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2021

Unit 3 General Principles and Processes of Isolation of Elements | p-Block Elements (Group 15 to 18)

General Principles and Processes of Isolation of Elements

A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry.

METALLURGY

The entire scientific and technological processes used for isolation of metal from its ores is called metallurgy.

Elements Modes of Metals

Native state

Least reactive elements like noble gases and noble metals occur in free state or native state.

Combined state

Highly reactive elements like fluorine, chlorine, sodium, etc. are found in combined state.

Minerals

Naturally occurring chemical substances in the earth's crust obtainable by mining.

Ores

The minerals from which we can obtain metal profitably and easily.

METALLURGICAL PROCESSES

- Crushing and grinding of the ore: Involves the breaking of huge lumps into small pieces using crushers or grinders which in turn reduced to fine powder using ball or stamp mill.
- Concentration of ore: Involves the removal of gangue from ore.

The different methods used in this process are:

Hydraulic washing: Based on the difference in the specific gravities of the gangue and the ore particles. Therefore, heavier ore particles settle down while lighter impurities are washed away. For example, oxide ores like haematite, tinstone and native ores of Au, Ag, etc.

Electromagnetic separation: Based on the difference in magnetic properties of the gangue and ore particles. Therefore, magnetic particles fall nearer to the roller while non-magnetic particles fall farther off. For example, magnetite (Fe₃O₄), haematite (Fe₂O₃), wolframite (FeWO₄), Froth floatation process: Based on the difference in wetting properties of gangue and ore particles. Therefore, ore particles rise to the surface in the form of froth and impurities remain in water. For example, sulphide ores.

Leaching: Based on the difference in chemical properties of gangue and ore particles. Used for extraction of Au, Ag (Mac Arthur Forest cyanide process) and pure alumina from bauxite ore (Baeyer's process).

chromite (FeO·Cr2O3), etc.

Extraction and isolation of metals: Involves extraction of metal in free state from concentrated ore. The following two chemical processes used are:

Based on

nature of ores

and impurities

present

- · Calcination: Process of heating the ore strongly below its melting point either in the absence of air or in the limited supply. e.g., carbonate and hydrated oxide ores.
- · Roasting: Process of heating the ore strongly below the melting point in a sufficient supply of air to bring about its oxidation and remove volatile impurities. e.g., sulphide ores.

Oxidation or de-electronation process

> Reduction process

Reduction of calcinated or roasted ore to metal using reducing agent. For example,

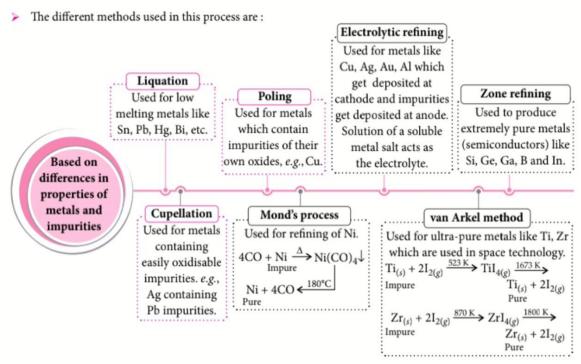
- Carbon or carbon monoxide is used for oxides of Fe, Cu, Zn, Mg, Co, etc.
- Electropositive metals like Na, Al, Mg or hydrogen are used for reduction of ores of Mn, Cr, Ti, Mo, W, etc.
- Water gas is used for nickel ores.
- Auto-reduction process is used for ores of Pb, Hg, Cu, etc.
- · Electrolytic reduction is used for highly electropositive metals.
- Hydrometallurgy or displacement method is used for Ag, Au, etc.



Extraction of cleaner copper with energy capture!

In February 2016, a toxin-free method for extraction of copper from raw ore and other procedures using molten salts have been developed. Recent method involves the chemical processes that produce huge mountains of waste mine tailings and lake-size waste water collections, accumulating high levels of toxins such as arsenic, cadmium and sulphuric acid. But latest method works by heating ore using molten salts to temperatures exceeding 1500°F such that copper is separated from the ore without use of water and dangerous chemicals. The technology also allows for the collection of surplus heat and using it to power steam turbines and generators. These technologies could really shift the paradigm with cleaner, more efficient methods for both mining and energy storage.

Refining of metals: Involves the purification of crude metals by removing the impurities present in it.



