Halogens (F_2, Cl_2, Br_2, I_2)

(Surendra Sharma)

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* Preparation of halogens:-

~ General methods

(i) Electrolytic oxidation of halides

Eg:-

$$KHF_2 \rightleftharpoons KF + HF$$

$$KF \rightleftharpoons K^+ + F^-$$

$$HF \rightleftharpoons H^+ + F^-$$

$$2F^- \rightleftharpoons F_2 + 2e^- \quad (\text{at anode})$$

$$2H^+ + 2e^- \rightleftharpoons H_2 \quad (\text{at cathode})$$

Note:-
Electrolysis of F_2 is done in anhydrous condition because F_2 reacts with water to give O_2 gas.

(ii) By chemical oxidation of Halides [Except F_2, since F_2 is strongest oxidising agent]

Cl_2, Br_2 & I_2 can be prepared by oxidation of halides with strong oxidising agents like MnO_2, $K_2Cr_2O_7$, $KMnO_4$, etc.

$$MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + 2H_2O + Cl_2$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2 \quad (\text{without heat})$$

$$K_2Cr_2O_7 + 14HCl \xrightarrow{\Delta} 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

~ Laboratory preparation of Cl_2, Br_2 & I_2

→ Principle: By heating respective halide salt with manganese dioxide and conc. sulphuric acid.

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + [O]$$

$$NaX + H_2SO_4 \longrightarrow NaHSO_4 + HX \quad]\times 2$$

$$2HX + [O] \longrightarrow H_2O + X_2$$

[Note:- NaX → NaCl, NaBr, KI]

$$MnO_2 + 3H_2SO_4 + 2NaX \xrightarrow{\Delta} 2NaHSO_4 + MnSO_4 + X_2 + 2H_2O$$

Manufacture of Bromine from Carnallite:-

Carnallite is the double salt of hydrated potassium magnesium chloride ($KCl.MgCl_2.6H_2O$). Naturally occuring carnallite contains smaller amount of KBr and $MgBr_2$ as impurities. When carnallite is subjected to crystallization the chlorides form salt while bromides remain in mother liquor. From mother liquor bromine is obtained by action of chlorine.

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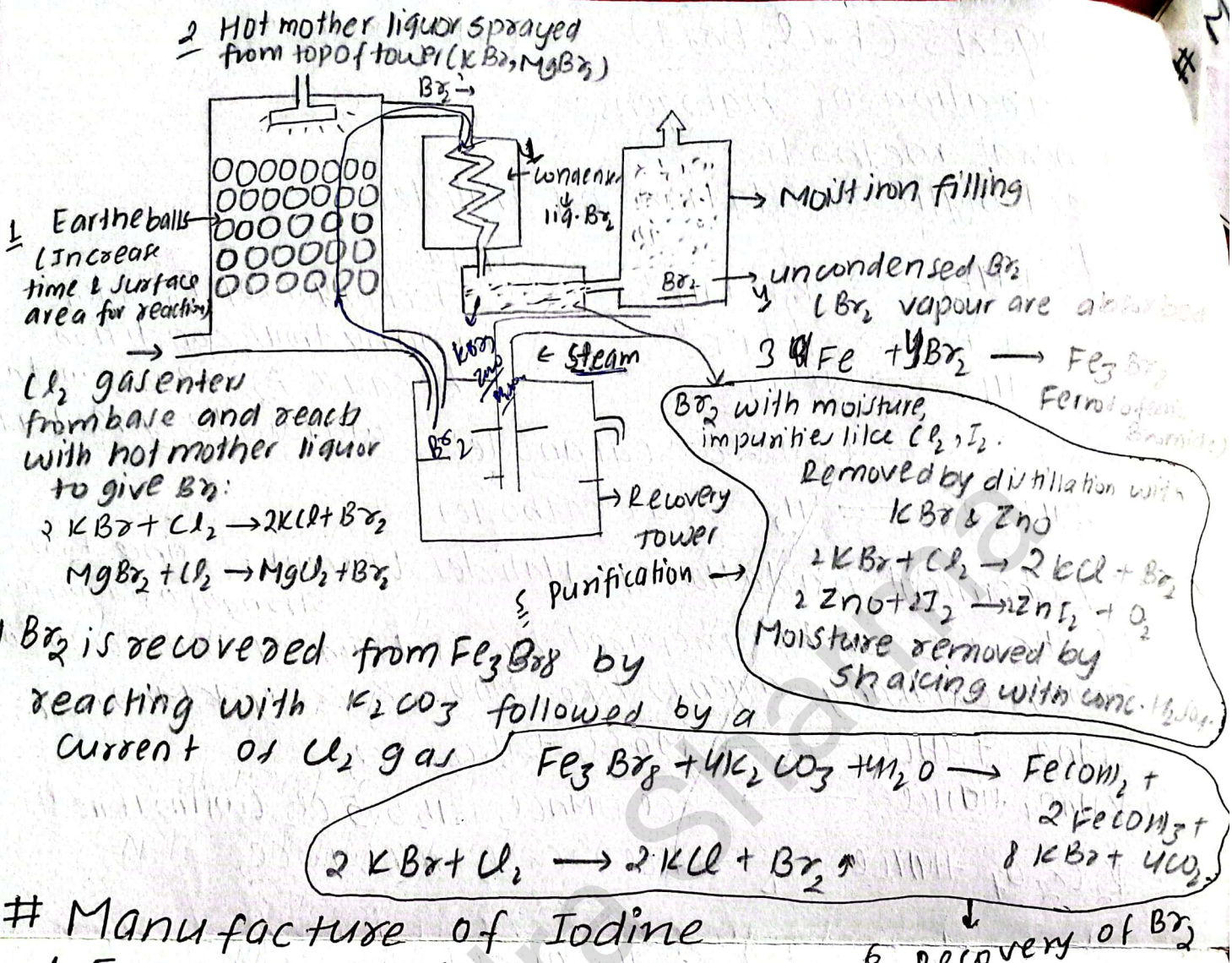


