HYDROGEN CHLORIDE

1. History and Occurrence

Hydrogen chloride [7647-01-0], HCl, exists in solid, liquid, and gaseous states and is very soluble in water. The aqueous solution, hydrochloric acid, owes its name to Davy whose studies in 1810 of chlorine and its compounds proved that the gas consists of only hydrogen and chlorine. The term muriatic acid, proposed by Lavoisier in 1789, to indicate the presence of chlorine in an inorganic compound, is used in the U.S. industry to refer to the commercial forms of hydrochloric acid. Similarly, the arbitrary specific gravity scale devised in the eighteenth century by the French chemist Baumé (°Bé) is still used to characterize the commercial grades of the acid, whereas the Twaddell density scale (°Tw) is less commonly used. The relationship between these density scales and the concentration of three standard grades of hydrochloric acid is summarized in Table 1.

Hydrogen chloride was discovered in the fifteenth century by the German alchemist Basilius Valentinus who treated the green vitriol, $FeSO_4 \cdot 7H_2O$, and common salt and obtained what was then called spirit of salt (1). In the seventeenth century, Glauber prepared hydrochloric acid from common salt [7647-14-5]

Table 1. **Density and Concentration of Commercial Grades of Hydrochloric Acid**

	Density unit[a]		
Specific gravity	°Bé	°Tw	HCl,%
1.1417	18	28.34	27.92
1.1600	20	32.00	31.45
1.1789	22	35.78	35.21

[a] $[145/(145-°Be)] = (0.005°\mathrm{Tw} + 1) =$ specific gravity.

and sulfuric acid [7664-93-9]. Commercial production of hydrochloric acid began in England in 1823. However in 1863, legislation was passed prohibiting the indiscriminate discharge of waste hydrogen chloride from the crude scrubbers into the atmosphere. This legislation forced manufacturers to develop uses for the HCl generated in the Leblanc process for soda ash which involved reaction between NaCl and H_2SO_4. The industrial synthesis of hydrogen chloride followed the development of the chlor-alkali electrolytic process early in the twentieth century (see CHLORINE). The route involving direct combination of H_2 and Cl_2, produced electrolytically, and the chemical routes based on reaction between alkali metal and/or alkaline-earth chlorides and H_2SO_4 or $NaHSO_4$, were used to produce high purity hydrochloric acid. However, as of the mid-1990s, these processes are becoming obsolete because of the large amounts of hydrogen chloride generated as by-product from several manufacturing processes, a typical example being, the industrial production of chlorinated hydrocarbons (see CHLOROCARBONS AND CHLOROHYDROCARBONS, SURVEY).

Hydrochloric acid is found naturally in the gases evolved from volcanoes, particularly those in Mexico and South America. Its formation is attributed to the high temperature reaction of water with the salts found in seawater. The original atmosphere of the earth is considered to have contained water (qv), carbon dioxide (qv), and hydrogen chloride in the ratio of 20:3:1, giving an early ocean consisting of about 1*N* HCl, which dissolved the crustal minerals, leading to the ocean salinity. Hydrogen chloride was also detected in the atmosphere of the planet Venus. The dissociation of HCl is considered the source of chlorine detected in the spectra of distant stars.

Hydrochloric acid is also present in the digestive system of most mammals (2). The gastric mucosa lining the human stomach produces about 1.5 L/d of gastric juices, containing an acid concentration in the range of 0.05 to 0.1 *N*. A deficiency of hydrochloric acid impairs the digestive process, particularly of carbohydrates and proteins, and excess acid causes gastric ulcers.

2. Physical and Thermodynamic Properties

2.1. Anhydrous Hydrogen Chloride.

Anhydrous hydrogen chloride is a colorless gas that condenses to a colorless liquid and freezes to a white crystalline solid. The physical and thermodynamic properties of HCl are summarized in Table 2 for selected temperatures and pressures. Figure 1 shows the temperature dependence of some of these properties.

The high thermal stability of hydrogen chloride is a consequence of the large enthalpy of its formation. The calculated percent dissociation at different temperatures is given in Table 3. The dissociation of gaseous hydrogen chloride into its elements is important for selecting proper materials of construction, because of the formation of free chlorine which is highly corrosive in the presence of moisture.

The dielectric constant of liquid hydrogen chloride is low relative to other solvents having similar ionization characteristics, and many organic compounds form conducting solutions in liquid hydrogen chloride. The narrow temperature range of the liquid phase, −94 to −85°C at atmospheric pressure, and the low

Table 2. **Physical and Thermodynamic Properties of Anhydrous Hydrogen Chloride**

Property	Value
melting point, °C	−114.22
boiling point, °C	−85.05
heat of fusion at −114.22°C, kJ/mol[a]	1.9924
heat of vaporization at −85.05°C, kJ/mol[a]	16.1421
entropy of vaporization, J/(mol · K)[a]	85.85
triple point, °C	−114.25
critical temperature, T_c, °C	51.54
critical pressure, P_c, MPa[b]	8.316
critical volume, V_c L/mol	0.069
critical density, g/L	424
critical compressibility factor, Z_c	0.117
ΔH°_f at 198 K, kJ/mol[a]	−92.312[c]
	−100.4[d]
ΔG°_f at 298 K, kJ/mol[a]	−95.303
S° at 298 K, J/(mol · K)[a]	186.786
dissociation energy at 298 K, kJ[a]	431.62[c]
	427.19[d]
compressibility coefficient	0.00787
internuclear separation, nm	0.12510
dipole moment, C · m[e]	3.716[c]
	3.74[d]
ionization potential, J[a]	20.51[c]
	20.45[d]
heat capacity, C_p, J/(mol · K)[a]	
vapor (constant pressure)	
at 273.16 K	29.162
at 973.2 K	30.554
liquid at 163.16 K	60.378
solid at 147.16 K	48.98
surface tension at 118.16 K, mN/cm(=dyn/cm)	23
viscosity, mPa · s(=cP)	
liquid at 118.16 K	0.405
vapor at 273.06 K	0.0131
vapor at 523.2 K	0.0253
thermal conductivity, mW/(m · K)	
liquid at 118.16 K	335
vapor at 273.16 K	13.4
density, g/cm^3	
liquid	
at 118.16 K	1.045
at 319.15 K	0.630
solid	
rhombic at 81 K	1.507
cubic at 98.36 K	1.48
cubic at 107 K	1.469
refractive index	
liquid at 283.16 K	1.254
gas at 273.16 K	1.0004456
dielectric constant	
liquid at 158.94 K	14.2
gas at 298.16 K	1.0046

Table 2 (*Continued*)

Property	Value
electrical conductivity, $(\Omega \cdot m)^{-1}$	
at 158.94 K	1.7×10^{-7}
at 185.56 K	3.5×10^{-7}

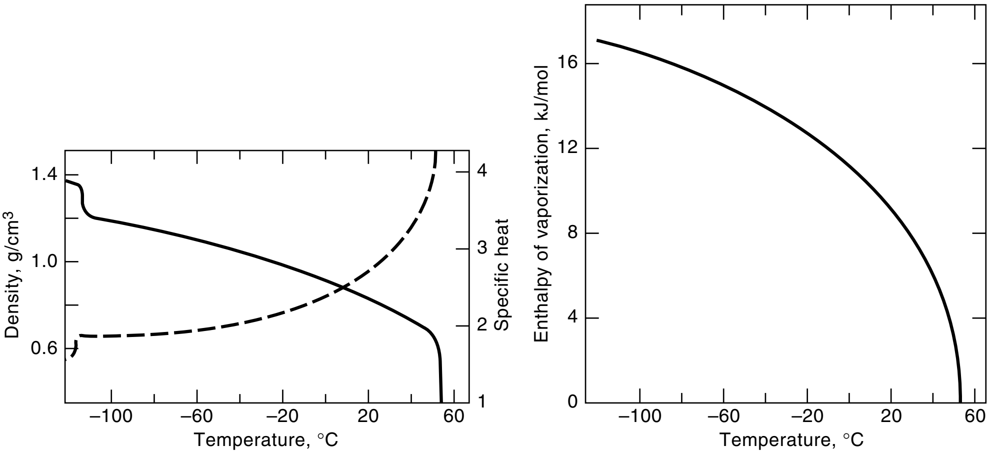
[a] To convert J to cal, divide by 4.184.
[b] To convert MPa to atm, divide by 0.101.
[c] Measured value.
[d] Calculated value. See Refs. 3 and 4.
[e] To convert $C \cdot m$ to debye, divide by 3.34×10^{-30}.

temperatures required for liquefaction (triple point = −114.25°C), however, severely limit studies in solutions of liquid hydrogen chloride. The liquid vapor pressure, P, from 160 to 260 K is given by

$$\log P = -905.53\, T^{-1} = 1.75 \log T - 0.0050077\, T + 3.78229$$

where P is in kPa and T is in Kelvin.

