Chapter-05

Chemistry of Non-metals

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Hydrogen

Hydrogen is the courless, tasteless, odourless and lightest gas which is also known as water producer gas. It is water insoluble and inflammable gas.

Different form of Hydrogen

1. Atomic Hydrogen

Hydrogen obtained by the dissociation of molecular hydrogen is called atomic hydrogen.

2. Nascent Hydrogen

It is the newly formed hydrogen in the reaction mixture. Nascent hydrogen are mono-atomic hydrogen that exists transiently after the reduction of hydrogen ion.

Example:

$Zn + dil.\ 2HCl \longrightarrow ZnCl_2 + 2[H]$ (Where, H = nascent hydrogen)

The nascent hydrogen is a more reactive and powerful reducing agent than ~~atomic~~ molecular hydrogen which can be proved by the following chemical reactions.

i. Reaction with acidified Potassium Permanganate solution

$KMnO_4 + H_2SO_4 + H_2 \longrightarrow$ No reaction

$2KMnO_4 + 3H_2SO_4 + 10[H] \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$

colourless

ii. Reaction with acidified Potassium dichromate Solution

$K_2Cr_2O_7 + H_2SO_4 + H_2 \longrightarrow$ No reaction

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

orange

green

iii. Reaction with ferric chloride Solution

$FeCl_3 + H_2 \longrightarrow$ No reaction

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

Yellow — Palegreen

Isotopes of Hydrogen

The atom of the same element having the same atomic number but a different mass number are called isotopes. There are 3 known isotopes of hydrogen.

i. Protium or ordinary hydrogen ($_1H^1$ or H)
ii. Deuterium or heavy hydrogen ($_1H^2$ or D)
iii. Tritium or radioactive hydrogen ($_1H^3$ or T)

Uses of Protium

- Hydrogenation of vegetable oils.
- Synthesis of ammonia by Haber's process
- As a rocket fuel

Uses of Deuterium

- As a moderator in the nuclear power plant.
- As a tracker to determine the mechanism of the reaction.

Uses of Tritium

- As a radioactive tracer
- To make hydrogen bomb

Heavy Water

Deuterium oxide is known as heavy water. It is represented by D_2O or $_1H^2_2O$

Uses

- Moderator in nuclear reactions

- Coolant in nuclear reactor.
- To prepare deuterium.

Oxygen and It's Allotropes

Oxygen is the representative atom of Group VIA (group 16) of the perodic table.

Allotropes are the atoms of same element with similar chemical properties but different physical properties.

Types of oxides

1. Acidic oxides

Acidic oxides are non-metallic oxides that combine with water to produce ~~an~~ an acid and react with base to produce salt and water.

Examples: ~~A~~ SO_2, SO_3, CO_2, CrO_3 etc.

2. Basic oxides

Basic oxides are metallic oxides that combine with water to produce base and react with acid to produce salt and water. Example: K_2O, MnO_4, CaO, CuO etc.

$Na_2O + H_2O \longrightarrow 2NaOH$ (base)

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$ (salt and water)

3. Amphoteric Oxides

Oxides that react with both acid as well as base to form salt and water are called amphoteric oxides.

Eg:

$ZnO + ~~2Na~~ H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

(basic)

$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

(acidic)

4. Neutral oxides

Oxides which neither react with acid ~~or~~ nor with the base are called neutral oxides.

Example: H_2O, CO, NO, N_2O etc.

5. Peroxides

Oxides that contain Peroxy linkage (-O-O-) and has a -1 oxidation number are called peroxides.

Example: H_2O_2, Na_2O_2, BaO_2

$Na_2O_2 + 2HCl \longrightarrow 2NaCl + H_2O_2$

$BaO_2 + 2HCl \longrightarrow BaCl_2 + ~~H_2S~~ H_2O_2$

6. Mixed or Compound Oxides

Oxides that are a mixture of two simpler oxides of the same element in different valency are called mixed oxide.

Example: Fe_3O_4 ferrosoferric oxide ($FeO + Fe_2O_3$), Pb_3O_4 Red Lead [$2PbO + PbO_2$]

$Fe_3O_4 + 8HCl \longrightarrow FeCl_3 + 2FeCl_3 + 4H_2O$

Applications of Hydrogen Peroxide [H_2O_2]

- It is used as an oxidizing agent.
- It is used as a bleaching agent.
- It is used as an antiseptic.
- It is used in the preparation of toothpaste.
- It is used for cleansing purpose for glass, lens etc.

Ozone

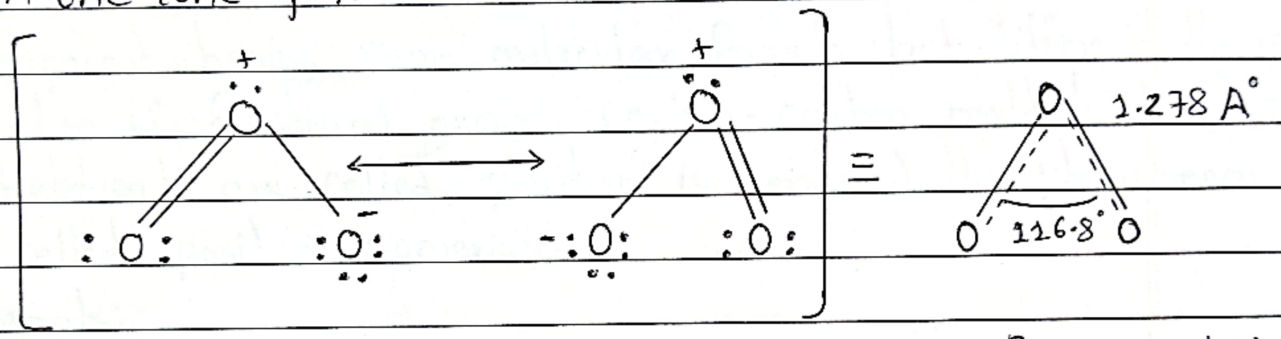
Ozone is the triatomic molecule and one of the allotrope of oxygen, having molecular formula O_3. It is formed naturally in the stratosphere by the action of UV radiation from the sun on oxygen.

$$O_2(g) \xrightarrow{UV} O + O$$

$$O_2 + O \longrightarrow O_3(g)$$

Structure of Ozone

It has bent structure with bond angle 116.8° and bond length is 1.278 A°. The central atom is sp^2 hybridized with one lone pair.



