Hydrogen

- Group → 1 (Alkali metals)
- Period → 1
- Non metal
- Hydrogen shows similar characteristics to both alkali metals (Gr. 1) and halogens (Gr. 17)
- Dihydrogen (H_2): Most abundant molecule in the universe. (70%)
- Isotopes: protium (^1_1H), deuterium (^2_1H), tritium ($^3H_1$)
  - protium → most abundant
  - deuterium → 0.0156% in terrestrial Hydrogen, mostly in form of HD
  - tritium → Only radioactive, emits β particle, $t_{1/2} = 12.33$ years.

PREPARATION»

- Granulated Zn and dilute HCl : $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$ → [Lab prep] [Mina Ashido]
- Zn and aqueous alkali ⟶ $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$ → [Lab prep]
- Electro-lysis of acidified water: $2H_2O(l) \xrightarrow{\text{ϟ}} 2H_2(g) + O_2(g)$ [Underwater Kaminari]
- High purity (>99.95%) H_2 is obtained by electrolysing warm aqueous barium hydroxide solution w/ nickel electrodes.
- Electrolysis of brine solution: ~~2Cl~~ $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2\bar{O}H(aq)$ [As a by product]
- Steam on hydrocarbon/coke at high T & catalyst: $C_nH_{2n+2} + nH_2O \xrightarrow[Ni]{1270K} nCO + (2n+1)H_2$

$$CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270K} \underbrace{CO(g) + 3H_2(g)}_{\text{water gas / synthesis gas / syngas}}$$

Ø Prep of Syngas from Coal (Coal Gasification):

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

▨ **Prep of Hydrogen**

Mina walked in the lab with a piece of Zinc to make H_2 and found Kaminari swimming in acidified water. After drying him for high purity bakugo and tetsu tetsu were called. They took him to Doctor Brown. There was steam coming out of his room, in such hotness he was drinking coke with his cat in lap. [MP]

PROPERTIES»

- Physical
  - Colourless, Odourless, tasteless
  - Combustible, insoluble in H_2O
  - Lighter than air,
- Chemical
  - (H–H bond dissociation enthalpy is the highest for single bond between two atoms of any element.)
  - Can Lose 1 e^- to form H^+, gain to form H^- or form covalent bond.

- **Reaction with Halogens**: $H_2(g) + X_2(g) \longrightarrow 2HX(g)$
  - Reaction with F occurs even in dark
  - Iodine needs catalyst.
- **Reaction with O_2**: $2H_2(g) + O_2(g) \xrightarrow{cat/\Delta} 2H_2O(l) + \Delta H$
- **Reaction with N_2**: $3H_2 + N_2 \xrightarrow[Fe]{673\,K,\ 200atm} 2NH_3 + \Delta H$ [Haber's Process]
- **Reaction with Metals**: $H_2(g) + 2M(g) \longrightarrow 2MH(g)$
- **Reaction with metal ion and metal oxids**: $H_2(g) + Pd^{2+}(aq) \longrightarrow Pd(s) + 2H^+(aq)$

$$yH_2(g) + M_xO_y(s) \longrightarrow xM(s) + yH_2O(l)$$

- **Reaction with Organic compounds**: Hydrogenation of vegetable oils using nickel as catalyst gives edible fats.
  - Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH{=}CH_2 \longrightarrow RCH_2CH_2-CHO \quad ⋮ \quad H_2 + RCH_2CH_2CHO \longrightarrow RCH_2CH_2CH_2OH$$

Uses of Hydrogen»

- synthesis of ammonia
- manufacture of vanaspati fat
- manufacture of organic compounds particularly methanol
- manufacture of metal hydrides.
- preparation of HCl
- Reducing heavy metal oxides to metal
- Atomic H and oxy-hydrogen torches used for cutting and welding.

  [Atomic H are allowed to recombines on the surface generating 4000K]
- Rocket fuel.
- Used in fuel cells for generating electrical energy

▨ **Uses of H_2**

Amelia takes a fat organo-metallic pipe to weld the rocket fuel tank lifted by hydrolic, but the electricity ran out

Hydrides ($EH_x \rightarrow E^{x+} + xH^-$)

classification
- Ionic or saline or saltlike hydrides
- Covalent or molecular hydrides
- Metallic or non-stoichiometric hydride

→ **Ionic or Saline Hydrides»**

- stoichiometric compounds with highly electropositive elem
- Generally ionic but covalent character found in light metal hydrides
- BeH_2, MgH_2 are polymeric
- Ionic ones are crystalline, non-volatile, non conducting in solid state.
- But melts of ionic ones conduct electricity and liberate H_2
- Saline hydrides react violently with H_2O producing H_2 gas.

$$NaH(s) + H_2O(aq) \longrightarrow NaOH(aq) + H_2(g)$$

- LiH is rather unreactive at moderate temperatures with O_2 or Cl_2. It is therefore, used in the synthesis of other useful hydrides.

$$8LiH + Al_2Cl_6 \longrightarrow 2LiAlH_4 + 6LiCl$$

$$2LiH + B_2H_6 \longrightarrow 2LiBH_4$$

Covalent / Molecular Hydries • covalent molecules formed with the p block elements. [CH_4, NH_3, H_2O, HF etc] → Form Hydrogen bond
• Being covalent, they are volatile

→ electron-deficient: Incomplete octate, electron ~~gee~~ acceptors, acts as lewis acid, group (13)
→ electron-precise: Complete octate, All group 14 hydrides
→ electron-rich: More than 8 e⁻s in last shell, group (15 – 17), electron donor, Lewis base

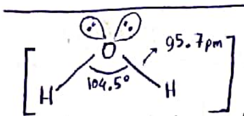
Metallic / Non-stoichiometric Hydrides • compounds with d block and f block [7, 8, 9th Group elements don't]
- From 6th group only Chromium forms CrH • Good conductors of heat and electricity.
- Almost always non-stoichiometric e.g. $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, $VH_{0.56}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$
- Some metals absorbs H_2 into their lattice, they are called interstitial hydrides. This property is used is widely used in catalytic reduction / hydrogenation.
- Pd, Pt can accommodate a very large volume of Hydrogen

WATER

• Human body has about 65%.

PROPS → Physical
→ tasteless, colourless liquid
→ high ~~mp~~ freezing point, b.p, heat of vap, heat of fusion, high specific heat capacity
→ high thermal conductivity, surface tension, dipole moment and dielectric const.
→ Anamelous behaviour

Structure ~~Chemical~~



- highly polar molecule • sp^3 hybridised
- In liquid face, there exist intermolecular H-bond.
- Dencity of ice is less than water.

Structure of Ice
Each O atom is sorrounded tetrahedrally by four O atoms.

Chemical

• **Amphoteric Nature**: Reacts ~~with~~ as an acid with NH_3 and as a base with H_2S.

$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$
$H_2O + H_2S \rightleftharpoons H_3O^+ + HS^-$

• **Auto-protolysis (self-ionization)**

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+ + OH^-$

• **Hydrolysis Reaction** Due to high dielectric constant, it has a very strong hydrating tendency.

$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$
$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$
$N^{3-} + 3H_2O \longrightarrow NH_3 + 3OH^-$

Hard Water Contains ~~carbonate~~, bicarbonates, ~~and~~ chlorides and sulphates. Doesn't readily form lather. (forms scum/precipitate with soap)
[Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipite out Ca/Mg stearate]

$2C_{17}H_{35}COONa\,(aq) + M^{2+}\,(aq) \longrightarrow (C_{17}H_{35}COO)_2M\downarrow + 2Na^+(aq)$ [M → Ca/Mg]

Classification ⟶ ① Temporary Hardness
② Permanent Hardness

• **Permanent Hardness** [Due to Mg/Ca chlorides/sulphates]
can be removed by
• Treating w/ washing soda (Na_2CO_3). Converts the solube salts into insoluble carbonates.

$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2NaCl$
$MSO_4 + Na_2CO_3 \longrightarrow MCO_3\downarrow + Na_2SO_4$

• **Redox involving H_2O** H_2O is easily reduced to H_2 by highly electropositive metals.

$2H_2O + 2Na \longrightarrow 2NaOH + H_2$

Oxidised to O_2 during photosynthesis and with F_2 too.

$2F_2 + 2H_2O \longrightarrow 4H^+ + 4F^- + O_2$

• **Hydrates Formation** From aqueous solution many salts can be crystallined as hydrated salts. classification →
→ coordinated water $[Cr(H_2O)_6]^{3+}3Cl^-$
→ interstitial water $BaCl_2 \cdot 2H_2O$
→ Hydrogen-bonded water $[Cu(H_2O)_4]^{2+}SO_4^{2-}$, $CuSO_4 \cdot 5H_2O$

Soft Water: Basically pure from minerals and readily forms lather with soap.

• **Temporary Hardness** [Due to Mg / Ca bicarbonate]
can be removed by
• Boiling By boiling, soluble $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ are converted into insoluble $Mg(OH)_2$ and ~~$Ca(HCO_3)_2$~~ $CaCO_3$ respectively, which forms precipitate.
• Clark's Method Calculated amount of added lime precipitates out ~~CaO~~ $CaCO_3$ and $Mg(OH)_2$

$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$
$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$

• **Calgon's method** Sodium hexameta phosphate ($Na_6P_6O_{18}$) commercially called 'calgon'. The following reactions occurs.

