METHYLENE CHLORIDE

1. Introduction

Methylene chloride [75-09-2] (dichloromethane, methylene dichloride), CH_2Cl_2, is a colorless, heavy liquid with a pleasant ethereal odor. Its outstanding solvent properties are the basis of its principal industrial interest. It was first prepared in 1840 by Regnault by chlorinating methyl chloride in sunlight. The compound was made in 1868 by Perkin by reducing chloroform with zinc dust and hydrochloric acid; he described this at the annual meeting of the British Association and reported its identity as "Regnault's chlorinated chloride of methyl." Butlerow made a thorough investigation of the compound in 1869. Methylene chloride became an industrial chemical of importance during World War II and, during the postwar period, its output underwent a fivefold expansion in the United States. Production reached its zenith in the late 1970s and early 1980s when the methylene chloride market began to shrink because of 1985 National Toxicology Program (NTP) study that indicated carcinogenicity in mice.

2. Physical and Chemical Properties

The physical properties of methylene chloride are listed in Table 1 and the binary azeotropes in Table 2. Methylene chloride is a volatile liquid. Although methylene chloride is only slightly soluble in water, it is completely miscible with other grades of chlorinated solvents, diethyl ether, and ethyl alcohol. It dissolves in most other common organic solvents. Methylene chloride is also an excellent solvent for many resins, waxes, and fats, and hence is well suited to a wide variety of industrial uses. Methylene chloride alone exhibits no flash or fire point. However, as little as 10 vol% acetone or methyl alcohol is capable of producing a flash point.

Methylene chloride is one of the more stable of the chlorinated hydrocarbon solvents. Its initial thermal degradation temperature is 120°C in dry air (1). This temperature decreases as the moisture content increases. The reaction produces mainly HCl with trace amounts of phosgene. Decomposition under these conditions can be inhibited by the addition of small quantities (0.0001–1.0%) of phenolic compounds, eg, phenol, hydroquinone, *p*-cresol, resorcinol, thymol, and 1-naphthol (2). Stabilization may also be effected by the addition of small amounts of amines (3) or a mixture of nitromethane and 1,4-dioxane. The latter diminishes attack on aluminum and inhibits iron-catalyzed reactions of methylene chloride (4). The addition of small amounts of epoxides can also inhibit aluminum reactions catalyzed by iron (5). On prolonged contact with water, methylene chloride hydrolyzes very slowly, forming HCl as the primary product. On prolonged heating with water in a sealed vessel at 140–170°C, methylene chloride yields formaldehyde and hydrochloric acid as shown by the following equation (6).

$$CH_2Cl_2 + H_2O \longrightarrow HCHO + 2\ HCl \qquad (1)$$

Table 1. **Properties of Methylene Chloride**

Property	Value
mol wt	84.92
bp at 101.3 kPa,[a] °C	39.8
fp, °C	−96.7
sp gr at 20°C	1.320
density at 20°C, kg/m^3	1315.7
vapor density (air = 1.02)	2.93
diffusivity in air, m^2/s	9×10^{-5}
refractive index at 20°C	1.4244
coefficient of cubical expansion at 20–35°C	0.0014
viscosity at 20°C mPa · s (=cP)	0.43
surface tension, mN/m (=dyn/cm)	
at 20°C	0.02812
at 30°C	0.02654
heat of vaporization at 20°C, kJ/kg[b]	329.23
thermal capacity, liq, 15–45°C (kJ/kg · K)[c]	1.171
heat capacity at 25°C, J/mol[c]	54.09
heat of combustion, MJ/kg[c]	7.1175
critical density, kg/m^3	472
critical temperature, °C	245.0
critical pressure, MPa[d]	6.171
vapor pressure, kPa[a]	
at 0°C	19.6
at 20°C	46.5
at 30°C	68.1
solubility in water at 20°C, g/kg	13.2
water solubility in methylene chloride at 20°C, g/kg	1.4
kauri-butanol value	136
autoignition temperature, °C	640
flash point (ASTM D1310-67)	none
explosive limits at 250°C, vol% in air	14–25
electrical properties at 24°C	
dielectric strength, V/cm[e]	94.488
specific resistivity at 24°C, Ω · cm	1.81×10^8
dielectric constant at 24°C, 100 kHz	10.7

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert kJ/kg to Btu/lb, multiply by 0.4302.
[c] To convert J to cal, divide by 4.184.
[d] To convert MPa to atm, divide by 0.101.
[e] To convert V/cm to V/100 mils, multiply by 0.254.

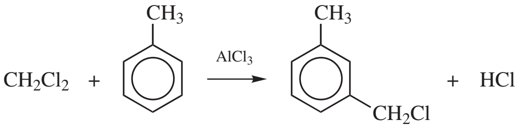
At 180°C, reaction with water results in formic acid, methyl chloride, methanol, hydrochloric acid, and some carbon monoxide.

