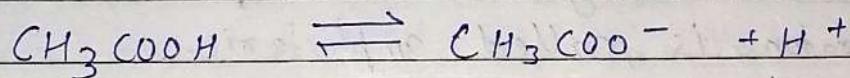
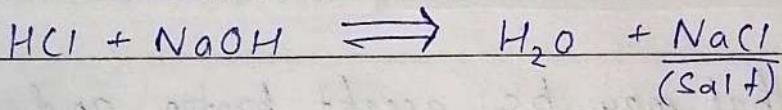
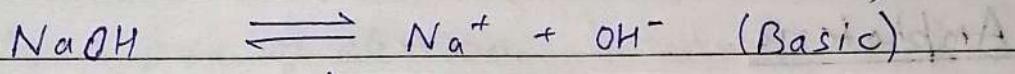
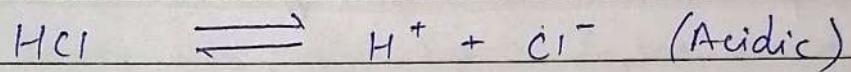


CH.2 → Acidity, Basicity, pH and Buffers.

Acid :-1. Arohenius theory :- (1887)

Acid are substances which on dissolution in water provide protons (H^+ , hydrogen ions) and Base are substances which on dissolving in water yields hydroxyl ions (OH^-).

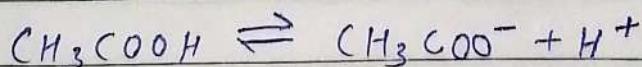
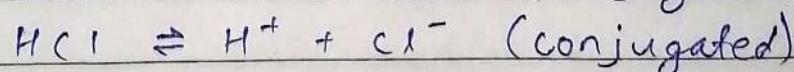
Example :-2. Bronsted - Lowry Theory

According to this theory an acid is a substance that donate a proton and base is a substance that accept a proton.

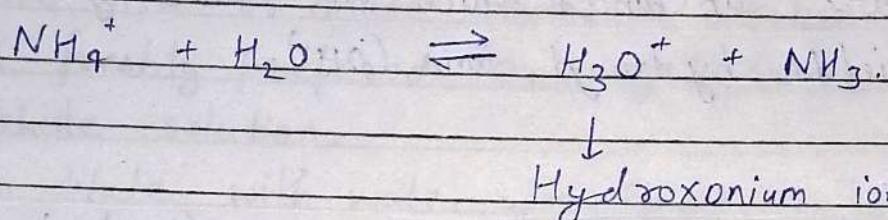
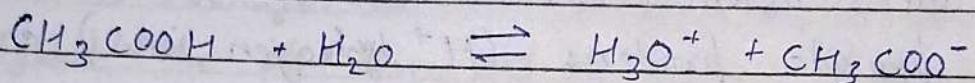
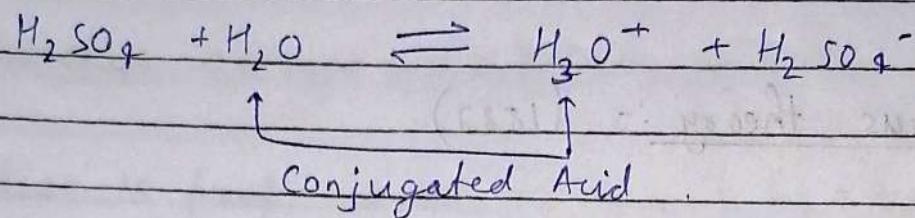
i.e → Acid is a proton donor.

Base is a proton acceptor.

Example :> Acid = $H^+ + \text{Base}$ (conjugated)



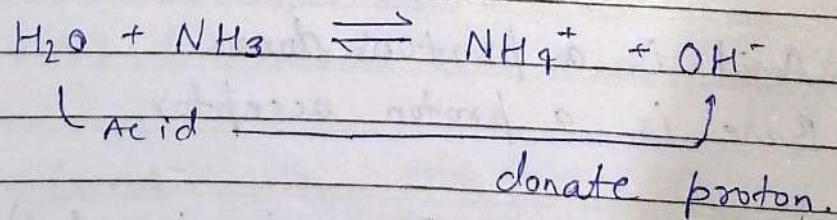
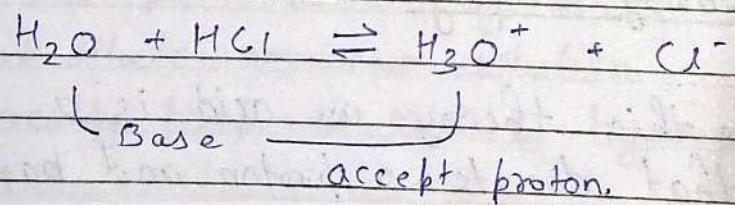
Ex :- Brønsted Base :- NH_3 , OH^- , Cl^-



Amphoteric.

A substance that may be accept proton and donate proton is called amphoteric.

Ex :- H_2O .



③ Lewis Acid - Base :-

An acid is an electron pair acceptor and a base is an electron pair donor. All compounds or ions containing unshared electron pairs are Lewis bases.

e.g. → hydroxyl ion, amines, ammonia, ethers, alcohol etc.

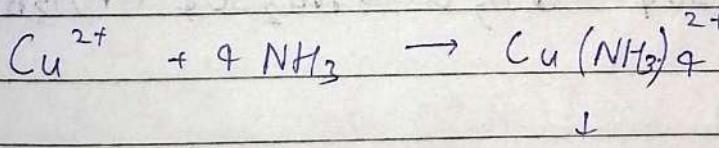
All Brønsted acids are electron pair acceptor and are also Lewis acids.

All Brønsted bases are also Lewis bases since they donate a pair of electrons.

Examples:-

BF_3 , ZnCl_2 , AlCl_3 and SO_3 accept pair of electrons from a donor species.

Ag^+ , Fe^{2+} , Na^+ and Zn^{2+} accept electron pairs from donor species (e.g. NH_3 , H_2O , Cl^- , CN^-)



Cupra-ammonium ion.

Boric Acid.