Resonance structure Resonance Hybrid

Ozone Layer depletion / Ozone hole

The ozone layer is depleting mainly due to man-made chlorofluorocarbons (CFCs), also known as freons which are the compounds of carbon, fluorine and chlorine.

Reactions:

$$CF_2Cl_2 \xrightarrow{UV} CF_2Cl + Cl$$

$$Cl + O_3 \longrightarrow O_2 + OCl$$

$$OCl \xrightarrow{UV} O + Cl$$

$$O + O_3 \longrightarrow 2O_2$$

Tailing of Mercury

$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$

When mercury is exposed to the atmosphere of ozone, it is

oxidized into mercurous oxide. Mercury loses its meniscus and sticks on the glass surface leaving a tail. This is called the tailing of mercury.

Compounds of nitrogen (Ammonia - NH_3)

Manufacture of ammonia by Haber's process:

Principle:

When a mixture of nitrogen and hydrogen in the ratio ~~2:3~~ of 1:3 by volume is heated to about 450°c under a pressure of 200-900 atm in the presence of finely divided iron as a catalyst and some molybdenum as a promoter, ammonia is formed.

$$N_2 + 3H_2 \underset{Fe/Mo}{\overset{450^\circ c,\ 200\text{-}900\ atm}{\rightleftharpoons}} 2NH_3 + 22\,kcal$$

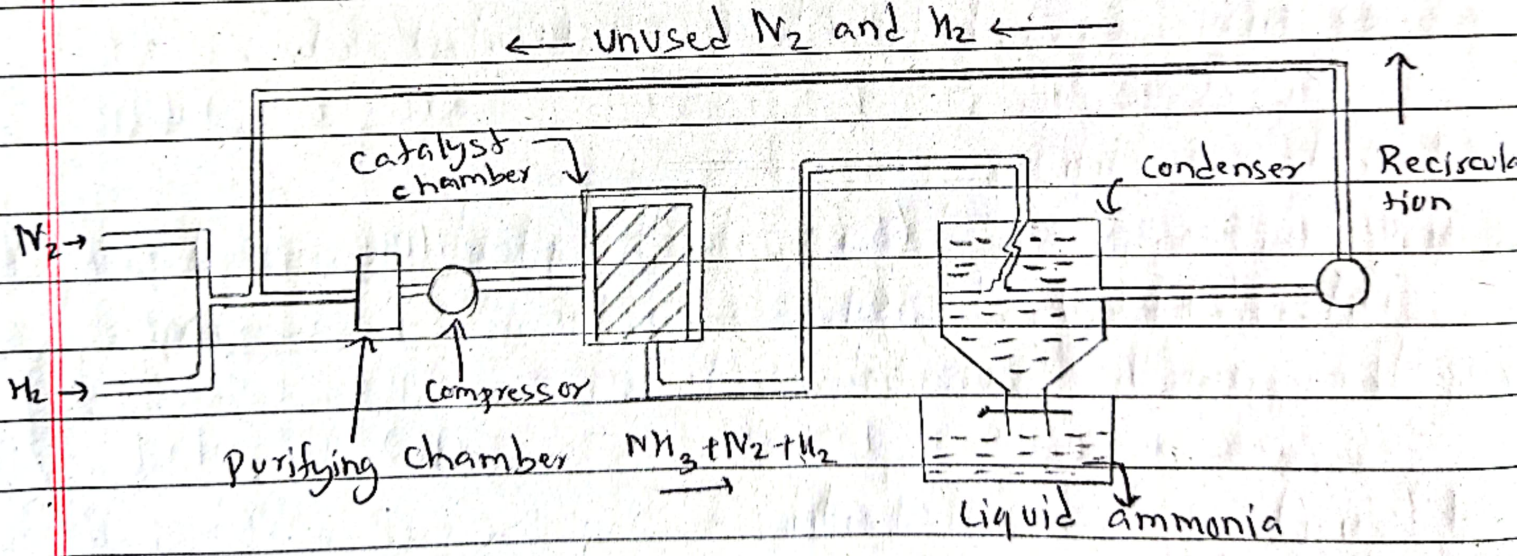


Fig: Manufacture of ammonia by Haber's process

Nitric Acid

Manufacture of Nitric Acid by Ostwald Process

Principle:

1. Catalytic oxidation of Ammonia

Ammonia is oxidized in the air in presence of platinum as a catalyst at 850°c to give nitric oxide.

