

Class XII
Chemistry
Ch 6: General Principles & Processes
Of Isolation of Elements

Top concepts:

1. Minerals: The naturally occurring chemical substances in the earth's crust which are obtained by mining are known as minerals. Metals may or may not be extracted profitably from them.
2. Ores: The rocky materials which contain sufficient quantity of mineral so that the metal can be extracted profitably or economically are known as ores.
3. Gangue: The earthy or undesirable materials present in ore are known as gangue.
4. Metallurgy: The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.
5. Chief Ores and Methods of Extraction of Some Common Metals:

| Metals | Occurrence | Extraction Method | Remark |
|-----------|---|---|---|
| Sodium | Rock salt: NaCl Feldspar: $\text{Na}_3\text{AlSi}_3\text{O}_8$ | Electrolysis of fused NaCl or NaCl/ CaCl_2 | Sodium is highly reactive, it reacts with water |
| Copper | Copper pyrites: CuFeS_2 Malachite: $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ Cuprite: Cu_2O Copper glance: Cu_2S | Roasting of sulphide partially and reduction $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$ | It is self reduction in a specially designed converter. Sulphuric acid leaching is also employed. |
| Aluminium | Bauxite: $\text{AlO}_x(\text{OH})_{3-2x}$ where $0 < x < 1$ Cryolite: Na_3AlF_6 Kaolinite: $[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5]$ | Electrolysis of Al_2O_3 dissolved in molten cryolite or in Na_3AlCl_6 | A good source of electricity is needed in the extraction of Al |
| Zinc | Zinc blende or Sphalerite: ZnS Zincite: ZnO Calamine: ZnCO_3 | Roasting and then reduction with C | The metal may be purified by fractional distillation. |
| Lead | Galena: PbS | Roasting of the sulphide ore and then reduction of the oxide | Sulphide ore is concentrated by froth floatation process |
| Silver | Argentite: Ag_2S | Sodium cyanide leaching of the sulphide ore and finally replacement of Ag by Zn | It involves complex formation and displacement |

| | | | |
|------|---|--|---|
| Gold | Native, small amounts in many ores such as those of copper and silver | Cyanide leaching, same as in case of silver | Gold reacts with cyanide to form complex |
| Iron | Haematite: Fe_2O_3 Magnetite: Fe_3O_4 Siderite: FeCO_3 Iron pyrites: FeS_2 | Reduction with the help of CO and coke in blast furnace. | Limestone is added as flux which removes SiO_2 as calcium silicate (slag) floats over molten iron and prevents its oxidation. Temperatures approaching 2170 K is required. |

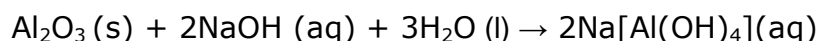
6. Steps of metallurgy:
 - a. Concentration of ore
 - b. Conversion of concentrated ore to oxide
 - c. Reduction of oxide to metal
 - d. Refining of metal
7. Concentration of ore: The process of removal unwanted materials like sand, clay, rocks etc from the ore is known as concentration, ore – dressing or benefaction. It involves several steps which depend upon physical properties of metal compound and impurity (gangue). The type of metal, available facilities and environmental factors are also taken into consideration.
8. Hydraulic washing (or gravity separation): It is based on difference in densities of ore and gangue particles. Ore is washed with a stream of water under pressure so that lighter impurities are washed away whereas heavy ores are left behind.
9. Magnetic separation: This method is based on the difference in magnetic and non – magnetic properties of two components of ore (pure and impure). This method is used to remove tungsten ore particles from cassiterite (SnO_2). It is also used to concentrate magnetite (Fe_3O_4), chromite (FeCr_2O_4) and pyrolusite (MnO_2) from unwanted gangue.
10. Froth Floatation Process: The principle of froth floatation process is that sulphide ores are preferentially wetted by the pine oil, whereas the gangue particles are wetted by the water. Collectors are added to

enhance the non-wettability of the mineral particles. Examples are pine oil, fatty acids and xanthates are added to it. Froth stabilizers are added to stabilize the froth. Examples are cresols, aniline. If two sulphide ores are present, it is possible to separate the two sulphide ores by adjusting proportion of oil to water or by adding depressants. For example- In the case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to froth but allows PbS to come with the froth.

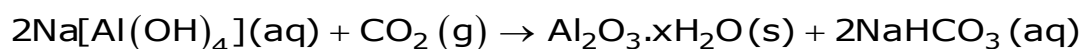
11. Leaching (Chemical separation): It is a process in which ore is treated with suitable solvent which dissolves the ore but not the impurities.