H_3BO_3 : Mol. weight = 61.83

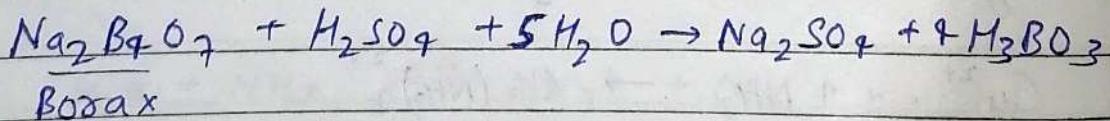
- Boric acid, occurs in nature as the mineral sassolite, contains not less than 95.5 percent and not more than the equivalent of 100.5% of H_3BO_3 , calculated with reference to the dried substance.

Preparation of Boric Acid (H_3BO_3)

① From Natural Sources :

It comes out with jets of steam, called soffioni, from the ground in certain parts of Tuscany. The condensed steam is concentrated by its own heat, cooled and crystallized boric acid is separated.

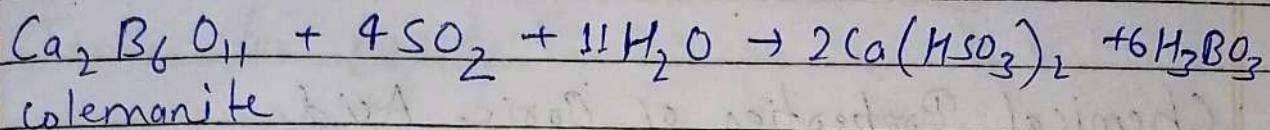
② By Decomposition of Borax :



- A mixture of concentrated sulphuric acid and water is added to a hot aqueous solution of borax. The hot solution is filtered, cooled and the crystallised boric acid is filtered off.

③ Form Colemanite :

By passing sulphur dioxide through colemanite suspended in water, crystals of boric acid separate out on cooling.



Physical Characters of Boric Acid:

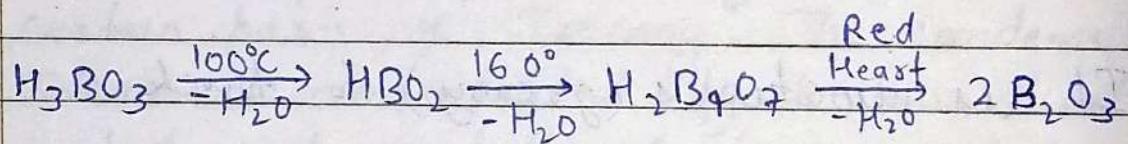
- Boric acid occurs as odourless, colourless, transparent plates, crystals or white granules or powder; some what pearly lustrous scales.
- It isunctions (greasy) to touch.
- Melting point 171°C .
- Sweetish in taste.
- It volatiled with steam; pH 5.1.
- Soluble 1 in 20 of water; 16 of alcohol and 4 of glycerol.
- Solubility in water is increased by HCl, citric, tartaric acids or by heat.

- Most solutions of boric acid contains only small amounts of tetraboric acid.
- Boric acid is stored in well - closed containers.

Chemical Properties of Boric Acid.

- ① It is a weak acid and in solution gives a slightly red colour with litmus.
- ② Heating of boric acid to certain temperatures produces various dehydration products:

For ex:-



Ortho Basic Acid	Meta Basic Acid	Tetra Basic acid	Red Anhydride.
------------------------	-----------------------	------------------------	-------------------

- ③ It changes trimeric paper brown which turns blackish when dipped in sodium hydroxide solution.

- ④ A mixture of ethyl alcohol and boric acid burns with a green flame due to formation of ethyl borate.

(3) The reaction of boric acid with equimolar amounts of glycerin at 140° - 150° produces a compound known as Boroglycerin glycerite. ($C_3H_5BO_3$) which is used as a suppository base.

Tests for purity:

- Test for arsenic; lead; heavy metals; sulphate; alcohol insoluble substances; acidity; clarity and colour of solution; organic matter.

For determining sulphate, an acidified solution is boiled and filtered. The filtrate complies with the limit test for sulphates.

Tests for Identification:

- ① Boric acid (0.1 g) is dissolved in methanol (5 ml) by heating to which a few drops of sulphuric acid have been added. On ignition the solution the flame has a green colour border.
- ② An aqueous solution of boric acid is acidic in nature (pH: between 3.8 and 4.8).

Incompatibility: Alkali carbonates and hydroxides.

Assay of Boric Acid:-

Boric Acid is a very weak acid and cannot be titrated accurately with a standard solution of a strong alkali if glycerol is first added to the boric acid before starting the titration.

① (I.P.) :- Accurately weighed sample (2g) is dissolved in a mixture of water (50 ml) and glycerin (100ml), previously neutralised to phenolphthalein solution. The solution is titrated with 1 N sodium hydroxide, using phenolphthalein solution as indicator. Each ml of 1N sodium hydroxide is equivalent to 0.06183 of H_3BO_3 .

② (B.P.):- An aqueous solution of boric acid (1g) and mannitol (10g) is titrated with 1N sodium hydroxide, using phenolphthalein as indicator. Sodium metaborate is formed by neutralizing one equivalent of sodium equivalent of sodium hydroxide. Each ml of 1N sodium hydroxide is equivalent to 61.8 mg % of H_3BO_3 .

Uses of Boric Acid

- Boric acid possesses weak bacteriostatic, fungistatic, astringent and antiseptic properties.
- It is externally used as a buffer and antimicrobial in eye-drops.
- An insecticide for cockroaches and black carpet beetles.
- It is used as mouth-washes, skin lotions for local anti-infective action; as douches for irrigating the bladder and vagina; in ointment for emollient and antiseptic action.
- Used in dusting powder due to its smooth-unctionous touch
- Boric acid is used in buffer systems such as ephinephrine bitartrate, ophthalmic solution; Aluminium acetate and Aluminium subacetate solutions.

