CARBON DISULFIDE

1. Introduction

Carbon disulfide [75-15-0] (carbon bisulfide, dithiocarbonic anhydride), CS_2, is a toxic, dense liquid of high volatility and flammability. It is an important industrial chemical and its properties are well established. Low concentrations of carbon disulfide naturally discharge into the atmosphere from certain soils, and carbon disulfide has been detected in mustard oil, volcanic gases, and crude petroleum. Carbon disulfide is an unintentional by-product of many combustion and high temperature industrial processes where sulfur compounds are present.

Carbon disulfide was first prepared nearly two hundred years ago by heating sulfur with charcoal. That general approach was the only commercial route to carbon disulfide until processes for reaction of sulfur and methane or other hydrocarbons appeared in the 1950s. Significant commercial production of carbon disulfide began around 1880, primarily for agricultural and solvent applications. Both the physical and chemical properties of carbon disulfide are utilized in industry. Commercial uses grew rapidly from about 1929 to 1970, when the principal applications included manufacturing viscose rayon fibers, cellophane, carbon tetrachloride, flotation aids, rubber vulcanization accelerators, fungicides, and pesticides. Production of carbon disulfide in the United States has declined in recent years. Other chemical fibers and films, as well as environmental and toxicity considerations related to carbon tetrachloride, have had significant impact on the demand for carbon disulfide.

2. Physical Properties

Pure carbon disulfide is a clear, colorless liquid with a delicate etherlike odor. A faint yellow color slowly develops upon exposure to sunlight. Low-grade commercial carbon disulfide may display some color and may have a strong, foul odor because of sulfurous impurities. Carbon disulfide is slightly miscible with water, but it is a good solvent for many organic compounds. Thermodynamic constants (1), vapor pressure (1,2), spectral transmission (3,4), and other properties (1,2,5–7) of carbon disulfide have been determined. Principal properties are listed in Table 1.

Table 1. **Properties of Carbon Disulfide**

Property		Values		References
		General		
melting point, K		161.11		5
latent heat of fusion, kJ/kg^a		57.7		5
boiling point at 101.3 kPa^b, °C		46.25		2
flash point at 101.3 kPa^b, °C		-30		8
ignition temperature in air, °C				2
10-s lag time		120		
0.5-s lag time		156		
critical temperature, °C		273		2
critical pressure, kPa^b		7700		2
critical density, kg/m^3		378		2
solubility H2O in CS^2				9
at 10°C, ppm		86		
at 25°C, ppm		142		
dielectric constant		2.641		10
Liquid at temperature, °C	0°C	20°C	46.25°C	
density, kg/m^3	1293	1263	1224	2
specific heat, J/kg·K^a	984	1005	1030	2
latent heat of vaporization, kJ/kg^a	377	368	355	1
surface tension, mN/M (=dyn/cm)	35.3	32.3	28.5	2
thermal conductivity, W/m·KW/(m·K)		0.161		2
viscosity, mPa·s(= cP)	0.429	0.367	0.305	2
refractive index, n^D	1.6436	1.6276		11
solubility in water, g/kg soln	2.42	2.10	0.48	2
vapor pressure, kPa^b	16.97	39.66	101.33	2
Gas at temperature, °C^c	46.25	200	400°C	
density, kg/m^3	2.97	1.96	1.37	1
specific heat, J/kg·KJ/(kg·K)^{a,d}	611	679	730	6
viscosity, mPa·s(= cP)	0.0111	0.0164	0.0234	7
thermal conductivity, W/m·KW/(m·K)	0.0073			7
Thermochemical data at 298 K^a				
heat capacity, C^0p, J/mol·KJ/(mol·K)^a		45.48		12
entropy, S^0, J/mol·KJ/(mol·K)^a		237.8		12
heat of formation, $H^0{}_f$, kJ/mol^a		117.1		12
free energy of formation, $G^0{}_f$, kJ/mol^a		66.9		12

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

[b] To convert kPa to atm, divide by 101.3

[c] At absolute pressure, 101.3 kPa.

