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CARBON TETRACHLORIDE

Carbon tetrachloride [56-23-5] (tetrachloromethane), CCl_4, at ordinary temperature and pressure is a heavy, colorless liquid with a characteristic nonirritant odor; it is nonflammable. Carbon tetrachloride contains 92 wt % chlorine. When in contact with a flame or very hot surface, the vapor decomposes to give toxic products, such as phosgene. It is the most toxic of the chloromethanes and the most unstable upon thermal oxidation. The commercial product frequently contains added stabilizers. Carbon tetrachloride is miscible with many common organic liquids and is a powerful solvent for asphalt, benzyl resin (polymerized benzyl chloride), bitumens, chlorinated rubber, ethylcellulose, fats, gums, rosin, and waxes.

Carbon tetrachloride was one of the first organic chemicals produced on a large scale. In the 1890s, commercial manufacturing processes were being investigated by the United Alkali Co. in England. At the same time it was also produced in Germany, exported to the United States, and retailed as a spotting agent under the trade name Carbona. Large-scale production of carbon tetrachloride in the United States began about 1907. By 1914, annual production fell just short of 4500 metric tons and was used primarily for dry cleaning and for charging fire extinguishers. During World War I, U.S. production of carbon tetrachloride expanded greatly; its use was extended to grain fumigation and the rubber industry. In 1934 it was supplanted as the predominant dry-cleaning agent in the United States by perchloroethylene, which is much less toxic and more stable. During the years immediately preceding World War II, trichloroethylene began to displace carbon tetrachloride from its then extensive market in the United States as a metal degreasing solvent. Carbon tetrachloride is more difficult to recover from degreasing operations, more readily hydrolyzed, and more toxic than trichloroethylene. The demands of World War II stimulated production and marked the beginning of its use as the starting material for chlorofluoromethanes, by far the most important application for carbon tetrachloride.

By the late 1940s, carbon tetrachloride was rapidly losing in competition not only with trichloroethylene but with perchloroethylene as well. In 1948 only 33% of the solvent used by the dry-cleaning industry was carbon tetrachloride and 60% was perchloroethylene; two years later the ratio of perchloroethylene to carbon tetrachloride was three to one. This technological change was not reflected in past sales of carbon tetrachloride, which exhibited a steady increase following World War II. It was at this time, ca 1950, that carbon tetrachloride found a new and rapidly expanding use as the starting material in the manufacture of fluorinated refrigerants, an application that by 1954 accounted for about half the total demand for carbon tetrachloride and over 95% of the demand today.

1. Physical and Chemical Properties

The physical properties of carbon tetrachloride are listed in Tables 1 and 2.

Carbon tetrachloride readily dissolves stannic chloride, $SnCl_4$, but not ferric chloride, $FeCl_3$. Carbon tetrachloride forms a large number of binary and several ternary azeotropic mixtures; a partial list of the former is shown in Table 3.

Table 1. Physical Properties of Carbon Tetrachloride

Property	Value
mol wt	153.82
mp, °C	
101.3 kPa[a]	−22.92
21.3 MPa[b]	−19.5
62.8 MPa[b]	0
117.5 MPa[b]	19.5
bp at 101.3 kPa[a], °C	76.72
refractive index at 15°C	1.46305
sp gr	
0/4°C	1.63195
20/4°C	1.59472
76/4°C	1.48020
autoignition temperature, °C	>1000
flash point, °C	none
density of solid, g/cm^3	
−186°C	1.831
−80°C	1.809
vapor density (air = 1)	5.32
surface tension, mN/m (=dyn/cm)	
0°C	29.38
20°C	26.77
60°C	18.16
specific heat, J/kg[c]	
20°C	866
30°C	837
critical temperature, °C	283.2
critical pressure, MPa[b]	4.6
critical density, kg/m^3	558
thermal conductivity, mW/(m·K)	
liquid, 20°C	118
vapor, bp	7.29
average coefficient of volume expansion	
0–40°C	0.00124
dielectric constant, ϵ	
liquid, 20°C	2.205
liquid, 50°C	1.874
vapor, 87.6°C	1.00302
heat of formation, kJ/mol[c]	
liquid	−142
vapor	−108
heat of combustion, liquid, at constant volume at 18.7°C, kJ/mol[c]	365
latent heat of fusion, kJ/mol[c]	2.535
latent heat of vaporization, kJ/kg[c]	194.7
solubility of CCl_4 in water at 25°C, g/100 g H_2O	0.08
solubility of water in CCl_4 at 25°C, g/100 g CCl_4	0.013