Br_2 is recovered from Fe_3Br_8 by reacting with K_2CO_3 followed by a current of Cl_2 gas

$Fe_3Br_8 + 4K_2CO_3 + 4H_2O \rightarrow FeCO_3 + 2Fe(OH)_3 + 8KBr + 4CO_2$

$2KBr + Cl_2 \rightarrow 2KCl + Br_2 \uparrow$

6 Recovery of Br_2

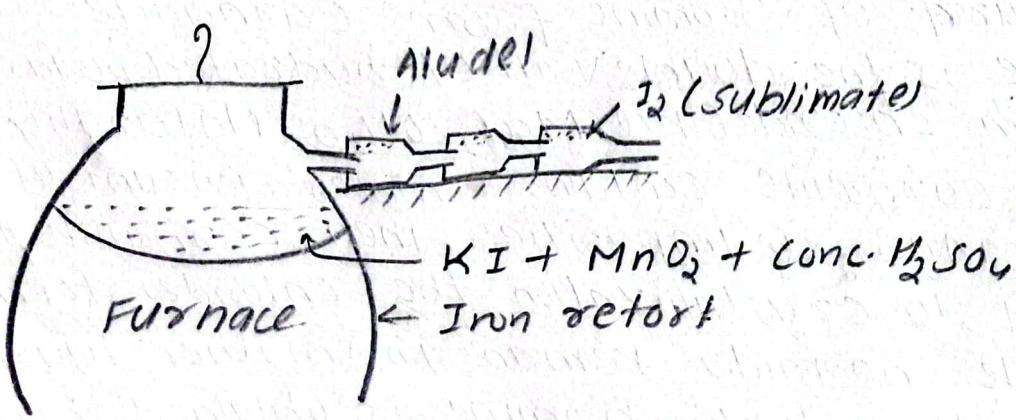
Manufacture of Iodine

1. From sea weeds

Sea weeds of Laminaria varieties contains Iodine in the foom of NaI & KI. For production of I_2 sea weeds are collected, ~~burnt and~~ dried and burnt. The ash is extracted with water and subjected to coystallization. More soluble NaI and KI remains in mother liquor. then,

$KI + 3H_2SO_4 + MnO_2 \xrightarrow{\Delta} 2KHSO_4 + MnSO_4 + I_2 + 2H_2O$

(mother liquor)



Manufacture of Iodine from Caliche :-
Sodium nitrate is called Chile salt petre. Crude chile salt petre is called caliche, which contains smallar amount of $NaIO_3$.

$$NaIO_3 + NaHSO_3 \longrightarrow Na_2SO_3 + HIO_3 \quad]\times 2$$

Sodium iodate

$$2HIO_3 \longrightarrow I_2 + H_2O + 5[O]$$

$$NaHSO_3 + [O] \longrightarrow NaHSO_4 \quad]\times 3$$

$$Na_2SO_3 + [O] \longrightarrow Na_2SO_4 \quad]\times 2$$

$$2NaIO_3 + 5NaHSO_3 \longrightarrow 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$$

Iodine obtained from above process contains impurities like ICl, IBr, ICN and sulphur which are removed by distillation with KI.

$$ICl + KI \xrightarrow{\Delta} KCl + I_2$$

$$ICN + KI \xrightarrow{\Delta} KCN + I_2$$

$$S + 2KI \longrightarrow K_2S + I_2$$

Chemical properties of Halogens

(1) Action with alkalis

* For Cl_2 and Br_2 $(X_2 \rightarrow Cl_2 \& Br_2)$

$$X_2 + 2NaOH \text{ (cold and dil.)} \longrightarrow NaX + H_2O + NaXO$$

Sodium hypohalite

$$3X_2 + 6NaOH \text{ (hot and conc.)} \longrightarrow 5NaX + 3H_2O + NaXO_3$$

Sodium halate

* For I_2

$$I_2 + NaOH \text{ (cold \& dil.)} \longrightarrow NaI + HOI$$

Hypoiodous acid

$$3I_2 + 6NaOH \text{ (hot and conc.)} \longrightarrow 5NaI + 3H_2O + NaIO_3$$

(Sodium Iodate)

(2) Oxidizing nature of halogen [Due to formation of nascent oxygen]

(i) $H_2S + X_2 \longrightarrow S + 2HX$ $[X_2 \rightarrow Cl_2, Br_2, I_2]$

Hydrogen sulphide — free sulphur

(ii) $SO_2 + X_2 + 2H_2O \longrightarrow H_2SO_4 + 2HX$

(iii) $Na_2SO_3 + H_2O + X_2 \longrightarrow Na_2SO_4 + 2HX$

Sodium sulphate

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(iv) $Cl_2 + H_2SO_4 + 2FeSO_4 \longrightarrow Fe(SO_4)_3 + 2HCl$
Light green → Yellow

(v) $Na_2S_2O_3 + H_2O + X_2 \longrightarrow S + Na_2SO_4 + 2HX$
Sodium thiosulphate → free sulphur [$X_2 \rightarrow Cl_2, Br_2$]

But,

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$
Sodium thiosulphate → Sodium tetrathionate

Note: In all oxidi... reactions.
1st step → $X_2 + H_2O \rightarrow 2HX + [O]$
2nd step → oxidizing step

3. Bleaching action of chlorine

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

Colouring material + O ⟶ Colourless substance (oxidised)

NOTE:- Bleaching action of chlorine is due to oxidation and permanent.

Uses of Halogen

F_2	Cl_2	Br_2	I_2
→ prepare CFC compounds used as refrigirant → NaF → insecticide → NF_3 & OF_3 → rocketfuel	→ purify drinking water → DDT (insecticides) → Bleaching agent	→ AgBr - photography → 1,2-dibromo ethane added to petrol to remove lead	→ Tincture of iodine (I_2 dissolved in ethyl alcohol) - antiseptic → NaI, KI - Treat goitre

Preparation of Haloacids (HX)

Laboratory Preparation

* HCl
- By heating NaCl with conc. H_2SO_4.

