CHLOROETHYLENES AND CHLOROETHANES

1. Ethylene Dichloride

1.1. Introduction. 1,2-Dichloroethane [107-06-2], ethylene chloride, ethylene dichloride, CH_2ClCH_2Cl, is a colorless, volatile liquid with a pleasant odor, stable at ordinary temperatures. It is miscible with other chlorinated solvents and soluble in common organic solvents as well as having high solvency for fats, greases, and waxes. It is most commonly used in the production of vinyl chloride monomer.

1.2. Physical and Chemical Properties. The physical properties of 1,2-dichloroethane are listed in Table 1.

Pyrolysis. Pyrolysis of 1,2-dichloroethane in the temperature range of 340–515°C gives vinyl chloride, hydrogen chloride, and traces of acetylene (3) and 2-chlorobutadiene. Reaction rate is accelerated by chlorine (4), bromine, bromotrichloromethane, carbon tetrachloride (5), and other free-radical generators. Catalytic dehydrochlorination of 1,2-dichloroethane on activated alumina (6), metal carbonate, and sulfate salts (7) has been reported, and lasers have been used to initiate the cracking reaction, although not at a low enough temperature to show economic benefits.

Hydrolysis. Heating 1,2-dichloroethane with excess water at 60°C in a nitrogen atmosphere produces some hydrogen chloride. The rate of evolution is

Table 1. **Properties of 1,2-Dichloroethane**[a]

Property	Value
melting point, °C	−35.3
boiling point, °C	83.7
density at 20°C, g/L	1.2529
n_D^{20}	1.4451
viscosity at 20°C mPa · s (= cP)	0.84
surface tension at 20°C, mN/m (= dyn/cm)	31.28
specific heat at 20°C, J/(g · K)[a]	
liquid	1.288
gas	1.066
latent heat of vaporization at 20°C, J/g[b]	323.42
latent heat of fusion, J/g[b]	88.36
critical temperature, °C	290
critical pressure, MPa[c]	5.36
critical density, g/L	0.44
flash point °C	
closed cup	17
open cup	21
explosive limits in air at 25°C, vol %	6.2–15.6
autoignition temperature in air, °C	413
thermal conductivity, liquid at 20°C, W/(m · K)[d]d	0.143
heat of combustion, kJ/g[b]	12.57
heat of formation, kJ/mol[b]	
liquid	157.3
vapor	122.6
dielectric constant	
liquid, 20°C	10.45
vapor, 120°C	1.0048
dipole moment, C · m[e]	5.24×10^{-30}
coefficient of cubical expansion, mL/g, 0–30°C	0.00116
vapor pressure, kPa[f]	
10°C	5.3
20°C	8.5
30°C	13.3
solubility at 20°C, g	
1,2-dichloroethane in 100 g H_2O	0.869
H_2O in 100 g 1,2-dichloroethane	0.160
azeotropes[g], bp, °C	
with 10.5% H_2O	72
with 5% H_2O and 17% ethanol	66.7

[a] See Ref. 11 for additional property data.
[b] To convert J to cal, divide by 4.184.
[c] To convert MPa to atm, multiply by 9.87.
[d] To convert W/(m · K) to Btu · ft)/(h · ft^2 · °F), divide by 1.73.
[e] To convert C · m to debyes, multiply by 3×10^{29}.
[f] To convert kPa to mm Hg, multiply by 7.5.
[g] See Ref. 2 for additional binary azeotropes.

dependent on the temperature and volume of the aqueous phase. Hydrolysis at 160–175°C and 1.5 MPa (15 atm) in the presence of an acid catalyst gives ethylene glycol, which is also obtained in the presence of aqueous alkali at 140–250°C and up to 4.0 MPa (40 atm) pressure (8).

Oxidation. Atmospheric oxidation of 1,2-dichloroethane at room or reflux temperatures generates some hydrogen chloride and results in solvent discoloration. A 48-h accelerated oxidation test at reflux temperatures gives only 0.006% hydrogen chloride (9). Addition of 0.1–0.2 wt. % of an amine, eg, diisopropylamine, protects the 1,2-dichloroethane against oxidative breakdown. Photooxidation in the presence of chlorine produces monochloroacetic acid and 1,1,2-trichloroethane (10).

Corrosion. Corrosion of aluminum, iron, and zinc by boiling 1,2-dichloroethane has been studied. Dry and refluxing 1,2-dichloroethane completely consumed a 2024 aluminum coupon in a 7-d study, whereas iron and zinc were barely attacked. Aluminum was attacked less than iron or zinc by refluxing with 1,2-dichloroethane containing 7% water. Corrosion rates in µm/yr (mils penetration per year or mpy) in dry solvent are 0.254 (0.01) for iron and 3.05 (0.12) for zinc. In the wet solvent, the corrosion rate for iron increases to 145 µm/yr (5.7 mpy) and for zinc to 1.2 mm/yr (47 mpy). Corrosion rate for aluminum in the wet solvent is 2.36 mm/yr (92 mpy) as compared to complete dissolution in the dry solvent.

Nucleophilic Substitution. The kinetics of the bimolecular nucleophilic substitution of the chlorine atoms in 1,2-dichloroethane with NaOH, $NaOC_6H_5$, $(CH_3)_3N$, pyridine, and CH_3COONa in aqueous solutions at 100–120°C has been studied (11). The reaction of sodium cyanide with 1,2-dichloroethane in methanol at 50°C to give 3-chloropropionitrile proceeds very slowly. Dimethyl sulfoxide as a solvent for the reaction greatly enhances nucleophilic substitution of the chlorine atom. Further reaction of sodium cyanide at room temperature gives acrylonitrile (qv), $CH_2{=}CHCN$ (12). 1,2-Dichloroethane reacts with toluene in the presence of Friedel-Crafts catalysts such as $AlBr_3$, $AlCl_3$, $GaCl_3$, and $ZrCl_3$ (13). Ammonolysis of 1,2-dichloroethane with 50% aqueous ammonia at 100°C is a primary commercial process for producing ethyleneamines (14).

1.3. Manufacture. 1,2-Dichloroethane is produced by the vapor- (15) or liquid-phase chlorination of ethylene. Most liquid-phase processes use small amounts of ferric chloride as the catalyst. Other catalysts claimed in the patent literature include aluminum chloride, antimony pentachloride, and cupric chloride and an ammonium, alkali, or alkaline-earth tetrachloroferrate (16). The chlorination is carried out at 40–50°C with 5% air or other free-radical inhibitors (17) added to prevent substitution chlorination of the product. Selectivities under these conditions are nearly stoichiometric to the desired product. The exothermic heat of reaction vaporizes the 1,2-dichloroethane product, which is purified by distillation.

$$H_2C{=}CH_2 + Cl_2 \xrightarrow[50-150^\circ C]{FeCl_3} ClH_2C{-}CH_2Cl$$

Oxychlorination of ethylene has become the second important process for 1,2-dichloroethane. The process is usually incorporated into an integrated vinyl chloride plant in which hydrogen chloride, recovered from the dehydrochlorination or cracking of 1,2-dichloroethane to vinyl chloride, is recycled to an oxychlorination unit. The hydrogen chloride by-product is used as the chlorine source in the chlorination of ethylene in the presence of oxygen and copper chloride catalyst:

$$2\,H_2C{=\!=}CH_2 + 4\,HCl + O_2 \xrightarrow[270^\circ C]{CuCl_2} 2\,ClH_2C{-\!-}CH_2Cl + H_2O$$