THERMODYNAMIC PRINCIPLES OF METALLURGY

- Thermodynamic principles:
 - With the help of thermodynamics, the temperature conditions and suitable reducing agents in the metallurgical processes can be decided.
 - Gibb's Helmholtz equation ($\Delta G^{\circ} = \Delta H^{\circ} T\Delta S^{\circ}$), is used to check the feasibility of a reaction.
 - ΔG° < 0 (Spontaneous reaction)
- Ellingham diagram: The graphical representation of Gibbs free energy change vs absolute temperature for a process is known as Ellingham diagram.

The ΔG° vs T graphs are straight lines unless the materials melt or vaporise (i.e., change from solid \rightarrow liquid or from liquid \rightarrow gas).

Salient features

Metal oxide with lower value of ΔG° is more stable than a metal oxide with higher ΔG° .

The coupling or combination of oxidation and reduction reactions helps in interpreting whether the given reducing agent can be useful or not. All the ΔG° vs T lines have slopes upwards because ΔG° becomes less and less negative with increase in temperature.

p-Block Elements (Group 15 to 18)

GROUP 15 ELEMENTS (PNICTOGENS)

Electronic configuration: N(7) - [He] $2s^22p^3$; P(15) - [Ne] $3s^23p^3$; As(33) - [Ar] $3d^{10}4s^24p^3$; Sb(51) - [Kr] $4d^{10}5s^25p^3$; **Bi(83)** - [Xe] $4f^{14}5d^{10}6s^26p^3$; **Mc(115)** - [Rn] $5f^{14}6d^{10}7s^27p^3$

PHYSICAL PROPERTIES

Physical state and metallic character:

N2 (unreactive gas), P4 (solid non-metal), As₄ and Sb₄ (solid metalloids), Bi (solid metal), Mc (Radioactive)

Atomicity: Nitrogen (diatomic gaseous molecule), phosphorus, arsenic, antimony (discrete tetratomic tetrahedral molecules).

Thermal and electrical conductivity: Increase down the group, as delocalisation of electrons increases.

Allotropy: Nitrogen (α and β -Nitrogen), phosphorus (white, red, scarlet, violet, α-black, β-black), arsenic (grey, yellow, black) antimony (metallic, yellow, explosive).

Atomic radioactive : Increase down the group, smaller than that of group 14 elements due to increased nuclear charge.

Melting and boiling points : M.pt. increases from N to As and then decreases whereas b. pt. increases from N to Sb and decreases very slightly.

Ionisation enthalpy: Decreases regularly down the group due to increase in size.



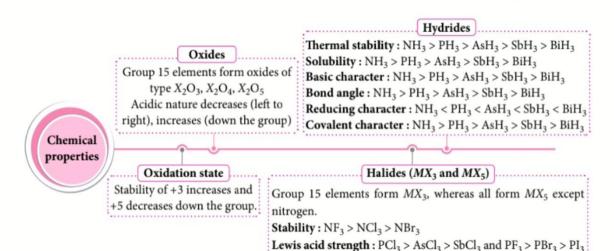
Group 15

Elements

 (ns^2np^3)

Decreases down the group.

CHEMICAL PROPERTIES



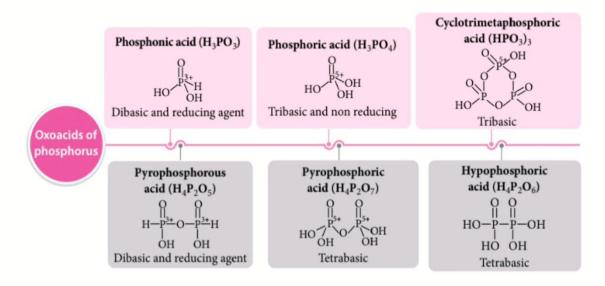
repulsions)

Lewis base strength: $NI_3 > NBr_3 > NCl_3 > NF_3$

Bond angle: $PF_3 < PCl_3 < PBr_3 < PI_3$ (increasing b.p. - b.p.

