

CHEM03CS General principles of Metallurgy P.C.II ①

Metallurgy : Process isolating metals from ore / prep. of alloy.

- Minerals : are materials, where the metals are extracted from them.
- Gangue : minerals along with earthly materials such as rock and gravels.
- Ores : Form of minerals concentrated to extract the metal from it economically.

All the ores are minerals, but all the minerals are not ores.

Extraction of Metals :-

The Source of metal & technique used to extract metals are determined by the nature of metals.

Source based on Standard electrode potential / free energy

classified as five main types based of SEP/DG.

TYPE I : very electro +ve metals, shows high -ve Standard reduction potential

Eg : Li -3.04 V , Na -2.71 V , K -2.92 V etc...

They occurs as Soluble Salts in nature: Such as chlorides, Carbonates, Sulfates, etc.... These are extracted by electrolytic technique.

TYPE II : Alkaline earths except Be, also have high -ve Std. red. Pot. (Mg: -2.37 V , Ba -2.9 V). Formed as insoluble Carbonates & Sulfates (MgSO₄ soluble) also ext. by electrolytic technique

(2)

TYPE III: Also electro +ve, but std. red. pot are less than type I & II metals (Al -1.66V , Ti -0.95V , Cr -0.74V)
main sources are oxides and mixed oxides.

Varieties of technique used to ext. such metals.
incl. electrolytic, chemical reduction using C, CO & more reactive metals.

TYPE IV: These are weaker metals as shown by their low -ve std. red. pot. (Zn -0.76V , Fe -0.44V , Co -0.28V) and are found with weaker anions. Principally as S^{2-} and less frequently as O^{2-} .

The MS is converted to MO prior to reduction with Carbon, CO & H_2 / converted to SO_4^{2-} for subsequent electrolytic treatment

TYPE V: These are unreactive metals and available in free state as shown by their +ve std. red. pot. (Ag $+0.8\text{V}$, Au $+1.5\text{V}$, Pt $+1.2\text{V}$)

not interpreted too rigidly.

Borderline: - Cu, Zn & Pb occurs as carbonates.

→ Only workable sources of Fe is O^{2-} & Ca^{2+}

→ Hg occurs in free state and also ext. from HgS .

⇒ Most abundant metal in earth crusts are Al, Fe, Ca, Mg, Na, K, Ti & Mn.

⇒ Sea water Na, Mg & Ca.

⇒ Sea bed Mn (since Mn eating bacteria)

→ Isolation of metals from ore (Three major steps)

ore → Dressed ore → impure ore → pure metal.

(i) Prep. of the ore / (conc. ore, (ii) conversion into suitable for redn (mostly oxides)

(iii) Production of the metal

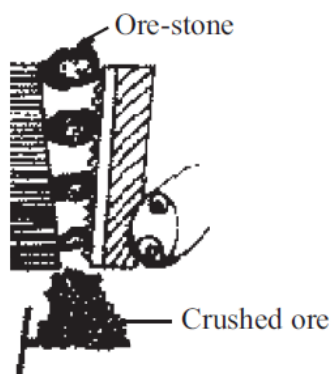
(iv) Purification of the metal

General principles of extraction of metals

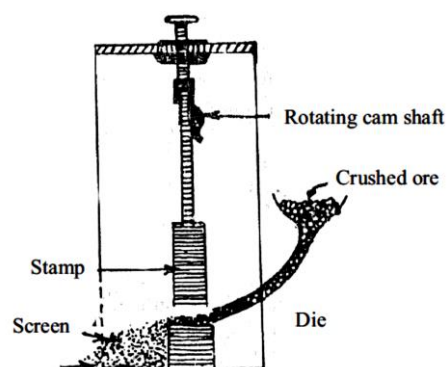
- (i) Crushing and pulverization
- (ii) Concentration or dressing of the ore
- (iii) Calcination or roasting of the ore
- (iv) Reduction of metal oxides to free metal
- (v) Purification and refining of metal.

Crushing and Pulverization

The ore is generally obtained as big rock pieces. These big lumps of the ore are crushed to smaller pieces by using ***jaw-crushers*** and *grinders*.



One of the plates of the crusher is stationary while the other moves to and fro and the crushed pieces are collected below



The crushed pieces of the ore are then pulverized (powdered) in a stamp mill

Concentration or Dressing of the Ore

Generally, the ores are found mixed with earthy impurities like sand, clay, lime stone etc. These unwanted impurities in the ore are called *gangue* or *matrix*.

The process of removal of gangue from powdered ore is called concentration or ore dressing.

several methods for concentrating the ores. The choice of method depends on the nature of the ore.

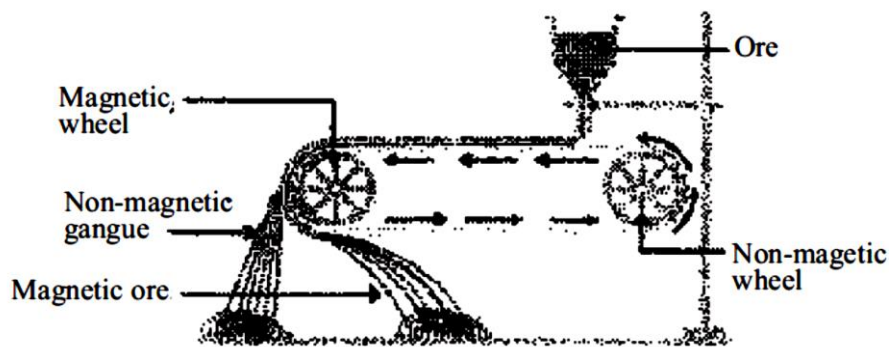
(i) Gravity separation (Hydraulic washing): concentration of heavier oxide ores, like haematite (Fe_2O_3) tinstone (SnO_2) and gold (Au).



(ii) Magnetic separation method:

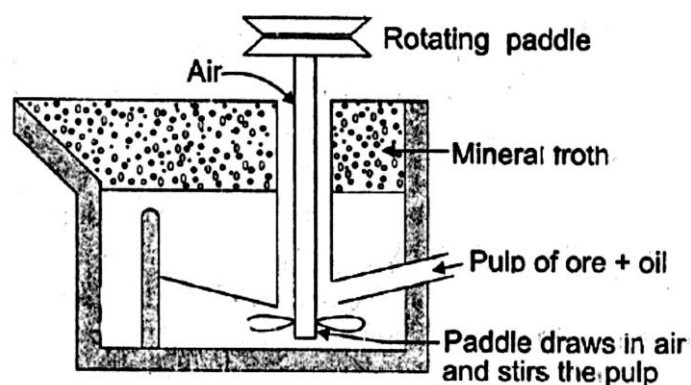
Those ores can be concentrated which either contain impurities which are magnetic or are themselves magnetic in nature.

For example, the tin ore, tin stone (SnO_2) itself is non-magnetic but contains magnetic impurities such as iron tungstate (FeWO_4) and manganese tungstate (MnWO_4).



(iii) Froth floatation method

This method is especially applied to **sulphide ores**, such as **galena** (PbS), **zinc blende** (ZnS), or **copper pyrites** (CuFeS_2). It is based on the different wetting properties of the surface of the ore and gangue particles. The sulphide ore particles are wetted preferentially by oil and gangue particles by water. In this process, finely powdered ore is mixed with either pine oil or eucalyptus oil. It is then mixed with water. Air is blown through the mixture with a great force. Froth is produced in this process which carries the wetted ore upwards with it. impurities (gangue particles) are left in water and sink to the bottom from which these are drawn off

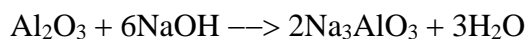


Enlarged view of an air bubble showing mineral particles attached to it

(iv) Chemical method :

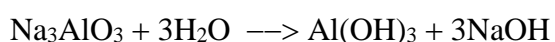
In this method the ore is treated with a suitable chemical reagent which dissolves the ore leaving behind insoluble impurities. The ore is then recovered from the solution by a suitable chemical method. This is applied for extraction of aluminium from bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$).

Bauxite is contaminated with iron (III) oxide (Fe_2O_3), titanium (IV) oxide (TiO_2) and silica (SiO_2). These impurities are removed by digesting the powdered ore with aqueous solution of sodium hydroxide at 420 K under pressure. Aluminium oxide dissolves in sodium hydroxide, whereas, iron (III) oxide, silica and titanium (IV) oxide remain insoluble and are removed by filtration.



Sodium aluminate

Sodium aluminate is diluted with water to obtain precipitate of aluminium hydroxide. It is filtered and ignited to obtain pure alumina.



