CLASS-XII

for

BRUSH UP

NEET/JEE 2020

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Unit 3

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

General Principles and Processes of Isolation of Elements

METALLURGY

- The natural substances in which the metals occur in the earth along with impurities are called minerals.
- The minerals from which the metals can be conveniently and economically extracted are called ores. Thus all ores are minerals but all minerals are not ores.
- An ore is contaminated with earthly or undesired materials known as gangue.
- The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

Types of Ores and their Examples

S. No.	Types of Ore	Examples
1.	Native metals	Cu, Ag, Au, As, Sb, Bi, Pd, Pt
2.	Oxides	Al_2O_3, Fe_2O_3, Fe_3O_4, SnO_2, MnO_2, TiO_2, FeO, Cr_2O_3
3.	Carbonates	$CaCO_3$, $MgCO_3$, $FeCO_3$, $PbCO_3$, $BaCO_3$, $SrCO_3$, $ZnCO_3$
4.	Halides	NaCl, KCl, AgCl, $MgCl_2.6H_2O$
5.	Sulphides	Ag_2S, Cu_2S, CuS, PbS, ZnS, HgS
6.	Sulphates	$BaSO_4$, $PbSO_4$, $CaSO_4.2H_2O$ $CuSO_4.2Cu(OH)_2$
7.	Silicates	$Be_2AlSi_6O_{18}$
8.	Phosphates	$CePO_4$, $LaPO_4$, $NdPO_4$, $PrPO_4$

STEPS INVOLVED IN METALLURGY

- Crushing the ore
- Dressing or concentration of the ore
- Isolation of the metal from the concentrated ore
- Purification or refining

Crushing the Ore

- The lumps of ores are broken into small pieces with the help of crushers or grinders.

Concentration of Ore

- The removal of undesired impurities (gangue) from the ores is known as concentration or dressing or benefaction. It can be done by both physical and chemical processes.

Physical Methods

- **Gravity separation :** This method is used for concentration of oxide and carbonate ores and separation is based on the difference in the specific gravities of the gangue and ore particles. Generally oxide and carbonates ores are concentrated by this method *e.g.*, cassiterite and haematite.

- **Magnetic separation :** It is useful when one component, either the ore or the impurity is magnetic in nature. Ferro-magnetic ores are concentrated by this method. *e.g.*, wolframite ($FeWO_4$) is separated from cassiterite (SnO_2) by this method.
- **Froth floatation :** Dense sulphide ores are concentrated by this method, and it is based on the preferential wetting properties of the ore and gangue particles with frothing agent and water. It is used to concentrate the dense ores such as galena and zinc blende.

Chemical Methods

- Chemical methods like leaching is used if the ore is soluble in some suitable solvent. This method involves the treatment of the ore with suitable reagent so as to make it soluble while impurities remain insoluble, and the ore is recovered from the solution by suitable chemical method.
  - Leaching of alumina from bauxite ore :

    $Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

    $NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$

    $2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$
  - Mac Arthur Forest cyanide process is used for extraction of Au or Ag and is based on the principle of leaching. *e.g.*,

    $4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow \underset{\text{Sod. argentocyanide}}{4Na[Ag(CN)_2]} + 4NaOH$

    $2NaAg(CN)_2 + Zn \longrightarrow \underset{\text{Soluble}}{Na_2[Zn(CN)_4]} + 2Ag\downarrow$

Isolation of the Metal from the Concentrated Ore

- Metals are usually extracted by reduction. Thus, the concentrated ores is converted into a ore which is suitable for reduction. Thus, isolation involves two major steps :

I. Conversion of ore into metal oxide

- The methods used are
  - **Calcination :** The process of converting concentrated ore into oxide by heating it strongly below its melting point in the absence of air is called calcination.

    $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2\uparrow$
  - **Roasting :** In this process the concentrated ore (usually sulphide) is heated strongly, in the presence of excess of air so that sulphide ore is converted into its oxide.

    $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_{2(g)}\uparrow$

II. Reduction of metal oxides

- **Chemical reduction**
  - **Reduction by carbon or smelting :**

    $ZnO + C \longrightarrow Zn + CO\uparrow$

    Released carbon monoxide also brings about the reduction :

    $ZnO + CO \longrightarrow Zn + CO_2\uparrow$

    Smelting is carried out in blast furnace at high temperature. So, that metal is produced in liquid state. Sometimes metal is obtained in vapour state, *e.g.*, Zn.
  - **Flux :** To remove the infusible impurity (gangue) from calcined or roasted ore, certain substances are mixed with concentrated ore which combine with earthy impurities to form easily fusible mass called slag. There are two types of flux :

    (i) Acidic flux : Acidic fluxes like silica (SiO_2) and borax ($Na_2B_4O_7{\cdot}10H_2O$) are used to remove basic earthy impurities (gangue) such as lime CaO, MgO, FeO, etc.

    $\underset{\text{Acidic flux}}{SiO_2} + \underset{\text{Basic gangue}}{MgO} \longrightarrow \underset{\text{Fusible slag}}{MgSiO_3}$

    (ii) Basic flux : Basic fluxes like lime (CaO), magnesium oxide (MgO) are used to remove acidic gangue such as SiO_2, P_4O_{10}, etc.

    $\underset{\text{Basic flux}}{CaO} + \underset{\text{Acidic gangue}}{SiO_2} \longrightarrow \underset{\text{Fusible slag}}{CaSiO_3}$
  - **Aluminium reduction method (Aluminothermy or Goldschmidt thermite process) :** This is the process of reducing certain metal oxides which cannot be reduced by carbon like TiO_2, Cr_2O_3 and Mn_3O_4 etc., by using aluminium powder as reducing agent.

    $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + \text{Heat}$

    $3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn + \text{Heat}$

  Metal halides can also be reduced to metal (Kroll's process).
- **Self-reduction method :** When the sulphide ores of less electropositive metals like Hg, Cu, Pb, Sb, etc., are heated in air, a part of the ore gets oxidized to oxide or sulphate, which then reacts with the remaining sulphide ore to give the metal and SO_2.

  $CuS + O_2 \longrightarrow CuO + SO_2$

  $CuO + CuS \longrightarrow 2Cu + SO_2$

- **Hydrometallurgy or Precipitation :** In this process, ore is treated with such chemical reagent that converts it to some soluble compound. Now addition of a more electropositive metal to the filtrate displaces less electropositive metal from the compound thus, metal gets precipitated.

$$CuO + H_2SO_4 \longrightarrow \underset{\text{Soluble}}{CuSO_4} + H_2O$$

$$CuSO_4 + Fe \longrightarrow Cu\downarrow + FeSO_4$$

Ag and Au are also recovered from the solution of their complex cyanide salts by zinc scrap.

- **Electrolytic reduction :** Highly reactive metals are reduced from their corresponding cations by electrolytic reduction. Al, Na, Mg, K, Ca, etc. are obtained by electrolysis of their molten oxides, halides, etc. These metals cannot be reduced with carbon because at high temperature they form carbides with carbon.

For example, sodium metal is obtained by electrolyzing molten sodium chloride.

$$Na^+Cl^-(\text{molten}) \longrightarrow Na^+ + Cl^-$$

At cathode : $Na^+ + e^- \longrightarrow Na$

At anode : $Cl^- \longrightarrow (1/2)Cl_2 + e^-$

Aluminium is also obtained by electrolytic reduction of Al_2O_3 dissolved in cryolite (Na_3AlF_6).

Peep Into Previous Years

1. The cyanide process of gold extraction involves leaching out gold from its ore with CN^- in the presence of Q in water to form R. Subsequently, R is treated with T to obtain Au and Z. Choose the correct option(s).
   (a) R is $[Au(CN)_4]^-$. (b) T is Zn.
   (c) Q is O_2. (d) Z is $[Zn(CN)_4]^{2-}$.
   (JEE Advanced 2019)

2. The composition of 'copper matte' is
   (a) $Cu_2S + FeS$ (b) $Cu_2S + Cu_2O$
   (c) $Cu_2S + FeO$ (d) $Cu_2O + FeS$
   (Karnataka CET 2016)

3. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with
   (a) carbon monoxide (b) copper (I) sulphide
   (c) sulphur dioxide (d) iron (II) sulphide.
   (AIPMT 2015, 2012)

