Chlorine

Contents

1 . Intrioduion ;

Chlorine (from the Greek word *khlôros*, meaning ' pale green') , is the chemical element with atomic number 17 and symbol **Cl**. It is a halogen, found in the periodic table in group 17 (formerly VII , VIIa , or VIIb) . As the chloride ion , which is part of common salt and other compounds, it is abundant in nature and necessary to most forms of life , including humans. In its elemental form (Cl_2 or " di chlorine ") under standard conditions, chlorine is a powerful oxidant and is used in bleaching and disinfectants. As a common disinfectant, chlorine compounds are used in swimming pools to keep them clean and sanitary . In the upper atmosphere , chlorine - containing molecules such as chlorofluorocarbons have been implicated in the destruction of the ozone layer.

Appearance	Pale green gas
Name , Symbol , Number	Chlorine , Cl , 17
Element Category	Halogen
Group , Period , Block	17 , 3 , p
Standard atomic weight	35.453 g · mol^{-1}
Electron configuration	[Ne] $3s^2$ $3p^5$
Electrons per shell	2 , 8 , 7
Phase	gas
Density	(0 °C , 101.325 kPa) 3.2 g / L
Melting Point	- 101.5 ° C
Boiling Point	- 34.4 ° C
Critical Point	416.9 K , 7.991 MPa
Heat of fusion	(Cl_2) 6.406 kJ · mol^{-1}
Heat of vaporization	(Cl_2) 20.41 kJ · mol^{-1}
Specific heat capacity	(25 °C) (Cl_2) 33.949 J·mol^{-1}·K^{-1}
Oxidation states	7 , 6 , 5 , 4 , 3 , 2 , 1 , -1 (strongly acidic oxide)
Electro Negativity	3.16 (Pauling scale)
Ionization energies	1 st : 1251.2 kJ · mol^{-1} 2 nd : 2298 kJ · mol^{-1} 3 rd : 3822 kJ · mol^{-1}
Covalent radius	102 ± 4 pm
Van der Waals radius	175 pm
Crystal structure	Ortho rhombic
Magnetic ordering	diamagnetic
Electrical resistivity	(20 ° C) > 10 Ω·m
Thermal conductivity	(300 K) 8.9 x 10^{-3} W·m^{-1}·K^{-1}
Speed of sound	(gas, 0 °C) 206 m / s

2 . Characteristics

At standard temperature and pressure, two chlorine atoms form the diatomic molecule Cl_2. This is a pale yellow - green gas that has its distinctive strong smell, the smell of bleach. The bonding between the two atoms is relatively weak (only of 242.580 ± 0.004 kJ / mol) which makes the Cl_2 molecule highly reactive.

Along with fluorine, bromine, iodine and astatine, chlorine is a member of the halogen series that forms the group 17 of the periodic table—the most reactive group of elements. It combines readily with nearly all elements .

Compounds with oxygen, nitrogen, xenon, and krypton are known, but do not form by direct reaction of the elements.[2] Chlorine, though very reactive, is not as extremely reactive as fluorine. Pure chlorine gas does, how ever, support combustion of organic compounds such as hydrocarbons, although the carbon component tends to burn incompletely, with much of it remaining as soot . At 10 °C and atmospheric pressure, one liter of water dissolves 3.10 L of gaseous chlorine, and at 30 °C, 1 L of water dissolves only 1.77 liters of chlorine.[4]

Chlorine is a member of the salt - forming halogen series and is extracted from chlorides through oxidation often by electrolysis. With metals, it forms salts called chlorides. As the chloride ion, Cl^-, it is also the most abundant dissolved ion in ocean water.

2 . 1 . Isotopes of chlorine :

Chlorine has isotopes with mass numbers ranging from 32 to 40. There are two principal stable isotopes, ^{35}Cl (75.77 %) and ^{37}Cl (24.23 %) , giving chlorine atoms in bulk an apparent atomic weight of 35.4527 g / mol.

Trace amounts of radioactive ^{36}Cl exist in the environment, in a ratio of about 7×10^{-13} to 1 with stable isotopes. ^{36}Cl is produced in the atmosphere by spallation of ^{36}Ar by interactions with cosmic ray protons. In the subsurface environment, ^{36}Cl is generated primarily as a result of neutron capture by ^{35}Cl or muon capture by ^{40}Ca. ^{36}Cl decays to ^{36}S and to ^{36}Ar, with a combined half-life of 308,000 years. The half-life of this hydrophilic nonreactive isotope makes it suitable for geologic dating in the range of 60,000 to 1 million years.

Additionally, large amounts of ^{36}Cl were produced by irradiation of seawater during atmospheric detonations of nuclear weapons between 1952 and 1958. The residence time of ^{36}Cl in the atmosphere is about 1 week. Thus, as an event marker of 1950s water in soil and ground water, ^{36}Cl is also useful for dating waters less than 50 years before the present. ^{36}Cl has seen use in other areas of the geological sciences, including dating ice and sediments.

2 . 2 Occurrence (Halide minerals)

In nature, chlorine is found primarily as the chloride ion, a component of the salt that is deposited in the earth or dissolved in the oceans — about 1.9 % of the mass of seawater is chloride ions. Even higher concentrations of chloride are found in the Dead Sea and in underground brine deposits. Most chloride salts are soluble in water, thus, chloride-containing minerals are usually only found in abundance in dry climates or deep underground . Common chloride minerals include *halite* (sodium chloride) , *sylvite* (potassium chloride), and *carnallite* (potassium magnesium chloride hexahydrate) . Over 2000 naturally-occurring organic chlorine compounds are known .

Industrially, elemental chlorine is usually produced by the electrolysis of sodium chloride dissolved in water. Along with chlorine, this chloralkali process yields hydrogen gas and sodium hydroxide, according to the following chemical equation:

$$2\ NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ NaOH$$

3 . History

The most common compound of chlorine, sodium chloride, has been known since ancient times; archaeologists have found evidence that rock salt was used as early as 3000 BC and brine as early as 6000 BC. The first compound of chlorine synthesized was probably hydrochloric acid (as a solution), which was prepared by the Persian alchemist Rhazes around 900 AD. Around 1200 AD, aqua regia (a mixture of nitric acid and hydrochloric acid) began to be used to dissolve gold,[*citation needed*] and today this is still one of the few reagents that will dissolve gold. Upon dissolving gold in aqua regia, chlorine gas is released along with other nauseating and irritating gases, but this wasn't known until much more recently.

Chlorine was first prepared and studied in 1774 by Swedish chemist Carl Wilhelm Scheele, and therefore he is credited for its discovery . He called it "*dephlogisticated muriatic acid air*" since it was a gas (then called " airs ") and it came from hydro chloric acid (then known as " muriatic acid ") . However, he failed to establish chlorine as an element, mistakenly thinking that it was the oxide obtained from the hydrochloric acid . He named the new element within this oxide as *muriaticum* . Regardless of what he thought, Scheele did isolate chlorine by reacting MnO_2 with HCl :

$$4\,H\,Cl + Mn\,O_2 \rightarrow Mn\,Cl_2 + 2\,H_2\,O + Cl_2$$

Scheele observed several of the properties of chlorine: the bleaching effect on litmus, the deadly effect on insects, the yellow green color, and the smell similar to aqua regia.

Claude Berthollet suggested that Scheele's *dephlogisticated muratic acid air* must be a combination of oxygen and an undiscovered element, *muriaticum* .

In 1809 Joseph Louis Gay - Lussac and Louis - Jacques Thénard tried to decompose *dephlogisticated muratic acid air* by reacting it with charcoal to release the free element *muriaticum* (and carbon dioxide) . They did not succeed and published a report in which they considered the possibility that *dephlogisticated muratic acid air* is an element, but were not convinced .

In 1810, Sir Humphry Davy tried the same experiment again, and concluded that it was an element, and not a compound . He named this new element as chlorine, from the Greek word χλωρος (*chlōros*) , meaning green – yellow . The name halogen, meaning salt producer, was originally defined for chlorine (in 1811 by Johann Salomo Christoph Schweigger), and it was later applied to the rest of the elements in this family. In 1822, Michael Faraday liquefied chlorine for the first time .

