

Chapter 6

General Principles and Processes of Isolation of Elements

Intext exercise

Question 1:

Which of the ores mentioned can be concentrated by magnetic separation method?

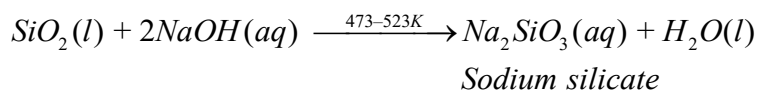
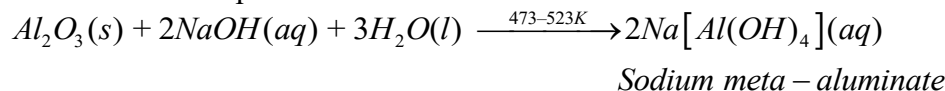
Solution 1:

Ores which are magnetic in nature can be separated from non-magnetic gangue particles by magnetic separation method. For ex: ores of iron such as haemetite (Fe_2O_3), magnetite (Fe_3O_4), siderite ($FeCO_3$) and iron pyrites (FeS_2) being magnetic can be separated from non-magnetic silica and other impurities by magnetic separation method.

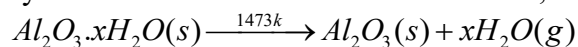
Question 2:

What is the significance of leaching in the extraction of aluminium?

Solution 2: Aluminium contains silica (SiO_2), iron oxide (Fe_2O_3) and titanium oxide (TiO_4) as impurities. These impurities can be removed by the process of leaching. During leaching, the powdered bauxite ore is heated with a concentrated (45%) solution of NaOH at 473-523 K, where alumina dissolves as sodium meta aluminate and silica as sodium silicate leaving Fe_2O_3 , TiO_2 and other impurities behind:



The impurities are filtered off and solution of sodium meta-aluminate is neutralised by passing CO_2 when hydrated alumina separates out while sodium silicate remains in solution. The hydrated alumina thus obtained is filtered, dried and heated to give back pure alumina.



Thus, by leaching, pure alumina can be obtained from bauxite ore.

Question 3:

The reaction, $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$ ($\Delta G^\theta = -421kJ$) is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature?

Solution 3:

This is explained on the basis of K_{eq} , the equilibrium constant. In the given redox reaction, all reactants and products are solids at room temperature, so, there is no equilibrium between the reactants and products and hence the reactions does not occur at RT. At high temperature, Cr melts and values of $T\Delta S$ increases. As a result, the value of $\Delta_r G^\theta$ becomes more negative and hence the reaction proceeds rapidly.

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Question 4:

Is it true that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO? What are those conditions?

Solution 4:

Yes, below $1350^\circ C$, Mg can reduce Al_2O_3 and above $1350^\circ C$, Al can reduce MgO. This can be inferred from ΔG° vs T plots.

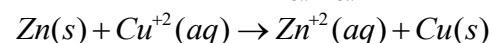
NCERT EXERCISE

Question 1:

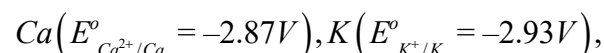
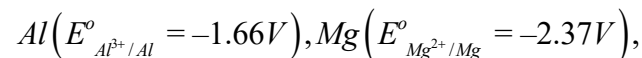
Copper can be extracted by hydrometallurgy but not zinc. Explain.

Solution 1:

Copper can be extracted by hydrometallurgy but not zinc, this is because $E^\circ_{Zn^{2+}/Zn} = -0.76V$ is lower than that of $E^\circ_{Cu^{2+}/Cu} = 0.34V$. Hence, zinc can replace Cu from solution of Cu^{+2} ions.



In order to displace zinc from zinc solution, a more reactive metal is required, such as



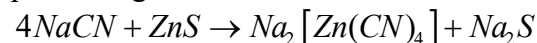
But with water, these metals (Al, Mg, Ca and K) forms their corresponding ions with the evolution of H_2 gas. Thus, Al, Mg, Ca, K, etc., cannot be used to displace zinc from zinc solution, and only copper can be extracted by hydrometallurgy but not the zinc.

Question 2:

What is the role of depressant in froth-floatation process?