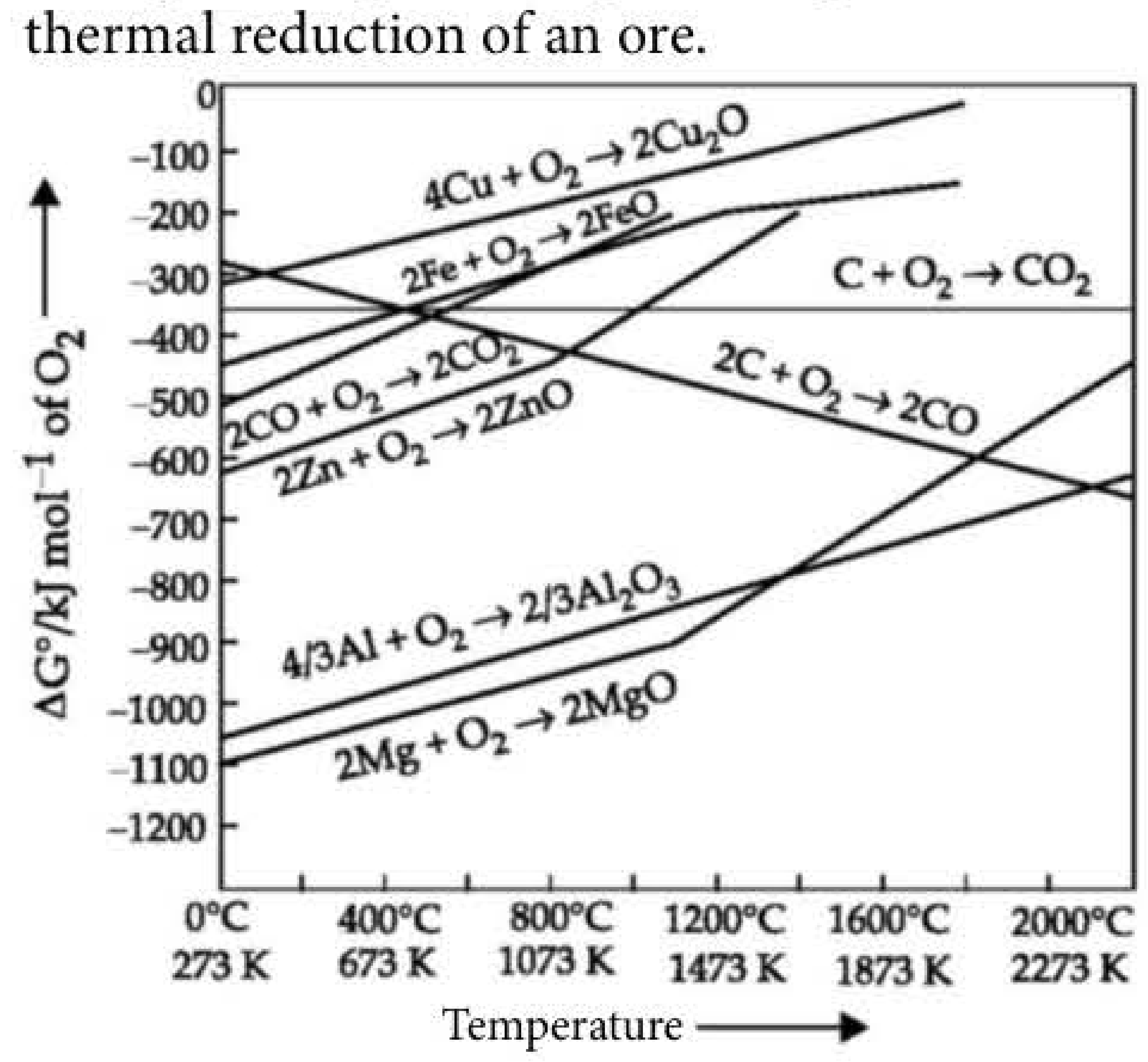
Electrochemical Principles of Metallurgy

- In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which can be understood through the equation: $\Delta G^\circ = -nFE^\circ$ where, n = no. of electrons and E° = electrode potential of the redox couple formed in the system. More reactive the metals, higher will be their negative E° values and thus, more difficult is their reduction. If the difference of the two E° values corresponds to a positive value and consequently negative ΔG° value, then the less reactive metal will go into the solution. In simple electrolysis, the M^{n+} ions are discharged at cathode.

$MO + C \longrightarrow M + CO$; $\Delta G_1 = +ve$
$CO + 1/2O_2 \longrightarrow CO_2$; $\Delta G_2 = -ve$

Thermodynamic Principles of Metallurgy

- The graphical representation of Gibbs energy *vs* temperature provides a basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram. Such a diagram helps us in predicting the feasibility of thermal reduction of an ore.



Gibbs energy (ΔG°) *vs.* T plot for formation of some oxides (Ellingham diagram)

- The criterion of feasibility is that at a given temperature, Gibbs energy of reaction must be negative.

Quotable Quote

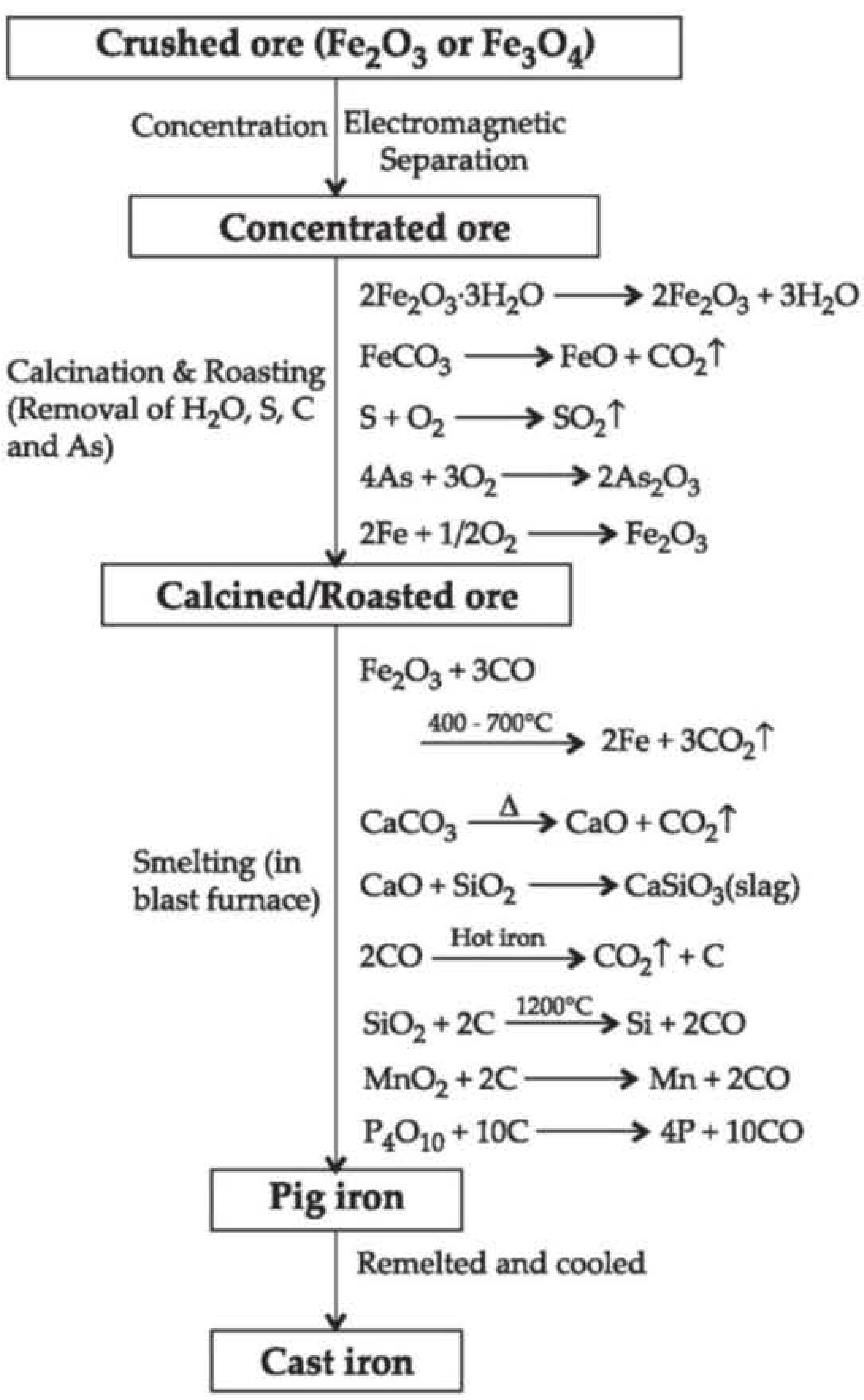
Anyone who has never made a mistake has never tried anything new.