$$NH_3 + 5O_2 \xrightarrow{Pt.\ 850^\circ c,\ 5\ atm} 4NO + 6H_2O$$

2. Oxidation of nitric oxide

Nitric oxide is oxidized into nitrogen dioxide in presence of oxygen

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

3. Absorption of nitrogen dioxide

Nitrogen dioxide is absorbed in water in presence of air to give nitric acid

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3 \text{ (Nitric Acid)}$$

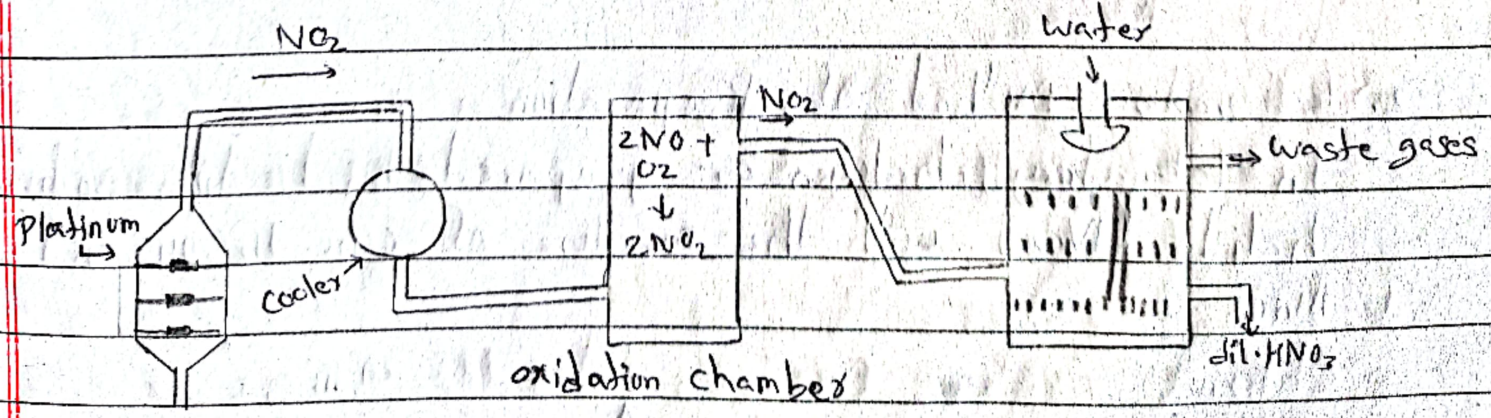


Fig: Manufacture of nitric acid by ostwald's Process

Chemical Properties

1. Oxidizing Agent

Halogen

General Characteristics of halogen

General Method of Preparation

1. By the oxidation of haloacids (HX)

Haloacids when reacts with oxidizing agent like $KMnO_4$, $K_2Cr_2O_7$, MnO_2 etc. gives halogens.

$$2KMnO_4 + 16HX \xrightarrow{\Delta} 2KX + 2MnX_2 + 8H_2O + 5X_2 \quad (X = Cl, Br, I)$$

$$MnO_2 + HX \longrightarrow MnX_2 + 2H_2O + X_2$$

$$K_2Cr_2O_7 + 14HX \longrightarrow 2KX + 2CrX_3 + 7H_2O + 3X_2$$

$$KClO_3 + 6HX \longrightarrow KCl + 3H_2O + 3X_2$$

2. Laboratory Method of Preparation

In laboratory, halogen are prepared by heating sodium halide (NaX) with the mixture of conc. H_2SO_4 and MnO_2

$$2NaX + 3H_2SO_4 + MnO_2 \xrightarrow{\Delta} 2NaHSO_4 + MnSO_4 + 2H_2O + X_2 \quad (X = Cl, Br, I)$$

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Chemical properties of Halogens

1. Action with H_2O, alkali, Ammonia

Chlorine and bromine decomposes water in presence of sunlight but iodine do not react with water.

$$Cl_2 + H_2O \xrightarrow{\text{Sunlight}} HClO + HCl$$

$$Br_2 + H_2O \xrightarrow{\text{Sunlight}} HBrO + HBr$$

$$I_2 + H_2O \longrightarrow \text{No reaction}$$

Chlorine or bromine react with cold and dilute alkali to give sodium hypohalide but with hot and conc. alkali gives sodium halide

(X = Cl and Br)

$$X_2 + NaOH \longrightarrow NaX + H_2O + NaXO$$
(cold and dilute)

$$3X_2 + 6NaOH \longrightarrow 5NaX + 3H_2O + NaXO_3$$
(Hot and conc.)

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

$$3I_2 + 6NaOH \text{ (Hot and Conc)} \longrightarrow 5NaI + 3H_2O + NaI$$
(sodium Iodate)

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Action with Ammonia

$8NH_3$ (excess) $+ 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$

$2NH_3 + 6Cl_2$ (excess) $\longrightarrow 2NCl_3 + 6HCl$

$8NH_3$ (excess) $+ 3Br_2 \longrightarrow N_2 + 6NH_4Br$

$2NH_3 + 3Br_2 \longrightarrow 2NBr_3 + 6HBr$

$2NH_3 + 3I_2 \longrightarrow 2NI_3 + 6HI$

Oxidizing Nature

Halogens are good oxidizing agents. Their oxidizing power is in the order : $F_2 > Cl_2 > Br_2 > I_2$.

a. With H_2S

Chlorine oxidized H_2S into sulphur.

$H_2S + Cl_2 \longrightarrow 2HCl + S$

b. With SO_2

Chlorine oxidises SO_2 into H_2SO_4

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

c. With Na_2SO_3

Chlorine oxidises Na_2SO_3 into Na_2SO_4

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

d. With $Na_2S_2O_3$

Chlorine oxidises $Na_2S_2O_3$ into Na_2SO_4

$Na_2S_2O_3 + H_2O + Cl_2 \longrightarrow 2HCl + Na_2SO_4 + S$

clw

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Bleaching Action

Chlorine changes colored compounds into colorless. This process is called bleaching. Bleaching action is permanent and is due to oxidation.

$$H_2O + Cl_2 \longrightarrow HCl + HOCl$$

$$HOCl \longrightarrow HCl + [O]$$

$$[O] + \text{Coloured substance} \longrightarrow \text{Colourless substance.}$$

Uses of Chlorine

- To purify drinking water
- As a bleaching agent
- To prepare chloroform, DDT etc.

Uses of Bromine

- AgBr is used in photography.
- Used in manufacture of dyes, drugs etc.
- To detect unsaturation in organic compounds.