Solution 2:

The role of depressant is to prevent one type of sulphide ore particles from forming the froth with air bubbles. NaCN is used as a depressant to separate lead sulphide (PbS) ore from zinc sulphide (ZnS) ore. NaCN forms a zinc complex, $Na_2 [Zn(CN)_4]$ on the surface of ZnS thereby preventing it from the formation of the froth.



*Sodium tetracyano –
zincate(II)*

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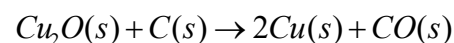
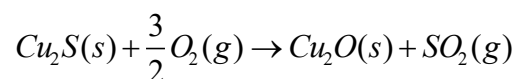
In this condition, only lead sulphide forms froth and thus can be separated from zinc sulphide ore.

Question 3:

Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?

Solution 3:

$\Delta_f G^\circ$ of Cu_2S is more negative than $\Delta_f G^\circ$ of CS_2 H_2S . So Cu_2S can not be reduced by carbon or hydrogen. $\Delta_f G^\circ$ of CO_2 is more negative than $\Delta_f G^\circ$ of Cu_2O . So Cu_2O can be reduced by carbon. So pyrites is first converted to oxide before reduction to copper.



Question 4:

Explain:

- (i) Zone refining
- (ii) Column chromatography

Solution 4:

(i) **Zone refining:** This method is used for production of semiconductors and other metals of very high purity, e.g., Ge, Si, B, Ca and In. It is based on the principle that the impurities are more soluble in the molten state (melt) than in the solid state of the metal. The impure metal in the form of bar is heated at one end with a moving circular heater, as the heater is slowly moved along the length of the rod, the pure metal crystallises out of the melt whereas the impurities pass into the adjacent molten zone. This process is repeated several times till the impurities are completely driven to one end of the rod which is then cut off and discarded.

(ii) **Chromatography:** It is based on the principle that the different components of a mixture are adsorbed to different extents on an adsorbent.

In column chromatography, an adsorbent, such as alumina (Al_2O_3) or silica gel is packed in a column. This forms the stationary phase. The mixture to be separated is dissolved in a suitable solvent (mobile phase) and applied to the top of the column. The adsorbed components are extracted (eluted) from the column with a suitable solvent (eluent). The component which is more strongly adsorbed on the column takes longer time to travel through the column than a component which is weakly adsorbed. Thus, the various components of the mixture are separated as they travel through adsorbent (stationary phase).

Question 5:

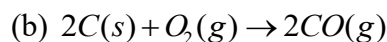
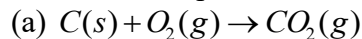
Out of C and CO which is a better reducing agent at 673K?

Solution 5:

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This can be explained thermodynamically, taking entropy and free energy changes into account



Case (i): Volume of CO_2 produced = Volume of O_2

Used.

$\therefore \Delta S$ is very small and ΔG does not change with temperature.

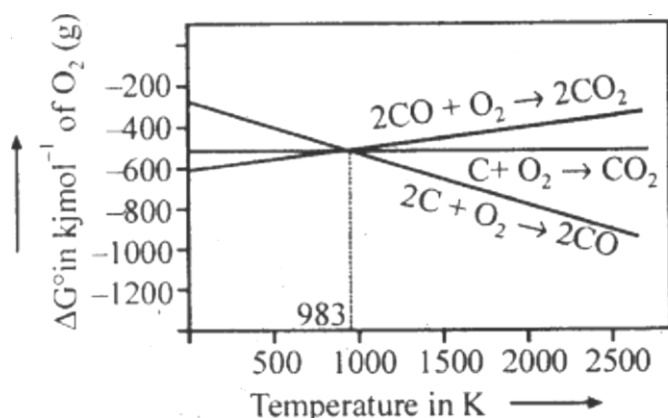
\therefore Plot of ΔG Vs T is almost horizontal.

Case (ii): Volume of CO produced = $2 \times$ volume of O_2 used.

$\therefore \Delta S$ is positive and hence ΔG becomes increasingly

Negative as the temperature increases.

\therefore Plot of ΔG Vs T slopes downwards.



As can be seen from ΔG Vs T plot (Ellingham diagram), lines for the reactions,

$C \rightarrow CO_2$ and $C \rightarrow CO$ cross at 983 K. Below 983 K, the reaction

(a) is energetically more favourable but above 673 K, reaction.