$NaCl + H_2SO_4 \xrightarrow{\text{low temp.}} NaHSO_4 + HCl\uparrow$

$2NaCl + H_2SO_4 \xrightarrow{\text{high temp.}} Na_2SO_4 + 2HCl\uparrow$

HCl gas is dried by passing HCl gas through conc. H_2SO_4.

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Preparation of HBr

- By heating NaBr with Phosphoric acid (H_3PO_4)

$$NaBr + H_3PO_4 \xrightarrow{\Delta} NaH_2PO_4 + HBr$$

- Lab. Preparation

- By action of Bromine on moist red phosphorus

$$P_4 \text{ (red)} + 6Br_2 \longrightarrow 4PBr_3 \text{ (Phosphorus tribromide)}$$

$$PBr_3 + 3H_2O \longrightarrow H_3PO_3 + 3HBr \quad]\times 4$$

$$P_4 + 6Br_2 + 12H_2O \longrightarrow 4H_3PO_3 + 12HBr$$

Dried by passing anhydrous $CaCl_2$ or P_4O_{10}.

Other H_2SO_4 can't be used because HBr is strong reducing agent. [H_2SO_4 - oxidizing agent]

$$H_2SO_4 + 2HBr \longrightarrow 2H_2O + SO_2 + Br_2$$

Similarly, CaO (quick lime) reacts with HBr

$$CaO + 2HBr \longrightarrow CaBr_2 + H_2O$$

(base) (acid)

Preparation of HI in lab.

- By action of water on the mixture of red phosphorus and iodine.

$$P_4 \text{ (red)} + 6I_2 \longrightarrow 4PI_3$$

$$PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI \quad]\times 4$$

$$P_4 + 6I_2 + 12H_2O \longrightarrow 4H_3PO_3 + 12HI$$

* Drying of HI gas is done as of HBr as HI is also reducing agent.

Test of X^- ion in aqueous solution ($AgNO_3$ test)

(i) For Cl^-

$$Cl^- + AgNO_3 \longrightarrow AgCl\downarrow + NO_3^-$$

(curdy white ppt)

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

[Soluble in Ammonia solution]

Diammine silver chloride

$$[Ag(NH_3)_2]Cl + HNO_3 \longrightarrow AgCl\downarrow + 2NH_4NO_3$$

[Reappears on adding HNO_3]

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(ii) For Br^-

$Br^- + AgNO_3 \longrightarrow \underset{\text{(light yellow ppt.)}}{AgBr\downarrow} + NO_3^-$

$AgBr + 2NH_4OH \longrightarrow \underset{\text{Diammine silver bromide}}{[Ag(NH_3)_2]Br} + 2H_2O$ [Slightly soluble in NH_4OH]

$[Ag(NH_3)_2]Br + HNO_3 \longrightarrow AgBr\downarrow + 2NH_4NO_3$ [Reappears on adding HNO_3]

(iii) For I^-

$I^- + AgNO_3 \longrightarrow \underset{\text{(Yellow ppt.)}}{AgI\downarrow} + NO_3^-$ [Insoluble in NH_4OH]

#HI as a powerful reducing agent

$HI + CuSO_4 \longrightarrow Cu_2I_2 + I_2 + H_2SO_4$

HBr and HCl can't reduce $CuSO_4$.

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Hydrogen (Water Producer Gk.) - Henry Cavendish

* Resembelence with Alkali
  - → one electron in valence shell
  - → Forms cation [$H - e^- \rightarrow H^+$]
  - → Liberated at cathode
  - → Reducing character
  - → Oxidation state (+1)

* Resembelence with Halogen
  - → one e⁻ less than Noble gas.
  - → Forms anion [$H + e^- \rightarrow H^-$]
  - → diatomic and non-metal
  - → Forms hydrines (as halides) with ~~alkali~~ metal

* Differences
  - → Non-metal & gaseous state
  - → Neutral oxide [Alkali oxide: basic]
  - → Forms covalent compound [Gen.]
  - → much smaller H^+
  - → High ionization energy (than Gr. I)

  - → Less tendency to gain electron
  - → Reducing agent [-X → oxidizing agent]
  - → Max. oxidation state (+1) [OF-X → +7]
  - → Neutral oxide [-X → Acidic oxide]
  - → No lone pair [H-H But :Cl—Cl:]

* Forms of Hydrogen

1. Atomic Hydrogen (H) → very reactive

$$\underset{\text{(molecular)}}{H_2} \xrightleftharpoons[\text{between tungsten electrodes [3000°C]}]{\text{Passing through electric arc}} \underset{\text{(Atomic)}}{2H}$$

- → Life time - short - 0.3sec. [Quickly returns to molecular]
- → Powerful reducing agent (than Nascent) [can reduce AgCl, CdS, etc.]
- → used as hydrogen torch for welding metals.

2. Nascent Hydrogen [Just liberated hydrogen]

→ more reactive and better reducing agent than molecular H_2.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2[H]$$

↳ Proof:-

(i) Reaction with acidified $KMnO_4$ solution

$$\underset{\text{Purple}}{2KMnO_4} + 3H_2SO_4 + 10[H] \longrightarrow K_2SO_4 + \underset{\text{colourless}}{2MnSO_4} + 8H_2O$$

$$KMnO_4 + H_2SO_4 + H_2 \longrightarrow \text{No reaction}$$

(ii) With acidified $K_2Cr_2O_7$ solution.

$$K_2Cr_2O_7 + 4H_2SO_4 + 6[H] \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + H_2 \rightarrow \text{No reaction.}$$

(iii) With $FeCl_3$ solution:

$$FeCl_3 + [H] \longrightarrow FeCl_2 + HCl$$

$$FeCl_3 + H_2 \longrightarrow \text{no reaction.}$$

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3. Ortho and Para Hydrogen [(22) and (25)]

→ Nuclei of Hydrogen molecule spinning in same direction (Parallel)

→ Nuclei of Hydrogen molecule spinning in opp. direction (Antiparallel)

→ Ordinary Hydrogen (75% ortho, 25% para)

→ higher energy (spin in same dir.)