12. Purification of Bauxite by Leaching: Baeyer's process:

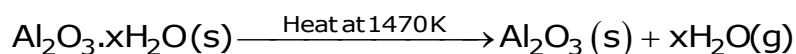
Step 1:



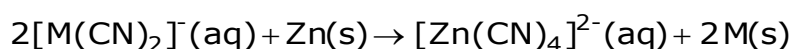
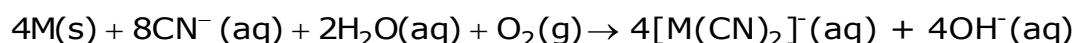
Step 2:



Step 3:



13. Concentration of Gold and Silver Ores by Leaching:



Where :

[M = Ag or Au]

14. Conversion of ore into oxide: It is easier to reduce oxide than sulphide or carbonate ore. Therefore, the given ore should be converted into oxide by suitable method:

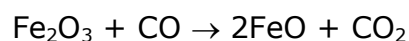
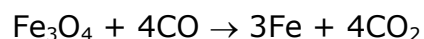
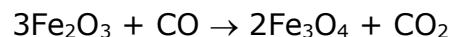
| Roasting | Calcination |
|---|--|
| It is a process in which ore is heated in a regular supply of air at a temperature below melting point of the metal so as to convert the given ore into oxide | It is a process of heating ore in limited supply of air so as to convert carbonate ores into oxides. |

| | |
|--|--|
| ore. | |
| Sulphide ores are converted into oxide by roasting | Carbonate ores are converted into oxide by roasting |
| It is also used to remove impurities as volatile oxides | It is also used to remove moisture and volatile impurities |
| E.g.: $2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2$ | E.g.: $\text{CaCO}_3 \xrightarrow{\text{heat}} \text{CaO} + \text{CO}_2$ |

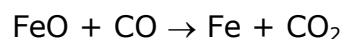
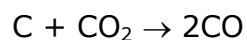
15. Reduction of oxide to metal: The process of converting metal oxide into metal is called reduction. It needs a suitable reducing agent depending upon the reactivity or reducing power of metal. The common reducing agents used are carbon or carbon monoxide or any other metals like Al, Mg etc.
16. Thermodynamic principles of metallurgy: Some basic concepts of thermodynamics help in understanding the conditions of temperature and selecting suitable reducing agent in metallurgical processes:
- Gibbs free energy change at any temperature is given by $\Delta G = \Delta H - T\Delta S$ where ΔG is free energy change, ΔH is enthalpy change and ΔS is entropy change.
 - The relationship between ΔG^\ominus and K is $\Delta G^\ominus = -2.303 RT \log K$ where K is equilibrium constant. $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, T is temperature in Kelvin.
 - A negative ΔG means +ve value of K i.e., products are formed more than the reactants. The reaction will proceed in forward direction.
 - If ΔS is +ve, on increasing temperature the value of $T\Delta S$ increases so that $T\Delta S > \Delta H$ and ΔG will become negative.
17. Coupled reactions: If reactants and products of two reactions are put together in a system and the net ΔG of two possible reactions is -ve the overall reaction will take place. These reactions are called coupled reactions.

18. Ellingham diagrams: The plots between $\Delta_f G^\ominus$ of formation of oxides of elements vs. temperature are called Ellingham diagrams. It provides a sound idea about selecting a reducing agent in reduction of oxides. Such diagrams help in predicting the feasibility of a thermal reduction of an ore. ΔG must be negative at a given temperature for a reaction to be feasible.
19. Limitations of Ellingham Diagrams: It does not take kinetics of reduction into consideration, i.e., how fast reduction will take place cannot be determined.
20. Reduction of iron oxide in blast furnace: Reduction of oxides takes place in different zones.

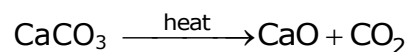
At 500 – 800 K (lower temperature range in blast furnace)



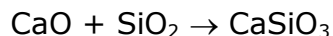
At 900 – 1500 K (higher temperature range in blast furnace)



Limestone decomposes to CaO and CO_2



Silica (impurity) reacts with CaO to form calcium silicate which forms slag. It floats over molten iron and prevents oxidation of iron.



Calcium silicate

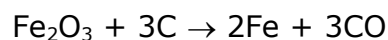
(Slag)

21. Types of iron:

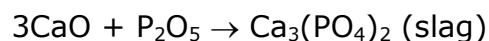
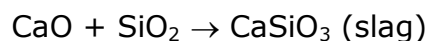
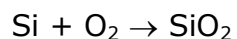
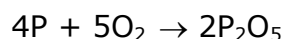
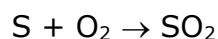
- a. Pig iron: The iron obtained from blast furnace is called pig iron. It is impure form of iron contains 4% carbon and small amount of S, P, Si and Mn. It can be casted into variety of shapes.

- b. Cast iron: It is made by melting pig iron with scrap iron and coke using hot air blast. It contains about 3% of carbon content. It is extremely hard and brittle.
- c. Wrought iron: It is the purest form of commercial iron. It is also called malleable iron.

It is prepared by oxidative refining of pig iron in reverberatory furnace lined with haematite which oxidises carbon to carbon monoxide.



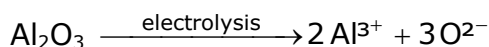
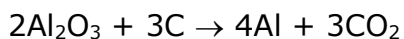
The substance which reacts with impurity to form slag is called flux e.g. limestone is flux.