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

Table 2. Viscosity and Vapor Pressure of CCl_4 as a Function of Temperature

Temperature, °C	Viscosity, mPa·s(= cP)	Vapor pressure, kPa[a]
−50		0.123
−20		1.323
0	1.329	4.41
20	0.965	11.94
40	0.739	28.12
60	0.585	58.53
100	0.383	
150		607.3
180	0.201	
200		1458

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

Table 3. Azeotropic Mixtures of Carbon Tetrachloride

Second component	Boiling point of azeotrope, °C	CCl_4, wt %
n-butyl alcohol	77	97.5
acetic acid	77	97
ethyl nitrate	75	84.5
ethyl alcohol	65	84
nitromethane	71	83
ethylene dichloride	76	79
acetone	56	11.5

Many polymer films, eg, polyethylene and polyacrylonitrile, are permeable to carbon tetrachloride vapor (1). Carbon tetrachloride vapor affects the explosion limits of several gaseous mixtures, eg, air-hydrogen and air-methane. The extinctive effect that carbon tetrachloride has on a flame, mainly because of its cooling action, is derived from its high thermal capacity (2).

As chlorination proceeds from methyl chloride to carbon tetrachloride, the length of the C–Cl bond is decreased from 0.1786 nm in the former to 0.1755 nm in the latter (3). At ca 400°C, thermal decomposition of carbon tetrachloride occurs very slowly, whereas at 900–1300°C dissociation is extensive, forming perchloroethylene and hexachloroethane and liberating some chlorine. Subjecting the vapor to an electric arc also forms perchloroethylene and hexachloroethane, as well as hexachlorobenzene, elementary carbon, and chlorine.

A cold mixture of carbon tetrachloride and water, seeded with crystals of chloroform hydrate, yields crystals of a hydrate that decomposes at 1.4–1.49°C and 101.3 kPa (760 mm Hg). Carbon tetrachloride is the chloromethane least resistant to oxidative breakdown. One gram of CCl_4 mixed with air and heated to 335°C in the presence of iron produces 375 mg of phosgene. Only 2.4 mg of phosgene is produced from 1 g of chloroform under the same conditions (4). When mixed with excess water and heated to 250°C, carbon tetrachloride decomposes to carbon dioxide and hydrochloric acid; if the quantity of water is limited, phosgene is produced. This decomposition also occurs when wet carbon tetrachloride is exposed to uv irradiation (253.7 nm) at ordinary temperatures (5). Chloromethanes, hexachloroethane, and perchloroethylene are formed with steam at high temperatures. A similar decomposition occurs when carbon tetrachloride vapor is heated with some metallic oxides, eg, aluminum and magnesium oxides. An aqueous suspension of carbon tetrachloride droplets exposed to ultrasonic irradiation at ordinary temperature decomposes to carbon dioxide, chlorine, hydrogen chloride, perchloroethylene, and hexachloroethane. Dry carbon tetrachloride does not react with most commonly used construction metals, eg, iron and nickel; it reacts very slowly with copper and lead. Like the other chloromethanes, carbon tetrachloride is reactive, sometimes explosively, with aluminum and its alloys (6–8). The presence of moisture is probably a necessary requirement for the reaction with aluminum. When carbon tetrachloride is in contact with metallic sodium or potassium, or with a liquid alloy of both metals, shock may produce an explosion (9). On heating with sodium amalgam, decomposition takes place with the formation of sodium chloride and the liberation of carbon; at 400°C an analogous reaction takes place with mercury alone.