Conversion of concentrated ore into metal oxide:

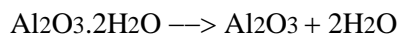
Calcination and Roasting of the Ore

The concentrated ore is converted into metal oxide by calcination or roasting.

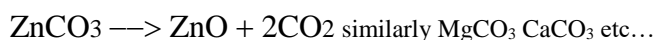
(A) Calcination :

Calcination involves heating of the concentrated ore in either limited supply of air or without air so that it loses moisture, water of hydration and gaseous volatile substances. The ore is heated to a temperature so that it does not melt. Two examples of calcination are given below:

(i) Removal of water of hydration



(ii) Expulsion of CO_2 from carbonate

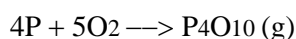
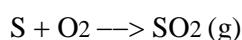
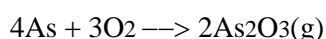
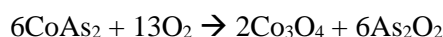


(B) Roasting:

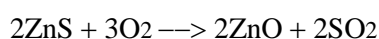
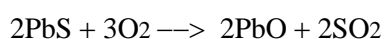
Roasting is a process in which the concentrated ore is heated in a free supply of air at a temperature insufficient to melt it. The following changes take place during roasting:

(i) Drying of the ore.

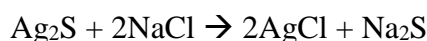
(ii) Removal of the volatile impurities like arsenic, sulphur, phosphorus and organic matter.



(iii) Conversion of the sulphide ores into oxides



(iv) sometimes ore is mixed with suitable salt and roasted in absence of air



Calcination and roasting are generally carried out in a reverberatory furnace or in a multiple hearth furnace.

(C) Smelting:

This process used for gauge is more reactive than metal to be recovered

An oxide is added deliberately and heated. The added oxide will combine with other unwanted impurities at molten condition. This will immiscible with metal oxide molten slag

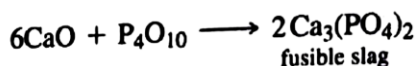
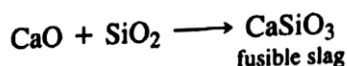
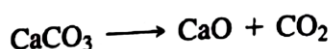
Non-metal oxide(acidic) + metal oxide(basic) \rightarrow fusible slag (easily melted)

e.g. FeO is impurities on extraction of Cu from its ore

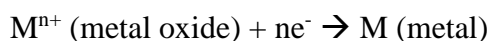


To remove unwanted acidic oxides like sand and P_2O_5

Smelting done in presence of lime

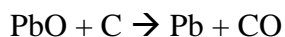
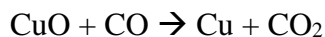


Reduction of a metal oxide: Consider following reaction



$$\text{ease of reduction of metal oxide } M^{n+} \text{ to metal } M \propto \frac{1}{\text{reactivity of metal}}$$

Thus less active metals such as Pb and Cu are reduced easily by less active reducing agent



Vice versa the highly reactive more electro positive metals such as Li, Na, Mg, Ca and Al cannot be easily formed from their oxides, using coke or carbon monoxide as reducing agents. Their compounds are reduced electrolytically (a powerful reduction process).

Metal	Oxide reduction process
Hg, Cu	Roasting of sulphides; reduction by S^{2-}
Cr, Mn, Ti, V	Reduction of oxides with more electropositive metals
Sn, Fe, Zn, Pb	Reduction with coke or carbon monoxide
W, Co	Reduction with molecular hydrogen
Li, Na, Mg, Ca, Al	Electrolytic reduction

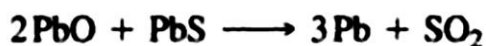
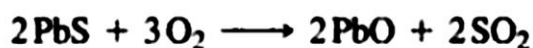
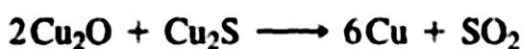
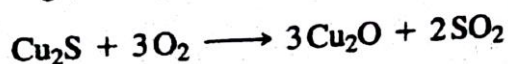
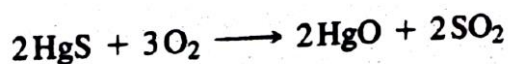
Note: The reduction with hydrogen is not a widely used because (i) many metals forms their hydrides at elevated reduction temperature, and (ii) the hydrogen used may react explosively with the oxygen in the air.

Methods of reduction

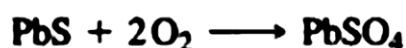
The production of metals from metal oxide by reduction is of four types:

- (i) Auto-reduction / self-reduction / air reduction method
- (ii) Chemical reduction method
- (iii) Electrolytic reduction method
- (iv) Special methods of reduction

(i) Auto-reduction / self-reduction / air reduction method: less electropositive (less reactive) metals such as metallic lead, antimony, copper and mercury etc... have low reactivity: therefore, their sulphide ores on roasting produce the metals directly through auto-reduction without the need for a reducing agent. Cinnabar (HgS), for example, produces Hg directly on heating it.

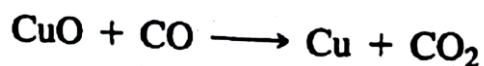
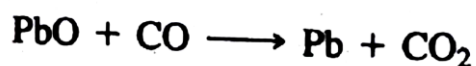
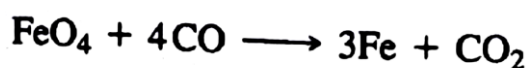
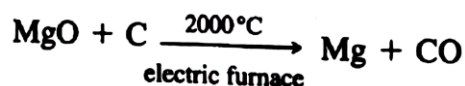
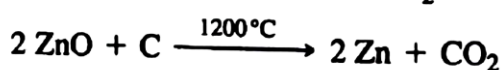
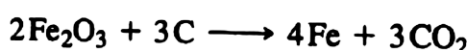


Or Pb can also be represented as follows



(ii) Chemical reduction method:

(a) Using carbon (coke) and carbon monoxide (CO), one of the oldest method, commercially viable, used up to furnace temperature at 2000 °C



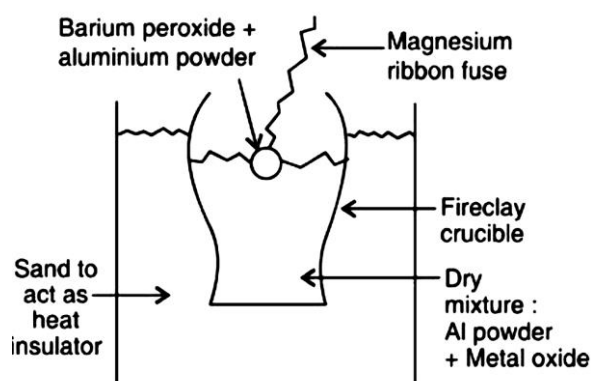
Disadvantages:

- (i) many metals combine with C and forms their carbides
- (ii) Expensive as it required very high temperature and necessary to use blast furnace.

(b) reduction with hydrogen: this method not used widely as afore mentioned reason

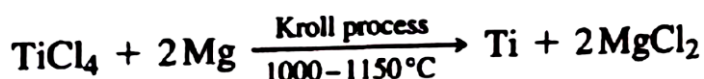


(c) **reduction by other metals:** (i) using Aluminum: Some metal-oxides are needed very high temperature for reduction using coke (e.g. Cr_2O_3 and Mn). The coke reduction is expensive for such reduction process, some metals have more oxophilic nature than carbon in such cases C is not possible to use. Therefore, reduction of metal oxides effected with the highly electropositive aluminium. When Al reduces the metal oxide and forms Al_2O_3 , a large amount of heat energy is liberated ($4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 1675 \text{ kJ mol}^{-1}$ exothermic, proceeds with explosive violence, needed only initial temperature to start reaction). The energy liberated is used for reduction of other metal oxides This metallurgical method is called the **thermite process / Goldschmidt / aluminothermic process** (fig)



(ii) using magnesium: Na and Mg used in similar manner, where the oxides are too stable to reduce in such cases Na and Mg used to reduce their chloride salts

Advantages: the by-products are NaCl , MgCl_2 which is soluble in water. As a result of the process easily washed with water from metals. As more electropositive metals they have higher reducing power.