Dry methylene chloride does not react with the common metals under normal conditions; however, a reaction with aluminum can be initiated, sometimes explosively, by the addition of small amounts of other halogenated solvents or an aromatic solvent (7). Iron catalyzes the reaction, and this can be significant in the handling and storage of methylene chloride and in the formulation of products, eg, in aluminum aerosol containers of pigmented paints, where the conditions necessary for the reaction are commonly found. A typical reaction in this

Table 2. **Binary Azeotropes of Methylene Chloride**

Second component			
Name	Bp, °C	Bp of azeotrope, °C	CH_2Cl_2, wt%
water	100.0	38.1	98.5
methanol	64.7	39.2	94.0
t-butyl alcohol	82.8	57.1	94.0
2-propanol	82.3	56.6	92.0
ethanol	78.4	54.6	88.5
iodomethane	42.5	39.8	79.0
propylene oxide	35.0	40.6	77.0
cyclopentane	49.5	38.0	70.0
diethyl ether	34.6	40.8	70.0
acetone	56.5	57.6	70.0
carbon disulfide	46.3	37.0	61.0
diethylamine	55.5	52.0	45.0

process is shown in equation 2.



(2)

Further dechlorination may occur with the formation of substituted diphenylmethanes. If enough aluminum metal is present, the Friedel-Crafts reactions involved may generate considerable heat and smoke and substantial amounts of hydrogen chloride, which reacts with more aluminum metal, rapidly forming $AlCl_3$. The addition of an epoxide inhibits the initiation of this reaction by consuming HCl. Alkali, alkaline-earth, magnesium, and zinc metals also present a potential reactivity hazard with chlorinated solvents such as methylene chloride.

The most common reaction of methylene chloride is its reaction with chlorine to give chloroform and carbon tetrachloride. This occurs by a free-radical process initiated by heat or light in the gas or liquid phase. Catalytic chlorination to these same products is also known (see CHLOROFORM).

In the gas phase, methylene chloride reacts with nitrogen dioxide at 270°C to yield a gaseous mixture consisting mainly of carbon monoxide, nitric oxide, and hydrogen chloride (8).

Methylene chloride is easily reduced to methyl chloride and methane by alkali metal ammonium compounds in liquid ammonia. When the vapor is contacted with reduced nickel at 200°C in the presence of excess hydrogen, hydrogen chloride and elementary carbon are produced. Heating with alcoholic ammonia at 100–125°C results in hexamethylenetetramine, $(CH_2)_6N_4$, a heterocyclic compound; with aqueous ammonia at 200°C, hydrogen chloride, formic acid, and methylamine are produced.

Bromochloromethane is produced by reaction of an excess of a mixture of methylene chloride and bromine with aluminum at 26 to 30°C (9).

When heated for eight hours at 200°C and 91.2 MPa (900 atm) in the presence of aluminum, methylene chloride reacts with carbon monoxide to yield chloroacetyl chloride, $CH_2ClCOCl$ (10).

Methylene chloride vapor reacts at 300–400°C with a mixture of silicon and reduced copper under a nitrogen atmosphere to give a mixture of organosilicon derivatives (11).

3. Manufacture

Methylene chloride is produced industrially in the United States by two methods. The older and currently lesser used method involves a direct reaction of excess methane with chlorine at high temperatures, approximately 400–500°C, or at somewhat lower temperatures either catalytically or photolytically. This process produces methyl chloride, chloroform, and carbon tetrachloride as coproducts. The temperature and raw material flow rates to the reactor can be controlled to maximize the production of the particular chloromethane desired. The reactor effluent also contains unreacted methane and hydrogen chloride. Methane is recovered by removing the HCl by water washing and then drying before recycling. The liquid chloromethane stream, which contains the methylene chloride and its coproducts, passes through a sequence of fractionating columns after washing, alkali scrubbing, and drying (see METHYL CHLORIDE).

The predominant method of manufacturing methylene chloride employs as a first step the reaction of hydrogen chloride and methanol to give methyl chloride. Excess methyl chloride is then mixed with chlorine and reacts to give methylene chloride, chloroform, and carbon tetrachloride as coproducts. This reaction is usually carried out in the gas phase thermally (12) but can also be done catalytically (13,14) or photolytically (15). Parallel reactor trains operating on different feeds, CH_4–CH_3Cl or CH_3Cl–CH_2Cl_2, are known (16,17). At low temperature and high pressure, the liquid-phase process (18,19) is capable of giving high selectivities to methylene chloride.