$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$
$M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$

↑ This complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution

● **Ion-exchange method**: This method is also known as zeolite / Permutit process. Hydrated sodium aluminium silicate is zeolite / permutit [$(NaAlSiO_4)$ can be written as NaZ]

~~zeolite~~ → $2NaZ + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na(aq)$ [M = Mg, Ca]

When all the Na is used, it is regenerated by NaCl

$$MZ_2(s) + 2NaCl(aq) \longrightarrow 2NaZ(s) + MCl_2(aq)$$

● **Synthetic Resins Method**: Ion exchange resin (RSO_3H) is changed to RNa by NaCl. It exchanges Na^+ with Ca^{2+} and Mg^{2+}

$$2RNa(s) + M^{2+}(aq) \longrightarrow R_2M(s) + 2Na^+(aq)$$

Pure de-mineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (H^+) and an anion exchange (OH^-) resins.

$$2RH(s) + M^{2+}(aq) \rightleftharpoons HR_2(s) + 2H^+(aq)$$

In this process, water is acidified, in anion exchange, it gets neutralised.

$$RNH_2(s) + H_2O(l) \rightleftharpoons RNH_3^+ \cdot OH^-(s)$$

$$RNH_3^+ \cdot OH^-(s) + X^-(aq) \rightleftharpoons RNH_3^+ \cdot X^-(s) + OH^-(aq)$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

● **Hydrogen Peroxide (H_2O_2)** [H—O—O—H]

● **PREP** » Ø Acidifying Barium Peroxide and removing water by evaporation under low press.

$$BaO_2 \cdot 8H_2O(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

Ø Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate at high current density on hydrolysis

Used for making D_2O_2

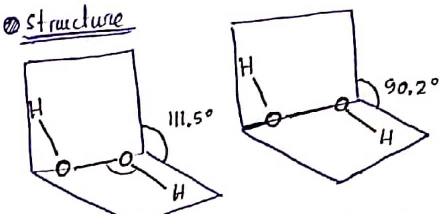
$$2HSO_4^-(aq) \xrightarrow{e} HO_3SOOSO_3H(aq) \xrightarrow{\text{Hydrolysis}} 2HSO_4^-(aq) + 2H^+(aq) + H_2O_2(aq)$$

$$K_2S_2O_8 + 2D_2O \longrightarrow 2KDSO_4 + D_2O_2$$

Ø INDUSTRIALLY, prepared by Auto-oxidation of 2-alkyl anthraquinols.

$$\text{2-ethylanthaquinol} \underset{H_2/Pd}{\overset{O_2(air)}{\rightleftharpoons}} H_2O_2 + (\text{oxidised product})$$

● **Structure**



● Gas Phase ● Solid phase

● **Physical Properties**
- → colourless (very pale blue)
- → forms a hydrate ($H_2O_2 \cdot H_2O$)
- → 30% solⁿ is marketed as 100 volume.

● **Chemical properties** [Acts as both oxidising & reducing agent]

→ Oxidising in acidic medium, $2Fe^{2+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{3+} + 2H_2O$ / $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

→ Reducing in acidic medium, $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$ / $HOCl + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$

→ Oxidising in basic medium, $2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$ / $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$

→ Reducing in basic medium, $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$ / $2MnO_4^- + 3H_2O_2 \longrightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

● **Storage** [Decomposes slowly on the exposure of light] $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$

→ In presence of metal or traces of alkali, the above reaction is catalysed. It is stored in wax-lined glass or plastic vessels in dark. Urea can be added as stabiliser. Kept away from dust cas it causes explosive decomposition.

● **Uses** → Used as hair bleach and mild disinfectant. Sold as an antiseptic with the name perhydrol
- → manufacture chemicals like sodium perborate and per carbonates (detergents)
- → synthesis of hydroquinone, tartaric acid, cephalospborin etc
- → bleaching agent for textile, paper pulp, leather, oils, fats etc
- → in pollution control, industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewag

● **Heavy water (D_2O)**
- → used as moderator in nuclear reactors, used in preparation of other deuterium.
- → prepared by exhaustive electrolysis of water or by-product in some fertilizer industries.

$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$ / $SO_3 + D_2O \longrightarrow D_2SO_4$ / $Al_4C_3 + 12D_2O \longrightarrow 3CD_4 + 4Al(OD)_3$

● **H_2 as a fuel**

S-Block

- Groups 1 & 2 — Group 1: Li, Na, K, Rb, Cs, Fr $[ns^1]$ (Alkali metals) — Group 2: Be, Mg, Ca, Sr, Ba, Ra $[ns^2]$ (Alkaline earth metals)
- Francium is radioactive, ^{223}Fr has a $t_{1/2}$ = 21 minutes
- Beryllium (Be) is rare (only 10^{-10}% of igneous rocks)
- Li shows similarities to Mg and Be to Al [Diagonal relationship] → Due to similar size and q/m ratio.

Group 1 : Alkali metals

- Higly electropositive metals and lose 1 electron to form M^+ ions.

TRENDS

→ Atomic / Ionic Radii : Increase down the group [Li < Na < K < Rb < Cs < Fr]. Ions are smaller than parent atom.

→ IE / IP : Decrease down the group [Li > Na > K > Rb > Cs > Fr]

→ Hydration Enthalpy: Decrease down the group [Li > Na > K > Rb > Cs > Fr]

- Lithium has max hydration enthalpy, thus Li salts are mostly hydrated $[LiCl \cdot 2H_2O]$

PHYSICAL PROPERTIES

- All are silvery white, soft and light metals.
- Density ~~decreases~~ increases from Li to Cs [Exception, K is lighter than Na]
- M.P and B.P.s are low due to weak metallic bonding.
- Impart characteric flame in oxidising flame due to shifting of excited electron and coming back.

Metal	Colour	λ(nm)
Li	Crimson Red	670.8
Na	Yellow	589.2
K	Violet	766.5
Rb	Red violet	780.0
Cs	Blue	455.5

CHEMICAL PROPERTIES

→ Reaction with Air:
- They ternish in dry air due to formation of oxides, which in turn reacts with moisture to form hydroxide.
- Na forms peroxide, Li forms monoxide, others form superoxides [O_2^- is stable w/ large cations (K, Rb, Cs)]

$4Li + O_2 \longrightarrow 2Li_2O$ (oxide) / $2Na + O_2 \longrightarrow Na_2O_2$ (peroxide) / $M + O_2 \longrightarrow MO_2$ (superoxide) [M = K, Rb, Cs]

- Li shows exceptional behaviour by reacting directly with N_2 of air to form nitride $[Li_3N]$
- Due to high reactivity towards air, these metals are kept submerged in Kerosene oil.

→ Reaction with Water:
- Alkali metals ~~for~~ react with water to form hydroxide and dihydrogen. $[2M + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2]$
- Na → least −ve $E^\ominus$ value, Reaction of Li with H_2O is ~~more~~ less vigourous than Na
- Li → most −ve $E^\ominus$ value, other metals react explosively. This is due to small size and very high Hydration energy,
- Also react with proton donors like alcohol, gaseous ammonia and terminal alkynes.

→ Reaction with H_2:
- They react with H_2 at about 673 K (400°C) (Li at 1073 K (800°C)) to form hydrides. [All ionic w/ high melting point]

$2M + H_2 \longrightarrow 2M^+H^-$

→ Reaction with Halogens:
- React vigorously to form ionic halides.
- Exception: Li-halides are somewhat covalent [Due to high Polarising power of Li^+ (Fazan's Rule)] [LiI is most covalent due to large anion]

~~→ Reaction~~

→ Reducing Nature:
- Strong reducing agents, Li strongest, Na weakest.

$M(s) \longrightarrow M(g)$ [Sublimation enthalpy]

$M(g) \longrightarrow M^+(g) + e^-$ [Ionisation enthalpy]

$M^+(g) + H_2O \longrightarrow M^+(aq)$ [Hydration enthalpy]

→ Solutions in liquid Ammonia:
- Dissolve in liq NH_3 giving deep blue solution which are conducting in nature.

$M + (x+y)NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$

- The blue colour is due to the ammoniated e^- which absorbs energy and thus imparts blue colour to the solution
- Solution is paramagnetic
- On standing slowly, liberates hydrogen resulting in formation of amide. $[M^+_{(am)} + e^- + NH_3(l) \longrightarrow MNH_{2(am)} + \frac{1}{2}H_2(g)]$
- In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

USES

- Li with Pb makes 'white metal' ball bearings for motor engine.
- Li with Al is used to make aircraft parts.
- Li with Mg alloy is used to make armour plates.
- Also (Li) used to make electrochemical cells.
- Na is used to make Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. → Used to be used as anti-knocking additive
- liquid Na is used as coolant if fast breeder nuclear reactors.
- K has vital role for biological systems.
- KCl → fertilizer
- KOH is used in the manufacture of soft soap, Also used as an excellent absorbent of CO_2
- Cs is used in devising photoelectric cells.