Uses of Iodine

- Manufacture of Iodoform.
- AgI is used in photography.
- Treatment of goitre.
- Used as an antiseptic.

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Hydrogen Halides (HCl, HBr, HI)

The diatomic inorganic compounds with the formula HX are called hydrogen halides.

Lab preparation of hydrogen chloride gas

HCl gas is prepared in the lab by heating common salt with concentrated sulphuric acid

$$NaCl + H_2SO_4 \xrightarrow{\text{low tempt.}} NaHSO_4 + HCl\,(g)$$

$$2NaCl + H_2SO_4 \xrightarrow{\text{high tempt.}} Na_2SO_4 + 2HCl\,(g)$$

Preparation of aqueous HCl

HCl gas is highly soluble in water. Its aqueous solution is called hydrochloric acid. In order to prepare aqueous HCl, an anti suction device should be made by attaching an inverted funnel to the delivery tube such that the rim of the funnel just touches the surface of the water in the beaker.

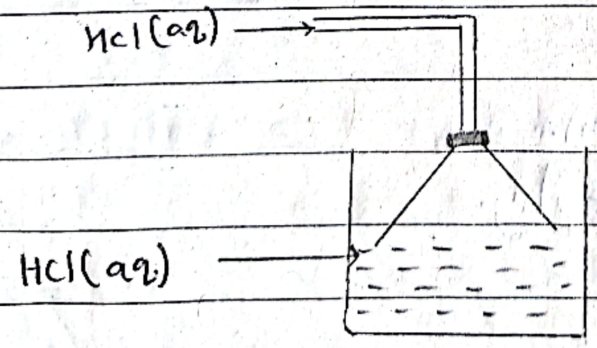

fig: Preparation of aq. HCl

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Preparation of HBr and HI

HBr and HI are more powerful reducing agents than HCl. Hence, they reduce conc. H_2SO_4 and evolves SO_2 gas. So, conc. H_2SO_4 is not used for the preparation of HBr and HI.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr \quad] \times 2$$
$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$
$$2HBr + [O] \longrightarrow Br_2 + H_2O$$
$$2NaBr + 3H_2SO_4 \longrightarrow 2NaHSO_4 + SO_2 + Br_2 + 2H_2O$$

Similarly,

$$KI + H_2SO_4 \longrightarrow KHSO_4 + HI$$
$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$
$$2HI \longrightarrow I_2 + H_2O$$
$$2KI + 3H_2SO_4 \longrightarrow 2KHSO_4 + SO_2 + I_2 + 2H_2O$$

However, HBr and HI can be prepared by the reaction of bromine and ~~iodine~~ iodide salt with non-oxidizing acid.

$$NaBr + H_3PO_4 \longrightarrow NaH_2PO_4 + HBr$$
$$NaI + H_3PO_4 \longrightarrow NaH_2PO_4 + HI$$

Lab Preparation of Hydrogen Bromide

HBr gas is prepared in the lab by the action of bromine on moist red phosphorous.

$P_4 + 6Br_2 \longrightarrow 4PBr_3$

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

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

Moist HBr gas is dried over anhydrous $CaCl_2$ or P_2O_5. Conc. H_2SO_4 or CaO can't be used for drying.

Lab preparation of Hydrogen Iodide

HI gas is prepared in the lab by the action of water on a mixture of red phosphorous and iodine

$P_4 + 6I_2 \longrightarrow 4PI_3$

$PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI$ | $\times 4$

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

Moist HI gas is dried over anhydrous $CaCl_2$ or P_2O_5. Conc. H_2SO_4 or CaO can't be used for drying.

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Chemical Properties

1. Acidic Nature

Hydrogen halides are soluble in water and their aqueous solution are called hydrohalic acid. HF is hydrofluoric acid, HCl is hydrochloric acid, HBr is hydrobromic acid and HI is hydroiodic acid.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Acidic strength of halogen acid:

$HF < HCl < HBr < HI$

i. Action with Base

$$HCl + NaOH \longrightarrow NaCl + H_2O$$
$$2HCl + Na_2O \longrightarrow 2NaCl + H_2O$$
$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$
$$HCl + NaHCO_3 \longrightarrow NaCl + H_2O + CO_2$$

ii. Action with metal

$$2Na + 2HCl \longrightarrow 2NaCl + H_2$$
$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

iii. They turn blue litmus to red, phenolphthalein from pink to colourless and methyl orange from yellow to orange.

2 Reducing Nature

Hydrogen halides are reducing nature

$HI > HBr > HCl > HF$

HCl reduces MnO_2, $KMnO_4$ and $K_2Cr_2O_7$

- With HCl

$$MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + [O]$$
$$[O] + 2HCl \longrightarrow Cl_2 + H_2O$$
$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

- With $KMnO_4$

$$2KMnO_4 + 6HCl \longrightarrow 2KCl + 2MnCl_2 + 3H_2O + 5[O]$$
$$[O] + 2HCl \longrightarrow H_2O + Cl_2 \quad] \times 5$$
$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 5Cl_2 + 5H_2O$$

- With $K_2Cr_2O_7$

$$K_2Cr_2O_7 + 8HCl \longrightarrow 2KCl + 2CrCl_3 + 4H_2O + 3[O]$$
$$[O] + 2HCl \longrightarrow H_2O + Cl_2 \quad] \times 3$$
$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

HBr and HI react similarly as HCl. HBr and HI can even reduce conc. H_2SO_4 and HNO_3 also.

- With conc. H_2SO_4

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$
$$[O] + 2HBr \longrightarrow H_2O + Br_2$$
$$H_2SO_4 + 2HBr \longrightarrow 2H_2O + SO_2 + Br_2$$

- With conc. HNO_3

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$$

$$[O] + 2HBr \longrightarrow H_2O + Br_2$$

$$2HNO_3 + 2HBr \longrightarrow 2H_2O + 2NO_2 + Br_2$$

HI is a more powerful reducing agent. Hence, it reduces copper sulphate too.