Hydrochloric Acid (HCl)

HCl ; Mol. weight = 36.46

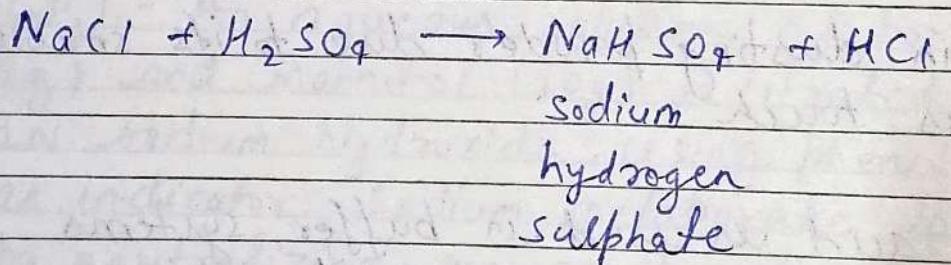
Synonyms : Measuring Muriatic acid ; Spirit of salt.

Hydrochloric acid is a solution of hydrogen chloride gas (HCl) in water.

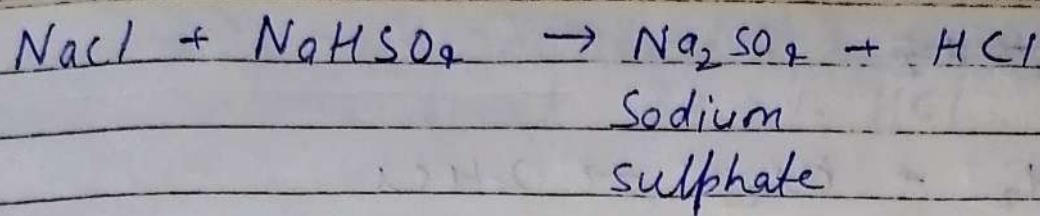
Preparation

1. From Sodium Chloride:

Hydrochloric acid is manufactured by treating concentrated sulphuric acid with sodium chloride (Leblanc Soda Process)



The pasty mass of sodium hydrogen sulphate is mixed with more quantity of sodium chloride and heated to redness to yield a further supply of hydrogen chloride leaving behind anhydrous sodium sulphate (salt cake).



Hydrochloric acid gas is collected in a chamber where cold water is spread over the gas. The dilute acid is obtained at the bottom.

The acid so obtained is spread down the tower to absorb more HCl gas for getting concentrated hydrochloric acid.

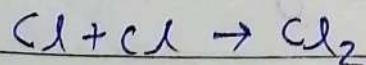
2. By Synthesis :

Large amount of hydrogen and chlorine gases are obtained as by-products by electrolysis of sodium chloride solution during the manufacture of caustic soda.

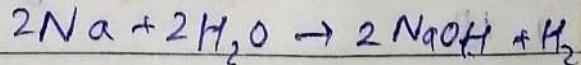
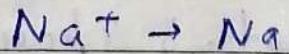
These gases are dried and then combined to produce hydrogen chloride gas. The gas cooled and water is spread over the gas. The solution of hydrochloric acid flows into storage tank.

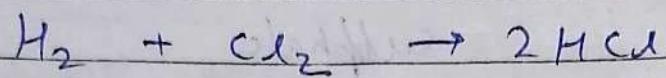
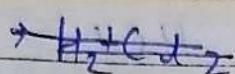


At the Anode



At the cathode





Physical Characters of HCl

- Hydrogen chloride is a colourless gas with an acid irritating odour and an acid taste.
- It is about 25% heavier than air.
- The gas can be liquified under pressure.
- It is very soluble in water.
- A 0.1 N aqueous solution is ionized at 18°C and conducts electricity.
- Muriatic acid is a technical grade of hydrochloric acid containing 35 to 38% of HCl and a number of impurities including chloride, arsenous and sulphurous acids and iron.
- Hydrochloric acid is a clear colourless fuming aqueous solution of hydrogen chloride with a pungent odour and sour taste; specific gravity is about 1.18.

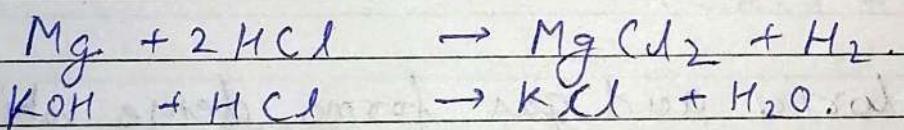
Reagent grade concentrated hydrochloric acid contains about 38.0% HCl.

Storage

Hydrochloric acid should be kept in a stopped container of glass or other inert material and stored at a temperature not exceeding 30°.

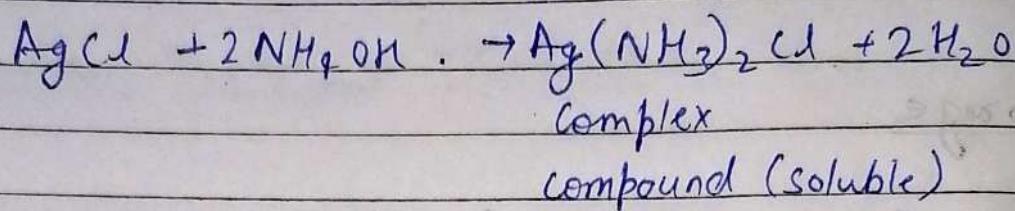
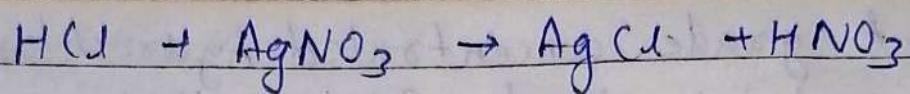
Chemical Properties of HCl

- It turns moist blue litmus to red.
- It reacts with metals and their salts like oxides, hydroxides and carbonates to form the chlorides of the metals.

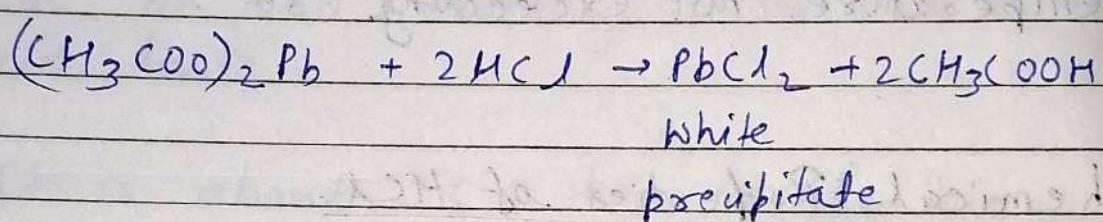


The hydrogen in the hydrochloric acid is displaced by metals yielding hydrogen gas.