(b) is favourable and preferred. Thus, below 673 K both C and CO can act as a reducing agent but since CO can be more easily oxidised to CO_2 than C to CO_2 , therefore, below 673K, CO is more effective reducing agent than carbon.

Question 6:

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

Solution 6:

The common elements present in the anode mud are antimony, selenium, tellurium, silver, gold and platinum. These elements settle down under anode as anode mud because they are less reactive and are not effected by $CuSO_4-H_2SO_4$ solution.

Question 7:

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

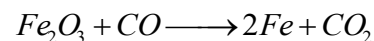
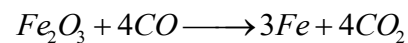
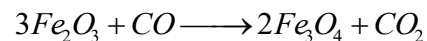
Solution 7:

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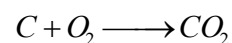
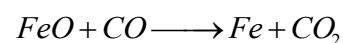
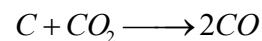
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In the blast furnace reduction of iron oxides take place at different temperature ranges as shown below.

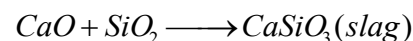
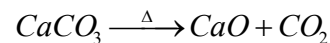
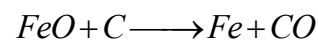
At 500-800K



At 900-1500K

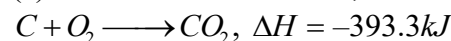


Above 1570K



The following reactions occur in the blast furnace:

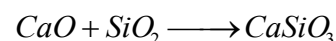
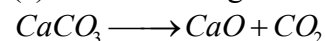
(a) In zone of combination,



(b) In zone of heat absorption,

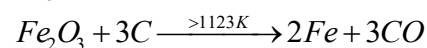
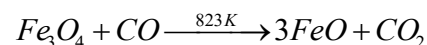
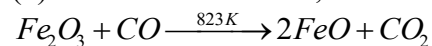


(c) In zone of slag formation,



Calcium Silicate (Slag)

(d) In zone of reduction,



Question 8:

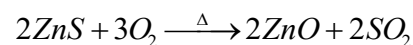
Write chemical reactions taking place in the extraction of zinc from zinc blende.

Solution 8:

The following processes are involved in the extraction of zinc from zinc blende:

(i) Concentration: Zinc blende ore is crushed and the concentration done by froth- floatation process.

(ii) Roasting: The concentrated ore is then roasted in presence of excess of air at about 1200 K as a result zinc oxide is formed.

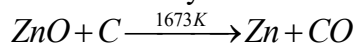


Zinc blende *Zinc oxide*

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(iii) Reduction: Zinc oxide obtained above is mixed with powdered coke and heated to 1673 K in a fire clay retort where it is reduced 'to zinc metal.



At 1673 K, zinc metal being volatile (boiling point 1180 K), distills over and is condensed.

(iv) Electrolytic refining: Impure zinc is made the anode while pure zinc strip is made the cathode. ZnSO_4 solution acidified with dil. H_2SO_4 is the electrolyte used. On passing electric current, pure zinc gets deposited on the cathode.

Question 9:

State the role of silica in the metallurgy of copper.

Solution 9:

During roasting, copper pyrites are converted into a mixture of FeO and Cu_2O . Thus, acidic flux silica is added during smelting to remove FeO (basic). FeO combines with SiO_2 to form famous silicate (FeSiO_3) slag which floats over molten matte.

Question 10:

What is meant by the term "chromatography"?

Solution 10:

Chromatography is a technique used for separation, purification, identification and characterization of the components of a mixture whether coloured or colourless. The term chromatography was originally derived from the Greek word 'chroma' meaning colour and 'graphy' for writing because the method was first used for the separation of coloured substances (plant pigments) into individual components.

Question 11:

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

Solution 11:

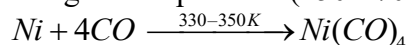
The stationary phase is selected in such a way that the impurities are more strongly adsorbed or are more soluble in the stationary phase than component to be purified. Thus, when the column is extracted, the impurities will be retained by the stationary phase while the pure component is easily eluted.

Question 12:

Describe a method for refining nickel.