ALBERT EINSTEIN

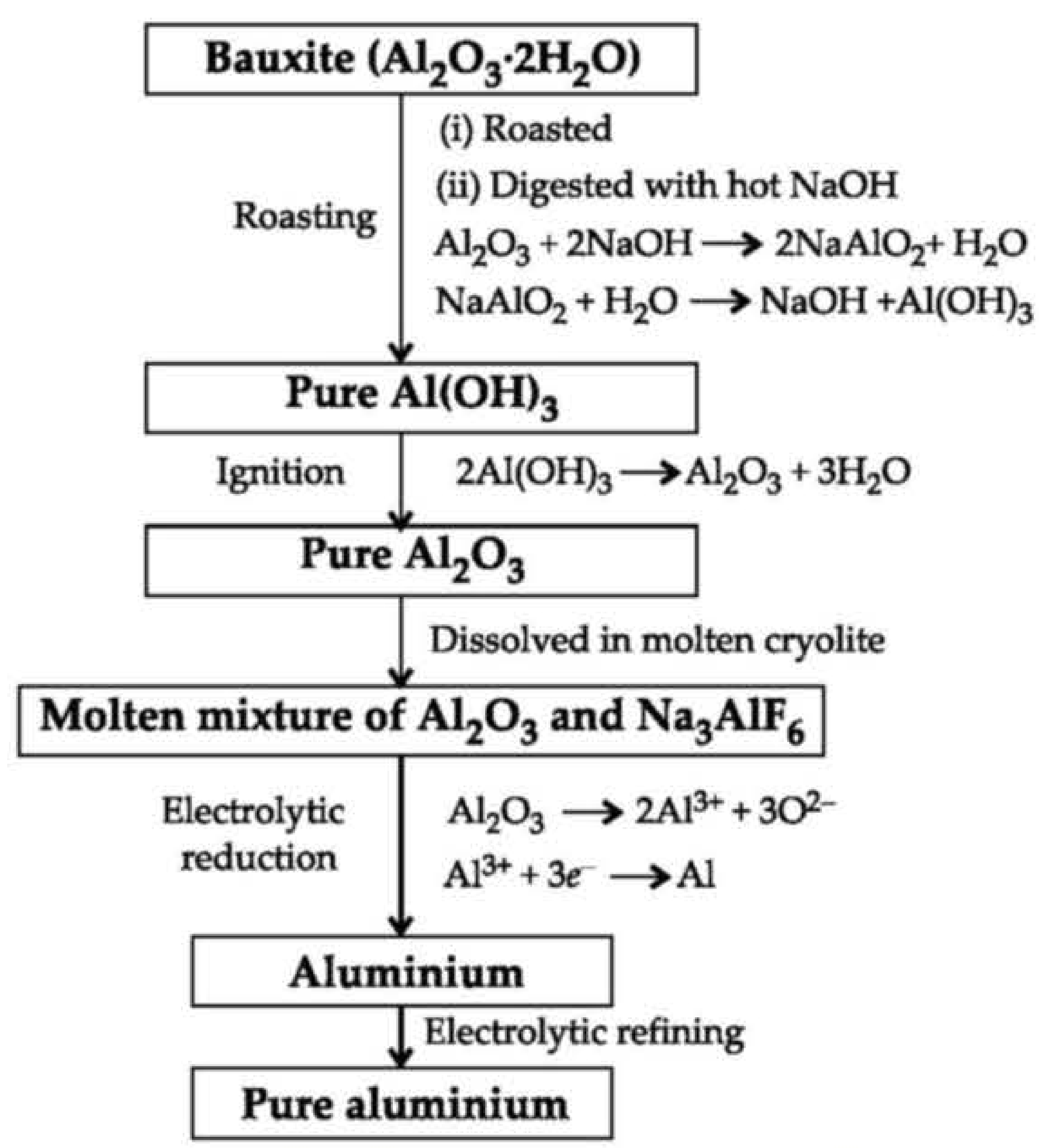
Refining of Crude Metals

S. No.	Methods	Metals purified
1.	Distillation	Zinc and mercury
2.	Electrolysis	Impure metal is made anode and the pure metal is cathode. The net result is the transfer of pure metal from anode to cathode. Copper, gold, silver, lead, zinc, aluminium
3.	Liquation	A low melting metal like tin and lead can be made to flow on a sloping surface and thus separated from higher melting impurities.
4.	Zone refining	Metals of high purity are obtained. Silicon, germanium, boron, gallium, indium are purified (which are used in semiconductors). It is based on the fact that impurities are more soluble in the melt than in the pure metal.
5.	Vapour phase refining	In Mond's process for the refining of nickel. $\underset{\text{(impure)}}{Ni + 4CO} \xrightarrow{80°C} Ni(CO)_4 \xrightarrow{200°C} \underset{\text{(pure)}}{Ni + 4CO\uparrow}$ In van Arkel method for zirconium. $\underset{\text{(impure)}}{Zr + 2I_2} \xrightarrow{600\ K} ZrI_4 \xrightarrow{1800\ K} \underset{\text{(pure)}}{Zr + 2I_2}$

Extraction of Iron (Fe)



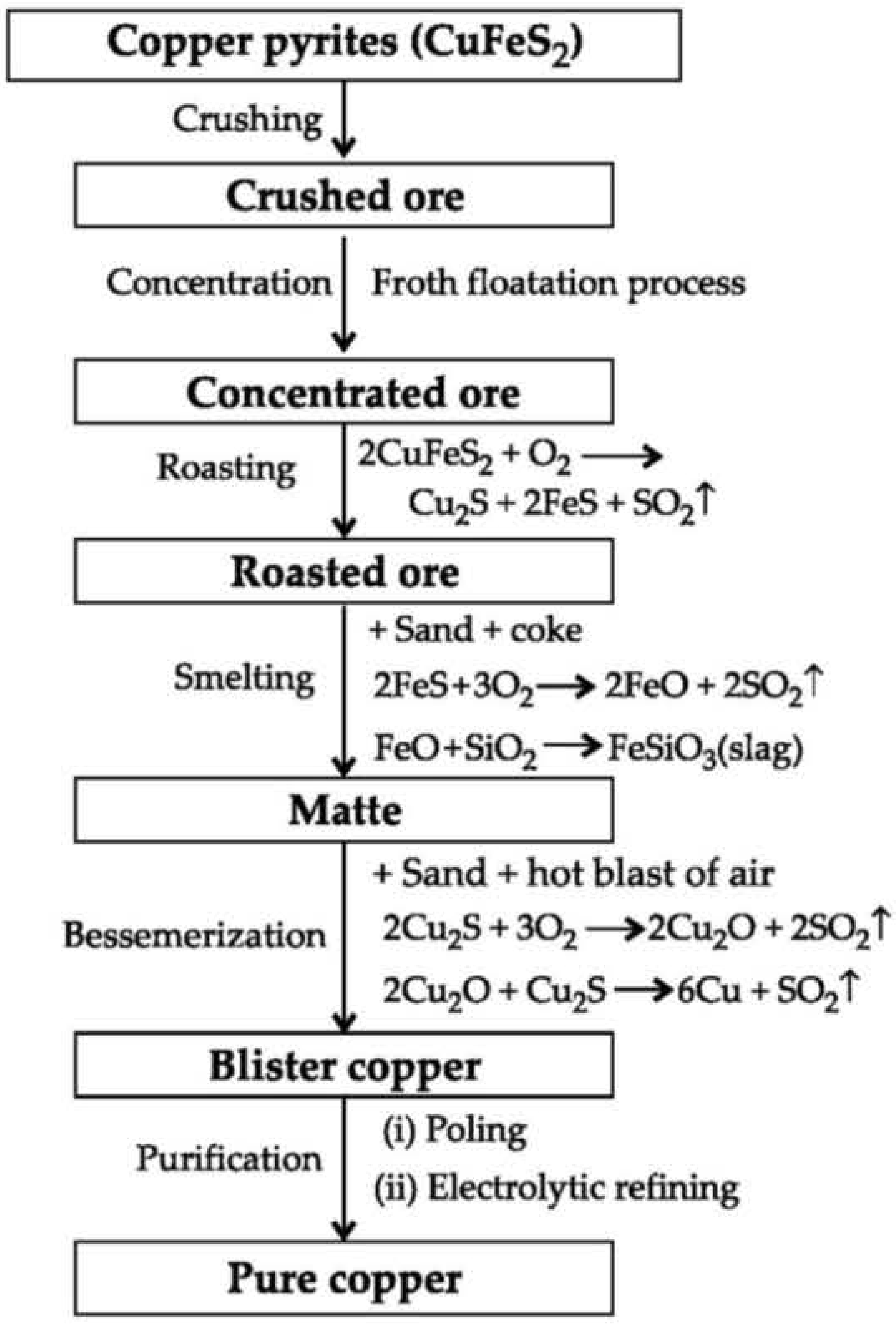
Extraction of Aluminium (Al)



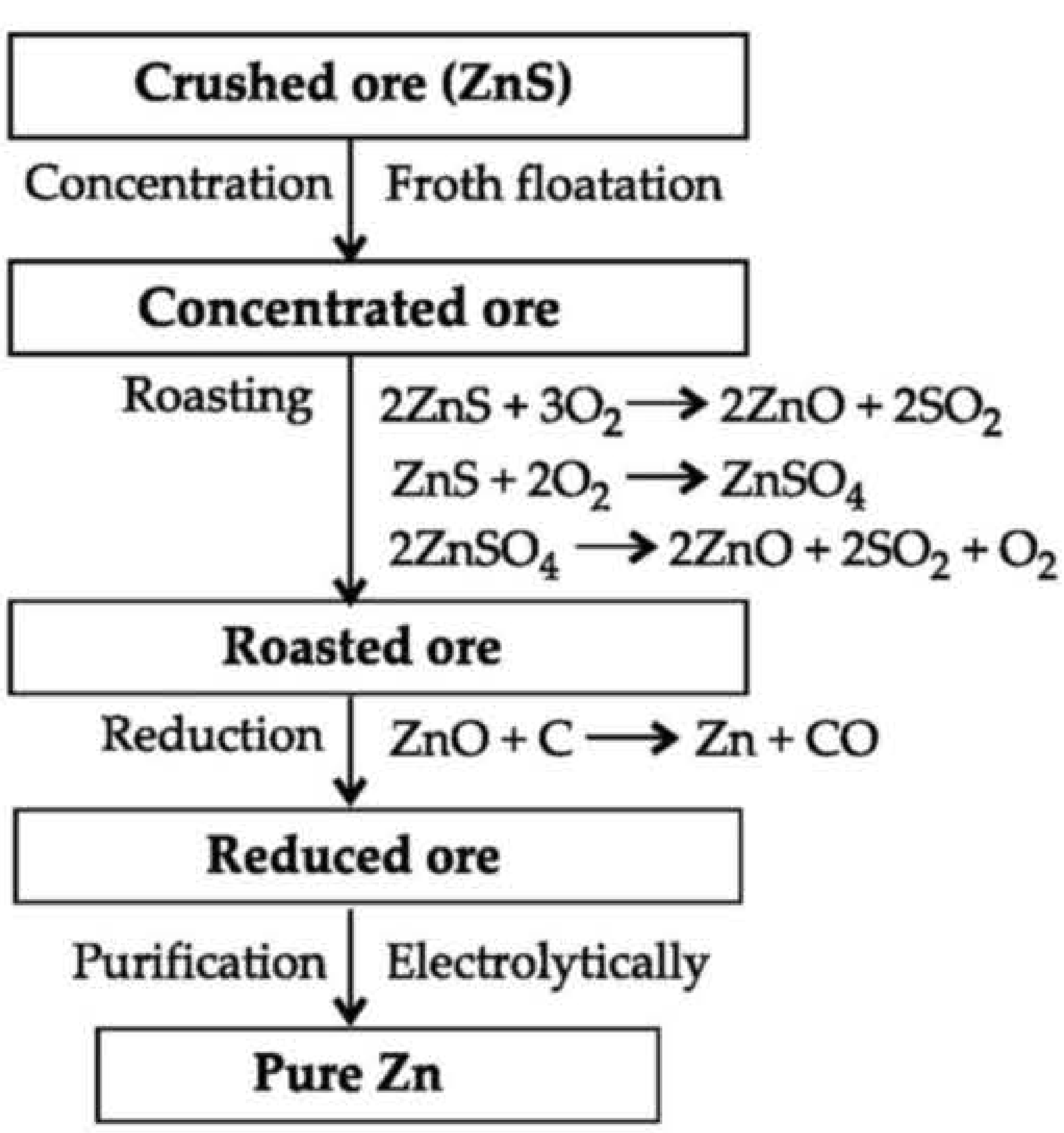
Monthly Test Drive CLASS XI ANSWER KEY

1. (a)	2. (d)	3. (c)	4. (a)	5. (b)
6. (a)	7. (b)	8. (b)	9. (a)	10. (c)
11. (d)	12. (c)	13. (a)	14. (a)	15. (d)
16. (b)	17. (b)	18. (a)	19. (b)	20. (b,c)
21. (a,b)	22. (a,c)	23. (a,c,d)	24. (5)	25. (5)
26. (3)	27. (c)	28. (a)	29. (b)	30. (d)

