p- block

BORON FAMILY / $ns^2 np^1$ / IIIA / 13th

3 → Anomalous → non metal

Al → 3rd most abundant element in crust (Oxy > Si) Al
→ 1st most abundant metal in the crust.

Ga → Liq (Room T to 200°C) → Used in Quartz thermostats
* used in high range thermometry

In

Tl → Highly toxic.

Physical Properties

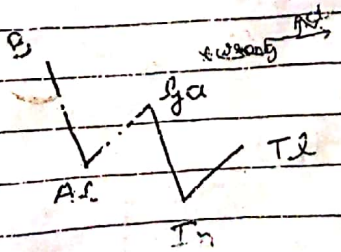
1) Atomic radius
Ionic radius ↓ Increases

B << Al > Ga < In < Tl
(almost same)

* SE (shielding effect) of $3d^{10}$ e^- is unable to compensate the increase in E.N.C. (effective nuclear charge)

2) Density ↓ Increases

3) I.E (3rd) ↓ Decreases



Tilted 'W'

* Allotropy is shown only by non-metals. (Not shown by elements showing metallic char.)

classmate Date Page

I.E. (1st)

~~A~~ wrong B > Tl > Ga > Al > In.

B - 1
Al - 4
Ga - 2
In - 5
Tl - 3

remember alternate numbering

SIGN H

4) E.N. ↓ Decreases B → ↑ Al → ↓ Tl

5) E.A. ↓ Decreases

6) B.P. ↓ Decreases

7) M.P. ↓ Decreases

B
↓
Al
Ga — In — Tl
Least.

8) Metallic Nature

B —Increases→ Al —Decreases→ Tl
↑
Non metal

a) Hydration Energy ↓ Decreases.

10) Allotropy – shown by Boron

Crystalline	Amorphous
Black	Brown
Hard	Less hard
Inert	Less Inert

11) Reactivity ↓ Increases

B – ×
Al, Ga, In, Tl – Reactive

13) Reducing Power [Except boron]
↓
Decreases due decrease in $E_{o.p.}$

12) Oxidation Number – $ns^2\ np^1$

B, Al] +3 >> +1
Ga, In] +3 > +1
Tl] +1 >> +3

+3 → +1: Decreases; Increases

* Chemical Properties

1) Reaction with O_2

High T
B — B_2O_3
Al (moist) — Al_2O_3 → Passive
Ga — Ga_2O_3 (+3) + Ga_2O (+1)
In — In_2O_3 + In_2O
Tl — Tl_2O + Tl_2O_3 → major

Carbon reactivity → Low
But reacts at high temp.

2) Reaction with H_2O.

H_2O —
- B — ~~No reaction~~
- Al — $Al_2O_3 + H_2$ (→ Passive)
- Ga → $Ga(OH)_3 + GaOH$
- In → $In(OH)_3 + InOH$
- Tl → $Tl(OH) + Tl(OH)_3$ (↳ major)

3) Reaction with ~~N~~ Carbon

Exam pov *

C ~~N_2~~ (↗ ~~Always~~ needs ~~high~~ temp.) —
- B — B_4C → Norbic. (Hard) → used in brakes
- Al — Al_4C_3
- Ga to Tl — ~~No reaction~~ → less thermal tolerance

4) Reaction with. NH_3

Exam pov *

NH_3 (↗ ~~Rea~~ high temp.) —
- B — $BN + H_2$
- Al — $AlN + H_2$
- Ga to Tl — No reaction

Reactivity ~~de~~ same as Nitrogen.

5) Reaction with ~~carbon~~ N_2

Exam pov *

N_2 ~~C~~ (↙ High) —
- B — BN
- Al — AlN
- Ga to Tl — ~~No reaction~~

6) Reaction with metal

Exam pov

Mg (High) —
- B — Mg_3B_2 (Boride)

Addition product

7) Reaction with acids

B] - only with oxidising acid. conc H_2SO_4, HNO_3 etc. (not HCl)
Al, Ga] - Any acid except HNO_3 → passive
In, Tl] - Any acid.

8) Reaction with ~~alkanes~~ alkalis

NaOH (High temp)
- B – $NaBO_2 + H_2$
- Al – $NaAlO_2 + H_2$
- Ga – $NaGaO_2 + H_2$

] Meta ....

- In, Tl – No reaction

9) Properties of hydrides [MH_3 - type] [suffix - ane]

Borane B – B_nH_{n+4} - Nido borane
B_nH_{n+6} - Arachno borane

Alane Al - $(AlH_3)_n$
Galane Ga - $(GaH_3)_n$
Indane In - InH_3
Thallane Tl - x will form TlH.

B, Al & Ga - Anionic hydride
- Good reducing agent
Eg: $Li^+[AlH_4]^-$, $Na^+[BH_4]^-$ etc.

Thermal stability - Decreases ↓

Addition product

7) Reaction with acids

B] - only with oxidising acid (not HCl) conc H_2SO_4, HNO_3 etc.

Al, Ga] - Any acid except HNO_3 → passive

In, Tl] - Any acid.

8) Reaction with ~~alkalies~~ alkalis

NaOH (High temp)

- B → $NaBO_2 + H_2$
- Al → $NaAlO_2 + H_2$
- Ga → $NaGaO_2 + H_2$

] Meta ....

- In, Tl] - No reaction

9) Properties of hydrides [MH_3 - type] (suffix - ane)

Borane B - [B_nH_{n+4} - Nido borane.
B_nH_{n+6} - Arachno borane

Alane Al - $(AlH_3)_n$

Galane Ga - $(GaH_3)_n$

Indane In - InH_3

Thallane Tl - x will form TlH.

B, Al & Ga - Anionic hydride
- good reducing agent

Eg: $Li^+[AlH_4]^-$, $Na^+[BH_4]^-$ etc

Thermal stability - Decreases !

can react with strong acid as well. acid

* $B_2O_3 + P_2O_5 \xrightarrow{\Delta} BPO_4$.
weak strong

Any compound of Boron is always e^- deficient.

classmate Date Page

10) Properties of oxides.

		Basic Nature	Solubility
soluble weak acidic	B_2O_3	Increases ↓	Decreases ↓
amphoteric	Al_2O_3, Ga_2O_3		
basic	In_2O_3, Tl_2O_3		

11) Properties of hydroxides

		Basic	Solubility
more acidic	$B(OH)_3$	Increases ↓	Decreases ↓
amphoteric	$Al(OH)_3$, $Ga(OH)_3$		
basic	$In(OH)_3$, $Tl(OH)_3$		

12) Properties of halides (MX_3)

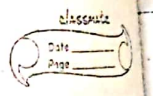
BX_3 - e^- deficient, Lewis acid, covalent, sp^2 and gives H_3BO_3 on hydrolysis.

$$\overset{+3}{B}X_3 + H_2O \rightarrow HX + H_3BO_3$$

* $BF_3 + H_2O \rightarrow BF_3.H_2O$ $(+ H_3BO_3 + HF.)$ less amount

due to H.B.

↓ exists as $H[BF_3OH]$



F^- → ionic

Al/Ga/In/Tl → Covalent

$Cl^-/Br^-/I^-$ → Aqueous. → Ionic

ex.

$AlCl_3 \xrightarrow{H_2O} [Al(H_2O)_6]Cl_3$

$\downarrow\uparrow$

$[Al(H_2O)_6]^{+3} + 3Cl^-$

* Lewis Acid:

$BF_3 < BCl_3 < BBr_3 < BI_3$

→ Due to back bonding.

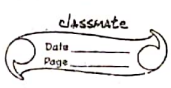
(condition of back bonding:
- e^- deficient of central atom
- energy gap should be less

B - $1s^2 2s^2 2p^1$
F - $1s^2 2s^2 2p^5$
] Almost same energy

* Lewis Acid or e^- deficiency of central atom.
* Back bonding or e^- deficiency of central atom

back bonding

* Resonance - BF_3
* Bond order - 4/3



* $AlCl_3 \xrightarrow{\text{Dimeric}} Al_2Cl_6$

BCl_3 → Not possible due to small size B << Cl.

* Anomalous Properties of Boron:

- Its radius is very less as compared to its group.
- Its ionisation energy is high.
- Its melting point is high.
- Its shows non-metal properties
- It can form allotropes
- It is least reactive.
- It requires high temp. to form oxide.
- It doesn't react with water.
- It form interstitial compound with carbon (B_4C)
- Its the only element which reacts with metals
- ~~This~~ It reacts only with oxidising acids.
- Its ~~is~~ hydride shows polymerising tendency.
- Its compounds are e^- deficient.
- Its oxides and hydroxides are soluble and acidic.
- It doesn't show ↓ reducing behaviour.
- Maximum covalency is 4 due to unavailability of vacant d-orbital.
- High tendency to form complex structure
- It forms anionic structure in aqueous medium.
- Boron forms monobasic acids.

Last step in extraction is always oxide forming.

* Compounds of Boron:

Borax – $Na_2B_4O_7 \cdot 10H_2O$ [$Na_2[B_4O_5(OH)_4]$]
Tincal – $Na_2B_4O_7 \cdot 10H_2O$ [Impurity of SiO_2]
Kernite – $Na_2B_4O_7 \cdot 4H_2O$ – $Na_2[B_4O_5(OH)_4]$
Mohnite – $Na_2B_4O_7 \cdot 5H_2O$
Colemanite – $Ca_2B_6O_{11} \cdot 5H_2O$ (OR) $Ca_2(B_3O_4(OH)_3)_2 \cdot 2H_2O$

* Extraction of Boron:

1) From Colemanite (double salt) → best → more purity

a) $Ca_2B_6O_{11} + Na_2CO_3 \xrightarrow{\Delta} CaCO_3 + NaBO_2 + Na_2B_4O_7$

$\downarrow CO_2$

$Na_2CO_3 + Na_2B_4O_7$

HCl conc ↓ ; H_2SO_4 conc ↓

$NaCl + H_2B_4O_7$ ← any one → $H_2B_4O_7 + Na_2SO_4$

$\downarrow H_2O$

H_3BO_3

$\downarrow \Delta$

$H_2O + B_2O_3$

$Ca_2B_6O_{11} + SO_2 + H_2O \rightarrow Ca(HSO_3)_2 + H_3BO_3$

$\downarrow \Delta$

$B_2O_3 + H_2O$

2) Reduction of B_2O_3.

i) thermal red^n.