Reactor designs have included fixed and fluidized beds. A fluidized-bed oxychlorination reactor developed by B. F. Goodrich is claimed to provide very good temperature control (18). A large number of patents deal with the catalyst technology (19–27), which usually includes $CuCl_2$ and minor amounts of by-product inhibitors, such as potassium, sodium, lithium, or magnesium. To reduce oxidation to carbon dioxide and carbon monoxide, plant designs may include two or three reactors in series, with the HCl and oxygen feeds split to the secondary reactor(s) to decrease the C_2H_4:oxygen ratio in each reactor. By-products of this reaction include carbon dioxide, carbon monoxide, ethyl chloride, 1,1,2-trichloroethane, and trichloroacetaldehyde (chloral). The reactor products are usually condensed, unreacted HCl and water are separated from the organics, and the 1,2-dichloroethane is purified by distillation. Unreacted ethylene and oxygen can be recycled to the reactor, or sent to a vent recovery system; however, a purge is needed in the recycle system to prevent inert gas buildup in the recycle stream. Air or pure oxygen can be used; oxygen-based systems lose less ethylene during the inert purge.

1.4. Economic Aspects.

A significant portion of ethylene chloride (EDC) is converted to vinyl chloride monomer which is used in the production of poly(vinyl chloride). Worldwide consumption of EDC reached a level of 32×10^6t in 1999. North America is the largest exporter of EDC. The Middle East is also a major exporter. It is cheaper for Asian companies to import EDC rather than make it (28).

Table 2 lists the U.S. producers and their capacities.

Table 2. **U.S. Producers of Ethylene Dichloride and Their Capacities**

Producer	Location	Capacity[a], $\times 10^3$t ($\times 10^6$lb)
Borden	Geismar, La.	535 (1,180)
Dow	Freeport, Tex. (2 plants)	2,041 (4,500)
Dow	Plaquemine, La.	1,043 (2,300)
Formosa Plastics	Baton Rouge, La.	816 (1,800)
Formosa Plastics	Point Comfort, Tex.	1,134 (2,500)
Georgia Gulf	Lake Charles, La.	771 (1,700)
Georgia Gulf	Plaquemine, La.	1,270 (2,800)
Occidental Chemical	Convent, La.	680 (1,500)
Occidental Chemical	Ingleside, Tex.	680 (1,500)
OxyMar	Ingleside, Tex.	1,542 (3,400)
OxyVinyls	Deer Park, Tex.	884 (1,950)
OxyVinyls	La Porte, Tex.	1,814 (4,000)
PHH Monomers	Lake Charles, La.	635 (1,400)
PPG	Lake Charles, La.	726 (1,600)
Vulcan	Geismar, La.	272 (600)
Westlake	Calvert City, Ky.	885 (1,950)
	Total	*15,730 (34,680)*

[a] Ref. 29.

Demand in 2000 was 6.97×10^3t, expected demand in 2004 is 8.13×10^3t.

Prices for the period 1995–2000 were a high of $.10/kg and a low of $0.05/kg (29).

Commercial technology using a direct ethylene to vinyl chloride monomer could reduce the demand for EDC. The market was soft in 2001 because of a decline in construction and the slowing of the economy. Growth through 2005 is expected at the rate of 3.5% (29).

1.5. Health and Safety Factors.

1,2-Dichloroethane at high vapor concentrations (above 200 ppm) can cause central nervous system depression and gastrointestinal upset characterized by mental confusion, dizziness, nausea, and vomiting. Liver, kidney, and adrenal injuries may occur at the higher vapor levels. The recommended 1991 AGCIH vapor exposure TWA standard for 1,2-dichloroethane was 10 ppm, with a STEL guideline of 40 ppm. The odor threshold for 1,2-dichloroethane is 50–100 ppm and thus odor does not serve as a good warning against possible overexposure.

1,2-Dichloroethane is one of the more toxic chlorinated solvents by inhalation (30). The highest nontoxic vapor concentrations in chronic exposure studies with various animals range from 100 to 200 ppm (31,32). 1,2-Dichloroethane exhibits a low single-dose oral toxicity in rats; LD_{50} is 680 mg/kg (30). Repeated skin contact should be avoided since the solvent can cause defatting of the skin, severe irritation, and moderate edema. Eye contact may have slight to severe effects.

1.6. Environmental Concerns.

Removal of metal chlorides from the bottoms of the liquid-phase ethylene chlorination process has been studied (33). A detailed summary of production methods, emissions, emission controls, costs, and impacts of the control measures has been made (34). Residues from this process can also be recovered by evaporation, decomposition at high temperatures, and distillation (35). A review of the by-products produced in the different manufacturing processes has also been performed (36). Several processes have been developed to limit ethylene losses in the inerts purge from an oxychlorination reactor (37,38).

1.7. Uses.

Production of vinyl chloride monomer comprises 94% of EDC use. Three percent goes to the production of ethylene amines; 1% goes to the production of 1,1,1-trichloroethane; 1% goes to the production of vinylidene chloride; 1% goes to miscellaneous uses (includes production of trichloroethylene and perchloroethylene) (29).

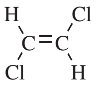
Worldwide environmental concerns have caused a reduction in the use of chlorine and chlorinated derivatives. Consumption of chlorinated solvents has been negatively impacted. The use of poly(vinyl chloride) is also under scrutiny (28).

2. Dichloroethylene

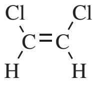
2.1. Introduction.

1,1-Dichloroethylene [75-35-4] is more commonly known as vinylidene chloride and is covered in an article in the *Encyclopedia* by that title.

1,2-Dichloroethylene [540-59-0] (1,2-dichloroethene) is also known as acetylene dichloride, dioform, α,β-dichloroethylene, and *sym*-dichloroethylene. It exists as a mixture of two geometric isomers: *trans*-1,2-dichloroethylene [156-60-5] (**1**) and *cis*-1,2-dichloroethylene [156-59-2] (**2**).



(**1**)



(**2**)

The isomeric mixture is a colorless, mobile liquid with a sweet, slightly irritating odor resembling that of chloroform. It decomposes slowly on exposure to light, air, and moisture. The mixture is soluble in most hydrocarbons and only slightly soluble in water. The cis–trans proportions in a crude mixture depend on the production conditions. The isomers have distinct physical and chemical properties and can be separated by fractional distillation.

2.2. Physical and Chemical Properties. 1,2-Dichloroethylene consists of a mixture of the cis and trans isomers, as manufactured. The physical properties of both isomeric forms are listed in Table 3. Binary and ternary azeotrope data for the cis and trans isomers are given in Table 4.

2.3. Manufacture. 1,2-Dichloroethylene can be produced by direct chlorination of acetylene at 40°C. It is often produced as a by-product in the chlorination of chlorinated compounds (40) and recycled as an intermediate for the synthesis of more useful chlorinated ethylenes (41). 1,2-Dichloroethylene can be formed by continuous oxychlorination of ethylene by use of a cupric chloride–potassium chloride catalyst, as the first step in the manufacture of vinyl chloride [75-01-4] (42).