Sulphur

Allotropes of Sulphur

1. Crystalline Sulphur
   i. Rhombic sulphur
   ii. Monoclinic sulphur

2. Amorphous sulphur
   i. Plastic sulphur
   ii. Milk of sulphur
   iii. ~~Co Hodial~~ Colloidal sulphur

Uses of sulphur

It is used to produce sulphuric acid.

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Preparation of H_2S gas by using kipp's apparatus:

Hydrogen sulphide gas is used in the lab for qualitative salt analysis. For this purpose, a small quantity of H_2S is required in frequent analysis. For the intermittent supply of H_2S gas, kipps apparatus is used.

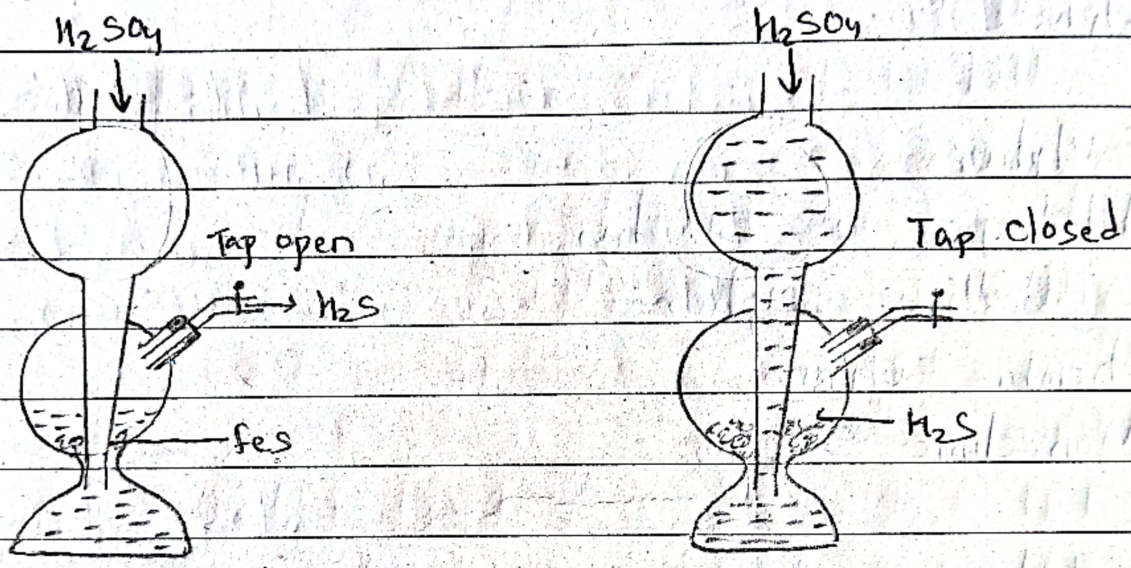

fig: Lab preparation of H_2S using kipp's apparatus

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

kipps apparatus contains three bulbs A, B and C. Upper bulb A has a long stem that reaches the bottom of bulb C. Middle bulb B contains iron sulphide. The apparatus is made air-tight.

Dilute H_2SO_4 is poured from bulb A till the piece of FeS are covered. The acid reacts with FeS and evolves H_2S gas which comes out from the tap when it is opened.

When the tap is closed, the pressure of the gas in bulb B, increases which forces the acid into bulb A. As a result, the contact of FeS and acid breaks. The gas evolves again until the tap is opened again.

Chemical Properties

1. Acidic Nature

The aqueous solution of H_2S is termed hydrosulphuric acid. It is a weak diprotic acid that ionizes ~~the into~~ in two steps:

$$H_2S \rightleftharpoons H^+ + HS^- \quad \text{(Bisulphide ion)}$$
$$HS^- \rightleftharpoons H^+ + S^{--} \quad \text{(sulphide ion)}$$

It reacts with a base to give two types of salt

$$H_2S + NaOH \longrightarrow NaHS \text{ (sodium bisulphide)} + H_2O$$
$$H_2S + NaOH \longrightarrow Na_2S \text{ (sodium sulphide)} + 2H_2O$$

More electropositive metals than hydrogen react with H_2S gas

$$Zn + H_2S \longrightarrow ZnS + H_2$$
$$2Na + H_2S \longrightarrow Na_2S + H_2$$

It reacts with basic oxide to ~~gr~~ give salt

$$CaO + H_2S \longrightarrow \text{~~CaO~~} CaS + H_2O$$
$$MgO + H_2S \longrightarrow MgS + H_2O$$

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2. H_2S as reducing Agent

i. Action with acidified Potassium Permanganate

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

$[O] + H_2S \longrightarrow H_2O + S \;]\times 5$

$2KMnO_4 + 4H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

ii. Action with acidified potassium dichromate

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

$[O] + H_2S \longrightarrow H_2O + S \;]\times 3$

$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2$
$+ 3S$

iii. Action with $FeCl_3$

$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$

iv. Action with halogens

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

$[O] + H_2S \rightarrow H_2O + S$

$Cl_2 + H_2S \longrightarrow HCl + S$

Also,

$Br_2 + H_2S \longrightarrow 2HBr + S$

$I + H_2S \longrightarrow 2HI + S$

v. Action with SO_2

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

H_2S as an analytical reagent

~~Salt analysis involves qva~~

i. H_2S as an analytical reagent for the detection of group II basic radicals:

Group II basic radicals are precipitated in the form of sulphide in an acidic medium.

$$Cu^{++} + H_2S \xrightarrow{HCl} CuS + 2H^+$$
(Black ppt.)