Chlorine was first used to bleach textiles in 1785 . In 1826, silver chloride was used to produce photographic images for the first time . Chloroform was first used as an anesthetic in 1847 . Chlorine was first used as a germicide to prevent the spread of puerperal fever in the maternity wards of Vienna General Hospital in Austria in 1847 , and in 1850 by John Snow to disinfect the water supply in London after an out break of cholera. The US Department of Treasury called for all water to be disinfected with chlorine by 1918 . Poly vinyl chloride (PVC) was invented in 1912, initially without a purpose.[12] Chlorine gas was first introduced as a weapon on April 22 , 1915 at Ypres by the German Army , and the results of this weapon were disastrous because gas masks had not yet been invented.

4 . Production :

4 . 1 . Gas extraction :

Chlorine can be manufactured by electrolysis of a sodium chloride solution (brine) . The production of chlorine results in the co - products caustic soda (sodium hydroxide, NaOH) and hydrogen gas (H_2) . These two products, as well as chlorine itself, are highly reactive. Chlorine can also be produced by the electrolysis of a solution of potassium chloride, in which case the co - products are hydrogen and caustic potash (potassium hydroxide) . There are three industrial methods for the extraction of chlorine by electrolysis of chloride solutions, all proceeding according to the following equations :

Cathode : $2\,H^+ (aq) + 2\,e^- \rightarrow H_2 (g)$
Anode : $2\,Cl^- (aq) \rightarrow Cl_2 (g) + 2\,e^-$

Over all process :

$$2\,NaCl \text{ (or KCl)} + 2\,H_2O \rightarrow Cl_2 + H_2 + 2\,NaOH \text{ (or KOH)}$$

***Mercury cell electrolysis** :*

Mercury cell electrolysis, also known as the Castner-Kellner process, was the first method used at the end of the nineteenth century to produce chlorine on an industrial scale.The" rocking " cells used have been improved over the years. Today, in the "primary cell", titanium anodes (formerly graphite ones) are placed in a sodium (or potassium) chloride solution flowing over a liquid mercury cathode. When a potential difference is applied and current flows, chlorine is released at the titanium anode and sodium (or potassium) dissolves in the mercury cathode forming an amalgam. This flows continuously into a separate reactor (" denuder " or " secondary cell ") , where it is usually converted back to mercury by reaction with water, producing hydrogen and sodium (or potassium) hydroxide at a commercially useful concentration (50 % by weight) . The mercury is then recycled to the primary cell .

The mercury process is the least energy - efficient of the three main technologies (mercury , diaphragm and membrane) and there are also concerns about mercury emissions .

It is estimated that there are still around 100 mercury-cell plants operating worldwide. In Japan, mercury - based chloralkali production was virtually phased out by 1987 (except for the last two potassium chloride units shut down in 2003) . In the United States, there will be only five mercury plants remaining in operation by the end of 2008. In Europe, mercury cells accounted for 43 % of capacity in 2006 and Western European producers have committed to closing or converting all remaining chloralkali mercury plants by 2020 .

Diaphragm cell electrolysis :

In diaphragm cell electrolysis, an asbestos (or polymer – fiber) diaphragm separates a cathode and an anode, preventing the chlorine forming at the anode from re - mixing with the sodium hydroxide and the hydrogen formed at the cathode.[20] This technology was also developed at the end of the nineteenth century. There are several variants of this process: the Le Sueur cell (1893), the Hargreaves-Bird cell (1901) , the Gibbs cell (1908) , and the Townsend cell (1904) . The cells vary in construction and placement of the diaphragm, with some having the diaphragm in direct contact with the cathode .

The salt solution (brine) is continuously fed to the anode compartment and flows through the diaphragm to the cathode compartment, where the caustic alkali is produced and the brine is partially depleted.

As a result, diaphragm methods produce alkali that is quite dilute (about 12 %) and of lower purity than do mercury cell methods. But diaphragm cells are not burdened with the problem of preventing mercury discharge into the environment. They also operate at a lower voltage, resulting in an energy savings over the mercury cell method , but large amounts of steam are required if the caustic has to be evaporated to the commercial concentration of 50 %.

Membrane cell electrolysis :

Development of this technology began in the 1970s. The electrolysis cell is divided into two "rooms" by a cation permeable membrane acting as an ion exchanger. Saturated sodium (or potassium) chloride solution is passed through the anode compartment, leaving at a lower concentration . Sodium (or potassium) hydroxide solution is circulated through the cathode compartment, exiting at a higher concentration. A portion of the concentrated sodium hydroxide solution leaving the cell is diverted as product, while the remainder is diluted with deionized water and passed through the electrolysis apparatus again.

This method is more efficient than the diaphragm cell and produces very pure sodium (or potassium) hydroxide at about 32 % concentration, but requires very pure brine .

Other electrolytic processes :

Although a much lower production scale is involved, electrolytic diaphragm and membrane technologies are also used industrially to recover chlorine from hydrochloric acid solutions, producing hydrogen (but no caustic alkali) as a co - product.

Furthermore, electrolysis of fused chloride salts (Downs process) also enables chlorine to be produced, in this case as a by - product of the manufacture of metallic sodium or magnesium.

5 . 2 . Other methods

Before electrolytic methods were used for chlorine production, the direct oxidation of hydrogen chloride with oxygen or air was exercised in the Deacon process :

$$4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O$$

This reaction is accomplished with the use of copper (II) chloride ($CuCl_2$) as a catalyst and is performed at high temperature (about 400 °C) . The amount of extracted chlorine is approximately 80 %. Due to the extremely corrosive reaction mixture, industrial use of this method is difficult and several pilot trials failed in the past. Nevertheless, recent developments are promising. Recently Sumitomo patented a catalyst for the Deacon process using ruthenium (IV) oxide (RuO_2) .

Another earlier process to produce chlorine was to heat brine with acid and manganese dioxide .

$$2\ NaCl + 2\ H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2\ H_2O + Cl_2$$

Using this process, chemist Carl Wilhelm Scheele was the first to isolate chlorine in a laboratory. The manganese can be recovered by the Weldon process .

In the latter half of the 19th century, prior to the adoption of electrolytic methods of chlorine production, there was substantial production of chlorine by these reactions to meet demand for bleach and bleaching powder for use by textile industries; by the 1880s the UK, as well as supporting its own (then not inconsiderable) domestic textile production was exporting 70,000 tons per year of bleaching powder . This demand was met by capturing hydrochloric acid driven off as a gas during the production of alkali by the Leblanc process, oxidizing this to chlorine (originally by reaction with manganese dioxide) , later by direct oxidation by air using the Deacon process (in which case impurities capable of poisoning the catalyst had first to be removed) , and subsequently absorbing the chlorine onto lime .

Small amounts of chlorine gas can be made in the laboratory by putting concentrated hydrochloric acid in a flask with a side arm and rubber tubing attached. Manganese dioxide is then added and the flask stoppered. The reaction is not greatly exothermic. As chlorine is denser than air, it can be collected by placing the tube inside a flask where it will displace the air. Once full, the collecting flask can be stoppered .

Another method for producing small amounts of chlorine gas in a lab is by adding concentrated hydrochloric acid (typically about 5M) to sodium hypochlorite or sodium chlorate solution.

4 . 3 . Industrial production

Large - scale production of chlorine involves several steps and many pieces of equipment. The description below is typical of a membrane plant. The plant also simultaneously produces sodium hydroxide (caustic soda) and hydrogen gas. A typical plant consists of brine production/treatment, cell operations, chlorine cooling & drying, chlorine compression & liquefaction, liquid chlorine storage & loading, caustic handling, evaporation, storage & loading and hydrogen handling.

Brine :

Key to the production of chlorine is the operation of the brine saturation/treatment system. Maintaining a properly saturated solution with the correct purity is vital, especially for membrane cells. Many plants have a salt pile which is sprayed with recycled brine. Others have slurry tanks that are fed raw salt.

The raw brine is partially or totally treated with sodium hydroxide, sodium carbonate and a flocculant to reduce calcium, magnesium and other impurities. The brine proceeds to a large clarifier or a filter where the impurities are removed. The total brine is additionally filtered before entering ion exchangers to further remove impurities. At several points in this process, the brine is tested for hardness and strength.