The trans isomer is more reactive than the cis isomer in 1,2-addition reactions (43). The cis and trans isomers also undergo benzyne, C_6H_4, cycloaddition (44). The isomers dimerize to tetrachlorobutene in the presence of organic peroxides. Photolysis of each isomer produces a different excited state (45,46). Oxidation of 1,2-dichloroethylene in the presence of a free-radical initiator or concentrated sulfuric acid produces the corresponding epoxide [60336-63-2], which then rearranges to form chloroacetyl chloride [79-04-9] (47).

The unstabilized grade of 1,2-dichloroethylene hydrolyzes slowly in the presence of water, producing HCl. Although unaffected by weak alkalies, boiling with aqueous NaOH may give rise to an explosive mixture because of monochloroacetylene [593-63-5] formation.

2.4. Storage and Handling. 1,2-Dichloroethylene is usually shipped in 208-L (55 gal) and 112-L (30 gal) steel drums. Because of the corrosive products of decomposition, inhibitors are required for storage. The stabilized grades of the isomers can be used or stored in contact with most common construction materials, such as steel or black iron. Storage stabilized 1,2-dichloroethylene compositions have been reported (48). Contact with copper or its alloys and with hot alkaline solutions should be avoided to preclude possible formation of explosive monochloroacetylene. The isomers do have explosive limits in air (Table 1). However, the liquid, even hot, burns with a very cool flame which

Table 3. **Physical Properties of the Isomeric Forms of 1,2-Dichloroethylene**

Property	Trans	Cis
mol wt	96.95	96.95
mp, °C	−49.44	−81.47
bp, °C	47.7	60.2
density, g/mL	1.2631	1.2917
15°C	1.44903	1.45189
20°C	1.44620	1.44900
viscosity, mPa · s (= cP)		
−50°C	1.005	1.156
−25°C	0.682	0.791
0°C	0.498	0.577
10°C	0.447	0.516
20°C	0.404	0.467
surface tension at 20°C, mN/m (= dyn/cm)	25	28
latent heat of vaporization[a], kJ/kg[b]	297.9	311.7
heat capacity at 20°C, kJ/(kg · K)[b]	1.158	1.176
vapor pressure, kPa[c]		
−20°C	5.3	2.7
−10°C	8.5	5.1
0°C	15.1	8.7
10°C	24.7	14.7
20°C	35.3	24.0
30°C	54.7	33.3
40°C	76.7	46.7
47.7°C	101	66.7
60.25°C		
soly of the isomer in water at 25°C, g/100 g	0.63	0.35
soly of water in the isomer at 25°C, g/100 g	0.55	0.55
steam distillation point at 101 kPa,[c] °C	45.3	53.8
flash point, °C	4	6
explosion limit in air, vol %[d]	5.6–12.8	

[a] At the boiling point.

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

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

[d] A cis-trans mixture (39).

self-extinguishes unless the temperature is well above the flash point. A red label is required for shipping 1,2-dichloroethylene.

2.5. Health and Safety Factors.

1,2-Dichloroethylene is toxic by inhalation and ingestion and can be absorbed by the skin. It has a TLV of 200 ppm (49). The odor does not provide adequate warning of dangerously high vapor

Table 4. **Azeotropes of *trans* and *cis*-1,2-Dichloroethylene Isomers**

		Binary azeotropes			
Second component	Bp, °C	Trans isomer in mixture wt%	Bp of azeotrope, °C	Cis isomer in mixture wt%	Bp of azeotrope, °C
methanol	64.5			87	51.5
ethanol	78.2	94.0	46.5	90.2	57.7
water	100.0	98.1	45.3	96.65	55.3

concentrations. Thorough ventilation is essential whenever the solvent is used for both worker exposure and flammability concerns. Symptoms of exposure include narcosis, dizziness, and drowsiness. Currently no data are available on the chronic effects of exposure to low vapor concentrations over extended periods of time.

1,2-Dichloroethylene appeared frequently in the 1980s literature largely because of its presence at ground water cleanup sites. The continued presence of 1,2-dichloroethylene may be a result of the biotransformation of tetrachloroethylene and trichloroethylene, which are much more common industrial solvents and are likely present because of past disposal practices (50,51).

2.6. Uses. 1,2-Dichloroethylene can be used as a low temperature extraction solvent for organic materials such as dyes, perfumes, lacquers, and thermoplastics (See ref. 52 for example). It is also used as a chemical intermediate in the synthesis of other chlorinated solvents and compounds (40).

Recently several patents have been issued (53–56) describing the use of 1,2-dichloroethylene for use in blends of chlorofluorocarbons for solvent vapor cleaning. One patent describes a method for cleaning acetate-based photographic film with *trans*-dichloroethylene (57). This art is primarily driven by the need to replace part of the chlorofluorocarbons because of the restriction on their production under the Montreal Protocol of 1987.

3. Trichloroethylene

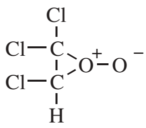
3.1. Introduction. Trichloroethylene [79-01-6], trichloroethene, $CHCl{=}CCl_2$, commonly called “tri,” is a colorless, sweet smelling (chloroformlike odor), volatile liquid and a powerful solvent for a large number of natural and synthetic substances. It is nonflammable under conditions of recommended use. In the absence of stabilizers, it is slowly decomposed (autoxidized) by air. The oxidation products are acidic and corrosive. Stabilizers are added to all commercial grades. Trichloroethylene is moderately toxic and has narcotic properties.

Trichloroethylene was first prepared by Fischer in 1864. In the early 1900s, processes were developed in Austria for the manufacture of tetrachloroethane and trichloroethylene from acetylene. Trichloroethylene manufacture began in Germany in 1920 and in the United States in 1925. Early uses of trichloroethylene were as an extraction solvent for natural fats and oils, such as palm, coconut, and soybean oils. It was later used for decaffeination of coffee, but this use has essentially been replaced by steam processes today. The demand for trichloroethylene was stimulated by the development of the vapor-degreasing process during the 1920s and by the growth of the dry-cleaning industry during the 1930s. By the mid-1950s, perchloroethylene had replaced trichloroethylene in dry-cleaning, and metal cleaning became the principal use for trichloroethylene.

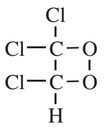
The demand for trichloroethylene grew steadily until 1970. Since that time trichloroethylene has been a less desirable solvent because of restrictions on emissions under air pollution legislation and the passage of the Occupational Safety and Health Act. Whereas previously the principal use of trichloroethylene was for vapor degreasing, 1,1,1-trichloroethane then became the most used solvent for vapor degreasing. The restrictions on production of 1,1,1-trichloroethane [71-55-6] from the 1990 Amendments to the Montreal Protocol on substances that deplete the stratospheric ozone and the U.S. Clean Air Act 1990 Amendments will lead to a phase out of 1,1,1-trichloroethane by the year 2005, which in turn will likely result in a slight resurgence of trichloroethylene in vapor-degreasing applications. The total production, however, will probably stay relatively low because regulations will require equipment designed to assure minimum emissions.