$B_2O_3 \xrightarrow{\Delta}$ Al – B + Al_2O_3 (crystalline)
Na – B + Na_2O } Amorphous (93%)
Mg – B + MgO }

↓
Moisson's Boron
But less purity since B can combine with metals.

ii) Electrolytic red^n

Anode – } Not specific.
Cathode – }
Electrolyte – B_2O_3 + MgO + MgF_2
Reducing agent

iii) Lab process:

$BF_3 + H_2 \xrightarrow[\text{arc}]{\text{Electric}} B + HF$

BORAX

BORAX

3 crystalline form

Prismatic Borax $Na_2B_4O_7 \cdot 10H_2O$ —60°C→ Octahedral Jeweller's Borax (in testing gold) $Na_2B_4O_7 \cdot 5H_2O$ —100°C→ Glass Borax $Na_2B_4O_7$

the last stage

steadily Δ

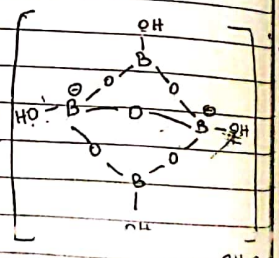
Bead test

$NaBO_2 + B_2O_3 + H_2O$

Reaction is used in detection of transition metal ions under the name of Borax Bead test.

* Structure of Borax $\{[Na_2(B_4O_5(OH)_4]\cdot 8H_2O\}$

1) No. of ↑ true water of crystallization - 8
2) No. of (BOB) linkages - 5
3) No. of (OH) linkages - 4
4) No. of σ bonds - 34
5) No. of lone pair of e^- - 34
6) No. of sp^3 atoms - 19
7) No. of sp^2 atoms - 2



If water present, always bicompounds are formed. (bisulphate, bicarbonate etc)

Boric acid is not a proton donor.

H_3BO_3 (Orthoboric Acid)

B — H_2SO_4 conc → $SO_2 + H_3BO_3$
B — HNO_3 conc → $NO_2 + H_3BO_3$
} x + conc → weak acid

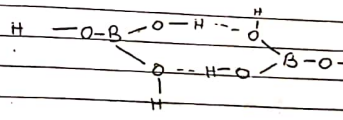
$BN + H_2O \longrightarrow H_3BO_3 + NH_3$

$BCl_3 + H_2O \longrightarrow H_3BO_3 + HCl$

$Ca_2B_6O_{11} + SO_2 + H_2O \longrightarrow Ca(HSO_3)_2 + H_3BO_3$

$Na_2B_4O_7 + HCl + H_2O \longrightarrow NaCl + H_3BO_3$

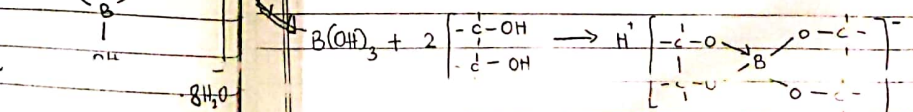
* Physical properties
- White, crystalline, less soluble (in soluble in cold water).
- Exist in dimeric / hexameric form - bcoz of H-B.



- Monobasic, Lewis acid, weak acidic, antiseptic.

$B(OH)_3 + H_2O \longrightarrow H[B(OH)_4] \rightleftharpoons H^+ + [B(OH)_4]^-$

* Acidic Strength ∝ cis 1,2 diol



Chelation

Adv Acid + Alcohol → Ester

* Chemical Properties

→ Heating effect

$H_3BO_3 \xrightarrow[\text{(1)}]{100°C} HBO_2$ ↗ $H-O-B=O$ Metaboric acid

Strongly ↓ | strong ↓ (2) ↙ | 160°C ↓ (3) (2) > (1)

$O=B-O-B=O \; H_2O + B_2O_3 \xleftarrow{\Delta} H_2B_4O_7$ Tetraboric

Any

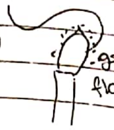
→ $H-O-B-O-B-O-B-O-B$ (ring of O)

→ Reaction with alcohol

* Exam POV

$H_3BO_3 + C_2H_5OH \xrightarrow{\Delta} (C_2H_5O)_3B + H_2O$

B–O–H + H–O–C₂H₅ (×3) — Ethyl Borate (inorganic ester)



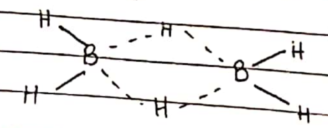
\# B_2H_6 [Diborane]

Best $NaBH_4 + I_2 \xrightarrow{\Delta} NaI + B_2H_6$

$BCl_3 + LiAlH_4 \xrightarrow{\Delta} LiCl + AlCl_3 + B_2H_6$

* $Mg_3B_2 + H_3PO_4 \xrightarrow{\Delta}$ Mixture of boranes

* colourless, crystalline



$3c - 2e^-$ - banana bond.

14

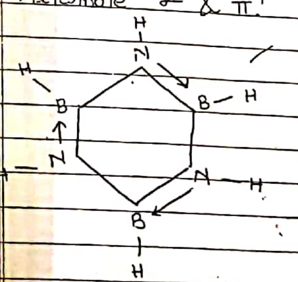
B_2H_6 —
- → O_2 → $B_2O_3 + H_2$
- → O_2 (excess) → $B_2O_3 + H_2O$ } exothermic → rocket propulsions
- → Cl_2 → $B_2H_5Cl + HCl$
- → Cl_2 (excess) → $BCl_3 + HCl$ → not B_2Cl_6 as not dimer [Proved before]
- → NaOH(Δ) → $NaBO_2 + H_2$
- → NH_3 (exc) [low T] → $B_2H_6 \cdot 2NH_3$
- → NH_3 (High T) → $(BN)_n + H_2$
- * → NH_3 [450K] → $B_3N_3H_6$

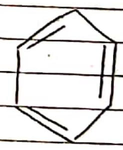
Borazole / Triborine triamine / Borazine / Inorganic benzene

Similarity b/w organic & inorganic benzene

cyclic, Planar, Iso-structural, Iso-electronic, Isosteric [Same no. of atoms & e⁻]

Alternate σ & π





- Polar	×
- Reactive	×
- Soluble	×
- Reaction with H_2O	×

→ $H_3BO_3 + NH_3 + H_2$

(BN)$_n$ – Inorganic Graphite

↳ crystalline (Borazon) – Hardest (more than diamond)

$B + N_2 \xrightarrow{\Delta} BN$

$B + NH_3 \rightarrow BN + H_2$

✱ $Na_2B_4O_7 + NH_4Cl \rightarrow NaCl + B_2O_3 + BN + H_2O$

→ colourless, crystalline

✱ No reaction with any mineral acids except HF
↓ inorganic acids.   ↓ Adduct (H.B.)

$BN + 4HF \rightarrow BN.4HF$ (OR) $NH_4[BF_4]$

ALUMINIUM (Al)

→ Corundum – Al_2O_3 present in
→ Ruby
→ Sapphire
→ Emerald

Extra:

→ Diaspar – $Al_2O_3 \cdot H_2O$ Mica : $K_2O \cdot Al_2O_3 \cdot SiO_2 \cdot 2H_2O$ (1:3:6)

→ Bauxite – $Al_2O_3 \cdot 2H_2O$

→ Gibbsite – $Al_2O_3 \cdot 3H_2O$

→ Cryolite – Na_3AlF_6 CaF_2 – Fluorspar

Ammonal – $NH_4NO_3 + Al$ (used in explosive)

Red liquor – $(CH_3COO)_3Al$ (used in dye ...) } Synthetic

✱ Extraction:

	Impurities	Process
Bauxite	$Fe_2O_3 >>> SiO_2$	Bayer's
	$SiO_2 >>> Fe_2O_3$	Serpeck's
	$SiO_2 + Fe_2O_3$	Hall's

✱ Extraction Imp. Exam POV

✱ Bayer's

Al_2O_3 (impure) $+ NaOH \xrightarrow{\Delta} NaAlO_2 + H_2O$ (Actually $Na[Al(OH)_4]$)

↓ H_2O

$Al(OH)_3 + NaOH$ (white ppt)

↓ Δ

$Al_2O_3 + H_2O$ (pure)

✱ Serpeck's

Al_2O_3 (impure) $+ N_2 + C \xrightarrow{\Delta} AlN + CO\uparrow$

↓ H_2O

$Al(OH)_3 + NH_3$

↓ Δ

$Al_2O_3 + H_2O$ (pure)

✱ H

* Hall's

$Al_2O_3 + Na_2CO_3 \xrightarrow{\Delta} NaAlO_2 + CO_2\uparrow$ (impure)

$\downarrow H_2O$

$Al(OH)_3 + NaOH$

$\downarrow \Delta$

$Al_2O_3 + H_2O$ (pure)

* Hall Heroult's Electrolytic Reduction

Anode - Carbon Rod

Cathode - Iron box lined with carbon

Electrolyte - $Al_2O_3 + Na_3AlF_6$ (cryolite) $+ CaF_2$ (Fluorspar)

- Decrease in fusion temp (2100 → 900)
- Increases conductivity

Electrorefining - (Hoop's Process)

Gold Schmid Alumina Thermite Welding Process

Al (reducing agent) →

- Fe_2O_3: $Al_2O_3 + Fe$
- B_2O_3: ~~B_2O_3~~ $Al_2O_3 + B$
- Mn_2O_3: $Al_2O_3 + Mn$

Exothermic

used in welding of Fe.

ALUM (Double Salt)

$M_2^{'}SO_4 \cdot M_2^{''}(SO_4)_3 \cdot 24H_2O$

M' - Monovalent [Na^+ to Cs^+, Tl^+, NH_4^+] etc.

M'' - Trivalent [Fe^{3+}, Cr^{+3}, Al^{+3}] etc. M3

Potash Alum - $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Soda Alum - $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

> K and Al → reference metals.
> Name changes according to metal.
> True soln. → when 1st mono, & 2nd tri
> If rules not followed, Pseudo alum

$FeSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ → Pseudo alum

* Mostly acidic soln.
→ Used in purifying water, heal wounds (coagulants) and fabrics.

CARBON FAMILY / ns^2np^2 / IV A / 14th

- C
- Si
- Ge
- Sn
- Pb

Solid

* Physical Properties

1) Atomic radii, Ionic radii] Increases

2) I.E. ↓ Increases

*

Sn
↓ ↑
Pb

3) E.N. ↓ Decreases

4) E.A. ↓ Decreases

5) Electropositivity ∝ Metallic ↓ Increases

C, Si] Non-metal

Ge, Sn] semi metal

Pb] metal

6) pπ - pπ bonding ↓ Decreases

eg ✡ carbon only eg. CO_2.

7) dπ - pπ bonding

↓ Increases except carbon

8) Reducing Power ↓ Decreases due to decreases $E_{o.p.}$

9) Oxidation no. $ns^2\ np^2$

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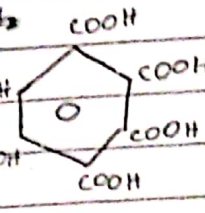
	+4	+2
C, Si: +4 >> +2		
Ge, Sn: +4 > +2	Stable Decr	Stable incr
Pb: +2 >> +4		

2 Catenation ∝ Bond Energy
↓ Decreases

3 Allotropy - Except Pb.
Most allotropes by Sn

- C
  - crystalline
    - Diamond
    - Graphite
    - Fullerene
  - Amorphous
    - coal
    - charcoal
    - Lamp-black
    - Soot

Diamond	Graphite (experimental)
- sp^3	- sp^2
- 3D	- 2D
- tetrahedral	- hexagonal planar
- hardest	- soft
- thermodynamically less stable	- more stable
- Bad conductor	- good conductor
- Ornamental use	- Lubricant

Inert (no reaction with conc HNO_3)	Reacts with HNO_3:  Maletic acid

Graphite ⟶ Diamond
1500 – 1600°C
500 – 600 atm

(chem prof ↗ thread)

Fullerene [Buckminster Fullerene]
name of architect, not ~~from~~ chemist.