→ less energy

→ Temp. increase → Para decrease, Ortho increase

* Para to Ortho
  → by mixing para H_2 with atomic H_2 or with paramagnetic substances.

*

$$\text{Ortho Hydrogen} \xrightarrow[\text{below 20K}]{\text{liquification}} \text{Para Hydrogen}$$

* Isotopes of Hydrogen has dif. physical properties

(1) Protium ($_1^1H$ or ordinary hydrogen H)
  → most abundant (99.98%)
  → manufacture NH_3
  → oxyhydrogen flame for welding
  → filling toy balloon
  → rocket fuel
  → hydrogenation of vegetable oil.

(2) Deuterium ($_1^2H$ or D)
  → second most abundant (0.015%)
  → Heavy hydrogen
  → moderator in nuclear power plants (D_2O)
  → tracer to determine reaction mechanism.

(3) Tritium ($_1^3H$ or T)
  → least abundant (10^{-16}%)
  → Radioactive - unstable (β)
  → short life period - 12.33 years
  → liberate huge amt. of energy (Hydrogen bomb)
  → Radioactive tracer in agriculture.

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Nitrogen ($1s^2, 2s^2, 2p^3$)

↓

lies in 15 or (VA) Group, second period, p-block elements

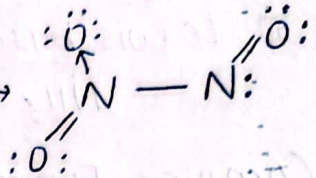
* Oxides of nitrogen

$\frac{1}{2}$ (Tot. electron economy − Tot. e⁻ available)

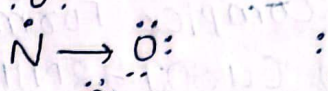
(1) Nitrous oxide → N_2O (O.N. of N → +1) → $:N \equiv N \rightarrow \ddot{O}:$

(2) Nitric oxide → NO (O.N. of N → +2) → $:N=\ddot{O}:$

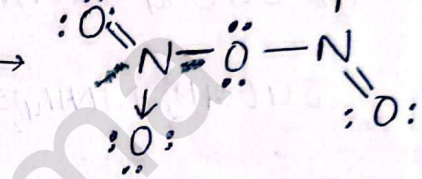
(3) Dinitrogen trioxide → N_2O_3 (O.N. of N → +3) →



(4) Nitrogen dioxide → (NO_2 - O.N of N → +4) →

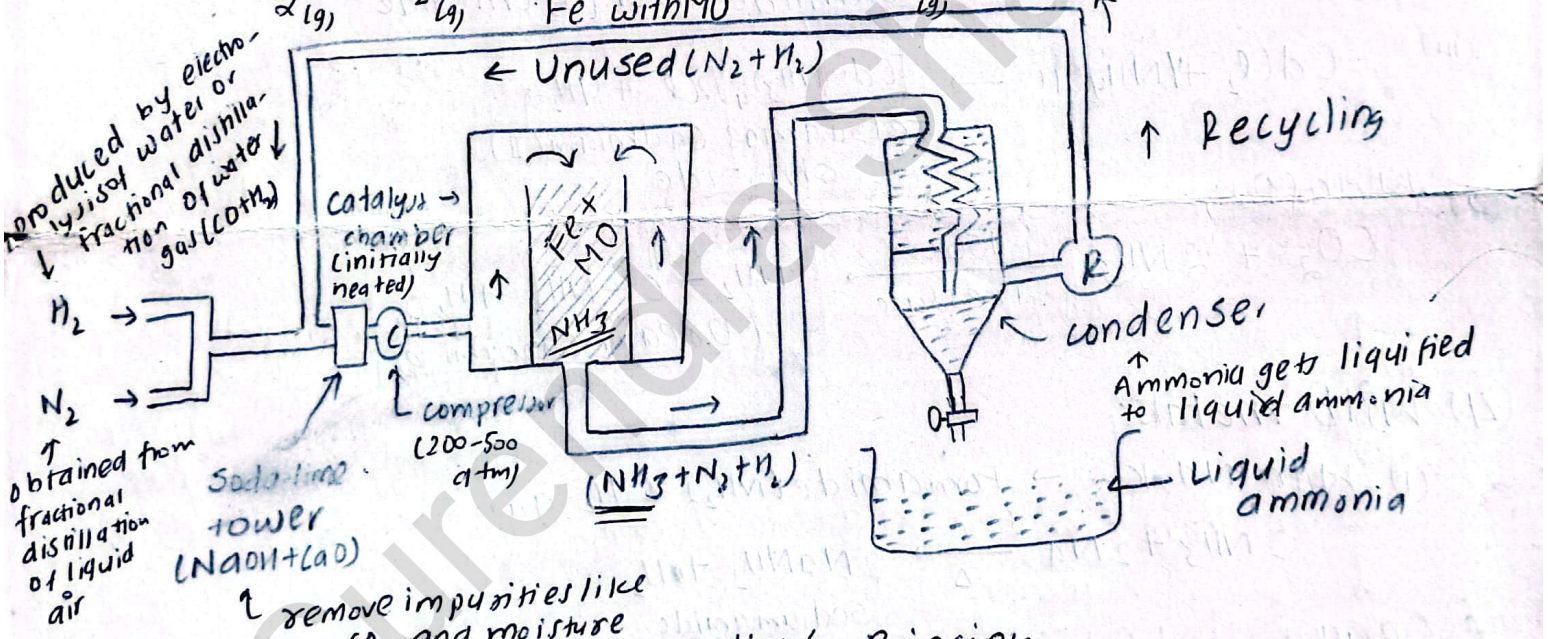


(5) Dinitrogen pentoxide → N_2O_5 (O.N. of N → +5) →



* Manufacture of NH_3 from Haber's process

$$N_{2(g)} + 3H_{2(g)} \underset{\text{Fe with MO}}{\overset{500^\circ C, 200\text{-}500 atm}{\rightleftharpoons}} 2NH_{3(g)} + \text{Heat}$$



Conditions: Ac. to Le Chatelier's Principle

(i) Low temperature (Min - 500°C to overcome slow reaction) → Exothermic

(ii) High pressure [Vol decrease on product side]

(iii) High concentration of N_2 and H_2

(iv) Catalyst - Iron + metal oxide (as promoter) → to speed up.