IMPORTANT COMPOUNDS OF NITROGEN AND PHOSPHORUS

Compounds	Preparations	Properties
Ammonia (NH ₃) O H N H H sp³ hybridisation (pyramidal)	Haber's process : $N_{2(g)} + 3H_{2(g)} \xrightarrow{773K} 2NH_{3(g)}$ $NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$ $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$ $Slaked lime$ $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$	[Ag(NH ₃) ₂] ⁺ AgCl NH ₃ O ₂ N ₂ H ₂ NHgOHgl NO NH ₄ Cl + N ₂ (If NH ₃ in excess)
Phosphine (PH ₃) P H H sp³ hybridisation (pyramidal)	$4H_3PO_3 \xrightarrow{478-483 \text{ K}} 3H_3PO_4 + PH_3$ $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$ $PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$ $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
Nitric acid (HNO ₃) H O-N O	$2KNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + K_2SO_4$ $4NH_{3(g)} + 5O_{2(g)} \xrightarrow{\text{Pt/Rh gauge}} 4NO_{(g)} + 6H_2O_{(g)}$ $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$ $3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$	$\begin{array}{c c} \text{H}_2\text{SO}_4 \leftarrow & & \text{FNO}_2 \\ + \text{NO}_2 & & \text{FNO}_3 \\ & & \text{FO}_2 \\ & & \text{COOH}_2 \\ & & \text{H}_2\text{SnO}_3 \\ & & \text{H}_2\text{O} + \text{NOCl} \\ & & + 2[\text{Cl}] \\ \end{array}$



GROUP 16 ELEMENTS (CHALCOGENS)

Electronic configurations: O(8) - [He] $2s^22p^4$; S(16) - [Ne] $3s^23p^4$; Se(34) - [Ar] $3d^{10}4s^24p^4$; Te(52) - [Kr] $4d^{10}5s^25p^4$; **Po(84)**-[Xe] $4f^{14}5d^{10}6s^26p^4$; **Lv(116)** - [Rn] $5f^{14}6d^{10}7s^27p^4$

PHYSICAL PROPERTIES

Allotropy: All elements show allotropy

Group 16

Elements

(ns²np⁴)

Electronegativity:

Decreases down the group.

Electron gain enthalpy: Increases from oxygen to sulphur and then decreases.

Melting and boiling points: Increase down the group upto Te and then decreases.

Physical state and metallic character:

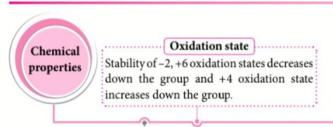
O2 (gas), S8 (solid non-metal), Se and Te (solid metalloids), Po (radioactive metal), Lv (radioactive)

Atomic radii: Increase down the group.

Ionisation enthalpy: Decreases down the group.

Atomicity: Oxygen (diatomic molecule), S, Se, Te (form polyatomic complex molecules).

CHEMICAL PROPERTIES



..... Hydrides **Boiling point**: $H_2O > H_2Te > H_2Se > H_2S$ Volatility: $H_2S > H_2Se > H_2Te > H_2O$ **Bond angle**: $H_2O > H_2S > H_2Se > H_2Te$ Acidic character: $H_2O < H_2S < H_2Se < H_2Te$ **Reducing power**: $H_2Te > H_2Se > H_2S > H_2O$

... Halides $(EX_6, EX_4 \text{ and } EX_2)$

Hexahalides stability: $SF_6 > SeF_6 > TeF_6$

Tetrahalides: SF₄(gas), SeF₄ (liquid), TeF₄ (solid).

SF₄ readily hydrolysed than SF₆.

Dihalides: All elements except selenium form:

Monohalides: Dimeric in nature and undergoes: disproportionation.

Oxides Monoxides: Except selenium, all elements form

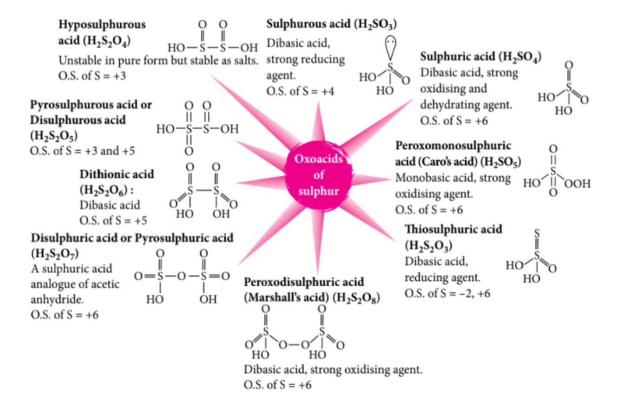
monoxides, MO. Dioxides: All elements form dioxides MO2, when

burnt in air. SO₂ (monomeric), SeO₂ (polymeric), TeO2 and PoO2 (ionic solids).