The entropy value of gaseous HCl is a sum of contributions from the various transitions summarized in Table 4. Independent calculations based on the spectroscopic data of $H^{35}Cl$ and $H^{37}Cl$ separately, show the entropy of HCl at 298 K to be 186.686 and 187.372 J/(mol·K) (44.619 and 44.783 cal/(mol·K), respectively. The low temperature (rhombic) phase is ferroelectric (6). Solid hydrogen chloride consists of hydrogen-bonded molecular crystals consisting of zigzag chains having an angle of 93.5° (6). Proton nmr studies at low temperatures have also shown the existence of a dimer $(HCl)_2$ (7).



(a) **(b)**

Fig. 1. (**a**) Variation of the density (—) and specific heat (-) of liquid HCl with temperature; (**b**) enthalpy of vaporization of HCl (5). To convert J to cal, divide by 4.184.

Table 3. **Thermal Stability of Gaseous Hydrogen Chloride**

Temperature, K	Log K_p	Dissociation, %
298	16.70	4.5×10^{-7}
473	10.70	4.5×10^{-4}
673	7.648	1.5×10^{-2}
873	5.981	0.10
1073	4.929	0.342
1273	4.205	0.73
1773	3.099	2.74
2273	2.461	5.55
2773	2.039	8.73
4000	1.59	14.7

Temperature dependence of viscosity of the gas over a wide range of temperatures is given by equation 1 where T is in Kelvin and η_0 is the value of η at 273 K.

$$\eta = \eta_0 (T/273.1)^{1.03} \tag{1}$$

Gaseous diffusion and thermal diffusion data may be found in References 8 and 9.

The vapor pressure of solid and liquid hydrogen chloride is described by equations 2 and 3, respectively,

$$\log p = -911.31\ \mathrm{T}^{-1} + 2.1875 + 4.313 \times 10^{-3}\mathrm{T} \tag{2}$$

$$\log p = -8.555 \times 10^{-1} + 2.553 \tag{3}$$

where p is the vapor pressure in mPa, and T the temperature in Kelvin. These equations are accurate over a wide temperature range (10). Temperature dependence of specific heat, C_p, for hydrogen chloride expressed in J/(mol · K) is given

Table 4. **Components of the Entropy of Hydrogen Chloride**

Entropy change	Temp, K	Value, J/(mol · K)[a]
0 K to transition point	0–98.36	30.79
solid transition: rhombic to cubic	98.36	12.09
transition to melting point	96.36–158.94	21.13
entropy of fusion	158.94	12.55
melting point to boiling point	158.94–188.11	9.87
entropy of vaporization	188.11	85.86
vapor	188.11–298	14.48
Total	*298*	*186.77*

[a] To convert J to cal, divide by 4.184.

Table 5. **Solubility of Hydrogen Chloride in Water**[a]

Temperature, °C	Solubility, g HCl/100 g solution	H_2O in vapor, mol%
−18.3	48.98	
−15	48.27	
−10	47.31	0.0070
0	45.15	0.0178
10	44.04	0.0460
20	42.02	0.1230
30	40.22	0.2850
40	38.68	0.6350
50	37.34	
60	35.94	

[a] At 101.3 kPa (1 atm).

by equation 4 (see Fig. 1a) (11).

$$C_p = 28.1663 + 1.8096 \times 10^{-3}\, T + 15.4692 \times 10^{-7}\, T^2 \qquad (4)$$

The value of the specific heat at constant pressure and constant volume is 1.404 at 0°C.

2.2. Hydrogen Chloride–Water System. Hydrogen chloride is highly soluble in water and this aqueous solution does not obey Henry's law at all concentrations. Solubility data are summarized in Table 5. The relationship between the pressure and vapor composition of unsaturated aqueous hydrochloric acid solutions is given in Reference 12. The vapor–liquid equilibria for the water–hydrogen chloride system at pressures up to 1632 kPa and at temperatures ranging from −10 to +70°C are documented in Reference 13.

Hydrogen chloride and water form four hydrates. The dihydrate is formed when a saturated solution is cooled at atmospheric pressure. It dissociates at −18.3°C in open vessels and has a melting point of −17.7°C in a sealed tube. The structure has been shown by x-ray analysis to be $(H_2O)_2H^+Cl^-$ (14). The monohydrate has a melting of −15.35°C; the trihydrate has a melting point of −24.9°C; the hexahydrate is very unstable and has a melting point of −70°C (14). Addition of hydrogen chloride to pure water lowers the freezing point until a eutectic temperature of about −85°C is reached at 25% HCl, a concentration that closely corresponds to the composition of the hexahydrate. Continued addition of HCl raises the freezing point first to that of the trihydrate and subsequently to that of the dihydrate (see Fig. 2).

Hydrogen chloride and water form constant boiling mixtures. The properties of these mixtures, determined with great accuracy, and often used as analytical standards (16), are summarized in Table 6 and graphically depicted in Figure 3.

An equation of state of the form $PV = RT$ was developed (17) for the vapor of concentrated and dilute hydrochloric acid which is valid up to a HCl mole fraction, x, of 0.23, at temperatures up to 780 K and pressures up to 15.0 MPa. A

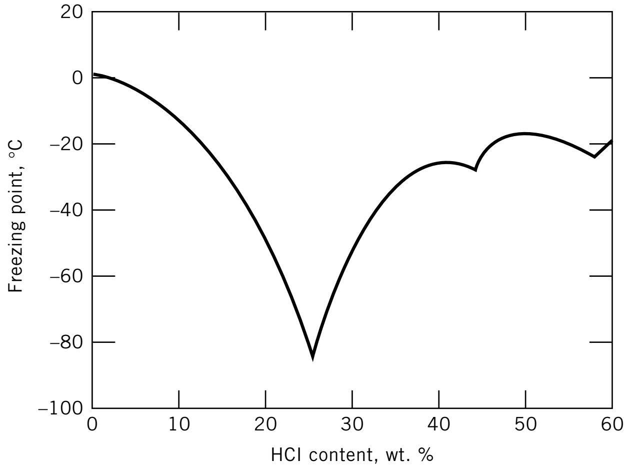


Fig. 2. Freezing point of aqueous solutions of HCl (15).

simplified Redlich-Kwong equation,

$$PV = RT + BP \tag{5}$$

where $B = b - aT^{1.5}R^{-1}$, and $a/(\mathrm{cm}^6 \cdot \mathrm{Pa} \cdot \mathrm{K}^{0.5} \cdot \mathrm{mol}^2) = 3283 - 4035\mathrm{x}_{\mathrm{HCl}}$; $b/(\mathrm{mol} \cdot \mathrm{cm}^3) = 139.8 - 218.4x_{\mathrm{HCl}}$; and $R = 8.3143\ \mathrm{MPa} \cdot \mathrm{cm}^3/(\mathrm{mol} \cdot \mathrm{K}))$, was found to describe these data. The saturation line is defined by equation 6 where P is in kPa and T is in Kelvin.

$$\log_{10}P = 3.515 - 2056T^{-1} + x_{\mathrm{HCL}}(2.064 - 988T^{-1}) \tag{6}$$

Hydrogen chloride is completely ionized in aqueous solutions at all but the highest concentrations. Thermodynamic functions have been determined

Table 6. **Properties of Constant Boiling Hydrochloric Acid**

Pressure, kPa[a]	Boiling point, °C	Density at 25°C	HCl, wt%
6.7	48.724	1.1118	23.42
33	81.205	1.1042	21.883
66	97.578	1.0993	20.916
93	106.424	1.0966	20.360
97		1.0963	20.293
101	108.584	1.0959	20.222
104			20.173
106	110.007	1.0955	20.155
133	116.185	1.0933	19.734

[a] To convert kPa to mm Hg, multiply by 7.5.