3.2. Physical and Chemical Properties. The physical properties of trichloroethylene are listed in Table 5. Trichloroethylene is immiscible with water but miscible with many organic liquids; it is a versatile solvent. It does not have a flash or fire point. However, it does exhibit a flammable range when high concentrations of vapor are mixed with air and exposed to high energy ignition sources.

The most important reactions of trichloroethylene are atmospheric oxidation and degradation by aluminum chloride. Atmospheric oxidation is catalyzed by free radicals and accelerated with heat and with light, especially ultraviolet. The addition of oxygen leads to intermediates (**3**) and (**4**).



(**3**)



(**4**)

Compound (**3**) decomposes to form dichloroacetyl chloride, which in the presence of water decomposes to dichloroacetic acid and hydrochloric acid (HCl) with consequent increases in the corrosive action of the solvent on metal surfaces. Compound (**4**) decomposes to yield phosgene, carbon monoxide, and hydrogen chloride with an increase in the corrosive action on metal surfaces.

In the presence of aluminum, oxidative degradation or dimerization supply HCl for the formation of aluminum chloride, which catalyzes further dimerization to hexachlorobutene. The latter is decomposed by heat to give more HCl. The result is a self-sustaining pathway to solvent decomposition. Sufficient quantities of aluminum can cause violent decomposition, which can lead to runaway reactions (58,59). Commercial grades of trichloroethylene are stabilized to prevent these reactions in normal storage and use conditions.

Amine-stabilized products, once the predominant grade, are sold today only in limited amounts. Most vapor-degreasing grades contain neutral inhibitor mixtures (60–62) including a free-radical scavenger, such as an amine or pyrrole, to prevent the initial oxidation reaction. Epoxides, such as butylene oxide and epichlorohydrin, are added to scavenge any free HCl and $AlCl_3$. Concern over the toxicity of these epoxides has eliminated the use of epichlorohydrin in the United States during the 1980s and may restrict butylene oxide in the future.

Trichloroethylene is not readily hydrolyzed by water. Under pressure at 150°C, it gives glycolic acid, $CH_2OHCOOH$, with alkaline hydroxides. Strong alkalies dehydrochlorinate trichloroethylene with production of spontaneously

Table 5. **Properties of Trichloroethylene**

Property	Value
molecular weight	131.39
melting point, °C	−86.5
boiling point, °C	87.3
specific gravity, liquid	
20/4°C	1.464
100/4°C	1.322
vapor density at bp, kg/m^3	4.61
n_D	
liquid, 20°C	1.4782
vapor, 0°C	1.001784
viscosity, mPa · s (= cP) liquid	
20°C	0.57
60°C	0.42
vapor at 100°C	0.01246
surface tension at 20°C, mN/m(= dyn/cm)	29.3
heat capacity, J/(kg · K)[a]	
liquid at 20°C	938
vapor at 100°C	693
critical temperature, °C	300.2
critical pressure, MPa[b]	4.986
thermal conductivity, W/(m · K)	
liquid at 20°C	0.115
vapor at bp	0.00851
coefficient of cubical expansion, liquid at 0–40°C	0.00119
dielectric constant, liquid at 16°C	3.42
dipole moment, C · m[c]	3.0×10^{-30}
heat of combustion, kJ/g[a]	−6.56
heat of formation, kJ/mol[a]	
liquid	−42.3
vapor	−7.78
latent heat of evaporation at bp, kJ/kg[a]	238
explosive limits, vol % in air	
25°C	8.0-saturation
100°C	8.0–44.8
vapor pressure[d], kPa[e]	
Antoine constants	
A	5.75373
B	1076.67
C	199.991
solubility, g	
H_2O in 100 g trichloroethylene	
0°C	0.010
20°C	0.0225
60°C	0.080
trichloroethylene in 100 g H_2O	
20°C	0.107
60°C	0.124

[a] To convert J to cal, divide by 4.184.
[b] To convert MPa to atm, divide by 0.101.
[c] To convert C · m to debye, divide by 3.336×10^{-30}.
[d] $\log_{10} P = A - B/(T + C)$, T in °C.
[e] To convert kPa to mm Hg, multiply by 7.5.

explosive and flammable dichloroacetylene. Reaction with sulfuric acid (90%) yields monochloroacetic acid, $CH_2ClCOOH$. Hot nitric acid reacts with trichloroethylene violently, producing complete oxidative decomposition. Under carefully controlled conditions, nitric acid gives trichloronitromethane (chloropicrin) and dinitrochloromethane (63). Dichloroacetylene, C_2Cl_2, can also be formed from trichloroethylene in the presence of epoxides and ionic halides (64).

In the presence of catalysts, trichloroethylene is readily chlorinated to pentachloro- and hexachloroethane. Bromination yields 1,2-dibromo-1,1,2-trichloroethane [13749-38-7]. The analogous iodine derivative has not been reported. Fluorination with hydrogen fluoride in the presence of antimony trifluoride produces 2-chloro-1,1,1-trifluoroethane [75-88-7] (65). Elemental fluorine gives a mixture of chlorofluoro derivatives of ethane, ethylene, and butane.

Liquid trichloroethylene has been polymerized by irradiation with ^{60}Co γ-rays or 20-keV x-rays (66). Trichloroethylene has a chain-transfer constant of <1 when copolymerized with vinyl chloride (67) and is used extensively to control the molecular weight of poly(vinyl chloride) polymer.

A variety of trichloroethylene copolymers have been reported, none with apparent commercial significance. The alternating copolymer with vinyl acetate has been patented as an adhesive (68) and as a flame retardant (69,70). Copolymerization with 1,3-butadiene and its homologues has been reported (71–73). Other comonomers include acrylonitrile (74), isobutyl vinyl ether (75), maleic anhydride (76), and styrene (77).

Terpolymers have been made with vinyl chloride–vinylidene chloride (78) and vinyl acetate–vinyl alcohol (79).

3.3. Manufacture. *From Acetylene.* As late as 1968, 85% of the production capacity in the United States was based on acetylene, but rising acetylene [74-86-2] costs reduced this figure to 8% by 1976 (80), and now most trichloroethylene is made from ethylene [74-85-1], 1,2-dichloroethane [107-06-2], or ethylene dichloride.

The acetylene-based process consists of two steps. First acetylene is chlorinated to 1,1,2,2-tetrachloroethane [79-34-5]. The reaction is exothermic (402 kJ/mol = 96 kcal/mol) but is maintained at 80–90°C by the vaporization of solvent and product. Catalysts include ferric chloride and sometimes phosphorus chloride and antimony chloride (81).

The product is then dehydrohalogenated to trichloroethylene at 96–100°C in aqueous bases such as $Ca(OH)_2$ (82) or by thermal cracking, usually over a catalyst (81) such as barium chloride on activated carbon or silica or aluminum gels at 300–500°C. The yield of trichloroethylene (80) is about 94% based on acetylene. A significant disadvantage of the alkaline process is the loss of chlorine as calcium chloride. In thermal cracking the chlorine can be recovered as hydrochloric acid, an important feedstock in many chemical processes. Since it poisons the catalysts during thermal cracking, all ferric chloride must be removed from the tetrachloroethane feed (81). Tetrachloroethane can also be cracked to trichloroethylene without catalysts at 330–770°C, but considerable amounts of tarry by-products are formed.