Graphite —electric arc⟶ Aggregation of atoms upto 360.

First found in C_{60} C_{70} form.

C_{60} (more common)	C_{70}
Purple	Red
→ Pentagonal + Hexagonal	→ Oval

* soluble in organic solvents.
→ Used in circuits and nano technology.

COAL :
Based on calorific value,

Anthracite > Bituminous > Lignite > Peat
90% carbon ↓ Almost 60%.

whenever O replaced by S, add prefix thio-

K_2CS_3 - Potassium thiocarbonate.

Charcoal → Animal
→ Plant (expensive)

* Used as adsorbing agent.
→ Used in production of sugar, face wash etc.

Lamp Black: Ink, Polish etc.
It has softest soot.

FUELS:

Water gas
Synthesis gas
Blue/Syn gas
$CO + H_2$ (45% + 50%) → Remaining 5% has hydrocarbons.

* Producer gas - $CO + N_2$ (35% + 65%)
* Coal gas - Hydrogen + other hydrocarbons
* Semi water gas - Mixture of syn gas + Producer gas
* C.N.G - CH_4 (85%)
* L.P.G - Butane + Isobutane + Propane
  ↑ odour due
  Markeptal - C_2H_5SH
  ↑ Thio Alcohol

CO: (C⩵O)

By dehydration:

$HCOOH \xrightarrow{\text{dehydrating}} CO + H_2O$

$K_4[Fe(CN)_6] + H_2SO_4 \rightarrow K_2SO_4 + FeSO_4 + HCN$

$HCN \xrightarrow{H_2O/H_2SO_4} HCOOH + NH_3$

$HCOOH \rightarrow CO + H_2O$, $NH_3 \rightarrow (NH_4)_2SO_4$

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \rightarrow CO + CO_2 + H_2O$$

By reduction:

$CaCO_3 + Zn \xrightarrow{\Delta} CaO + ZnO + CO$

$\xrightarrow{\Delta} CaO + CO_2 \xrightarrow{Zn} CaO + ZnO + CO$

From $K_4[Fe(CN)_6]$

$K_4[Fe(CN)_6] + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$

(H_2SO_4: conc; H_2O: used in second step)

best quality of CO.

- colourless, odourless, poisonous
- unsaturated, lone pair (best) donor (ligands), neutral
- Highest bond energy among all diatomic molecule.
- ☆ Adsorbed by ammonical Cu_2Cl_2

Chemical properties:

CO →

Add^n:
- → S → COS [carbonyl sulphide]
- → Cl_2 → $COCl_2$ [Phosgene → poisonous]
- → Cu_2Cl_2 → $Cu_2Cl_2.CO$
- → $2H_2$ [ZnO + Cr_2O_3] → $CO.2H_2$ → CH_3OH
- → H_2 → $CO.H_2$ → HCHO
- ☆ → NaOH (P & T) → CO.NaOH → HCOONa $\xrightarrow{360°C}$ HCOONa | HCOONa → $H_2 + Na_2C_2O_4$ [$CaCl_2$]

ligand:
- → Fe → $[Fe(CO)_5]$
- → Ni → $[Ni(CO)_4]$

Red^n:
- → Fe_2O_3 → Fe + CO_2

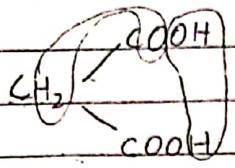
CO will try to [illegible]

Affinity of CO 200 times that of O_2: That's why poisonous. Haemoglobin combines with CO. Chloroform makes phosgene in presence of oxygen.

Carbon Sub-oxide → less requirement O_2.

$[C_3O_2 \rightarrow \overset{-2}{O}=\overset{+2}{C}=\overset{0}{C}=\overset{+2}{C}=\overset{-2}{O}]$

From Malonic Acid



$\xrightarrow[\text{conc.}]{H_2SO_4} 2H_2O + C_3O_2$

Foul smelling gas.

→ colourless, poisonous, insoluble

$C_3O_2 \xrightarrow{200^\circ C} CO_2 + C$

Dry ice / Solid CO_2 / "DRI-KOLD" (commercial name) at 0°C & 50 atm.

→ sublimating nature & refrigeration.

Silicon (Si)

Glass (liquid [super cooled liquid] → viscous)
- $Na_2O.CaO.6SiO_2$
- $Na_2SiO_3.CaSiO_3.4SiO_2$

Silica gel - $SiO_2.xH_2O$

Kieselguhr → amorphous silica

1) Geligrite - mix of nitrobenzene & kieselguhr
2) Dynamite - glyceryl trinitrate & glyceryl dinitrate absorbed on kieselguhr.

Raw materials
- Acidic oxides - B_2O_3, P_2O_5, SiO_2 etc.
- Basic oxides - CaO, Na_2O etc.
- Colouring oxides
  - Blue - Cu^{2+}
  - Red - Cu^{+}
  - Yellow - Cd^{+2}
  - Black - Ni^{+2}
  - Pink/Violet - Mn^{+2}

Borosil - Boron silicate. (and cars)
Toughened glass (used in AC coaches)

Washing soda + lime stone + sand + cullets (Preparation of glass)
↓ 1400°C
liquid
↓ slow cooling (Annealing)
Shape

* HF - etching of glass
↑ only solvent of glass.

→ Classified as:

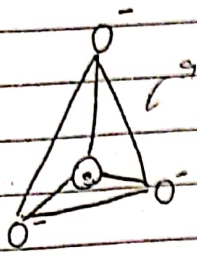
1) Soda / Soft glass - Na-Ca silicate - Cheap, bottle, windowsel.
2) Potash / Hard glass - K-Ca silicate - Resistivity against Acid / Alkalis. (making test tubes)
3) Jena glass - Zn-Ba silicate - Shock absorber
4) Flint glass - Pb-Ba silicate - high refractive index.
5) Crookes's glass - Ce-Ba silicates - U.V. protection.

→ SILICATES:
* Derivatives of Silicilic Acid H_4SiO_4.

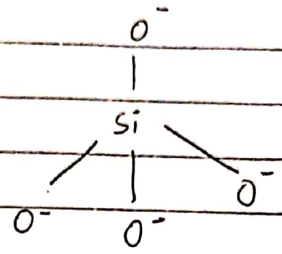
SiO_4^{4-} - silicate / sp^3 / tetrahedral

$ZrSiO_4$ - Artificial diamond

Glass is basic in nature.



representation in 2D



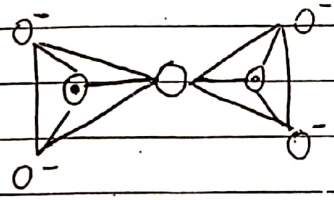
• → Si

O → oxy

> Classification:

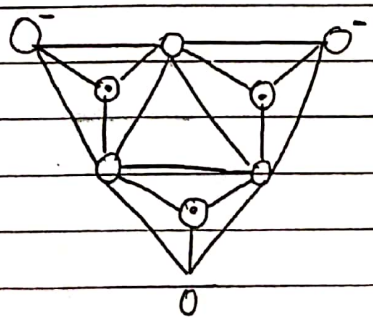
1> ortho-silicate - Contain single unit of SiO_4^{4-} (SiO_4^{4-}) ex - Zircon ($ZrSiO_4$) + Phenacite (Be_2SiO_4)

2> Pyro/Island of silicate - Contains 2 units of SiO_4^{4-} ex - Thortivitite $Sc_2.Si_2O_4$



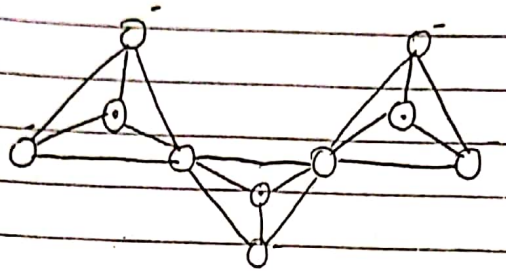
$(Si_2O_7)^{-6}$.

3> Ring Silicate - Formula $(SiO_3)_n^{2n-}$



ex - Beryl $3BeO.Al_2O_3.6SiO_2$.

4) Chain Silicate Formula $(SiO_3)_n^{2n-}$



ex: Waterglass - Na_2SiO_3
* synthetic.

5) 2D - silicate - ex: Talcum - $Mg(Si_2O_5)_2 \cdot Mg(OH)_2$
(3 ~~e~~ oxygen in plane).

6) 3D - silicate - Asbestos, Zeolite.
(4 oxygen in plane).

SILICONES (Synthetic Polymer) → Relate to ketones
└ R_2SiO

→ Preparation:

② From Grignard Reagent ($RMgX$)

i)

$R-MgCl + SiCl_4$

$\downarrow -MgCl_2$

$R-Si-Cl_3$

$\downarrow H_2O$

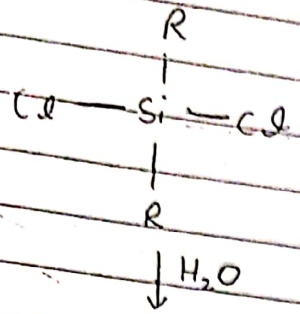
$R-Si(OH)-OH$

$\downarrow$ Polymerisation

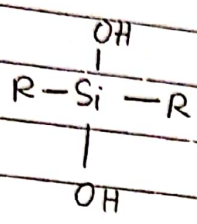
$R-Si(=O)-O\}_n$ Cross linked polymers.

2) $2RMgCl + SiCl_4$

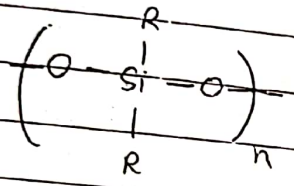
$\downarrow -MgCl_2$



$\downarrow H_2O$



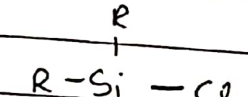
$\downarrow$ Polymerisation



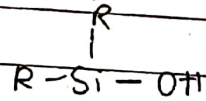
Chain / linear polymer

3) $3RMgCl + SiCl_4$

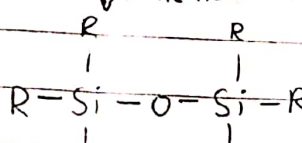
$\downarrow -MgCl_2$



$\downarrow H_2O$



$\downarrow$ Dimerisation



Dimer (used as stopper)

Nail paint remover - Acetone

$(CH_3COO)_2Pb$ - Sugar of lead

$2PbCO_3 \cdot Pb(OH)_2$ - white lead

PbS - galena, $PbSO_4$ - Anglesite

$PbCO_3$ - Cerussite

Plumbosolvency (solubility of lead)

$\propto \frac{NH_4^+, org.\ comp, NO_3^-}{PO_4^{3-}, CO_3^{2-}, SO_4^{2-}}$

$PbO + O_2 \xrightarrow{470^\circ} Pb_3O_4$

Strongly

$Pb + O_2 \xrightarrow{300^\circ} Massicot$

$\xrightarrow{900^\circ} Litharge$

Sugar of lead

$CH_3COOH \xrightarrow{\Delta}$ PbO → $(CH_3COO)_2Pb + H_2O$

$PbCO_3 \rightarrow (CH_3COO)_2Pb + H_2O + CO_2$

colourless, crystalline, soluble, poisonous sweet in taste.