* Properties:

→ pungent smell → highly soluble in water (H-bond)

→ lighter than air → Easily liquifiable

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* Chemical properties of NH_3 :-

(1) Basic nature

(i) $NH_3 + H_2O \longrightarrow NH_4OH$ (basic in nature)

(ii) Combines with acid to give salt

$NH_3 + HCl \longrightarrow NH_4Cl$ (Dence white fume)

(iii) Lewis base : Donates lone pair electrons

$\ddot{N}H_3 \rightarrow BF_3$

(2) Complex Formation → with salts of d-block elements (Cu, Ag, Cd)

(i) $CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$

Bluish white ppt.

$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

Excess — Tetraamine copper(II) sulphate (deep blue coloration)

(ii) $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$

Diamine silver (I) chloride

(iii) $CdCl_2 + 4NH_4OH \longrightarrow [Cd(NH_3)_4]Cl_2 + 4H_2O$

Tetraamine Cadmium(II) chloride

(3) With CO_2 :-

$$CO_2 + 2NH_3 \xrightarrow[\text{Pressure}]{150^\circ C} NH_2-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$

(Urea or Carbamide)

(4) With metals:

(i) With Na, K .. → Formamide (NH_2^-) & H_2 gas

$$2NH_3 + 2Na \xrightarrow{\Delta} 2NaNH_2 + H_2$$

Sodium amide

But, With Mg & Li → Forms nitride

$$2NH_3 + 3Mg \xrightarrow{\Delta} Mg_3N_2 + 3H_2$$

(5) Ammonia solution as precipitant :→ gives hydroxide from some salt

(i) $FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3\downarrow + 3NH_4Cl$

Reddish brown

(ii) $AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow + 3NH_4Cl$

Gelatenous white

(iii) $FeSO_4 + 2NH_4OH \rightarrow Fe(OH)_2 + (NH_4)_2SO_4$

Dirty green

(iv) $ZnCl_2 + 2NH_4OH \rightarrow Zn(OH)_2\downarrow + 2NH_4Cl$

White

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#) Reducing characters:→ Reduces other and itself gets oxidized

(i) $4NH_3 + 3O_2 \xrightarrow{\Delta} 2N_2 + 6H_2O$

(ii) $4NH_3 + 5O_2 \xrightarrow[800°C]{Pt\text{-}gauze} 4NO + 6H_2O$

(iii) $2NH_3 + 3CuO \xrightarrow{\Delta} N_2 + 3Cu + 3H_2O$
(heated) (oxidised)

(7) Action with halogen:-

Excess X_2 : $NH_3 + 3X_2 \longrightarrow 3HX + NX_3$
nitrogen trihalide

Excess NH_3 : $8NH_3 + 3X_2 \longrightarrow N_2 + 6NH_4X$ (Ammonium halide)

For Cl_2 & Br_2 and For fluorine NH_3 reacts violently i.e. Excess NH_3 case only.

* For I_2 : $NH_3 + I_2 \longrightarrow NH_3 \cdot NI_3 + 3HI$
Nitrogen triiodide ammonate

When $NH_3 \cdot NI_3$ rubbed.

$8NH_3 \cdot NI_3 \xrightarrow{Rubbed} 5N_2 + 9I_2 + 6NH_4I$ (explodes with noise liberating violet vapour of iodine)

(8) With Bleaching Powder ($CaOCl_2$)

$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + \underline{N_2}\uparrow$

(9) Mercurous nitrate paper

$Hg_2(NO_3)_2 + NH_3 \longrightarrow Hg + Hg(NH_2)NO_3 + NH_4NO_3$
Mercuric ammino nitrate

Black

(10) Nessler's reagent

$2K_2HgI_4 + 3KOH + NH_3 \longrightarrow HgO-Hg(NH_2)I + 7KI + 2H_2O$
Million's base
(Brown ppt.)

Structure

Oxyacids of nitrogen:-

(i) HNO_2 (Nitrous acid)

(ii) HNO_3 (Nitric acid)

(iii) HNO_4 (Pernitric acid)

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Nitric acid (HNO_3)

* Manufacture by Ostwald's process

Principle:

(1) catalytic oxidation of NH_3 to NO

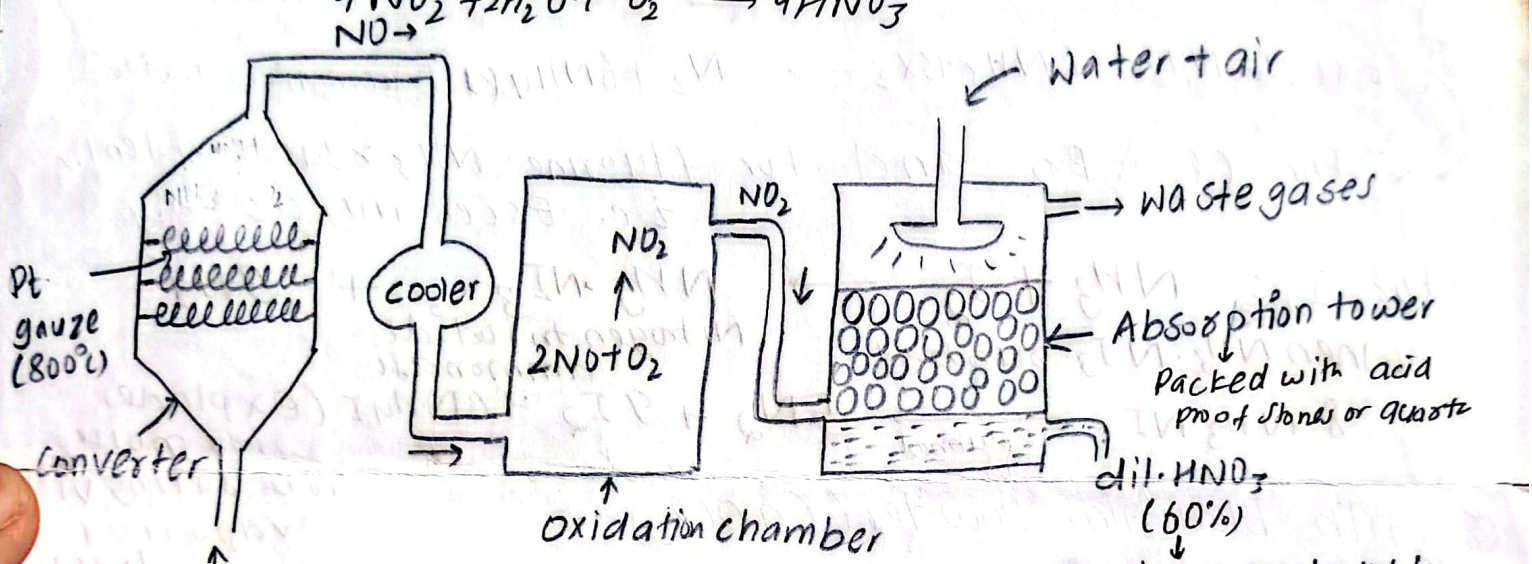
$$4NH_3 + 5O_2 \xrightarrow[800^\circ C]{Pt\text{-}gauze} 4NO + 6H_2O$$

(2) Oxidation of nitric oxide:

$$2NO + O_2 \longrightarrow 2NO_2$$

(3) Absorption of NO_2

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$



* Properties

→ colourless or brown (due to decomposition into NO_2)

→ Soluble in water → corrosive

* Chemical properties

1. Decomposition of nitric acid (conc.),

$$4HNO_3 \xrightarrow[\text{or } h\nu]{\Delta} 4NO_2 + 2H_2O + O_2$$

. So, nitric acid is stored in brown coloured bottle.

2. Acidic properties

(i) Blue litmus → red; pink phenolphthalein → colourless; Yellow methyl orange → pink

(ii) $HNO_3 + KOH \rightarrow KNO_3 + H_2O$ [Reacts with base to give salt & water]

(iii) Dissociates to H_3O^+ ion: $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

3) Reaction with Mg and Mn to produce H_2 gas.

$Mg + \text{very dilute } 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2\uparrow$

$Mn + \text{very dilute } 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2\uparrow$

(4) Strong Oxidizing agent

Concentration	Reduced products
conc. HNO_3	NO_2 (Nitrogen dioxide)
Mod. conc. HNO_3	NO (Nitric oxide)
dil. HNO_3	N_2O (Nitrous oxide)
very very dil. HNO_3	$NH_3 \rightarrow NH_3 + HNO_3 \rightarrow NH_4NO_3$

Electrochemical series

Li	K	Ba	Sr	Ca	Na	Mg	Al	Zn	Fe	Sn	Pb	H	Cu	Hg	Ag	Pt	I	Br	Cl	Au	F

Above hydrogen (more electropositive) ⟵ ⟶ below hydrogen (less electropositive)

Nascent hydrogen formation theory

$Metal + HNO_3 \rightarrow Metal\ nitrate + [H]$

$HNO_3 + [H] \rightarrow \text{reduced product} + H_2O$

Nascent oxygen formation theory

$HNO_3 \rightarrow \text{Reduced product} + H_2O + [O]$

$Metal + [O] \rightarrow Metal\ oxide$

$Metal\ oxide + HNO_3 \rightarrow Metal\ nitrate + H_2O$

(a) Reaction with Zinc (Zn)

with conc. HNO_3

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

with mod. HNO_3

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

with dil. HNO_3

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

with very very dil. HNO_3

$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

Similar is with Mg [(1,4), (3,8), (4,10), (4,10)]

(b) Reaction with Iron (Fe)

with conc. HNO_3

$Fe + 6HNO_3 \longrightarrow \underset{\text{Ferrosoferic oxide}}{Fe_3O_4} + 3H_2O + 3NO_2$

Fe_3O_4 deposits on the surface of the iron which prevents further reaction. Thus iron is passive (inert) with conc. HNO_3.

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Reaction with Gold, Platinum, etc like Noble metals

$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2[Cl]$]x3

(Conc) (Conc)

Nitrosyl chloride

Aquaregia

$Au + 3[Cl] \longrightarrow AuCl_3$]x2

$AuCl_3 + HCl \longrightarrow H[AuCl_4]$]x2

Chloroauric acid

$2Au + 11HCl + 3HNO_3 \longrightarrow 3NOCl + 6H_2O + 2H[AuCl_4]$

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F. Test for NO_3^- ion (Ring test)

→ In testing solution, double vol. of H_2SO_4 is added and solution is cooled under tap water. Then freshly prepared ferrous sulphate solution is added from side of test tube. Formation of brown-ring at junction indicate presence of NO_3^- ion.

$$NO_3^- + H_2SO_4 \longrightarrow HNO_3 + HSO_4^- \quad]\times 2$$

$$2HNO_3 \longrightarrow \underline{2NO} + H_2O + 3[O]$$

$$2\,FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O \quad]\times 3$$

$$2NO_3^- + 6\,FeSO_4 + 5H_2SO_4 \longrightarrow 2NO + 3\,Fe_2(SO_4)_3 + 4H_2O + 2HSO_4^-$$

$$FeSO_4 + NO \rightarrow FeSO_4 \cdot NO$$

Nitrosyl ferrous sulphate
(Brown ring)

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Carbon

Allotrophy: Property of an element to show different physical forms of same element.

