Kirk-Othmer Encyclopedia of Chemical Technology.

TETRACHLOROETHYLENE

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. These two properties combined with its excellent solvent properties account for its dominant use in the dry-cleaning industry as well as its application in metal cleaning and vapor degreasing.

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. Demand for tetrachloroethylene peaked in the 1980s. The decline in demand can be attributed to use of tighter equipment and solvent recovery in the dry-cleaning and metal cleaning industries and the phaseout of CFC 113 (trichlorotrifluoroethane) under the Montreal Protocol.

1. Physical and Chemical Properties

The physical properties of tetrachloroethylene are listed in Table 1. 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 (1).

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 (2). However, the unstabilized compound, in the presence of water for prolonged periods, slowly hydrolyzes to yield trichloroacetic acid [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] (3).

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 **(1)** and **(2)** are intermediates of this autoxidation. Compound **(1)** rear-ranges to form trichloroacetyl chloride and oxygen, whereas compound **(2)** breaks down to form two molecules of phosgene.

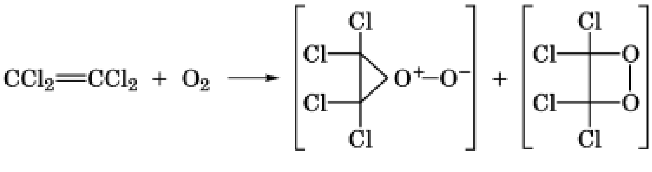
Table 1. Properties of Tetrachloroethylene

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.



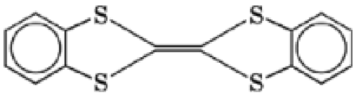
(1) **(2)**

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 (4). Tetrachloroethylene also reacts explosively with metallic potassium at its melting point, however it does not react with sodium (5).

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] (6). 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) (7).

Tetrachloroethylene reacts with formaldehyde and concentrated sulfuric acid at 80°C to form 2,2-dichloropropanoic acid [75-99-0] (8). Copolymers with styrene, vinyl acetate, methyl acrylate, and acrylonitrile are formed in the presence of dibenzoyl peroxide (9, 10).

Tetrachloroethylene is heated at 110–120°C with *o*-benzenedithiol, in the presence of sodium ethoxide, to form 2,2′-bis-1,3-benzdithiolene (11).



The addition of stabilizers to tetrachloroethylene inhibits corrosion of aluminum, iron, and zinc which otherwise occurs in the presence of water (12). 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.

2. 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.

2.1. 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

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

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

2.2. 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 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.

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

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

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

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

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

3. 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)

Table 2. Tetrachloroethylene World Production Capacity and Demand[a] by Region, 10^3 t

Area	Capacity	Demand
United States	327	252
Western Europe	599	257
Japan	96	101
Total	*1012*	*610*

[a] In 1987 (13).

Table 3. United States Tetrachloroethylene Producers and Their Capacitiesa[a], 10^3 t

Producer	1988 Capacity[b]
Dow Chemical Co.	
Pittsburg, Calif.	22.7[c]
Plaquemine, La.	40.8
Occidental Chemical Corp.	
Deer Park, Tex.	81.6
PPG Industries, Inc.	
Lake Charles, La.	90.7
Vulcan Materials Co.	
Geismar, La.	68.0
Wichita, Kans.	22.7

[a] Ref. 13.

[b] Capacities are flexible, depending on feedstocks and operating conditions.

[c] In 1990, Dow announced its intention to shut down this facility.

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. Economic Aspects

World capacity and demand for tetrachloroethylene were approximately 1100 and 845 thousand metric tons in 1974, respectively. Although demand increased into the mid-1980s, since then demand for tetrachloroethylene has decreased significantly as a result of the phaseout of chlorofluorocarbons, the use of more efficient dry-cleaning equipment, and increased reclamation of waste solvent. World capacity and demand as of 1988 are provided in Table 2 Several United States' manufacturers have shut down facilities in the last fifteen years. Current manufacturers and their capacities are listed in Table 3. United States' production and sales history is shown in Table 4.

Table 4. United States Tetrachloroethylene Production and Sales[a], 10^3 t

Year	Production	Sales	Price[b] $/ton
1974	333.1	321.5	243
1976	303.4	259.7	391
1978	333.4	249.1	276
1980	347.1	268.1	507
1982	265.3	229.0	441
1984	260.0	196.7	683
1986	187.8	219.9	683
1988	225.8	256.3	683
1989	218.3	197.1	683
1990c	132.3		683

[a] Courtesy of the U.S. International Trade Commission.
[b] List price: tanks, industrial-grade, consumers, delivered.
[c] 1990 production through third quarter report.

5. 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 (14). Typical commercial grades should not contain more than 50 ppm water, 0.0005 wt % acidity (as HCl), or 0.001 wt % insoluble residue.

6. Uses

Approximately 50% of the demand for tetrachloroethylene is in the dry-cleaning industry where about 80% of all dry cleaners use it as their primary cleaning agent. Use as a feedstock for chlorofluorocarbon production accounts for 30% of current demand. Metal cleaning and miscellaneous applications represent 12 and 8% of demand, respectively. The miscellaneous applications include such varied uses as transformer insulating fluid, chemical maskant formulations, and as a process solvent for desulfurizing coal.

7. Toxicity

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 (15). 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 (16–22). Alcohol consumed before or after exposure may increase adverse effects.

The OSHA permissible exposure limit (PEL) for tetrachloroethylene is 25 ppm (8-h TWA) (23). 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 (24). The odor threshold for tetrachloroethylene ranges from about 5 to 70 ppm (15). 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 (25). Victims of overexposure should be removed from the area, given artificial respiration or oxygen if necessary, and a physician should be consulted (26).

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 (17, 18). Approximately 20% of the absorbed material is subsequently metabolized and eliminated through the kidneys (27–29). 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 (30–32). 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 (33, 34). 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 (35).

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 (36).

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 (37), 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 (38). Packed tower aeration and granular activated carbon are considered the best available technologies for removal of tetrachloroethylene from drinking water.

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