①

ELLINGHAM diagram

Thermodynamics of metallurgy

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = \text{Spontaneousness of reaction} \left\{ \begin{array}{l} < 0 \text{ } \begin{array}{l} \text{-ve} \\ \text{Spontaneous} \end{array} \\ = 0 \text{ } \text{Equilibrium} \\ > 0 \text{ } \begin{array}{l} \text{non-spontaneous} \\ \text{+ve.} \end{array} \end{array} \right.$$

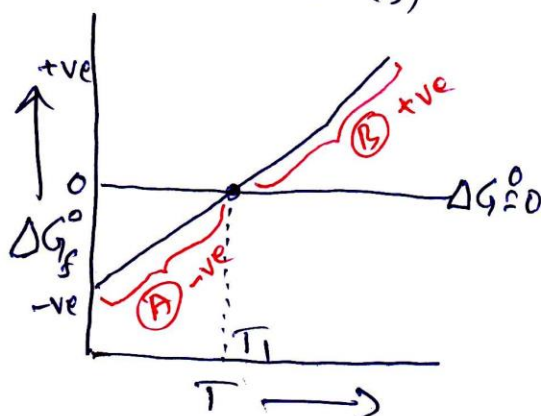
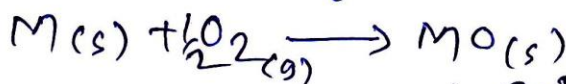
Ellingham provided the thermodynamic concept to understand the formation of metal oxide at different temperature. Also used this diagram to find Suitable reducing agent to reduce the metal oxide (MO) to metal (M)

Ellingham plot is $\Delta G_f^\circ \text{ Vs. } T$

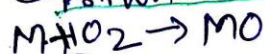
ΔG_f° = Gibb's free energy of ^{metal}oxide formation from 1 mole of O_2

T = temperature

Consider following reaction



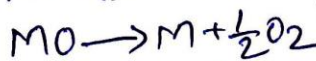
(A) part Forward reac



$$\Delta G = -ve$$

∴ Spontaneous

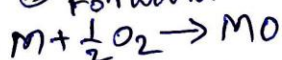
reverse reaction



$$\Delta G = +ve$$

∴ non-spontaneous

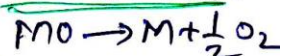
(B) part Forward rea



$$\Delta G = +ve$$

∴ non-spontaneous

reverse reac



$$\Delta G = -ve$$

∴ Spontaneous

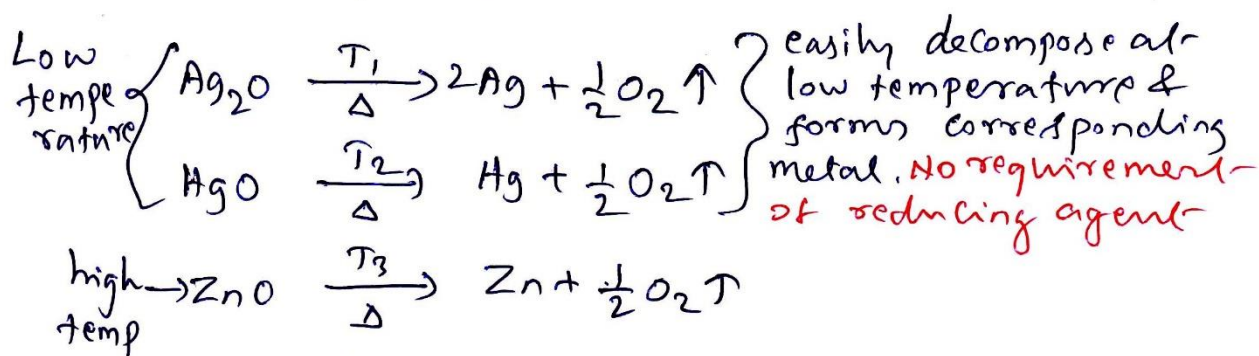
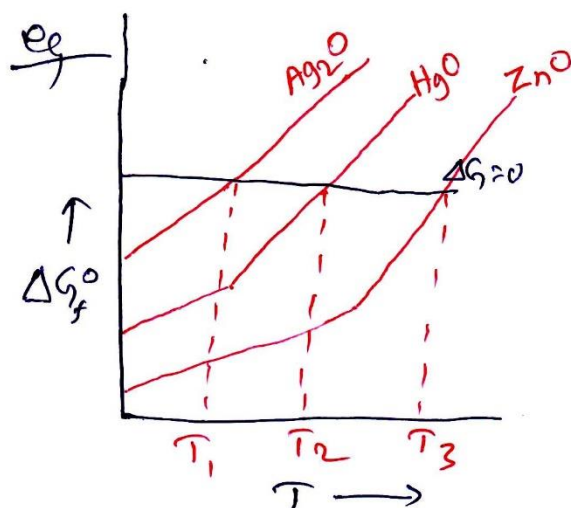
From the figure

(1) Before temperature T_1 , the forward reaction

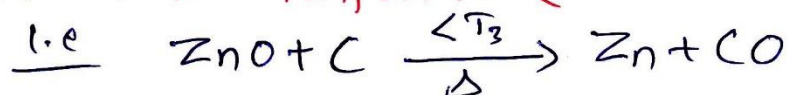
i.e. $M + \frac{1}{2}O_2 \rightarrow MO$ is spontaneous.

(2) After temperature T_1 , the reverse reaction

i.e. $MO \rightarrow M + \frac{1}{2}O_2$ is spontaneous.



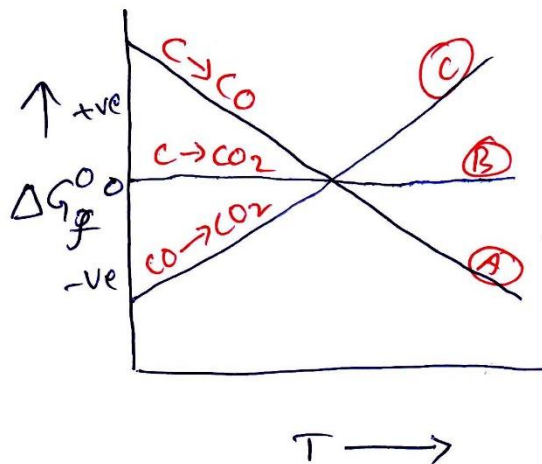
ZnO decomposes at very high temperature which is economically not feasible. \therefore used some external reducing agent to form the Zn from ZnO at low temperature



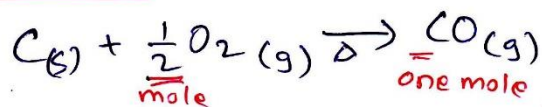
choosing best reducing agent

(2)

consider following Ellingham diagram for Coke 'C' oxidation



reaction (A) $C \rightarrow CO$



Standard molar entropies of gases much larger than those of solids
 \therefore entropies of reaction compared

change in moles of no of gas in the reaction.

$$i.e. \Delta n_g = n_p - n_r = 1 - \frac{1}{2} = \frac{1}{2} \text{ moles}$$

\downarrow \downarrow \downarrow
 change of no. of moles of reactant-
 moles product

increased

randomness of atoms in a molecule.

$\text{solid} < \text{liquid} < \text{Gas}$.

randomness highest for gases

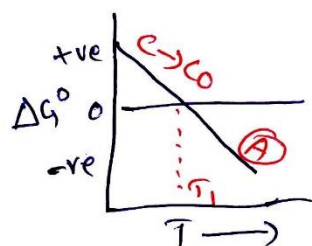
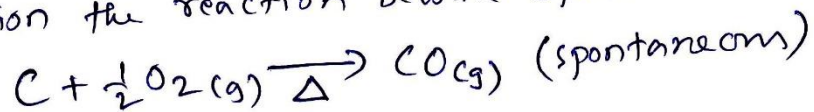
randomness \propto disorder \propto Entropy

\therefore in product ΔS increased, i.e. +ve

From eq $\Delta G^\circ = \Delta H^\circ - T\Delta S$ $\rightarrow +ve$ $T\Delta S$ is +ve \therefore ΔG° decreases.
 \uparrow
 $+ve$ inc. ($C + O_2 \rightarrow CO$)
 part is more -ve

As ΔG° decreases the reaction become Spontaneous.

∴ Increasing the temperature of following reaction the reaction become Spontaneous

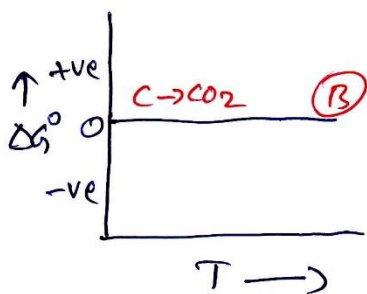


initially at $T=0$ $\Delta G = +ve$ no reaction
upon inc. temp beyond $T=T_1$, the
 $\Delta G = -ve$ and reaction become
spontaneous.