[d] $C_p/C_v = 1.21$ at 100°C (2).

Carbon disulfide is completely miscible with many hydrocarbons, alcohols, and chlorinated hydrocarbons (9,13). Phosphorus (14) and sulfur are very soluble in carbon disulfide. Sulfur reaches a maximum solubility of 63% S at the 60°C atmospheric boiling point of the solution (15). Solubility data for carbon disulfide in liquid sulfur at a CS_2 partial pressure of 101 kPa (1 atm) and a phase diagram for the sulfur–carbon disulfide system have been published (16). Vapor–liquid equilibrium and freezing point data are available for several binary mixtures containing carbon disulfide (9).

Under extremely high pressures of about 5.5 GPa (5.4×10^4 atm) and temperatures up to 175°C, a black, solid form of carbon disulfide has been observed (17).

3. Chemical Properties

The low flash point temperature of−30°C at atmospheric pressure and wide flammability range of carbon disulfide deserve special attention (18). The flash point is lowered if the pressure is decreased or the oxygen content enriched. The flammability limits or explosive ranges depend on conditions of temperature, pressure, and geometry of the enclosure. Flammability limits of 1.06–50.0 vol % carbon disulfide in air are reported for upward propagation and 1.91–35.0 vol % for downward propagation in a 75-mm diameter glass tube (19). The upper flammability limit can be significantly decreased by dilution with carbon dioxide (20). Maximum explosive force occurs at a 4–8% concentration of carbon disulfide in air, at which a maximum absolute pressure increase of 730 kPa (7.2 atm) has been measured (21).

Hot surfaces and electric sparks are potential ignition sources for carbon disulfide. The ignition temperature depends on specific conditions, and values from 90 to 120°C in air have been reported (2,22). Data on carbon disulfide oxidation and combustion have been summarized (18). Oxidation products are generally sulfur dioxide [7446-09-5] and carbon dioxide [124-38-9]:

$$CS_2 + 3\ O_2 \longrightarrow 2\ SO_2 + CO_2 \qquad (1)$$

Carbonyl sulfide and carbon monoxide [630-08-0] can also form under certain conditions.

Thermodynamic calculations for reactions forming carbon disulfide from the elements are complicated by the existence of several known molecular species of sulfur vapor (23,24). Thermochemical data have been reported (12). Although carbon disulfide is thermodynamically unstable at room temperature, the equilibrium constant of formation increases with temperature and reaches a maximum corresponding to 91% conversion to carbon disulfide at about 700°C. Carbon disulfide decomposes extremely slowly at room temperature in the absence of oxidizing agents.

Carbon disulfide chemistry is thoroughly described in several publications, which include many references (15,25–28). Several important reactions are mentioned here.

Carbon disulfide is essentially unreactive with water at room temperature, but above about 150°C in the vapor phase some reaction occurs forming carbonyl sulfide (carbon oxysulfide) [463-58-1] and hydrogen sulfide [7783-06-4]. Carbonyl sulfide is an intermediate in the hydrolysis reaction:

$$CS_2 + H_2O \longrightarrow COS + H_2S \tag{2a}$$

$$COS + H_2O \longrightarrow CO_2 + H_2S \tag{2b}$$

At temperatures of 300–600°C in the presence of an activated alumina catalyst, carbon dioxide and hydrogen sulfide are formed in almost quantitative yields (29):

$$CS_2 + 2\,H_2O \longrightarrow CO_2 + 2\,H_2S \tag{3}$$

This is a desirable side reaction in the first catalytic reactor of the Claus sulfur recovery process.