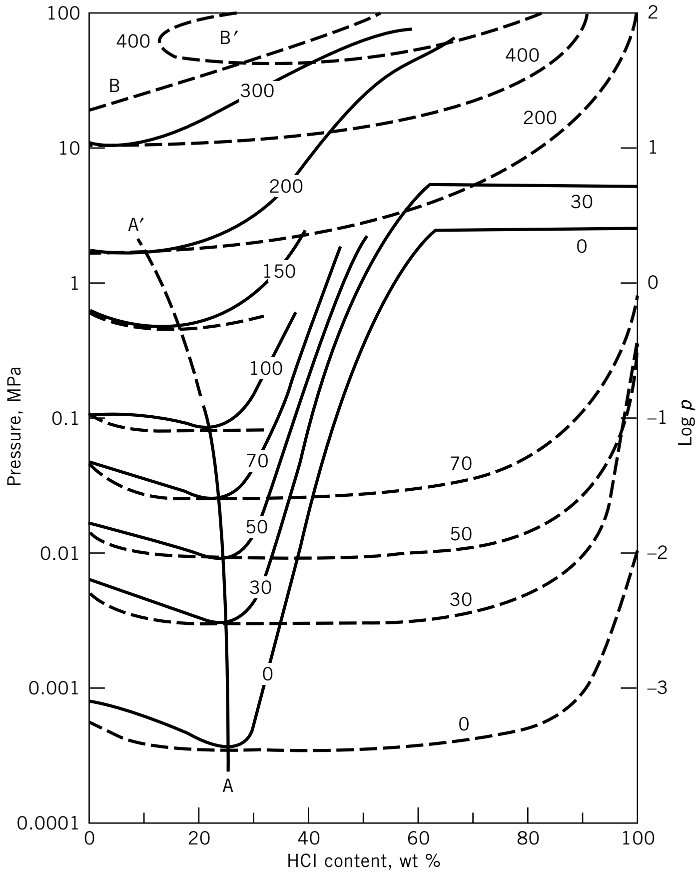


Fig. 3. Vapor–liquid-phase diagram for the HCl–H_2O system (5) where (‐) represents the demarcation between the two-phase region and the gas phase; (—) denotes the demarcation of the two-phase region from the liquid phase; and the numbers associated with the curves correspond to temperatures in °C. A–A′ connects the azeotropic points and B–B′ represents the critical segregation curve above the critical point of water, ie, point B occurs at 341.1°C at 21.43 MPa.

electrochemically for equations 7 and 8. Values are given in Table 7.

$$\mathrm{HCl(g)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} \qquad (7)$$

$$\mathrm{HCl(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} \qquad (8)$$

The viscosity of hydrochloric acid solutions, η, increases slightly with increasing concentration and is related to the molar concentration c by

$$(\eta - \eta_0)\eta_0 = 0.0030 + 0.0625\,c^{0.5} + 0.0008c \qquad (9)$$

where η_0 is the viscosity of the water, 0.8904 mPa · s(=cP) at 25°C. The surface tension of dilute hydrochloric acid solutions is very close to that of water

Table 7. **Thermodynamic Functions of Aqueous Hydrochloric Acid**

	Value	
Property[a]	equation 7	equation 8
ΔH°, kJ/mol	−74.852	−57.32
ΔG°, kJ/mol	−35.961	−39.7
ΔS°, J/(mol·K)	−130.33	−56.53

[a] To convert J to kcal, divide by 4.184.

(71.97 mN/m · (=dyn/cm) at 25°C) and decreases slightly as the concentration of HCl increases.

The variation of the dielectric constant of the $HCl + H_2O$ mixtures is not appreciably different from that of pure water (78.30) at 25°C until the hydrogen chloride concentration reaches a minimum of 0.2%. It increases slightly over the dielectric constant of water as the concentration increases.

The specific heat of aqueous solutions of hydrogen chloride decreases with acid concentration (Fig. 4). The electrical conductivity of aqueous hydrogen

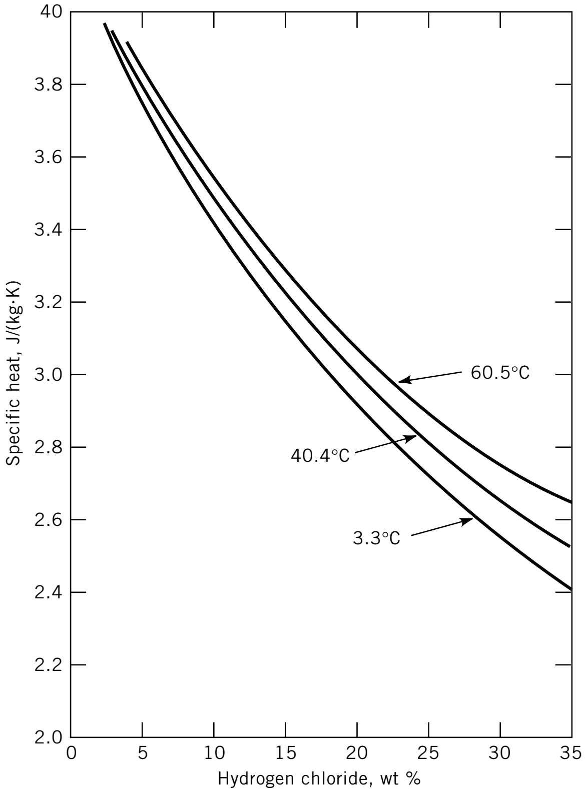


Fig. 4. Specific heat of aqueous solutions of hydrogen chloride.

Table 8. **Equivalent Conductivity of Hydrochloric Acid**

Concentration, wt%	Equivalent conductivity, $(\Omega \cdot cm)^{-1}$	
	25°C	65°C
0	426.2	666.8
0.91	377.4	578.2
3.58	332.3	509.2
7.90	270.0	416.3
13.60	200.1	310.8
20.66	134.7	209.5
28.63	83.5	130.0

chloride increases with temperature. Equivalent conductivity of these solutions are summarized in Table 8. Other physicochemical data related to HCl may be found in the literature (5).

2.3. Hydrogen Chloride–Water–Inorganic Compound Systems.

Salts. Salting out metal chlorides from aqueous solutions by the common ion effect upon addition of HCl is utilized in many practical applications. Typical data for ferrous chloride [13478-10-9], $FeCl_2$, potassium chloride [7447-40-7], KCl, and NaCl are shown in Table 9. The properties of the $FeCl_2 \cdot HCL \cdot H_2O$ system are important to the steel-pickling industry (see METAL SURFACE TREATMENTS, CASE HARDENING; STEEL). Other metal chlorides that are salted out by the addition of hydrogen chloride to aqueous solutions include those of magnesium, strontium, and barium.

Metal chlorides which are not readily salted out by hydrochloric acid can require high concentrations of HCl for precipitation. This property is used to recover hydrogen chloride from azeotropic mixtures. A typical example is the calcium chloride [10043-52-4] addition used to break up the HCl—H_2O azeotrope

Table 9. **Dependence of Solubility of Metal Chlorides on Hydrogen Chloride Concentration in Aqueous Solutions**

Concentration of HCl, wt%	Temperature, °C	Solubility of M_xCl_y, wt%
	Ferrous chloride	
3	21.5	34.0
12	22.7	20.6
20	22.1	10.6
	Potassium chloride	
0	25.0	26.8
11.5	25.0	9.59
21.8	25.0	1.92
	Sodium chloride	
0	25.0	26.46
11.1	25.0	10.63
17.1	25.0	4.73

and permit recovery of HCl gas by distillation (see DISTILLATION, AZEOTROPIC, AND EXTRACTIVE).

Salts of acids other than hydrochloric acid commonly show increased solubility in hydrochloric acid. This phenomenon has been explained by the Debye-Hückel theory for strong electrolytes (17–19).

Chlorine. The solubility of chlorine [7782-50-5] in hydrochloric acid is an important factor in the purification of by-product hydrochloric acid. The concentration of chlorine in solution, S, is proportional to the partial pressure of chlorine, ρ, in the gas phase and follows Henry's law, $S = Hp$, in the temperature range of 30–90°C, and at partial pressures of chlorine of <101.3 kPa (1 atm) for HCl concentrations varying in the range of 2–10 N. Henry's coefficient, H, is a function of temperature and HCl concentration, C, as expressed by equation 10:

$$H = \alpha C + B \tag{10}$$

where

$$\log \alpha = -1.21 \times 10^{-2} T - 1.603 \tag{11}$$

and

$$B = 2.14 \times 10^{2} T^{-1.21} \tag{12}$$

The units for B are g/L Cl_2 at 101 kPa (1 atm) and the unitless α represents the ratio of the concentration in g/L of Cl_2 to HCl at atmospheric pressure. The temperature is expressed in degrees Celsius. The empirical equation for the Gibbs free energy change was found to be linear with temperature for ΔG° in kJ/mol, T in Kelvin.

$$\Delta G^\circ = 8.983 + 0.121T \tag{13}$$

The entropy change of 121J/(mol·K) (28.9 cal/(mol·K)) is temperature independent.

The effect of pressure on the solubility of chlorine in hydrochloric acid has been reported for pressures varying from about 100 to 6500 kPa (1–6.5 atm) (20). At pressures above 200 kPa, there is a linear dependence of pressure on the solubility in the acid concentration range of 0.1–5.0 N.

2.4. Hydrogen Chloride-Organic Compound Systems. The solubility of hydrogen chloride in many solvents follows Henry's law. Notable exceptions are HCl in polyhydroxy compounds such as ethylene glycol (see GLYCOLS, OTHER GLYCOLS), which have characteristics similar to those of water. Solubility data of hydrogen chloride in various organic solvents are listed in Table 10.