After the ion exchangers, the brine is considered pure, and is transferred to storage tanks to be pumped into the cell room. Brine, fed to the cell line, is heated to the correct temperature to control exit brine temperatures according to the electrical load. Brine exiting the cell room must be treated to remove residual chlorine and control pH levels before being returned to the saturation stage. This can be accomplished via dechlorination towers with acid and sodium bisulfite addition. Failure to remove chlorine can result in damage to the cells. Brine should be monitored for accumulation of both chlorate anions and sulfate anions, and either have a treatment system in place, or purging of the brine loop to maintain safe levels, since chlorate anions can diffuse through the membranes and contaminate the caustic, while sulfate anions can damage the anode surface coating.

Cell room :

The building that houses many electrolytic cells is usually called a cell room or cell house, although some plants are built outdoors. This building contains support structures for the cells, connections for supplying electrical power to the cells and piping for the fluids. Monitoring and control of the temperatures of the feed caustic and brine is done to control exit temperatures. Also monitored are the voltages of each cell which vary with the electrical load on the cell room that is used to control the rate of production. Monitoring and control of the pressures in the chlorine and hydrogen headers is also done via pressure control valves.

Direct current is supplied via a rectified power source. Plant load is controlled by varying the current to the cells. As the current is increased, flow rates for brine and caustic and deionized water are increased, while lowering the feed temperatures.

Cooling and drying :

Chlorine gas exiting the cell line must be cooled and dried since the exit gas can be over 80° C and contains moisture that allows chlorine gas to be corrosive to iron piping. Cooling the gas allows for a large amount of moisture from the brine to condense out of the gas stream. This reduces both the cooling requirements and feed flow of sulfuric acid required in the drying towers. Cooling also improves the efficiency of both the compression and the liquefaction stage that follows. Chlorine exiting is ideally between 18° C and 25° C. After cooling the gas stream passes through a series of towers with counter flowing sulfuric acid. The sulfuric acid is fed into the final tower at 98% and the first tower typically has a strength between 66 % and 76 % depending on materials of construction. These towers progressively remove any remaining moisture from the chlorine gas. After exiting the drying towers the chlorine is filtered to remove any remaining sulfuric acid.

Compression and liquefaction :

Several methods of compression may be used: liquid ring, reciprocating, or centrifugal. The chlorine gas is compressed at this stage and may be further cooled by inter - and after- coolers. After compression it flows to the liquefiers, where it is cooled enough to liquefy. Non condensable gases and remaining chlorine gas are vented off as part of the pressure control of the liquefaction systems. These gases are routed to a gas scrubber, producing sodium hypochlorite, or used in the production of hydrochloric acid (by combustion with hydrogen) or ethylene dichloride (by reaction with ethylene) .

Storage and loading :

Liquid chlorine is typically gravity - fed to storage tanks. It can be loaded into rail or road tankers via pumps or padded with compressed dry gas .

Caustic handling , evaporation , storage and loading

Caustic, fed to the cell room flows in a loop that is simultaneously bled off to storage with a part diluted with deionized water and returned to the cell line for strengthening within the cells. The caustic exiting the cell line must be monitored for strength, to maintain safe concentrations. Too strong or too weak a solution may damage the membranes. Membrane cells typically produce caustic in the range of 30% to 33% by weight. The feed caustic flow is heated at low electrical loads to control its exit temperature. Higher loads require the caustic to be cooled, to maintain correct exit temperatures . The caustic exiting to storage is pulled from a storage tank and may be diluted for sale to customers who require weak caustic or for use on site. Another stream may be pumped into a multiple effect evaporator set to produce commercial 50 % caustic. Rail cars and tanker trucks are loaded at loading stations via pumps.

Hydrogen handling :

Hydrogen produced may be vented unprocessed directly to the atmosphere or cooled, compressed and dried for use in other processes on site or sold to a customer via pipeline, cylinders or trucks. Some possible uses include the manufacture of hydrochloric acid or hydrogen peroxide, as well as desulfurization of petroleum oils, or use as a fuel in boilers or fuel cells. In Porsgrunn the byproduct is used for the hydrogen fueling station at Hynor.

Energy consumption :

Production of chlorine is extremely energy intensive . Energy consumption per unit weight of product is not far below that for iron and steel manufacture and greater than for the production of glass or cement .

Since electricity is an indispensable raw material for the production of chlorine, the energy consumption corresponding to the electrochemical reaction cannot be reduced. Energy savings arise primarily through applying more efficient technologies and reducing ancillary energy use.

5 . Compounds

For general references to the chloride ion (Cl^-) including references to specific chlorides, see chloride. For other chlorine compounds see chlorate (Cl O −3) , chlorite (Cl O −2) , hypochlorite ($Cl\ O^-$) , and perchlorate (Cl O−4), and chloramine ($NH_2\ Cl$) .

Other chlorine - containing compounds include :

- Fluorides : chlorine monofluoride (Cl F) , chlorine trifluoride ($Cl\ F_3$) , chlorine pentafluoride ($Cl\ F_5$)
- Oxides: chlorine dioxide ($Cl\ O_2$), dichlorine monoxide ($Cl_2\ O$) , dichlorine heptoxide ($Cl_2\ O_7$)
- Acids: hydro chloric acid (HCl) , chloric acid ($HCl\ O_3$) , and perchloric acid ($H\ Cl\ O_4$)

5 . 1 . Oxidation states

Oxidation state	Name	Formula	Example compounds
− 1	chlorides	Cl^-	ionic chlorides, organic chlorides , hydrochloric acid
0	chlorine	Cl_2	elemental chlorine
+ 1	hypochlorites	$Cl\ O^-$	sodium hypochlorite , calcium hypochlorite
+ 3	chlorites	$Cl\ O^{-2}$	sodium chlorite
+ 5	chlorates	$Cl\ O^{-3}$	sodium chlorate , potassium chlorate , chloric acid
+7	perchlorates	$Cl\ O^{-4}$	potassium perchlorate, perchloric acid , magnesium perchlorate organic perchlorates , ammonium perchlorate

Chlorine exists in all odd numbered oxidation states from −1 to + 7 , as well as the elemental state of zero. Progressing through the states, hydrochloric acid can be oxidized using manganese dioxide, or hydrogen chloride gas oxidized catalytically by air to form elemental chlorine gas. The solubility of chlorine in water is increased if the water contains dissolved alkali hydroxide. This is due to disproportionation :

$$Cl_2 + 2\ OH^{-} \rightarrow Cl^{-} + ClO^{-} + H_2O$$

In hot concentrated alkali solution disproportionation continues:

$$2\ Cl\ O^{-} \rightarrow Cl^{-} + Cl\ O^{-2}$$
$$Cl\ O^{-} + Cl\ O^{-2} \rightarrow Cl^{-} + Cl\ O^{-3}$$

Sodium chlorate and potassium chlorate can be crystallized from solutions formed by the above reactions. If their crystals are heated, they undergo the final disproportionation step.

$$4\ Cl\ O^{-3} \rightarrow Cl^{-} + 3\ Cl\ O^{-4}$$

This same progression from chloride to perchlorate can be accomplished by electrolysis. The anode reaction progression is:

Reaction	Electrode potential
$Cl^{-} + 2\ OH^{-} \rightarrow Cl\ O^{-} + H_2\ O + 2\ e^{-}$	+ 0.89 volts
$Cl\ O^{-} + 2\ OH^{-} \rightarrow Cl\ O^{-2} + H_2\ O + 2\ e^{-}$	+ 0.67 volts
$Cl\ O -2 + 2\ OH^{-} \rightarrow Cl\ O^{-3} + H_2\ O + 2\ e^{-}$	+ 0.33 volts
$Cl\ O -3 + 2\ OH^{-} \rightarrow Cl\ O^{-4} + H_2\ O + 2\ e^{-}$	+ 0.35 volts

Each step is accompanied at the cathode by

$$2\ H_2O + 2\ e^{-} \rightarrow 2\ OH^{-} + H_2\ (-\ 0.83\ \text{volts})$$

6 . Applications and uses

6 . 1 . Production of industrial and consumer products

Chlorine's principal applications are in the production of a wide range of industrial and consumer products . For example, it is used in making plastics, solvents for dry cleaning and metal degreasing, textiles, agrochemicals and pharmaceuticals, insecticides, dyestuffs, household cleaning products, etc.