COMPOUNDS OF ALKALI METAL

→ **Oxides & Hydroxides**
- Li form oxide (Li_2O) and peroxide (Li_2O_2), Na forms peroxide (Na_2O_2) and superoxide (NaO_2), Others form only superoxides.
- Increasing stability of peroxide and hydroxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects.

formation of hydroxide by hydrolysis of oxide

$M_2O + H_2O \longrightarrow \underline{2M^+ + 2OH^-}$ / $M_2O_2 + 2H_2O \longrightarrow \underline{2M^+ + 2OH^-} + H_2O_2$ / $2MO_2 + 2H_2O \longrightarrow \underline{2M^+ + 2OH^-} + H_2O_2 + O_2$

- The oxides and peroxides are colourless whep pure, but the superoxides are yellow or orange in colour.
- Superoxides are paramagnetic (O_2^-). • Hydroxides made for oxides and H_2O are all white crystalline solids.
- Alkali metal hydroxides are strongest of all bases and dissolve freely in H_2O, releases heat on intense hydration.

→ **Halides**
- Crystalline colourless solids with high melting point.
- All these halides have high negative enthalpies of formation: $\Delta_f H^\ominus$ values for fluorides become less negative as we go down the group but that for chlorides, Bromides and Iodides are reverse.
- For a given metal $\Delta_f H^\ominus$ always becomes less negative from flouride to iodide
- m.p & b.p → Fluoride > Chloride > Bromide > Iodide → All are soluble in water.

$\boxed{\text{EXC}}$ Low solubity of LiF in water is due to its high lattice enthalpy whereas low solubility of CsI is due to smaller Hydration enthalpy of its two ions.

- Other halides of Li are soluble in ethanol, acetone and ethylacetate; LiCl is soluble in pyridine also.

→ **Salts of Oxo-Acids**
- Acidic proton and oxo group both are attached to the same hydroxyl group.

[~~H_2OC_3~~
$H_2CO_3 \rightarrow OC(OH)_2$
$H_2SO_4 - O_2S(OH)_2$

- Alkali metals form salts with all the oxo acids (Generally soluble).
- Carbonates and bicarbonates are highly stable to heat. • As electropositivety increase down the group, stability increases.
- Li_2CO_3 is not stable, being small cation it polaries CO_3^{2-} ion leading to formation of more stable Li_2O and CO_2
- $LiHCO_3$ doesn't exist as a solid.

Anomalous Properties of Li

→ Cause: • exceptionally small size. • High polarising power (~~[illegible]~~) (e/r ratio). • Diagonal relationship with Mg.

→ Points:
- Increased covalent character which results in solubility in organic compounds. • Li is least reactive • strongest reducing agent among Grp1
- harder and higher m.p, b.p than other alkali metals
- Forms nitride on combusttion like no other ~~metal~~, alkali metal.
- LiCl is deliquescent and crystallises as a hydrate ($LiCl.2H_2O$); othe alkali metal chlorides don't form solid hydrogen carbonate.
- $LiHCO_3$ is not obtained in the solid form whill all other elements form solid hydrogen carbonate.
- Li unlike other alkali metals don't form ethynide on reaction with ethyne.
- $LiNO_3$ gives Li_2O on heating, other dcompose [$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$ / $2NaNO_3 \longrightarrow 2NaNO_2 + O_2$]
- LiF and Li_2O are much less soluble due to covalency.

Similarities between Li and Mg
- Both Li and Mg are harder, and lighter than other elements in respective group.
- Both react slowly with water. Oxides and hydroxides are much less soluble. hydroxides decompose on heating.
- The oxides Li_2O and M_2O do not combine with excess O_2
- Both Li_2O are soluble in ethanol
- Both LiCl and $MgCl_2$ are delequest and crystalline.

COMPUNDS OF Na

→ **Washing Soda ($Na_2CO_3 \cdot 10H_2O$)**
- Generally prepared by sovley process.
- Advantage of low solubility of $NaHCO_3$ is taken, as, it gets precipitated in the reaction of NaCl and $(NH_4)HCO_3$. $(NH_4)HCO_3$ is created by passing CO_2 to a conc solution of NaCl ~~sta~~saturated with NH_3

$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$ / $(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$ / $NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$

- $NaHCO_3$ crystal separates. These are heated to give Na_2CO_3 [$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$]
- In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$.

$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + H_2O$

- Solvay process can't be extended to the manufacture of K_2CO_3 bcz $KHCO_3$ is too soluble to be precipitated by the addition of NH_4HCO_3 to a satured solution of KCl.

→ **Sodium Chloride (NaCl)** ○ Most abundant source is sea water containing 2.7 to 2.9% by mass of NaCl.

- In tropical counties, it is prepared by solar evapouration [50 lakh tons/year in India]
- ~~Co~~ Crude sodium chloride, generally obtained from crystallisation of brine solution, contains Na_2SO_4, $CaSO_4$, $CaCl_2$, $MgCl_2$ as impurities.
- $CaCl_2$, $MgCl_2$ are impurities because they are deliquesent (absorbs moicture)
- To obtain pure NaCl, crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with HCl gas. Crystals of pure sodium chloride separate out. Calcium and ~~mg~~ $MgCl_2$, being more soluble, remains in solution.
- Sodium chloride melts at 1081 K, solubility = 36g, solubility doesn't increase appreciably with increase in temp.

Uses: ○ Used as common salt ○ Used in preparation of Na_2O_2, NaOH and Na_2CO_3

→ **Caustic Soda (NaOH)** ○ prepared commercially by electrolysis of NaCl in Caster-Kellner cell.
↗ Na and Hg forms amalgum at cathode
↘ ~~Cl~~ Cl_2 is evolved at anode

Cathode : $Na^+ + e^- \xrightarrow{Hg}$ Na-amalgam / Anode : $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

- Treated with water, 2Na-amalgam + $2H_2O \longrightarrow 2NaOH + 2Hg + H_2$
- NaOH is white translucent solid, m.p = 591 K, readily soluble in water to give strong alkaline solution.
- Crystals of NaOH are deliquescent, NaOH at the surface reacts with CO_2 in atmosphere to form Na_2CO_3.

Uses: ○ Manufacture of Soap, paper, artificial silk ○ in petroleum refining ○ Purification of bauxite ○ In texttile industries for mercerising cotton fabrics ○ for preparation of pure fat, oils ○ As a laboratory reagent.

→ **Baking Soda ($NaHCO_3$)** ○ Decomposes on heating to release CO_2 making cakes or pastries fluffy.

- Made by saturating a solution of Na_2CO_3 with CO_2, white crystalline $NaHCO_3$ power, being less soluble, seperates out.

$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$ ○ Mild antiseptic and used in fire extinguishers.

○ **Biological Importance of Na and K**

- Na ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and ammino acids into cells
- K^+ ions are the most abundant cations within cell fluids, where they activate enzymes, participate in the oxidation of glucose to produce ATP and with Na^+, are responsible for the transmissions of nerve signals.
- The ionic gradiant across various blood cells demonstrate that a discriminatory mechanism called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by resting animal and about 15 kg per 24 h in human.

Group - 2

○ Electronic conf: ns^2 ○ Elements: Be, Mg, Ca, Sr, Ba, Ra

TRENDS → Atomic Radii/Ionic Radii: Be < Mg < Ca < Sr < Ba < Ra [All are smaller than corresponding Alkali metals]

→ IE : ~~Ionation~~ Ionisation Enthalpy decreases down the group. [Ra > Ba]

→ Hydration Enthalpies: $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ [More than alkali metals] → Thus their salts are generally hydrated unlike alkali metal

PHYSICAL PROPERTIES: ○ Generally are silvery white, lustrous and relatively soft but harder than alkali metals.

- Be, Mg are greyish ○ M.Ps and B.Ps are higher than corresponding alkali metals due to smaller size.
- Electropositive charachter increases down the group from Be to Ba
- Ca, Sr, Ba impart characteristic brick red, crimson and apple green colours respectively to the flame. The e^-s in Be and Mg are too tightly ~~bon~~ held to be excited and then release energy, hence no colour.
- High conductivity and typical metal properties.

CHEMICAL PROPERTIES [Less reactive than alkali metals / Reactivity increases down the group]

→ Rxn w/ Air and H_2O: ○ Be, Mg are kinetically inert to air and water due to formation of oxide film on their surface.

- But powdered Be burns brilliantly on ignition in air to give BeO and Be_3N_2
- Mg is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2.
- Ca, Sr, Ba are readily attacked by air to form oxide and nitride. React also with H_2O with increasing vigour even in cold to form hydroxides.

→ Rxn w/ Halogen: $[M + X_2 \longrightarrow MX_2]$ ○ But Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_4, and ~~Be_2~~ $BeCl_2$ is conviniently made from the oxide. $[BeO + C + Cl_2 \xrightarrow{600-800K} BeCl_2 + CO]$

→ Rxn w/ H_2: ○ All except Be combine to form hydride MH_2. ○ BeH_2 can be prepared by rxn of $BeCl_2$ with $LiAlH_4$

→ **Reducing Nature :** • Weaker reducing agent than corresponding alkali metals. • BeO has rather less negative reduction potential than other alkaline earth metals but its reducing nature is due to large hydration energy associated with small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal.

→ **Sol^n in liquid NH_3** • dissolves in liq. NH_3 to give deep blue black solution forming ammoniated ions.
$M + (x+y)NH_3 \longrightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^-$ • From these sol^n, the ammoniates $[M(NH_3)_6]^{2+}$ can be removed.