Carbon tetrachloride can be reduced to chloroform using a platinum catalyst (10) or zinc and acid. With potassium amalgam and water, carbon tetrachloride can be totally reduced to methane. It is widely employed as an initiator in the dehydrochlorination of chloroethanes at 400–600°C:

$$\mathrm{CH_2ClCH_2Cl} + \xrightarrow{\mathrm{CCl_4}} \mathrm{CH_2{=}CHCl} + \mathrm{HCl} + \mathrm{CCl_4}$$

When treated with aluminum bromide at 100°C, carbon tetrachloride is converted to carbon tetrabromide [558-13-4]; reaction with calcium iodide, CaI_2, at 75°C gives carbon tetraiodide [507-25-5]. With concentrated hydroiodic acid at 130°C, iodoform [75-47-8], CHI_3, is produced. Carbon tetrachloride is unaffected by gaseous fluorine at ordinary temperatures. Replacement of its chlorine by fluorine is brought about by reaction with hydrogen fluoride at a temperature of 230–300°C and a pressure of 5.17–6.89 MPa (750–1000 psi), producing mainly dichlorodifluoromethane (11, 12). Replacement of more than two chlorine atoms in carbon tetrachloride with fluorine from hydrogen fluoride requires other techniques (13).

Carbon tetrachloride forms telomers with ethylene and certain other olefins (14–16). The mixture of liquid products derived from ethylene telomerization may be represented $CCl_3(CH_2CH_2)_nCl$ in which n is a small number. Reaction of ethylene and carbon tetrachloride takes place under pressure and is induced by the presence of a peroxygen compound, eg, benzoyl peroxide (17–19) or metal carbonyls (14, 15).

Benzene reacts with carbon tetrachloride in the presence of anhydrous aluminum chloride to give triphenylchloromethane; no tetraphenylmethane is formed (20). At elevated temperatures, carbon tetrachloride attacks silica gel forming a silicon oxychloride (21).

2. Manufacture

For many years chlorination of carbon disulfide was the only process used to manufacture carbon tetrachloride. In the 1950s, chlorination of hydrocarbons, particularly methane, became more popular in the United States. Many hydrocarbons and chlorinated hydrocarbons are now used to feed chlorination reactors to make carbon tetrachloride.

2.1. Chlorination of Hydrocarbons or Chlorinated Hydrocarbons

Chlorination at pyrolytic temperatures is often referred to as chlorinolysis because it involves a simultaneous breakdown of the organics and chlorination of the molecular fragments. A number of processes have been described for the production of carbon tetrachloride by the chlorinolysis of various hydrocarbon or chlorinated hydrocarbon waste streams (22–24), but most literature reports the use of methane as the primary feed. The quantity of carbon tetrachloride produced depends somewhat on the nature of the hydrocarbon starting material but more on the conditions of chlorination. The principal by-product is perchloroethylene with small amounts of hexachloroethane, hexachlorobutadiene, and hexachlorobenzene. In the Hüls process, a 5:1 mixture by volume of chlorine and methane reacts at 650°C; the temperature is maintained by control of the gas flow rate. A heat exchanger cools the exit gas to 450°C, and more methane is added to the gas stream in a second reactor. The use of a fluidized-bed-type reactor is known (25, 26). Carbon can be chlorinated to carbon tetrachloride in a fluidized bed (27).

2.2. Oxychlorination of Hydrocarbons

Methane was oxychlorinated with HCl and oxygen over a 4:3:3 CuCl–$CuCl_2$–KCl molten mixture to give a mixture of chlorinated methanes, 60 mol % of which was carbon tetrachloride (28). Aqueous 20% HCl was used in the multistep process as the source of the acid. Anhydrous HCl is more typically used. Other oxychlorination processes can be made to yield high percentages of carbon tetrachloride starting from any of several hydrocarbon feeds (29–31). The typical reaction temperature is 400–600°C (see Chlorocarbons and chlorohydrocarbons, Methyl chloride; Methylene chloride; AND Chloroform).

