

VOLUME - I

Metallurgy

FORMULAE TO REMEMBER

Metal	Ore	Composition	Metal	Ore	Composition
Aluminium	Bauxite	Al ₂ O ₃ .nH ₂ O		Zinc blende or Sphalerite	ZnS
	Diaspore	$Al_2Si_2O_5(OH)_4$	Zinc	Calamine	ZnCO ₃
	Kaolinite	Al ₂ O ₃		Zincite	ZnO
	Haematite	Fe ₂ O ₃		Galena	PbS
	Magnetite	Fe ₃ O ₄	Lead	Anglesite	PbSO ₄
-	Siderite	FeCO ₃		Cerrusite	PbCO ₃
Iron	Iron pyrite	FeS ₂	Tin	Cassiterite (Tin stone)	SnO ₂
	Limonite	Fe ₂ O ₃ .3H ₂ O		Silver glance (Argentite)	Ag ₂ S
Copper	Copper pyrite	CuFeS ₂		Pyrargyrite (Ruby silver)	Ag ₃ SbS ₃
	Copper glance	Cu ₂ S	Silver	Chlorargyrite (Horn Silver)	AgCl
	Cuprite	Cu ₂ O		Stefinite	Ag ₅ SbS ₄
	Malachite	CuCO ₃ .Cu(OH) ₂		Proustite	Ag ₃ AsS ₃
	Azurite	2CuCO ₃ .Cu(OH) ₂			

MUST KNOW DEFINITIONS

Mineral	:	A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc is called a mineral .
Ores	:	Minerals that contains a high percentage of metal, from which it can be extracted conveniently and economically are called ores .
Concentration of Ore	:	The preliminary step in metallurgical process is removal of these impurities. This removal process is known as concentration of ore .
Roasting	:	Roasting is the method, usually applied for the conversion of sulphide ores into their oxides. The concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.
Calcination	:	Calcination is the process in which the concentrated ore is strongly heated in the absence of air.

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Refining process : Removal of such impurities a process .		associated with the isolated crude metal is called refining			
		of variation of the standard Gibbs free energy of reaction for al oxides with temperature is called Ellingham diagram.			
Application of Ellingham diagram Electrolytic refining	 Ellingham diagram helps of temperature range for reduct In electrolytic refining of the Cathode : Pure metal Anode : Impure metal 				
PUB		eous solution of salt of the metal NTLY ASKED QUESTIONS			
_	Mark NDDECT A NSWED	 c) Electrochemical process d) Acid leaching [Ans. (a) Carbon reduction] 			
 c) Fe₂O₃.2H₂O 2. Roasting of sulphid colourless gas. Aqua The gas (A) is a) CO₂ b) SO₃ 3. Wolframite ore is seprocess of a) Smelting b) Calcination c) Roasting d) Electromagnetic 	Imposition $[HY. '19; May-'22]$ b) $Al_2O_3.nH_2O$ d) None of these $[Ans. (b) Al_2O_3.nH_2O]$ e ore gives the gas (A).(A) is aeous solution of (A) is acidic. $[FRT-'22]$ c) SO_2 d) H_2S $[Ans. (c) SO_2]$ eparated from tinstone by the $[PTA - 2; Mar-2020]$	 6. Extraction of gold and silver involves leaching with cyanide ion. Silver is later recovered by (NEET-'17) a) Distillation b) Zone refining c) Displacement with zinc d) liquation [Ans. (c) Displacement with zinc] 7. The following set of reactions are used in refining Zirconium [Aug-'21] Zr (impure) + 2I₂ - 523K → ZrI₄. ZrI₄ - 1800K → Zr (pure) + 2I₂ This method is known as a) Liquation b) Van Arkel process c) Zone refining d) Mond's process [Ans. (b) van Arkel process] 8. The incorrect statement among the following is 			
4. Which one of the	ne following ores is best th – floatation method? <i>[Govt.MQP_'19; FRT-'22]</i> b) Haematite d) Cassiterite <i>[Ans.</i> (c) Galena] om ZnO by <i>[FRT & July '22]</i>	 <i>[QY. '19; Sep-2020]</i> a) Nickel is refined by Mond's process. b) Titanium is refined by Van Arkel's process. c) Zinc blende is concentrated by froth floatation. d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution. [<i>Ans.</i> (d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution. 			