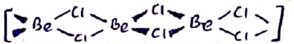
USES

• Be is used in manufacture of alloys. • Copper-beryllium alloys are used in the prep of high strength springs.
• Metallic Be is used for making windows X-ray tubes. • Mg forms alloys with Al, Zn, Mn and Sn
• Mg-Al alloys being light are used in air-craft construction. • Mg (Powder/Ribbon) is used in flash powders and bulbs, incendiary bombs and ~~single~~ signals. • Suspention of $Mg(OH)_2$ in H_2O (Milk of Magnesia) used as Antacid.
• $MgCO_3$ is used in toothpaste. • Ca is used in extraction of metals from oxides which are difficult to reduce with C.
• Ca and Ba metal used to remove air from vaccum tubes. • Ra salts are used in radiotherapy (Treatment of Cancer)

COMPOUNDS OF ALKALINE EARTH METAL

Specially covalent in nature

→ **Oxides & Hydroxides :** • Burn in O_2 to form MO (monoxide). • Except BeO, they have rock salt structure. • BeO is amphoteric, others are ionic
• Oxides have quite high enthalpies of formation, are ~~quite~~ very stable to heat.
• All oxides except BeO are basic, form sparingly soluble hydroxides reacting with H_2O $[MO + H_2O \longrightarrow M(OH)_2]$
• solubility, thermal stability and basic character increase with increase in At. no from $Mg(OH)_2$ to $Ba(OH)_2$
• Less basic and less stable than Grp. 1 • $Be(OH)_2$ being amphoteric
$$\left[\begin{array}{l} Be(OH)_2 + 2OH^- \longrightarrow [Be(OH)_4]^{2-} \rightarrow \text{(Beryllate ion)} \\ Be(OH)_2 + 2HCl + 2H_2O \longrightarrow [Be(OH)_4]Cl_2 \end{array}\right]$$

→ **Halides :** • Except BeX_2, all halides of Grp. 2 are ionic in nature. • BeX_2 is covalent and soluble in organic solvents.
• $BeCl_2$ has a chain structure in solid state  • In vapour phase, it forms chlorobridged dimer which dissosiates at order of 1200K. • Tendency to form halide hydrates gradually decreases down [$MgCl_2 \cdot 8H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ $BaCl_2 \cdot 2H$
• Insted of ~~dn~~ dehydration hydrated halides of Be and Mg on heating suffer hydrolysis.
• Fluorides are relatively less soluble than chlorides owning high lattice energies.

→ **Salts of Oxoacids**

→ **Carbonate :** • Insoluble in water, can be precipitated by addition of a sodium or ammonium carbonate soluble salts of these metals.
• The solubility of carbonates decreases with increase in at. no. • All the carbonates decompose on heating to give CO_2 and oxide
• $BeCO_3$ is unstable and kept in CO_2 atmosphere. • Thermal Stability increases with increasing cationic size.

→ **Sulphate :** • All white solids and stable to heat. • $BeSO_4$, and $MgSO_4$ are readily soluble in water.
Thus soluble.
• Solubility decrease from $CaSO_4$ to $BaSO_4$. • In Be^{2+} and Mg^{2+} ~~ions overcome~~ hydration enthalpies overcome lattice ~~energy~~ enthalpy

→ **Nitrates :** • Made by dissolution of the of the carbonates in dil nitric acids. • $Mg(NO_3)_2$ crystallises with 6 H_2O molecules, $Ba(NO_3)_2$ crystallises as adhydrous salt. • All decompose on heating $[2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2]$

• Anomalous Behaviour of Be : [• Diagonal relationship with Al]

Easily hydrolysed

• Exceptionally small atom and ionic size, Due to high ionisation enthalpy and small size it forms largely covalent compounds
• Due to absence of d orbital, does not exibit coordination no more than four. other members can have coordination no of 6.
• Unlike other member, oxides and hydroxide of Be are amphoteric.

• Diagonal Relationship b/w Be and Al :

• Be^{2+} and Al^{3+} have similar charge / radius ratio
• Al and Be are not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
• $Be(OH)_2$ dissolved in excess of alkali to give Beryllate ion $[Be(OH)_4]^{2-}$
• Chlorides of Be and Al have Cl^- bridged chloride structure in vapour state. Both chlorides are nonpolar, strong Lewis base. Used as Friedel Craft catalysts.
• Be^{2+} and Al^{3+} have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}.

COMPOUNDS OF Calcium

CO₂ is removed quickly.

→ **Quick Lime (CaO) :** • Preped by heating lime stone ($CaCO_3$) in a rotary kiln at 1070 - 1270K $[CaCO_3 \overset{heat}{\rightleftharpoons} CaO + CO_2]$
• CaO is a white amorphous solid. mp = 2870K. On exposure to air, it absorbs moisture and carbon dioxide.
$[CaO + H_2O \longrightarrow Ca(OH)_2 \;/\; CaO + CO_2 \longrightarrow CaCO_3]$ • Addition of limited water breaks lump of lime, its called slaking of lime
• Quick lime slaked with soda is known as sodalime • Being basic oxide, it combines with acidic oxides at high Temp.
$[CaO + SiO_2 \longrightarrow CaSiO_3 \;/\; 6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$

→ **Uses :** • For manufacturing cement and is the cheapest form alkali • Manufacturing of sodium carbonate (Na_2CO_3) and (NaOH),
• In purification of sugar and in manufacture of dye stuffs

→ **Slaked lime, $Ca(OH)_2$:** • Prepared by adding CaO to H_2O, white amorphous powder, sparingly soluble in water.
• The aqueous solution is known as lime water and a suspension of $Ca(OH)_2$ in H_2O is known as milk of lime.
• On passing CO_2, it turns milky due to formation of $CaCO_3$ $[Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O]$
• On passing excess CO_2, the ppt dissolves to form $Ca(HCO_3)_2$ $[CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$
Bleaching Power.
• Milk of lime reacts with Cl_2 to form hypochlorite, a constituent of bleaching powder $[Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}$ $+ 2H_2O$

→ **Uses :** • preparation of mortar, a building material. • used in white ash due to its disinfectant nature.
• Used in glass making, in tanning industry, prep of bleaching powder and purification of sugar

→ **Calcium Carbonate. ($CaCO_3$):** • $CaCO_3$ occurs in nature in several forms like lime stone, chalk, marble etc.

- Can be prepared by passing CO_2 through $Ca(OH)_2$ or by addition of Na_2CO_3 to $CaCl_2$
  $[Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \,/\, CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl]$
- $CaCO_3$ is a white fluffy powder, almost insoluble in water. When heated at 1200k, it decomposes.
  $[CaCO_3 \xrightarrow{1200K} CaO + CO_2]$
- Reacts with dilute acid to liberatte CO_2 $[CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \,/\, CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2]$

→ **Uses:**
- Used as building material in form of marble and manufacture of quick lime.
- $CaCO_3$ and $MgCO_3$ is used as a flux in the extraction of metals such as iron
- Specially ppt. $CaCO_3$ is used in making high quality paper.
- Used as antacid, mild abrasive in tooth paste, a constituent of chewing gum and filler in cosmetics.

→ **Calcium Sulphate (Plaster of Paris)($CaSO_4 \cdot \frac{1}{2} H_2O$):** • Hemi-hydrate of $CaSO_4$, obtained by heating gypsum, $CaSO_4 \cdot 2H_2O$ at 393 K
$[2(CaSO_4 \cdot 2H_2O) \longrightarrow 2(CaSO_4) \cdot H_2O + 3H_2O]$

- Above 393K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed [dead burnt plaster]
- Has remarkable property of settling with water. On mixing with adequate quantity of water it forms plastic mass that gets into a hard solid in 5 to 15 minutes.

→ **Uses:** • In building industry as plaster. • Used to immobilise the affected part of organ where there is a bone fracture of sprain, also employed in dentistry, in ornamental works and making casts of statues and busts

- Cement: Cement is a product obtained by combining a meterial rich in lime, CaO with other materials such as clay which contains silica, SiO_2 along with the oxides of aluminium.
  - The raw materials for the manufacture are limestone and clay. which are mixed together to form 'cement clinker'. which is mixed with 2-3% by weight of gypsum $(CaSO_4 \cdot 2H_2O)$ to form cement.
  - Ingredients of Portland cement (i) dicalcium silicate (Ca_2SiO_4) 26% (ii) tricalcium silicate (Ca_3SiO_5) 51% and (iii) tricalcium aluminate $(Ca_3Al_2O_6)$ 11%
  - Settling of Cement: When mixed with water, it settles to a hard mass. This is due to the hydration of the molecules of the constituents and rearrangements.
  - The purpose of adding gypsum is only to slow down the process of settling of the cement so that it gets sufficient hardening.

• **Biological Importance of Mg and Ca:**
• An adult body contains 25g of Mg and 1200g of Ca. • All enzymes that utilise ATP in phosphate transfer require Mg as a cofactor. • Main pigment for the absorption of light in plants is chlorophyll which contains Mg. • About 99% of body Ca is present in bones and teeth, it also plays important roles in neuromascular function, interneuronal transmission, cell membrane integrity and blood coagulation. • Ca concentration in blood plasma is regulated at about 100 mgL^{-1}, It is maintained by ~~by~~ two hormones: calcitonin and parathyroid.

P-Block

Group 15 elements (N, P, As, Sb, Bi) [ns^2np^3] : → down the group, there is a shift from non-metallic to metallic through metaloidic character. N, P are non metals, As, Sb is metalloids and Bi is a typical metal.