Chlorination of Ethylene. Dichloroethane, produced by chlorination of ethylene, can be further chlorinated to trichloroethylene and tetrachloroethylene.

The exothermic reaction is carried out at 280–450°C. Temperature is controlled by a fluidized bed, a molten salt bath, or the addition of an inert material such as perchloroethylene. The residence time in the reactor varies from 2 to 30 seconds, depending on conditions (81). Catalysts include potassium chloride and aluminum chloride (83), Fuller's earth (84), graphite (85), activated carbon (86), and activated charcoal (84).

Maximum conversion to trichloroethylene (75% of dichloroethane feed) is achieved at a chlorine to dichloroethane ratio of 1.7:1. Tetrachloroethylene conversion reaches a maximum (86% conversion of dichloroethane) at a feed ratio of 3.0:1 (81).

Oxychlorination of Ethylene or Dichloroethane. Ethylene or dichloroethane can be chlorinated to a mixture of tetrachoroethylene and trichloroethylene in the presence of oxygen and catalysts. The reaction is carried out in a fluidized-bed reactor at 425°C and 138–207 kPa (20–30 psi). The most common catalysts are mixtures of potassium and cupric chlorides. Conversion to chlorocarbons ranges from 85–90%, with 10–15% lost as carbon monoxide and carbon dioxide (81). Temperature control is critical. Below 425°C, tetrachloroethane becomes the dominant product, 57.3 wt% of crude product at 330°C (87). Above 480°C, excessive burning and decomposition reactions occur. Product ratios can be controlled but less readily than in the chlorination process. Reaction vessels must be constructed of corrosion-resistant alloys.

3.4. Shipping and Storage. Shipment of trichloroethylene is usually by truck or rail car and also in 208-liter (55-gallon) steel drums. Mild steel tanks, if appropriately equipped with vents and vent driers to prevent the accumulation of water, are adequate for storage. Precautions, such as diking, should be taken to provide for adequate spill containment at the storage tank. Seamless black iron pipes are suitable for transfer lines, gasketing should be of Teflon, Viton, or other solvent impermeable material. Centrifugal or positive-displacement pumps made from cast iron, steel, or stainless steel are suitable for use. Aluminum should never be used as a construction material for any halogenated hydrocarbon. Glass containers, amber or green, are suitable for small quantities, such as in a laboratory, but care should be taken for spill containment in the event of breakage.

Containers should bear warning labels against breathing vapors, ingesting the liquid, splashing solvent in eyes or on skin and clothing, and using it near an open flame, or where vapors will come in contact with hot metal surfaces (>176°C).

Precautions in handling any waste products in conformance with federal, state, and local regulations should be included.

Although the flammability hazard is very low, ignition sources should not be present when trichloroethylene is used in highly confined or unventilated areas. Tanks in which flammable concentrations could develop should be grounded to prevent build-up of static electric charges. Under no circumstances should welding or cutting with a torch take place on any storage container or process equipment containing trichloroethylene.

3.5. Economic Aspects. Table 6 lists the U.S. producers of trichloroethylene and their capacities. PPG capacity is flexible and can be swung between TCE and tetrachlorethylene production (88).

Table 6. **U.S. Producers of Trichloroethylene and Their Capacities**[a]

Producer	Location	Capacity, $\times 10^3$t ($\times 10^6$lb)
Dow	Freeport, Tex.	59 (130)
PPG	Lake Charles, La.	91 (200)
Total		*150 (330)*

[a] See Ref. 88.

There has been a significant increase in global use of TCE as a feedstock for the production of hydrofluorocarbons, particularly HFC-134a, which is used as a replacement for CFC-12 in refrigerants. This use has climbed steadily over the past few years and will continue to be strong. However as the CFC-12 is largely replaced, growth could drop to 6%/yr.

The use of TCE in metal cleaning is expected to decrease as users have installed new work procedures and equipment to limit fugitive emissions.

Demand for 2001 was 91×10^3 t. Demand for 2005 is expected to be 111×10^3 t. Prices have remained stable at $0.29/kg (88).

3.6. Specifications and Standards. Commercial grades of trichloroethylene, formulated to meet use requirements, differ in the amount and type of added inhibitor. The grades sold in the United States include a neutrally inhibited vapor-degreasing grade and a technical grade for use in formulations. U.S. Federal Specification O-T-634b lists specifications for a regular and a vapor-degreasing grade.

Apart from added stabilizers, commercial grades of trichloroethylene should not contain more than the following amounts of impurities: water 100 ppm; acidity, ie, HCl, 5 ppm; insoluble residue, 10 ppm. Free chlorine should not be detectable. Test methods have been established by ASTM to determine the following characteristics of trichloroethylene: acid acceptance, acidity or alkalinity, color, corrosivity on metals, nonvolatile-matter content, pH of water extractions, relative evaporation rate, specific gravity, water content, water-soluble halide ion content, and halogen content (89).

The passage of the Resource Conservation and Recovery Act in 1978 and its implementation in 1980 generated an increase in the recycling of trichloroethylene, which, in turn, defined the need for specifications for recycled solvent. Reagents, methods, and kits for detecting trichloroethylene and tetrachloroethylene have been described in a patent (90).

3.7. Health and Safety Factors. Trichloroethylene is acutely toxic, primarily because of its anesthetic effect on the central nervous system. Exposure to high vapor concentrations is likely to cause headache, vertigo, tremors, nausea and vomiting, fatigue, intoxication, unconsciousness, and even death. Because it is widely used, its physiological effects have been extensively studied.

Exposure occurs almost exclusively by vapor inhalation, which is followed by rapid absorption into the bloodstream. At concentrations of 150–186 ppm, 51–70% of the trichloroethylene inhaled is absorbed. Metabolic breakdown occurs by oxidation to chloral hydrate [302-17-0], followed by reduction to trichloroethanol [115-20-8], part of which is further oxidized to trichloroacetic acid [76-03-9] (91,92). Absorbed trichloroethylene that is not metabolized is eventually eliminated through the lungs (93). The OSHA permissible exposure limit (PEL) eight-hour TWA concentration has been set at 50 ppm for eight-hour exposure ACGIH TLV is 50 ppm also (94).

It is estimated that concentrations of 3000 ppm cause unconsciousness in less than 10 minutes (89). Anesthetic effects have been reported at concentrations of 400 ppm after 20-min exposure. Decrease in psychomotor performance at a trichloroethylene concentration of 110 ppm has been reported in one study (100), whereas other studies find no neurotoxic effects at concentrations of 200 ppm (96–99).

Victims of overexposure to trichloroethylene should be removed to fresh air, and medical attention should be obtained immediately. A self-contained positive pressure breathing device should be used wherever high vapor concentrations are expected, eg, when cleaning up spills or when accidental releases occur.