Extraction of Copper (Cu)



Extraction of Zinc (Zn)



Peep Into Previous Years

4. Match the refining methods (Column I) with metals (Column II).

	Column I (Refining methods)		Column II (Metals)
(I)	Liquation	(a)	Zr
(II)	Zone refining	(b)	Ni
(III)	Mond process	(c)	Sn
(IV)	van Arkel method	(d)	Ga

(a) (I) - (c); (II) - (a); (III) - (b); (IV) - (d)
(b) (I) - (b); (II) - (c); (III) - (d); (IV) - (a)
(c) (I) - (b); (II) - (d); (III) - (a); (IV) - (c)
(d) (I) - (c); (II) - (d); (III) - (b); (IV) - (a)

(JEE Main 2019)

5. Considering Ellingham diagram, which of the following metals can be used to reduce alumina?
(a) Fe (b) Zn (c) Mg (d) Cu

(NEET 2018)

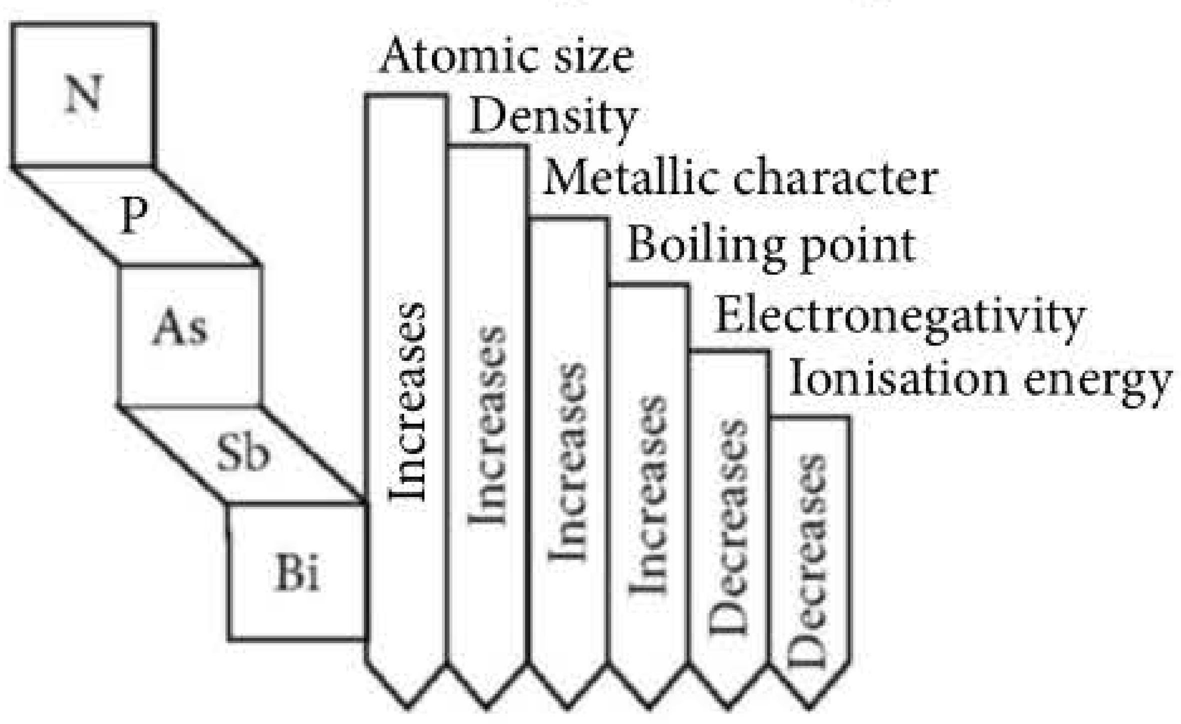
Points For Extra Scoring

- **Refractory material :** These are the substances which bear very high temperature without melting and becoming soft. Hence, the furnace is lined with refractory material.
- **Pyrometallurgy :** The process of extraction of metals using heat is called pyrometallurgy. It involves roasting, calcination, smelting, reduction and refining of metals from sulphide, carbonate, oxide ores, etc.
- **Pickling :** The process of removing layers of basic oxides from metal surfaces before electroplating is called pickling.
- **Slagging :** The removal of impurities from a mineral by forming molten salts is called slagging.
- **Anodising :** The process of producing an oxide coating on a metallic surface by making it the anode in an electrolytic bath during electrolysis is called anodising.
- **Amalgamation :** The process of combining metals present in their native ores with mercury to form alloys (amalgams) is called amalgamation. This process is applicable in the extraction of noble metals like Au and Ag.
- **Pulverisation :** The process of grinding the crushed ore into fine powder is called pulverisation.

Group 15 Elements (Nitrogen Family)

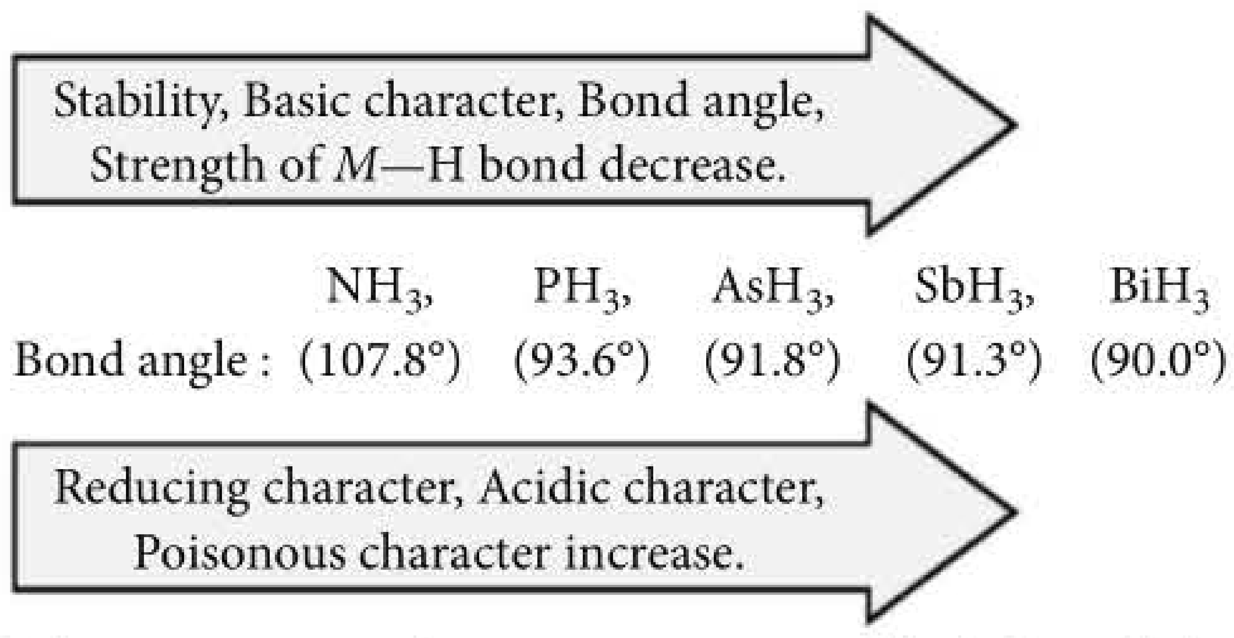
- Group 15 of the periodic table consists of six elements *viz*. nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi) and Moscovium (Mc)
- **Electronic configuration :** The electronic configuration of these elements is ns^2np^3.

General Trends in Physical Properties



Chemical Properties

- **Hydrides :** Form MH_3 type hydrides.
  - **Melting point :** $PH_3 < AsH_3 < SbH_3 < NH_3$
  - **Boiling point :** $BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$



- **Halides :** Nitrogen forms MX_3 type of halides while rest other form both MX_3 and MX_5 types of halides.

Property	Gradation	Reason
Stability of trihalides of nitrogen	$NF_3 > NCl_3 > NBr_3$	Large size difference between N and the halogens
Lewis acid strength	$PCl_3 > AsCl_3 > SbCl_3$	$PF_3 > PBr_3 > PI_3$
Bond angle among the halides of phosphorus	$PF_3 < PCl_3 < PBr_3 < PI_3$	Due to decreased bond pair-bond pair repulsion as these move away from P due to increased electronegativity of X

- **Oxides :** All the elements of this group form oxides, of the type M_2O_3, M_2O_4 and M_2O_5.

Property	Gradation	Reason
Acidic strength of trioxides	$N_2O_3 > P_2O_3 > As_2O_3$	Electronegativity of central atom decreases
Acidic strength of oxides of nitrogen	$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$	Oxidation state of central atom increases
Thermal stability of pentoxide	$P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5 > Bi_2O_5$	Stability of oxides of a higher oxidation state *i.e.*, M_2O_5 decreases with increasing atomic number

Anomalous Behaviour of Nitrogen

- Small size.
- High electronegativity.
- Absence of *d*-orbitals in the valence shell.
- Tendency to form multiple bonds.