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9.	Which of the following reduction is not thermodynamically feasible? [<i>PTA</i> - 3] a) $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$	16.	(a) Mond process(b) Electrolytic refining(c) Van-Arkel process(d) Liquation
	b) $Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al$ c) $3TiO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Ti$ d) none of these [Ans. (b) $Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al]$	17.	[Ans. (c) Van-Arkel process] Considering Ellingham diagram, which of the following metals can be used to reduce aluminas (NEET-'18)
10.	Sulphide ores of metals are usually concentrated by froath floatation process. Which one of the following sulphide ore offers an exception and is concentrated by chemical leaching. $[PTA - 4]$ a) Argentite b) galena	1.	a) Fe b) Cu c) Mg d) Zn [Ans. (c) Mg] 2 MARKS What are the differences between minerals and ores? [QY_'19; Sep-2020; FRT, May-'22]
	c) Copper pyrites d) Sphalerite	Ans.	
11	[Ans. (a) Argentite]		Minerals Ores
11.	Which method of purification represented by the equation? [PTA - 5] $Ti(impure) + 2l_2 \xrightarrow{550K} Til_4$ $\xrightarrow{1800K} Ti(pure) + 2I_2$		A naturally occurring Ore contains a high substance obtained by percentage of metal, mining which contains the metal in free state extracted conveniently or in the form of compounds.
	a) Cupellation b) Zone refining		All minerals are not ores All ores are Minerals
	c) Van - Arkel method		It contains a low It contains a high
	d) Mond's process		percentage of metal.
	[Ans. (c) Van - Arkel method]		Ex : Mineral of Al is Ex : Ore of Al is bauxite
12.	The process of converting hydrated aluminia		bauxite and china clay
	into anhydrous alumina is called.[PTA - 6]a) Roastingb) Smeltingc) Auto-reductiond) Calcination	2.	Which type of ores can be concentrated by froth floatation method? Give two examples for such ores. <i>[FRT-'22]</i>
	[Ans. (d) Calcination]	Ans.	(i) Sulphide ores can be concentrated by froth
13.	Elements like silicon and Germanium to be used		floatation method.
	as a semiconductor is purified by		(<i>ii</i>) Ex : Lead sulphide galena (PbS) and zind blende (ZnS).
	a) heating under vaccum [PTA - 1]b) Van - Arkel method	3.	Describe a method for refining nickel. [PTA - 3; May-'22]
	c) Zone refining	Ans.	Mond process for refining nickel :
14	d) Electrolysis [Ans. (c) Zone refining] The metal which is used in packing metarial for		(i) The impure nickel is heated in a stream of
± 1°•	food items : [Sep-2020]		carbon monoxide at around 350K.
	(a) Zn (b) Zr (c) Al (d) Au		<i>(ii)</i> The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl.
	[Ans. (c) Al]		(<i>iii</i>) The solid impurities are left behind.
15.	CaO + SiO ₂ \rightarrow ? [FRT-'22] (flux) (gangue) (slag)		$\operatorname{Ni}_{(s)} + 4\operatorname{CO}_{(g)} \xrightarrow{350 \text{ K}} [\operatorname{Ni}(\operatorname{CO})_4]_{(g)}$
	(a) CaSiO ₂ (b) CaSiO ₃		(iv) On heating the nickel tetracarbonyl around
	$(a) \operatorname{Call}_2$ $(b) \operatorname{Call}_3$		460K, the complex decomposes to give pure
	(c) Ca_2SiO_4 (d) Ca_3SiO_4		metal.

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4. What is the role of graphite rods in the electro metallurgy of aluminium? *[PTA - 1]*

- Ans. (i) Graphite rods act as **anode** during electrolytic reduction of alumina.
 - At anode, O₂ gas is produced which react with *(ii)* the carbon of anode (rods) to produce CO_2 gas.
 - (iii) So these graphite rods are consumed slowly and need to be replaced from time to time.

Define roasting. **5**. [PTA - 4]

Ans. In roasting, the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.

$$2Pbs + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2 \uparrow$$

6. Explain calcination with an example. [PTA - 4]

- Ans. (i) Calcination is the process in which the concentrated ore is strongly heated in the absence of air.
 - (*ii*) During this process, the water of crystallisation present in the hydrated oxide escapes as moisture.
 - (iii) Any organic matter (if present) also get expelled leaving behind a porous ore.
 - (iv) This method can also be carried out with a limited supply of air.
 - (v)During calcination of carbonate ore, carbon dioxide is expelled

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2\uparrow$$

5 MARKS

Explain zone refining process with an example. 1. [PTA - 6; Mar-2020; FRT-'22]

- This method is based on the Fractional Ans. (i) Crystallisation. The impure metal is melted and allowed to solidify, the impurities prefer to remain in the molten region.
 - The impure metal is taken in the form of a rod. *(ii)*
 - When the metal rod is heated with a heater the (iii) metal melts.
 - (iv) The heater is slowly moved from one end to the other end.
 - The impurity dissolves in the molten zone. (v)
 - (vi) When the heater moves, the molten zone also moves.
 - (vii) This process is repeated again and again to get pure metal.