$(CH_3COO)_2Pb \xrightarrow{\Delta} (CH_3)_2CO + PbCO_3$

White Lead

$Na_2CO_3 + (CH_3COO)_2Pb + H_2O \rightarrow 2PbCO_3 + Pb(OH)_2 + CO_2 + CH_3COONa$

→ white pigment, soluble.

$2PbCO_3 \cdot Pb(OH)_2 \xrightarrow{\Delta}$ (it strong heating → then CO as well) $Pb_3O_4 + CO_2 + H_2O$

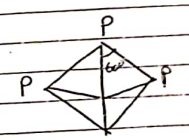
PNICOGENS - $F/ns^2np^3/VA/15^{th}$

↳ Bad Smelling comp.

(N) - Diatomic gas

P, As, Sb - Tetra atomic tetrahedral solid ... ex - P_4

Bi - diatomic



Physical Properties :

1) Atomic Radius, Ionic radius ↓ Increases

2) I.E. ↓ Decreases

3) E.N. ↓ Decreases

4) E.A. ↓ Decreases

(N, P)

5) Catenation or Bond Energy
↓ Decreases (N > P)

6) Melting Point ↓ Increases
N —Increases→ As —Decreases→ Bi

7) Boiling Point ↓ Increases
N —Increases→ Sb —Decreases→ Bi

8) pπ - pπ bonding ↓ Decreases
* shown by nitrogen only

9) dπ - pπ bonding ↓ Increases
* except nitrogen

10) Electro(+ve) or Metallic. ↓ Increases

N, P] Non-metal
As, Sb] Semi metal
Bi] Metallic

11) Allotropy - Except Bi

1. Oxidation no.

N, P] -3 to +5 >> +3
As, Sb] +5 > +3
Bi] +3 >> +5

ns^2 np^3
+5 : Stab Dec
+3 : Stab increases

Chemical Properties:

1) Properties of oxides : X_2O_3, X_2O_4, X_2O_5

* Acidic nature ↓ Decreases

N, P] Acidic
As, Sb] Amphoteric
Bi] Basic

* Nitrogen (N)

$N_2O_3 < N_2O_4 < N_2O_5$ = Acidic

N_2O & NO - neutral
NO & NO_2 - odd e^-, Paramagnetic, unstable
↓ Dimeric ↓
N_2O_2 N_2O_4 - Diamagnetic
(colourless) diamagnetic

remove max water.

$-N_2O$ - Nitrous Oxide

$\overline{T}$ - Laughing gas

$N_2 + [O]$

Nitroso booster, laughing - 'used by dentist'

Hysterica (stretches muscle).

$NH_4NO_3 \xrightarrow{\Delta} 2H_2O + N_2O$

$NH_4NO_2 \xrightarrow{\Delta} 2H_2O + N_2$

* All the oxides of N are soluble.

N_2O_5 — $H_2O \rightarrow HNO_3$

N_2O_5 — $NaOH \rightarrow NaNO_3 + H_2O$

N_2O_3 — $H_2O \rightarrow HNO_2$

N_2O_3 — $NaOH \rightarrow NaNO_2 + H_2O$

NO_2 / N_2O_4 — $H_2O \rightarrow HNO_2 + HNO_3$

NO_2 / N_2O_4 — $NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$

Phosphorous (P)

$P_2O_3 \xrightarrow{\text{Dimeric}} P_4O_6$

$P_2O_5 \xrightarrow{\text{Dimeric}} P_4O_{10}$

P_2O_5 — Dehydrating agent.

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2) Properties of halides

a) Trihalides:

Stab - $NF_3 > NCl_3 > NBr_3 > NI_3$ (stable)

- unstable
- explosion

- Lewis base, tetrahedral
- soluble except NF_3 & PF_3 → why? → SF_6 also cannot be hydrolysed.

H_2O →
- $NCl_3 \rightarrow NH_3 + HOCl$
- $PCl_3 \rightarrow H_3PO_3 + HCl$
- $AsCl_3 \rightarrow H_3AsO_3 + HCl$
- $SbCl_3 \rightarrow SbOCl + HCl$
- $BiCl_3 \rightarrow BiOCl + HCl$

b) Pentahalides

- formed by all except N & Bi
  - *N → due to unavailability of vacant 'd'.
  - Bi → due to $+3 \gg +5$

* Pentahalides are less stable due to bond strain

$PCl_5 \longrightarrow PCl_3 + Cl_2$

sp^3d (120° & 90°)

- Easily hydrolysed

ex: PCl_5 (Partial hydrolysis)
- H_2O (moist) → $POCl_3 + HCl$
- H_2O (excess) → $H_3PO_4 + HCl$

* solid PCl_5 - $[PCl_4][PCl_6]$
solid PBr_5 - $[PBr_4][Br]$
solid PI_5 - $[PI_4][I]$

3) Properties of hydrides.

	Thermal Stab	Bond energy	Reducing Power	Poisonous	Bond Angle — 107	Solubility
NH_3	Decreases	Decreases	Increases	Increases	Decreases — 90	All insoluble except (NH_3) Due to H.B.
PH_3						
AsH_3						
SbH_3						
BiH_3						

	B.P.	
Lewis Basic		PH_3
		AsH_3
Decreases	Increases	(NH_3) due to H.B.
		SbH_3
		BiH_3

4) Oxo - acids

N

*Imp
$H_2N_2O_2$ - Hypo Nitrous Acid (cis-trans)
$H_2N_2O_4$ - Nitroxylic acid (Explosive)
HNO_2 - Nitrous acid H-O-N=O
HNO_3 - Per nitrous acid / Nitric acid
HNO_4 - Per nitric acid H-O-O-N(=O)=O

Per nitrous: H-O-O-N=O
Nitric: H-O-N(=O)=O

N_2 needs minimum 1100°C to react with O_2.

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P

H_3PO_2 - Hypophosphorous acid → ?

H_3PO_3 - Phosphorous Acid

H_3PO_4 - Phosphoric acid

$H_4P_2O_7$ - Pyrophosphoric acid

HPO_3 - Metaphosphoric acid

$H_4P_2O_7$

HPO_3

$H_4P_2O_5$ - Pyrophosphorous acid

$H_4P_2O_6$ - Hypophosphoric acid → ?

Acid - H_2O = Meta

$H_3PO_4 - H_2O = HPO_3$

$H_3BO_3 - H_2O = HBO_2$

Acide - Oxide = Meta

$Na_3AlO_3 - Na_2O = NaAlO_2$

2 Acid - H_2O = Pyro

$2H_3PO_4 - H_2O = H_4P_2O_7$

$2H_3PO_3 - H_2O = H_4P_2O_5$

N_2

By heating

$NH_4Cl + NaNO_2 \xrightarrow{\Delta} NaCl + NH_4NO_2 \xrightarrow{\Delta} 2H_2O + N_2$

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

orange

$Ba(N_3)_2 \xrightarrow{\Delta} Ba + N_2$

→ Azide

Best

From Urea

$NH_2CONH_2 + HNO_2 \rightarrow H_2CO_3 + N_2$

From HNO_3

$Cu + HNO_3 \rightarrow CuO + N_2 + H_2O$

(very dilute)

By oxidⁿ:

NH_3 →
- $\rightarrow CuO \rightarrow Cu + N_2 + H_2O$
- $\rightarrow X_2 \rightarrow N_2 + NH_4Cl$
- * $\rightarrow CaOCl_2 \rightarrow N_2 + CaCl_2 + H_2O$

→ colourless, odourless, insoluble.

* Inert due to high bond energy

→ ↔ Chemical properties:

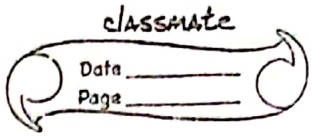
N_2 →
- $\rightarrow O_2 \rightarrow NO$
- $\rightarrow Li \rightarrow Li_3N$
- $\rightarrow Be \rightarrow Be_3N_2$
- $\rightarrow B \rightarrow BN$
- * $\rightarrow CaC_2 \rightarrow (CaCN_2 + C)$ Nitrolim (Fertilizer)

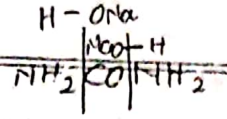
NH_3:

By hydrolysis:

H_2O →
- $\rightarrow Mg_3N_2 \rightarrow NH_3 + Mg(OH)_2$
- $\rightarrow BN \rightarrow H_3BO_3 + NH_3$

NH_2CONH_2 contains 42% N.





From urea → good source of NH_3

$$NH_2CONH_2 + NaOH \rightarrow Na_2CO_3 + NH_3$$

(H, O, H)

From NH_4^+ comp

NH_4 comp $\xrightarrow{Alkali}$ NH_3

NH_4Cl (S.A + W.B)

- $NaOH \rightarrow NH_3 + NaCl + H_2O$
- $PbO \rightarrow NH_3 + PbCl_2 + H_2O$

Haber's

$N_2 + H_2 \xrightarrow[\text{Low-T, High-P}]{\text{catalyst (Fe), promoter (MO)}} NH_3$

Physical properties:

Colourless, Pungent, soluble (bcoz of H.B.).

Moist NH_3 can be dehydrated by using

- Anhy. CaO (best)
- Anhy. $CaCl_2$ (adduct ↗ complex)
- Anhy P_2O_5
- Conc H_2SO_4

(last two: acidic)

Chemical properties.

NH_3, Δ

- $Li \rightarrow Li_2NH + H_2$ (imide)
- $Na \rightarrow NaNH_2 + H_2$ (amide)
- $Be \rightarrow Be_3N_2 + H_2$
- $B \rightarrow BN + H_2$
- $HCl \rightarrow NH_4Cl$
- $H_2O \rightarrow NH_4OH$

cyanamide

* NH_3 —
  - $CO_2 \rightarrow NH_4CNO \rightarrow NH_2CONH_2$
  - X_2 excess $\rightarrow NX_3 + HX$ (halogen only Cl, Br)
  - $I_2 \rightarrow NH_3.NI_3 + HI$ (explosive)

$NH_3 + X_2 \longrightarrow N_2 + NH_4X$
(excess NH_3; X_2 = oxidising agent)

* Reaction with Aqu. NH_3 / NH_4OH

Remember FeCrAl, $A+B \rightarrow C+D$

* Imp — NH_3 (aq) or NH_4OH (insoluble hydroxides):
  - $FeCl_3 \rightarrow NH_4Cl + Fe(OH)_3$ ← Red brown
  - $CrCl_3 \rightarrow NH_4Cl + Cr(OH)_3$ ← green
  - $AlCl_3 \rightarrow NH_4Cl + Al(OH)_3$ ← white

  (ppts.)