Methylene chloride can also be made by reducing either chloroform or carbon tetrachloride with hydrogen over a platinum catalyst (20) or with metal hydrides (21). Chloroform is slowly reduced to methylene chloride upon warming with trisilane, Si_3H_8, in the absence of air as shown in equation 3.

$$4\ CHCl_3 + Si_3H_8 \longrightarrow 4\ CH_2Cl_2 + Si_3H_4Cl_4 \qquad (3)$$

Oxychlorination of methane can yield significant amounts of methylene chloride. A number of patents were obtained by Lummus in the mid-1970s on a high temperature, molten salt oxychlorination process (22,23). Catalyst development work has continued and generally consists of mixtures of Cu, Ni, Cr, or Fe promoted with an alkali metal (24–27). There are no industrial examples of this process at the present time.

Very high selectivities to methylene chloride can be obtained by the reaction of phosgene and formaldehyde at ca 170°C over a variety of activated carbons (28).

$$COCl_2 + CH_2O \longrightarrow CH_2Cl_2 + CO_2$$

Table 3. **U.S. Methylene Chloride Producers**[a]

Producer	Capacity, 10^3 t/yr ($\times 10^6$ lb)
The Dow Chemical Company, Freeport, Tex.	68 (150)
The Dow Chemical Company, Plaquemine, La.	68 (150)
Vulcan, Geismar, La.	45.4 (100)
Vulcan, Wichita, Kans.	61.2 (135)
Total	*242.6*

[a] Ref. 30.

Ferrous hydroxide in the presence of alkaline hydroxides or carbonates reportedly reduces carbon tetrachloride to methylene chloride (29).

4. Economic Aspects

Table 3 lists the U.S. producers of methylene chloride and their rated yearly capacities. Since the product mix of a typical chloromethanes process is very flexible, production may be adjusted according to the demand for methylene chloride and chloroform. The demand for methylene chloride has taken a broad downturn as a result of the 1985 NTP carcinogenicity tests. The 1998 and 1999 demands were 98,430 t and 94,350 t, respectively. Forecast demand for 2003 is 90,700 t. The historical growth rate (1994–1999) was −2.7% per year. Growth rate through 2003 is expected to be 0% (30).

4.1. Price. For the period, 1994–1999, the high price for methylene chloride was \$0.20/kg (\$0.43/lb) and the low was \$0.18/kg (\$0.40/lb), tanks, delivered.

5. Transportation and Handling

All persons who have occasion to use or handle methylene chloride 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.

Because of its low boiling point, methylene chloride should be stored in a cool place away from direct sunlight. Storage containers may be constructed of mild or plain steel that are galvanized or suitably lined. Aluminum is not recommended for bulk storage. All bulk storage tanks should be equipped with a vent dryer packed with calcium chloride or other appropriate desiccant to exclude moisture. Alternatively, the tank may utilize a dry inert gas pad with an appropriate pressure vacuum relief valve. Methylene chloride is transported in drums, truck transports, rail cars, barges, and oceangoing ships. Recommended hose-type is seamless stainless steel, Teflon, seamless bronze, or seamless steel with asbestos, Teflon, Viton, or Neoprene gaskets (31).

6. Specifications

Although methylene chloride is considered a very stable compound, small amounts of stabilizers are usually added at the time of manufacture. Additional

Table 4. **Methylene Chloride Specifications**

Property	Value
distillation range at 101 kPa (1 atm), IBP-DP	39.4–40.4°C
specific gravity at 25/25°C	1.319–1.322
acidity as HCl, max	5 ppm
nonvolatile matter, max	10 ppm
water, max	100 ppm
APHA color, max	10
free halogens	negative to test
residual odor	negative to test

stabilizers may be used to provide adequate protection against corrosion or solvent breakdown in specific applications. See Table 4 for specification of a representative commercial grade of methylene chloride.

Gas chromatographic or infrared techniques are commonly used to monitor the purity of methylene chloride shipments.

7. Analytical Methods

The most widely used method of analysis for methylene chloride 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.

8. Health and Safety Factors

Methylene chloride is one of the least toxic chlorinated methanes. The LD_{50} in rats is in the range of 1.6–3.0 g/kg body weight. The fatal dose for a 68-kg person ranges from 80 mL (1.5–2.5 oz) to 470 mL (1 pint). Methylene chloride is painful and irritating if splashed directly into the eye. The ACGIH threshold limit value (TLV) for methylene chloride is 50 ppm by volume for an eight-hour exposure. The OSHA permissible exposure level is 25 ppm time-weighted average (32).

High levels of methylene chloride vapors have an anesthetic action. The odor threshold is approximately 300 ppm. At concentrations between 310 and 800 ppm, the odor is clearly identifiable but not unpleasant. In the range of 900 to 1200 ppm, the odor is pronounced and anesthetic effects with accompanying dizziness begins after 20 minutes of exposure. Excessive exposure to levels greater than 2300 ppm causes lightheadedness, dizziness, nausea, headaches, and tingling or numbness of extremities. Mental alertness and physical coordination may also be impaired. Exposure to very high concentrations could result in unconsciousness or death.