6 . 2 . Purification and disinfection

Chlorine is an important chemical for water purification (such as water treatment plants) , in disinfectants, and in bleach. Chlorine in water is more than three times more effective as a disinfectant against *Escherichia coli* than an equivalent concentration of bromine, and is more than six times more effective than an equivalent concentration of iodine .

Chlorine is usually used (in the form of hypochlorous acid) to kill bacteria and other microbes in drinking water supplies and public swimming pools. In most private swimming pools chlorine itself is not used , but rather sodium hypochlorite, formed from chlorine and sodium hydroxide, or solid tablets of chlorinated isocyanurates. Even small water supplies are now routinely chlorinated .

It is often impractical to store and use poisonous chlorine gas for water treatment, so alternative methods of adding chlorine are used. These include hypochlorite solutions, which gradually release chlorine into the water, and compounds like sodium dichloro-s-triazinetrione (dihydrate or anhydrous) , sometimes referred to as " dichlor ", and trichloro - s - triazinetrione, sometimes referred to as " trichlor ". These compounds are stable while solid and may be used in powdered, granular, or tablet form. When added in small amounts to pool water or industrial water systems, the chlorine atoms hydrolyze from the rest of the molecule forming hypochlorous acid ($HOCl$) which acts as a general biocide killing germs, micro-organisms, algae, and so on.

6 . 3 . Chemistry

Elemental chlorine is an oxidizer. It undergoes halogen substitution reactions with lower halide salts. For example, chlorine gas bubbled through a solution of bromide or iodide anions oxidizes them to bromine and iodine respectively .

Like the other halogens, chlorine participates in free-radical substitution reactions with hydrogen-containing organic compounds. This reaction is often — but not invariably — non -regioselective, and hence, may result in a mixture of isomeric products. It is often difficult to control the degree of substitution as well, so multiple substitutions are common. If the different reaction products are easily separated, e.g. by distillation, substitutive free-radical chlorination (in some cases accompanied by concurrent thermal dehydro chlorination) may be a useful synthetic route. Industrial examples of this are the production of methyl chloride, methylene chloride, chloroform and carbon tetrachloride from methane, allyl chloride from propylene, and trichloro ethylene and tetra chloro ethylene from 1 , 2 – dichloro ethane.

Like the other halides, chlorine undergoes electrophilic additions reactions, most notably, the chlorination of alkenes and aromatic compounds with a Lewis acid catalyst. Organic chlorine compounds tend to be less reactive in nucleophilic substitution reactions than the corresponding bromine or iodine derivatives, but they tend to be cheaper. They may be activated for reaction by substituting with a tosylate group, or by the use of a catalytic amount of sodium iodide.

Chlorine is used extensively in organic and inorganic chemistry as an oxidizing agent and in substitution reactions because chlorine often imparts many desired properties to an organic compound, due to its electronegativity.

Chlorine compounds are used as intermediates in the production of a number of important commercial products that do not contain chlorine. Examples are: polycarbonates, polyurethanes, silicones, polytetrafluoroethylene, carboxymethyl cellulose and propylene oxide.

6 . 4 . Use as a Weapon

Poison gas in World War I :

Chlorine gas, also known as **bertholite**, was first used as a weapon in World War I by Germany on April 22, 1915 in the Second Battle of Ypres. As described by the soldiers it had a distinctive smell of a mixture between pepper and pineapple. It also tasted metallic and stung the back of the throat and chest. Chlorine can react with water in the mucosa of the lungs to form hydrochloric acid, an irritant which can be lethal. The damage done by chlorine gas can be prevented by a gas mask, or other filtration method, which makes the overall chance of death by chlorine gas much lower than those of other chemical weapons. It was pioneered by a German scientist later to be a Nobel laureate, Fritz Haber of the Kaiser Wilhelm Institute in Berlin, in collaboration with the German chemical conglomerate IG Farben, who developed methods for discharging chlorine gas against an entrenched enemy. It is alleged that Haber's role in the use of chlorine as a deadly weapon drove his wife, Clara Immerwahr, to suicide. After its first use, chlorine was utilized by both sides as a chemical weapon, but it was soon replaced by the more deadly gases phosgene and mustard gas .

Iraq War 2007

Chlorine gas has also been used by insurgents against the local population and coalition forces in the Iraq War in the form of Chlorine bombs. On March 17, 2007, for example, three chlorine filled trucks were detonated in the Anbar province killing two and sickening over 350 . Other chlorine bomb attacks resulted in higher death tolls, with more than 30 deaths on two separate occasions.[38] Most of the deaths were caused by the force of the explosions rather than the effects of chlorine, since the toxic gas is readily dispersed and diluted in the atmosphere by the blast. The Iraqi authorities have tightened up security for chlorine, which is essential for providing safe drinking water for the population.

6 .5 . Chlorine Cracking

The element is widely used for purifying water owing to its powerful oxidizing properties, especially potable water supplies and water used in swimming pools. Several catastrophic collapses of swimming pool ceilings have occurred owing to stress corrosion cracking of stainless steel rods used to suspend them.[*citation needed*] Some polymers are also sensitive to attack, including acetal resin and polybutene. Both materials were used in hot and cold water domestic supplies, and stress corrosion cracking caused widespread failures in the USA in the 1980s and ' 90s. One example shows an acetal joint in a water supply system, which when it fractured, caused substantial physical damage to computers in the labs below the supply. The cracks started at injection molding defects in the joint and grew slowly until finally triggered. The fracture surface shows iron and calcium salts which were deposited in the leaking joint from the water supply before failure .

6 . 6 Other uses

Chlorine is used in the manufacture of numerous organic chlorine compounds, the most significant of which in terms of production volume are 1,2 – dichloro ethane and vinyl chloride, intermediates in the production of PVC. Other particularly important organochlorines are methyl chloride, methylene chloride, chloroform, vinylidene chloride, trichloroethylene, perchloroethylene, allyl chloride, epichloro hydrin , chloro benzene, dichloro benzenes and tri chloro benzenes.

Chlorine is also used in the production of chlorates and in bromine extraction.

7 . Health effects

Chlorine is a toxic gas that irritates the respiratory system. Because it is heavier than air, it tends to accumulate at the bottom of poorly ventilated spaces. Chlorine gas is a strong oxidizer, which may react with flammable materials .

Chlorine is detectable in concentrations of as low as 1 ppm. Coughing and vomiting may occur at 30 ppm and lung damage at 60 ppm. About 1000 ppm can be fatal after a few deep breaths of the gas . Breathing lower concentrations can aggravate the respiratory system, and exposure to the gas can irritate the eyes .

Chlorine's toxicity comes from its oxidizing power. When chlorine is inhaled at concentrations above 30ppm it begins to react with water and cells which change it into hydrochloric acid (H Cl) and hypo chlorous acid (H Cl O) .

When used at specified levels for water disinfection, although chlorine reaction with water itself usually doesn't represent a major concern for human health, other materials present in the water can generate disinfection by - products that can damage human health .

Chloric acid

Chloric acid , $HClO_3$, is an oxoacid of chlorine, and the formal precursor of chlorate salts. It is a strong acid ($pK_a \approx -1$) and oxidizing agent . It is prepared by the reaction of sulfuric acid with barium chlorate, the insoluble barium sulfate being removed by precipitation :

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow 2H\,ClO_3 + Ba\,SO_4$$

Another method is the heating of hypo chlorous acid, of which productions include chloric acid and hydrogen chloride:

$$3H\,ClO \rightarrow H\,ClO_3 + 2\,H\,Cl$$

It is stable in cold aqueous solution up to a concentration of approximately 30 %, and solution of up to 40 % can be prepared by careful evaporation under reduced pressure. Above these concentrations, and on warming, chloric acid solutions decompose to give a variety of products, for example :

$$8\,H\,ClO_3 \rightarrow 4\,H\,ClO_4 + 2H_2O + 2\,Cl_2 + 3\,O_2$$
$$3\,H\,ClO_3 \rightarrow H\,ClO_4 + H_2O + 2\,ClO_2$$

The decomposition is controlled by kinetic factors: indeed, chloric acid is never thermo dynamically stable with respect to disproportionation .