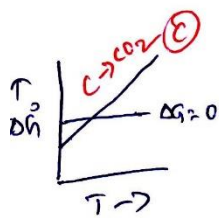
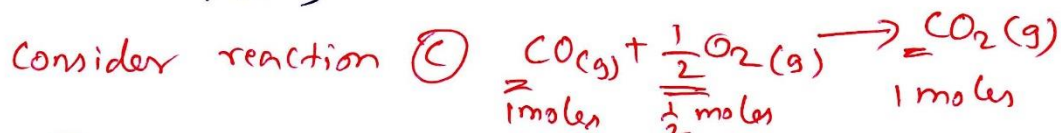


$$\Delta n(g) = n_p - n_r = 1 - 1 = 0 \text{ There is no change in randomness.}$$

$$\Delta S^\circ = 0 \quad \Delta H^\circ = 0$$



no change in ΔG° upon inc temperature. i.e. in equilib-
rium.



$$\Delta n(g) = n_p - n_r = 1 - (1 + \frac{1}{2}) = -\frac{1}{2} \text{ moles decreased}$$

randomness decreased ∴ $\Delta S = -ve$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

ΔH° is $+ve$ (inc. ∴ +ve)
 ΔS° is $-ve$ (X)
 $\therefore \Delta G^\circ = \text{increased } +ve$
 non-spontaneous.

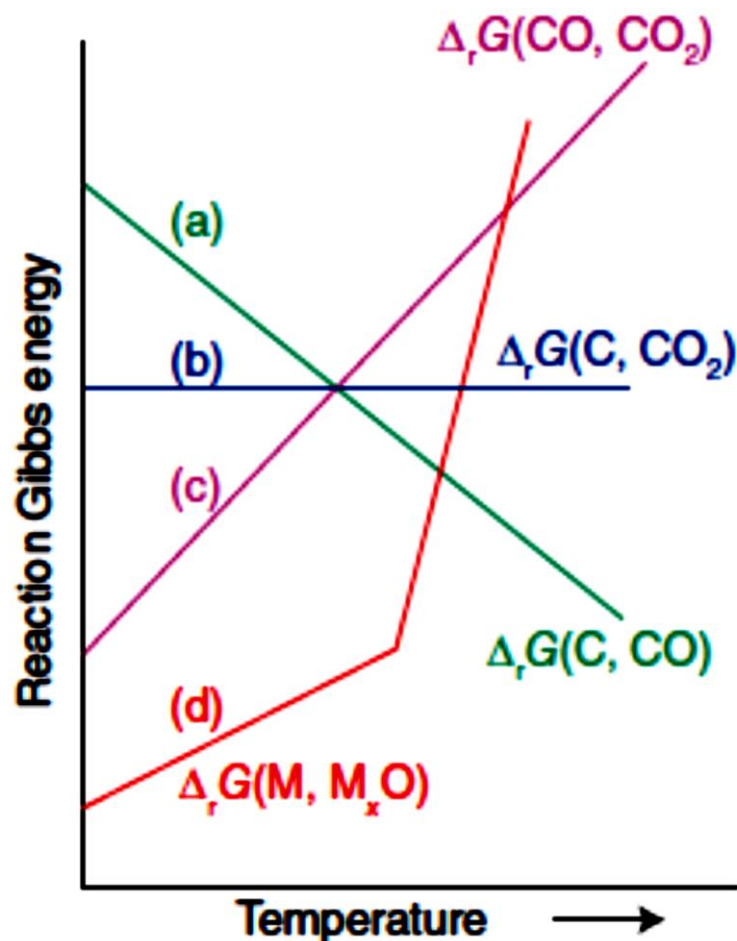


Figure: Part of an Ellingham diagram showing the standard Gibbs energy for the formation of a metal oxide and the three carbon oxidation Gibbs energies. The slopes of the lines are determined largely by whether there is net gas formation or consumption in the reaction. A phase change generally results in a kink in the graph (because the entropy of the substance changes).

From the figure

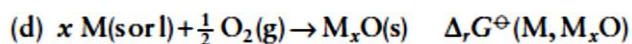
The standard reaction entropy of (d), in which there is a net consumption of gas, is negative, and hence the plot has a positive slope ($M + \frac{1}{2} O_2 \rightarrow MO$, ΔS is going to negative as product there is no gas, therefore, ΔG is positive). The kinks in the lines, where the slope of the metal oxidation line changes, are where the metal undergoes a phase change, particularly melting, and the reaction entropy changes accordingly.

- For temperatures at which the C/CO line lies below the metal oxide line, carbon can be used to reduce the metal oxide and itself is oxidized to carbon monoxide.
- For temperatures at which the C/CO₂ line lies below the metal oxide line, carbon can be used to achieve the reduction, but is oxidized to carbon dioxide.
- For temperatures at which the CO/CO₂ line lies below the metal oxide line, carbon monoxide can reduce the metal oxide to the metal and is oxidized to carbon dioxide.

To achieve a negative $\Delta G < 0$ for the reduction of a metal oxide with carbon or carbon monoxide, one of the following reactions

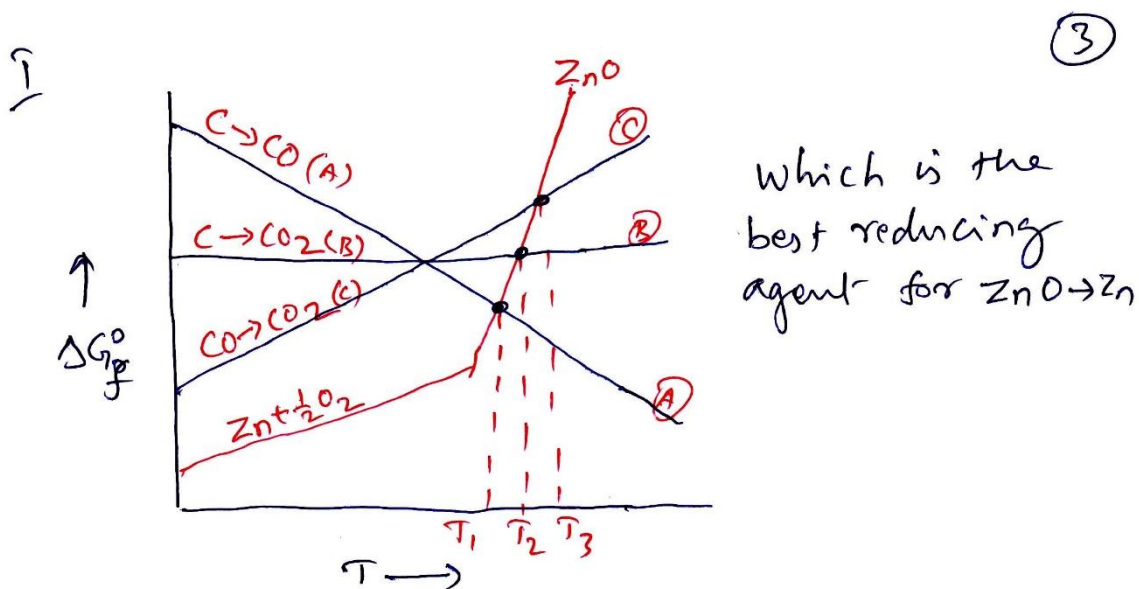
- (a) $\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)} \quad \Delta_r G^\ominus(\text{C, CO})$
 (b) $\frac{1}{2} \text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \frac{1}{2} \text{CO}_2(\text{g}) \quad \Delta_r G^\ominus(\text{C, CO}_2)$
 (c) $\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta_r G^\ominus(\text{CO, CO}_2)$

must have a more negative ΔG than a reaction of the form



under the same reaction conditions. If that is so, then one of the reactions will have a negative standard reaction Gibbs energy

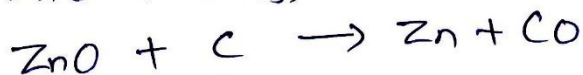
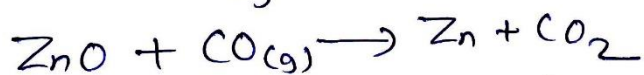
- (a-d) $\text{M}_x\text{O(s)} + \text{C(s)} \rightarrow x \text{M(sor l)} + \text{CO(g)} \quad \Delta_r G^\ominus(\text{C, CO}) - \Delta_r G^\ominus(\text{M, M}_x\text{O})$
 (b-d) $\text{M}_x\text{O(s)} + \frac{1}{2} \text{C(s)} \rightarrow x \text{M(sor l)} + \frac{1}{2} \text{CO}_2(\text{g}) \quad \Delta_r G^\ominus(\text{C, CO}_2) - \Delta_r G^\ominus(\text{M, M}_x\text{O})$
 (c-d) $\text{M}_x\text{O(s)} + \text{CO(g)} \rightarrow x \text{M(sor l)} + \text{CO}_2(\text{g}) \quad \Delta_r G^\ominus(\text{CO, CO}_2) - \Delta_r G^\ominus(\text{M, M}_x\text{O})$



Note:-

① → The metal oxide placed higher in the diagram can be reduced by element involved in the formation of oxide present in lower of the diagram.