The main points of difference are :

- Nitrogen is a gas while other members are solids.
- Nitrogen exists as diatomic molecule while other elements except bismuth form tetra-atomic molecules such as P_4, As_4 and Sb_4.
- The catenation property is more pronounced in nitrogen. Chains containing upto eight nitrogen atoms are known but in other elements catenation is limited to two atoms only.
- Nitrogen does not form pentahalides.
- Nitrogen exhibits a large number of oxidation states from –3 to +5 *i.e.*, +5, +4, +3, +2, +1, 0, –1, –2 and –3.

Ammonia (NH_3)

- **Preparation :**
  - $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$
  - Manufacture (Haber's Process) :

    $N_2 + 3H_2 \xrightarrow[\text{200-300 atm}]{\text{Fe + Mo, 750 K}} 2NH_3 + 24\text{ kcal}$
- **Physical Properties :**
  - It is a colourless, pungent smelling gas which brings tears to the eyes.

- It is lighter than air and highly soluble in water due to formation of hydrogen bonds.

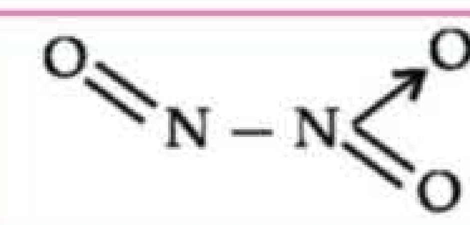
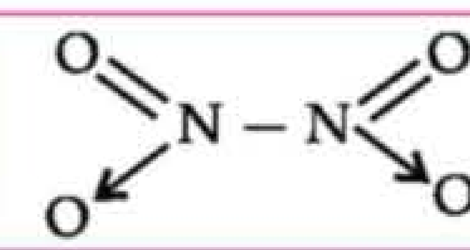
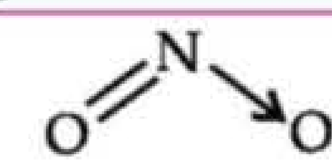
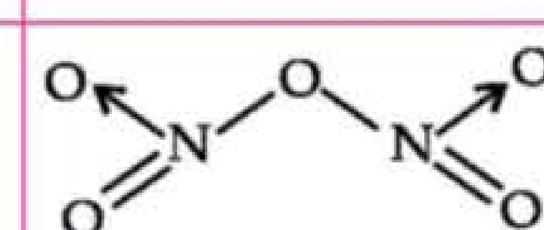
- **Chemical Properties :**
  - It forms salts with mineral acids.
    $NH_3 + HCl \longrightarrow NH_4Cl$
    $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
  - It ionises partially in water yielding a weakly basic solution.
    $NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Nitric Acid (HNO_3)

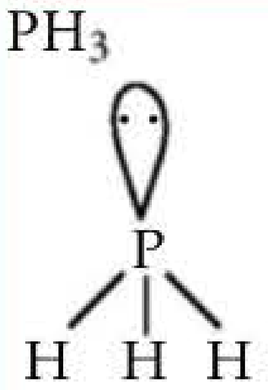
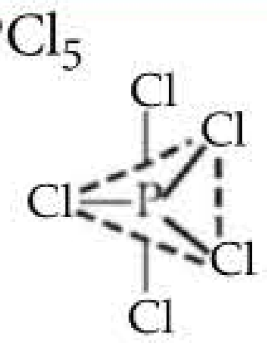
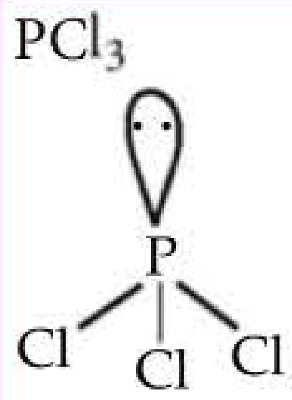
- **Preparation :**
  - **Laboratory preparation :**
    $2KNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + K_2SO_4$
  - **Ostwald's process :**
    $4NH_3 + 5O_2 \xrightarrow{\text{Pt gauze, 1075 K}} 4NO + 6H_2O$
    $2NO + O_2 \rightleftharpoons 2NO_2$
    $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$
- **Physical Properties :**
  - Anhydrous acid is a colourless, fuming liquid with a pungent smell, soluble in water in all proportions.
  - Aqueous solution containing 68% HNO_3 forms an azeotropic mixture.
- **Chemical Properties :** It is a very strong acid and very strong oxidizing agent as it decomposes to give nascent oxygen easily.

$HNO_{3(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$
$3Cu + 8HNO_3(\text{dilute}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
$Cu + 4HNO_3(\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$
$3SO_2 + 2HNO_3 + 2H_2O \rightarrow 3H_2SO_4 + 2NO$

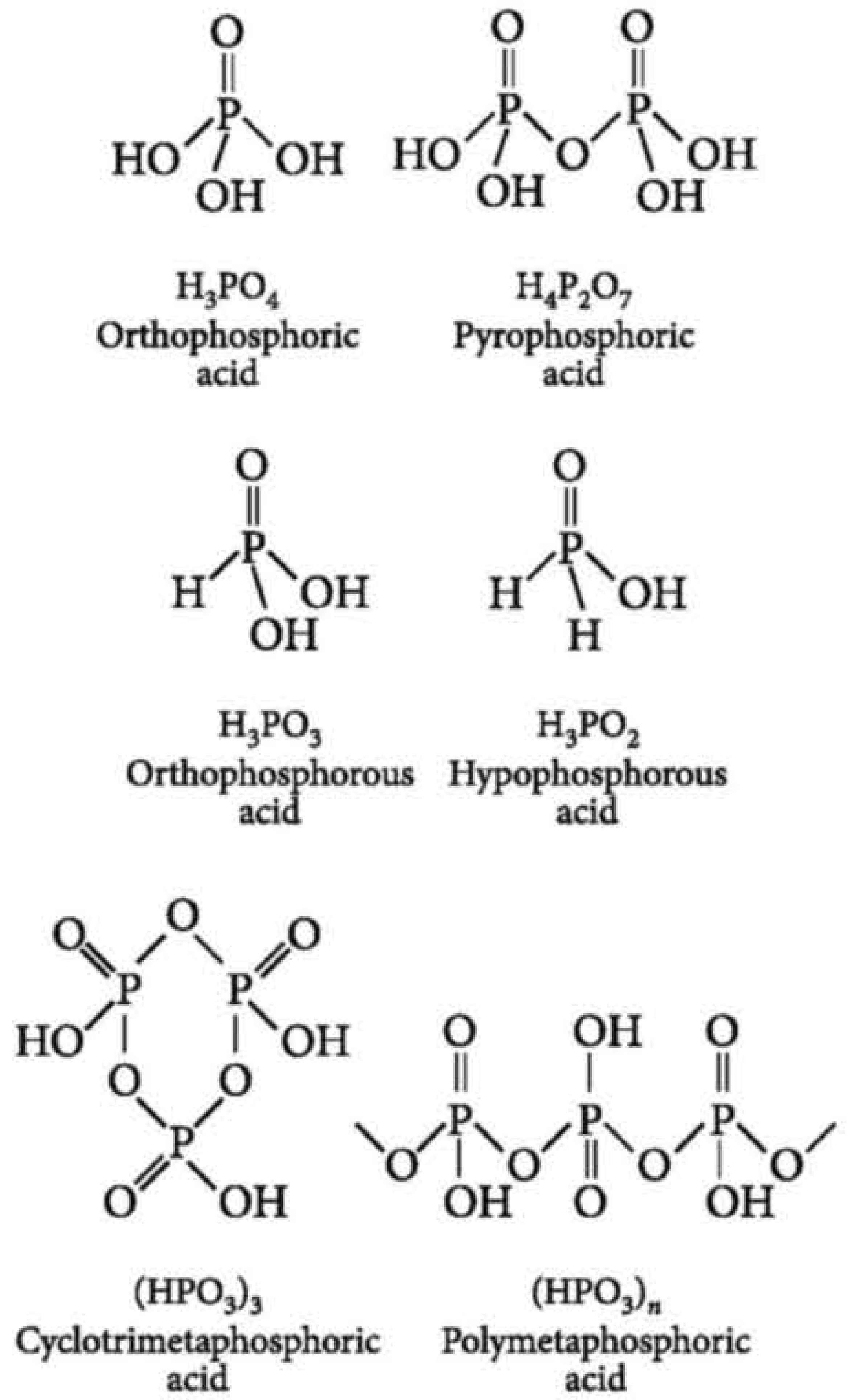
Oxides of Nitrogen

Oxides	O.S. of N	Physical appearance	Structure
N_2O Nitrous oxide	+1	Colourless gas	$N \equiv N \rightarrow O$
NO Nitric oxide	+2	Colourless gas	$N = O$
N_2O_3 Dinitrogen trioxide	+3	Blue coloured solid	
N_2O_4 Dinitrogen tetraoxide	+4	Colourless solid	
NO_2 Nitrogen dioxide	+4	Brown gas	
N_2O_5 Dinitrogen pentaoxide	+5	Colourless gas	

Some Important Compounds of Phosphorus

Compound	Preparation	Properties	Uses
PH_3 	$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$ $Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$ $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (sodium hypophosphite) $PH_4I + KOH \rightarrow KI + H_2O + PH_3$	$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$ $3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$ $PH_3 + HBr \rightarrow PH_4Br$ $PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$ $PH_3 + 16HNO_3 \rightarrow P_2O_5 + 16NO_2 + 11H_2O$	Used in smoke screens and Holme's signals.
PCl_5 	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ (white or red) $P_4 + 10\,SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$	$PCl_5 + 4H_2O\ (\text{excess}) \rightarrow H_3PO_4 + 5HCl$ $PCl_5 + SO_2 \rightarrow SOCl_2 + POCl_3$ $6PCl_5 + P_4O_{10} \rightarrow 10POCl_3$ $PCl_5 + Zn \rightarrow ZnCl_2 + PCl_3$	Used as chlorinating and dehydrating agent.
PCl_3 	$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ $3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$ $3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$	Used as reagent in organic synthesis and as a precursor of PCl_5, $POCl_3$ and $PSCl_3$.

