

**BACHLEOR OF SCIENCE
SEMESTER-III
PAPER NO.: US03CICH01 (3 CREDITS, 70 MARKS)
(HEAVY AND FINE CHEMICALS)**

Unit-1:

Acids: Manufacture, Properties and uses of Nitric acid, Sulphuric acid, Phosphoric acid, Hydrochloric acid

Sulfuric Acid

Introduction

- Of all the heavy industrial chemicals, sulfuric acid is perhaps the most fundamentally important, in that it has a number of large-scale uses not only within the chemical industry but in other industries as well.
- By far the most important user is the phosphate fertilizer industry.
- Other important applications of sulfuric acid are found in petroleum refining, pigment production, steel pickling, nonferrous metals extraction, and the manufacture of explosives, detergents, plastics, and man-made fibers.
- Many specialty areas of the chemical industry also use varying amounts of sulfuric acid including the production of dyes, pharmaceuticals, and fluorine chemicals.

Properties

Physical Properties

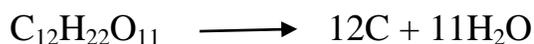
- Pure sulfuric acid H_2SO_4 , Mw 98.08, is a colorless, water-white, slightly viscous liquid, melting point $10.4\text{ }^\circ\text{C}$, boiling point $279.6\text{ }^\circ\text{C}$, and density 1.8356.
- It can be mixed with water in any ratio.

- Aqueous sulfuric acid solutions are defined by their H₂SO₄ content in weight-percent terms. Anhydrous (100 %) sulfuric acid is even today sometimes referred to as “monohydrate,” which simply means that it is the monohydrate of sulfur trioxide.
- Sulfuric acid will dissolve any quantity of SO₃, forming oleum (“fuming sulfuric acid”).
- The physical properties of sulfuric acid and oleum are dependent on the H₂SO₄ and SO₃ concentrations, the temperature, and the pressure.

Chemical Properties

1. Dehydrating agent –

- Sulphuric acid has a great affinity for water and the reaction is extremely exothermic.
- A large amount of heat is produced on mixing acid with water. So in preparing dilute solutions of H₂SO₄ the acid should be added to water slowly with constant stirring. Never add water to the acid.
- The evolution of heat is due to the formation of mono and di hydrates H₂SO₄.H₂O and H₂SO₄.2H₂O.
- The formation of these hydrates also explains the dehydrating nature of sulphuric acid. Therefore it is used for drying almost all gases, except NH₃ and H₂S.
- Its corrosive action on skin is also due to dehydration of skin which then burns and produces itching sensation.
- Due to dehydrating property, it chars sugar to give carbon.



- Similarly, paper, starch, wood etc. are charred by conc. H₂SO₄ due to the removal of water. It is also used in removing water from various substances such as oxalic acid and formic acid.



2. Oxidising agent

- Since sulphuric acid gives O_2 on strong heating, hot cone. H_2SO_4 also acts as an oxidising agent.

3. Pickling agent

- Pickling is the process in which layers of basic oxides are removed before electroplating, enamelling, galvanising and soldering. This is done by sulphuric acid.

4. Acidic nature

- It is a strong dibasic acid and forms two series of salts with alkalis. These are bisulphates (HSO_4^-) and sulphates (SO_4^{2-}).

Manufacture

The manufacture of sulphuric acid is carried out by two processes:

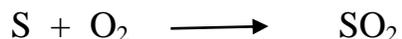
1. The Lead Chamber process or by
2. The Contact process.

The Lead Chamber process.

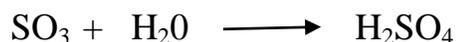
The Lead Chamber process for the manufacture of sulphuric acid dates back about 200 years. Although less efficient than the contact process, it is still of considerable commercial importance.

THEORY

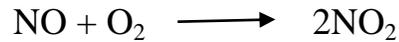
- Sulphur dioxide is obtained by burning sulphur or roasting pyrites.



- The sulphur dioxide thus formed is then oxidised by oxides of nitrogen to sulphur trioxide. The latter then reacts with steam to produce sulphuric acid.



- Nitric oxide obtained takes oxygen from air and gets oxidized back to nitrogen dioxide.



- In this manner, oxides of nitrogen take oxygen from air and pass it to sulphur dioxide and act as oxygen carrier.
- The main principle of the process is that the moist sulphur dioxide is oxidized by the oxygen of the air into sulphur trioxide in the presence of oxides of nitrogen acting as catalyst. Sulphur trioxide thus formed, combined with water to form sulphuric acid.