Carbon disulfide slowly reacts with alkali hydroxides to form trithiocarbonates and alkali carbonates:

$$3\,CS_2 + 6\,KOH \longrightarrow 2\,K_2CS_3 + K_2CO_3 + 3\,H_2O \tag{4}$$

Trithiocarbonates can also be prepared from aqueous alkali sulfides:

$$CS_2 + K_2S \longrightarrow K_2CS_3 \tag{5}$$

Industrially important dithiocarbonates (xanthates) result from reaction with various alcoholic alkalies:

$$CS_2 + NaOH + C_2H_5OH \longrightarrow C_2H_5OC(S)SNa + H_2O \tag{6}$$

Of great commercial significance is preparation of sodium cellulose xanthate [9032-37-5] solution (viscose) by reaction with alkali cellulose:

$$CS_2 + R_{cellulose}ONa \longrightarrow R_{cellulose}OC(S)SNa \tag{7}$$

Cellulose is subsequently regenerated from the viscose solution in sulfuric acid and carbon disulfide is liberated. These are the basic steps in manufacturing viscose rayon. The production of regenerated cellulose is estimated to account for more than 75% of the total carbon disulfide consumption worldwide (see FIBERS, REGENERATED CELLULOSICS).

Carbon disulfide and chlorine react in the presence of iron catalysts to give carbon tetrachloride [56-23-5] and sulfur monochloride [10025-67-9]:

$$2\,CS_2 + 6\,Cl_2 \longrightarrow 2\,CCl_4 + 2\,S_2Cl_2 \tag{8}$$

This is followed by a second reaction where sulfur monochloride becomes the chlorinating agent:

$$CS_2 + 2\,S_2Cl_2 \longrightarrow CCL_4 + 6\,S \tag{9}$$

Reactions 8 and 9 have been used in the large-scale production of carbon tetrachloride since the early 1900s. As a result of decreased demand for carbon tetrachloride, this process is no longer used in the United States (see CARBON TETRACHLORIDE).

If bromine is used in equation 8, carbon tetrabromide [558-13-4] is formed. With a minor amount of iodine present, and in the absence of iron catalyst, carbon disulfide and chlorine react to form trichloromethanesulfenyl chloride (perchloromethyl mercaptan [594-42-3]), CCl_3SCl, which can be reduced with stannous chloride or tin, and hydrochloric acid to form thiophosgene (thiocarbonyl chloride [463-71-8], $CSCl_2$, an intermediate in the synthesis of many organic compounds (see SULFUR COMPOUNDS).

Carbon disulfide reacts with concentrated ammonia to give ammonium thiocyanate [1762-95-4] and ammonium trithiocarbonate [13453-08-2] in a reaction promoted by alumina catalysts:

$$2\,CS_2 + 4\,NH_3 \longrightarrow NH_4SCN + (NH_4)_2CS_3 \tag{10}$$

At approximately 160°C, some of the ammonium thiocyanate is converted to thiourea [62-56-6], H_2NCSNH_2, in low yield. With alcoholic ammonia, ammonium dithiocarbamate [513-74-6] forms:

$$CS_2 + 2\,NH_3 \longrightarrow NH_2C(S)SNH_4 \tag{11}$$

Carbon disulfide reacts with primary and secondary amines to yield substituted ammonium salts of *N*-substituted dithiocarbamic acids, $RNHC(S)SNH_3R$ and $R_2NC(S)SNH_2R_2$:

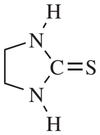
$$CS_2 + 2\,RNH_2 \longrightarrow RNHC(S)SNH_3R \tag{12}$$

Industrially important alkali salts result if alkali hydroxide is present, such as the reaction with dimethylamine [124-40-3] forming sodium dimethyl dithiocarbamate [128-04-1]:

$$CS_2 + (CH_3)_2NH + NaOH \longrightarrow (CH_3)_2NC(S)SNa + H_2O \tag{13}$$

Analogous reactions form sodium methyldithiocarbamate [137-42-8] from methylamine, and disodium ethylenebis(dithiocarbamate) [142-59-6] from ethylenediamine. Iron, manganese, and zinc salts can be prepared from the sodium salts; heavy metals form characteristically colored compounds with dithiocarbamates.