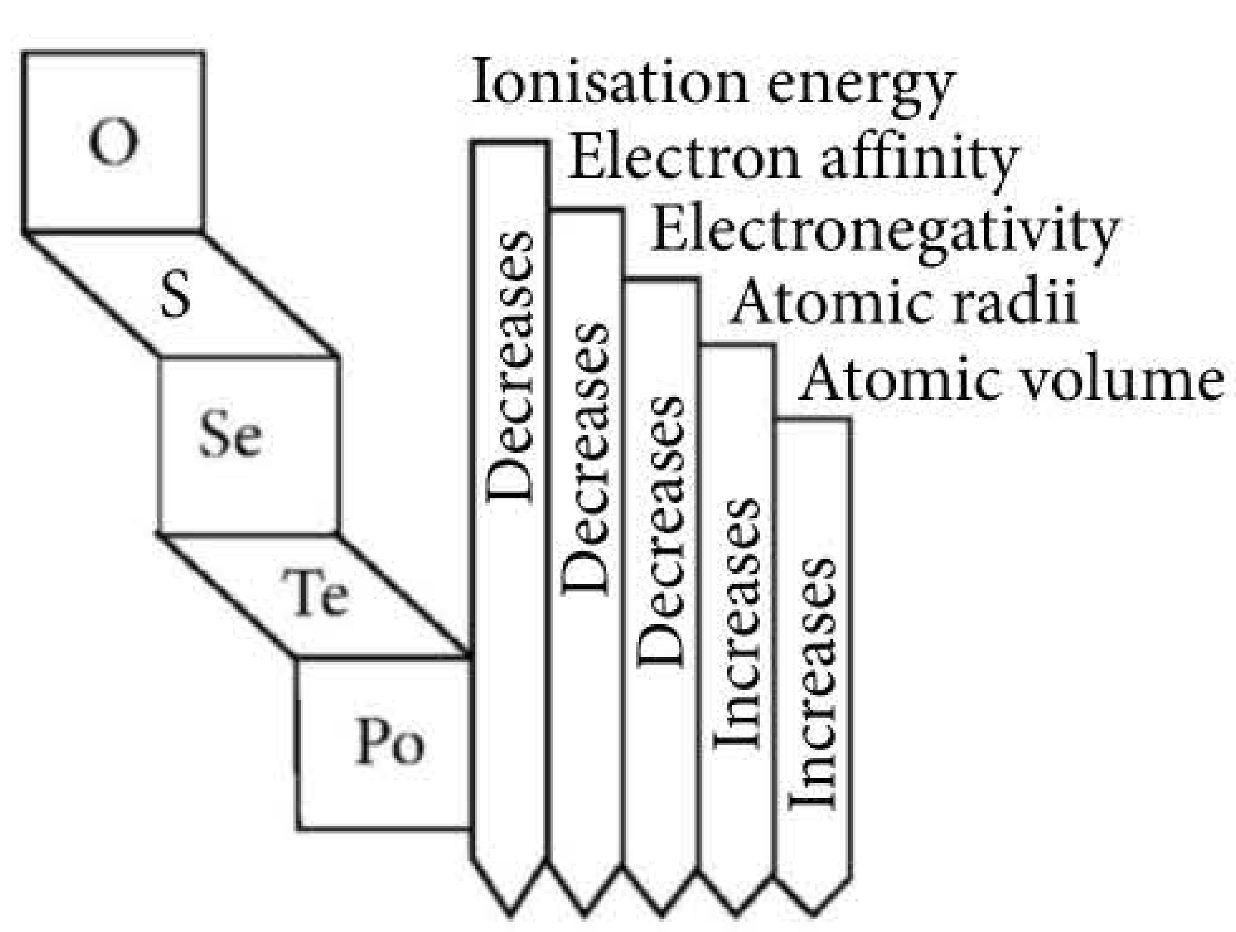
Oxoacids of Phosphorus



GROUP 16 ELEMENTS (OXYGEN FAMILY)

- The elements oxygen (O), sulphur (S), Selenium (Se), tellurium (Te) and polonium (Po) and Livermorium (Lv) constitute group 16 of the periodic table.
- **Electronic configuration :** Their valence shell electronic configuration is ns^2np^4 where n = 2 to 6.

General Trends in Physical Properties



Chemical Properties

- **Hydrides :** All the elements form stable hydrides of the type H_2M, where M is sp^3 hybridised.

Stability decreases →

H_2O, H_2S, H_2Se, H_2Te

Poisonous nature, acidic character, reducing character increase →

- **Halides :** Form MX_6, MX_4 and MX_2 types of halides :
  - **Dihalides :** All elements except selenium form dihalides.
  - **Tetrahalides :** SF_4(gas), SeF_4(liquid), TeF_4 (solid). SF_4 is readily hydrolysed than SF_6.
- **Oxides :** Form MO, MO_2 and MO_3 types oxides.

Anomalous Behaviour of Oxygen

- Oxygen is a diatomic gas while others are solids.
- Oxygen exhibits oxidation states of –2, –1 and +2 only while other members show both negative and positive oxidation states like –2, +2, +4 and +6.
- Due to high electronegativity of oxygen, hydrogen bonding is present in water.
- Oxygen is highly non-metallic due to high value of electronegativity.
- Oxygen is paramagnetic while others are diamagnetic.

Dioxygen (O_2)

- **Laboratory preparation :**

  $2Na_2O_{2(s)} + 2H_2O_{(l)} \longrightarrow 4NaOH_{(aq)} + O_{2(g)}$

  $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

- **Physical Properties :**
  - It is a colourless, odourless and tasteless gas. However liquid oxygen has a pale colour.
  - It exists as diatomic molecule (O_2).
- **Chemical Properties :**

  O_2 is not very active under ordinary conduction as its bond dissociation energy is high. It only reacts at high temperature, but once the reaction starts it continues of its own as the combination of oxygen is always exothermic.

  $2Mg + O_2 \longrightarrow 2MgO$; $4P + 5O_2 \longrightarrow 2P_2O_5$

  $4Al + 3O_2 \longrightarrow 2Al_2O_3$; $2NO + O_2 \longrightarrow 2NO_2$

  $4HCl + O_2 \xrightarrow[CuCl_2]{700\ K} 2H_2O + Cl_2$

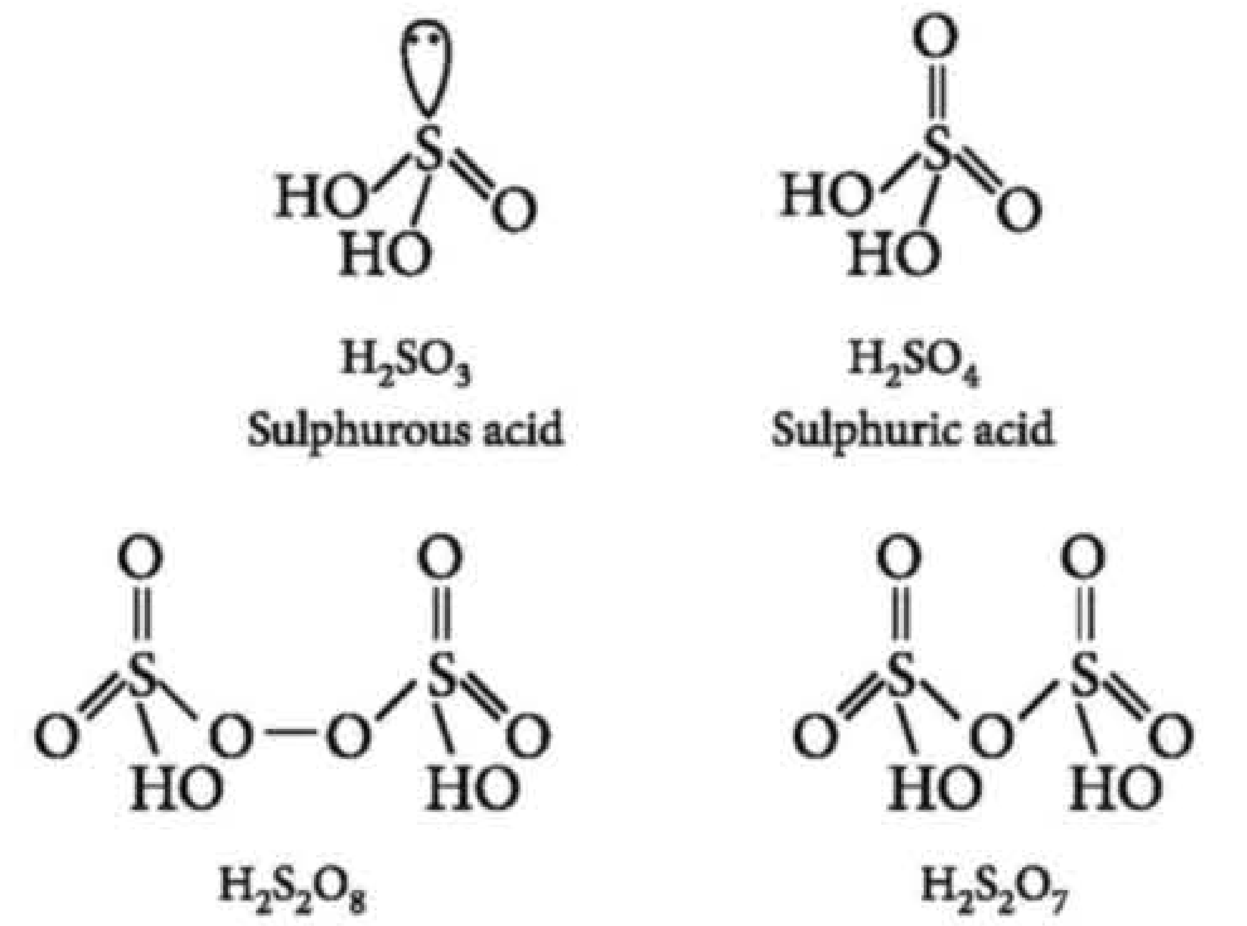
- **Uses**
  - For artificial respiration in hospitals and by mountaineers, pilots and divers.
  - Liquid dioxygen is used as a rocket fuel.