3. Chemical Properties

3.1. Reactions of Anhydrous Hydrogen Chloride. *Inorganic Compounds.* Hydrogen chloride reacts with inorganic compounds by either heterolytic or homolytic fission of the H—Cl bond. However, anhydrous HCl

Table 10. **Solubilities of Hydrogen Chloride in Common Solvents**[a]

	Solubility, mol HCl/mol solvent		
Compound	0°C	20°C	Other[b]
water	0.409	0.3578	
dimethylformamide	2.41		
diethyl ether	1.123	0.67	
methanol	0.92	0.74	
ethanol	0.97	0.82	
2-propanol	1.00	0.83	
n-octanol	1.00		
ethyl acetate	0.73	0.49	
propyl acetate	0.76	0.53	
acetic acid		0.14	
benzene	0.065	0.039	
octane		0.029	
dodecane		0.031	
1,1,1-trichloroethane		0.031	
1,1,2,2-tetrachloroethane		0.027	
hexane		0.017	
n-hexadecane			0.024_{29} 0.014_{102} 0.010_{177}
toluene		0.054	
diisopropyl ether			0.978_{10}
dibutyl ether			0.893_{10}
dioxane			1.046_{10}
tetrahydrofuran			1.284_{10}
chloroform			0.028_{15} 0.023_{25}
carbon tetrachloride		0.025	 0.016_{50}

[a] Ref. 5.

[b] Temperatures in °C given as subscript.

has high kinetic barriers to either type of fission and hence, this material is relatively inert.

Reactions with Salts of Main Group Anions. Anhydrous HCl protonates the Group 15 (V) hydrides, MH_3, where M = N, P, and As (see HYDRIDES).

$$MH_3 + HCl \longrightarrow MH_4^+ + Cl^- \qquad (14)$$

Reactions of HCl and nitrides, borides, silicides, germanides, carbides, and sulfides take place at significant rates only at elevated (≥650°C) temperatures. The products are the metal chlorides and the corresponding hydrides. The reactions most studied are those involving nitrides of aluminum, magnesium, calcium, and titanium, where ammonia (qv) is formed along with the corresponding metal chloride.

The reaction of HCl and silicon, germanium, and boron hydrides is catalyzed by aluminum chloride and is useful for preparing chloro-substituted silanes and germanes.

$$MH_4 + HCl \longrightarrow MH_3Cl + H_2 \tag{15}$$

$$MH_3Cl + HCl \longrightarrow MH_2Cl_2 + H_2 \tag{16}$$

Reaction with Metal Oxides. The reaction of hydrogen chloride with the transition-metal oxides at elevated temperatures has been studied extensively. Fe_2O_3 reacts readily at temperatures as low as 300°C to produce $FeCl_3$ and water. The heavier transition-metal oxides require a higher reaction temperature, and the primary reaction product is usually the corresponding oxychlorides. Similar reactions are reported for many other metal oxides, such as Sb_2O_3, BeO, Al_2O_3, and TiO_2, which lead to the formation of relatively volatile chlorides or oxychlorides.

Reaction with Metals. Thermodynamic considerations for the reaction

$$M + nHCl \longrightarrow MCl_n + n/2H_2 \tag{17}$$

indicate that most metals should react with HCl. However, this reaction is kinetically slow at all but elevated temperatures. The reaction of the vapors of sodium and potassium metals has been reported (21). Hydrogen chloride reacts with powdered silicon at 250°C to give $SiHCl_3$ and $SiCl_4$ (22).

Reaction with Oxidizing Agents. Hydrogen chloride and oxygen react in the gaseous state to liberate chlorine:

$$4\,HCl + O_2 \longrightarrow 2\,Cl_2 + 2\,H_2O \tag{18}$$

The rate of this reaction is significantly enhanced over catalysts such as copper chloride which is the basis for the Deacon process for producing Cl_2 from HCl. The relationship between the equilibrium constant K_p and the temperature in Kelvin for the reaction is expressed by equation 19.

$$\log K_p = 5500/T - 4.31\ \log T + 0.0015T + 5.18 \tag{19}$$

The Weldon-Pechiney process for manufacturing Cl_2 from HCl involves the use of MnO_2 as the oxidizing agent instead of the O_2 employed in the Deacon reaction.

Reaction with Other Inorganic Halogen Compounds. Anhydrous HCl forms addition compounds at lower temperatures with halogen acids such as HBr and HI, and also with HCN. These compounds are stable at room temperature.

Reaction with Oxyacids and Salts. Hydrogen chloride reacts with sulfur trioxide yielding liquid chlorosulfuric acid [7790-94-5].

$$HCl + SO_3 \longrightarrow ClSO_3H \tag{20}$$

The reaction can also be carried out with oleum, distilling the chlorosulfuric acid as it forms. Reaction with oxidizing oxyacids such as HNO_3 liberates chlorine.

Anhydrous sulfates of the heavy metals form addition compounds with HCl that can be released by heating the complex to elevated temperatures. The complex $CuSO_4 \cdot 2HCl$ has been used for storage and transport of HCl (23).

Reaction with Organic Compounds. Addition to Olefins and Acetylenes. Hydrogen chloride adds to carbon–carbon double and triple bonds in a variety of organic compounds. Both 1,2- and 1,4-additions are possible with conjugated dienes. The specific orientation follows the Markonikov rule, which states that halogen attaches itself to the site having lower electron density. This reaction was initially used to make vinyl chloride from acetylene and hydrogen chloride but has since been replaced by oxychlorination (or oxyhydrochlorination) technology, using ethylene (qv) and HCl (or chlorine) as the raw materials. Oxychlorination accounts for more consumption of HCl than any other process (21–26).

Acetylene and hydrogen chloride historically were used to make chloroprene [126-99-8]. The olefin reaction is used to make ethyl chloride from ethylene and to make 1,1-dichloroethane from vinyl chloride. 1,1-Dichloroethane is an intermediate to produce 1,1,1-trichloroethane by thermal (26) or photochemical chlorination (27) routes.

Replacement of Aliphatic Hydroxyl with Chloride. Lower alcohols such as methanol (qv) can be converted to the corresponding alkyl chlorides by carrying out the reaction

$$ROH + HCl \longrightarrow RCL + H_2O \tag{21}$$

using either a liquid (28) or a solid catalyst (29). The generally used liquid catalyst is zinc chloride although ferric chloride has been used in the past. Solid catalysts include metal chlorides deposited on a carrier such as carbon, silica gel, pumice, alumina, polyphosphoric acids, and activated alumina. In the case of higher alcohols, catalysts such as zinc chloride are used to promote the reaction in the liquid phase.

Chloromethylation Reactions. The introduction of the chloromethyl group to both aliphatic and aromatic compounds is carried out by reaction of paraformaldehyde [30525-89-4] and hydrogen chloride. This method is used for synthesizing methyl chloromethyl ether [107-30-2], benzyl chloride [100-44-7], and chloromethyl acetate.

3.2. Hydrochloric Acid.

Reaction with Inorganic Compounds. Most metals and alloys react with aqueous hydrochloric acid via

$$M + nH_3O^+ \longrightarrow M^{n+} + nH_2O + n/_2H_2 \tag{22}$$

This is essentially a corrosion reaction involving anodic metal dissolution where the conjugate reaction is the hydrogen (qv) evolution process. Hence, the rate depends on temperature, concentration of acid, inhibiting agents, nature of the surface oxide film, etc. Unless the metal chloride is insoluble in aqueous solution eg, Ag or Hg^{2+}, the reaction products are removed from the metal or alloy surface by dissolution. The extent of removal is controlled by the local hydrodynamic conditions.

Oxides and hydroxides react with HCl to form a salt and water as in a simple acid–base reaction. However, reactions with low solubility or insoluble oxides and hydroxides is complex and the rate is dependent on many factors similar to those for reactions with metals. Oxidizing agents such as H_2O_2, H_2SeO_4, and V_2O_5 react with aqueous hydrochloric acid, forming water and chlorine.

Electrolytic Processes. HCl can be electrolyzed to produce H_2 and chlorine.

$$2\,HCl \longrightarrow H_2 + Cl_2 \tag{23}$$

Electrolytic cells for this reaction are manufactured by Hoechst-Uhde (see ELECTROCHEMICAL PROCESSING, INORGANIC) (30,31).

Reaction with Organic Compounds. Many organic reactions are catalyzed by acids such as HCl. Typical examples of the use of HCl in these processes include conversion of lignocellulose to hexose and pentose, sucrose to inverted sugar, esterification of aromatic acids, transformation of acetaminochlorobenzene to chloroanilides, and inversion of methone [1074-95-9].

4. Manufacturing and Processing

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.