2.3. Carbon Disulfide Chlorination

The chlorination of carbon disulfide [75-15-0] is a very old method of producing carbon tetrachloride that is still practiced commercially in the United States. In this process CS_2 reacts continuously with chlorine in an annular reactor at 105–130°C. Product CCl_4 is separated by distillation to a CS_2 content of 0–5 ppm. By-product S_2Cl_2 is reduced in a reactor at 450°C with hydrogen without a catalyst to give sulfur of 99.985% purity (32). Other processes use ferric chloride as a catalyst (33, 34).

3. Economic Aspects

Chlorofluorocarbon gases (CFCs),such as CFC-12 dichlorodifluoromethane [75-71-8], CCl_2F_2, and CFC-11 fluorotrichloromethane [75-69-4], CCl_3F, were introduced as aerosol propellants in the late 1950s and early 1960s. From 1960 to 1970, carbon tetrachloride, the feedstock for these compounds, averaged a growth rate of 10.7% per year (Table 4). From 1970 to 1974, as less expensive propellants became available, production of fluorocarbon propellants increased at a rate of only about 7.2%/yr even though overall aerosol consumption grew ca 10%/yr during the same period. In 1978 the use of chlorofluorocarbons in aerosols was essentially banned by the EPA. During the period 1979 to 1988 the compounded growth rate for carbon tetrachloride production was $-0.7\%/\mathrm{yr}$ (35). This is projected to decrease to $-3\%/\mathrm{yr}$ for the years 1989 to 1993. Production of CFC-11 and -12 is slated to be phased out by the year 2000, though it will probably decrease faster than that as replacement HCFCs become available. The U.S. producers of carbon tetrachloride and their capacities appear in Table 5. All methylene chloride and chloroform producers also make a small amount of carbon tetrachloride as a by-product. Those producers are not listed in Table 5 since the amount of carbon tetrachloride made is small and varies depending on the ratio of methylene chloride to chloroform made.

In 1978 there were 10 producing carbon tetrachloride plants in the United States. The number has decreased to the six listed, though the total capacity has decreased only about 10%.

List prices do not reflect actual market conditions because of overcapacity and the shrinking nature of the market. Although present U.S. carbon tetrachloride capacity of 271,900 t/yr is far in excess of demand, many installations are capable of producing other chlorinated hydrocarbons such as perchloroethylene.

4. Standards and Analysis

The most widely used method of analysis for carbon tetrachloride is gas chromatography. A capillary column medium that does a very good job in separating most chlorinated hydrocarbons is methyl silicone or methyl (5% phenyl) silicone. The detector of choice is a flame ionization detector. Typical molar response factors for the chlorinated methanes are methyl chloride, 2.05; methylene chloride, 2.2; chloroform, 2.8; and carbon tetrachloride, 3.1, where methane is defined as having a molar response factor of 2.00. Most two-carbon chlorinated hydrocarbons have a molar response factor of about 1.0 on the same basis.

Table 4. U.S. Carbon Tetrachloride Production and Price Statistics[a]

Year	Total production, 10^3 t	Total sales, 10^3 t	Total value, 10^6 $	Unit value, $/kg
1960	168.8	151.3	27.14	0.18
1965	269.3	231.1	37.49	0.15
1970	458.7	381.6	44.09	0.11
1975	411.2	219.6	65.9	0.31
1976	388.6	208.2	60.3	0.29
1977	367.76	175.22	49.08	0.29
1978	335.01	165.18	41.70	0.24
1979	324.76	159.47	40.02	0.24
1980	322.54	174.70	44.13	0.24
1981	330.22	175.28	48.78	0.29
1982	267.02	141.04	39.89	0.29
1983	260.38	156.43	44.46	0.29
1984	324.11	159.65	54.47	0.35
1985	293.46	163.79	58.22	0.35
1986	284.99	225.39	68.87	0.31
1987	305.52	326.28	102.07	0.31
1988	346.08	386.03	129.43	0.33

[a] Courtesy of U.S. International Trade Commission.