$$Hg^{++} + H_2S \xrightarrow{HCl} HgS + 2H^+$$
(Black ppt.)

$$Pb^{++} + H_2S \xrightarrow{HCl} PbS + 2H^+$$
(Black ppt.)

$$Cd^{++} + H_2S \xrightarrow{HCl} CdS + 2H^+$$
(Yellow ppt)

$$Sn^{++} + H_2S \longrightarrow SnS + 2H^+$$
(Brown ppt)

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ii) H_2S as an analytical reagent for the detection of group III B basic radicals:

Group III B basic radicals are precipitated in the form of sulphide in an alkaline medium.

$$Zn^{++} + H_2S \xrightarrow{NH_4Cl + NH_4OH} ZnS + 2H^+$$
(White ppt)

$$Co^{++} + H_2S \longrightarrow CoS + 2H^+$$

$$Ni^{++} + H_2S \longrightarrow NiS + 2H^+$$
(Black ppt)

$$Mn^{++} + H_2S \longrightarrow MnS + 2H$$

Chemical Properties

1. Acidic Nature

It gets dissolved in water to form sulphurous acid

$$SO_2 + 2H_2O \longrightarrow H_2SO_3$$

Sulphurous acid is diprotic acid and ionizes in two steps:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$ (Bisulphite ion)

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$$ (sulphite ion)

It reacts with base to give two types of salt

$$H_2SO_3 + NaOH \longrightarrow NaHSO_3 + H_2O$$ (sodium bisulphate)

$$NaHSO_3 + NaOH \longrightarrow Na_2SO_3 + H_2O$$ (sodium sulphite)

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2. Reducing Nature

i. Action with halogens.

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

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

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

ii. Action with acidified Potassium Permanganate

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

$[O] + SO_2 + H_2O \longrightarrow H_2SO_4] \times 5$

$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

iii. Action with acidified potassium dichromate

$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[$

$[O] + SO_2 + H_2O \longrightarrow H_2SO_4] \times 3$

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2$

iv. Action with ferric sulphate

$Fe_2(SO_4)_3 + SO_2 + 2H_2O \longrightarrow 2H_2SO_4 + 2FeSO_4$

v. Action with potassium iodate

$2KIO_3 + 5SO_2 + 4H_2O \longrightarrow K_2SO_4 + 4H_2SO_4 + I_2$

3. Oxidizing Nature

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

$SO_2 + 2Mg \longrightarrow 2MgO + S$

$SO_2 + 2Fe \longrightarrow 2FeO + S$

$SO_2 + 4HI \longrightarrow 2H_2O + 2I_2 + S$

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Bleaching Nature

1. Bleaching by reduction:

In presence of moisture, sulphur dioxide gas bleaches vegetable colouring matter.

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$

Colouring substance + $[H] \longrightarrow$ colourless substance

ii. Bleaching by addition reaction

Colored compound + $SO_2 \longrightarrow$ Colourless compound

Uses of SO_2

i. Manufacture of sulphuric acid

ii. As bleaching agent

iii. As a disinfectant, fungicides and preservation of ~~food~~ food.

iv. As antichlor (removing chlorine)

Sulphuric Acid

Manufacture of Sulphuric acid by Contact Process

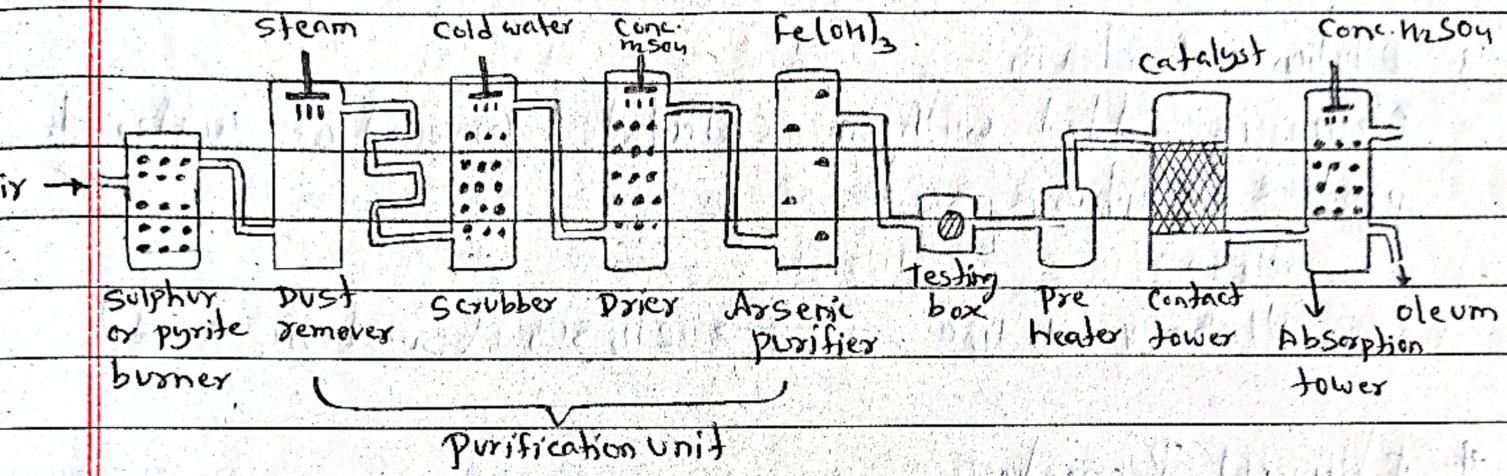

Fig: Manufacture of Sulphuric Acid by Contact Process

Principle:

1. **Production of sulphur dioxide**

Sulphur dioxide gas can be prepared either by burning sulphur or by the roasting of iron pyrite.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 \text{ (iron pyrite)} + 11\,O_2 \longrightarrow 2Fe_2O_3 + 8\,SO_2$$