The Contact Process for Sulfuric Acid

- Essentially all sulfuric acid today is manufactured by the contact process.
- A review of the contact process is presented by Phillips and Bland (1984).
- The raw material for this procedure is elemental sulfur, sulfur dioxide, or pyrite (FeS_2).
- The sources of these materials are as follows:
 1. Sulfur from mines.
 2. Sulfur or hydrogen sulfide recovered from petroleum desulfurization.
 3. Recovery of sulfur dioxide from coal or oil-burning public utility stack gases.
 4. Recovery of sulfur dioxide from the smelting of metal sulfide ores:



5. Isolation of SO_2 from pyrite.

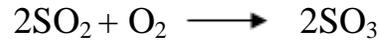
Steps in the Contact Process

As the steps in this process are as follow.

1. Burning of sulfur



2. Catalytic oxidation of SO₂ to SO₃ (vessel 2)



3. Hydration of SO₃

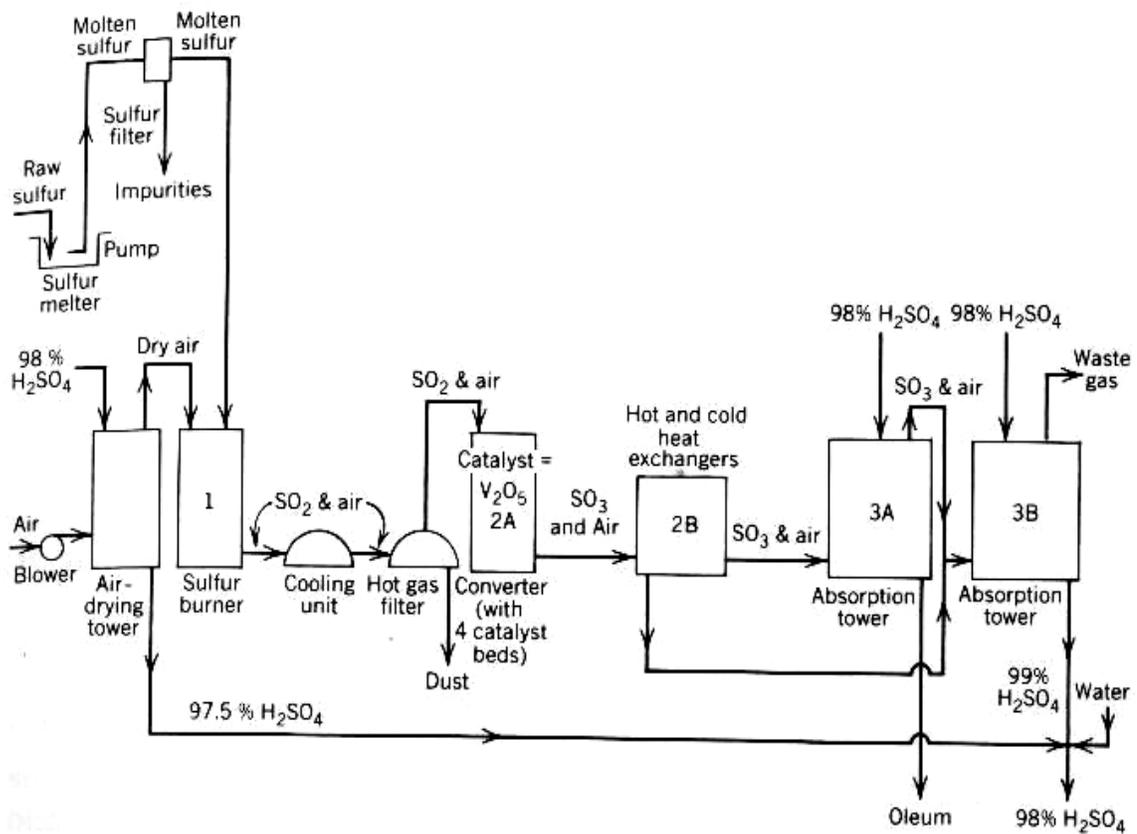


Figure: - Flow chart for sulfuric acid manufacture by the contact process. Piping between catalyst layers from 2A to 2B, and also to 3rd unit (3) not shown.