Other Names	Chloric (V) acid
Molecular Formula	$H\,ClO_3$
Molar Mass	84.5 g mol^{-1}
Appearance	Colourless solution
Density	1 g / mL , solution
Solubility in Water	> 40 g / 100 ml (20 °C)
Acidity (pK_a)	*ca.* −1
Main hazards	Oxidant

Chlorous acid

1 . Introduction :

Chlorous acid is a chemical compound with the formula $HClO_2$ It is a weak acid. Chlorine possesses oxidation state +3 in this acid. The pure substance is unstable, disproportionating to hypo chlorous acid (Cl oxidation state +1) and chloric acid (Cl oxidation state +5) :

$$2\ H\ ClO_2\ (aq) \rightarrow H\ ClO\ \ (aq) + H\ ClO_3\ (aq)$$

Chlorite salts such as sodium chlorite are stable conjugate bases derived from this acid. These salts are sometimes used in the production of chlorine dioxide.

2 . Preparation

$HClO_2$ can be prepared through reaction of barium chlorite and dilute sulfuric acid:

$$Ba\ (\ ClO_2\ )_2 + H_2\ SO_4 \rightarrow Ba\ SO_4 + 2\ H\ ClO_2$$

3 . Stability

Chlorine is the only one of the four halogens to form an isolable acid of formula HXO_2 . Fluorine does not have the bonding capacity to do so, whereas the hypothetical bromous acid and iodous acid have never been isolated and only a few salts of bromous acid, bromites, are known, and no iodites .

Molecular Formula	$H\ Cl\ O_2$
MolarMass	68.5 g / mol
Acidity (pK_a)	1.96

Hydro Chloric Acid

Contents

1 . Introduction :

Hydro chloric acid is the solution of hydrogen chloride (HCl) in water. It is a highly corrosive, strong mineral acid and has major industrial uses. It is found naturally in gastric acid.

Historically called **muriatic acid** or **spirits of salt** , hydro chloric acid was produced from vitriol and common salt. The alchemist Jabir ibn Hayyan first formally described it in the eighth century. During the Middle Ages, it was used by alchemists in the quest for the philosopher's stone, and later by European scientists including Glauber, Priestley, and Davy in their scientific research .

With major production starting in the Industrial Revolution, hydrochloric acid is used in the chemical industry as a chemical reagent in the large-scale production of vinyl chloride for PVC plastic, and MDI / TDI for polyurethane. It has numerous smaller - scale applications, including household cleaning, production of gelatin and other food additives , de caling , and leather processing. About 20 million metric tones of hydrochloric acid are produced annually .

Other Names	Muriatic acid , Spirit (s) of Salt , Chlorane
Molecular Formula	HCl in water (H_2O)
Molar Mass	36.5 g / mol (HCl)
Appearance	Clear colorless to light - yellow liquid
Density	1.18 g / cm^3
Melting point	− 27.32 °C , 38 % solution.
Boiling point	110 °C , 20.2 % solution; 48 °C , 38 % solution.
Solubility in Water	Miscible
Acidity (pK_a)	− 8.0
Viscosity	1.9 mPa·s at 25 °C , 31.5 % solution
EU Classification	Corrosive (**C**)

2 . **History**

Hydrochloric acid was first discovered around A.D. 800 by the alchemist Jabir ibn Hayyan (Geber) , by mixing common salt with sulfuric acid (" vitriol ") . Jabir discovered many important chemicals, and recorded his findings in over twenty books, which carried his chemical knowledge of hydrochloric acid and other basic chemicals for hundreds of years. Jabir's invention of the gold-dissolving aqua regia, consisting of hydrochloric acid and nitric acid, was of great interest to alchemists searching for the philosopher's stone.

In the Middle Ages, hydrochloric acid was known to European alchemists as *spirits of salt* or *acidum salis* (salt acid). Both names are still deployed, notably in non - English languages, such as

German: *Salzsäure* and Dutch : *Zoutzuur*. Gaseous HCl was called *marine acid air*. The old (pre - systematic) name *muriatic acid* has the same origin (*muriatic* means "pertaining to brine or salt") , and this name is still sometimes used. Notable production was recorded by Basilius Valentinus, the alchemist-canon of the Benedictine priory Sankt Peter in Erfurt, Germany, in the fifteenth century. In the seventeenth century, Johann Rudolf Glauber from Karlstadt am Main, Germany, used sodium chloride salt and sulfuric acid for the preparation of sodium sulfate in the Mannheim process, releasing hydrogen chloride gas. Joseph Priestley of Leeds, England prepared pure hydrogen chloride in 1772, and in 1818 Humphry Davy of Penzance, England, proved that the chemical composition included hydrogen and chlorine .

During the Industrial Revolution in Europe, demand for alkaline substances increased. A new industrial process by Nicolas Leblanc (Is soundun , France) enabled cheap large - scale production of sodium carbonate (soda ash) . In this *Leblanc process* , common salt is converted to soda ash, using sulfuric acid, limestone, and coal, releasing hydrogen chloride as a by -product. Until the British Alkali Act 1863 and similar legislation in other countries , the excess HCl was vented to air. After the passage of the act, soda ash producers were obliged to absorb the waste gas in water, producing hydrochloric acid on an industrial scale .

In the twentieth century, the Leblanc process was effectively replaced by the Solvay process without a hydrochloric acid by-product. Since hydrochloric acid was already fully settled as an important chemical in numerous applications, the commercial interest initiated other production methods, some of which are still used today. After 2000 , hydrochloric acid is mostly made by absorbing by-product hydrogen chloride from industrial organic compounds production .

Since 1988, hydrochloric acid has been listed as a Table II precursor under the 1988 United Nations Convention Against Illicit Traffic in Narcotic Drugs and Psychotropic Substances because of its use in the production of heroin, cocaine, and methamphetamine.[6]

3 . Chemistry

Acid titration:

Hydrogen chloride (HCl) is a mono protic acid, which means it can dissociate (*i.e.,* ionize) only once to give up one H^+ ion (a single proton) . In aqueous hydrochloric acid, the H^+ joins a water molecule to form a hydronium ion, H_3O^+ :

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

The other ion formed is Cl^-, the chloride ion. Hydrochloric acid can therefore be used to prepare salts called *chlorides,* such as sodium chloride. Hydrochloric acid is a strong acid, since it is essentially completely dissociated in water .

Monoprotic acids have one acid dissociation constant, K_a, which indicates the level of dissociation in water. For a strong acid like HCl, the K_a is large. Theoretical attempts to assign a K_a to HCl have been made . When chloride salts such as Na Cl are added to aqueous HCl they have practically no effect on pH, indicating that Cl^- is an exceedingly weak conjugate base and that H Cl is fully dissociated in aqueous solution. For intermediate to strong solutions of hydrochloric acid, the assumption that H^+ molarity (a unit of concentration) equals HCl molarity is excellent, agreeing to four significant digits .

Of the seven common strong mineral acids in chemistry, hydrochloric acid is the mono protic acid least likely to undergo an interfering oxidation - reduction reaction. It is one of the least hazardous strong acids to handle; despite its acidity, it consists of the non - reactive and non - toxic chloride ion. Intermediate strength hydrochloric acid solutions are quite stable upon storage, maintaining their concentrations over time. These attributes, plus the fact that it is available as a pure reagent, mean that hydrochloric acid makes an excellent acidifying reagent . Hydro chloric acid is the preferred acid in titration for determining the amount of bases . Strong acid titrants give more precise results due to a more distinct endpoint. Azeotropic or " constant – boiling " hydrochloric acid (roughly 20.2 %) can be used as a primary standard in quantitative analysis, although its exact concentration depends on the atmospheric pressure when it is prepared . Hydrochloric acid is frequently used in chemical analysis to prepare (" digest ") samples for analysis. Concentrated hydrochloric acid dissolves many metals and forms oxidized metal chlorides and hydrogen gas, and it reacts with basic compounds such as calcium carbonate or copper (II) oxide, forming the dissolved chlorides that can be analyzed .

4 . Physical properties

The physical properties of hydrochloric acid, such as boiling and melting points, density, and pH depend on the concentration or molarity of H Cl in the acid solution. They range from those of water at very low concentrations approaching 0% HCl to values for fuming hydrochloric acid at over 40 % HCl .