The distinctive odor of trichloroethylene may not necessarily provide adequate warning of exposure, because it quickly desensitizes olfactory responses. Fatalities have occurred when unprotected workers have entered unventilated areas with high vapor concentrations of trichloroethylene or other chlorinated solvents. For a complete description of proper entry to vessels containing any chlorinated solvent, see ASTM D4276-84, Standard Practice for Confined Area Entry (89).

Ingestion of large amounts of trichloroethylene may cause liver damage, kidney malfunction, cardiac arrhythmia, and coma (93); vomiting should not be induced, but medical attention should be obtained immediately.

Protective gloves and aprons should be used to prevent skin contact, which may cause dermatitis (101–103). Eyes should be washed immediately after contact or splashing with trichloroethylene.

The National Cancer Institute reported in 1975 that massive oral doses of trichloroethylene caused liver tumors in mice but not in rats (104). Trichloroethylene was tested again in the 1980s by the National Toxicology Program (NTP) with similar results (105,106). The EPA has classified trichloroethylene as B2, a probable human carcinogen. The International Agency for Research on Cancer (IARC) classifies it as group 3, ie, unclassifiable as to human carcinogenicity. Teratogenicity studies conducted with trichloroethylene by The Dow Chemical Company showed no significant effects on fetal development (107). During the 1980s several epidemiology studies were conducted on worker populations exposed to trichloroethylene (108–110). Each of these studies failed to show a positive link between human exposure in the work place and cancer. Human mutation data has been reported, however (5).

During the 1980s a significant amount of work was done on developing methods for treatment of contaminated groundwater and also on setting standards for trichloroethylene under the Safe Drinking Water Act. The EPA has set a maximum contaminant level goal (MCLG) at 0 based on the animal carcinogenic effects (111). The maximum contaminant level (MCL) is currently set at five micrograms per liter.

3.8. Uses. Approximately 67% of the trichloroethylene produced in the United States is consumed in the vapor degreasing of fabricated metal parts (see METAL SURFACE TREATMENTS); 30% is divided equally between exports and miscellaneous applications and 3% is used as a polymerization modifier (84). A variety of miscellaneous applications include use of trichloroethylene as a component in adhesive and paint-stripping formulations, a low temperature heat-transfer medium, a nonflammable solvent carrier in industrial paint systems, and a solvent base for metal phosphatizing systems. Trichloroethylene is used in the textile industry as a carrier solvent for spotting fluids and as a solvent in waterless preparation dying and finishing operations. Cleaning or drying compositions as a replacement for CFCs has been described (112).

Trichloroethylene was approved for use for many years as an extraction solvent for foods. In late 1977, the Food and Drug Administration (FDA) banned its use as a food additive, directly or indirectly, prohibiting the use in hop extraction, decaffeination of coffee, isolation of spice oleoresins, and other applications. The FDA also banned the use of trichloroethylene in cosmetic and drug products (84).

Trichloroethylene is widely used as a chain-transfer agent in the production of poly(vinyl chloride). There has been a significant increase in the use of trichloroethylene as a feedstock in the production of hydrofluorocarbons, the replacements for chlorofluorcarbons implicated in the depletion of stratospheric ozone. HFC-134a (hydrotetrafluoroethane) is one of these products. It replaces CFC-12 as a refrigerant in the United States. This application has been growing steadily, but will slow as CFC-12 is replaced completely.

4. Tetrachloroethylene

4.1. Introduction. Tetrachloroethylene [127-18-4], perchloroethylene, $CCl_2{=\!=}CCl_2$, is commonly referred to as “perc” and sold under a variety of trade names. It is the most stable of the chlorinated ethylenes and ethanes, having no flash point and requiring only minor amounts of stabilizers.

Tetrachloroethylene was first prepared in 1821 by Faraday by thermal decomposition of hexachloroethane. Tetrachloroethylene is typically produced as a coproduct with either trichloroethylene or carbon tetrachloride from hydrocarbons, partially chlorinated hydrocarbons, and chlorine. Although production of tetrachloroethylene and trichloroethylene from acetylene was once the dominant process, it is now obsolete because of the high cost of acetylene.

4.2. Physical and Chemical Properties. The physical properties of tetrachloroethylene are listed in Table 7. It dissolves a number of inorganic materials including sulfur, iodine, mercuric chloride, and appreciable amounts of aluminum chloride. Tetrachloroethylene dissolves numerous organic acids, including benzoic, phenylacetic, phenylpropionic, and salicylic acid, as well as a variety of other organic substances such as fats, oils, rubber, tars, and resins. It does not dissolve sugar, proteins, glycerol, or casein. It is miscible with chlorinated organic solvents and most other common solvents. Tetrachloroethylene forms approximately sixty binary azeotropic mixtures (113).

Stabilized tetrachloroethylene, as provided commercially, can be used in the presence of air, water, and light, in contact with common materials of construction, at temperatures up to about 140°C. It resists hydrolysis at temperatures up to 150°C (114). However, the unstabilized compound, in the presence of water for prolonged periods, slowly hydrolyzes to yield trichloroacetic acid

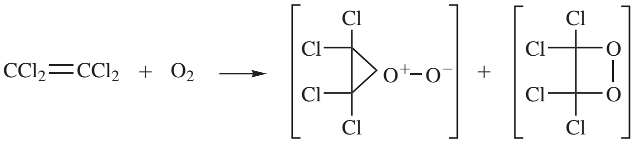
Table 7. **Properties of Tetrachloroethylene**

Property	Value
molecular weight	165.83
melting point, °C	−22.7
boiling point at 101 kPa[a], °C	121.2
specific gravity, liquid, at °C	
10/4	1.63120
20/4	1.62260
30/4	1.60640
120/4	1.44865
vapor density at bp at 101 kPa, kg/m^3	5.8
viscosity, mPa · s (= cP)	
liquid, °C	
15	0.932
25	0.839
50	0.657
75	0.534
vapor at 60°C	9900
surface tension, mN/m (= dyn/cm)	
15°C	32.86
30°C	31.27
thermal capacity, kJ/(kg · K)[b]	
liquid at 20°C	0.858
vapor at 100°C	0.611
thermal conductivity, mW/(m · K)	
liquid	126.6
vapor at bp	8.73
heat of combustion	
constant pressure with formation of aq HCl, kJ/mol[b]	679.9
constant volume at 18.7°C, kJ/mol[b]	831.8
latent heat of vaporization at 121.2°C, kJ/mol[b]	34.7
critical temperature, °C	347.1
critical pressure, MPa[c]	9.74
latent heat of fusion, kJ/mol[b]	10.57
heat of formation, kJ/mol[b]	
vapor	−25
liquid	12.5
n_D at 20°C	1.50547
dielectric constant at 1 kHz, 20°C	2.20
electrical conductivity at 20°C, 10^{15} $(\Omega \cdot m)^{-1}$	55.8
coefficient of cubical expansion at 15–90°C, av	0.001079
vapor pressure, *kPa*[c], at °C	
−20.6	0.1333
13.8	1.333
40.0	5.466
60.0	13.87
80.0	30.13
100.0	58.46
121.2	101.3
solubility at 25°C, mg	
C_2Cl_4 in 100 g H_2O	15
H_2O in 120 g C_2Cl_4	8

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert kJ to kcal, divide by 4.184.
[c] To convert MPa to atm, divide by 0.101.