Trioxides: Sulphur, selenium, tellurium form trioxides, MO_3 .

IMPORTANT COMPOUNDS OF OXYGEN AND SULPHUR

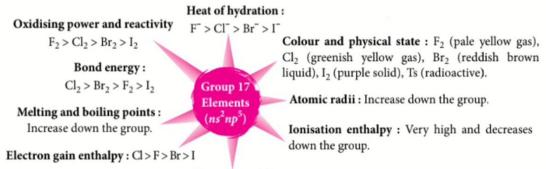
Compounds	Preparation	Properties
Ozone (O ₃) O 116.8° O 218 pm O Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö Ö	Silent electric discharge 2O ₃	$O_{3} \xrightarrow{NO} O_{2} + NO_{2}$ $\xrightarrow{H_{2}S} H_{2}O + S + O_{2}$ $\xrightarrow{KOH} KO_{3}$ $\xrightarrow{PbS} PbSO_{4}$ $\xrightarrow{HCl + SnCl_{2}} SnCl_{4}$ $\xrightarrow{CH_{2}=CH_{2}} HCHO$
Sulphuric acid (H ₂ SO ₄) Sulphuric acid Sulphuric acid	Contact process: $2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$ $1 + 2SO_4 \xrightarrow{H_2O} H_2SO_7$	$\begin{array}{c} \text{NaOH} & \text{NaHSO}_4 + \text{H}_2\text{O} \\ \text{2NaOH} & \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \\ \text{Zn} & \text{ZnSO}_4 + \text{H}_2 \\ \hline \\ C_{12}\text{H}_{22}\text{O}_{11} & \text{12C} + 11\text{H}_2\text{O} \\ \hline \\ S_8 & \text{SO}_2 + \text{H}_2\text{O} \\ \hline \\ \text{Na}_2\text{S} & \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} \\ \hline \\ BaCl_2 & \text{BaSO}_4 + \text{HCl} \\ \hline \\ K_4[Fe(\text{CN})_6] & \text{K}_2\text{SO}_4 + \text{FeSO}_4 + \\ \hline \\ \text{(NH}_4)_2\text{SO}_4 + \text{CO} \uparrow \\ \end{array}$



GROUP 17 ELEMENTS (HALOGENS)

Electronic configuration: $F(7) - [He] 2s^2 2p^5$; $Cl(17) - [Ne] 3s^2 3p^5$; $Br(35) - [Ar] 3d^{10} 4s^2 4p^5$; $I(53) - [Kr] 4d^{10} 5s^2 5p^5$; $At(85) - [Xe] 4f^{14} 5d^{10} 6s^2 6p^5$; $Ts(117) - [Rn] 5f^{14} 6d^{10} 7s^2 7p^5$

PHYSICAL PROPERTIES



Electronegativity: Decreases down the group.

CHEMICAL PROPERTIES

Chemical

properties

..... Oxidation state

F shows only - 1 oxidation state (except +1 in HOF while other elements show -1, +1, +3, +5 and +7oxidation states also.

...... Hydrogen halides

Boiling points: HF > HI > HBr > HCl Melting points: HI > HF > HBr > HCl **Bond lengths**: HI > HBr > HCl > HF

Bond dissociation enthalpy: HF > HCl > HBr > HI

Acidic strength: HI > HBr > HCl > HF Thermal stability: HF > HCl > HBr > HI Reducing power : HI > HBr > HCl > HF

..... Oxides

OF₂, O₂F₂ Cl2O, ClO2, Cl2O6 and Cl2O7

Br₂O, BrO₂, BrO₃

I2O4, I4O9

All are covalent and powerful oxidising agents.