4.1. Synthesis from Hydrogen and Chlorine. Less than 10% of the U.S. production capacity of HCl is made by the direct reaction of the elements.

$$H_2 + Cl_2 + \longrightarrow 2\,HCl + 184\ \text{kJ}\ (44\ \text{kcal}) \tag{24}$$

Because this reaction is highly exothermic, the equilibrium flame temperature for the adiabatic reaction with stoichiometric proportions of hydrogen and chlorine can reach temperatures up to 2490°C where the equilibrium mixture contains 4.2% free chlorine by volume. This free hydrogen and chlorine is completely converted by rapidly cooling the reaction mixture to 200°C. Thus, by properly controlling the feed gas mixture, a burner gas containing over 99% HCl can be produced. The gas formed in the combustion chamber then flows through an absorber/cooler to produce 30–32% acid. The HCl produced by this process is known as burner acid.

Commercially, the burner chamber and the absorber cooler sections are combined as a single unit for small-scale production. However, in large capacity plants, these units are separated. A typical commercial unit is schematically described in Figure 5 (32).

In general, silica has proved to be a good material of construction for the burner. Cast iron, steel, or graphite was sometimes used. Gaseous HCl produced by this method is very pure and can be used to manufacture pure hydrochloric acid by the adiabatic absorption process (33) or falling film absorption process (34).

4.2. Decomposition of Metal Chlorides by Acids. Two commercial processes employing the acidic decomposition of metal chlorides are the salt–

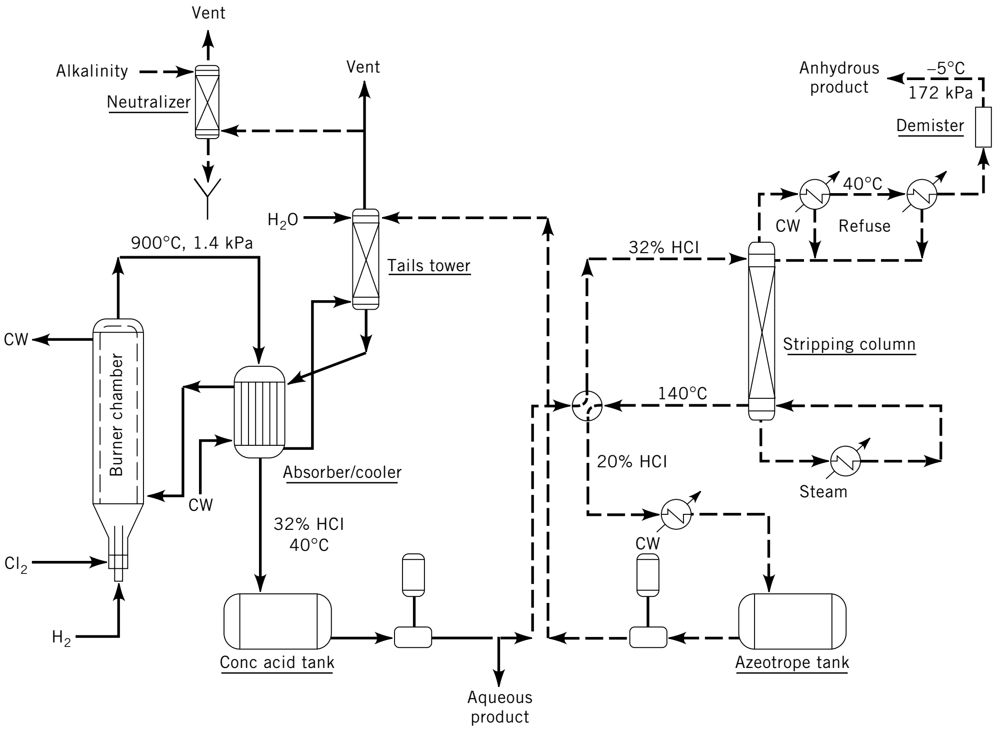


Fig. 5. Schematic of the process of producing HCl from H_2 and Cl_2 where CW denotes cold water (32). To convert kPa to psig, multiply by 0.145.

sulfuric acid process and the Hargreaves process. Although these processes are declining in importance, they are used mainly because of the industrial demand for salt cake [7757-82-6] by the paper (qv) and Glass (qv) industries. In the United States, however, little HCl is produced this way.

The Salt–Sulfuric Acid Process. The reaction between NaCl and sulfuric acid occurs in two stages, both endothermic.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \tag{25}$$

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl \tag{26}$$

The first of these reactions takes place at temperatures of about 150°C, the second reaction proceeds at about 550–660°C. Typical furnaces used to carry out the reaction include cast-iron retorts; the Mannheim mechanical furnace, which consists of an enclosed stationary circular muffle having a concave bottom pan and a domed cover; and the Laury furnace, which employs a horizontal two-chambered rotating cylinder for the reaction vessel. The most recent design is the cannon fluid-bed reactor in which the sulfuric acid vapor is injected with the combustion gases into a fluidized bed of salts. The Mannaheim furnace has also been used with potassium chloride as the feed.

The Hargreaves Process. This process, which follows the scheme given by equation 27, is exothermic.

$$4\,\mathrm{NaCl} + 2\,\mathrm{SO_2} + \mathrm{O_2} + 2\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{Na_2SO_4} + 4\,\mathrm{HCl} \qquad (27)$$

This reaction is self-sustaining without the need for additional heating once the reactants are heated to 430–450°C; 10–12% HCl is produced by this process as compared to 30–60% HCl from the Mannheim furnace process.

4.3. 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 (qv), and the manufacture of phosphoric acid [7664-38-2] and esters of phosphoric acid (see PHOSPHORIC ACIDS AND PHOSPHATES).

4.4. 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 noncatalytic processes have been developed (34–37) to treat these wastes to produce hydrogen chloride (see HAZARDOUS WASTE INCINERATORS).

4.5. 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% H_2O 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. The stripped acid which is close to the azeotropic composition, is recycled to the absorber.

Stripping is accomplished by dehydration using sulfuric acid (38), lithium chloride [7447-41-8] (39), and tertiary amines containing from 14–32 carbon atoms in an organic solvent immiscible with water followed by thermal treatment of the HCl–organic complex (40).

4.6. Purification.

Anhydrous Hydrogen Chloride. Gaseous HCl from all the manufacturing processes described invariably contains moisture, and sometimes organic species. H_2SO_4 drying can be used to remove small amounts of water, reducing the residual water content to less than 0.02%. If the water content is high, it can be removed as concentrated hydrochloric acid by cooling the gas mixture before drying with sulfuric acid. Addition of chlorosulfuric acid to this stream reduces the water content to less than 10 ppm (41). This mixture also removes unsaturated organics such as ethylene and vinyl chloride (42) and certain organic compounds such as monochloroacetic acid (43).

Chlorine can be removed by either activated carbon adsorption or by reaction with olefins such as ethylene over-activated carbon at temperatures of 30−200°C (44). Addition of liquid high boiling paraffins can reduce the chlorine content in the HCl gas to less than 0.01% (45).

Solid absorbents generally remove the organics from HCl. Polystyrene foam is effective for removal of aromatic compounds (46) and synthetic zeolites have been used for removal of toluene and chlorosilane (47). Activated carbon is effective for removal of chloroacetylene (48). Low boiling organic compounds can be removed by scrubbing HCl using a high boiling organic liquid (49) and low boiling unsaturated organics such as ethylene and vinyl chloride can be converted to high boiling saturates by reaction with HCl in the presence of $AlCl_3$ (50). These reaction products can be removed by Adsorption (qv) on granulated activated carbon. Because HCl has a lower boiling point than any of the organic impurities present, impurities such as $COCl_2$ and CCl_4 can be removed by compressing and cooling the gas to partially or completely liquefy the HCl (51). A two-stage solvent scrubbing process, having solvents resistant to chlorination such as CCl_4 and C_4Cl_6 (52), can also be used for purifying crude HCl gas containing both chlorine and chlorocarbons.

Crude HCl recovered from production of chlorofluorocarbons by hydrofluorination of chlorocarbons contains unique impurities which can be removed by processes described in References 53−62. $ClCN{-}Cl_2$ mixtures generated by reaction of hydrogen cyanide and Cl_2 during the synthesis of $(ClCN)_3$ can be removed from the by-product HCl, by fractional distillation and recycling (see CYANIDES) (59).

Hydrochloric Acid. Use of air or purified HCl gas as stripper is practiced to remove volatile dissolved organics and chlorine from aqueous HCl (63). Coalescing and decanting is needed for complete removal of suspended organics (64). A countercurrent stripping system is recommended to minimize the loss of hydrogen chloride (65). Whereas residual organics and chlorine can be removed by adsorption on activated carbon, aromatic impurities have also been removed from hydrochloric acid by extraction with a liquid paraffin (66). By-product HCl from chloroflurocarbon processes contains residual hydrogen fluoride which can be removed from the acid by contacting with a $CaCl_2$ solution (67) or with activated alumina or silica gel (68) (see FLUORINE COMPOUNDS, ORGANIC).