(viii) The process is carried in an inert gas atmosphere to prevent the oxidation of metals.

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Example :

Ans. (i)

Elements such as Germanium (Ge), Silicon (Si) and Galium (Ga) are refined using this process.

2. Give the uses of zinc.

- [PTA 4] Metallic zinc is used in galvanising metals
- such as iron and steel structures to protect them from rusting and corrosion.
 - *(ii)* Zinc is also used to produce die-castings in the automobile, electrical and hardware industries
 - (iii) Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment.
 - (iv) Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.
 - (v)Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion.

3. Explain the electrometallurgy of aluminium. [Govt.MQP '19]

Ans. Hell - Herold Process :

Cathode : Iron tank lined with carbon

- Anode : Carbon blocks
- Electrolytes : 20% solution of alumina obtained from bauxite + Molten cryolite + Calcium chloride (lowers the melting point of the mixture)

Temperature: Above 1270 K

Ionisaiton of alumina

$$Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$$

Reaction at cathode

 $2Al^{3+}$ (melt) + $6e^{-} \longrightarrow 2Al_{(1)}$

Reaction at anode

$$6O^{2-}$$
 (melt) $\longrightarrow 3O_2 + 12e^{-1}$

Since carbon acts as anode the following (i) reaction takes place.

$$C_{(s)} + O^{2-} (melt) \longrightarrow CO + 2e^{-}$$

$$C_{(s)} + 2O^{2-} \text{ (melt)} \longrightarrow CO_2 + 4e^{-}$$

- (ii) During electrolysis anodes are slowly consumed due to the above two reactions.
- (iii) Aluminium is formed at the cathode and settles at the bottom.

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- (iv) Net electrolysis reaction is $4Al^{3+} (melt) + 6O^{2-} (melt) + 3C_{(s)}$ $\longrightarrow 4Al_{(l)} + 3CO_{2(g)}$
- 4. Describe the role of the following in the process mentioned.
 - (i) Silica in the extraction of copper.
 - (ii) Cryolite in the extraction of aluminium. $[QY_1]$
 - (iii) Iodine in the refining of Zirconium. [QY_'19]

(iv) Sodium cyanide in froth floatation.

- *Ans. (i)* Silica, is used as an acidic flux is used to remove slag during the process of roasting.
 - (ii) Lowers the melting point to 1173K and improves the electrical conductivity of the aluminium.
 - *(iii)* To form a volatile compound which on further heating decomposes to give pure Zn.
 - *(iv)* Sodium cyanide is used as an depressing agent in froth flotation. It prevents other metal sulphides coming to the froth.

For Example, when impurities such as ZnS is present in galena (PbS), sodium cyanide (NaCN) is added to depresses the flotation property of ZnS by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of zinc sulphide.

- 5. Explain the principle of electrolytic refining with an example. [HY-'19; July-'22]
- *Ans. (i)* Electrolytic refining is carried out in an electrolytic cell.
 - (ii) Anode : Impure metal
 Cathode : Thin strips of pure metal
 Electrolyte : Aqueous solution of the salts of the metal.
 - (*iii*) The metal of interest dissolves from the anode, pass into the solution while the same amount of metal ions from the solution will be deposited at the cathode.
 - *(iv)* During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.
 - (v) Electrolytic refining of silver as an example.Cathode : Pure silverAnode : Impure silver rods

Electrolyte : Acidified aqueous solution of silver nitrate.

(vi) When a current is passed through the electrodes the following reactions will take place Reaction at anode

 $Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + 1e^{-}$

Reaction at cathode

$$Ag^{+}_{(aa)} + 1e^{-} \longrightarrow Ag_{(s)}$$

- (vii) During electrolysis, at the anode the silver atoms lose electrons and enter the solution.
- (*viii*) The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode.
- 6. Explain electrolytic refining of silver.

- Ans. (i) Electrolytic refining of silver as an example.
 Cathode : Pure silver
 Anode : Impure silver rods
 Electrolyte : Acidified aqueous solution of
 - (ii) When a current is passed through the electrodes the following reactions will take place

Reaction at anode

$$Ag_{(s)} \longrightarrow Ag^{+}_{(aa)} + 1e^{-}$$

Reaction at cathode

$$Ag^{+}_{(aa)} + 1e^{-} \longrightarrow Ag_{(s)}$$

- 7. Explain extraction of copper from copper pyrites. [PTA 5]
- Ans. (i) In this method, a flux (a chemical substance that forms an easily fusible slag with gangue) and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating at an elevated temperature (above the melting point of the metal) in a smelting furnace.
 - *(ii)* For example the oxide of iron can be reduced by carbon monoxide as follows.