Oxidising power: $Cl_2O > Cl_2O > Cl_2O_6 > Cl_2O_7$ Stability: $Cl_2O < ClO_2 < Cl_2O_6 < Cl_2O_7$

Oxoacids

Acid strength: HClO₄ > HClO₃ > HClO₂ > HClO;

HOCl > HOBr > HOI

Oxidising power : $HOCl \cong HOBr > HOI$;

 $BrO_4^- > IO_4^- > ClO_4^-$

HClO₄ < HClO₃ < HClO₂ < HClO

IMPORTANT COMPOUNDS OF HALOGEN FAMILY

Compounds	Preparation	Properties
Chlorine (Cl ₂)	Laboratory method: $2\text{NaCl} + 3\text{H}_2\text{SO}_4 + \text{MnO}_2$ → $2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$	$\begin{array}{c} \text{Cl}_2 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{HCl} \\ \text{Cl}_2 + \text{H}_2\text{S} \longrightarrow 2\text{HCl} + \text{S} \\ \text{Cl}_2 + 2\text{NaOH}_{(dil.)} \longrightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O} \\ 3\text{Cl}_2 + 6\text{NaOH}_{(conc.)} \longrightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O} \\ \text{Cl}_2 \xrightarrow{\text{H}_2\text{O}} 2\text{HCl} + [\text{O}] \xrightarrow{\text{Coloured} \\ \text{substance}} \text{Colourless} \end{array}$
Hydrogen Chloride (HCl)	$NaCl + H_2SO_4 \xrightarrow{420 \text{ K}} NaHSO_4 + HCl$ $NaHSO_4 + NaCl \xrightarrow{823 \text{ K}} Na_2SO_4 + HCl$	Colourless and pungent smelling gas, easily liquifiable, extremely soluble in water. $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$ $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$

Oxoacids of halogens :

Oxidation state of halogen	Chlorine	Bromine	Iodine	Name of acid
+1	HClO	HBrO	HIO	Hypohalous
+3	HClO ₂	-	-	Halous
+5	HClO ₃	HBrO ₃	HIO ₃	Halic
+7	HClO ₄	HBrO ₄	HIO ₄ H ₅ IO ₆	Perhalic

INTERHALOGEN COMPOUNDS

Covalent Strong oxidising Diamagnetic Reactive than nature in nature in nature halogens in solution or in liquid state.	in nature

	Types of interhalogen compounds		
AX ₅	AX 3	AX ₇	AX_3
sp a Square pyramidal	<i>sp</i> ³ Linear	sp³d³ Pentagonal bipyramidal	<i>sp³d</i> T-shaped
X X X X X X X X X X	A_{X}	$X \xrightarrow{X} X$	\mathcal{O}_{X}^{X}

GROUP 18 ELEMENTS (NOBLE OR INERT GASES)

Electronic configuration : He(2) - $1s^2$; **Ne(10)** - [He] $2s^22p^6$; **Ar(18)** - [Ne] $3s^23p^6$; **Kr(36)** - [Ar] $3d^{10}4s^24p^6$; $\mathbf{Xe(54)} - [\mathrm{Kr}] 4d^{10} 5s^2 5p^6; \mathbf{Rn(86)} - [\mathrm{Xe}] 4f^{14} 5d^{10} 6s^2 6p^6; \mathbf{Og(118)} - [\mathrm{Rn}] \ 5f^{14} 6d^{10} 7s^2 7p^6$

PHYSICAL PROPERTIES

Physical state: All are monoatomic gases and Og is radioactive

Group 18

Elements

 $(ns^2 np^6)$

Ease of liquefication:

Increases down the group.

Ionisation enthalpy:

Decreases down the group.

Atomic radii:

Increase down the group.

Electron gain enthalpy: Positive

Melting and boiling points: Very low due to

weak dispersion forces.

COMPOUNDS OF XENON

Compound	Preparation	Properties
Xenon difluoride (XeF $_{\!2})$	$Xe + F_2 \xrightarrow{673 \text{ K}, 1 \text{ bar}} XeF_2$ (Xe in excess)	Linear, sp ³ d
Xenon tetrafluoride (XeF ₄)	$Xe + 2F_2 \xrightarrow{873 \text{ K}} XeF_4$ (1:5)	Square planar, dsp ²
Xenon hexafluoride (XeF $_6$)	$Xe + 3F_2 \xrightarrow{573 \text{ K}} XeF_6$ (1:20)	Distorted octahedral, sp^3d^3
Xenon trioxide (XeO ₃)	$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$	Pyramidal, sp ³
Xenon oxydifluoride (XeOF ₂)	$XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$	T -shaped, sp^3d
Xenon oxytetrafluoride (XeOF ₄)	$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$	Square pyramidal, sp ³ d ²
Xenon dioxydifluoride (XeO_2F_2)	$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$	Distorted trigonal bipyramidal, sp^3d