4.7. Materials of Construction. *Gaseous Hydrogen Chloride.* Cast iron (qv), mild steel, and steel alloys are resistant to attack by dry, pure HCl at ambient conditions and can be used at temperatures up to the dissociation temperature of HCl. The corrosion rate at 300°C is reported to be 0.25 cm/yr and no ignition point has been found for mild steel at 760°C, at which temperature HCl is dissociated to the extent of 0.2%.

When moisture films are formed, water vapor can accelerate the corrosion rate. Hence, it is necessary to maintain the temperature above the dew point of the gas mixture by at least 20°C, to prevent the formation of moisture films. A temperature of 130°C or above, at atmospheric pressure, can be used for all mixtures of HCl gas and water vapor because the azeotropic boiling point is 108.6°C. The boiling point of azeotropic mixtures can be used as a guide at other pressures (see Table 6).

HCl gas reacts with metal oxides to form chlorides, oxychlorides, and water. Therefore, all the steel equipment should be pickled to remove the oxide scales before it is put in service. Because oxidizing agents in the HCl gas such as oxygen or chlorine significantly affect the corrosion rate, it is essential that the operating temperature of the steel equipment be kept below the temperature (316°C) at which ferric chloride is vaporized from the metal surface.

Stainless steel alloys show excellent corrosion resistance to HCl gas up to a temperature of 400°C. However, these are normally not recommended for process equipment owing to stress corrosion cracking during periods of cooling and shut down. The corrosion rate of Monel is similar to that of mild steel. Pure (99.6%) nickel and high nickel alloys such as Inconel 600 can be used for operation at temperatures up to 525°C where the corrosion rate is reported to be about 0.08 cm/yr (see NICKEL AND NICKEL ALLOYS).

Anhydrous HCl is stored in liquid form under pressure at −25°C and these pressure containers are rated for 2–24 MPa (300–350 psig). The material of construction for this purpose is carbon steel which should be ductile at very low (−87°C) temperatures.

Aqueous Hydrochloric Acid. Metals. Most metals react with aqueous HCl following equation 22. The reaction rate is dependent on the concentration of the acid, oxidizing, reducing, or complexing agents, and corrosion inhibitors, in addition to the metallurgical characteristics of the material and the prevailing hydrodynamic conditions (see CORROSION AND CORROSION CONTROL).

Tantalum and zirconium exhibit the highest corrosion resistance to HCl. However, the corrosion resistance of zironium is severely impaired by the presence of ferric or cupric chlorides. Tantalum–molybdenum alloys containing more than 50% tantalum are reported to have excellent corrosion resistance (see MOLYBDENUM AND MOLYBDENUM ALLOYS) (69). Pure molybdenum and tungsten are corrosion resistant in hydrochloric acid at room temperature and also in 10% acid at 100°C but not in boiling 20% acid.

Corrosion resistance of iron can be improved by alloying with Ni, Cr, Mo, Cu, Mn, W, and Sb. A Japanese stainless steel containing, on a wt% basis, 16–18 Ni, 9–11 Cr, 6–8 Mo, 2 Mn, 1 Si, and 0.04 P is reported to exhibit good resistance to hot hydrochloric acid (70).

Nickel-based alloys have superior corrosion resistance to iron-based alloys. The only alloys recommended for hot hydrochloric acid use are Ni–Mo alloys containing 60–70% Ni and 25–33% Mo. Chlorimet (63 Ni, 32 Mo, 3 Fe) and Hastelloy (60 Ni, 28 Mo, 6 Fe) are found to be stable at all acid concentrations in the absence of air and iron chlorides. Electroless nickel, a Ni–P alloy containing 2–10% P, shows excellent resistance to hot hydrogen chloride (71). The corrosion resistance increases with phosphorus content. This coating can be deposited on cast iron, wrought iron, mild steel, stainless steels, brass, bronze, and Aluminum (qv).

Although lead chloride is moderately soluble in the acid, lead is also used occasionally in hydrochloric acid service. Addition of 6–25% Sb increases the corrosion resistance. Air and ferric chloride accelerate the corrosion. Durichlor (14.5% Si, 3% Mo, 82% Fe), a silica-based alloy, shows excellent resistance to hot hydrochloric acid in the absence of ferric chloride.

Plastics and Elastomers. Common plastics and elastomers (qv) show excellent resistance to hydrochloric acid within the temperature limits of the materials. Soft natural rubber compounds have been used for many years as liners for concentrated hydrochloric acid storage tanks up to a temperature of 60°C (see RUBBER, NATURAL). Semihard rubber is used as linings in pipe and equipment at temperatures up to 70°C and hard rubber is used for pipes up to 50°C and pressures up to 345 kPa (50 psig). When contaminants are present, synthetic elastomers such as neoprene, nitrile, butyl, chlorobutyl, hypalon, and ethylene–propylene–diene monomer (EPDM) are preferred to natural rubber. Standard plastics such as polypropylene, poly(vinyl chloride), Saran, and acrylonitrile–butadiene–styrene (ABS) show good resistance to hydrochloric acid. The fluorocarbon plastics exhibit extremely high corrosion resistance and a high upper temperature limit of operation.

Carbon and Graphite. Carbon and graphite rendered impervious with 10–15% phenolic, epoxy, or furan resin are among the most important materials for hydrochloric acid service up to 170°C. The most important applications of these materials for hydrochloric acid service are heat exchangers and centrifugal pumps.

Glass and Ceramics. Glass and ceramic-coated equipment is widely used for handling hydrochloric acid. The glass lining is normally 0.5–1.0 mm (20–40 mil) thick and can be applied to various base metals. A variety of glasses is used by different equipment fabricators and the corrosion resistance varies with the type of glass (see REFRACTORY COATINGS). Fused-cast Refractories (qv) such as alumina, silica, zirconia, and chrome alumina are also used for hydrochloric acid service for lining equipment such as brick-lined towers. Monolithic refractories have also been used for special applications such as stoneware vessels.

5. Economic Aspects

The market for hydrogen chloride in the United States, Western Europe, and Japan amounted to 16.6×10^6 tons in 2000. Hydrochloric acid is used primarily to produce chlorinated organics such as ethylene dichloride and chlorinated inorganics such as calcium chloride. Generation of HCl from 1995 to 2000 increased by 8.7% due in large part to the fluorocarbons and isocyanate sectors (72).

Table 11 gives U.S. production data for hydrochloric acid for 2002. Most manufactured HCl is captive capacity. The plants listed in Table 11 are suppliers to the merchant market, but some capacity is used in-house. More than 90% of the HCl is by-product production. The balance comes from intentional manufacturing. Most producers of by-product HCl rely on distributors to market their product (73).

Demand for HCl in 2001 was 2154 tons. Projected demand for 2005 is 2295 tons. Demand equals production plus imports less exports. Imports for 2000 equaled 69 tons, for 2005, projection is for 100 tons. Exports for 2000 equaled 50 tons, for 2005, projection is for 52 tons. Growth through 2005 is expected at the rate of 1.1%/yr (73).

Table 11. **U.S Production of HCl and their Capacities, t 100% basis**[a]

Producer	Location	Capacity; t
BASF Polymers	Geismar, La.	160
Bayer Polyurethane	Baytown, Tex.	91
Dow Chemical	Freeport, Tex.	1288
	La Port, Tex.	68
DuPont Fluoroproducts	Corpus Christi, Tex.	109
	Louisville, Ky.	68
Huntsman Polyurethanes	Geismar, La.	145
Lyondell Chemical	Lake Charles, La.	95
Pioneer Americas	Henderson, Nev.	45
Vulcan Chemicals	Whichita, Kan.	148
Small producers	43 locations	816
Total		3033

[a] Excluding data for co-product HCl that is generated and recycled in integrated ethylene dichloride/vinyl chloride monomer plants. Co-product HCl capacity at 12 vinyl chloride monomer plants equaled 4331 t.

In Western Europe, the increase in HCl was less than in the U.S. Vinyl chloride monomer production stagnated and production of chlorinated methanes and ethanes declined. The generation of HCl from salt and sulfuric acid tends to be more important in Western Europe. In Japan, production of HCl increased somewhat in the late 1990s. Supply and demand numbers should not change significantly in the future (72).

Table 12 gives an example of processing costs. As capital costs increase, operating costs decrease; those costs involved in the production of HCl by various routes are presented in Table 12 for some nominal production capacities. These data indicate the direct route from H_2 and Cl_2 to be most economic among all the technologies considered here. Details, including the assumptions involved in estimating the various costs in Table 12, may be found in the literature (74,75).

The historical price (1996–2001) of HCl was about \$125 for a high and \$65 for a low price of 22° Bé (73). Prices depend on plant location, transportation burden, and on-site demand. These factors all influence the selling price significantly, sometimes carrying zero or negative value.