Table 5. U.S. Producers of Carbon Tetrachloride[a]

Producer	Location	Capacity, 10^3 t/yr
The Dow Chemical Company	Pittsburg, Calif.	36.4
The Dow Chemical Company	Plaquemine, La.	45.5
Vulcan Materials	Geismar, La.	40.9
Vulcan Materials	Wichita, Kans.	27.3
Akzo	LeMoyne, Ala.	118.2
LCP	Moundsville, W.Va.	3.6
Total		*271.9*

[a] Ref. 35.

A good technical grade of carbon tetrachloride contains not more than the following amounts of impurities: 1 ppm acidity as HCl, 1 ppm carbon disulfide if manufactured by carbon disulfide chlorination, 20 ppm bromine, 200 ppm water, and 150 ppm chloroform. The residue should not exceed 10 ppm on total evaporation. The product should give no acid reaction with bromophenol blue, and the starch iodine test should indicate the absence of free chlorine.

When heated with pyrocatechol [720-80-9], copper powder, and alcoholic sodium hydroxide, carbon tetrachloride gives a blue color that changes to red on addition of hydrochloric acid. This color reaction is not produced by chloroform. Quantitative analysis of carbon tetrachloride may be done by first decomposing the sample free of organic and inorganic chlorides, heating in a sealed tube with alcoholic potash, and subsequently determining the potassium chloride formed as the silver halide. The Zeiss interference refractometer has been used to determine the concentration of carbon tetrachloride vapor in air (36).

5. Health and Safety Factors

All persons who have occasion to use or handle carbon tetrachloride should be thoroughly instructed and adequately supervised in the proper methods of handling the substance to prevent or minimize exposure to the liquid or its vapors and in the proper methods of disposing of this chemical.

Carbon tetrachloride is the oldest and was the most extensively used chlorinated solvent in degreasing and dry-cleaning operations for many years. Consequently, its narcotic and toxic properties have been the subject of much investigation. Careful investigations have repeatedly shown carbon tetrachloride to be one of the most harmful of the common solvents (37).

Carbon tetrachloride is toxic by inhalation of its vapor and oral intake of the liquid. Inhalation of the vapor constitutes the principal hazard. Exposure to excessive levels of vapor is characterized by two types of response: an anesthetic effect similar to that caused by compounds such as diethyl ether and chloroform; and organic injury to the tissues of certain organs, in particular the liver and kidneys. This type of injury may not become evident until 1–10 days after exposure. The nature of the effect is determined largely by the vapor concentration but the extent or severity of the effect is determined principally by the duration of exposure (38).

Organic injury may result from single prolonged exposure to carbon tetrachloride vapor or from repeated short duration exposures. Serious and fatal injuries are usually the result of a single prolonged exposure. Vapor concentrations of only a few hundred parts per million may be sufficient to cause injury. Symptoms of exposure include nausea and vomiting, headache, burning of eyes and/or throat, drowsiness, abdominal pain or discomfort, weakness, and muscle stiffness and soreness. Prolonged or repeated exposure to carbon tetrachloride vapor or liquid may result in subacute or chronic poisoning. Consequently, a threshold limit value of 5 ppm by volume of carbon tetrachloride in air has been established by ACGIH as a maximum safe concentration for daily eight-hour exposure. The OSHA permissible exposure level is 2 ppm.

Occasional brief contacts of liquid carbon tetrachloride with unbroken skin do not produce irritation, though the skin may feel dry because of removal of natural oils. Prolonged and repeated contacts may cause dermatitis, cracking of the skin, and danger of secondary infection. Carbon tetrachloride is apparently absorbed through the skin but at such a slow rate that there is no significant hazard of systemic poisoning in normal industrial operations.