[76-03-9] and hydrochloric acid. In the absence of catalysts, air, or moisture, tetrachloroethylene is stable to about 500°C. Although it does not have a flash point or form flammable mixtures in air or oxygen, thermal decomposition results in the formation of hydrogen chloride and phosgene [75-44-5] (115).

Under ultraviolet radiation in the presence of air or oxygen, tetrachloroethylene undergoes autoxidation to trichloroacetyl chloride [76-02-8]. This reaction, which accounts for the slow decomposition of tetrachloroethylene under prolonged storage in the presence of light and air or oxygen, is inhibited in commercial products by the addition of amines or phenols as stabilizers. Peroxy compounds (**5**) and (**6**) are intermediates of this autoxidation. Compound (**5**) rear-ranges to form trichloroacetyl chloride and oxygen, whereas compound (**6**) breaks down to form two molecules of phosgene.



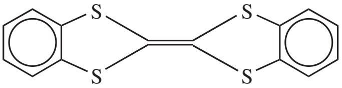
(**5**) (**6**)

Reaction with hydrogen at 220°C in the presence of reduced nickel catalyst results in total decomposition to hydrogen chloride and carbon. An explosive reaction occurs with butyllithium in petroleum ether solution (116). Tetrachloroethylene also reacts explosively with metallic potassium at its melting point, however it does not react with sodium (117).

Photochlorination of tetrachloroethylene, observed by Faraday, yields hexachloroethane [67-72-1]. Reaction with aluminum bromide at 100°C forms a mixture of bromotrichloroethane and dibromodichloroethane [75-81-0] (118). Reaction with bromine results in an equilibrium mixture of tetrabromoethylene [79-28-7] and tetrachloroethylene. Tetrachloroethylene reacts with a mixture of hydrogen fluoride and chlorine at 225–400°C in the presence of zirconium fluoride catalyst to yield 1,2,2-trichloro-1,1,2-trifluoroethane [76-13-1] (CFC 113) (119).

Tetrachloroethylene reacts with formaldehyde and concentrated sulfuric acid at 80°C to form 2,2-dichloropropanoic acid [75-99-0] (120). Copolymers with styrene, vinyl acetate, methyl acrylate, and acrylonitrile are formed in the presence of dibenzoyl peroxide (121,122).

Tetrachloroethylene is heated at 110–120°C with *o*-benzenedithiol, in the presence of sodium ethoxide, to form 2,2′-bis-1,3-benzdithiolene (123).



The addition of stabilizers to tetrachloroethylene inhibits corrosion of aluminum, iron, and zinc which otherwise occurs in the presence of water (124). Where water in excess of the solubility limit is present, forming separate layers, hydrolysis and corrosion rates increase. System design and construction materials should consider these effects.

4.3. Manufacture.

Many processes have been used to produce tetrachloroethylene. One of the first was chlorination of acetylene (C_2H_2) to form tetrachloroethane, followed by dehydrochlorination to trichloroethylene. If tetrachloroethylene was desired, the trichloroethylene was further chlorinated to pentachloroethane and dehydrochlorinated. This process is no longer used in the United States; Hooker Chemical closed down the last plant in 1978.

In Japan, Toagosei is reported to produce trichloroethylene and tetrachloroethylene by chlorination of ethylene followed by dehydrochlorination. In this process the intermediate tetrachloroethane is either dehydrochlorinated to trichloroethylene or further chlorinated to pentachloroethane [76-01-7] followed by dehydrochlorination to tetrachloroethylene. Partially chlorinated by-products are recycled and by-product HCl is available for other processes.

The following processes are commonly used today.

Chlorination of Ethylene Dichloride. Tetrachloroethylene and trichloroethylene can be produced by the noncatalytic chlorination of ethylene dichloride [107-06-2] (EDC) or other two-carbon (C2) chlorinated hydrocarbons. This process is advantageous when there is a feedstock source of mixed C2 chlorinated hydrocarbons from other processes and an outlet for the by-product HCl stream. Product ratios of tri- and tetrachloroethylene are controlled by adjusting the Cl_2: 2:EDC ratio to the reactor. Partially chlorinated by-products are recycled to the chlorinator. The primary reactions are

$$CH_2ClCH_2Cl + 3\ Cl_2 \longrightarrow Cl_2C{=\!=}CCl_2 + 4\ HCl$$

$$CH_2ClCH_2Cl + 2\ Cl_2 \longrightarrow CHCl{=\!=}CCl_2 + 3\ HCl$$

Chlorination of C1–C3 Hydrocarbons or Partially Chlorinated Derivatives. Tetrachloroethylene and carbon tetrachloride are produced with or without a catalyst at high temperatures (550–700°C) from light hydrocarbon feedstocks or their partially chlorinated derivatives. This is one of the most versatile processes, allowing for a wide range of mixed chlorinated hydrocarbon wastes from other processes to be used as feedstocks. However the phase out of CFC-11 and CFC-12, most of carbon tetrachloride use, has caused producers to maximize perchloroethylene production and minimizing or eliminating production of carbon tetrachloride (125). The large quantities of HCl produced requires integration with other HCl consuming processes. As with the previous process, product distribution is controlled by controlling feedstock ratios, and partially chlorinated by-products are recycled to the chlorinator. As examples, reaction of EDC or propane are shown in the following.

$$3\ CH_2ClCH_2Cl + 11\ Cl_2 \longrightarrow 2\ Cl_2C{=\!=}CCl_2 + 2\ CCl_4 + 12\ HCl$$

$$CH_3CH_2CH_3 + 8\ Cl_2 \longrightarrow Cl_2C{=\!=}CCl_2 + CCl_4 + 8\ HCl$$

Oxychlorination of C2 Chlorinated Hydrocarbons. Tetrachloroethylene and trichloroethylene can be produced by reaction of EDC with chlorine or HCl and oxygen in the presence of a catalyst. When hydrochloric acid is used, additional oxygen is required. Product distribution is varied by controlling reactant ratios. This process is advantageous in that no by-product HCl is produced,

Table 8. **U.S. Producers of Tetrachloroethylene and Their Capacities**[a]

Producer	Location	Capacity, $\times 10^3$t ($\times 10^6$ lb)
Dow Chemical	Plaquemine, La.	40.8 (90)
PPG Industries	Lake Charles, La.	90.7 (200)
Vulcan Materials	Geismar, La.	63.5 (140)
Total		*195 (430)*

[a] Ref. 125.

and it can be integrated with other processes as a net HCl consumer. The reactions may be represented as follows:

$$CH_2ClCH_2Cl + Cl_2 + O_2 \longrightarrow Cl_2C{=\!=}CCl_2 + 2\,H_2O$$

$$CH_2ClCH_2Cl + 1/2\ Cl_2 + 3/4\ O_2 \longrightarrow CHCl{=\!=}CCl_2 + 3/2\,H_2O$$

4.4. Shipping and Storage. Tetrachloroethylene is shipped by barge, tank car, tank truck, and 55-gallon (208-L) steel drums. It may be stored in mild steel tanks that are dry, free of rust, and equipped with a chemical (such as calcium chloride) vent dryer and controlled evaporation vent. Appropriate secondary containment including dikes and sealed surfaces should be provided in accordance with federal and local standards to prevent potential groundwater contamination in the event of a leak. Piping and centrifugal or positive displacement pumps should be constructed of ductile iron or carbon steel with gasket materials made of impregnated cellulose fiber, cork base materials, or Viton resin.