6. Analytical Methods

6.1. Solution of Hydrogen Chloride.

The concentration of aqueous solutions of hydrogen chloride can be estimated from specific gravity tables for most industrial needs. HCl in aqueous solutions is determined quantitatively by volumetric analysis using standard alkali, whereas HCl in methanol or acetic acid media is estimated from conductometric titrations using standard solutions of lithium, sodium, or potassium acetate. Precise determination of chloride ion concentration in solutions containing mixtures of halides can be accomplished by differential potentiometry to determine the end point, using silver nitrate as the reagent.

Table 12. **Capital and Operating Costs[a] for HCl Production by Process[b]**

Process	Concentration, °Bé	Capacity, t × 10^3/yr	Capital cost,[c] \$ × 10^6	Net production cost,[d] \$/kg	Product cost,[e] \$/kg
		Hydrochloric acid			
direct	22	9.9	2.8	0.23	0.30
		19.9	3.9	0.19	0.24
Mannheim	22	9.9	10.5	0.34	0.61
		19.9	17.3	0.26	0.48
salt by a fluidized bed	22	9.9	7.9	0.29	0.49
		19.9	11.6	0.21	0.36
Hargreaves	22	9.9	14.1	0.42	0.78
		19.9	23.2	0.30	0.59
incineration gas	18	7.6	4.7	0.21	0.36
		15.2	6.9	0.15	0.27
spent pickle liquor	18[f]	6.6	6.2	0.32	0.55
		13.2	9.3	0.20	0.37
		Anhydrous HCl			
direct	100[f]	19.9	4.3	0.20	0.25
		33.0	5.7	0.18	0.22
incineration gas	100[f]	6.9	6.0	0.37	0.59
		13.9	9.2	0.27	0.43

[a] Materials costs employed in these estimates in \$/kg are, Cl_2, 0.10; H_2, 0.30; slaked lime, 0.044; salt, 0.02; H_2SO_4, 0.062; S, 0.064; $FeCl_3$, 1.08; ferric oxide, 0.088; Na_2SO_4, 0.044; utility costs are cooling water, 0.1¢/m^3; steam at 1 MPa (150 psig), \$7.52/t; electricity, 3¢/kWh; process water, 1.4¢/m^3; fuel oil, \$2.36/GJ; and natural gas, \$2.23/GJ.

[b] Ref. 74.

[c] Includes off sites.

[d] This includes labor costs, variable costs, overhead, taxes, and depreciation.

[e] This is a sum of the production cost and return-on-investment (ROI) before taxes at 25%/yr of total capital costs.

[f] Units are wt%.

6.2. Determination in the Atmosphere.

Trace amounts of HCl in the atmosphere are detected using krypton homologues as detectors (76), Zn, Al, and Cu kryptonates respond to HCl concentrations in the range of 97–250 ppb; or from photometric determination of NH_4Cl (77) formed by reaction of ammonia and HCl in a helium reservoir (see NOBLE-GAS COMPOUNDS). A congo red indicator for chlorimetric determination of HCl in air has been found effective for concentrations as low as 5 ppm (78). Colorimetric procedures have also been developed for determining HCl in air by absorption in water containing a suitable indicator such as methyl red. Absorption of gaseous HCl on a filter treated with KOH–triethanoloamine is used to determine the HCl in ambient air at the ppb level (79). To trap the HCl in the atmosphere, a nylon filter can also be used. The filter, after exposure to HCl, is sonicated in water to extract the HCl which is analyzed by conventional methods (80).

6.3. Determination of Impurities.

Impurities in hydrochloric acid primarily arise from the products of the manufacturing process used to produce it. Because most hydrogen chloride is a by-product of processes making chlorinated organic compounds, HCl contains a significant amount of organics. Organic compounds containing chlorine, at the ppm level, can be analyzed by the reduction of $KMnO_4$ to MnO_2 in alkaline solution (81).

Aromatic compounds can be determined from the uv absorption spectrum of the aliphatic hydrocarbon extract of the HCl sample. Organic chloride impurities which are of particular concern in food-grade hydrochloric acid, can be determined by the FDA procedure employing two extractions with cold petroleum ether to measure impurities in the 5–10 ppm range (82). Reagent-grade hydrochloric acid is generally analyzed for metallic impurities by methods such as inductively coupled plasmas (icp). Other procedures can also be used to determine trace metals at levels of 10^{-6}–10^{-7} % (83,84) (see TRACE AND RESIDUE ANALYSIS).

7. Storage and Handling

All Department of Transportation (DOT), Environmental Protection Agency (EPA), and Occupational Safety and Health Act (OSHA) rules and regulations should be reviewed prior to handling hydrochloric acid and all the regulations must be followed. All employees handling HCl must be trained to ensure that they are familiar with the appropriate materials safety data sheets and applicable regulations.

The Department of Transportation classifies HCl as a corrosive material and requires that it be transported in DOT-approved delivery vessels. Tank cars must conform to 103B, 103B-W, or DOT 111A60W5 specifications. Tank trailers must conform to DOT MC-310, MC-311, MC-312, or DOT-412 specifications with display of a corrosive placard on both sides, front, and rear of the tank. The United Nations identification number for muriatic acid is UN1789, which must appear on all shipping papers and placards.

Tables 13 and 14 list many of the typical materials of construction used in the industry and the corresponding relative resistance to hydrochloric acid (15).

8. Health and Safety Factors

Hydrogen chloride in air is an irritant, severely affecting the eye and the respiratory tract. The inflammation of the upper respiratory tract can cause edema and spasm of the larynx. The vapor in the air, normally absorbed by the upper respiratory mucous membranes, is lethal at concentrations of over 0.1% in air, when exposed for a few minutes. HCl is detectable by odor at 1–5 ppm level and becomes objectionable at 5–10 ppm. The maximum concentration that can be tolerated for an hour is about 0.01% which, even at these levels, causes severe throat irritation. The maximum allowable concentration under normal working conditions has been set at 5 ppm per OSHA and ACGIH (85).

Hydrogen chloride in the lungs can cause pulmonary edema, a life threatening condition. In order for HCl in air to reach the lungs, it must be transported

Table 13. **Corrosion Resistance of Metals to HCl**[a,b]

	HCl concentration, wt %		
Material	1–20	>20	>2[c]
aluminum 3003	NR	NR	NR
carbon-graphite, resin impregnated	A[d]	A[d]	A[d]
carbon steel 1018	NR	NR	NR
copper nickel, 90/10 or 70/30	B-NR	NR[e]	NR
Hastelloy B	A	A[f]	B[f]
Hastelloy C	A	A	C[g]
Inconel	B-NR	NR	NR
Monel	NR	NR	NR
nickel	A-B	C-NR	NR
stainless steel 303, 304, 316	NR	NR	NR
tantalum	A	A[h]	A
titanium	B-C	C-NR[i]	NR
zirconium	A[j]	A[k]	A

[a] A is little to no attack; B, good resistance; C, limited resistance; and NR, not recommended (15).
[b] At a temperature of 21°C for metals unless otherwise indicated.
[c] At a temperature of 79.4°C unless otherwise indicated.
[d] Up to 249°C.
[e] At 37 wt% HCl.
[f] Up to 100 wt% HCl.
[g] Up to 10 wt% HCl.
[h] Up to 149°C.
[i] At 39 wt% HCl.
[j] Up to 100°C.
[k] Up to 37 wt% HCl at 100°C.

either as an aerosol or as a deposit on soot particles of less than 3 μm in diameter. A procedure for the removal of 99% of the HCl from municipal waste incinerators has been developed (86). Lime is employed as a dry adsorbent which is collected in a filter bag system.

Hydrogen chloride in air can also be a phytotoxicant (87). Tomatoes, sugar beets, and fruit trees of the Prunus family are sensitive to HCl in air.

Exposure of concentrated hydrochloric acid to the skin can cause chemical burns or dermatitis. Whereas the irritation is noticed readily, the acid can be water flushed from the exposed area. Copious use of running water is the only recommended safety procedure for any external exposure. Ingestion is seldom a problem because hydrochloric acid is a normal constituent of the stomach juices. If significant quantities are accidentally swallowed, it can be neutralized by antacids.