In most situations, adequate, usually forced, ventilation is necessary to prevent excessive exposure. Persons who drink alcohol excessively or have liver, kidney, or heart diseases should be excluded from any exposure to carbon tetrachloride. All individuals regularly exposed to carbon tetrachloride should receive periodic examinations by a physician acquainted with the occupational hazard involved. These examinations should include special attention to the kidneys and the liver. There is no known specific antidote for carbon tetrachloride poisoning. Treatment is symptomatic and supportive. Alcohol, oils, fats, and epinephrine should not be given to any person who has been exposed to carbon tetrachloride. Following exposure, the individual should be kept under observation long enough to permit the physician to determine whether liver or kidney injury has occurred. Artificial dialysis may be necessary in cases of severe renal failure.

6. Handling and Storage

Although in the dry state carbon tetrachloride may be stored indefinitely in contact with some metal surfaces, its decomposition upon contact with water or on heating in air makes it desirable, if not always necessary, to add a small quantity of stabilizer to the commercial product. A number of compounds have been claimed to be effective stabilizers for carbon tetrachloride, eg, alkyl cyanamides such as diethyl cyanamide (39), 0.34–1% diphenylamine (40), ethyl acetate to protect copper (41), up to 1% ethyl cyanide (42), fatty acid derivatives to protect aluminum (43), hexamethylenetetramine (44), resins and amines (45), thiocarbamide (46), and a ureide, ie, guanidine (47).

Small quantities of carbon tetrachloride can be shipped in 1, 5, and 55 gallon (208 L) metal containers. Larger quantities are shipped by tank truck, tank car, barge, and ship. Seamless stainless steel, Teflon, or seamless bronze hose is recommended with asbestos, Teflon, Viton, or neoprene gaskets. Special precautions should be taken to prevent contact with aluminum, magnesium metal, and their alloys (48).

7. Uses

Carbon tetrachloride was formerly used for metal degreasing, dry-cleaning fluid, fabric spotting fluid, fire extinguisher fluid, grain fumigant, and reaction medium. However, as its toxicity became recognized, it was replaced by less toxic chlorinated hydrocarbons in metal and fabric cleaning applications. During the 1950s the demand for carbon tetrachloride as a raw material in the manufacture of chlorofluorocarbons increased and the net result was continued growth for the product. In 1970, carbon tetrachloride was banned from all use in consumer goods in the United States. Its current principal applications include chlorofluorocarbon production (CFC-11 and -12) and some small use as a reaction medium or chemical intermediate. Chlorofluorocarbons 11 and 12, trichloromonofluoromethane [75-69-4], and dichlorodifluoromethane [75-71-8], respectively, are made by the catalytic reaction of hydrogen fluoride with carbon tetrachloride. These products will decline significantly long term as the Montreal Protocol takes effect.

8. Regulation

Carbon tetrachloride, as are the other chlorinated methanes, is heavily regulated at the national, state, and local level. The manufacturing, storage, and disposal of carbon tetrachloride may be regulated. Carbon tetrachloride is reportable under SARA 312 (inventory) and 313 (emissions). In addition, the nonpermitted release of carbon tetrachloride is reportable at a 10 pound (4.5 kg) quantity under CERCLA. Finally, fugitive monitoring regulations and programs may apply to individual facilities. The discharge of carbon tetrachloride to the waterways may be regulated under OCPSF guidelines or other permitted parameters. Disposal of carbon tetrachloride and carbon tetrachloride-containing wastes may be regulated under RCRA as a discarded commercial chemical (U0211), a nonspecific source waste (F001), or as an extractable at 0.5 mg/L under the TCLP (D019). The potential exposure to carbon tetrachloride by workers may be regulated by OSHA or the state Industrial Hygiene Department. In addition, various state and local regulations may impose other reporting and regulatory standards. Contacting the Environmental or Regulatory Compliance Department before importing, purchasing, selling, using, or disposing of carbon tetrachloride is highly recommended.

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