Ozone (O_3)

- Pale blue gas with characteristic strong smell, slightly soluble in water but more soluble in turpentine oil, glacial acetic acid and CCl_4.

$$O_3 \xrightarrow{NO} O_2 + NO_2$$
$$O_3 \xrightarrow{H_2S} H_2O + S + O_2$$
$$O_3 \xrightarrow{PbS} PbSO_4$$
$$O_3 \xrightarrow{KOH} KO_3$$
$$O_3 \xrightarrow[H_2O/Zn]{CH_2=CH_2} HCHO$$
$$O_3 \xrightarrow{(HCl + SnCl_2)} SnCl_4$$

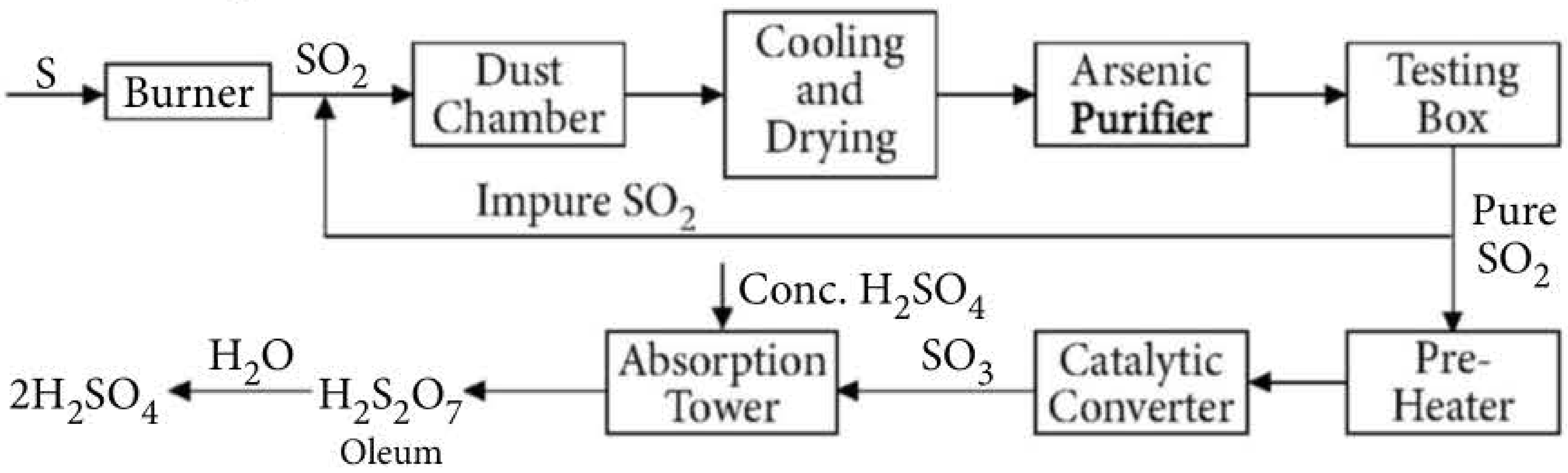
Oxoacids of Sulphur

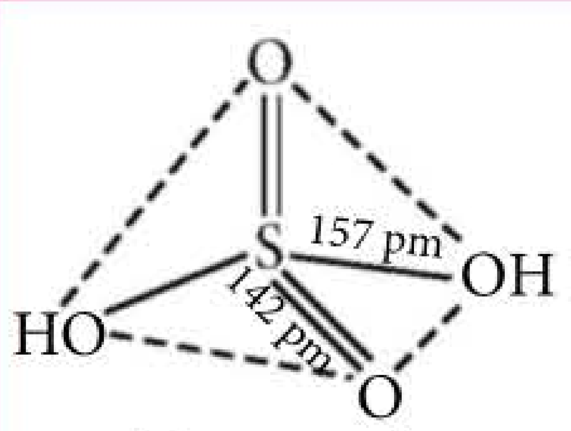
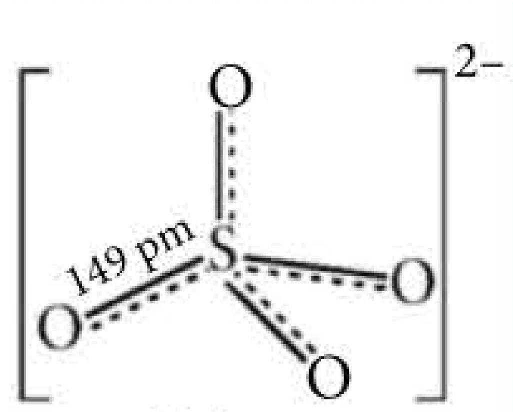


H_2SO_3 Sulphurous acid; H_2SO_4 Sulphuric acid; $H_2S_2O_8$ Peroxodisulphuric acid; $H_2S_2O_7$ Pyrosulphuric acid (Oleum)

Sulphuric Acid (H_2SO_4)

- **Preparation :** Contact process :



Structure	Properties	Uses
 Sulphuric acid  Sulphate ion	$H_2SO_4 \xrightarrow{NaOH} NaHSO_4 + H_2O$ $\xrightarrow{NaHCO_3} Na_2SO_4 + CO_2 + H_2O$ $\xrightarrow{Zn} ZnSO_4 + H_2$ $\xrightarrow{C_{12}H_{22}O_{11}} 12C + 11H_2O$ $\xrightarrow{S_8} SO_2 + H_2O$ $\xrightarrow{Na_2S} Na_2SO_4 + H_2S$ $\xrightarrow{BaCl_2} BaSO_4 + 2HCl$ $\xrightarrow{K_4[Fe(CN)_6]} K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO\uparrow$	It is used as oxidising agent, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids, etc.

Peep Into Previous Years

6. The species analogous to paramagnetic behaviour like O_2 is
(a) monoclinic sulphur (b) rhombic sulphur
(c) colloidal sulphur (d) gaseous sulphur.
(AMU(Engg.) 2019)

7. The number of S $=$ O and S — OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are
(a) (4 and 2) and (4 and 2)
(b) (2 and 4) and (2 and 4)
(c) (4 and 2) and (2 and 4)
(d) (2 and 2) and (2 and 2). ***(JEE Main 2017)***

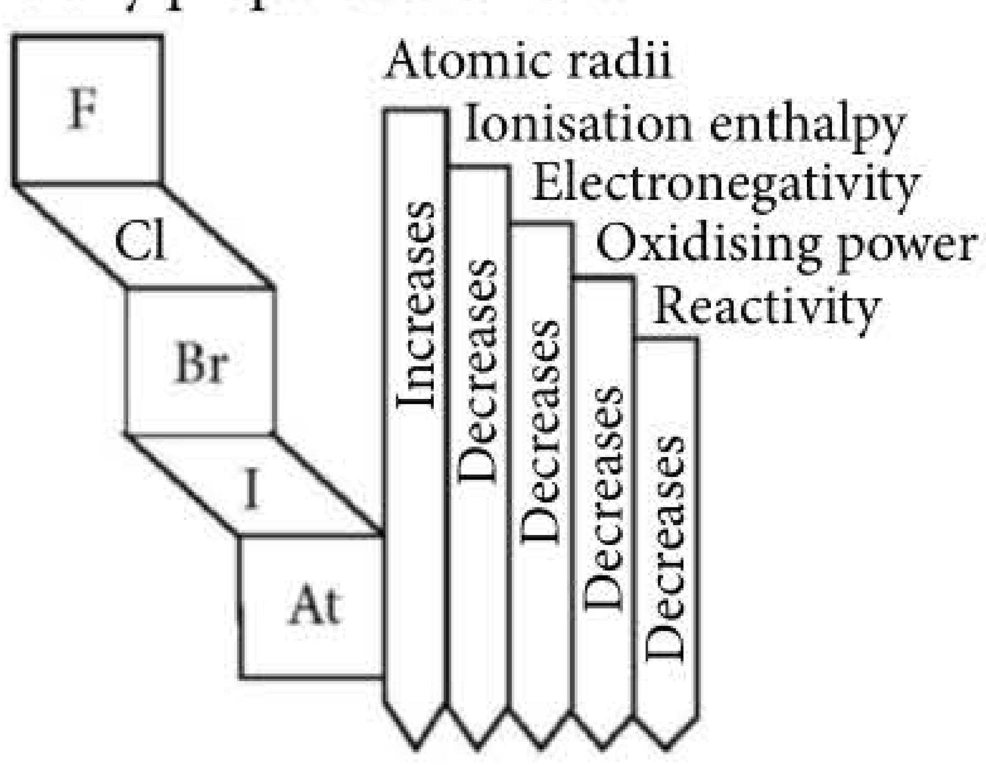
8. When copper is heated with conc. HNO_3 it produces
(a) $Cu(NO_3)_2$, NO and NO_2
(b) $Cu(NO_3)_2$ and N_2O
(c) $Cu(NO_3)_2$ and NO_2
(d) $Cu(NO_3)_2$ and NO ***(NEET-I 2016)***

Group 17 Elements (Halogen Family)

- Group 17 of the periodic table consists of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At) and Tennessine (Ts).
- **General electronic configuration :** ns^2np^5

General Trends in Physical Properties

- They are collectively known as halogens (sea salt forming elements). Astatine is radioactive and artificially prepared element.