* Soluble (co-ordination, use ligand):
  - $\overset{+2}{Cu}SO_4 \rightarrow [Cu(NH_3)_4]SO_4$
  - $\overset{+2}{Cd}SO_4 \rightarrow [Cd(NH_3)_4]SO_4$
  - $\overset{+1}{Ag}Cl \rightarrow [Ag(NH_3)_2]Cl$

  many are more hydroxide so remember insoluble.

* Nessler's Reagent:
  - $K_2HgI_4 + KOH \rightarrow Hg_2NH_2OI + KI$ (Iodide of Millon's base)
  - $HgCl_2 \rightarrow HgNH_2Cl$ white
  - $Hg_2Cl_2 \rightarrow HgNH_2Cl + Hg$ grey

Raschig's Process → N_2H_4 (OR) $\overset{-2}{NH_2}-\overset{-2}{NH_2}$ (Hydrazine)

Very imp — unique character

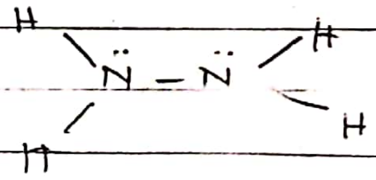
$NaOCl + HNH_2 \xrightarrow{glue} NaOH + NH_2Cl$ ← prevents decomposition of hydrazine

(sodium hypochloride) (Ammonia)

$NH_2Cl \xrightarrow{+NH_3} HCl + NH_2-NH_2$ (unstable)

→ Physical properties

1) Colourless, basic, soluble. →H.B.



Only one hydride of N which shows acidic property N_2H_4

→ Chemical Properties

N_2H_4 → H_2SO_4 → $N_2H_4 . H_2SO_4$

N_2H_4 → HNO_2 → $N_3H + N_2 + H_2O$

Hydrazoic acid (N_3H): (Linear struc)

$NaNH_2 + N_2O \rightarrow NaN_3 \xrightarrow{H_2SO_4} NaHSO_4 + N_3H$

→ colourless, acidic, soluble.

acid: $NaNH_2$ / N_3H

metal → salt

$AgNO_3 \rightarrow AgN_3 + HNO_3$

$Mg \rightarrow Mg(N_3)_2 + H_2$

This is the only way to prepare azides.

HNO_2 [Exist in sol^n]

$NaNO_2 + HCl \rightarrow NaCl + HNO_2$

$N_2O_3 + H_2O \rightarrow HNO_2$

$Ba(NO_2)_2 + H_2SO_4$ (dil) → $HNO_2 + BaSO_4$ ↑ insoluble → so best

→ Physical properties:

Colourless, weak acidic, soluble, diamagnetic.

→ Chemical Properties :

$HNO_2 \longrightarrow N_2O_3 + H_2O$

$\Downarrow$

$NO + NO_2$

para ↳ shows colour

* Self Oxidⁿ - Redⁿ :

$\overset{+3}{HNO_2} \longrightarrow \overset{+5}{HNO_3} + \overset{+2}{NO} + H_2O$

* Oxidation Properties :

$HNO_2 \longrightarrow H_2O + NO + [O]$

HNO_2 —
- $KNO_2 \rightarrow KNO_3$
- $K_2SO_3 \rightarrow K_2SO_4$
- $S \rightarrow H_2SO_4$
- $SO_2 \rightarrow H_2SO_4$
- $P \rightarrow H_3PO_4$
- $Na_3ASO_3 \rightarrow Na_3ASO_4$

* Reduction Properties : (with strong oxidant)

$HNO_2 + [O] \rightarrow HNO_3$

HNO_2 —
- $KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_2O$
- $MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O_2$
- $Br_2 + H_2O \rightarrow HBr$
- $O_3 \rightarrow O_2$

→ strong water

HNO_3 (Aqua Fortis):

↓ viscous

→ Birkland Eyde's process:

$N_2 + O_2 \xrightarrow{1100^\circ C} NO \xrightarrow{cooling} NO_2 \xrightarrow{H_2O} HNO_3 + HNO_2$

~~N_2O_4~~

→ Ostwald's Process: → Modern way

$NH_3 + O_2 \xrightarrow[\text{dec. temp.}]{[Pt]\ \Delta} NO + H_2O \xrightarrow{cooling} NO_2 \xrightarrow{O_2} N_2O_5 \xrightarrow{H_2O} HNO_3$ (65%) $\xrightarrow{P_2O_5}$ 99%

Anhydrous – colourless, odourless, viscous, acidic.

* Chemical Properties:

oxid. prop.
- Dil → $NO + H_2O + [O]$
- Conc → $NO_2 + H_2O + [O]$

Oxidising prop.

HNO_3 (conc) →
- $C \rightarrow CO_2$
- $S \rightarrow H_2SO_4$
- $SO_2 \rightarrow H_2SO_4$
- $P \rightarrow H_3PO_4$
- $I_2 \rightarrow HIO_3$
- $B \rightarrow H_3BO_3$
- $SnCl_2 + HCl \rightarrow SnCl_4$

* → Nitrating properties: Depends on
- concentration
- nature of metal
- Temperature.

Exam POV

- V.D → 7 – 8%
- D → 20%

a) $Mg/Mn \xrightarrow{V.D}$ Nitrates $+ H_2$

b) $Zn/Fe/Sn$

- V.D → $NH_4NO_3 + Zn^{+2}/Fe^{+2}/Sn^{+2}$ (Nitrates) } Lower O.N
- D → $N_2O + Zn^{+2}/Fe^{+2}/Sn^{+2}$ (Nitrates) } Lower O.N
- C → $NO_2 + Zn^{+2}/Fe^{+3}/Sn^{+4}$ (Nitrates) } higher O.N.
  - Sn^{+4} → H_2SnO_3

* Exam POV.

c) $Cu/Ag/Hg/Pb$

- D → $NO + Cu^{+2}/Ag^{+}/Hg^{+}/Pb^{+2}$ (Nitrates)
- C → $NO_2 + Cu^{+2}/Ag^{+}/Hg^{+2}/Pb^{+2}$ (Nitrates)

* → passive formed after 2nd. reaction

d) Al/Cr/Fe/Co etc → No rxn. due to passive layer formation

e) Au/Pt/Rh etc → No rxn due to insoluble nature
↳ Soluble in aqua-regia

$HNO_3 + HCl$ (1 : 3) — Resulting compound soluble in HCl → so more quantity.

$HNO_3 + HCl \rightarrow NOCl + H_2O + [Cl]$

$Au + [Cl] \rightarrow AuCl_3$ +
$AuCl_3 + HCl \rightarrow H[AuCl_4]$
$HNO_3 + HCl + Au \rightarrow NOCl + H_2O + H[AuCl_4]$
↳ $Pt \rightarrow NOCl + H_2O + H_2[PtCl_6]$

Phosphorous:

Chloro Apatite $Ca_3(PO_4)_2 + CaCl_2$ (3:1) → $Ca_{10}Cl_2(PO_4)_6$

Fluoro Apatite $Ca_3(PO_4)_2 + CaF_2$ (3:1)

Phosphorite $Ca_3(PO_4)_2$

↓

Bone ash

* Extraction:

a) $Ca_3(PO_4)_2 + H_2SO_4 \rightarrow CaSO_4 + H_3PO_4 \xrightarrow{\Delta, -H_2O} HPO_3$

$HPO_3 \xrightarrow{coke} P_4 + H_2O + CO$

b) $Ca_3(PO_4)_2 + SiO_2 + C \xrightarrow{\Delta} CaSiO_3 + CO\uparrow + P_4$

Physical Properties

③ Polymer P & T P_4 ① Inert + T ④ Polymer

Black ← White → Red

(metallic)

↓ light

Yellow

P_4 ②

Reactivity :-

↘ Highly compact polymer

White	Red
Waxy solid	Brittle
Pungent	x
Poisonous	x
Soluble in CS_2	x
Reactive	x
Rxn with NaOH	x
Chemiluminescence	x

→ Chemical Properties:

H_3PO_3 —
- $\xrightarrow{200^\circ C} H_3PO_4 + PH_3$
- $Cl_2 + H_2O \rightarrow H_3PO_3 + HCl$ (oxi)
- $CuSO_4 + H_2O \rightarrow H_3PO_4 + Cu + H_2SO_4$
- $AgNO_3 + H_2O \rightarrow H_3PO_4 + Ag + HNO_3$
- $HgCl_2 + H_2O \rightarrow H_3PO_4 + HCl + Hg_2Cl_2$
- $Hg_2Cl_2 + H_2O \rightarrow H_3PO_4 + HCl + Hg$

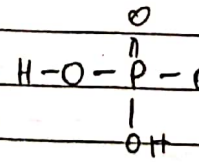
* H_3PO_4 (Phosphoric Acid)

$Ba_3(PO_4)_2 + H_2SO_4 \rightarrow BaSO_4 + H_3PO_4$

$PCl_5 + H_2O \xrightarrow{\text{(excess)}} HCl + H_3PO_4$ (which one best?)

$P_2O_5 + H_2O \rightarrow H_3PO_4$ (not cold)

→ Colourless, soluble, acid, tribasic



No P–H. So, no oxi or red shown. So, substitution

\+ Chemical properties

H_3PO_4 —
- $\xrightarrow{250^\circ C} H_4P_2O_7 + H_2O$
- $\xrightarrow{600^\circ C} HPO_3 + H_2O$
- $\xrightarrow{\text{strongly}} P_2O_5 + H_2O$
- $BaCl_2 \rightarrow Ba_3(PO_4)_2 + HCl$
- $AgNO_3 \rightarrow Ag_3PO_4 + HNO_3$

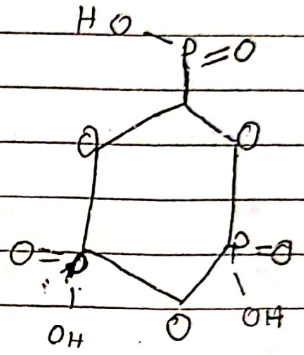
classmate
Date
Page

* HPO_3 [Meta Phosphoric acid]

$H_3PO_3 + Br_2 \longrightarrow HPO_3 + 2HBr$
oxi prop.