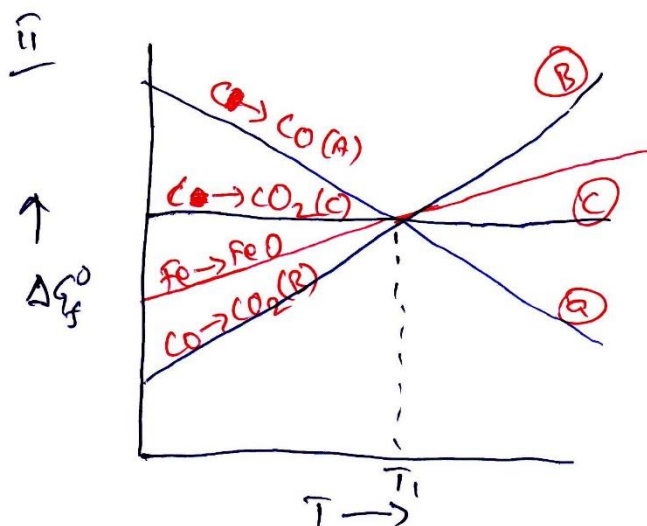
② → Always give priority to low temperature & $\Delta G = -ve$ / more $-ve$ from above diagram.



According to note: 1: All the 3 materials (A), (B), (C) act as reducing agent for ZnO

According to note: 2 lower temperature T_1 given priority, where ΔG also more $-ve$ with respect to other two.

∴ Coke 'c' is best reducing agent at temperature T_1 ∴ $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$ is best route



Out of 'C' and 'CO' which one is the best reducing agent to recover Fe from FeO?



Both (A) i.e. C as well as CO (B) present down to the $\text{Fe} \rightarrow \text{FeO}$, However 'C' act as reducing agent $T > T_1$, where $\Delta G = -ve$.

But CO act as reducing agent at $T < T_1$, where $\Delta G = -ve$

\therefore To reduce FeO to Fe 'CO' is best agent

Observations from Ellingham diagram

1. If temperature increases, Gibb's free-energy change of metal oxide formation decreases, implying that the stability of the metal oxide decreases with the temperature increase except $C \rightarrow CO_2$ and $C \rightarrow CO$.
2. $\Delta G^\circ \propto T$. At certain temperature the slope of the line changes (kink) infers physical state of the metal is changed (as with mercury which becomes a vapour at $350^\circ C$). The change in slope is due to a large increase in the entropy of the system.
3. For some metals, the graph crosses the $\Delta G^\circ = 0$ line as the temperature is increased; this indicates that the oxide will decompose above a certain temperature. Below this temperature, the free energy of formation of the oxide is negative and so the oxide is stable. All oxides, theoretically, are expected to decompose at sufficiently high temperatures. Practically, the oxides of Ag, Au and Hg decompose at moderate temperatures, easily attainable; consequently, these metals can be obtained by the thermal decomposition of their oxide ores.
4. The oxide of a metal which is above another metal in the Ellingham diagram can be reduced by the latter. Thus, Mg can reduce Cr_2O_3 ; Al can reduce Fe_2O_3 . For such a reduction, the free-energy change [metal(m1) oxide + metal(m2) \rightarrow metal(m1) + metal(m2)oxide] is negative. For example, in the reduction



the ΔG° of the reaction

$$\begin{aligned} &= 3 \Delta G_f^\circ(MgO) - \Delta G_f^\circ(Cr_2O_3) \\ &= (3 \times -570 \text{ kJ mol}^{-1}) - (-1,056 \text{ kJ mol}^{-1}) \\ &= -654 \text{ kJ mol}^{-1} \end{aligned}$$

Consider the hypothetical reaction



$$\begin{aligned} \text{The } \Delta G^\circ \text{ of this reaction} &= \Delta G_f^\circ(HgO) - \Delta G_f^\circ(MgO) \\ &= -59 - (-569 \text{ kJ mol}^{-1}) \\ &= 510 \text{ kJ mol}^{-1} \end{aligned}$$

This ΔG° value is positive and therefore Hg cannot reduce MgO.

Uses of Ellingham Diagram

1) Alumino Thermic Process

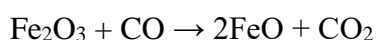
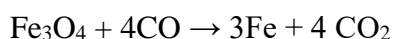
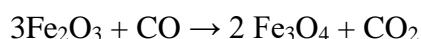
The Ellingham curve on the graph actually lies lower than most of the other metals such as iron. This essentially means Aluminium can be used as a reducing agent for oxides of all the

metals that lie above it in the graph. Since aluminium oxide is more stable it is used in the extraction of chromium by a thermite process.

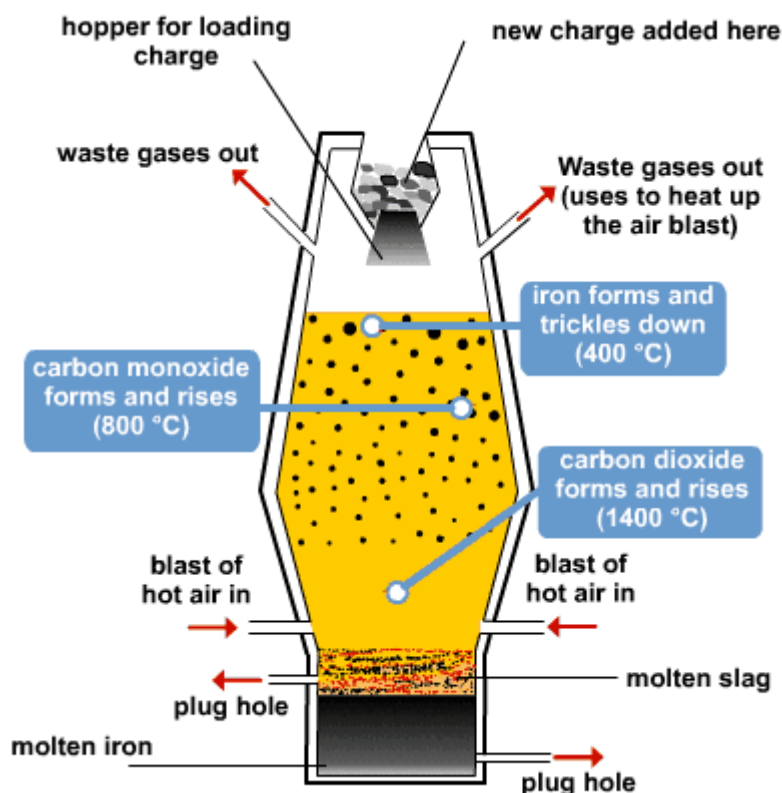
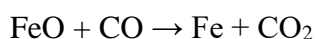
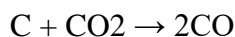
2) Extraction of Iron

Extraction of iron from its oxide is done in a blast furnace. Here the ore mixes with coke and limestone in the furnace. Actually, the reduction of the iron oxides happens at different temperatures. The lower part of the furnace is kept at a much higher temperature than the top. This process was developed after understanding the reactions with the help of thermodynamics. These reactions are as follows

At temperatures of 400-800 K



At temperatures of 800-1500 K

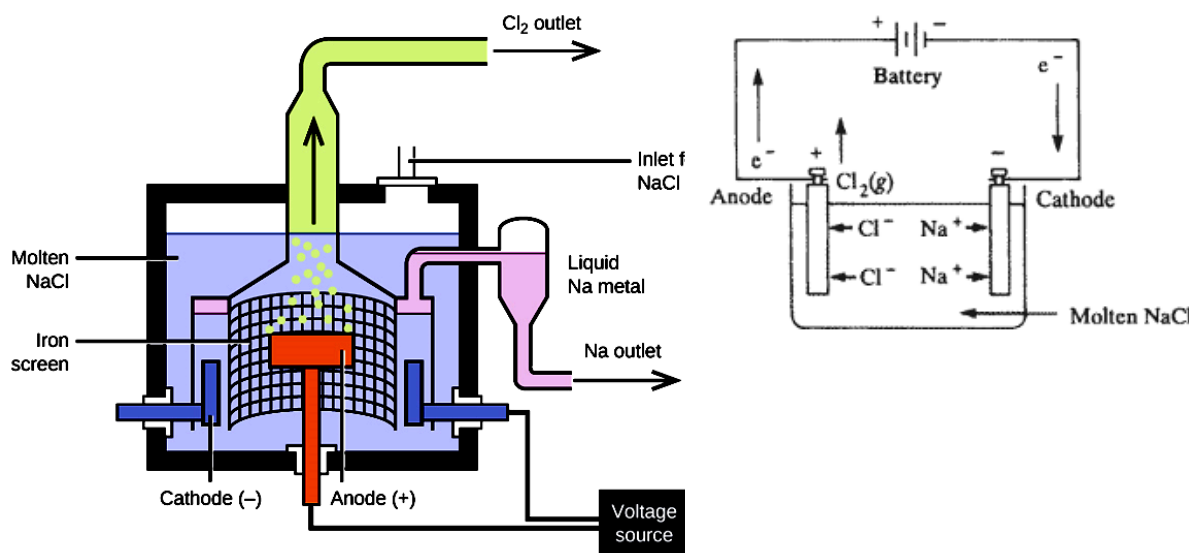


Limitations of Ellingham Diagram

- It does not consider the kinetics of the reactions.
- Also, it does not provide complete information about the oxides and their formations. Say for example more than one oxide is possible. The diagram gives us no representation of this scenario