Process Details

Step 1. Dry SO_2 is needed for the catalytic oxidation. With sources 1 and 2 above, dry air is used in the combustion process. Water will cause corrosion because of acid formation. If sulfur contains carbonaceous impurities, the molten material has to be filtered to avoid poisoning the catalyst and forming water from burning hydrogen.

Step 2. When using sulfur from sources 1 and 2, purification of the SO_2 gas is normally not needed. Other sources of SO_2 require wet scrubbing followed by treatment of the gas with electrostatic precipitators to remove fine particles. The catalyst used is vanadium pentoxide and the pressure is 1.2-1.5 atmospheres. The temperature has to be kept around 410-430°C. If it rises above 430°C, the equilibrium is displaced away from SO_3 . The value has to reach around 410°C for the catalyst to be activated. This process is strongly exothermic. Consequently, the catalytic reactor (2A) is designed as a four-stage fixed-bed unit. The gas has to be cooled between each step. Four passes, together with "double absorption," described below, are necessary for overall conversion of 99.5-99.8% (three passes, 97-98%). The temperature rises to over 600° with the passage of the gas through each catalyst bed. The doubled absorption consists of cooling the gases between each bed back to the desired range by sending them through the heat exchanger (2B), and then back through the succeeding beds. Between the third and fourth beds, the gases are cooled and sent to an absorption tower like unit (3). This is not shown on diagram. This is to shift the equilibrium to the right by absorbing SO_3 . The gases are then sent to the heat exchanger to warm them to 410-430° and then on to the fourth catalyst bed.

Step 3. After the catalytic oxidation process, the resulting SO_3 is hydrated by absorption in packed towers filled with 98-99% sulfuric acid. This is the H_2SO_4 azeotrope of minimum total vapor pressure. The catalytic oxidation has to proceed in high yield to avoid air pollution problems. SO_2 has a low solubility in 98% H_2SO_4 . At lower acid concentrations, sulfuric acid and SO_3 form a troublesome mist and at higher concentrations emissions of SO_3 and H_2SO_4 vapor become significant. The absorption acid concentration is kept within the desired range by exchange as needed between the H_2SO_4 in the drying acid vessel that precedes the combustion chamber with the H_2SO_4 in the absorption tower. The acid strength can be adjusted by controlling the streams of H_2SO_4 to give acid of 91 to 100% H_2SO_4 with various amounts of added SO_3 and water. The conversion of sulfur to acid is over 99.5%.

Uses of Sulfuric Acid

- The largest single consumer of sulfuric acid by far is the fertilizer industry.
- Most goes into the production of phosphoric acid, which in turn is used to manufacture such fertilizer materials as triple superphosphate and mono- and diammonium phosphates.
- Lesser amounts are used for producing superphosphate and ammonium sulfate. About 60 % of the sulfuric acid produced is utilized in fertilizer manufacture.
- Sulfuric acid are used as an acidic dehydrating reaction medium in organic chemical and petrochemical processes involving such reactions as nitration, condensation, and dehydration, as well as in oil refining, in which it is used for refining, alkylation, and purification of crude-oil distillates.
- In the inorganic chemical industry sulfuric acid is used notably in the production of TiO_2 pigments, hydrochloric acid, and hydrofluoric acid.

- In the metal processing industry, sulfuric acid is used for pickling and descaling steel, for leaching copper, uranium, and vanadium ores in hydrometallurgical ore processing, and in the preparation of electrolytic baths for nonferrous-metal purification and plating.
- Certain wood pulping processes in the paper industry require sulfuric acid, as do some textile and chemical fiber processes and leather tanning.

Nitric Acid

Introduction

- Nitric acid is a strong acid that occurs in nature only in the form of nitrate salts.
- Nitric acid is the most important and useful oxyacid of nitrogen.
- It is of great commercial importance as it is used in the manufacture of various fertilizers (ammonium nitrate and phosphate, nitrophosphate), explosives (TNT nitroglycerine, cellulose polynitrate, ammonium picrate etc.), fibres, plastics and dyestuffs.
- A growing and potentially very important use of nitric acid is the replacement of sulphuric acid in acidulation of phosphate rock.
- Nitric acid was known to the ancient Egyptians because of its special ability to separate gold and silver.

Physical Properties.

- Nitric acid Mw 63.013 is miscible with water in all proportions.
- Pure nitric acid is colourless, fuming and pungent smelling liquid.
- The impure nitric acid is yellow due to dissolved oxides of nitrogen, mainly NO₂.
- It has a corrosive action on skin and causes painful blisters.