~~H_3PO_2~~ $H_4P_2O_7$] $\xrightarrow{600^\circ C}$ $HPO_3 + H_2O$
H_3PO_4]

$P_2O_5 + H_2O \longrightarrow HPO_3$
cold



→ colourless, crystalline, soluble, solid.
→ Exist in trimeric form $(HPO_3)_3$

* H_3PO_4, HPO_3, $H_4P_2O_7$ all show same O.N. of P. So will show same chemical properties.

Carbon family → Chemical Properties.

1) Properties of oxides
– $\overset{+2}{M}O$ & $\overset{+4}{M}O_2$ type

	MO	MO_2	
C	✓	✓	] Gaseous (pπ-pπ bonding)
Si	* high T	✓	] Solid (dπ-pπ bonding)
Ge	✓	✓	
Sn	✓	✓	
Pb	✓	✓	

$\overset{+2}{Pb} > \overset{+4}{Pb}$

$\overset{+4}{PbO_2}$ – Powerful oxidant
– gives O_2 with HNO_3

2) Rxn wid acids

C, Si] — only with oxidising acids (conc H_2SO_4 / conc HNO_3)

fe] — Any conc acid

Sn, Pb] — Any acid

3) Rxn with alkalies

C — No Rxn

Si — $Na_2SiO_3 + H_2$

NaOH — fe, Sn — $Na_2\overset{+4}{M}O_3 + Na_2\overset{+2}{M}O_2$

Pb — $Na_2\overset{+2}{M}O_2 + Na_2\overset{+4}{M}O_3$

Major product

4) Rxn with steam

C — $CO + H_2$

H_2O — Si, fe, Sn — $MO_2 + H_2$

Pb — Passive

5) Properties of halides — MX_4

★ All form except $PbBr_4$ & PbI_4.

Pb^{+4} - Power ful oxidant

Br^-/I^- - Powerful reductant

] $PbBr_4$ & PbI_4 not possible

But $PbCl_4$ exists.

Stability :

Reason → (Size)

$MF_4 > MCl_4 > MBr_4 > MI_4$ (Size)

$CCl_4 > SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$ +4 stab ↓ decreases

($SiCl_4$ to $PbCl_4$) ↓ easily hydrolysed → $M(OH)_4 + HCl$

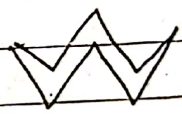
CCl_4 → Fe (steam) → $COCl_2 + HCl$ (phosgene)

CCl_4 → no reaction w/ no hydrolysis → Due to unavailability of vacant d-orbitals

CHALCOGEN / ns^2np^6 / VIA / 16th

O } Diatomic gas

S, Se, Te] octahedral solid, staggered ring like struc ex – S_8



Po] Radioactive

* Physical Properties

1) Atomic rad, Ionic rad ↓ Increases
2) I.E ↓ Decreases
3) E.N. ↓ Decreases
4) E.A. ✗ ↓ Decrease

✗ Oxygen least →?

5) M.P. & B.P. ↓ Increases

6) pπ - pπ bonding ↓ Decreases

7) dπ - pπ bonding ↓ Increases except O_2

8) Electro +ve nature & metallic nature ↓ Increases

O, S] Non-metal

Se, Te] Semi-metal

Po] Metal

9) Allotropy → Shown by All. (except Po)

10) Oxid. no.

O = -2 to +2

S, Se, Te] -2 to +6

* Chemical Properties

1) Prop. of oxides

→ All form oxides except oxygen.

- MO_2 & MO_3 type

☆ Soluble

☆ acidic nature: ↓ Decreases →

2) Prep. of halides

O → F → Fluorides [OF_2, O_2F_4 etc.] unstable, explo.

O → Cl/Br/I → No halide formation, gives oxides. → X_2O_3, X_2O_5, X_2O_7 etc.

Reason: more O.N. to E.N.

	F	Cl	Br	I
S_2X_2	✓	✓	✓	✓
SX_2	✓	✓	✓	✗
SX_4	✓	✓	✗	✗
SX_6	✓	✗	✗	✗

* SeX_4 & SeX_2 – Cl & Br.

3) Prep. of hydrides,

	Thermal stab	Bond energy	Bond angle	Acidic nature	M.P. & B.P.	Red. power
H_2O	↓ Decr.	↓ Decr.	104.5° ↓ Decreases due to decrease in E.N.	↑ Increases	↑ Increases * H_2O (max)	↓ Increases
H_2S						
H_2Se						
H_2Fe						

← Poisonous, colourless, colourless

4) Oxo-acids (except oxygen).

O → S (prep.) ... Prefix thio

H_2SO_3 – Sulphurous acid

$H_2S_2O_2$ – Thio sulphurous acid

$H_2S_2O_5$ – Pyro sulphurous acid.

H_2SO_4 – Sulphuric acid

$H_2S_2O_3$ – Thio sulphuric acid

$H_2S_2O_7$ – Pyro sulphuric acid.

whenever S-S → thionic

S-S
- $H_2S_2O_6$ – Dithionic acid
- $H_2S_{(n=2)}O_6$ – Polythionic acid

n=4,5,6 → name according to no.

O-O
- H_2SO_5 Peroxo Monosulphuric acid / Caro's acid
- $H_2S_2O_8$ Peroxo Disulphuric acid / Marshal's acid.

O_2 (Dioxygen)

By heating:

- $LiNO_3 \rightarrow Li_2O + NO_2 + O_2$
- $NaNO_3 \rightarrow NaNO_2 + O_2$
- Lab $KClO_3 \rightarrow KCl + O_2$
- $MnO_2 \rightarrow Mn_3O_4 + O_2$ (→ MnO + Mn_2O_3)
- Imp $KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
- $K_2Cr_2O_7 \rightarrow K_2CrO_4 + Cr_2O_3 + O_2$
- $PbO_2 \rightarrow$, $Pb_3O_4 \rightarrow$ } $\rightarrow PbO + O_2$
- $Ag_2O \rightarrow Ag + O_2$
- $HgO \rightarrow Hg + O_2$
- $BaO_2 \rightarrow BaO + O_2$

} only oxides which give metal on heating

By chem rxn.

$H_2O_2 \rightarrow$
- $KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + H_2O + O_2 + K_2SO_4$
- $MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + O_2$

→ colourless gas, paramagnetic, soluble.
Blue liquid & Blue violet solid
* Absorbed by Pyrogallol

→ Chem prop.

O_2 —
- $N_2 \rightarrow NO$
- $C \rightarrow CO \rightarrow CO_2$ if an oxi reagent.
- $Li \rightarrow Li_2O$
- $Na \rightarrow Na_2O$
- $NaO \rightarrow Na_2O_2$

O_3 (Ozone)

$3O_2 \xrightleftharpoons[\text{Silent electric discharge}]{} 2O_3$

$3O_2$ → Dry-cold

$2O_3$ → 5–10 %

Siemen's ozoniser
Brodie's ozoniser

↓ Fractional dist.

By reduction more you get $O_2 + O_3$.

$F_2 + H_2O \rightarrow O_2 + O_3 + H_2F$

P.P.

- Diamagnetic, unstable, Insoluble
- Soluble in turpentine oil, CCl_4 etc.
- Blue violet liq / solid
- Pungent, Poisonous

C.P:

$O_3 \longrightarrow O_2 + [O]$ ∴ Responsible for dry permanent bleaching and oxidation

O_3 →
- $P + H_2O \rightarrow O_2 + H_3PO_4$
- $S + H_2O \rightarrow O_2 + H_2SO_4$
- $SO_2 + H_2O \rightarrow O_2 + H_2SO_4$
- $KI + H_2SO_4 \rightarrow K_2SO_4 + I_2 + H_2O + O_2$
- $FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O + O_2$
- $O_3 + KI\ (Alk.) \rightarrow KIO_3 + KIO_4$
- $I_2 + H_2O \rightarrow HIO_3$
- $I_2\ (dry) \rightarrow I_4O_9\ [I^{+3}(IO_3^-)_3]$ ← iodine iodate
- $CdS \rightarrow CdSO_4$
- $PbS \rightarrow PbSO_4$
- $H_2S \rightarrow S + H_2O$
- $NaNO_2 \rightarrow NaNO_3$
- $SnCl_2 + HCl \rightarrow SnCl_4 + H_2O$ } NO O_2 formed
- $SO_2\ (dry) \rightarrow SO_3$
- $Hg \rightarrow HgO + O_2$ ← Tailing of Hg (used to fill Hg in thermometer)

O_2 – common product.

Reducing properties – with peroxide only.

$BaO_2 + O_3 \longrightarrow O_2 + BaO$

Reactivity

H_2O_2	O_3
$KMnO_4/H^+$ ✓	X
$K_2Cr_2O_7/H^+$ ✓	X
Hg X	✓

H_2S :

Sb_2S_3 —Δ→ H_2 → H_2S + Sb
Sb_2S_3 —Δ→ HCl → H_2S + $SbCl_3$

$FeS + H_2SO_4 \xrightarrow{dil} FeSO_4 + H_2S$

Kipp's Apparatus

P.P

Colourless, pungent (rotten egg like)
Poisonous, Insoluble, acidic.

C.P

$H_2S \rightarrow S + [H]$

H_2S →
- $X_2 \rightarrow S + HX$
- $O_2 \rightarrow S + O_2 + H_2O$
- $SnCl_4 \rightarrow S + SnCl_2 + HCl$
- $H_2O_2 \rightarrow S + H_2O$
- $KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_2O$

Metal / Metal oxides $\xrightarrow{H_2S}$ Metal Sulphides

H_2S →
- $Na \rightarrow Na_2S + H$
- $Na_2O \rightarrow Na_2S + H_2O$

Any oxo salt + Acid → Gaseous non-metal oxide (same O.N.) + Salt + H_2O

SO_2

H_2SO_4 (high conc. (hot)) →
- $Cu \rightarrow SO_2 + H_2O + CuSO_4$
- $Ag \rightarrow SO_2 + H_2O + Ag_2SO_4$
- $Hg \rightarrow SO_2 + H_2O + HgSO_4$

(Hg is polarise to hydrogen.)

$NaHSO_3$, Na_2SO_3 + $HCl \rightarrow SO_2 + H_2O + NaCl$

☆ $FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

→ P.P.
- colourless, Pungent (Burning sulphur like)
- suffocating, soluble, acidic.

→ C.P. – Reducing Prop.