Occurance: → N_2 is 78% of the atmosphere by volume. it occurs in earth's crust as $NaNO_3$, KNO_3. It is also found in proteins.

→ P appears in members of the apatite family [$Ca_9(PO_4)_6 \cdot CaX_2$ (X = F, Cl or OH)] it is an essential constituent of animal and plant matter (bones, cells).

→ As, Sb and Bi are found mainly as sulphide minerals.

atomic and ionic radii : → increase down the group. considerable increase from N to P and minute in As to Bi (due to d and f orbitals)

ionisation enthalpy: → decrases down the group. due to half filled p orbital, IE is considerably high than group 14. ($\Delta H_1 < \Delta H_2 < \Delta H_3$)

electronegativity: → decreases down the group, not profound in heavier element

physical properties : → N_2 is ~~solid~~ gas, others are diatomic solids. metallic character increases down the group. → b.p increases down the group.

→ m.p. increases upto As then decreases upto Bi.

→ all other than N show allotropy.

CHEMICAL PROPERTIES

ox states and trends in chemical reactivity → common oxidation states are −3, +3, +5. ~~de~~ tendency to exibit −3 ox. state decreases down the group. Bi almost doesn't.

→ stability of +5 ox state decreases down the group. only Bi(V) compound is BiF_5. stability of +3 ox state increases down the group (due to inert pair effect)

→ N also exhibits +1, +2, +4 ox. states reacting with O_2

→ P shows +1 and +4 in some oxoacids

→ all ox states of N from +1 to +4 disproportionate in acid solution.

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

→ similarly in P, nearly all ox states disproportionate in alkali and acid.

→ N is stricted to a maximum covalency of 4 since only 4 (1s + 3p) orbitals are available. others with d orbital can expand their octate.

anomalous properties of nitrogen → due to small size and high electronegativity, high ionisation enthalpy and non-availability of d orbitals. N has unique ability to form pπ−pπ multiple bond with itself and other elements with small size and high electronegativity (e.g. C, O). thus N_2 exist with high bond dissociation enthalpy.

→ P−P, As−As and Sb−Sb form single bond, Bi forms metallic bond. Single N−N is weaker than P−P because of high interelectronic repulsion of the non-bonding electrons. As a result, catenation tendency is weaker in N.

→ due to absense of d orbital in valence shell, it cannot form dπ−pπ ~~bor~~ bond as the others. P and As can form dπ−dπ bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

reactivity towards H_2: → all form hydride of form EH_3. stability of the hydrides decreases from NH_3 to BiH_3. the reducing nature of the hydrides increases down the group.
→ basicity order: $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$

reactivity towards O_2: → all form two types of oxides: E_2O_3 and E_2O_5. oxide with higher ox. state is more acidic. acidic character decreases down the group.
→ E_2O_3 of N, P are purely acidic, As, Sb are amphoteric, Bi is basic.

reactivity towards halogens: → these form EX_3 and EX_5. N doesn't form NX_5 due to absence of d orb.
→ EX_5 are ~~EX_3~~ more covalent than EX_3. except NX_3 all trihalides are stable (NF_3 is stable though)(~~Tri~~ EX_3 except BiF_3 are covalent).

reactivity towards metals: → all form binary compounds exhibiting −3 ox state e.g. Ca_3N_2, Ca_3P_2..

DINITROGEN

preparation: → produced commercially by liquification and fractional distillation of air.
→ treating an aqueous solⁿ of NH_4Cl with sodium nitrile ($NaNO_2$)

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

→ by thermal decomposition of $(NH_4)_2Cr_2O_7$ [ammonium dichromate]

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

→ very pure N_2 by thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

properties: → has two stable isotopes: ^{14}N and ^{15}N. very less soluble in water. low freezing and boiling points. rather inert at room temp.
→ reactivity increases rapidly with temperature. at high Temp, it directly combines with some metals to form predominantly ionic nitrides and covalent ones with non-metals.

$$6Li + N_2 \xrightarrow{\Delta} 2Li_3N \; / \; 3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$

→ it combines with H_2 at 500°C in presence of catalyst (Haber's process)

$$N_2(g) + 3H_2(g) \underset{cat}{\overset{500°C}{\rightleftharpoons}} 2NH_3(g)$$

→ N_2 combines with O_2 at about 2000K to form NO.

$$N_2 + O_2(g) \overset{\Delta}{\rightleftharpoons} 2NO(g)$$

AMMONIA

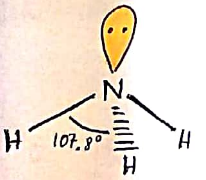
preparation: → in nature, due to decay of nitrogenous compounds e.g. urea.

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

→ in small scale, ammonium salts decompose when treated w/ NaOH, $Ca(OH)_2$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$



→ On large scale, it is manufactured by Habers Process.

$$N_2(g) + 3H_2(g) \underset{400°C}{\overset{200\,atm}{\rightleftharpoons}} 2NH_3(g)$$ [catalyst → K_2O, Al_2O_3]

properties: → colourless, pungent odour. possesses hydrogen bonds causing high b.p.
→ highly soluble in water, in aq solⁿ is weakly basic due to form OH −

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

→ It precipitates the hydroxides of many metals from their salt. e.g.

$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{white ppt}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$

$$FeCl_3(aq) + NH_4OH(aq) \longrightarrow Fe_2O_3 \cdot xH_2O(s) + NH_4Cl(aq)$$

→ due to presence of lone pair on N atom, acts as lewis base. By donating the electron pair, it forms linkage with metal ions and this finds application in detection of metal ions such as Cu^{2+}, Ag^{2+}:

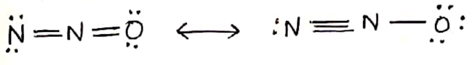
$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$
blue — deep blue

$Ag^+ + Cl^- \longrightarrow AgCl(s)$ white ppt
colourless

$AgCl(s) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]Cl\ (aq)$
colourless

Oxides of Nitrogen

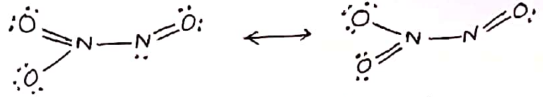
Dinitrogen oxide (N_2O): colourless gas (neutral)
oxidation state: +1   preparation: $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$


$\ddot{N}=N=\ddot{O} \longleftrightarrow :N\equiv N-\ddot{O}:$

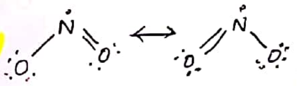
Nitrogen monoxide (NO): colourless gas (neutral)
oxidation state: +2   preparation: $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$


$:N=\ddot{O}: \longleftrightarrow :\dot{N}=\ddot{O}:$

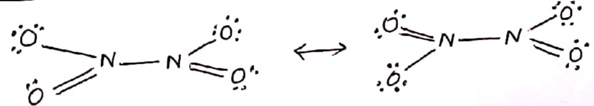
Dinitrogen trioxide (N_2O_3): blue solid (acidic)
oxidation state: +3   preparation: $2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$



Nitrogen dioxide (NO_2): brown gas (acidic)
oxidation state: +4   preparation: $2Pb(NO_3)_2 \xrightarrow{400K} 4NO_2 + 2PbO + O_2$

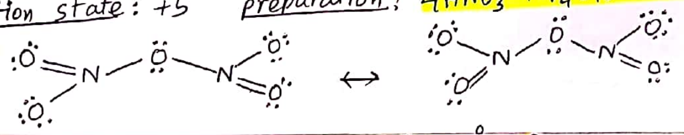


Dinitrogen tetroxide (N_2O_4): colourless solid/liquid (acidic)
oxidation state: +4   preparation: $2NO_2 \underset{\Delta}{\overset{cool}{\rightleftharpoons}} N_2O_4$



[NO_2 contains odd number of valance electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons]

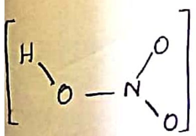
Dinitrogen pentoxide (N_2O_5): colourless solid (acidic)
oxidation state: +5   preparation: $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$



NITRIC ACID

preparation: → Lab prep by heating KNO_3 or $NaNO_3$ and conc H_2SO_4

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$


gaseous state

→ On large scale, it is prepared by Ostwald's process.

$4NH_3 + 5O_2(g) \xrightarrow[500K,\ 9\,bar]{Pt/Rh\ gauge\ catalyst} 4NO + 6H_2O$

$2NO + O_2 \rightleftharpoons 2NO_2$

$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$

properties: → conc nitric acid is a strong oxidising agent and attacks most metals except noble metals. the products depend upon the concentration of the acid, temp and nature of the material undergoing oxidation.

$3Cu + 8HNO_3(dil) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

$Cu + 4HNO_3(conc) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

→ Zn reacts with dilute nitric acid to give NO_2 and with conc acid to give NO_2

$$4Zn + 10HNO_3\,(dil) \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3\,(conc) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

→ some metals (e.g. Cr, Al) do not dissolve in conc nitric acid because of the formation of a passive film of oxide on the surface.

→ conc HNO_3 also oxidises non-metals and other compounds.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

→ the familiar 'Brown Ring Test' for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex. the test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube.