Concentration			Density	Molarity	Viscosity	Specific heat	Vapor pressure	Boiling point	Melting point
kg HCl / kg	kg HCl/m^3	Baumé	Kg / l	Mol / dm^3	mPa·s	kJ / (kg · K)	Pa	° C	° C
10 %	104.80	6.6	1.048	2.87	1.16	3.47	0.527	103	− 18
20 %	219.60	13	1.098	6.02	1.37	2.99	27.3	108	− 59
30 %	344.70	19	1.149	9.45	1.70	2.60	1,410	90	− 52
32 %	370.88	20	1.159	10.17	1.80	2.55	3,130	84	− 43
34 %	397.46	21	1.169	10.90	1.90	2.50	6,733	71	− 36
36 %	424.44	22	1.179	11.64	1.99	2.46	14,100	61	− 30
38 %	451.82	23	1.189	12.39	2.10	2.43	28,000	48	−26

Hydro chloric acid as the binary (two – component) mixture of HCl and H_2O has a constant - boiling azeo trope at 20.2 % HCl and 108.6 °C . There are four constant - crystallization eutectic points for hydrochloric acid, between the crystal form of $HCl·H_2O$ (68 % HC), $HCl·2H_2O$ (51 % HCl), $HCl·3H_2O$ (41% HCl), $HCl·6H_2O$ (25 % HCl), and ice (0 % HCl). There is also a meta stable eutectic point at 24.8 % between ice and the $HCl·3H_2O$ crystallization .

5 . Production

Hydro chloric acid is prepared by dissolving hydrogen chloride in water. Hydrogen chloride can be generated in many ways, and thus several precursors to hydro chloric acid exist. The large - scale production of hydro chloric acid is almost always integrated with the industrial scale production of other chemicals .

5 . 1 . Industrial market

Hydrochloric acid is produced in solutions up to 38 % HCl (concentrated grade). Higher concentrations up to just over 40 % are chemically possible, but the evaporation rate is then so high that storage and handling need extra precautions, such as pressure and low temperature. Bulk industrial-grade is therefore 30 % to 34 %, optimized for effective transport and limited product loss by HCl vapors. Solutions for household purposes in the US, mostly cleaning, are typically 10 % to 12 %, with strong recommendations to dilute before use. In the United Kingdom, where it is sold as " Spirits of Salt " for domestic cleaning, the potency is the same as the US industrial grade .

Major producers worldwide include Dow Chemical at 2 million metric tones annually (2 Mt / year) , calculated as HCl gas, and FMC, Georgia Gulf Corporation, Tosoh Corporation, Akzo Nobel , and Tessenderlo at 0.5 to 1.5 Mt / year each. Total world production, for comparison purposes expressed as HCl, is estimated at 20 Mt / year, with 3 Mt / year from direct synthesis, and the rest as secondary product from organic and similar syntheses. By far, most hydro chloric acid is consumed captively by the producer. The open world market size is estimated at 5 Mt/year .

6 . Applications

Hydrochloric acid is a strong inorganic acid that is used in many industrial processes. The application often determines the required product quality .

6 . 1 . Pickling of steel

One of the most important applications of hydrochloric acid is in the pickling of steel, to remove rust or iron oxide scale from iron or steel before subsequent processing, such as extrusion, rolling, galvanizing, and other techniques. Technical quality HCl at typically 18 % concentration is the most commonly used pickling agent for the pickling of carbon steel grades .

$$Fe_2 O_3 + Fe + 6 H Cl \rightarrow 3 Fe Cl_2 + 3 H_2O$$

The spent acid has long been re-used as iron (II) chloride (also known as ferrous chloride) solutions, but high heavy - metal levels in the pickling liquor has decreased this practice.

The steel pickling industry has developed hydrochloric acid regeneration processes, such as the spray roaster or the fluidized bed HCl regeneration process, which allow the recovery of HCl from spent pickling liquor. The most common regeneration process is the pyro hydrolysis process, applying the following formula :

$$4 Fe Cl_2 + 4 H_2O + O_2 \rightarrow 8 HCl + 2 Fe_2O_3$$

By recuperation of the spent acid, a closed acid loop is established . The iron (III) oxide by - product of the regeneration process is valuable, used in a variety of secondary industries.[3]

6 . 2 . Production of organic compounds

Another major use of hydro chloric acid is in the production of organic compounds such as vinyl chloride for PVC. This is often captive use, consuming locally produced hydro chloric acid that never actually reaches the open market. Other organic compounds produced with hydro chloric acid include bisphenol A for poly carbonate, activated carbon, and ascorbic acid, as well as numerous pharmaceutical products .

$2 CH_2 = CH_2 + 4 HCl + O_2 \rightarrow 2 Cl CH_2 CH_2 Cl + 2 H_2O$
(vinyl chloride by oxy chlorination)
wood + HCl + heat → activated carbon (chemical activation)

6 . 3 . Production of inorganic compounds

Numerous products can be produced with hydrochloric acid in normal acid - base reactions, resulting in inorganic compounds. These include water treatment chemicals such as iron (III) chloride and poly aluminium chloride (PAC) .

$$Fe_2 O_3 + 6 HCl \rightarrow 2 Fe Cl_3 + 3 H_2O$$

(iron (III) chloride from magnetite)

Both iron (III) chloride and PAC are used as flocculation and coagulation agents in sewage treatment , drinking water production , and paper production.

Other inorganic compounds produced with hydrochloric acid include road application salt calcium chloride, nickel (II) chloride for electroplating, and zinc chloride for the galvanizing industry and battery production .

$$Ca CO_3 + 2 HCl \rightarrow Ca Cl_2 + CO_2 + H_2O$$

(calcium chloride from limestone)

6 . 4 . pH Control and neutralization

Hydrochloric acid can be used to regulate the basicity (pH) of solutions.

$$OH^- + H Cl \rightarrow H_2 O + Cl^-$$

In industry demanding purity (food , pharmaceutical , drinking water) , high - quality hydrochloric acid is used to control the pH of process water streams. In less - demanding industry, technical quality hydrochloric acid suffices for neutralizing waste streams and swimming pool treatment .

6 . 5 . Regeneration of ion exchangers

High - quality hydrochloric acid is used in the regeneration of ion exchange resins. Cation exchange is widely used to remove ions such as Na^+ and Ca^{2+} from aqueous solutions, producing demineralized water . The acid is used to rinse the cations from the resins .

Na^+ is replaced by H^+
Ca^{2+} is replaced by 2 H^+

Ion exchangers and demineralized water are used in all chemical industries, drinking water production, and many food industries

6 . 6 . Other

Hydro chloric acid is used for a large number of small - scale applications, such as leather processing, house hold cleaning , and building construction . Oil production may be stimulated by injecting hydro chloric acid into the rock formation of an oil well , dissolving a portion of the rock , and creating a large-pore structure. Oil well acidizing is a common process in the North Sea oil production industry .

Many chemical reactions involving hydro chloric acid are applied in the production of food , food ingredients , and food additives. Typical products include aspartame, fructose , citric acid , lysine , hydrolyzed vegetable protein as food enhancer , and in gelatin production . Food - grade (extra – pure) hydro chloric acid can be applied when needed for the final product .

7 . Presence in living organisms

Gastric acid is one of the main secretions of the stomach. It consists mainly of hydrochloric acid and acidifies the stomach content to a pH of 1 to 2.

Chloride (Cl^-) and hydrogen (H^+) ions are secreted separately in the stomach fundus region at the top of the stomach by parietal cells of the gastric mucosa into a secretory network called canaliculi before it enters the stomach lumen .

Gastric acid acts as a barrier against microorganisms to prevent infections and is important for the digestion of food. Its low pH denatures protein and thereby makes them susceptible to degradation by digestive enzymes such as pepsin. The low pH also activates the enzyme precursor pepsinogen into the active enzyme pepsin by self - cleavage. After leaving the stomach, the hydrochloric acid of the chyme is neutralized in the duodenum by sodium bicarbonate .

The stomach itself is protected from the strong acid by the secretion of a thick, protective mucus layer, and by secreting induced buffering with sodium bicarbonate. Heartburn or peptic ulcers can develop when these mechanisms fail. Drugs of the antihistaminic and proton pump inhibitor classes can inhibit the production of acid in the stomach, and antacids are used to neutralize existing acid .