$SO_2 + H_2O \rightarrow H_2SO_3 \xrightarrow{H_2O} H_2SO_4 + [H]$

responsible for reduction & temporary moist bleaching

SO_2 →
- $FeCl_3 + H_2O \Rightarrow H_2SO_4 + FeCl_2 + HCl$
- $SnCl_4 + H_2O \rightarrow H_2SO_4 + SnCl_2 + HCl$
- $H_2O_2 \rightarrow H_2SO_4 + H_2O$
- $KMnO_4 + H_2SO_4 \rightarrow H_2SO_4 + K_2SO_4 + MnSO_4 + H_2O$
- Cl_2 (dry) $\rightarrow SO_2Cl_2$
- PbO_2 (dry) $\rightarrow PbSO_4$

SO_2 + Metal → Metal oxide + Metal sulphide
(except for I_A)

Oxidation prop. – with strong reductant

SO_2 →
- → $Mg\ (II_A) \rightarrow MgO + MgS$
- → Fe (d-block) → $FeO + FeS$
- → $K\ (I_A) \rightarrow K_2SO_3 + K_2S_2O_3$
- → $H_2S \rightarrow S + H_2O$

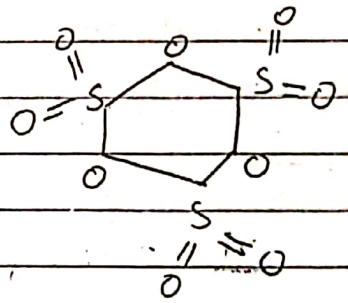
To SO_3:

$H_2SO_4 \xrightarrow{P_2O_5 \text{ OR } H_3PO_4} H_2O + SO_3$

$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_3$

$SO_2 + O_2 \xrightarrow{[Pt]} SO_3$

colourless, acidic, soluble
exist in trimeric form $(SO_3)_3$



SO_3 (acidic) →
- → $\xrightarrow{\Delta} SO_2 + O_2$
- → basic PbO → $PbSO_4$
- * → $HCl \rightarrow SO_3.HCl$ (OR) $SO_2(OH)Cl$
- → $H_2O \rightarrow H_2SO_4$
- → $H_2SO_4 \rightarrow H_2S_2O_7$
- → $NaOH \rightarrow Na_2SO_4 + H_2O$

↗ King of chemical

H_2SO_4 (oil of vitriol)

old process

→ Lead chamber process

$$S + O_2 \rightarrow SO_2$$

$$SO_2 \xrightarrow[\Delta]{O_2\ [NO]} SO_3 \xrightarrow{H_2O} H_2SO_4$$

65–70%

↑ Brown oil of vitriol.

→ Contact process

$$S + O_2 \rightarrow SO_2$$

Best but expensive

$$SO_2 \xrightarrow[\Delta]{O_2\ [V_2O_5/Pt]} SO_3 \xrightarrow{H_2SO_4} H_2S_2O_7$$

↓ Strength can be controlled.

PP.

– Anhy – colourless, viscous, soluble, acidic, good conductor, H.B.

* High affinity for water (Exo.)

C.P. :– oxi. prop.

$$H_2SO_4 \rightarrow H_2O + SO_2 + [O]$$

H_2SO_4 (Hot conc.) →
- Cu → $CuSO_4$
- Ag → Ag_2SO_4
- Hg → $HgSO_4$
- P → H_3PO_4
- I_2 → HIO_3
- B →
- C →

we cannot break peroxides.

Dehydrating properties:

$$HCOOH \xrightarrow[\text{conc}]{H_2SO_4} CO + H_2O$$

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[\text{conc}]{H_2SO_4} CO + CO_2 + H_2O$$

$C_6H_{12}O_6$ (wooden table, chair etc.) $\xrightarrow[\text{conc}]{H_2SO_4}$ $C + H_2O$

$C_{12}H_{22}O_{11}$ $\xrightarrow[\text{conc}]{H_2SO_4}$ $C + H_2O$

→ Caro's Acid / Peroxo Mono sulphuric Acid

Prep:

derivative of H_2SO_4

$$H-O-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-Cl + H-O-O-H \rightarrow H-O-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-O-O-H \xrightarrow{H_2O} H_2SO_4 + H_2O_2$$

don't use H_2SO_4 becoz strong → so exothermic

→ Marshal's acid / Peroxo Di sulphuric acid:

Prep.

$$\begin{matrix} O \\ \| \\ O-S-Cl \\ \| \\ O \end{matrix} + H-O-O-H \rightarrow \begin{matrix} O \\ \| \\ Cl-S-OH \\ \| \\ O \end{matrix} \rightarrow \begin{matrix} O \\ \| \\ H-O-S-O-O-S-OH \\ \| \qquad\qquad \| \\ O \qquad\qquad O \end{matrix}$$

(OR) excess H_2O → $\downarrow H_2O$

13/4/17

VII-A / 17th / Halogen Family:

Super halogen

- F → Colourless gas
- Cl → Yellow green gas
- Br → Brown liq.
- I → Violet solid
- At* → Radioactive

Halogen (sea-salt's producer)

* Physical Properties:

1) Atomic radius ↓ Increase.
   Ionic radius ↓

2) I.E ↓ Decreases

3) E.N. ↓ Decreases

4) E.A. ↓ Decreases

   F
   Cl ↑

5) Electro(tv^e) Nature ↓ Increases

6) Metallic Nature ↓ Increases
   (can be shown by iodine)

7) Bond Energy ↓ Decreases

$$Cl_2 > Br_2 > F_2 > I_2$$

8) Oxidation power ↓ Decreases

9) Reactivity ↓ Decreases

$F_2 > \underbrace{Cl_2 > Br_2}_{\text{Same}} > I_2$

6) Oxid. no.

F = -1 & 0

X = -1 to 7.

* Chemical Properties

i) Rxn with H_2O

H_2O —
- $F_2 \rightarrow HF + O_2 + O_3$
- $Cl_2/Br_2 \rightarrow HX + H\overset{+1}{X}O$
- $I_2 \rightarrow$ No Rxn

2) Rxn with CH_4

CH_4 —
- $F_2 \rightarrow C + HF$ (Possible in dark also)
- $Cl_2/Br_2 \rightarrow CH_3X + HX$ (Possible in light.)
- $I_2 \rightarrow$ No Rxn.

3) Properties of oxides.

F : No oxide formation.

OF_2, O_2F_2 etc.

- Fluorides
- unstable
- good oxidation & fluorinating agent.

$X = X_2O_3$, X_2O_5, X_2O_7 etc.

- oxides, soluble
- acidic
- gives oxo-acid with water.

4) Properties of hydrides

	thermal stab	Bond energy	Acidic Nature	Reducing	Poisonous	M.P. & B.P.
HF	Dec ↓	Dec ↓	Inc ↓	Inc ↓	Inc ↓	* HF max
HCl						
HBr						In.
HI						

5) Rxn with alkali

$$X_2 \xrightarrow{NaOH\ (c\text{-}D,\ \text{cold-dil})} NaX + NaXO + H_2O$$

$$X_2 \xrightarrow{NaOH\ (H\text{-}C,\ \text{hot conc.})} NaX + NaXO_3 + H_2O$$

$$F_2 \xrightarrow{NaOH\ (\text{cold-dil})} NaF + H_2O + OF_2$$

$$F_2 \xrightarrow{NaOH\ (\text{hot conc-dil})} NaF + H_2O + O_2$$

* Glauber's salt - Na_2SO_4.

$HClO_4$ is Strongest acid.

Oxo - acids [Except 'F']

	Acidic nature	thermal Stab.	Oxid Powers.
$H^{+1}XO$	Increases	Increases	Decreases
$H.X^{+3}O_2$			
$HX^{+5}O_3$			
$HX^{+7}O_4$			

→ more stable then less tendency to donate

↓ Stability of (conj base(anion) increases.

↗ can also check by ~~bondorder~~ B.O ∝ Stab

F_2

→ By the ~~the~~ electrolysis of $KHF_2 + H_2F_2$ (1:5)

↓ Fermi Salt.

$KHF_2 \xrightarrow{!} KF + HF$

$H^+ + F^- \longrightarrow F_2$

$\longrightarrow H_2$ → only process to form F_2

* Physical Properties:

→ colourless (light yellow), soluble, pungent, poisonous, reactive.

* Chemical Properties:

→ Reaction with all elements → fluorides

F_2 —H.O→ $HF + O_2 + O_2$

F_2 —CH_4→ $C + HF$

Remember H_2F_2 formed instead of HF.

medium to pass F_2

* C_6H_6 (ice) → C_6F_{12} + HF

F_2 * $KXO_3 + H_2O \rightarrow KXO_4 + HF$

* $KHSO_4 \rightarrow K_2S_2O_8 + HF$

→ only reaction where peroxide formed.

Cl_2

→ By oxidation

MnO + HCl

HCl → $MnO_2 \rightarrow Cl_2 + MnCl_2 + H_2O$

$Pb_3O_4 \rightarrow Cl_2 + PbCl_2 + H_2O$

$PbO_2 \rightarrow Cl_2 + PbCl_2 + H_2O$

$KMnO_4 \rightarrow Cl_2 + MnCl_2 + KCl + H_2O$

→ From bleaching powder

$CO_2 \rightarrow Cl_2 + CaCO_3$

$CaOCl_2$ — HCl dil → $Cl_2 + CaCl_2 + H_2O$

H_2SO_4 dil → $Cl_2 + CaSO_4 + H_2O$

→ Deacon's process:

(remember)

$HCl + O_2 \xrightarrow[\Delta]{CuCl_2} Cl_2 + H_2O$

→ By electrolysis

$NaCl + H_2O \rightarrow NaOH + H_2 + Cl_2$

* Upper halogen can displace lower halogen.

→ By hydrolysis:

H_2O — PCl_3, PCl_5, $SiCl_4$ — Under H_2O

* Physical properties:
→ Yellow-green, soluble
→ Acidic, pungent
→ Poisonous
* ice cold - $Cl_2 \cdot 8H_2O$

* Chemical properties:
→ Directly reacts with all elements except C, O, N & Zero group.

* $Cl + H_2O \longrightarrow HCl + [O]$

Cl_2 —
- $C_2H_5Br \rightarrow C_2H_5Cl + Br_2$
- $FeCl_2 \rightarrow FeCl_3$
- $SnCl_2 \rightarrow SnCl_4$
- $H_2S \rightarrow S + HCl$
- $C_2H_4 \rightarrow C_2H_4Cl_2$ (broke π bonds)
- $CO \longrightarrow COCl_2$
- $Na_2SO_3 + H_2O \rightarrow Na_2SO_4 + HCl$
- $Na_3ASO_3 + H_2O \rightarrow Na_3ASO_4 + HCl$
- $I_2 + H_2O \longrightarrow HIO_3 + HCl$
- $P + H_2O \rightarrow H_3PO_4 + HCl$
- $SO_2 + H_2O \rightarrow H_2SO_4$ + HCl
- $S + H_2O \longrightarrow H_2SO_4 + HCl$

Br_2

a) From Sea water - $MgBr_2$, KBr etc.

b) From Carnallite - $KCl.MgCl_2.6H_2O$.

0.25 % $MgBr_2$ → in uncombined form

↓ best source.

Cl_2 → $KBr \rightarrow KCl + Br_2$

$MgBr_2 \rightarrow MgCl_2 + Br_2$

* Purification:

Br_2 (Impure) $+ Na_2CO_3 \xrightarrow{\Delta}$ NaBr + $NaBrO_3$ + CO_2

→ $H_2SO_4 \rightarrow Na_2SO_4 + Br_2$

→ Brown liq, pungent, poisonous.