With silver nitrate, hydrochloric acid gives a white precipitate soluble in ammonium hydroxide and insoluble in nitric acid.



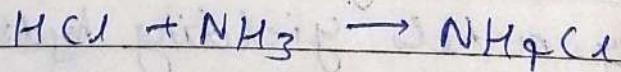
with lead acetate, it gives a white precipitate soluble in hot water.



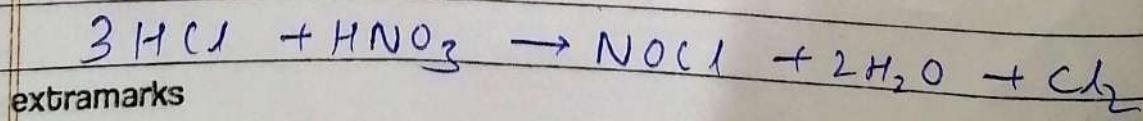
3. Fluorine decomposes hydrochloric acid to form chloride.



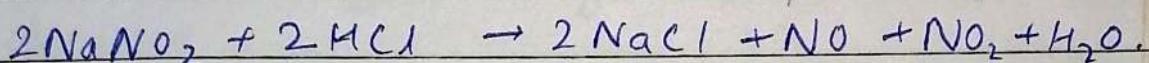
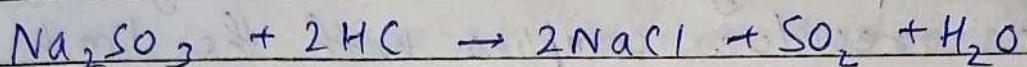
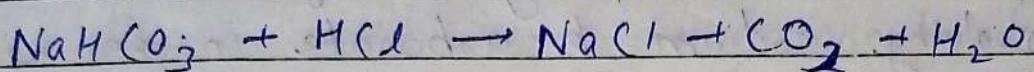
4. Hydrochloric acid gas forms dense white fumes of ammonium chloride with ammonia



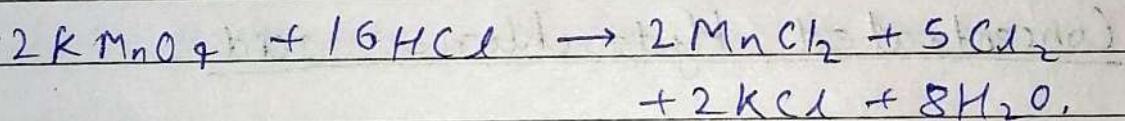
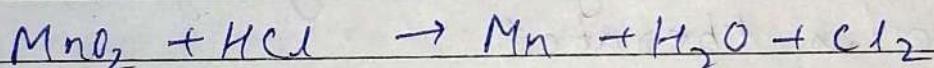
5. A mixture of concentrated hydrochloric acid (3 parts) and concentrated nitric acid (1 part) is called aqua regia which is used for dissolving noble metals, gold and platinum as their chlorides.



⑥ Hydrochloric acid decomposes salts of weaker acids such as carbonates, bicarbonates, sulphides, sulphites, nitrates and thiosulphates.



Hydrochloric acid gives chlorine when warmed with oxidizing agents, such as manganese dioxide or potassium permanganate.



Tests for purity

Weight per ml; tests for free chlorine; bromide; iodide, sulphate, heavy metals; arsenic, lead, oxidizable substances, clarity and colour and non-volatile matter.

For determining bromide and iodide, chloroform and chlorinated lime solution are added with constant shaking. The chloroform layer does not become brown or violet.

- The presence of sulphite is found out by treating the acid with barium chloride solution and 0.001 N iodine.
- Sulphate as an impurity is detected by dissolving sodium bicarbonate in the acid and evaporating the solution to dryness. The residue complies with the limit test for sulphates.

Incompatibility:-

The chloride ion is precipitated with silver mercurous mercury and lead salts. It is oxidized by oxidizing agents, chlorine is liberated.

Concentrated Hydrochloric acid.

- Concentrated hydrochloric acid is an aqueous solution of hydrogen chloride in water. It contains not less than 35.1% w/w and not more than 38.1% w/w of HCl.

Tests for Identification

1. When neutralized and diluted, it gives the reactions of chlorides.

2. When added to potassium permanganate, chlorine is evolved.

Assay :

Hydrochloric acid is a strong monoprotic acid which can be assayed conveniently by titrating against sodium hydroxide solution using methyl red as an indicator.

Accurately weighed 4g is added to 40ml of water in a stoppered flask and titrated with 1N sodium hydroxide using methyl orange. Each ml of 1N sodium hydroxide is equivalent to 0.3646g of HCl.



Uses :-

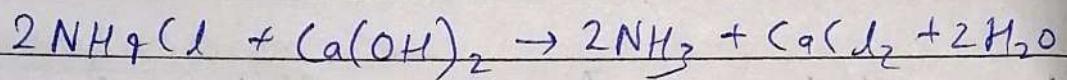
- Used as a pharmaceutical aid or as acidifying agent.
- In dilute form it is used for the treatment of achlorhydria (absence of HCl from the stomach juice).
- It is given intravenously in the management of metabolic alkalosis (increase in alkalinity of the blood).

Ammonium Hydroxide

NH_4OH ; Mol. Weight = 35.0

Preparation :-

1. In laboratory ammonia is prepared by heating ammonium chloride with calcium hydroxide.

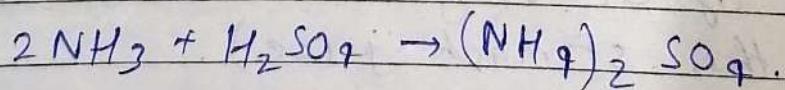


2. Commercially ammonia is obtained from the 'ammonical liquor' which is a big by-product during the production of coal-gas.

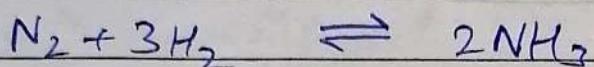
Ammonical gas is obtained by passing the hot gas through cooling pipes. Lime water is added to the ammonical liquor and steam is passed through the mixture.