2. **Oxidation of sulphur dioxide**

Sulphur dioxide is oxidized to sulphur trioxide in presence of vanadium pentoxide as a catalyst at about 450°c and 2 atm pressure.

$$2\,SO_2 + O_2 \underset{2\,atm}{\overset{V_2O_5,\ 450^\circ c}{\rightleftharpoons}} 2\,SO_3 + 45\,kcal$$

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3. Absorption of sulphur trioxide

Sulphur trioxide is absorbed by conc. sulphuric acid to form pyrosulphuric acid called oleum.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \text{ (oleum)}$$

4. Dilution of oleum

Oleum is added with a calculated amount of water to produce sulphuric acid.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4 \text{ (sulphuric acid)}$$

Chemical Properties

1. Acidic Nature

It is strong diprotic acid and ionizes in two steps. It is soluble in water, turns blue litmus red and has sour taste.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^- \text{ (Bisulphate ion)}$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^- \text{ (sulphate ion)}$$

It gives two types of salt with base

$$H_2SO_4 + NaOH \longrightarrow NaHSO_4 \text{ (sodium bisulphate)} + H_2O$$
$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 \text{ (Sodium sulphate)} + 2H_2O$$

It neutralizes alkalis, basic oxides to form salt and water. It evolves CO_2 from carbonates and bicarbonates and SO_2 from sulphites and bisulphites.

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2CO_2 + H_2O$

$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$

$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O$

$2NaHSO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2SO_2 + H_2O$

Dilute sulphuric acid gives hydrogen gas with active metal

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$

2. Concentrated sulphuric acid as an oxidizing agent

i. Action with Metal

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + SO_2 + 2H_2O$

ii. Action with non-metals (C, P, S)

- With carbon

$H_2SO_4 \longrightarrow SO_2 + H_2O + [O] \times 2$

$2[O] + C \longrightarrow CO_2$

$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

- With Phosphorous

$H_2SO_4 \longrightarrow SO_2 + H_2O + [O] \times 10$

$10[O] + P_4 + 6H_2O \longrightarrow 4H_3PO_4$

$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$

- With sulphur

$H_2SO_4 \longrightarrow SO_2 + H_2O + [O] \times 2$

$2[O] + S \longrightarrow SO_2$

$S + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$

iii. Action with reducing agents.

- With H_2S

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

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

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

- With HI

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

$[O] + 2HI \longrightarrow H_2O + I_2$

$H_2SO_4 + HI \longrightarrow 2H_2O + SO_2 + I_2$

3. Concentrated sulphuric acid as dehydrating agent

i. It removes water of crystallization of hydrates salts

$CuSO_4.5H_2O + H_2SO_4 \longrightarrow CuSO_4 + H_2SO_4.5H_2O$

ii. It removes water from glucose, fructose or ~~Sucro~~ sucrose and form carbon

~~C_6H_2O~~

$C_6H_{12}O_6$ (glucose) $+ H_2SO_4$ (conc.) $\longrightarrow 12C + H_2SO_4.11H_2O$

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Sodium thiosulphate or Hypo ($Na_2S_2O_3$)

- Uses

i. Estimation of iodine
ii. Photography
iii. Antichlor in bleaching industry to remove chlorine

Carbon

Carbon is located in group 14 or IVA and 2nd period in the modern periodic table. It is a p-block element. Its valency is 4.

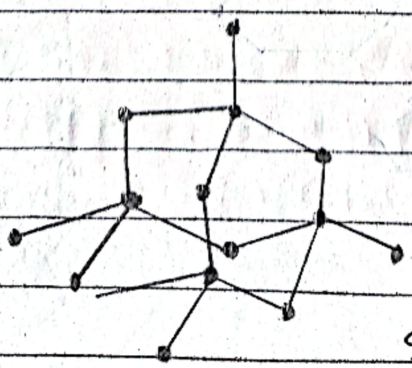
Allotropes of carbon

A. Crystalline forms

1. Diamond

It is the purest form of carbon and it is the hardest compound known.

In diamond, each carbon atom is tetrahedrally linked wi four surroundings carbon atoms. The bond angle is 109.5° and c-c bond length is 1.54°A. Carbon atoms are linked with four other carbon atoms through a strong covalent bond which makes the diamond extremely hard with a hig melting point.



Structure of diamond

Properties

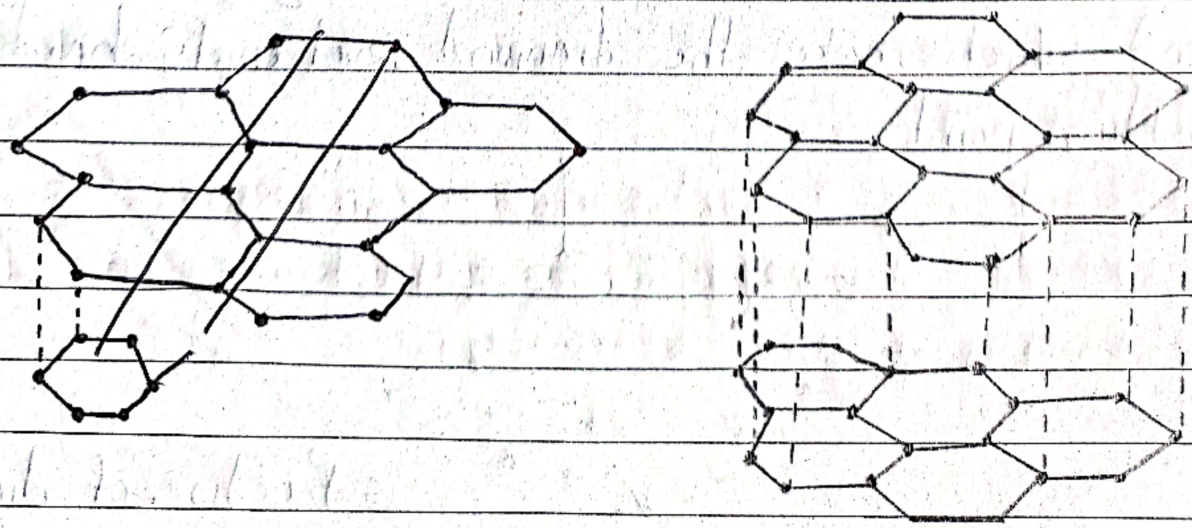
i. It is the hardest substance known with a high melting points.
ii. It is transparent to X-rays.
iii. It is very unreactive
iv. It is a bad conductor of electricity
v. It has a high density and a high refractive index