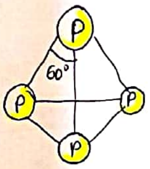
$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{brown}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

Phosphorus

Allotropic forms:

white phosphorus: → translucent white, waxy, poisonous, insoluble in water but soluble in CS_2 and glows in dark.



→ It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

→ it is less stable and therefore, more reactive than others because of angular strain in the P_4 molecule (angles 60°). It readily chatches fire in air to give dense white fumes of P_4O_{10}

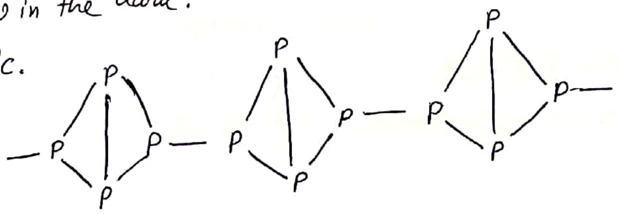
$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

red phosphorus:

→ obtained by heating white phosphorus at 573K in inert atmosphere for several days. when it is headed under high pressure, a series of phases of black P is formed.

→ Red P posseses iron grey lusture. odourless, non-poisonous and insoluble in water as well as in ~~carbon~~ CS_2. Red P is less reactive than white P. doesn't glow in the dark.

→ It is polymaric.



black phosphorus: → it has two forms e.g. α-black and β-black. α-black phosphorus is formed when red ~~ph~~ P is heated in a sealed tube at 803K. it can be sublimed in air and has opaque monoclinic or rhombo~~dr~~hedral crystals. does not oxidise in air,

→ β-black P is prepared by heating white P at 473K under high P. It does not burn in air upto 673K.

Phosphine

preparation: → by the reaction of Calcium phosphide (Ca_3P_2) with H_2O or dilute HCl

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$

→ lab prep: by heating white P with conc NaOH in inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

→ when pure, it is non inflammable but becomes inflammable owing to the presence of P_2H_4 of P_4 vapours. to purify it from impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH. gives PH_3. $PH_4I + KOH \longrightarrow KI + H_2O + PH_3$

properties: → colourless gas, rotten fish smell and is highly pisonous. it explodes in contact with traces of oxidising agent like HNO_3, Cl_2 and Br_2 vapours.

→ slightly soluble in water. solution of PH_3 in water decomposes in presence of light giving red P and H_2.

→ when absorbed in $CuSO_4$ or $HgCl_2$ solution, the corresponding phosphides formed

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

$$3Hg_2Cl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

→ phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g. $PH_3 + HBr \longrightarrow PH_4Br$

Phosphorus Halides

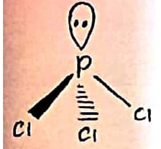
[PX_3] preparation: → passing dry Cl over heated white P. $P_4 + 6Cl_2 \longrightarrow 4PCl_3$

→ action of thionyl chloride ($SOCl_2$) with white P.

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

properties: → colourless oily liquid and hydrolyses in the presence of moisture.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$



→ reacts with organic compounds containing –OH group.

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

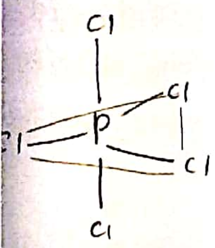
$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

[PX_5] preparation: → reaction of white P with excess of dry chlorine. $P_4 + 10Cl_2 \longrightarrow 4PCl_5$

→ by action of SO_2Cl_2 on P. $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

properties: → yellowish white powder, in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$; $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$



→ when heated, it sublimes but decomposes on stronger heating. $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

→ reacts with organic compounds containing –OH group converting to Cl-derive

$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$

$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

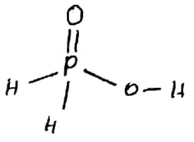
→ finely divided metals on heating with PCl_5 give corresponding chlorides.

$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$ / $Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$

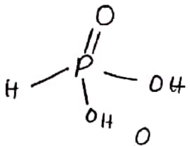
→ it has trigonal bipyramidal structure ~~and~~. In solid state, it exists ~~as~~ an ionic solid $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+ \rightarrow$ tetrahedral, $[PCl_6]^- \rightarrow$ octa.

Oxoacids of Phosphorus.

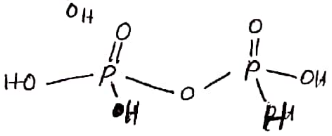
Hypophosphorus acid. (H_3PO_2): (+1) preparation: white P_4 + alkali oxidation no: +1



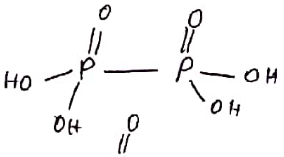
Orthophosphorus acid (H_3PO_3): (+3) preparation: $P_2O_3 + H_2O$ ox. no: +3



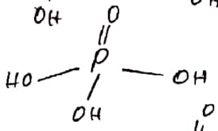
Pyrophosphorus acid ($H_4P_2O_5$): (+3) preparation: $PCl_3 + H_3PO_3$ ox. no: +3



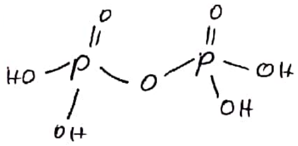
Hypophosphoric acid ($H_4P_2O_6$): (+4) prep: red P_4 + alkali.



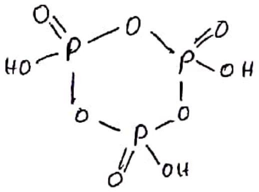
Orthophosphoric acid (H_3PO_4): (+5) prep: $P_4O_{10} + H_2O$



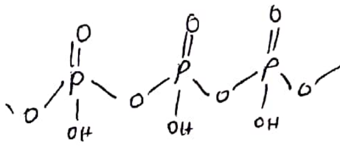
Pyrophosphoric acid ($H_4P_2O_7$): (+5) prep: heat phosphoric acid.



Metaphosphoric acid ($(HPO_3)_n$): (+5) prep: phosphorus acid $+ Br_2 + \Delta$ in sealed tube



cyclotrimetaphosphoric acid



polymetaphosphoric acid.

properties: → acids in +3 ox state disproportionate. e.g. $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$

→ acids with P–H bond have strong reducing properties e.g. H_3PO_2 w/ 2 P–H bonds.

$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$

Group 16

elements: O, S, Se, Te, Po   electronic configuration: ns^2np^4

atomic and ionic radii: increases down the group. Oxygen is exceptionally small.

Ionisation enthalpy: increases down the group. IE of grp 16 is lower compared to grp 15.

electron gain enthalpy: because of compact nature, O atom has less negative electron gain enthalpy than S. from S onwards the value again becomes less negative upto Po.

electronegativity: next to F, O has the highest EN value amongst the elements. EN decreases down the group. metallic character increases from O to Po.

physical properties:
→ O, S are non metals, Se, Te are metalloids, Po is a metal.
→ Po is radioactive and short lived.
→ all these elements exhibits allotropy
→ mp and bp increase with atomic number. large difference b/w the mp and bp of O and S may be explained on the basis of atomicity [O_2 diatomic, S_8 polyatomic

CHEMICAL PROPERTIES

Oxidation state & chemical reactivity:
→ stability of −2 ox. state decreases down the group. Po doesn't. O only shows −2. exception: OF_2 (+2)
→ others show +2, +4, +6 ox states. +4 and +6 are more common. S, Se, Te generally show +4 with oxygen and +6 with F. stability of +6 oxidation state decreases down the group and that of +4 increases (inert pair effect).

anomalous behaviour of oxygen:
→ due to small size, high electronegativity. due to this H-bond exists in H_2O but not H_2S.
→ absence of d orbital limits its covalency to 4 and in practice, it rarely exceeds 2.

reactivity w/ hydrogen:
→ all form hydrides of the type H_2E (E = O, S, Se, Te, Po), acidic character increases down
→ the increase in acidic character down the group can be explained in terms of decrease in bond enthalpy for dissociation of H-E bond down the group.
→ the thermal stability of hydries also decreases from H_2O to H_2Po due to this.
→ all hydrides except water possesses reducing property and this character increases from H_2S to H_2Te.

reactivity w/ oxygen:
→ all form oxides of EO_2 and EO_3 type. O_3 and SO_2 are gases while SeO_2 is solid.
→ reducing property of dioxide decreases from SO_2 to TeO_2. SO_2 is reducing while TeO_2 is an oxidising agent.
→ besides EO_2, S, Se and Te form EO_3. both are acidic in nature.

reactivity w/ halogens:
→ they form a large number of halides of type EX_6, EX_4 and EX_2.
→ stability of halides decreases in the order $F^- > Cl^- > Br^- > I^-$. among EX_6, ECl_6 are only stable halides. all EF_6 are gaseous in nature. SF_6 is exceptionally stable for steric reasons.
→ among EX_4, SF_4 is a gas, SeF_4 a liquid, TeF_4 a solid.
→ all except O forms dichlorides and dibromides.
→ the well known monohalides are dimeric in nature eg. S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2. these undergo disproportionation as given below.

$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$$

Dioxygen

preparation: → lab preps: by heating O-containing salts such as chlorates, nitrates and permanganates.

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

→ lab prep: by thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$$2Ag_2O \longrightarrow 4Ag + O_2 \qquad 2Pb_3O_4 \longrightarrow 6PbO + O_2$$

$$2HgO \longrightarrow 2Hg + O_2 \qquad 2PbO_2 \longrightarrow 2PbO + O_2$$

→ lab prep: H_2O_2 is readily decomposed into H_2O and O_2 with finely divided metal and MnO_2 as catalyst. $2H_2O_2 \longrightarrow 2H_2O + O_2$

→ on large scale it can prepared from water or air via electrolysis.