The mixture of steam and ammonia evolved is bubbled through sulphuric acid.

From it, ammonium sulphate is produced which is the most important commercial ammonium salt and used as fertiliser.

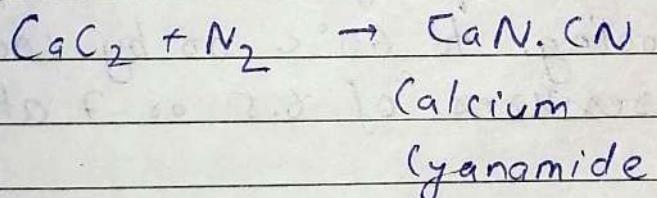


③ Ammonia is also synthesized by Haber's process in which nitrogen and hydrogen are combined in the presence of a catalyst (iron and molybdenum) at 450° - 500°C at 200-900 atmospheric pressure.

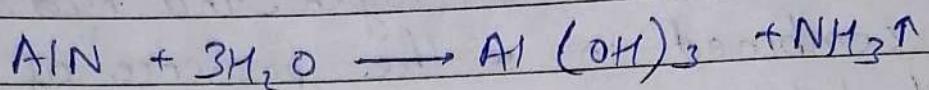
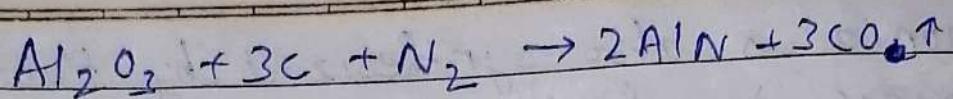


The reaction is reversible and exothermic. The ammonia produced is stored in liquid form in metal cylinders or absorbed in water, or converted into ammonium salts by combination with acids.

④ Hydrolysis of cyanamide with super heated steam gives ammonia. Atmospheric nitrogen is passed over calcium carbide and heated to a high temperature in an electric furnace to yield calcium cyanamide which is used as a fertilizer.

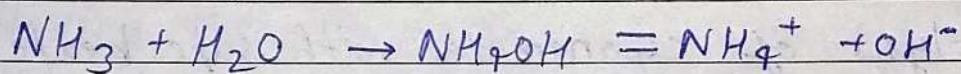


⑤ Ammonia is also obtained as a by-product in the purification of bauxite (Serpel's process). Bauxite and coke are heated in a current of nitrogen to form aluminium nitride which is hydrolyzed with water.



Physical Characters:

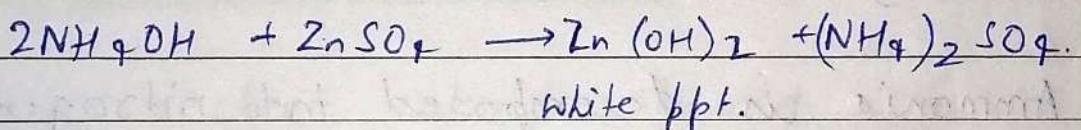
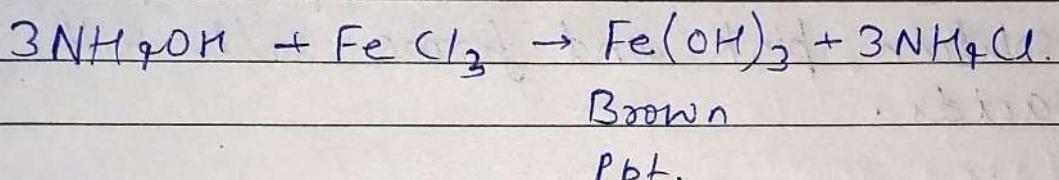
- Ammonia is a colourless gas; very pungent odour; lighter than air; specific gravity is 0.596; extremely soluble in water. One volume of water dissolves 1300 volumes of ammonia at 0°C and 760 mm to form ammonium hydroxide which is a base.



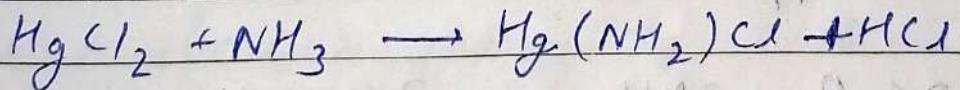
- Mixture of ammonia and air explode when ignited under favourable conditions.
- The gas may be liquefied at atmospheric pressure by cooling to 60°C or by cooling to 10°C at pressures of 6.5 or 7 atmospheres.
- Liquid ammonia is a good solvent and ionizing medium.

Chemical Properties:

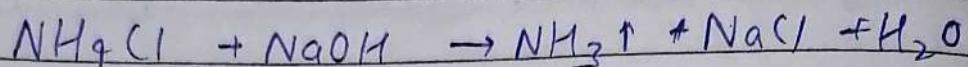
Ammonia molecule possesses an unshared pair of electrons, therefore, it acts as a ligand in forming soluble complex ion with many metal cations, e.g. Cu, Ag, Zn, Cd, Cr, Ni, Co, Mn and Pt. The hydroxides or insoluble salts of these metals dissolve in ammonia solution. It reacts with certain metallic salts and precipitates hydroxides of the metals.



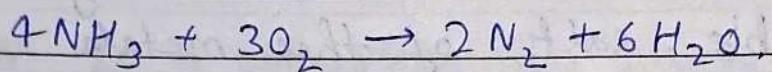
- Ammonia forms ammonia-basic salts by ammonolysis when reacts with mercuric chloride.



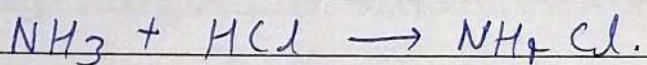
- Salt of ammonia reacts as acid in the presence of bases. Depending upon the particular salt, the pH of aqueous solutions of ammonia compounds will range from neutral to acidic.



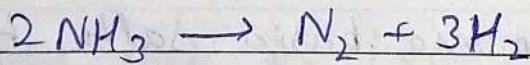
- Ammonia is burnt in an atmosphere of oxygen :



- Ammonia is a typical weak base. It turns red litmus blue, phenolphthalein solution pink and forms salts with acids.