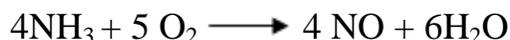
Chemical Properties.

- **Acidic properties.** Nitric acid is a strong monobasic acid and ionisation in aqueous solution.
- **Oxidising properties.** It acts as a powerful oxidising agent, due to the formation of nascent oxygen.
- **Action on metals.** Nitric acid reacts with almost all the metals, except noble metals, like Pt and Au. The metals are oxidized to their corresponding positive metal ions while HNO_3 is reduced to NO , NO_2 , N_2O , NH_2OH or NH_3 , depending upon the conditions such as temperature, nature of metal and concentration of the acid.

Industrial Production

Nitric acid is made by the oxidation of ammonia, using platinum or platinum-10% rhodium as catalyst, followed by the reaction of the resulting nitrogen oxides with water. The industrial production of nitric acid by the Ostwald process is described in this section. The process involves three chemical steps.

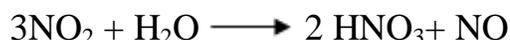
1) Catalytic oxidation of ammonia with atmospheric oxygen to yield nitrogen monoxide:



2) Oxidation of the nitrogen monoxide product to nitrogen dioxide or dinitrogen tetroxide:



3) Absorption of the nitrogen oxides to yield nitric acid:



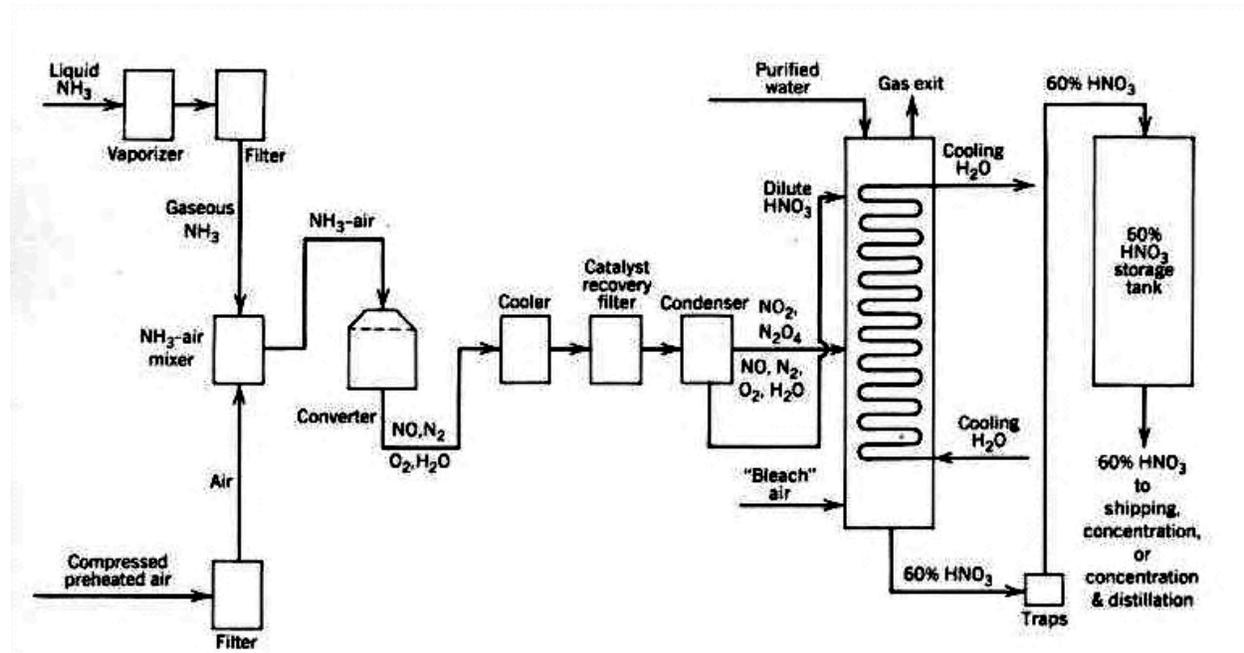


FIGURE Flow chart for nitric acid manufactured by oxidation of ammonia.

Brief Process Description

1. Into the ammonia-air mixer is fed vaporized filtered liquid ammonia and preheated filtered compressed air. This mixture is led to the converter.
2. The converter contains the catalyst gauzes. This is where reaction (1) occurs. As shown in Figure the gases leaving the converter are NO with enough oxygen for reaction (2), as well as nitrogen from the air and from reaction (6), and water mainly from reaction (1) (temperature, 920°. pressure, 1-4 atm). This is to compress gases because of equipment size limitations. Pressure does not affect the reaction as there is little volume change; see Eq.(1). The gases are cooled.