8 . Safety

Concentrated hydrochloric acid (fuming hydrochloric acid) forms acidic mists. Both the mist and the solution have a corrosive effect on human tissue, with the potential to damage respiratory organs, eyes, skin, and intestines. Upon mixing hydrochloric acid with common oxidizing chemicals, such as sodium hypochlorite (bleach, NaClO) or potassium permanganate ($KMnO_4$) , the toxic gas chlorine is produced.

$$NaClO + 2\,HCl \rightarrow H_2O + NaCl + Cl_2$$

$$2\,KMnO_4 + 16\,HCl \rightarrow 2\,MnCl_2 + 8H_2O + 2\,KCl + 5\,Cl_2$$

Personal protective equipment such as rubber or PVC gloves, protective eye goggles, and chemical-resistant clothing and shoes are used to minimize risks when handling hydro chloric acid .

The hazards of solutions of hydro chloric acid depend on the concentration. The following table lists the EU classification of hydrochloric acid solutions .

The United States Environmental Protection Agency rates and regulates hydro chloric acid as a toxic substance .

Hypo Chlorous Acid

Contents

1 . Introduction :

Hypo chlorous acid is a weak acid with the chemical formula HClO. In the swimming pool industry, Hypo chlorous acid is referred to as HOCl . It forms when chlorine dissolves in water . HOCl is used as a bleach, an oxidizer, a deodorant, and a disinfectant.

Other Names	Hydrogen hypochlorite Hydrogen chlorate (I)
Molecular Formula	HClO
Molar Mass	52.5 g / mol
Appearance	Colorless aqueous solns
Density	Variable
Solubility in Water	Soluble
Acidity (pK_a)	7.497
Main hazards	Oxidizer

Addition of chlorine to water gives both hydro chloric acid HCl and hypo chlorous acid :

$$Cl_2 + H_2O = HClO + HCl$$

2 . Production Using Electrolysis

Solutions of hypo chlorites can be produced by electrolysis of an aqueous chloride solution. Chlorine gas is produced at the anode, while hydrogen forms at the cathode. Some of the chlorine gas produced will dissolve forming hypochlorite ions through the above reaction. The geometry of the cell is critical to ensure that as much of the chlorine as possible dissolves, rather than simply bubbling out of the cell.

At the anode : $2\ Cl^- \ \text{--->}\ Cl_2 (g) + 2e^-$

At the cathode : $2H^+ + 2e^- \ \text{--->}\ H_2 (g)$

It can be seen that over time, the electrolyte will become increasingly basic.

There are a number of potential hazards and challenges associated with this process. It should not be attempted by untrained persons.

- The electrochemical environment of the cell is highly corrosive, particularly at the anode. Few materials are suitable as an anode electrolyte. Graphite can be used, but will degrade quickly (which also results in contamination of the cell with finely divided carbon particles). Graphite supported lead dioxide electrodes have been reported to be more effective.
- If the reaction conditions are not controlled, the produced hypochlorite can react with the hydroxide ions to form chlorate ions. These can additionally be electrochemically oxidized to perchlorate ions (within the same cell) .
- Hypochlorite is a powerful oxidizing agent, and will attack the dyes used in pH paper and damage pH sensors, making measurement and control of the conditions difficult.

- Hydrogen gas is highly flammable, and can form explosive mixtures with both air and chlorine over a wide range of concentrations.
- Chlorine gas is highly toxic and corrosive.

3 . Uses

In organic synthesis , HOCl converts alkenes to chloro hydrins .

In biology, hypo chlorous acid is generated in activated neutrophils by myelo peroxidase - mediated per oxidation of chloride ions, and contributes to the destruction of bacteria and this is used in water treatment such as the acid being the active sanitizer in hypochlorite - based swimming pool products.

4 . Chemical reactions

In aqueous solution, hypo chlorous acid partially dissociates into the anion *hypochlorite* O Cl $^-$:

$$H\,ClO\ Ocl^- + H^+$$

Salts of hypo chlorous acid are also called **hypo chlorites**. One of the best - known hypo chlorites is Na ClO , the active ingredient in bleach. In the presence of sunlight, hypo chlorous acid decomposes into hydro chloric acid and oxygen, so this reaction is sometimes seen as :

$$2\,Cl_2 + 2\,H_2O\ \ 4\,HCl + O_2$$

H ClO is considered to be a stronger oxidant than chlorine.

HClO reacts with HCl to form chlorine gas :

$$HClO + HCl \rightarrow H_2O + Cl_2$$

4 . 1 . Reactivity of HClO with bio molecules

Hypo chlorous acid reacts with a wide variety of biomolecules including DNA, RNA , fatty acid groups, cholesterol and proteins .

4 . 1 . 1 . Reaction with protein sulfhydryl groups

Knox et al . first noted that HClO is a sulfhydryl inhibitor that, in sufficient quantity, could completely inactivate proteins containing sulfhydryl groups. This is because HClO oxidises sulfhydryl groups, leading to the formation of disulfide bonds[23] that can result in crosslinking of proteins. The HClO mechanism of sulfhydryl oxidation is similar to that of chloramine, and may only be bacteriostatic, because, once the residual chlorine is dissipated, some sulfhydryl function can be restored . One sulfhydryl-containing amino acid can scavenge up to four molecules of HOCl . Consistent with this, it has been proposed that sulfhydryl groups of sulfur-containing amino acids can be oxidized a total of three times by three HClO molecules, with the fourth reacting with the α-amino group. The first reaction yields sulfenic acid (R - SOH) then sulfinic acid ($R-SO_2H$) and finally $R - SO_3H$. Each of those intermediates can also condense with another sulfhydryl group, causing cross-linking and aggregation of proteins. Sulfinic acid and $R - SO_3H$ derivatives are produced only at high molar excesses of HClO , and disulfides are formed primarily at bacteriocidal levels . Disulfide bonds can also be oxidized by HClO to sulfinic acid . Because the oxidation of sulfhydryls and disulfides evolves hydrochloric acid, this process results in the depletion HClO.

4 . 1 . 2 . Reaction with protein amino groups

Hypo chlorous acid reacts readily with amino acids that have amino group side - chains, with the chlorine from HClO displacing a hydrogen, resulting in an organic chloramine . Chlorinated amino acids rapidly decompose, but protein chloramines are longer-lived and retain some oxidative capacity. Thomas et al . concluded from their results that most organic chloramines decayed by internal rearrangement and that fewer available NH2 groups promoted attack on the peptide bond, resulting in cleavage of the protein. McKenna and Davies found that 10 mM or greater H ClO is necessary to fragment proteins in vivo. Consistent with these results, it was later proposed that the chloramine undergoes a molecular rearrangement, releasing HCl and ammonia to form an amide . The amide group can further react with another amino group to form a Schiff base, causing cross - linking and aggregation of proteins .

4 . 1 . 3 . Reaction with DNA and Nucleotides

Hypochlourous acid reacts slowly with DNA and RNA as well as all nucleotides in vitro . GMP is the most reactive because HClO reacts with both the heterocyclic NH group and the amino group. In similar manner, TMP with only a heterocyclic NH group that is reactive with H ClO is the second-most reactive. AMP and CMP, which have only a slowly reactive amino group are less reactive with HClO . UMP has been reported to be reactive only at a very slow rate . The heterocyclic NH groups are more reactive than amino groups, and their secondary chloramines are able to donate the chlorine.[9] These reactions likely interfere with DNA base pairing, and, consistent with this, Prütz has reported a decrease in viscosity of DNA exposed to HClO similar to that seen with heat denaturation. The sugar moieties are unreactive and the DNA back bone is not broken . NADH can react with chlorinated TMP and UMP as well as HClO. This reaction can regenerate UMP and TMP and results in the 5 - hydroxy derivative of NADH. The reaction with TMP or UMP is slowly reversible to regenerate H ClO. A second slower reaction that results in cleavage of the pyridine ring occurs when excess HClO is present. NAD + is inert to H ClO .

4 . 4 . 1 . Reaction with lipids

Hypochlorous acid reacts with unsaturated bonds in lipids, but not saturated bonds, and the OCl^- ion does not participate in this reaction. This reaction occurs by hydrolysis with addition of chlorine to one of the carbons and a hydroxyl to the other. The resulting compound is a chlorhydrin. The polar chlorine disrupts lipid bilayers and could increase permeability. When chlorhydrin formation occurs in lipid bilayers of red blood cells, increased permeability occurs. Disruption could occur if enough chlorhydrin is formed. The addition of preformed chlorhydrins to red blood cells can affect permeability as well. Cholesterol chlorhydrins have also been observed, but do not greatly affect permeability, and it is believed that Cl_2 is responsible for this reaction .