Solution 12:

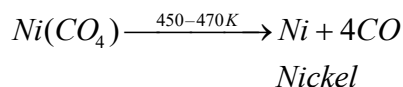
When impure nickel is heated in presence of CO at 330-350 K, it forms volatile nickel tetracarbonyl leaving behind the impurities. The nickel tetracarbonyl thus obtained is then heated to higher temperature (450-470K), then it undergoes thermal decomposition to give pure nickel.



(impure) Nickel tetracarbonyl

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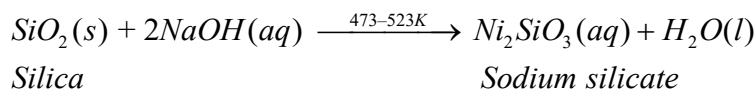
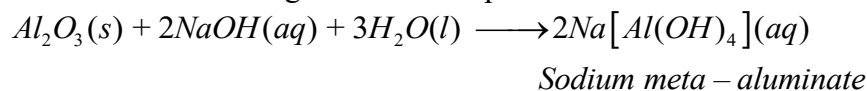
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**Question 13:**

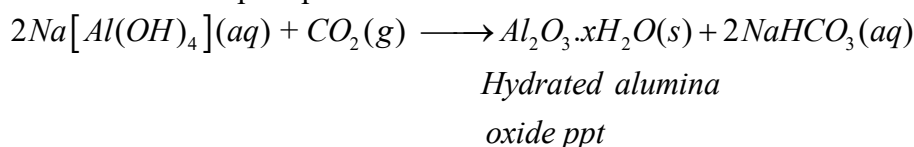
How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.

Solution 13:

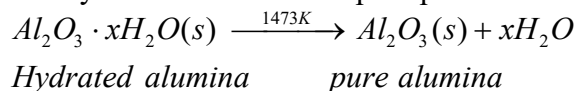
Pure alumina can be separated from silica in bauxite by Baeyer's process. The bauxite ore associated with silica is heated with a concentrated solution of NaOH at 473–523 K and 35–36 bar pressure. Under these conditions, alumina dissolves as sodium meta-aluminate and silica as sodium silicate leaving behind the impurities.



The resulting solution is filtered to remove the undissolved impurities, sodium meta-aluminate can be precipitated as hydrated aluminium oxide by passing CO₂ vapours. The sodium silicate formed cannot be precipitated and can be filtered off.



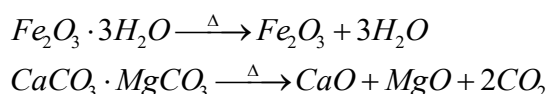
The hydrated alumina thus precipitated is filtered, dried and heated to give back pure

**Question 14:**

Giving examples, differentiate between 'roasting' and 'calcination'.

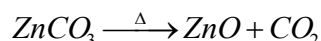
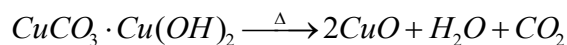
Solution 14:

Calcination is a process of converting carbonates and hydroxide ores of metals to their respective oxides by heating them, strongly below their melting points either in absence or limited supply of air.

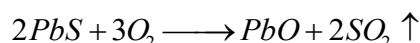
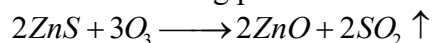


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Roasting is a process of converting sulphide ores into its metallic oxides by heating strongly below its melting point in excess of air.



Question 15:

How is 'cast iron' different from 'pig iron'?

Solution 15:

The iron obtained from blast furnace is called pig iron. It contains about 4% carbon and many other impurities in smaller amount (eg., S, P, Si and Mn). Cast iron is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Question 16:

Differentiate between minerals' and ores'.

Solution 16:

Minerals: The natural substances in which the metals or their compounds occur in the earth is called minerals.

Ores: The minerals from which the metals can be conveniently and economically extracted are called ores.

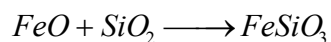
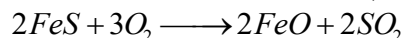
Note: All ores are minerals but all minerals are not ores.

Question 17:

Why copper matte is put in silica lined converter?