→ industrially, O_2 is obtained by fractional distilation of liquified air after removing CO_2 and water vapour.

properties: → $2Ca + O_2 \longrightarrow 2CaO$; $4Al + 3O_2 \longrightarrow 2Al_2O_3$; $P_4 + 5O_2 \longrightarrow P_4O_{10}$

$C + O_2 \longrightarrow CO_2$; $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$;

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$; $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Simple Oxides: → generally, non-metal oxides are acidic but oxides of some metals in high oxidation state have some acidic character (e.g. Mn_2O_7, CrO_3, V_2O_5)

→ generally, metal oxides are basic.

→ some show dual behaviour known as amphoteric oxides. e.g.

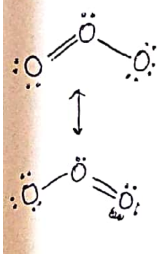
$$Al_2O_3 + 6HCl + 9H_2O \longrightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$$

$$Al_2O_3 + 6NaOH + 3H_2O \longrightarrow 2Na_3[Al(OH)_6]$$

→ some oxides neither acidic nor basic known as neutral oxides. eg. CO, NO, N_2O.

Ozone

→ too reactive to remain in atmosphere at sea level. at about 20 km, ozone layer is formed.



preparation: → passing dry O_2 through a silent electrical discharge, conversion of O_2 to O_3 (10%) occurs. the product is known as ozonised oxygen.

$$3O_2 \longrightarrow 2O_3$$

→ as the conversion in endothermic, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition.

→ for >10%, a battery of ozonisers can be used and pure ozone can be condensed in a vessel surrounded by liquid oxygen.

properties: → pale blue gas, dark blue liquid and violet-~~gas~~ black solid. it has a characteristic smell and in small concentration is harmless. however above 100 ppm, breathing becomes uncomfortable resulting in headache and nausea.

→ ozone is thermodynamically unstable wrt O_2 since in decomposition ΔH is -ve and ΔS is positive. $\Delta G < 0$. thus high concentration of O_3 is explosive.

→ due to tendency to liberate atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. e.g.

$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$

$$2I^- + H_2O + O_3 \longrightarrow 2OH^- + I_2 + O_2$$

→ nitrogen oxides (particularly nitric acid) combine rapidly with O_3.

$$NO + O_3 \longrightarrow NO_2 + O_2$$

→ freons used in aerosol sprays and as refrigerants damages ozone layer.

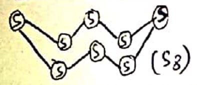
Sulphur

→ forms numerous allotropes of which yellow rhombic (α-sulphur) and monoclinic (β-sulphur) forms are most important. rhombic sulphur is stable at room temperature.

rhombic sulphur (α-sulphur): → yellow in colour, formed on evaporation of solution of roll sulphur in CS_2.

→ insoluble in water but dissolves to some extent in ⌬, R-OH and R-O-R'.

→ readily soluble in CS_2.

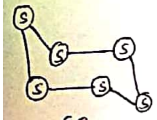


monoclinic sulphur (β-sulphur) → soluble in CS_2, prepared by melting rhombic sulphur in dish and cooling, till crust is formed. two holes are made in the crust and the remaining liquid is poured out. On removing the crust, colourless needle ~~sp~~ shaped crystal of β-sulphur. transforms into α-sulphur below 369K.

→ at 369K, both forms are stable, it is known as transition temperature

→ both forms have S_8 molecules with different structure (puckered and crown)

→ in synthesised cyclo-S_6, it becomes chair form. above 1000K, S_2 is dominant.



(S_6)

Sulphur Dioxide

preparation: → SO_2 is formed with a little (6–8%) SO_3 when S is burnt in air or oxygen.

$$S + O_2 \longrightarrow SO_2$$

→ lab prep: treating a sulphite with dilute sulphuric acid

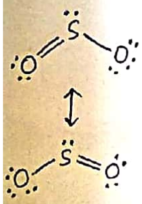
$$SO_3^{2-} + 2H^+ \longrightarrow H_2O + SO_2$$

→ industrially, produced as a ~~p~~ by product of roasting of sulphide ores.

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

properties: → colourless, pungent smelling, soluble in water. forms H_2SO_3 with water.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$



→ reacts readily with NaOH solution forming sodium sulphite which reacts with more SO_2 forming $NaHSO_3$.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

→ reacts with Cl_2 in presence of charcoal (catalyst) to give sulphuryl chloride (SO_2Cl_2). it is oxidised to SO_3 by O_2.

$$SO_2 + Cl_2 \xrightarrow{\text{charcoal}} SO_2Cl_2$$

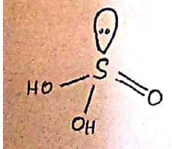
$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

→ moist SO_2 behaves as a reducing agent. it converts Fe(III) ions to Fe(II) and decolourises acidified $KMnO_4$ solution.

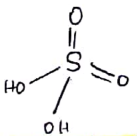
$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

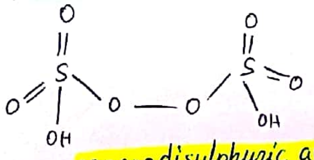
Oxoacids of Sulpher



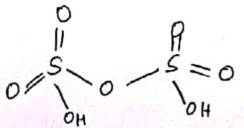
sulphurous acid
(H_2SO_3)



sulpuric acid.
(H_2SO_4)



peroxodisulphuric acid
($H_2S_2O_8$)



Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

Sulphuric Acid

manufacture: → by the Contact Process which involves 3 steps.:
i) burning of sulphur or sulphide ores in air to generate SO_2.
ii) conversion of SO_2 to SO_3 by the reaction with O_2 with V_2O_5 as catalyst.
iii) absorption of SO_3 in H_2SO_4 to give Oleum ($H_2S_2O_7$)

(ii) is the key step [$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$, $\Delta_rH^\ominus = -196.6\ kJ\,mol^{-1}$]. the reaction is exothermic, reversible and forward reaction leads to decrease in volume. therefore, low T and high P are favourable. (generally 2bar and 720K is used) dilution of oleum gives H_2SO_4 of the desired concentration (96–98% pure).

properties: → colourless, dissolves in water with large evolution of heat. [conc acid into water + stir]
→ chemical reactions are due to (i) low volatility (ii) strong acid (iii) strong affinity to water (iv) ability to act as oxidising agent.
→ due to low volatility, can be used to make more volatile acids from their salts.

$$2MX + H_2SO_4 \longrightarrow 2HX + M_2SO_4 \quad [X = F, Cl, NO_3]$$

→ it is strong dehydrating agent (wet gases can be dried up provided they don't react) it removes water from organic compounds. $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$
→ hot concentrated sulphuric acid acts as a moderately strong oxidising agent. (intermidiate between phosphoric and nitric acid). H_2SO_4 is reduced to SO_2.

$$Cu + 2H_2SO_4 \xrightarrow{(conc)} CuSO_4 + SO_2 + 2H_2O$$

$$S + 2H_2SO_4\,(conc) \longrightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4\,(conc) \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

uses: → mainly in making fertilizers, petroleum refining, manufacture of pigments, paints, detergent industry

Group 17 Elements

occurance: → F, Cl are fairly abundant. At is radioactive. F is normaly present as insoluble fluorides (CaF_2, Na_3AlF_6 etc) and small quantity is present in soil, river water, bones and teeth of animals.
→ sea water contains chlorides, bromides and iodides of Na, K, Mg and Ca (mainly NaCl)

electronic config → ns^2np^5

atomic and ionic radii: → smallest atomic radii in respective ~~group~~ periods. F is extremely small.
→ atomic and ionic radii increases down the group.

ionisation enthalpy: → very high ionisation enthalpy. decreases down the group.

electron gain enthalpy: → maximum electron gain enthalpy in respective ~~group~~ periods because they need only one electron for octate. becomes less negative down the group
→ negative electron gain enthalpy of F is less than Cl due to small size.

electronegativity: → highlyly electronegative, decreases down the group. F is most electronegative.

physical properties: → all halogens are coloured. (F_2 yellow, Cl_2 greenish yellow, Br_2 red, I_2 violet).
→ F and Cl react with H_2O, Br and I are sparingly soluble in H_2O. but soluble in various organic solvents such as chloroform, CCl_4, CS_2 and hydrocarbons.
→ enthalpy of dissosiation of F_2 is less than that of Cl_2 (X—X). $F_2 < Cl_2 > Br_2 > I_2$

CHEMICAL PROPERTIES

ox. state and trend in chemical reactivity: → all halogens exhibit −1 ox state. however Cl, Br and I exhibit +1, +3, +5 and +7 also. higher oxidation state of Cl, Br, I are realised mainly when the halogens combine with small and highly electronegative F or O atoms.

→ all halogens are highly reactive. reactivity decreases down the group.