- Ammonia is decomposed into nitrogen and hydrogen at red heat.



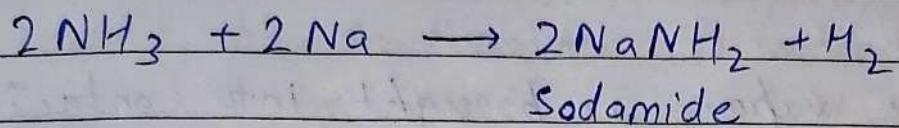
- Ammonia is oxidized when passed over heated copper oxide.



- Both chlorine and bromine oxidise ammonia to give nitrogen.



- When ammonia is passed over heated sodium or potassium at 300°C , amides are produced.



- Liquid ammonia dissolves alkali and alkaline earth metals to form blue solutions which decomposes slowly in the presence of impurities, yielding hydrogen and amide of the metal,
e.g. NaNH_2 .

Strong Ammonia Solution

It is a clear colourless liquid with a strongly pungent characteristic odour, containing 27 to 30% w/w of ammonia. It is not quite saturated with the gas at ordinary temperatures. The most concentrated commercial solution contains about 35% of NH_3 and has a specific gravity of 0.880. It is stored at a temperature not exceeding 20° in airtight containers.

Test for Identification

1. Strongly alkaline, even when freely diluted with water.
2. When the vapour is brought into contact with gaseous hydrochloric acid; dense white fumes are produced.

Test for purity:

Weight per ml ; tests for arsenic; heavy metals; pyridine and homologous; tarry matter; non-volatile matter.

Assay:-

Strong ammonia solution is assayed via residual titration. The solution (2g.) is added to 1M hydrochloric acid (50 ml), taking precautions during the addition to avoid loss of ammonia and the excess of acid titrated with 1M sodium hydroxide using methyl red solution as indicator. Each ml of 1M hydrochloric acid is equivalent to 17.03 mg of NH_3 .

Dilute Ammonia Solution

It is prepared by diluting strong Ammonia solution with freshly boiled and cooled purified water. It contains 9.5 to 10.5 l. of NH_3 ; stored at a temperature not exceeding 20°C in well closed containers.

Uses :-

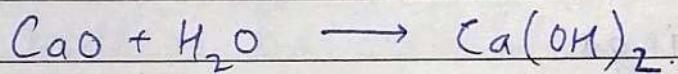
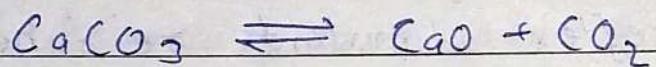
Dilute solutions of ammonia have been used as reflex stimulants, ~~as~~ subfacients and counter-irritants and to neutralize insect stings.

- Strong ammonia solution is used in the preparation of Aromatic ammonia spirit and commercial ammonical silver nitrate solution. Dilute ammonia solution may be used as reflex stimulant in fainted persons.
- It is also used in the manufacture of nitric acid; sodium bicarbonate and ammonium salts of acids, Aromatic spirit of ammonia and strong ammonium acetate solution.
- Ingestion of strong solutions of ammonia causes severe pain in the mouth, throat and gastrointestinal tract, with cough, vomiting and shock.

CALCIUM HYDROXIDE (SLAKED LIME)

Ca(OH)_2 , Mol. weight = 74.09

Calcium hydroxide contains not less than 90% of Ca(OH)_2 . It is maintained manufactured by spraying water on to a quicklime which is itself is prepared by heating limestone. The lumps of quicklime break into powder and heat is evolved. This process is known as slaking.



Water is absorbed by the oxide with the evolution of excess of heat; swelling of CaO lumps and finally disintegration into a fine powder take place.

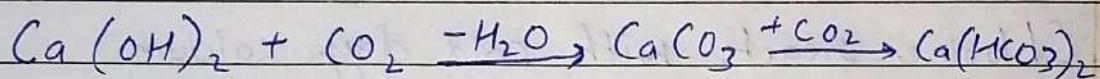
Physical Characters:

Calcium hydroxide occurs as crystals or soft, odourless, granules or powder with slightly bitter alkaline taste. It is almost entirely soluble in water (1 in 600); soluble in aqueous solution of glycerol and sugars. The aqueous solution is alkaline to phenolphthalein and readily absorbs CO₂ from air forming CaCO_3 .

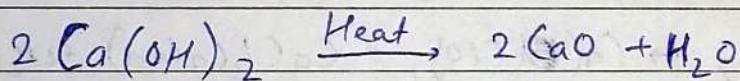
- Solubility of $\text{Ca}(\text{OH})_2$ diminishes with increasing temperature.
- It is preserved in air tight container.

Chemical Properties :-

1. Calcium hydroxide absorbs carbon dioxide from air forming calcium carbonate. In presence of excess of CO_2 , soluble calcium bicarbonate is formed.

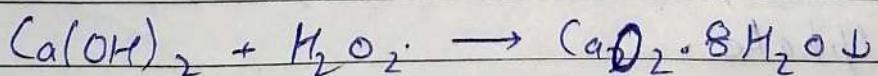


2. Calcium Hydroxide loses water when ignited forming calcium oxide.

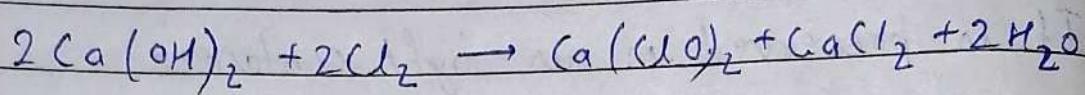


When calcium hydroxide is mixed with 3 to 4 times its weight of water, the suspension is called Milk of lime.

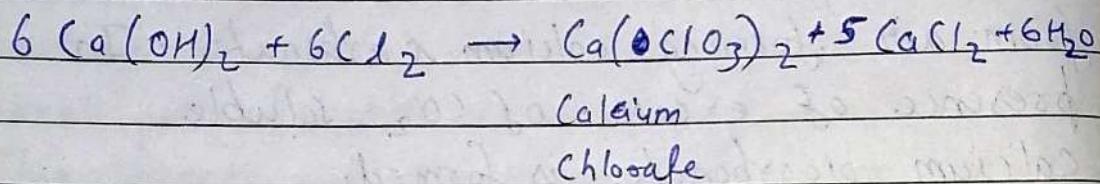
3. When H_2O_2 is added to a solution of calcium hydroxide, calcium peroxide is precipitated.