$$\operatorname{Fe_2O}_{3(s)} + 3\operatorname{CO}_{(g)} \longrightarrow 2\operatorname{Fe}_{(s)} + 3\operatorname{CO}_{2(g)\uparrow}$$

(*iii*) In this extraction, a basic flux, limestone (CaO) is used. Since the silica gangue present in the ore is acidic in nature, the limestone combines with it to form calcium silicate (slag).

$$\begin{array}{c} \operatorname{CaO}_{(s)} + \operatorname{SiO}_{2(s)} \longrightarrow \operatorname{CaSiO}_{3(s)} \\ \\ \operatorname{Flux} & \operatorname{Gangue} & \operatorname{Slag} \end{array}$$

(iv) In the extraction of copper from copper pyrites, the concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux.

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(vi) The remaining metal sulphides Cu_2S and FeS are mutually soluble and form a copper matte. $2CuFeS_{2(2)} + O_{2(2)} \longrightarrow$

$$2FeS_{(l)} + Cu_2S_{(l)} + SO_{2(g)}$$

$$2FeS_{(l)} + 3O_{2(g)} \longrightarrow 2FeO_{(l)} + 2SO_{2(g)}$$

$$FeO_{(s)} + SiO_{2(s)} \longrightarrow FeSiO_{3(s)}$$
Flux Gangue Slag

- (*vii*) The matte is separated from the slag and fed to the converting furnace.
- (*viii*) During conversion, the FeS present in the matte is first oxidised to FeO.
- (*ix*) This is removed by slag formation with silica.
- (x) The remaining copper sulphide is further oxidised to its oxide which is subsequently converted to metallic copper.

$$2\operatorname{Cu}_{2}\operatorname{S}_{(l,s)} + 3\operatorname{O}_{2(g)} \longrightarrow 2\operatorname{Cu}_{2}\operatorname{O}_{(l,s)} + 2\operatorname{SO}_{2(g)}$$
$$2\operatorname{Cu}_{2}\operatorname{O}_{(l)} + \operatorname{Cu}_{2}\operatorname{S}_{(l)} \longrightarrow 6\operatorname{Cu}_{(l)} + \operatorname{SO}_{2(g)}$$

- (*xi*) The metallic copper is solidified and it has blistered appearance due to evolution of SO₂ gas formed in this process. This copper is called blistered copper.
- 8. Explain how gold ore is leached by cyanide process [Govt. MQP_'19]
- Ans. (i) Gold is usually found in native state.
 - (*ii*) The leaching process is intended to concentrate the gold metal.

$$4\operatorname{Au}_{(s)} + 8\operatorname{NaCN}_{(aq)}^{-} + 2\operatorname{H}_{2}\operatorname{O}_{(aq)} + \operatorname{O}_{2(g)} \longrightarrow$$
$$4\operatorname{Na}\left[\operatorname{Au}(\operatorname{CN})_{2}\right]_{(aq)}^{-} + 4\operatorname{NaOH}_{(aq)}^{-}$$

 $2Na [Au(CN)_2] + Zn -$

 $Na_2[Zn(CN)_4] + 2Au \downarrow$

(*iii*) In this reaction, gold is reduced to its elemental state and the process is called cementation.

9. How is Ni purified by Mond process?

[FRT-'22]

Ans. The impure nickel is heated in a stream of carbon monoxide at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

Ni (s) + 4 CO (g) \longrightarrow [Ni(CO)₄] (g)

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

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10. Write a note on gravity separation method. [May-'22]

- Ans. (i) In gravity separation method, the ore having high specific gravity is separated from the gangue that has low specific gravity by washing with running water.
 - (*ii*) Ore is crushed to a finely powdered form and treated with rapidly flowing current of water.
 - *(iii)* During this process the lighter gangue particles are washed away by the running water.
 - (*iv*) This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite (Fe_2O_3), tin stone (SnO_2) etc.

11. How is acid leaching done for the sulphide ores? (or) Expalin Acid Leaching with an example.

[July-'22]

Ans. (i) Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.

$$2ZnS(s) + 2H_2SO_4(aq) + O_2(g) \longrightarrow$$
$$2ZnSO_4(aq) + 2S(s) + 2H_2O$$

(*ii*) In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

12. How are ores concentrated by magnetic separation method? *[FRT-'22]*

- *Ans. (i)* This method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities.
 - *(ii)* For example tin stone can be separated from the wolframite impurities which is magnetic.
 - (*iii*) Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non magnetic siliceous impurities. The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one is magnetic.
 - (iv) The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it as shown in the figure.

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