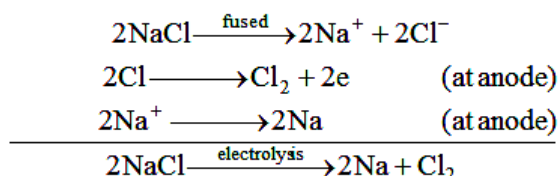
(d) Electrolytic reduction:

The reactive high electro positive metals (high up in the activity series) cannot be produced by any of the above methods. Because in order to reduce their oxide there is necessary of huge amount of heat and at very high temperature, these metals forms an undesired products. Extraction of such metal can be done by carrying out electrolytic reduction of their anhydrous molten oxides or chlorides. During electrolysis, the cathode supplies electrons to metal ions for their reduction to the metal.

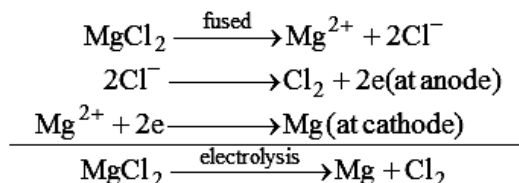


Examples:

(i) Sodium metal is obtained by the electrolysis of molten sodium chloride.



(ii) Magnesium metal is obtained by the electrolysis of molten magnesium.



(iii) Aluminium oxide (Al_2O_3) is reduced to aluminium by the electrolysis of molten aluminium oxide.

The aluminium ions present in aluminium oxide go to the cathode and are reduced there to aluminium atoms.

Note: During electrolytic reduction of the molten salts, the metals are always liberated at the cathode.

Electrolysis can be performed in following medium:

(i) Aqueous medium: This is the most convenient and cheapest medium to conduct the electrolysis. However, the products formed should not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulfates.

(ii) Other solvent medium: several non aqueous solvents were uses for electrolysis.

(iii) Fused melts: Elements that are highly reactive with water and solvents are produced from electrolysis of fused melts. E.g. Na, Mg, Al etc...

for driving a reduction by coupling it through electrodes and external circuitry to a reactive or a physical process with a more negative ΔG . The free energy available from the external source can be assessed from the **potential difference** it produces across the electrodes using the thermodynamic relation

$$\Delta G = -nFE$$

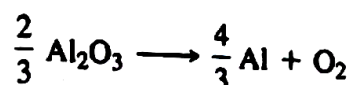
Therefor, total Gibb's energy change of the coupled internal and external process is

$$\Delta G + \Delta G_{\text{ext}} = \Delta G - nFE_{\text{ext}}$$

If the potential difference of external source is exceeds, $E_{\text{ext}} = \frac{\Delta G}{nF}$

The reaction is thermodynamically feasible and process occurs.

**Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C .
The reaction for decomposition is**



$\Delta G = +960 \text{ kJ}$ at 500°C .

Hence, the change in oxidation number of aluminium is 3 per mole. Since $4/3$ moles of Al are produced $n = 3 \times 4/3 = 4$

$$E_{\text{ext}} = \frac{960 \text{ KJ}}{4 \times 96.49 \text{ kcal/mol}} = 2.5 \text{ V}$$

A potential difference of at least 2.5 V must be applied to the oxide to bring about reduction.

Ref: Sohn, H. Y. (2001). Hydrometallurgical Principles. Encyclopedia of Materials: Science and Technology, pages 3976–3981

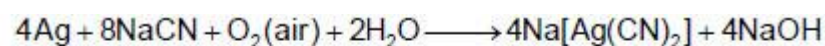
Hydrometallurgy: The use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials

Hydrometallurgy divided into three general areas:

- **Leaching**

The selective dissolution (lixiviation) of the metal constituent of an ore by suitable chemical reagents (mineral acid, base, sodium cyanide solution or chlorine in presence of water etc.) in aqueous medium

e.g. (i) Silver and Gold are leached from their native ores, with dilute solution of Sodium cyanide (NaCN) or Potassium cyanide (KCN) in presence of Oxygen (O₂) from air, when their soluble complex cyanides are obtained. The method is called Mac-Arthur Forest Cyanide process. Silver or Gold ore treated with NaCN to get water soluble 4Na[Ag(CN)₂] or 4Na[Au(CN)₂]



(ii) The isolation of Al from bauxite ore: Bauxite ore of Aluminium contains Silica (SiO₂), Iron oxides and Titanium oxides (TiO₂) as impurities. When the powdered bauxite ore is digested with concentrated solution of NaOH at about 473K-523K temperature and 35–36 bars of pressure. Al₂O₃ dissolves in the solution as Sodium aluminate & SiO₂ as Sodium silicate leaving the impurities behind.



(Alumina)

(sodium aluminate)

- **Solution concentration and purification**

After leaching, the leach liquor must normally undergo concentration of the metal ions that are to be recovered. Additionally, undesirable metal ions sometimes require removal.

- **Metal or metal compound recovery**

Metal recovery is the final step in a hydrometallurgical process. Metals are recovered from concentrated solution using suitable metal recovery step, such as chemical reduction, electrolysis, gaseous reduction, and precipitation.

For example, (i) a major target of hydrometallurgy is copper, which is conveniently obtained by electrolysis. Cu²⁺ ions reduce at **mild potentials** (electrolytic reduction), leaving behind other contaminating metals such as Fe²⁺ and Zn²⁺.

(ii) Silver (Ag) & Gold (Au) are recovered from their solutions by chemical reduction of 4Na[Ag(CN)₂] or 4Na[Au(CN)₂] by adding **zinc** which displaces them



Advantages:

1. More economical and environmentally friendlier (calcination and smelting is not required, this causes air pollution) with respect to other metallurgical process
2. This method operates at relatively low, often ambient, temperatures, with respect to some other method involved
3. Low grade ores can be treated with this method. E.g. Low-grade uranium ores, are being exploited on a limited basis in Texas by methods that involve pumping sodium carbonate (leachant for uranium ore) directly into the deposit without bringing the ore to the surface.
4. Hydrometallurgy is the only method some time *by-passes the mineral enrichment* operations for enriching ores, such as crushing, grinding, and flotation. For instance, ore may simply be fractured and treated in place by aqueous solutions at a considerable cost savings
5. Hydrometallurgical processes have the flexibility for treatment of complex ores and for production of a variety of by-product metals. Complex ores and concentrates in which a variety of recoverable metals are present can be effectively processed by hydrometallurgical routes.
6. This method has successfully separated closely related metals, such as individual rare earths (zirconium from hafnium, and niobium from tantalum), from their corresponding ores.
7. In hydrometallurgical plants, solutions and slurries generally are transferred easily in closed pipeline systems. In other cases, the sludge and molten slag (solid), gases such as SO_2 , As_2O_3 and other organic volatiles formed are not easily transported

Disadvantages:

1. Hydrometallurgical plants require sophisticated control schemes to maintain satisfactory operation.
2. There is no economic gain in processing a reasonably high-grade resource, with a hydrometallurgical one.
3. Engineering of hydrometallurgical plants is more complex and requires the full understanding of scale up relationships as well as processing requirements.
4. Hydrometallurgical processes can often generate significant amounts of liquid or solid wastes that may pose serious disposal problems.