5 . Mode of disinfectant action

Escherichia coli exposed to hypo chlorous acid lose viability in less than 100 ms due to inactivation of many vital systems . Hypo chlorous acid has a reported LD_{50} of 0.0104 ppm - 0.156 ppm and 2.6 ppm caused 100 % growth inhibition in 5 minutes . However it should be noted that the concentration required for bactericidal activity is also highly dependent on bacterial concentration .

5 . 1 . Inhibition of glucose oxidation

In 1948, Knox et al . proposed the idea that inhibition of glucose oxidation is a major factor in the bacteriocidal nature of chlorine solutions. He proposed that the active agent or agents diffuse across the cyto plasmic membrane to inactivate key sulfhydryl-containing enzymes in the glycolytic pathway. This group was also the first to note that chlorine solutions (H OCl) inhibit sulfhydryl enzymes. Later studies have shown that, at bacteriocidal levels, the cytosol components do not react with HOCl . In agreement with this, McFeters and Camper found that aldolase, an enzyme that Knox et al. proposes would be inactivated, was unaffected by H OCl in vivo. It has been further shown that loss of sulfhydryls does not correlate with inactivation . That leaves the question concerning what causes inhibition of glucose oxidation. The discovery that H OCl blocks induction of β - galactosidase by added lactose led to a possible answer to this question. The uptake of radio labeled substrates by both ATP hydrolysis and proton co-transport may be blocked by exposure to H OCl preceding loss of viability. From this observation, it proposed that H OCl blocks uptake of nutrients by inactivating transport proteins . The question of loss of glucose oxidation has been further explored in terms of loss of respiration. Venkobachar et al. found that succinic dehydrogenase was inhibited in vitro by H OCl, which led to the investigation of the possibility that disruption of electron transport could be the cause of bacterial inactivation. Albrich et al . subsequently found that H OCl destroys cyto chromes and iron-sulfur clusters and observed that oxygen uptake is abolished by H OCl and adenine nucleotides are lost. Also observed was, that irreversible oxidation of cyto chromes paralleled the loss of respiratory activity. One way of addressing the loss of oxygen uptake was by studying the effects of HOCl on succinate dependent electron transport.[37] Rosen et al.[31] found that levels of reductable cyto chromes in H Ocl - treated cells were normal, and these cells were unable to reduce them. Succinate dehydrogenase was also inhibited by H Ocl , stopping the flow of electrons to oxygen. Later studies revealed that Ubiquinol oxidase activity ceases first, and the still - active cyto chromes reduce the remaining quinone. The cytochromes then pass the electrons to oxygen, which explains why the cytochromes cannot be reoxidized, as observed by Rosen et al. However, this line of inquiry was ended when Albrich et al . found that cellular inactivation precedes loss of respiration by using a flow mixing system that allowed evaluation of viability on much smaller time scales. This group found that cells capable of respiring could not divide after exposure to H OCl.

5 . 2 . Depletion of adenine nucleotides

Having eliminated loss of respiration Albrich et al . proposes that the cause of death may be due to metabolic dysfunction caused by depletion of adenine nucleotides. Barrette et al.[34] studied the loss of adenine nucleotides by studying the energy charge of H OCl - exposed cells and found that cells exposed to H OCl were unable to step up their energy charge after addition of nutrients. The conclusion was that exposed cells have lost the ability to regulate their adenylate pool, based on the fact that metabolite uptake was only 45 % deficient after exposure to HOCl and the observation that H OCl causes intracellular ATP hydrolysis. Also confirmed was that , at bacteriocidal levels of H OCl, cytosolic components are unaffected. So it was proposed that modification of some membrane - bound protein results in extensive ATP hydrolysis, and this, coupled with the cells inability to remove AMP from the cytosol, depresses metabolic function. One protein involved in loss of ability to regenerate ATP has been found to be ATP synthetase . Much of this research on respiration reconfirms the observation that relevant bacteriocidal reactions take place at the cell membrane .

5 . 3 . Inhibition of DNA replication

Recently it has been proposed that bacterial inactivation by HOCl is the result of inhibition of DNA replication. When bacteria are exposed to HOCl, there is a precipitous decline in DNA synthesis that precedes inhibition of protein synthesis, and closely parallels loss of viability . During bacterial genome replication, the origin of replication (oriC in *E. Coli*) binds to proteins that are associated with the cell membrane, and it was observed that H OCl treatment decreases the affinity of extracted membranes for oriC , and this decreased affinity also parallels loss of viability. A study by Rosen et al.[40] compared the rate of H OCl inhibition of DNA replication of plasmids with different replication origins and found that certain plasmids exhibited a delay in the inhibition of replication when compared to plasmids containing oriC. Rosen’s group proposed that inactivation of membrane proteins involved in DNA replication are the mechanism of action of H OCl .

5 . 4 . Protein Unfolding and Aggregation

H OCl is known to cause post-translational modifications to proteins, notably cysteine and methionine oxidation. A recent examination of H OCl's bactericidal role revealed it to be a potent inducer of protein aggregation. Hsp 33 , a chaperone known to be activated by oxidative heat stress, protects bacteria from the effects of H OCl by acting as a holdase , effectively preventing protein aggregation. Strains of E. coli and Vibrio cholerae lacking Hsp 33 were rendered especially sensitive to H OCl . Hsp 33 protected many essential proteins from aggregation and inactivation due to H OCl, which is a probable mediator of H OCl's bactericidal effects .

6 . Safety

HOCl is a strong oxidizer and can form explosive mixtures.

Per chloric acid

Contents

1 . Introduction :

Per chloric acid , $HClO_4$, is an oxoacid of chlorine and is a colorless liquid soluble in water. It is a strong acid comparable in strength to sulfuric and nitric acids. It is useful for preparing per chlorate salts, but it is also dangerously corrosive and readily forms explosive mixtures.

Molecular Formula	$HClO_4$
Molar Mass	100.5 g / mol
Appearance	Colorless liquid
Density	1.67 g / cm^3
Melting Point	−112 °C
Boiling Point	19 °C (decomp)
Solubility in Water	Miscible
EU Classification	Oxidant (**O**) Corrosive (**C**)

2 . Production

Per chloric acid is produced by treatment of sodium perchlorate with sulfuric acid and by the electrochemical oxidation of aqueous chlorine.

3 . Acidity

Perchloric acid is a superacid, and one of the strongest Brønsted - Lowry acids. Its pK_a is −10 .

Anhydrous per chloric acid is an oily liquid. It forms a series of at least five hydrates, several of which have been characterized crystallographically. The dihydrate is representative: the solid consists of the per chlorate anion linked to H_2O and H_3O^+ centers via hydrogen bonds. Per chloric acid forms an azeotrope with water, consisting of about 72.5 % per chloric acid. This form of the acid is stable indefinitely and is commercially available. Such solutions are hygroscopic, that is, if left unsealed, concentrated acid dilutes itself by absorbing water from the air.

4 . Laboratory preparation

The concentrated acid can be prepared by distillation of a solution of sodium per chlorate in concentrated sulfuric acid.

$$\mathrm{Na\ ClO_4 + H_2SO_4 \rightarrow Na\ HSO_4 + H\ ClO_4}$$

In a related method, barium per chlorate reacts with dilute sulfuric acid to precipitate barium sulfate, leaving per chloric acid. It also can be made by mixing nitric acid with ammonium per chlorate. The reaction gives nitrous oxide and per chloric acid due to a concurrent reaction involving the ammonium ion.

5 . Safety

Anhydrous and monohydrated perchloric acid are explosive, but the usual aqueous solutions are stable in the absence of organic compounds. It is very corrosive to skin and eyes. Upon contact with perchloric acid, organic materials such as cloth and wood ignite. Salts of perchloric acid are also powerful oxidizers that can be explosive. Perchlorate salts tend to be more stable than their chlorate counterparts, which has led to their increased use in pyrotechnic compositions due to safety concerns.

Due to these hazards, per chloric acid is usually handled under fume hoods with wash - down and air scrubbing capabilities that are not available on standard laboratory fume hoods. The crystalline form of the acid, which is explosive and shock sensitive, can precipitate on hood surfaces; washing down the hood interior returns any crystalline form to solution, thus eliminating the explosion hazard.