- **Bond energy :** $Cl_2 > Br_2 > F_2 > I_2$
- **Electron gain enthalpy :** $Cl > F > Br > I$

Chemical Properties

- **Hydrogen halides :**
  Boiling Point : HF > HI > HBr > HCl
  Melting point : HI > HF > HBr > HCl

Bond length, acidic strength and reducing power increase →

HF, HCl, HBr, HI

Bond dissociation enthalpy and thermal stability decrease →

Anomalous Behaviour of Fluorine

- Fluorine is most reactive of all the halogens due to low dissociation energy of F – F bond.
- It exhibits only –1 oxidation state while other members show oxidation state from –1 to +7.
- Fluorine shows H-bonding whereas other halogens do not.
- Fluorine shows a covalency of one only due to absence of *d*-orbital, on the other hand other halogen members can show a maximum covalency of 7.
- HF is the weakest acid of all halogen acids.
- Fluorine has the highest tendency for ionic compound formation due to high electronegativity.

Chlorine (Cl_2)

- **Preparation :**
  $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$
  $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
  – **Weldon's process :**
  $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
- **Properties :**
  It is a yellowish green poisonous gas, soluble in water, its aqueous solution is known as chlorine water.
  $2NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$
  (hot & conc.)
  $2KOH + Cl_2 \longrightarrow KCl + KClO + H_2O$
  – Bleaching action of chlorine :
  $H_2O + Cl_2 \longrightarrow 2HCl + H + [O]$
  Colouring Matter + Nascent Oxygen ⟶ Colourless Matter

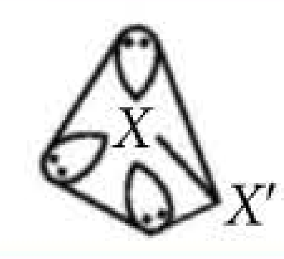
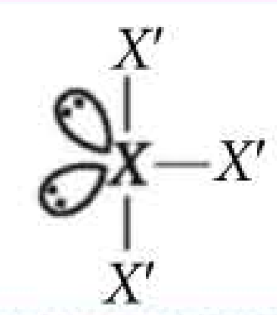
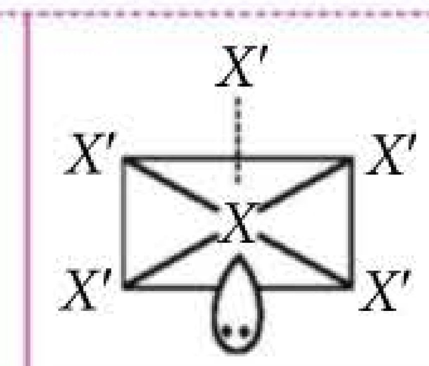
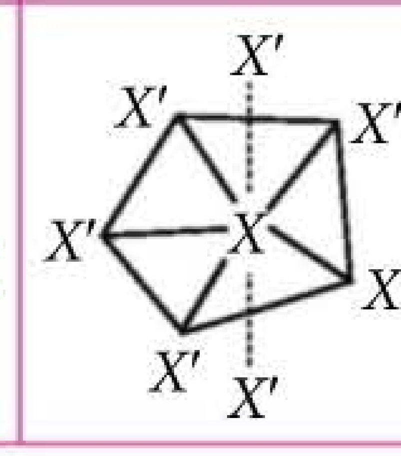
Hydrochloric Acid (HCl)

- **Preparation :** By direct combination of hydrogen and chlorine.
  – $H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Sunlight}} 2HCl_{(g)}$
  – $NaCl + H_2SO_4 \xrightarrow{420\text{ K}} NaHSO_4 + HCl$
- **Properties :** Anhydrous HCl does not show acidic properties. Only aqueous HCl or in presence of moisture, HCl behaves as an acid.
  – $Mg + 2HCl \longrightarrow MgCl_2 + H_2\uparrow$
  – $CaO + 2HCl \longrightarrow CaCl_2 + H_2O$
  – $AgNO_3 + HCl \longrightarrow HNO_3 + AgCl\downarrow$
  – $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
  When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, *e.g.* gold, platinum.
  $Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$

Interhalogen Compounds

- These compounds are regarded as halides of more electropositive (*i.e.* less electronegative) halogens.
- **Preparation :**
  $Cl_2 + F_2 \xrightarrow{473\text{ K}} 2ClF$; $I_2 + 3Cl_2 \longrightarrow 2ICl_3$
  (equal volume) (excess)
  $Cl_2 + 3F_2 \xrightarrow{573\text{ K}} 2ClF_3$; $Br_2 + 3F_2 \longrightarrow 2BrF_3$
  (excess) (diluted with water)
  $I_2 + Cl_2 \longrightarrow 2ICl$; $Br_2 + 5F_2 \longrightarrow 2BrF_5$
  (equimolar) (excess)

- **Structures :**

Type	Hybridisation	Shape	Structure
XX'	sp^3	Linear	
XX'_3	sp^3d	T-shaped	
XX'_5	sp^3d^2	Square pyramidal	
XX'_7	sp^3d^3	Pentagonal bipyramidal	

Oxyacids of Halogens

Variation of the general properties of oxyacids of halogens				
Halogen	**Hypohalous acids (X = +1)**	**Halous acids (X = +3)**	**Halic acids (X = +5)**	**Perhalic acid (X = +7)**
Cl	HClO	$HClO_2$	$HClO_3$	$HClO_4$
Br	HBrO	—	$HBrO_3$	—
I	HIO	—	HIO_3	HIO_4

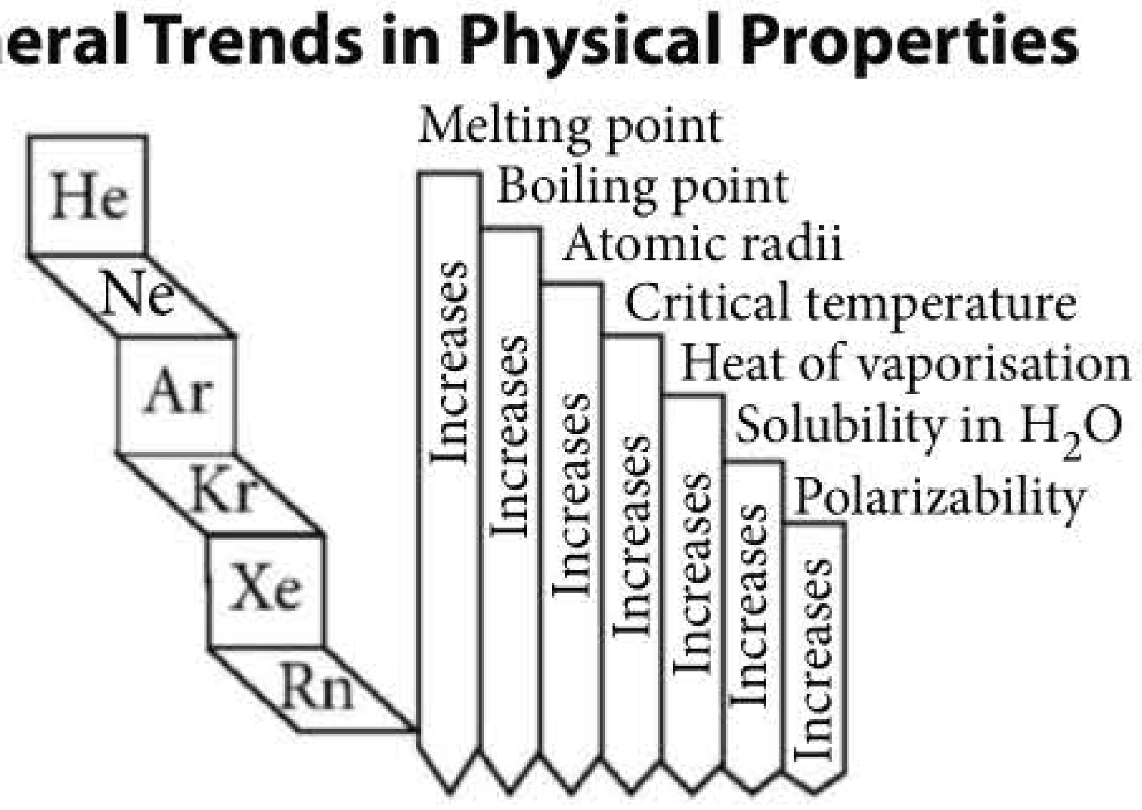
– Oxidation number of the central atom increases (+1, +3, +5, +7) →
– Thermal stability increases →
– Covalent character of X—O bond increases →
– Oxidising power decreases →
– Basicity decreases →
– Electronegativity of the central atoms remains the same —

↓ Electronegativity of the central atom decreases —
↓ Thermal stability decreases —
↓ Oxidising power decreases —
↓ Acidic strength decreases —
— Oxidation number of the central atom remains the same —

Group-18 Elements (Noble Gases)

- The elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Ra) and Oganesson (Og) constitute group 18 (or zero) of the periodic table.
- All the noble gases, except He have eight electrons (closed shell) with electronic configuration $ns^2\ np^6$ where n = 2 to 6. Helium, however has only two electrons and hence its electronic configuration is $1s^2$.

General Trends in Physical Properties



Chemical Properties

- Noble gases are generally inert and do not participate in the reactions easily. The inertness of noble gases is due to the following reasons :
  - The atoms of noble gases have stable closed shell electronic configuration.
  - Noble gases have exceptionally high ionization energies.
  - Noble gases have very low electron affinities.

  But later on few compounds of noble gases were discovered. *e.g.*, $Xe + PtF_6 \longrightarrow Xe^+[PtF_6]^-$