Methylene chloride, applied to both intact and abraded skin of rabbits in doses as large as 0.5 g/kg body weight per day, five times per week, for a period of 90 days, caused no apparent adverse effects. Absorption through the skin is not usually a hazard when good working practices are followed.

A determination that carbon monoxide might be a metabolite of methylene chloride in humans (33) suggests that unacceptable levels of carboxyhemoglobin would exist in the blood of persons exposed to methylene chloride vapors at concentrations greater than 500 ppm for extended periods of time. These conditions are rarely encountered in most industrial applications. However, as with any organic solvent, adequate ventilation should be provided to ensure compliance with all industrial and governmental regulations.

Studies in which pregnant rats and mice were exposed to 1250 ppm of methylene chloride for seven hours a day on days 6–15 of gestation indicated no significant maternal, embryonal, or fetal toxicity (34). Methylene chloride was shown to be nonteratogenetic to either animal at the concentration studied.

The National Toxicology Program (NTP) reported on tests on mice and rats that there was an increase in the spontaneous incidence of benign tumors in male and female rats and an increase in malignant liver and lung tumors in B6C3F1 mice. NTP concluded that these data demonstrated clear evidence of carcinogenicity in mice and female rats and some evidence in male rats (35).

Like many organic solvents, including hexane, heptane, benzene, xylene, toluene, gasoline, and particularly some of the other chlorinated and fluorinated solvents, methylene chloride may cause cardiac arrhythmias in the presence of elevated epinephrine when inhaled at concentrations as high as 20,000 ppm (36).

Fatalities have occurred when unprotected workers have entered an unventilated tank or piece of equipment that contained high vapor concentrations of a chlorinated solvent such as methylene chloride.

9. Environmental Concerns and Regulations

Methylene chloride, as are the other chlorinated methanes, is heavily regulated at the national, state, and local level. The manufacturing, storage, and disposal of methylene chloride may be regulated. Methylene chloride is reportable under SARA 312 (inventory) and 313 (emissions). In addition, the nonpermitted release of methylene chloride is reportable at a 1000 pound (455 kg) quantity under CERCLA. Finally, fugitive monitoring regulations and programs may apply to individual facilities. The discharge of methylene chloride to the waterways may be regulated under OCPSF guidelines or other permitted parameters. Disposal of methylene chloride and methylene chloride-containing wastes may be regulated under RCRA as a discarded commercial chemical (U080) or as a nonspecific source waste (F001 and F002). The potential exposure to methylene chloride 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 methylene chloride is strongly recommended.

10. Uses

For use in paint strippers, one of its first applications, methylene chloride is blended with other chemical components to maximize its effectiveness against specific coatings. Typical additives include alcohols, acids, amines or ammonium hydroxide, detergents, and paraffin wax. Paint stripping formulations without methylene chloride have not as yet been shown to be as effective as those with methylene chloride. A quasi-azeotropic mixture containing methylene chloride for the treatment of solid surfaces has been decribed (37).

Methylene chloride is used as a solvent in cements for clear plastics and is often blended with other solvents to help dissolve the resin used in contact adhesives (30).

Methylene chloride is used as an extraction solvent for the decaffeination of coffee, spices, and beer hops because of its strong solvency power and stability (38–40) manufacture of photographic film as well as a carrier solvent in the textile industry. It is also used as a solvent for vapor degreasing of metal parts. Methylene chloride may also be blended with petroleum and other chlorinated hydrocarbons for use as a dip-type cleaner in the metal-working industry. Use in this area is falling because of recycling and recovery efforts on the part of end users. Aerosol applications are expected to continue to decline because of a government cancer-labeling requirement on consumer goods containing methylene chloride. The reduction in the use of 1,1,1-trichloroethane because of the Montreal Protocol and clean air legislation may increase the use of methylene chloride. Other applications include low pressure refrigerants, air-conditioning installations, and as a low temperature heat-transfer medium.

There are several uses for methylene chloride in chemical processing, including the manufacture of polycarbonate plastic from bisphenol and phosgene, the manufacture of photoresist coatings, and as a solvent carrier for the manufacture of insecticide and herbicide chemicals (Table 5). Methylene chloride is also used by the pharmaceutical industry as a process solvent in the manufacture of steroids, antibiotics, vitamins, and to a lesser extent as a solvent in the coating of tablets (41). Other uses include grain fumigation (42) and oil dewaxing (43).

Table 5. **Uses of Methylene Chloride (2000)**

paint stripper	30%
adhesives	20%
aerosols	10%
pharmaceuticals	10%
chemical processing	10%
metal degreasing	10%
urethane foam blowing agent	5%
other	5%

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