3. The oxidation of NO to NO₂ takes place after the gases leave the cooler, as well as the absorption in water to give nitric acid. Note the line from the bottom of the condenser for dilute nitric acid. This is from the water from reaction (1) with the NO₂.

4. The absorption tower has enough water so that 60% nitric acid will result, and also enough air to convert all remaining NO to NO₂. The pressure is 10 atm. to give more efficient absorption.

A more concentrated acid is obtained by distillation. The yield is 94-95% nitric acid. The product is 60% HNO₃. An acid of up to 65% strength can be obtained if the absorbing system is cooled to 2°C.

Uses

- The principal use of nitric acid is as a starting material in the manufacture of nitrogen fertilizers large amounts are reacted with ammonia to yield ammonium nitrate.
- Weak acid (ca. 60 % HNO₃) is most suitable for this purpose. Smaller amounts of weak acid are used to digest crude phosphates.
- About 75 – 85 % of the nitric acid produced is used in the fertilizer sector.
- In addition, porous ammonium nitrate prills are still an important component of explosives.
- Nitric acid is used as a nitrating agent in the preparation of explosives and organic intermediates such as nitroalkanes and nitroaromatics.
- It is also used in the production of adipic acid.
- Other applications include use as a chemical in metallurgy and in rocket fuel production

Hydrochloric Acid

Hydrochloric acid, also known as muriatic acid, is a solution of hydrogen chloride (HCl) in water. Hydrogen chloride (HCl) exists in solid, liquid, and gaseous states and is very soluble in water.

Properties

Physical Properties

- HCl gas is a colourless, pungent smelling gas with acidic taste.
- It fumes in moist air and is extremely soluble in water. One volume of water dissolves 452 volumes of the gas at room temperature.
- It is heavier than air.
- With water it gives a constant boiling mixture (containing 20.2% of the acid and boiling at 382K). Dilute solutions of the acid cannot, therefore, be concentrated by boiling beyond 20.2 %.
- It can be easily liquefied to a colourless liquid (b.p 189 K) and frozen to white crystalline solid. (m.p. 162 K).

Chemical Properties

- Hydrogen chloride is thermally stable up to approximately 1500 °C, but appreciable dissociation occurs above this temperature.
- Completely dry hydrogen chloride is not very reactive: mild steel is not measurably attacked. Moreover, reactions involving dry hydrogen chloride often take place only in the presence of catalysts.
- In contrast, a solution of hydrogen chloride in a polar solvent is a strong acid and, therefore, an aggressive reagent.

Manufacture of HCl acid

Hydrogen chloride is produced by the direct reaction of hydrogen and chlorine, by reaction of metal chlorides and acids, and as a by-product from many chemical manufacturing processes such as chlorinated hydrocarbons.

1. **Synthesis from Hydrogen and Chlorine.** Less than 10% of HCl is made by the direct reaction of the elements. There is large demand in the market for water white acid. Such acid is obtained by synthetic method and most of the plants are based on this process.