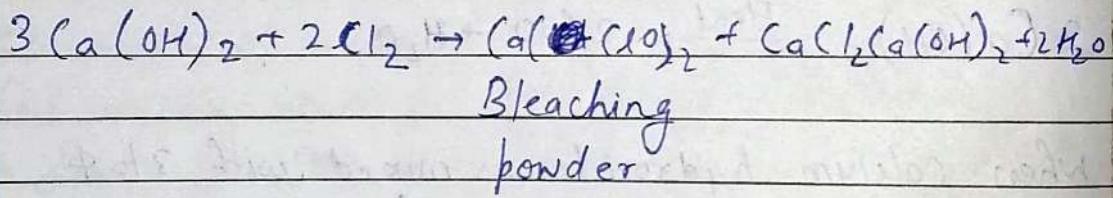
4. Chlorine reacts with cold Milk of lime to form calcium hypochlorite.



With hot Milk of lime chlorine yields calcium chlorate.



Chlorine reacts with cold dry calcium hydroxide to form a mixture of calcium hypochlorite and basic calcium chloride (bleaching powder).



Test for purity:

Tests for aluminium, iron, phosphate, and matter insoluble in hydrochloric acid; heavy metals; arsenic; lead; chloride; and sulphate.

Test for Identification :

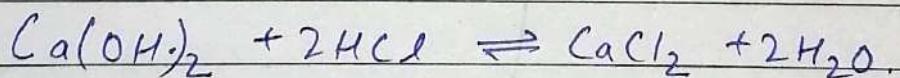
A solution in acetic acid gives the reactions of calcium.

Assay :

Calcium hydroxide solutions are basic, pH 12.3, and are neutralized by acids.

- i.) Accurately weighed sample (3g) is shaken with alcohol (10 ml),
- ii) 10.1. solution of sucrose (490 ml) is added.
- iii) The mixture is shaken vigorously for 5 minutes and then at frequent intervals during four hours.
- iv) The solution (250 ml) is filtered off and titrated with 1N HCl, using phenolphthalein solution as indicator.

Each ml of 1N HCl is equivalent to 0.03705 g. of $\text{Ca}(\text{OH})_2$.



Calcium Hydroxide Solution

It contains not less than 0.15 per cent w/v of $\text{Ca}(\text{OH})_2$, containing in each 100 ml, not less than 140 mg of $\text{Ca}(\text{OH})_2$.

Uses:-

1. Calcium hydroxide is internally used as an antacid; as lime water in inflate infantile diarrhoea and vomiting (astringent).
2. In skin lotions, ~~and oily~~ soaps, dentistry, as pesticides, as egg preservative.
3. Calcium is used medicinally as a fluid electrolyte and a topical astringent.

Sodium Hydroxide (caustic Soda)

Chemical formula: NaOH ; Mol. weight: 40.

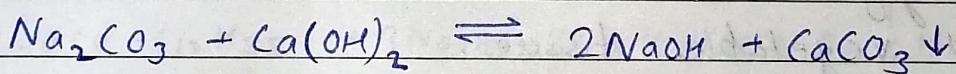
Standard :-

Contains not less than 97.0 percent of total alkali calculated as NaOH and not more than 2 S.I. of Na_2CO_3 .

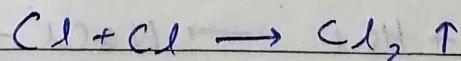
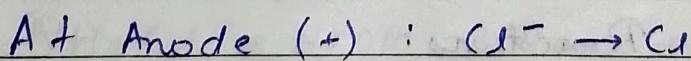
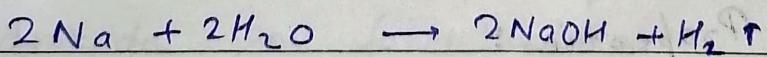
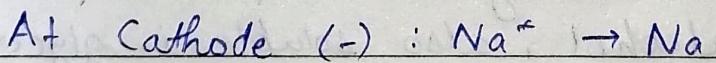
Preparation :

- When milk of lime is added to hot Sodium carbonate solution (20%), sodium carbonate solution (20%), sodium hydroxide and precipitate of calcium carbonate are obtained.

The reaction is reversible.



- Electrolysis of sodium chloride (NaCl)



Electrolytic cell

↓

Mercury diaphragm cell → Caster - Kellner cell

Cathode made of mercury.

Anode made of graphite.

NaCl solution is also known as Brine solution.

* Physical Character:

Day sodium hydroxide is very deliquescent, white sticks, pellets, spherical particles, masses or scales.

Melting point → 318°C.

Strongly alkaline and corrosive to animal and vegetable tissue.

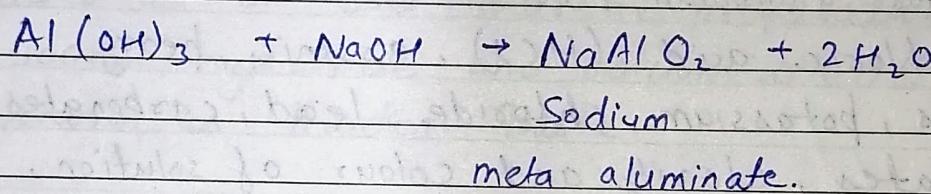
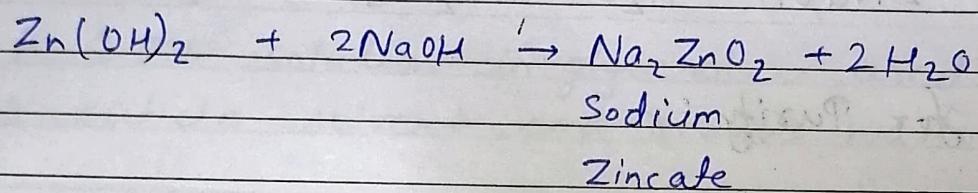
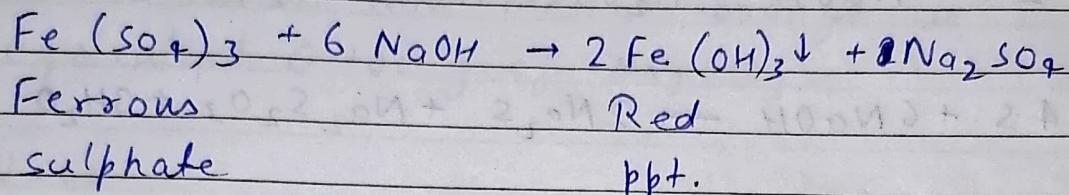
Solubility:- 1 gm dissolve in 0.3 ml of water, 0.3 ml boiling water, 7.2 ml absolute alcohol, also soluble in glycerol.