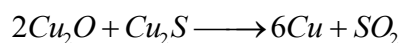
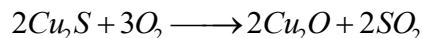
Solution 17:

Copper matte consists of Cu_2S along with some unchanged FeS . When a blast of hot air is passed through molten matte placed in silica lined converter, FeS present in matte is oxidised to FeO which combines with silica (SiO_2) to form slag.



Silica Slag

When whole of iron has been removed as slag, some of the Cu_2S undergoes oxidation to form Cu_2O which then reacts with more Cu_2S to form copper metal.



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Thus, copper matte is heated in silica lined converter to remove FeS present in matte as $FeSiO_3$ slag.

Question 18:

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

Solution 18:

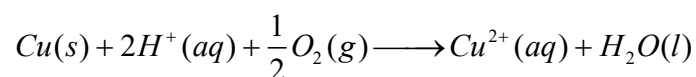
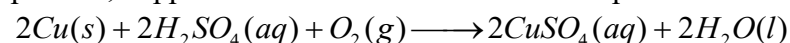
- (a) It lowers the fusion (melting) point of the bath from 2323 K to about 1140 K.,
 (b) It makes alumina a good conductor of electricity.
-

Question 19:

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

Solution 19:

Leaching in case of low grade copper ores is carried out with acids in presence of air. In this process, copper is oxidised to Cu^{2+} ions which pass into the solution.



Question 20:

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

Solution 20:

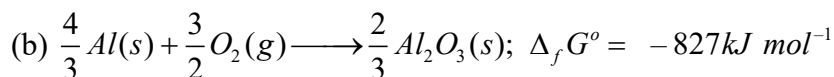
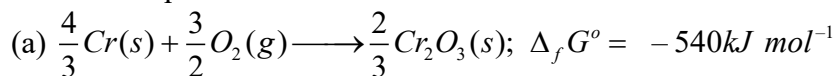
This is because the standard free energy of formation of CO_2 from CO is higher than that of standard free energy of formation of ZnO from Zn.

Question 21:

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

Solution 21:

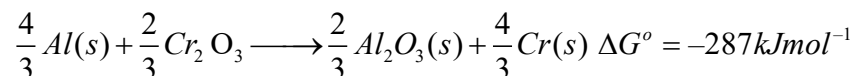
Chemical equation for the formation of Cr_2O_3 and Al_2O_3 are as follows:



Subtracting equation (a) from equation (b), we get

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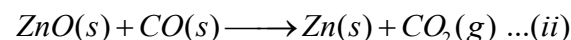
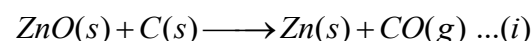
As can be seen $\Delta_r G^\circ$ is negative, thus, reduction of Cr_2O_3 by Al is possible.

Question 22:

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

Solution 22:

The two reduction reactions are



In the first case, there is increase in the magnitude of ΔS° while in the second case, it almost remains the same. In other words ΔG° will have more negative value in the first case when C(s) is used as the reducing agent than in the second case when CO(g) acts as the reducing agent. Therefore, C(s) is a better reducing agent.

Question 23:

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.

Solution 23:

We can study the choice of a reducing agent in a particular case using Ellingham diagram. It is evident from the diagram that metals for which the standard free energy of formation of their oxides is more negative can reduce those metal oxides for which the standard free energy of formation of their respective oxides is less negative it means that any metal will reduce the oxides of other metals which lie above it in the Ellingham diagram. This is because the standard free energy change ($\Delta_r G^\circ$) of the combined redox reaction will be negative by an amount equal to the difference in $\Delta_r G^\circ$ of the two metal oxides. Thus both Al and Zn can reduce FeO to Fe but Fe cannot reduce Al_2O_3 to Al and ZnO to Zn. In the same way, G can reduce ZnO to Zn but not CO.

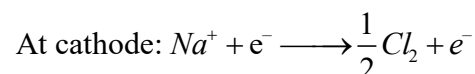
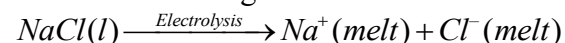
Note: Only that reagent will be preferred as reducing agent which will lead to decrease in free energy value ΔG° at a certain specific temperature.

Question 24:

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?