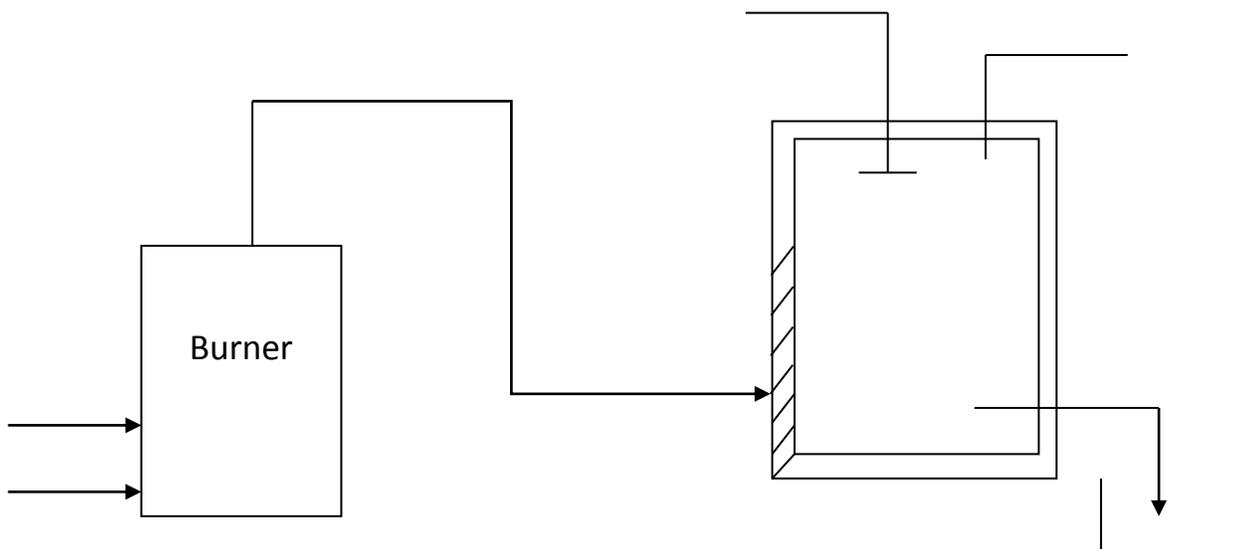
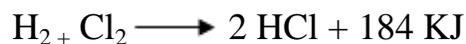
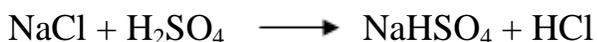


Figure show the flow sheet of a synthetic hydrochloric acid plant.

The plant consists of combustion chamber of structural carbon provided with cooling device which may consist even of cold water circulation in the shell. The gases are always kept above dew point to avoid corrosion. The hydrogen and chlorine gas enter the bottom in such proportions that slight excess of hydrogen is maintained. The reaction is started by igniting the burner with an external air-hydrogen torch. The HCl gas is conveyed to the absorber through connection pipe. With almost pure

HCl acid gas (98 per cent), the absorption is rapid and external cooling may be employed. The strength of acid produced is generally 32-33 per cen.

2. **Decomposition of Metal Chlorides by Acids.** Two commercial processes employing the acidic decomposition of metal chlorides are the salt-sulfuric acid process.
3. **The Salt-Sulfuric Acid Process.** The reaction between NaCl and sulfuric acid occurs in two stages, both endothermic.



4. **Hydrogen Chloride as By-Product from Chemical Processes.** Over 90% of the hydrogen chloride produced in the United States is a by-product from various chemical processes. The crude HCl generated in these processes is generally contaminated with impurities such as unreacted chlorine, organics, chlorinated organics, and entrained catalyst particles. A wide variety of techniques are employed to treat these HCl streams to obtain either anhydrous HCl or hydrochloric acid. Some of the processes in which HCl is produced as a by-product are the manufacture of chlorofluorohydrocarbons, manufacture of aliphatic and aromatic hydrocarbons, production of high surface area silica, and the manufacture of phosphoric acid and esters of phosphoric acid.
5. **Hydrogen Chloride Produced from Incineration of Waste Organics.** Environmental regulations regarding the disposal of chlorine-containing organic wastes has motivated the development of technologies for burning or pyrolyzing the waste organics and recovering the chlorine values as

hydrogen chloride. Several catalytic and non-catalytic processes have been developed to treat these wastes to produce hydrogen chloride.

6. **Hydrogen Chloride from Hydrochloric Acid Solutions.** Gaseous hydrogen chloride is obtained by partially stripping concentrated hydrochloric acid using an absorber–desorber system. The stripper is operated at a pressure of 100–200 kPa (1–2 atm) for improved recovery of HCl. The overhead vapors consisting of 97% HCl and 3% H₂O are cooled to remove most of the water as concentrated HCl, and the residual water vapor is removed by drying the gas with sulfuric acid.

Uses

Hydrogen chloride and the aqueous solution, muriatic acid, find application in many industries.

- In general, anhydrous HCl is consumed for its chlorine value, whereas aqueous hydrochloric acid is often utilized as a nonoxidizing acid.
- It is used in metal cleaning operations, chemical manufacturing, petroleum well activation, and in the production of food and synthetic rubber.
- It is used for the manufacture of chlorine and chlorides, eg. Ammonium chloride used in dry cell.
- In the manufacture of glucose from corn starch.
- For extracting glue from bones and purifying boneblack.
- A saturated solution of zinc chloride in dilute HCl is used for cleaning metals before soldering or plating.
- As a constituent of *aqua regia* which is used for dissolving noble metals.
- It is also used in medicine and as a reagent in the laboratory.