Methods of purification of metals:

Kroll Process:

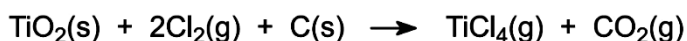
The Kroll Process

Most titanium is manufactured from rutile ores containing titanium dioxide using a lengthy four stage process:

- a) chlorination of TiO_2
- b) purification of TiCl_4
- c) reduction of TiCl_4 to titanium sponge
- d) processing of titanium sponge

(a) Chlorination of rutile

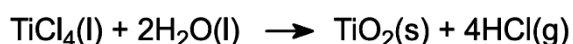
TiO_2 is thermally very stable and impossible to reduce using coke, CO, H_2 and even with electropositive metals. Conversion of TiO_2 into titanium(IV) chloride, makes production of titanium more viable, as the chloride is more readily reduced. The dry ore is fed into a chlorinator together with coke forming a fluid bed. Once the bed has been preheated, the heat of reaction with chlorine is sufficient to maintain the temperature at 1300 K:



(b) Purification of titanium(IV) chloride

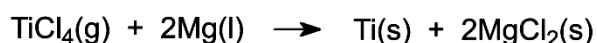
It is purified by distillation, The final product is pure (>99.9%) titanium(IV) chloride which can be used either to make titanium or oxidized to give titanium dioxide for pigments.

Storage tanks must be totally dry as the product undergoes rapid hydrolysis in the presence of water, generating dense white fumes of hydrogen chloride:



(c) Reduction of titanium(IV) chloride to titanium sponge

The reduction should conduct under the argon atmosphere, as Ti is highly reactive at this temperature even with nitrogen. Titanium(IV) chloride is a volatile liquid. It is heated to produce a vapour which is passed into a stainless steel reactor containing excess molten magnesium preheated to about 800 K. Exothermic reactions giving titanium(III) and titanium(II) chlorides cause a rapid temperature rise to about 1100 K. These chlorides undergo reduction slowly, so the temperature is raised to 1300 K to complete the reduction process. Even so, it is a lengthy process:



After 36-50 hours the reactor is removed from the furnace and allowed to cool for at least four days.

The unreacted magnesium and the chloride/titanium mixture is recovered, crushed and leached with dilute hydrochloric acid to remove magnesium chloride.

Alternatively, magnesium chloride, together with unreacted magnesium, is removed from the titanium by high temperature vacuum distillation. The magnesium chloride is electrolysed to generate magnesium for the reduction stage and the chlorine is recycled for the ore chlorination stage.

The titanium is purified by high temperature vacuum distillation. The metal is in the form of a porous granule which is called sponge. This may be processed on site, or sold on to other companies for conversion to titanium products.

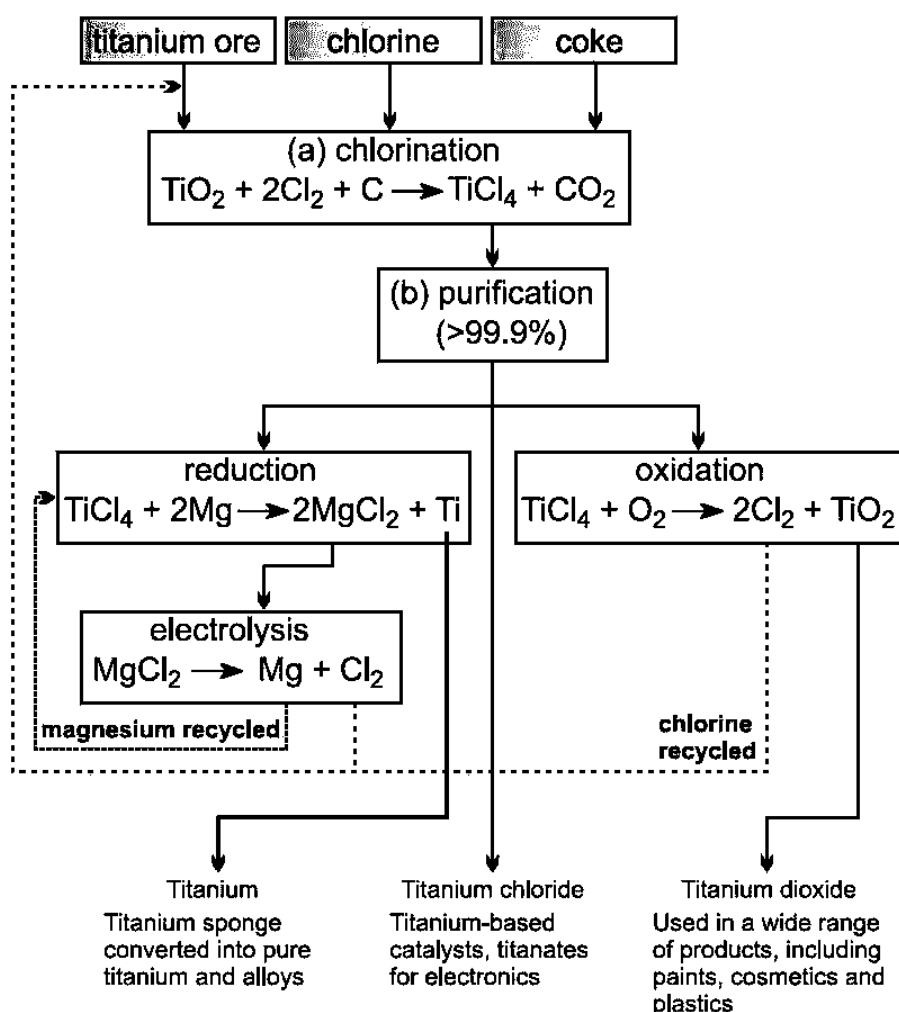


Figure Summary of the conversion of titanium ore into useful products.

(d) Processing of titanium sponge

As titanium sponge reacts readily with nitrogen and oxygen at high temperatures, the sponge must be processed in a vacuum or an inert atmosphere such as argon immediately.

Parting Process:

The gold obtained from its ore generally contaminated with silver, copper, lead and zinc. Lead and zinc are removed by the cupellation process while silver and copper are removed by parting process as described:

Parting use to be done with two different methods

- (i) parting with mineral acids such as sulfuric acid and nitric acid
- (ii) parting with chlorine gas

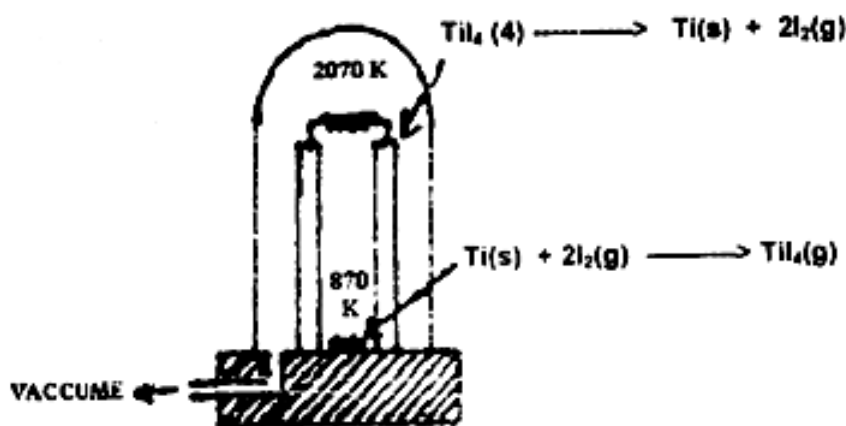
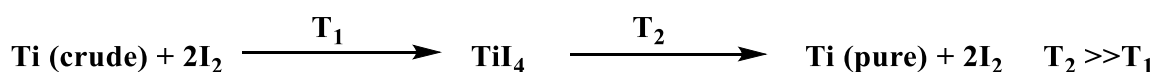
(i) Parting with Sulphuric Acid or Nitric Acid Principle behind this method is that, gold is not attacked either by sulphuric acid or by nitric acid, while copper and silver are dissolved. However, if the gold content is more than 25%, there is no effect of these acids on the impure sample having Cu and Ag. Therefore, the impure sample is alloyed with silver so as to reduce the gold content to about 25%. The alloyed sample is treated with boiling concentrated sulphuric acid or nitric acid. As a result, copper and silver are dissolved into acid solution while gold is left behind as insoluble and is fused with borax. Since this process reduces the gold content to 25%, the process is also known as **quartation**.

(ii) Parting with Chlorine The impure gold is fused with borax and dry chlorine gas is passed through it. The chlorine of lead and zinc are passed out as fumes while silver chloride forms a layer on the surface of fused gold. The gold remains unaffected as AuCl_3 is unstable at high temperatures. The silver chloride layer is skimmed off and the pure gold is tapped out and casted into ingots.

van Arkel–de Boer process (also known as iodide process or the crystal bar process): At first this method used for production of small quantities of ultra-pure titanium and zirconium. This process is based on the reversibility of a reaction between a metal and iodine. Formation of the metal iodide occurs at a relatively low temperature, and decomposition of the iodide occurs at a much higher temperature. It primarily involves the formation of the *metal iodides* and their subsequent *decomposition to yield pure metal*. This process was superseded commercially by the Kroll process

This method utilizes *chemical transport reaction. i.e. Crude metal* is heated to *low temperature* with a suitable substance so that the pure metal present in it may be converted into stable volatile compound leaving behind impurities. The compound so formed is then *decomposed by heating to high temperature* get the pure metal.