4.5. Economic Aspects. U.S. producers of tetrachloroethylene are listed in Table 8.

Tetrachloroethylene's primary use is as a precursor to manufacture fluorocarbons, particularly HFC-134a, which is used as a replacement for CFC-12 in refrigeration systems. This use has been growing at a rate of 9% in the United States. This rate will probably slow to 4% as the replacement of CFC-12 is complete.

Conversion to more efficient dry-cleaning equipment has resulted in a decline of 65% in the use of tetrachlorethylene as a dry-cleaning agent in the last decade. No alternative has the versatility and low cost of tetrachloroethylene so it will still be used in this application.

Chlorinated solvents are not favored because of their negative impact on the environment and health. Tetrachloroethylene is listed by the EPA as a substitute for 1,1,1-trichlorethane in adhesives, coatings, inks and metal degreasing and as a substitute for CFC-13.

Demand in 2001 was 152×10^3 t. In 2205, demand is expected to be 166×10^3 t. Growth is expected at a rate of 2% through 2005 (125).

Prices for the period 1996–2001 ranged from \$0.15/kg to 0.17/kg (125).

4.6. Specifications. Commercial grades of tetrachloroethylene include a vapor degreasing grade; a dry-cleaning grade; an industrial grade for use in formulations; a high purity, low residue grade; and a grade specifically formulated for use as a transformer fluid. The various grades differ in the amount and type of added stabilizers. U.S. Federal Specification OT-236A covers tetrachloroethylene.

ASTM has established standard test methods to determine acid acceptance, acidity, alkalinity, color, corrosivity to metals, nonvolatile matter content, pH of water extractions, relative evaporation rate, boiling point range, specific gravity, water content, water-soluble halide ions, and halogens (126). Typical commercial grades should not contain more than 50 ppm water, 0.0005 wt% acidity (as HCl), or 0.001 wt % insoluble residue.

4.7. Health and Safety Factors. Overexposure to tetrachloroethylene by inhalation affects the central nervous system and the liver. Dizziness, headache, confusion, nausea, and eye and mucous tissue irritation occur during prolonged exposure to vapor concentrations of 200 ppm (127). These effects are intensified and include incoordination and drunkenness at concentrations in excess of 600 ppm. At concentrations in excess of 1000 ppm the anesthetic and respiratory depression effects can cause unconsciousness and death. A single, brief exposure to concentrations above 6000 ppm can be immediately dangerous to life. Reversible changes to the liver have been reported following prolonged exposures to concentrations in excess of 200 ppm (128–134). Alcohol consumed before or after exposure may increase adverse effects.

The OSHA permissible exposure limit (PEL) for tetrachloroethylene is 25 ppm (8-h TWA) (135). The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) is 50 ppm. In addition they recommend a 15 minute, short-term exposure limit (STEL) of 200 ppm (94,136). The odor threshold for tetrachloroethylene ranges from about 5 to 70 ppm (127). Therefore odor alone does not provide adequate warning of potential overexposure in the workplace. Air sampling of the work environment should be performed in order to determine the need for protective equipment. Fatalities have occurred when workers have entered unventilated tanks or equipment containing high vapor concentrations of tetrachloroethylene without utilizing a self-contained breathing apparatus (137). Victims of overexposure should be removed from the area, given artificial respiration or oxygen if necessary, and a physician should be consulted (138).

Repeated exposure of skin to liquid tetrachloroethylene may defat the skin causing dermatitis. When frequent or prolonged contact is likely, gloves of Viton, nitrile rubber, or neoprene should be used, discarding them when they begin to deteriorate. Tetrachloroethylene can cause significant discomfort if splashed in the eyes. Although no serious injury results, it can cause transient, reversible corneal injury. If contact with skin or eyes occurs, follow standard first-aid practices.

Ingestion of small amounts of tetrachloroethylene is not likely to cause permanent injury; however, ingestion of large amounts may result in serious injury or even death. All containers should be properly labeled. If solvent is swallowed, consult a physician immediately. Do not induce vomiting. If solvent is aspirated it is rapidly absorbed through the lungs and may cause systemic effects and chemical pneumonia.

Exposure to tetrachloroethylene as a result of vapor inhalation is followed by absorption into the bloodstream. It is partly excreted unchanged by the lungs

(129,130). Approximately 20% of the absorbed material is subsequently metabolized and eliminated through the kidneys (139–141). Metabolic breakdown occurs by oxidation to trichloroacetic acid and oxalic acid.

Three significant studies have been conducted on the potential carcinogenic effects of tetrachloroethylene in laboratory animals (142–144). Two of these studies showed increases in observed liver and/or kidney tumors at high dosage levels. The third study showed no significant differences between exposed and control groups of animals at inhalation exposure levels up to 600 ppm. Tetrachloroethylene is classified in Group 2B, a "possible human carcinogen" by the International Agency for Research on Cancer (IARC). The National Toxicology Program (NTP) lists tetrachloroethylene as "reasonably anticipated to cause cancer in humans." Pharmacokinetic studies suggest the effects observed in laboratory animals are not directly applicable to humans (145,146). During the early 1990s, the Environmental Protection Agency (EPA), under its *Guidelines for Carcinogenic Risk Assessment*, had not made a final decision on the classification for this chemical (147).

No teratogenic effects were observed in mice and rats exposed to vapor concentrations of 300 ppm. Exposure levels having no effect on the mother are not anticipated to affect the fetus (148).

4.8. Environmental Regulations. Tetrachloroethylene is subject to inventory and release reporting under Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA). Tetrachloroethylene waste is considered hazardous waste under the Resource Conservation and Recovery Act of 1984 (RCRA). The preferred methods of disposal are through licensed reclaimers or permitted incinerators. The EPA revised the reportable quantity (RQ) for tetrachloroethylene to 100 lbs in 1989. Although tetrachloroethylene does not contribute to smog formation, and the EPA recommended exemption from Volatile Organic Compounds (VOC) regulations in 1983 (149), it continues to be controlled as a VOC. Under the Clean Air Act Amendment of 1990, tetrachloroethylene is considered a hazardous air pollutant. Under this act, the EPA will develop standards to control tetrachloroethylene emissions in dry-cleaning and metal cleaning applications. Under the Safe Drinking Water Act, EPA has established a maximum contaminant level (MCL) of 0.005 mg/L and a goal of 0 mg/L for tetrachloroethylene (150). Packed tower aeration and granular activated carbon are considered the best available technologies for removal of tetrachloroethylene from drinking water.

4.9. Uses. Use of tetrachlorethylene as a feedstock for chlorofluorocarbon production accounts for 65% of demand. Approximately 15% is used in the dry-cleaning industry. Metal cleaning applications account for 10% of consumption and miscellaneous uses account for 10%. Miscellaneous uses include transformer insulating fluid, chemical maskant formulations, and in a process for desulfurizing coal (125).

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