→ due to high acceptance of one electron, are strong oxidising agent ~~nature~~ F is the strongest oxidising halogen, oxidises other halide ions in solution or even is solid state. a halogen oxidises halide ions of higher at. no

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 \quad (X = Cl, Br, I)$$

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 \quad (X = Br, I)$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

→ relative oxidising power of halogens can further be illustrated by their reaction with water. F oxidises water to O_2 whereas Cl, Br form hydrohalic and hydrohalous acids. I doesn't react sponteneously, I_2 can be oxidised by O_2

$$2F_2 + H_2O \longrightarrow 4H^+ + 4F^- + O_2$$

$$X_2 + H_2O \longrightarrow HX + HOX \quad (X = Cl, Br)$$

$$4I^- + 4H^+ + O_2 \longrightarrow 2I_2 + 2H_2O$$

anomalous behaviour of fluorine: → due to small size, high electronegativity, low F-F bond dissociation enthalpy and non availability of d orbital.

→ IE, EN and electrode potential are high~~ly~~-er than expected.

→ most reactions of F are exothermic (due to small and strong bond formed with other elements).

→ It forms only one oxoacid while others from a number of them.

→ HF is a liquid (due to H-bonding), while other ~~by~~ HX are gases.

reactivity towards H_2 ~~hydrogens~~: → all react to give HX but affinity for H_2 decreases from F to I. HX dissolve in H_2O to form hydrohalic acid.

→ acidic strength : HF < HCl < HBr < HI. stability decreases down the group.

reactivity towards O_2: → forms many oxides but most are unstable, F forms two oxides OF_2 and O_2F_2 only OF_2 is thermally stable. both are strong fluorinating agents. O_2F_2 oxidises Pu to PuF_6 (used in removing Pu from nuclear fuel)

→ Cl, Br, I form oxides of +1 to +7. decrese in stability in order I > Cl > Br.

→ higher oxides tend to be more stable.

→ Cl oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive ox. agent and tend to explode. Cl_2O is used as bleaching agent for paper pulps, textiles, water treatment

→ Br oxides, Br_2O, BrO_2, BrO_3 are least stable ~~stable~~ halogen oxides.

→ I oxides, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good ox. agent and is used in estimation of CO.

reactivity towards metals: → forms metal halides e.g. $Mg + Br_2 \longrightarrow MgBr_2$

→ ionic character MF > MCl > MBr > MI. ~~It me~~ metals with higher ox. state is more ~~stable and more~~ covalent.

reactivity towards halogens: → they combine to form compounds of types XX', XX'_3, XX'_5 and XX'_7. where X is a larger size and X' is smaller size halogens.

Chlorine

preparation: → heating MnO_2 with concentrated HCl. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
however NaCl and conc H_2SO_4 is used in stead of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

→ by the action of HCl on $KMnO_4$.

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

manufacture: → Deacon's process: oxidation of HCl gas by atmospheric O_2 with $CuCl_2$ cat. at ~~72K~~ 723K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

→ Electrolytic process: Cl_2 is obtained by electrolysis of brine (conc. NaCl solution). Cl_2 is liberated at anode.

properties: → greenish yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It is 2-5 times heavier than air. can be easily liquified.

→ reacts with metals and non-metals to form chlorides.

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$ $\quad P_4 + 6Cl_2 \longrightarrow 4PCl_3$

$2Na + Cl_2 \longrightarrow 2NaCl$ $\quad S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$

$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$

→ It has great affinity for hydrogen. reacts with H-compounds forming HCl

$H_2 + Cl_2 \longrightarrow 2HCl$ $\quad H_2S + Cl_2 \longrightarrow 2HCl + S$ $\quad C_{10}H_{16} + 8Cl_2 \longrightarrow 16HCl + 10C$

→ with excess ammonia, Cl_2 gives N_2 and NH_4Cl but with excess Cl_2, NCl_3 (explosive) is formed.

$\underset{(excess)}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$ $\quad NH_3 + \underset{(excess)}{3Cl_2} \longrightarrow NCl_3 + 3HCl$

→ with cold and dilutes, Cl_2 produces a mixture of chloride and hypochlorite but ~~not~~ with hot and concentrated alkalies it gives choride + chlorate.

$\underset{(cold + dil)}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

$\underset{(hot + conc)}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

→ with dry slaked lime it gives bleaching powder $[Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O]$

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

→ Cl_2 reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$C_2H_4 + Cl_2 \xrightarrow{\text{room temp}} C_2H_4Cl_2$$

→ Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of Cl_2.

→ it oxidises ferrous to ferric and sulphite to sulphate. sulphur to SO_3, Iodine to iodate. In presence of H_2O, they form H_2SO_4 and HIO_3.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

→ It is a powerful bleaching agent; bleaching action is due to oxidation.

$$Cl_2 + H_2O \longrightarrow 2HCl + O$$

Coloured substance + O ⟶ Colourless substance.

Hydrogen Chloride

preapation: lab: by heating NaCl with concentrated sulphuric acid.

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$

properties: → bleaches veg and organic matter in presence of moisture. bleaching effect of Cl_2 is permanent.

→ colourless ang pungent smelling gas, easily liquified and extremely soluble in water and ionises.

$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

→ it's aqueous solution is called hydrochloric acid.

→ when 3 parts of conc 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

$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$

$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

→ decomposes salts of weaker acid e.g. carbonates, hydrogencarbonates, sulphites etc.

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$

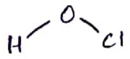
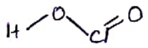
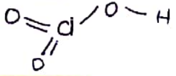
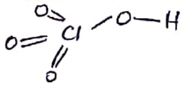
$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$

Oxoacids of Halogens

→ due to high EN and small size, F^- forms only one oxoacid. HOF known as fluoric (I) acid or hypofluorous acid. Others form several oxoacids which cannot be isolated in pure form. they are stable is their salts and in aqueous solution.

Halic (I) acid (hypohalous)	HOF (hypoflourous)	HOCl (hypochlorous)	HOBr (hypobromous)	HOI (hypoiodous)
Halic (III) acid (Halous)		HOClO (chlorous)	—	—
Halic (V) acid (Halic)		$HOClO_2$ (chloric acid)	$HOBrO_2$ (bromic)	$HOIO_2$ (iodic)
Halic (VII) acid (Perhalic)		$HOClO_3$ (perchloric)	$HOBrO_3$ (perbromic)	$HOIO_3$ (periodic)

INTERHALOGEN COMPONNDS

preparation: → by direct combination or by the action of halogen on lower interhalogen compounds.

$Cl_2 + F_2 \xrightarrow{437K} 2ClF$ aqual volume

$I_2 + 3Cl_2 \longrightarrow 2ICl_3$ (ex)

$Cl_2 + 3F_2 \xrightarrow{573K} 2ClF_3$ (ex)

$Br_2 + 3F_2 \longrightarrow 2BrF_3$ (dil)

$I_2 + Cl_2 \longrightarrow 2ICl$ (equimolar)

$Br_2 + 5F_2 \longrightarrow 2BrF_5$ (ex)

properties: → covalent molecules and diamagnetic in nature. generally more reactive than halogens (except F) cos ~~F~~ X − X' bond is weaker than X − X (~~ce~~ except F − F).

→ all undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (XX'_3), halate (when XX'_5) and perhalate (when XX'_7)

$XX' + H_2O \longrightarrow HX' + HOX$

GROUP 18 ELEMENTS

occurance: → all except Rn occur in the atmosphere. He and sometimes Ne are found in minerals of radioactive origin e.g. pitchblende, monazite, cleveite.

→ commercial source of helium is natural gas. Rn is obtained as a decay product of ^{226}Ra

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

electron configuration: → ns^2np^6 except helium which is $1s^2$.

atomic radii: → increases down the group

ionisation enthalpy: → exhibit very high ionisation enthalpy. decreases down the group.

electron gain enthalpy: → no tendency to accept electron therefore, have large positive values of EGA.

physical properties: → all monoatomic, colourless, odourless and tasteless. sparingly soluble in H_2O. very low m.p and b.p. He has the lowest b.p. (4.2K) of any known substance.

→ it has unusual property of diffusing through most commonly used lab materials such as rubber or plastics.

chemical properties: → there are several Xe compounds. compounds of Kr are fewer. only KrF_2 has been studied in detail.

→ Compounds of Rn has not been isolated just identified (e.g. RnF_2).

Xenon-F compounds: → forms XeF_2, XeF_4 and XeF_6 but combination under appropriate experimental conditions.

$$\underset{\text{(excess)}}{Xe(g)} + F_2(g) \xrightarrow{673K,\ 1bar} XeF_2(s)$$

$$\underset{(1:5\ \text{ratio})}{Xe(g) + 2F_2(g)} \xrightarrow{873K,\ 7bar} XeF_4(s)$$

$$\underset{(1:20\ \text{ratio})}{Xe(g) + 3F_2(g)} \xrightarrow{573,\ 60\text{-}70bar} XeF_6(s)$$

→ XeF_6 can also be prepared by interaction of XeF_4 and O_2F_2 at 143K

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

→ XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 25°C they are powerful fluorinating agents. readily hydrolysed even by traces of H_2O.

$$2XeF_4(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$$

→ Xe fluorides react with F ion acceptors to form cationic species and fluoride ion donors to form fluoranions.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$$

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^- \quad (M = Na, K, Rb\ or\ Cs)$$

Xenon-O compounds: → Hydrolysis of XeF_4 and XeF_6 with H_2O gives XeO_3.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

→ partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2

→ XeO_3 is a colourless explosive solid and has a pyramidal molecular structure.

→ $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.