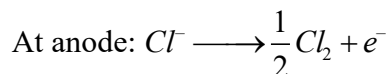
Solution 24:

Down process is used for the preparation of sodium metal, where chlorine is obtained as a by-product. This process involves the electrolysis of a fused mixture of NaCl and CaCl₂ at 873 K. Sodium is discharged at the cathode while Cl₂ is obtained at the anode as a by-product.



Chapter 6

General Principles and Processes of Isolation of Elements



If, an aqueous solution of NaCl is electrolysed, H_2 is evolved at the cathode while Cl_2 is obtained at the anode.

Question 25:

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

Solution 25:

In the electrometallurgy of aluminium, oxygen gas is evolved at anode. O_2 reacts with graphite or carbon (graphite electrodes) to form carbon monoxide and carbon dioxide. In case if some other metal carbon (graphite electrodes) to form carbon monoxide and carbon dioxide. In case if some other metal aluminium oxide (Al_2O_3) which will pass into the reaction mixture resulting into wastage of Al. Since graphite is cheaper than aluminium, its wastage or can be tolerated.

Question 26:

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

- (i) Zone refining
- (ii) Electrolytic refining
- (iii) Vapour phase refining

Solution 26:

(i) **Zone refining:** This method is used for production of semiconductors and other metals of very high purity, e.g., Ge, Si, B, Ca and In,

It is based on the principle that the impurities are more soluble in the molten state (melt) than in the solid state of the metal.

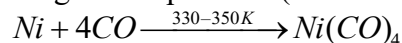
The impure metal in the form of bar is heated at one end with a moving circular heater. As the heater is slowly moved along the length of the rod, the pure metal crystallises Out of the melt whereas the impurities pass into the adjacent molten zone. This process is repeated several times till the

impurities are completely driven to one end of the rod which is then cut off and discarded.

(ii) **Electrolytic refining:** Many metals, such as Cu, Ag, Au, Al, Pb, etc., are purified by this method. The impure metals is made the anode while a thin sheet of pure metal acts as a cathode. The electrolytic solution consists of a salt or a complex salt solution of the metal. On passing the current, the pure metal is deposited on the cathode while the impurities fall down as anode mud.

(iii) **Vapour-phase refining:** The crude metal is freed from impurities by first converting it into a suitable volatile compound by heating it with a specific reagent at a lower temperature and then decomposing the volatile compound at some higher temperature to give the pure metal.

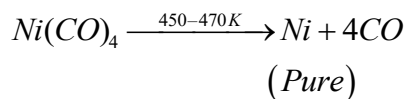
(a) Mond's process: When impure nickel is heated is a current of CO at 330-350 K, it forms volatile nickel tetracarbonyl complex leaving behind the impurities. The complex then heated to a higher temperature (450.470K) when it undergoes thermal decomposition giving pure nickel.



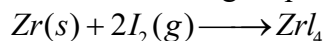
(*impure*)

Chapter 6

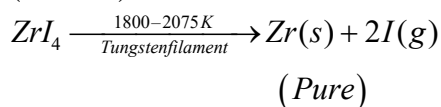
General Principles and Processes of Isolation of Elements



(b) Van Arkel method: This method is Used for preparing ultra-pure metals by removing all the oxygen and nitrogen present as impurities in metals like zirconium and titanium (which are used in space technology). Crude Zr is heated in an evacuated vessel with iodine at 870 K. Zirconium tetraiodide thus formed is separated. It is then decomposed by heating over a tungsten filament at 1800–2075 K to give pure Zr.



(Impure)

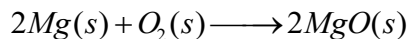
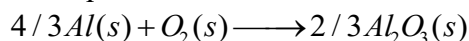


Question 27:

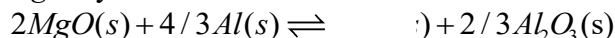
Predict conditions under which Al might be expected to reduce MgO .

Solution 27:

The equations for the formation of the two oxides are



If we look at the plots for the formation of the two oxides of the Ellingham diagram, we find that they intersect at certain point. The corresponding value of ΔG° becomes zero for the reduction of MgO by Al metal.



This means that the reduction of MgO by Al metal can occur below this temperature. Aluminium (Al) metal can reduce MgO to Mg above this temperature because $\Delta^\circ G$ for Al_2O_3 is less as compared to that of MgO