* Chemical Properties:

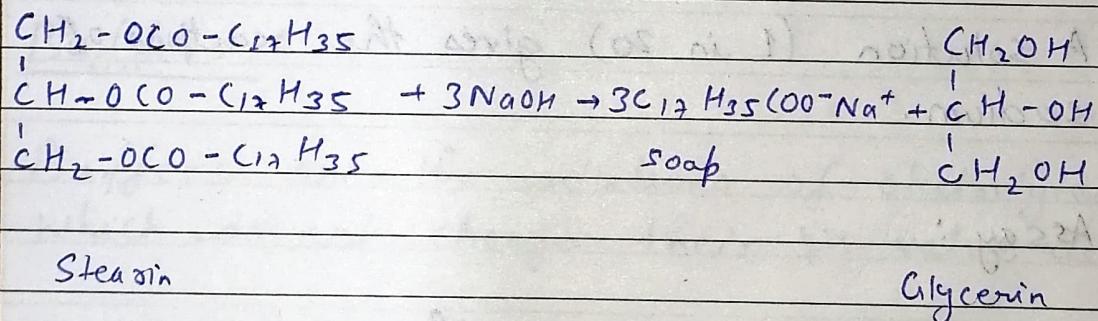
1. Neutralization Reactions:



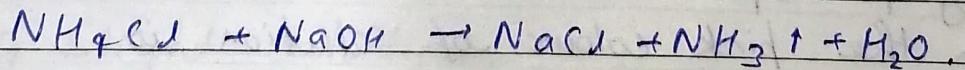
2. It precipitates hydroxides of metals by reacting with salts of all metals in solution.



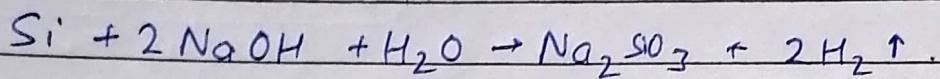
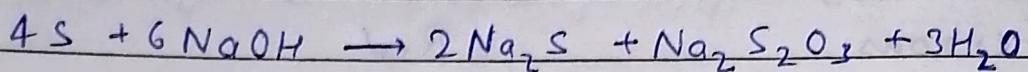
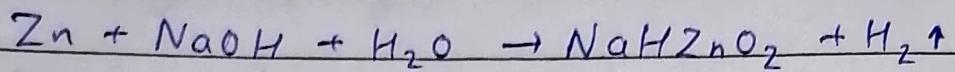
Saponification:



3. Ammonium salts are decomposed with sodium hydroxide and form ammonia.



4. Sodium Hydroxide solution reacts with zinc, aluminium, tin and silicon to form hydrogen.



* Test for Purity :

Test for aluminium, iron, matter insoluble in hydrochloric acid (HCl), arsenic, heavy metals, potassium chloride, lead, carbonates, sulphates, clarity and colour of solution.

* Test for identification :

A solution (1 in 20) gives the reactions of sodium.

* Assay :

A weighed amount of the substance (1.5g) dissolve in CO_2 free water (40ml) is titrated with 1N Sulphuric acid using phenolphthalein solution as indicator. When the pink colour of solution is discharged, volume of acid solution required recorded, methyl orange solution added on the titration is continued until a persistent pink colour is produced.

extramarks

Each ml of 1N H_2SO_4 is equivalent to 0.040 g of total alkali, calculated as $NaOH$ and each ml of acid consumed in the titration with methyl orange is equivalent 0.106 g of Na_2CO_3 .

* Uses :

1. A 2.5% solution in glycerol is used as a cuticle solvent and remove warts.
2. Used as an ~~ex~~ esthetic preparation of sodium hydroxide and calcium oxide, known as London baste.
3. Used for adjusting the pH of solution.

Buffers :

Buffers are the solutions of electrolytes which do not change their pH value as:

- (i) Standing for a long time.
- (ii) Exposure to atmospheric condition.
- (iii) Slight dilution.
- (iv) Addition of small amount of acids or bases.

Basic Buffer:

pH value of basic buffer is greater than.

Ex:- NH_3OH and NH_3Cl .

Buffer capacity.

Moles of strong acid or strong base required to change the pH of one litre of buffer solution by one unit.

Physiological Buffers:

Blood ($\text{pH} \rightarrow 7.3 - 7.4$)

Carbonic acid buffer system
 Na_2CO_3 and NaHCO_3

$\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ and $\text{H}_2\text{NCH}_2\text{COO}^-$

H_3PO_4 and Na_2HPO_4

H_3N^+ and $\text{H}_2\text{NCH}_2\text{COO}^-$

Standard Buffer Solution

Standard buffer solution are solⁿ of std. pH. They are used for reference purposes in pH measurements and for carrying out many pharmacopelial traits which require adjustments to specific pH.

e.g.:

- ① Hydrochloric acid buffer (pH range 1.2 to 2.2)
- ② Acid phthalate buffer (pH - 2.2 to 4.0)
- ③ Neutralized phthalate Buffer (pH - 4.2 to 5.8)
4. Phosphate buffer (pH - 5.8 to 8.0)
5. Alkaline Borate Buffer (pH - 8.0 to 10.0)
6. Acetate buffer (pH → 2.8)
other acetate buffer (pH - 3.5 to 5.0)
7. Glycine Buffer solution (Aminoacetate buffer solⁿ) (pH - 2.0 → 2.5)
8. Imidazole Buffer (pH → 7.4)