Accordingly, to purify crude titanium metal. Ti is heated with iodine to about 500K to form TiI_4 volatile compound. TiI_4 leaving behind the impurities. TiI_4 is further heated to 1700K when it decomposes to give pure titanium.



Purification occurs in this process mainly due to three reasons:

- (i) The impurities such as oxygen, nitrogen, and carbon present as oxide, nitride, and carbide present in the crude metal should not react with iodine at the temperature T_1 .
- (ii) Even if some of the impurities form their iodides at the lower temperature, they are too stable to decompose at the higher temperature, T_2
- (iii) some of the impurities, which are sufficiently volatile, do not remain in the high temperature zone, even if their iodine compounds are thermally decomposed.

The following conditions are strictly applicable for this iodide refining process described above,

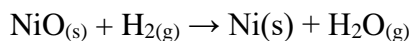
- (i) The metal should form volatile iodides

- (ii) Melting point of the metal must have higher than the dissociation temperatures of the corresponding iodide
- (iii) Volatile iodides are formed at manageable temperatures
- (iv) the iodides easily decompose at elevated temperatures
- (v) the vapor pressures of the metals are very low at the decomposition temperatures of the iodides

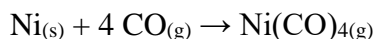
The Mond's process also known as the carbonyl process: this technique used for both extraction of nickel from ore and purification of nickel from crude.

This process converts nickel oxides into pure nickel in three steps

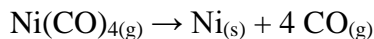
1. Nickel oxide treated with Syngas ($\text{H}_2 + \text{CO}$) at 473 K to give crude nickel, together with other impurities such as Fe, Co, etc....



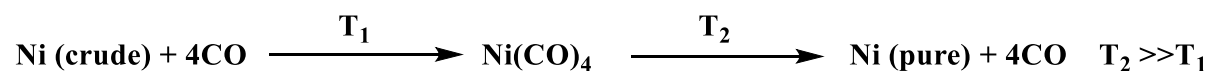
2. The crude nickel along with other impurities reacts with CO at ~323 K to form the gas nickel carbonyl, leaving the other impurities as solids.



3. The nickel carbonyl obtained in above process subjected to decompose at ~500 K, to get back nickel and carbon monoxide:



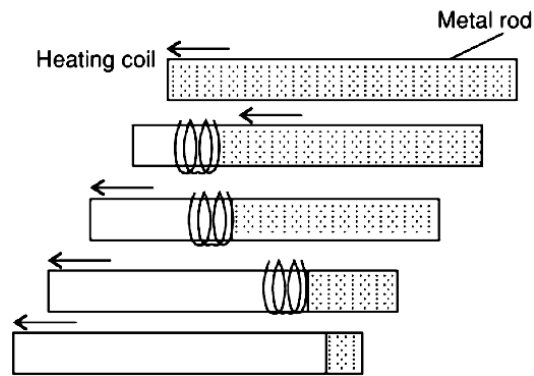
Steps 2 and 3 illustrate a chemical transport reaction, exploiting the properties that (1) carbon monoxide and nickel readily combine to give a volatile complex and (2) this complex degrades back to nickel and carbon monoxide at higher temperatures.



Process and conditions are almost similar to van Arkel-de method

Zone refining method:

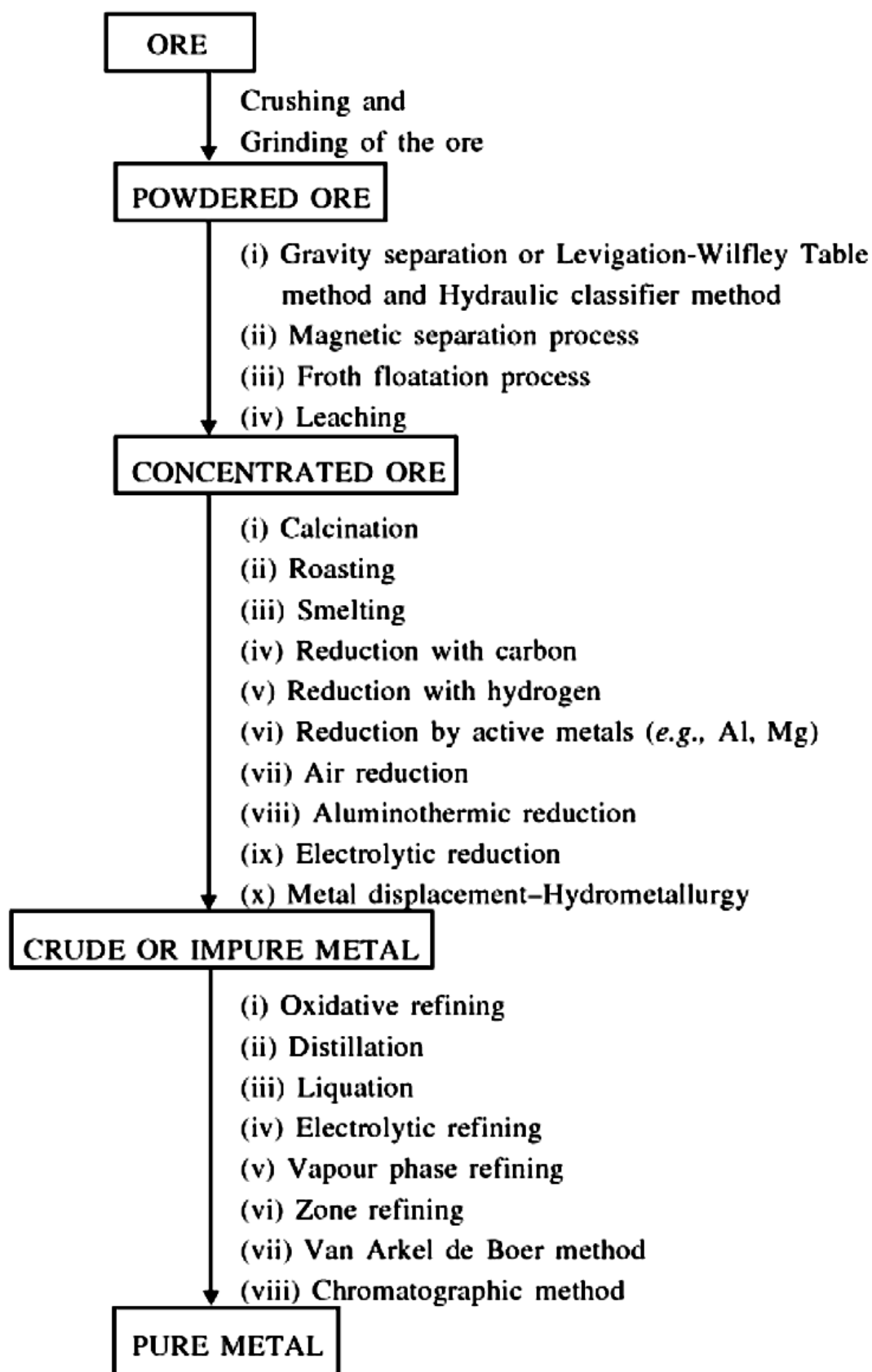
This method exploit the principle of fractional crystallization, that the impurities have greater solubility in the molten metal than in the solid metal. Therefore, as the impure molten metal rod solidifies partly, the impurities migrate to the molten zone of the rod. Ultrapure silicon, germanium, indium and gallium required for semiconducting industries are purified using this method with impurities in ppm level.



The rod form of the crude metal slowly moved across an electrical heating coil as shown in the figure, that melts the metal. The molten metal acting as solvent and impurities getting dissolved on it. When the rod comes out from the heating coil, it cools and the pure metal crystallizes in the colder emerging rod end, with the impurities migrating to the hot molten zone of the rod, which is still in the heating coil.

The crystal lattice formed on cooling does not accommodate the impurities easily. When the molten zone containing more impurities than the cold zone reaches the end of the rod, it is allowed to cool. The process of heating and cooling of the rod is repeated, to allow the migration of all the impurities to one end of the rod. Then, the impure rod end is cut off and discarded. The remaining metal has 99.99% purity.

Flow Sheet Diagram of Metallurgical Process



CONCEPT MAP