ii. Graphite

It is known as black lead. It is the most stable allotrope of carbon.

Structure of graphite

In graphite, each carbon atom is linked with three other carbon atoms directly in the same plane to give hexagonal rings. These rings are arranged to form co-planar sheets or layers. These layers are held together by vander Waals force of attraction. The bond angle is 120° and C-C bond length is 1.41 A°



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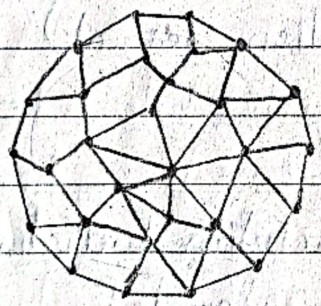
Properties
i) It is greyish black solid
ii) It is soft and slippery in nature
iii) It is a good conductor of electricity
iv. It is resistance towards almost all chemical reagents.

iii. Buckminster Fullerence
It is the latest discovered allotrope of carbon. It is ~~genera~~ generally consists of a closed cage-like structure as Soccer ball. It consists of 60 carbon atoms as 20 hexagons and 12 pentagons.



Structure of fullerence

Properties
Soluble in organic solvent Easily

Amorphous form of carbon
i. Coal
ii. Coke
iii. Lamp-black
iv. Gas-Carbon

v. Charcoal

Carbon Monoxide

Chemical Properties

1. Reducing Nature

i. It reduces metallic oxide into free metal.

$ZnO + CO \longrightarrow Zn + CO_2$

$PbO + CO \longrightarrow Pb + CO_2$

ii. It reduces Tollens reagent (ammoniacal silver) into metallic silver.

$2[Ag(NH_3)_2]OH$ (Tollens reagent) $+ CO \rightarrow 2Ag$ (silver mirror) $+ 4NH_2O + CO_2 + NH_3$

iii. It reduces Fehling's solution (alkaline solution of $CuSO_4$) into red ppt. of cuprous oxide.

$2Cu(OH)_2$ (Fehling's solution) $+ CO \rightarrow Cu_2O$ (Red ppt.) $+ 2H_2O + CO_2$

iv. It reduces steam at high temperatures

$CO_2 + H_2O \longrightarrow CO_2 + H_2$

v. It reduces I_2O_5 into I_2

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$

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2. Reaction with metals

$4CO + Ni \longrightarrow Ni(CO)_4$ (Nickel tetracarbonyl)

$5CO + Fe \longrightarrow Fe(CO)_5$ (Iron pentacarbonyl)

$8CO + 2Co \longrightarrow Co_2(CO)_8$ (Dicobalt octacarbonyl)

3. Action with Non-metals

$2CO + O_2 \xrightarrow{\Delta} 2CO_2$

$CO + 2H_2 \xrightarrow{\Delta} CH_3OH$ (Methyl alcohol)

$CO + Cl_2 \xrightarrow{\text{sunlight}} COCl_2$ (Phosgene)

$Co + S \xrightarrow{\Delta} COS$ (Carbonyl sulphide)

Uses of CO

i. As a fuel in water gas

ii. In the extraction of metals

iii. To prepare metal Carbonyl

iv. As a ~~reag~~ reducing reagent

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Phosphorous

Allotropes of Phosphorus

There are many allotropic forms of phosphorous. Among them, white or yellow and red phosphorous are most important.

1. Yellow or White Phosphorus

This is generally obtained by either electro-thermal process or retort process.

2. Red Phosphorus

It is obtained by heating white phosphorous at 240 - 250°C in presence of an inert atmosphere ~~at 240 - 250°C~~ and little iodine.

$$\text{White P} \xrightarrow[\text{iodine}]{CO_2 \text{ or } N_2,\ 240^\circ C} \text{Red P} + 2.73 \text{ kcal}$$

3. Black Phosphorus
4. Violet Phosphorus
5. Scarlet Phosphorus

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Phosphine

Laboratory preparation of Phosphine gas

Theory:

When white phosphorous is heated with caustic soda, Phosphine gas is formed.

P_4 (white) + $3NaOH + 3H_2O \longrightarrow PH_3$ (Phosphine) + $3NaH_2PO_2$ (sodium hypophosphite)

Chemical Properties

1. Basic Nature

Phosphine is less basic than ammonia because its lone pair of electron is less available for donation.

$PH_3 + HCl \longrightarrow PH_4Cl$ (Phosphonium chloride)

$PH_3 + H_2O \rightleftharpoons PH_4^+$ (phosphonium ion) $+ OH^-$

2. Action with Cl_2

$PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$

$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

3. Phosphine as a reducing agent

With $CuSO_4$

$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2$ (black ppt.) $+ 3H_2SO_4$

With $HgCl_2$

$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2$ (red ppt.) $+ 6HCl$

4. Action with oxygen

$$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$$

$$PH_3 + 2O_2 \longrightarrow H_3PO_3$$

Uses of Phosphine

i. As reducing agent

ii. To prepare PCl_3, PCl_5, P_2O_5 etc.