Allotrophs of carbon:

* Crystalline: Diamond, Graphite, Fullerene, Graphene
* Amorphous: Charcoal, Lampblack, Coal, Coke

Diamond: hardest substance; used as gem and to cut glass

Fullerene: Latest allotroph consisting of hollow cage of carbon atoms arranged in hexagon & pentagon [C_{60}]; used as super conductor, to trap metal ions (Ca, Au).

Carbon monoxide (CO)

(i) $C + CO_2 \xrightarrow{\Delta} 2CO$ (C = coke)

(ii) $C + O_2 \xrightarrow{\Delta} CO$ (O_2 = limited)

(iii) $4CO + O_2 \xrightarrow{\Delta} 4CO_2$

* $Ag(NH_3)_2OH + CO$ (Tollen's reagent) $\rightarrow Ag\downarrow + NH_3 + CO_2 + H_2O$
* $Cu(OH)_2 + CO \xrightarrow{\Delta} Cu_2O + H_2O + CO_2\uparrow$ (from Fehling solution)

* Laboratory preparation:

(1) From oxalic acid ($\begin{matrix}COOH\\COOH\end{matrix}$)

$$\begin{matrix}COOH\\COOH\end{matrix} + H_2SO_4 \xrightarrow{\Delta} CO + CO_2 + [H_2SO_4 \cdot H_2O]$$

(H_2SO_4 = conc, dehydrating agent)

[NaOH removes impurities of O_2 as Na_2CO_3]

(2) From Formic acid.

$$HCOOH + H_2SO_4 \xrightarrow{100^\circ C} H_2SO_4 \cdot H_2O + CO\uparrow$$

(Methanoic acid; H_2SO_4 = conc, dehydrating agent)

↑ collected by downward displacement of water.

* properties:-

(i) $CO + NaOH \xrightarrow{\Delta} HCOONa$ (sodium formate)

(ii) $ZnO + CO \longrightarrow Zn + CO_2$ [Reduces metaloxides (PbO, Fe_3O_4, Fe_2O_3) to free metal]

(CO easily forms CO_2 (oxidised))

(iii) $CO + 2H_2 \xrightarrow[\Delta]{ZnO + Cu} CH_3OH$ (Methanol)

($CO + 2H_2$ = water gas)

(iv) $CO + Cl_2 \xrightarrow{h\nu} COCl_2$ (phosgene gas)

(v) $Ni + 4CO \xrightarrow{\Delta} Ni(CO)_4$ Nickel tetracarbonyl [with metal] [$Fe(CO)_5$], $Co_2(CO)_8$]

(vi) $C + H_2O \xrightarrow{\Delta} CO + H_2$ (water gas)

(C = red hot coke; H_2O = steam)

(vii) CO + haemoglobin $\longrightarrow$ carboxy haemoglobin (stable complex)

(poisonous) ↓ reduces oxygen content of blood resulting suffocation

Oxygen [Joseph Priestly] (Surendra Sharma)

→ most abundant element in the earth crust

* Oxides are the binary compounds of oxygen with other elements which are less electronegative than oxygen.

* Classification of ~~oxygen~~ oxides:-

(1) Acidic oxides: → combine with water to give acid
→ Oxides of non-metal
→ react with bases to give salt and water
Eg: CO_2, N_2O_3, N_2O_5, NO_2, SO_2, SiO_2, SO_3, P_4O_{10}, ClO_2, etc.
→ Ex: Metallic (of d block) oxides (CrO_3, Mn_2O_7, V_2O_5 show acidic behaviour)

(2) Basic oxides:
→ Oxides of metal
→ Dissolve in water to give base
→ react with acid to give salt and water.
Eg: Na_2O, CaO, etc
$Na_2O + H_2O \rightarrow 2NaOH$.
$Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$

(3) Neutral oxides
→ Neither show acidic nor basic properties i.e. they do not react with acid or base to give salt and water.
Eg: H_2O, NO, N_2O, CO, etc.

(4) ~~Rea~~ Amphotheric oxides: reacts with both acid and base to give salt and water.
Eg: ZnO, PbO, Al_2O_3, SnO, SnO_2, BeO, Cr_2O_3, etc.
$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$
$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$
$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$
$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$
Sodium meta aluminate.

(5) Mixed oxides:
→ made by combination of more than one simpler oxides of the same elements. Eg: Fe_3O_4 ($FeO + Fe_2O_3$), Pb_3O_4 ($2PbO + PbO_2$)

(6) Peroxides
→ contain peroxide (-O-O-) linkage → react with dil acid (HCl, H_2SO_4, etc.) to give H_2O_2
→ oxidation number of Oxygen is -1
Eg: H_2O_2, Na_2O_2, BaO_2, etc. Eg: $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

(7) Super oxides: Higher no. of oxygen than expected [Ox. $O_2 \rightarrow -\frac{1}{2}$]
[KO_2, CsO_2, etc]

(8) Sub oxides: Less no. of oxygen than expected. [C_3O_2, Pb_2O]

#Note: Left to Right on period → Metallic character decreases → Basic character decreases
Top to bottom in group; metallic character increases; basic character increases

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Sulphur (S) → S_8

↓

$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

Oxidation states → -2, +2, +4, +6 (has d orbital)

8	O
16	S
34	Se
52	Te
84	PO

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*Allotrophs of Sulphur

A. Crystalline

1. Rhombic (α sulphur) → most stable
2. Monoclinic (β sulphur) → needle shaped sulphur

→ All allotrophs of sulphur are soluble in CS_2 except plastic sulphur

B. Non-crystalline or amorphous → no sharp melting point

3. Plastic sulphur (γ-sulphur) → zig-zag chain of sulphur atoms
4. Colloidal sulphur → changes into rhombic on long standing
5. Milk of sulphur → white; changes slowly into rhombic at room temp.