→ Less-soluble

* ice-cold - $Br_2.8H_2O$.

* Chemical properties:

$Br_2 + H_2O \rightarrow HBr + [O]$

* same as Cl_2.

I_2

→ By Oxd^n.

KI
- $Cl_2 \rightarrow KCl + I_2$
- $O_3 + H_2O \rightarrow I_2 + O_2 + KOH$
- * $CuSO_4 \rightarrow I_2 + Cu_2I_2 + K_2SO_4$
  - $O_2 \rightarrow CuO + I_2$

→ From seaweeds (laminaria species)

KI & NaI

↓ Δ

Residue (KELP)

Cl_2
- $NaI \Rightarrow NaCl + I_2$
- $KI \rightarrow KCl + I_2$

* P.P.

→ Violet solid, least soluble, acidic, pungent, poisonous.

* Chemical Properties

$I_2 + H_2O \rightarrow HI + [O]$

I_2
- $FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + HI$
- $Na_2SO_3 + H_2O \rightarrow Na_2SO_4 + HI$
- $H_2S \rightarrow HI + S$
- $NaNO_2 + H_2O \rightarrow NaNO_3 + HI$
- * $Na_2S_2O_3 \rightarrow Na_2S_4O_6 + NaI$

Reducing properties (- with strong oxidant)

*Imp.

I_2
- $KClO_3 \rightarrow KIO_3 + Cl_2$
- $O_3 + H_2O \rightarrow O_2 \downarrow + HIO_3$
- $HNO_3 \rightarrow NO_2 + HIO_3$
- $Cl_2 + H_2O \rightarrow HCl + HIO_3$

HX

→ Hydrogen Halides

Aqu → Hydrohalic acid

H_2F_2

CaF_2 + H_2SO_4 conc → $CaSO_4 + H_2F_2$

CaF_2 + H_3PO_4 conc → $Ca_3(PO_4)_2 + H_2F_2$

$KHF_2 \xrightarrow{Pt\ \Delta} KF + HF$

$AgF + H_2 \xrightarrow{\Delta} Ag + HF$

HCl

NaCl + H_2SO_4 conc → $Na_2SO_4 + HCl$

NaCl + H_3PO_4 conc → $Na_3PO_4 + HCl$

H_2O + PCl_3 → $H_3PO_3 + HCl$

H_2O + PCl_5 → $H_3PO_4 + HCl$

H_2O + $SiCl_4$ → $H_4SiO_4 + HCl$

By redn

Cl_2 + $SO_2 + H_2O$ → $H_2SO_4 + HCl$

Cl_2 + H_2S → $S + HCl$

classmate
Date
Page

* HBr

NaBr → H_3PO_4 conc → Na_3PO_4 + HBr

NaBr → H_2SO_4 conc → Na_2SO_4 + HBr

(strong acid)

HBr → $Br_2 + H_2O$

$H_2O + PBr_3 \longrightarrow H_3PO_3 + HBr$

$H_2S + Br_2 \longrightarrow S + HBr$

* HI

NaI → H_3PO_4 conc → Na_3PO_4 + HI

NaI → H_2SO_4 conc → Na_2SO_4 + HI

HI → $I_2 + H_2O$

* Bleaching Powder

$Ca(OCl)_2 \cdot H_2O + CaCl_2\,Ca(OH)_2 \cdot x H_2O$

$\longrightarrow CaOCl_2$

→ Hassen Clever Process
Beckmann's Process

$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$

dry

PP

Pungent (NH₃ like), soluble, pale yellow

* good source of Cl_2 (Available Chlorine)

* C·P

Calcium chlorate.

$CaCl_2 + Ca(ClO_3)_2$

$[CoCl_2] \rightarrow CaCl_2 + O_2$

Exam POV — $CaOCl_2$

- $CO_2 \rightarrow CaCO_3 + Cl_2$
- $HCl \rightarrow CaCl_2 + Cl_2 + H_2O$
- $H_2SO_4 \rightarrow CaSO_4 + Cl_2 + H_2O$

Oxid. prop $CaOCl_2 \rightarrow CaCl_2 + [O]$

$CaOCl_2$

- $NH_3 \rightarrow CaCl_2 + N_2 + H_2O$
- $C_6H_5CH_3 \rightarrow CaCl_2 + C_6H_5CHO$

* ClO_2 [yellow gas, deep red liquid]

$AgClO_2 + Cl_2 \xrightarrow{\Delta} AgCl + ClO_2$

$NaClO_2 + Cl_2 \rightarrow NaCl + ClO_2$

→ Pungent, yellow gas, paramagnetic, odd e^-.
→ unstable, good oxid. & bleaching agent.
→ sp^3, V-shaped, acidic.

ClO_2 (+4)

- spark → $Cl_2 + O_2$
- $H_2O \rightarrow \overset{+5}{HClO_3} + \overset{+3}{HClO_2}$
- $NaOH \rightarrow \overset{+5}{NaClO_3} + \overset{+3}{NaClO_2}$
- $Mg \rightarrow Mg(ClO_2)_2$

Simil b/w NO_2 & ClO_2

- odd e^-
- Paramagnetic
- colour
- ② acids with H_2O
- ② salts with NaOH

* ClO_2

$$ClO_2 + O_3 \xrightarrow{0^\circ C} O_2 + Cl_2O_7$$

- Pungent, unstable, odd e^-, paramagnetic
- Easily form dimer $[ClO_3 \rightarrow Cl_2O_6]$

ClO_3 —
- $\Delta \rightarrow Cl_2 + O_2$
- $H_2O \rightarrow HClO_4 + HClO_3$
- $NaOH \rightarrow NaClO_4 + NaClO_3$

INTERHALOGEN COMPOUNDS

→ Formed by the combination of different ~~half~~ halogens.

Condition - AX_n

Size : $A > X$ $n = 1, 3, 5, 7$

E.N. : $A < X$

AX - IF, ClF, BrF etc.

AX_3 - IF_3, ClF_3, BrF_3

AX_5 - IF_5, $BrCl_5$, ICl_5 etc.

AX_7 - IF_7, ClF_7, BrF_7 etc.

Properties:
- Mostly coloured except fluorides
- Polar in nature
- shows conductivity
- Stability $\propto$ E.NG
- Reactive in nature (less than F_2)
- soluble
- gives (2) acid with water
  → Halogen acid & oxo acid

H_2O —
- $\overset{+3}{Cl}\overset{-1}{F_3} \rightarrow HF + HClO_2$
- $\overset{+5}{I}\overset{-1}{Cl_5} \rightarrow HCl + HIO_3$
- $\overset{+1}{Cl}\overset{-1}{F} \rightarrow HF + HClO$

* Pseudo halogen: $(CN)_2$, $(SCN)_2$, $(SeCN)_2$, $(OCN)_2$ etc.

Pseudo halides: CN^-, SCN^-, OCN^- etc.

→ Sim. with true halogens:
1) Exist in all phases
2) Shows colour
3) Isomorph (Same struc) in nature
4) gives monobasic acid with H^+ [HCl, HCN]
5) Salts with metals [AgCl & AgCN]

AgCl: soluble in NH_3; Insoluble in H_2O

6) Preparation is also same

$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$

$Pb(CN)_4 \xrightarrow{\Delta} Pb(CN)_2 + (CN)_2$

Zero / $ns^2 np^6$ / Rare / Inert / Noble gases.

Universe - He > Ne > Ar > Kr > Xe > Rn

(less than 1% in air)

He

Ne

Ar → Max. in air

Kr

Xe

Rn* - radioactive

He, Ne

↓

clevite, monazite, ...

→ present, not as ...

P.P

1) Mono atomic, insoluble odourless gases.
2) Atomic radius ↓ Increases
3) I.E. ↓ Decreases
4) E.A. ↓ Decreases
5) E.N. ↓ Decreases
6) Density ↓ Increases
7) M.P. & B.P. ↓ Increases
8) Adsorbing tendency ↓ Increases

9) liquifying tendency ↓ Increases

10) Reactivity ↓ Increases

* First known comp. – $Xe[PtF_6]$ ↙ $O_2[PtF_6]$

- separation → charcoal adsorbtion method
  → Fractional distillation

* XeF_2 → Xenon difluoride

$Xe + F_2 \xrightarrow{Ni/400°C} XeF_2$
1 : 2

$O_2F_2 + Xe \xrightarrow{118°C} XeF_2 + O_2$

P.P : colourless, crystalline, soluble

C.P.

XeF_2
- Δ → $Xe + F_2$
- F_2 → XeF_4
- * H_2O → $Xe + H_2F_2 + O_2$

common product :- Xe

Xe inert
F reacts
with Xe
poti. XeF_2
- $Pt \rightarrow PtF_4$
- $Hg \rightarrow HgF_2$
- NO } odde → NOF
- NO_2 } → NO_2F
- $2SO_3 \rightarrow S_2O_5F_2 + O_2$
- $I_2 \rightarrow IF$
- $C_6H_6 \rightarrow C_6H_5F + H_2F_2$

→ Adduct forming tend: (odd e^-)

Lewis acid + Lewis base

XeF_2 — $2SbF_5 \rightarrow XeF_2 . 2SbF_5$

$IF_5 \rightarrow XeF_2 . IF_5$

* XeF_4

$Xe + F_2 \xrightarrow{Ni/400^\circ C} XeF_4$

1 : 10

$XeF_2 + F_2 \longrightarrow XeF_4$

→ colourless, crystalline, solid

* XeF_4 — $F_2 \rightarrow XeF_6$

$Xe \rightarrow XeF_2$ → shud be O_2.

* $H_2O \rightarrow H_2F_2 + O_2 + Xe + XeO_3$

→ Rest are same as XeF_2

Adduct

XeF_4 — $PF_5 \rightarrow XeF_4 . PF_5$

$AsF_5 \rightarrow XeF_4 . AsF_5$

$SbF_5 \rightarrow XeF_4 . SbF_5$

* XeF_6

$Xe + F_2 \xrightarrow{Ni/400^\circ C} XeF_6$

1 : 20

$XeF_4 + F_2 \longrightarrow XeF_6$

→ colourless, crystalline, solid

C.P.

* Imp

$XeF_6 \begin{cases} \xrightarrow{+4} SiO_2 \rightarrow SiF_4 + XeO_3 \\ Xe \rightarrow XeF_4 \end{cases}$

$XeF_6 + H_2O \longrightarrow H_2F_2 + XeOF_4 \xrightarrow{H_2O} XeO_2F_2 \xrightarrow{H_2O} XeO_3 + H_2F_2$

20 times more explosive than TNT.

explo

$XeF_6 + NaOH + H_2O \rightarrow Na_4 \overset{+8}{Xe}O_6 \cdot 8H_2O$

~~Sodium perchlorate~~

perxenate

→ Other reactions same as XeF_2

→ Do uses from book.