The metal is removed and freed from slag by passing through rollers.

22. Electrolytic Reduction (Hall – Heroult Process): Purified bauxite ore is mixed with cryolite (Na_3AlF_6) or CaF_2 which lowers its melting point and increases electrical conductivity. Molten mixture is electrolysed using a number of graphite rods as anode and carbon lining as cathode.

The graphite anode is useful for reduction of metal oxide to metal.

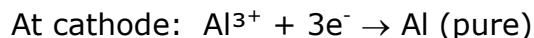
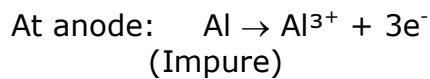


At cathode: $\text{Al}^{3+} \text{ (melt)} + 3\text{e}^- \rightarrow \text{Al} \text{ (l)}$

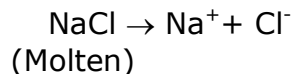
At anode: $\text{C(s)} + \text{O}^{2-} \text{ (melt)} \rightarrow \text{CO (g)} + 2\text{e}^-$

$\text{C(s)} + 2\text{O}^{2-} \text{ (melt)} \rightarrow \text{CO}_2 \text{ (g)} + 4\text{e}^-$

Graphite rods get burnt forming CO and CO_2 . The aluminium thus obtained is refined electrolytically using impure Al as anode, pure Al as cathode and molten cryolite as electrolyte.

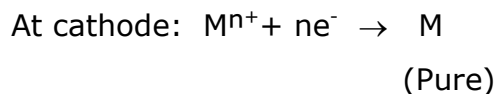
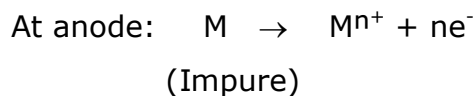


23. Electrolysis of molten NaCl:



Thus sodium metal is obtained at cathode and Cl_2 (g) is liberated at anode.

24. Refining: It is the process of converting an impure metal into pure metal depending upon the nature of metal.
25. Distillation: It is the process used to purify those metals which have low boiling points, e.g., zinc, mercury, sodium, potassium. Impure metal is heated so as to convert it into vapours which changes into pure metal on condensation and is obtained as distillate.
26. Liquation: Those metals which have impurities whose melting points are higher than metal can be purified by this method. In this method, Sn metal can be purified. Tin containing iron as impurities heated on the top of sloping furnace. Tin melts and flows down the sloping surface where iron is left behind and pure tin is obtained.
27. Electrolytic refining: In this method, impure metal is taken as anode, pure metal is taken as cathode, and a soluble salt of metal is used as electrolyte. When electric current is passed, impure metal forms metal ions which are discharged at cathode forming pure metal.



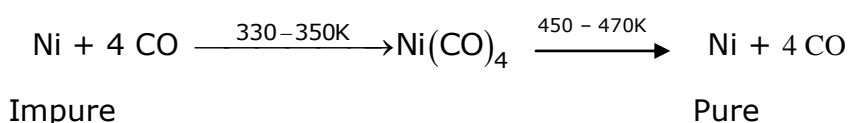
28. Zone refining: It is based on the principle that impurities are more soluble in the melt than in the solid state of the metal.

The impure metal is heated with the help of circular heaters at one end of the rod of impure metal. The molten zone moves forward along with

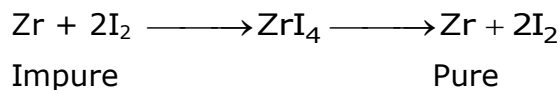
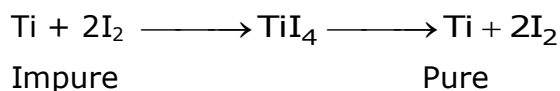
the heater with impurities and reaches the other end and is discarded. Pure metal crystallizes out of the melt.

The process is repeated several times and heater is moved in the same direction. It is used for purifying semiconductors like B, Ge, Si, Ga and In.

29. Vapour phase refining: Nickel is purified by Mond's process. Nickel, when heated in stream of carbon monoxide forms volatile $\text{Ni}(\text{CO})_4$ which on further subjecting to higher temperature decomposes to give pure metal.



30. van- Arkel method: It is used to get ultra pure metals. Zr and Ti are purified by this process. Zr or Ti are heated in iodine vapours at about 870 K to form volatile ZrI_4 or TiI_4 which are heated over tungsten filament at 1800K to give pure Zr or Ti.



31. Chromatographic method: It is based on the principle of separation or purification by chromatography which is based on differential adsorption on an adsorbent. In column chromatography, Al_2O_3 is used as adsorbent. The mixture to be separated is taken in suitable solvent and applied on the column. They are then eluted out with suitable solvent (eluant). The weakly adsorbed component is eluted first. This method is suitable for such elements which are available only in minute quantities and the impurities are not very much different in their chemical behaviour from the element to be purified.