Hydrogen Sulphide (H_2S)

*Laboratory preparation:-

$$FeS + H_2SO_4(dil) \longrightarrow FeSO_4 + H_2S$$

Why not conc.? → due to oxidising action: $H_2SO_4 + H_2S \rightarrow \underbrace{2H_2O + SO_2}_{\text{oxidised}} + S$

con HNO_3? → NO, oxidising action: $2HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S$

→ Collected by upward displacement of air.

Purification:- FeS is contaminated with Zn, Fe, etc that react with dil. acid to liberate H_2, HC and moisture.

Purified by passing through magnesium oxide in water:

$$MgO + 2H_2S \longrightarrow \underset{\text{Magnesium bisulphide}}{Mg(HS)_2} + H_2O$$

$$Mg(HS)_2 \xrightarrow{60^\circ C} MgS + H_2S$$

Drying: By using P_2O_5 or anhydrous $CaCl_2$.

Not CaO and conc. H_2SO_4? → $H_2S + CaO \longrightarrow H_2O + CaS$

$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$

For intermittent supply of H_2S gas for qualitative salt analysis Kipp's apparatus is used. It avoids

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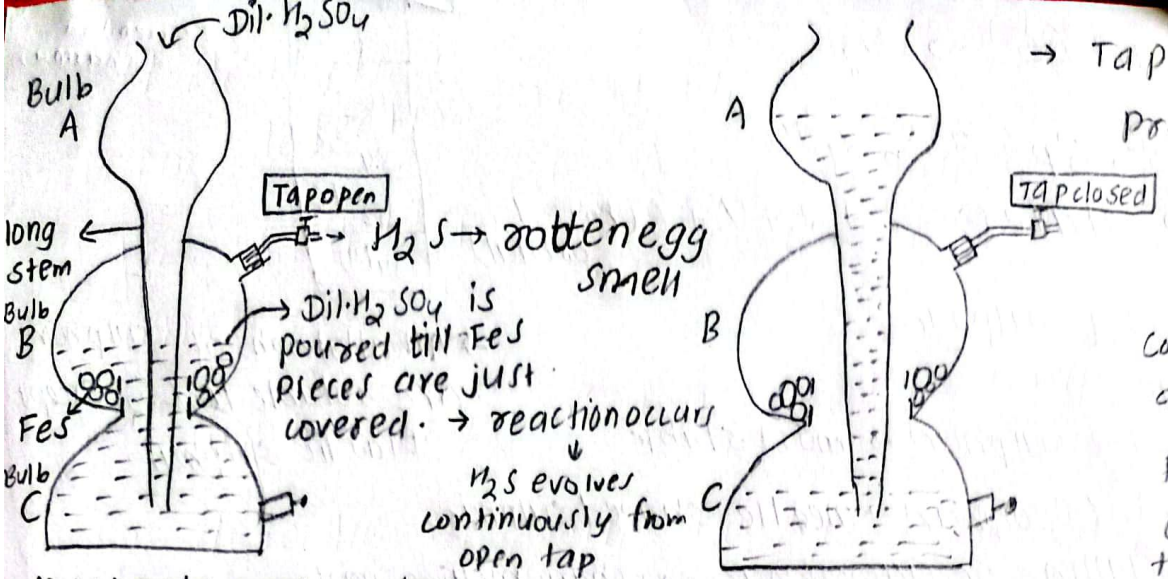

#Kipp's apparatus

Chemical properties

1. Combustibility

$H_2S + O_2 \xrightarrow[\text{in limited air}]{\text{burning}} H_2O + 2S\downarrow$

$2H_2S + O_2 \xrightarrow[\text{in excess air}]{\text{burning}} 2H_2O + 2SO_2$] Blue coloured flame

2. Acidic nature: (weak diprotic acid)

Gives two series of salt: (K_2, Na, ..) $KOH + H_2S \rightarrow KHS + H_2O$

$KOH + H_2S \rightarrow K_2S + H_2O$

With Metals more electropositive than H_2 gives $H_2\uparrow$ (Na, Pb, Zn, etc)

3. Reducing properties: S^{--} easily supply e^- to other and itself is oxidized to free sulphur.

(i) Halogen: $H_2S + X_2 \longrightarrow 2HX + S\downarrow$ ($X_2 = Cl_2, Br_2, I_2$)

(ii) SO_2 : $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S\downarrow$

(iii) conc. HNO_3 : $2HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S\downarrow$

(iv) conc. H_2SO_4 : $H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S\downarrow$

(v) Acidified $KMnO_4$ (pink colour is discharged):

$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$H_2S + [O] \longrightarrow H_2O + S$] x 5

$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

(vi) Acidified $K_2Cr_2O_7$ (disappearance of orange colour → green)

$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

(vii) $FeCl_3$: $2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$

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4. Analytical reagent: (qualitative analysis of basic radicals)

(i) For detection of group II basic radicals [Cu^{++}, Hg^{++}, Pb^{++}; black ppt, Cd^{++}, As^{++}; Yellow ppt] in form of sulphides.

Role of dil. HCl:- To suprevent ionization of weak acid H_2S, which decreases concentration of S^{--} ions but existed S^{--} will be sufficient to precipitate group II metal ions as sulphides.

(ii) For detection of group IIIB basic radicals [Zn^{++}; white ppt, Co^{++}, Ni^{++}; black ppt and Mn^{++}; flesh coloured] in form of sulphides.

Passing H_2S in alkaline medium of NH_4OH and NH_4Cl:- monitor concentration of S^{--} such that the value is enough to precipitate group IIIB metal sulphides.

* Test of H_2S

a. Lead acetate: $H_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{black ppt.}}{PbS\downarrow} + 2CH_3COOH$

(b) Sodium nitroprussside: $S^{--} + [Fe(CN)_5NO]^{--} \longrightarrow \underset{\text{violet colour.}}{[Fe(CN)_5NOS]^{----}}$

SO_2 (Sulphur dioxide)

↳ Study from book (Ayam) : all.

H_2SO_4 → Book

$H_2S_2O_3 \cdot 5H_2O$ → Book.

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