9. Uses

Hydrogen chloride and the aqueous solution, muriatic acid, find application in many industries. In general, anhydrous HCl is consumed for its chlorine value,

Table 14. **Corrosion Resistance of Nonmetals to HCl**[a,b]

	HCl concentration, wt%		
Material	1–20	>20	>2[c]
acid-proof brick			
carbon		A[d] (499)	
fireclay		A[d] (1371)	
epoxy	A (to 21)	A[d] (21)	NR (93)
	B-C (50)	AB[e] (66)	
glass		A[d] (232)	
glass-reinforced epoxy or polyester		A (104)	
graphite		A[d] (399)	
Halar, E-CTFE	A (93)	A (to 540)	A (93)
KEL-F	A (21)	A[f] (149)	A (93)
Kynar	A (to 135)	A[f] (135)	A (to 135)
neoprene		A[d] (to 104)	
Noryl	A (93)	A[d] (93)	A[d] (93)
nylon	A[g] (21)	NR[h] (21)	NR (93)
polycarbonate	A (93)	A[i] (93)	A[i]
polyethylene			
UHMW	A (21)	A[j] (49)	A[j]
HMW	A[j] (66)	AB[k] (66)	
polypropylene	A-C (to 79)	B-NR[l] (to 62)	A-C[m]
polysulfone	A (93)	A[d] (93)	A[d] (93)
poly(vinyl chloride)	A (to 60)	A-B[j] (to 60)	NR (93)
rubber-lined carbon steel	A (to 66)	A[d] (to 66)	
Ryton	A (93)	A[d] (93)	A (93)
Teflon			
TFE	A (93)	A[f] (to 127)	A (93)
FEP	A (21)	A[f] (to 93)	A (93)
PFA	A (to 120)	A[d] (to 120)	A (93)
Tefzel, ETFE	A (21)	A[j] (106)	A (93)

[a] A is little to no attack; B, good resistance; C, limited resistance; and NR, not recommended (15).
[b] Temperatures in °C are given in parentheses.
[c] At a temperature of 79.4°C unless otherwise indicated.
[d] At 37 wt% HCl.
[e] At 50 wt% HCl.
[f] At 100 wt% HCl.
[g] At 10 wt% HCl.
[h] At >10 wt% HCl.
[i] At 20 wt% HCl.
[j] Concentrated HCl.
[k] At 40 wt% HCl.
[l] At 35 wt% HCl.
[m] To 40 wt% HCl.

whereas aqueous hydrochloric acid is often utilized as a nonoxidizing acid. The latter is used in metal cleaning operations, chemical manufacturing, petroleum well activation, and in the production of food and synthetic rubber.

Most of the HCl produced is consumed captively, ie, at the site of production, either in integrated operations such as ethylene dichloride–vinyl chloride monomer (EDC/VCM) plants and chlorinated methane plants or in separate

HCl consuming operations at the same location. Captive use of anhydrous HCl accounts for most of the total demand. Percentages of HCl use excluding ethylene dichloride production for 2001 were organic chemicals, 29%; inorganic chemicals, 12%; food processing, 11%; brine treatment, 10%; steel pickling, 8%; oil well acidulation, 4%; swimming pools, 2%, and miscellaneous, including semiconductors, catalysts, mineral processing and regeneration of ion-exchange resins used in water treatment, 24%.

9.1. Anhydrous Hydrogen Chloride. *Ethylene Dichloride and Vinyl Chloride.* In the United States, all ethylene dichloride [107-60-2] (EDC) is produced from ethylene, either by chlorination or oxychlorination (oxyhydrochlorination). The oxychlorination process is particularly attractive to manufacturers having a supply of by-product HCl, such as from pyrolysis of EDC to vinyl chloride [75-01-4] monomer (VCM), because this by-product HCl can be fed back to the oxychlorination reactor. EDC consumption follows demand for VCM. VCM is, in turn, used in the manufacture of PVC resins. Essentially all HCl generated during VCM production is recycled to produce precursor EDC (see CHLOROCARBONS AND CHLOROHYDROCARBONS, SUREVEY; VINYL ACETAL POLYMERS).

Methyl Chloride. Most of the HCl consumed in the manufacture of methyl chloride [74-87-3] from Methanol (qv) is a recycled product. The further reaction of methyl chloride with chlorine to produce higher chlorinated methanes generates significant amounts of HCl which are fed back into methyl chloride production. Another source of recycled HCl is silicone production based on methyl chloride.

Chlorine. Several methods are available for generating chlorine from HCl. These include electrolysis of metallic chloride solutions, electrolysis of hydrochloric acid, oxidation of hydrogen chloride to chlorine with nitric acid, and oxidation of hydrogen chloride to chlorine using oxygen in the presence of catalysts (Deacon process and the modified Deacon process). Details related to electrolytic and chemical routes for manufacturing Cl_2 from HCl are given in the literature (88) (see CHLORINE).

Chlorinated C_2. Perchloroethylene (PCE) and trichloroethylene (TCE) can be produced either separately or as a mixture in varying proportions by reaction of C_2-chlorinated hydrocarbons, eg, C_2-chlorinated waste streams or ethylene dichloride, with a mixture of oxygen and chlorine or HCl.

Ethyl Chloride. Most ethyl chloride [75-00-3] is produced by the hydrochlorination of Ethylene (qv) using anhydrous HCl. Historically, the primary use of ethyl chloride was for the manufacture of tetraethyllead (TEL), a primary component of antiknock mixes in gasolines. Use has declined as a result of the environmental concern regarding lead and TEL is no longer produced in the United States. Other uses of ethyl chloride include the production of ethyl cellulose, which is formulated into lacquers, Adhesives (qv), Inks (qv), and varnishes.

Miscellaneous. Other uses for anhydrous HCl include use in cottonseed delinting and disinfecting (see COTTON), as a catalyst promotor for Petroleum (qv) isomerization, in the production of agricultural chemicals, and in the preparation of hydrochloride salts in the pharmaceutical industry (see PHARMACEUTICALS). It is also used in the production of ethylene chlorohydrin (see CHLOROHYDRINS), intermediate in the production of polysulfide Elastomers (qv). In addition, anhydrous HCl is used in the electronic industry as an etching and cleaning agent during the production of silicon wafers and semiconductors and for the cleaning the circuit boards. Anhydrous HCl is also used in the production of trichlorosilane and chlorosulfonic acid.

9.2. Aqueous Hydrochloric Acid. The largest captive use of aqueous HCl is for brine acidification prior to electrolysis in chlorine/caustic cells and the largest merchant markets for HCl are steel pickling and oil-well acidizing.

Brine Treatment. The principal use of aqueous HCl is for the acidification of brine prior to feeding it to the electrolytic cells for producing chlorine and caustic soda. Almost all of this HCl comes from captive sources.

Metal Cleaning. In steel pickling, the hydrochloric acid readily dissolves all of the various oxides present in the scale formed during the hot rolling process. Using suitable inhibitors such as alkyl pyridines, HCl reacts very slowly with the base metal rendering the surface so clean that it must be passivated with a mild alkaline rinse.

Hydrochloric acid is also used in other metal cleaning processes which range from large-scale process equipment such as tube and shell heat exchangers to solder fluxing agents and household cleaners for plumbing fixtures. Use of HCl for metal cleaning purposes is projected to decline in view of the problems associated with the disposal of the spent acid. Some steel mills regenerate spent acid and hence require only makeup HCl.

Oil-Well Acidizing. HCl is used both to clean out old oil wells and to encourage the flow of crude oil or gas to the well. Oilfield service companies use HCl concentrations in the range of 5–27% depending on geological and other factors. HCl consumption follows rig activity for oil production and is dependent on the price of crude oil.

Food. The food industry uses hydrochloric acid for processing a variety of products such as high fructose corn syrup for sweetening soft drinks (see CARBONATED BEVERAGES), hydrolyzed vegetable protein and soy sauce, gelatin, acidification of vegetable juices and can foods, and artificial Sweeteners (qv) (see FOOD PROCESSING).

Production of Calcium Chloride. Calcium chloride [10043-52-4] is produced by reaction of limestone and hydrochloric acid (see ALCOHOLS, HIGHER ALIPHATIC, SURVEY AND NATURAL ALCOHOLS MANUFACTURE). The HCl consumption varies depending on the quality of limestone used (see LIME AND LIMESTONE). The largest use of calcium chloride is for highway deicing and other uses including dust control, oil recovery, concrete treatment, and tire ballasting. Demand for HCl to produce calcium chloride for deicing depends on the weather conditions during the year, coupled with environmental constraints which include increasing regulatory restrictions (89,90).

Minerals and Metals. HCl is consumed in many mining operations for ore treatment, extraction, separation, purification, and water treatment (see MINERALS RECOVERY AND PROCESSING). Significant quantities are also used in the recovery of molybdenum (see MOLYBDENUM AND MOLYBDENUM ALLOYS) and gold (see GOLD AND GOLD COMPOUNDS).

Miscellaneous. Hydrochloric acid is used for the recovery of semiprecious metals from used catalysts, as a catalyst in synthesis, for catalyst regeneration (see FLUID CATALYTIC CRACKING (FCC) UNITS, REGENERATION), and for pH control (see HYDROGEN-ION ACTIVITY), regeneration of Ion-exchange (qv) resins used in wastewater treatment, electric utilities, and for neutralization of alkaline products or waste materials. In addition, hydrochloric acid is also utilized in many production processes for organic and inorganic chemicals.

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