Ethylenediamine reacts with carbon disulfide in alcoholic solution to give ethylenethiourea (2-imidazolidinethione [96-45-7]).



In boiling excess aniline, thiocarbanilide (1,3-diphenyl-2-thiourea [102-08-9]) is formed:

$$CS_2 + 2\,C_6H_5NH_2 \longrightarrow SC(NHC_6H_5)_2 + H_2S \tag{14}$$

If sulfur is present, another industrially important compound results, 2-mercapto benzothiazole (2-benzothiazolethiol [149-30-4]).

Carbonyl sulfide is a coproduct of many carbon disulfide oxidation reactions. Some examples are

$$CS_2 + MgO \longrightarrow COS + MgS \tag{15}$$

$$CS_2 + ClSO_3H \longrightarrow COS + SO_2 + S + HCl \tag{16}$$

$$CS_2 + (NH_2)_2CO \longrightarrow COS + NH_4SCN \tag{17}$$

With alkyl mercuric hydroxide:

$$CS_2 + RHgOH \longrightarrow COS + RHgSH \tag{18}$$

Carbon disulfide reacts with Grignard reagents to prepare the corresponding dithiocarboxylic acids:

$$CS_2 + RMgBr \longrightarrow RC(S)SMgBr \longrightarrow RC(S)SH \tag{19}$$

For example, dithiobenzoic acid [121-68-6] results from the reaction of carbon disulfide, phenyl bromide, ether, and magnesium.

Sodium azidodithiocarbonate [38093-88-8] is prepared by the reaction of aqueous sodium azide [26628-22-8] at 40–50°C:

$$CS_2 + NaN_3 \longrightarrow NaSCSN_3 \tag{20}$$

Sodium azidodithiocarbonate decomposes with evolution of nitrogen gas on addition of iodine, thus providing a useful qualitative test for the presence of residual carbon disulfide in aqueous solutions (25).

Carbon disulfide reacts with alkanols or dialkyl ethers at 250–500°C over activated alumina catalyst to give dialkyl sulfides. For example, methanol yields dimethyl sulfide [75-18-3].

Hydrogen reduces carbon disulfide at high temperatures by the following reactions:

$$CS_2 + 2\,H_2 \rightleftarrows 2H_2S + C \tag{21}$$

$$CS_2 + 4\,H_2 \rightleftarrows 2H_2S + CH_4 \tag{22}$$

Hydrogenation at lower temperature and in the presence of catalysts yields organic sulfur compounds. With a reduced nickel catalyst at 180°C, methanedithiol

[6725-64-0] is formed:

$$CS_2 + 2\,H_2 \longrightarrow CH_2(SH)_2 \tag{23}$$

With a cobalt catalyst at 250°C, methanethiol (methyl mercaptan [74-93-1]) results:

$$CS_2 + 3\,H_2 \longrightarrow CH_3SH + H_2S \tag{24}$$

Dimethyl sulfide [75-18-3], thioethers, thioformaldehyde [865-36-1], and thiophene [110-02-1] are among other possible carbon disulfide hydrogenation products.

4. Manufacture

The earliest method for manufacturing carbon disulfide involved synthesis from the elements by reaction of sulfur and carbon as hardwood charcoal in externally heated retorts. Safety concerns, short lives of the retorts, and low production capacities led to the development of an electric furnace process, also based on reaction of sulfur and charcoal. The commercial use of hydrocarbons as the source of carbon was developed in the 1950s, and it was still the predominate process worldwide in 1991. That route, using methane and sulfur as the feedstock, provides high capacity in an economical, continuous unit. Retort and electric furnace processes are still used in locations where methane is unavailable or where small plants are economically viable, for example in certain parts of Africa, China, India, Russia, Eastern Europe, South America, and the Middle East. Other technologies for synthesis of carbon disulfide have been advocated, but none has reached commercial significance.

4.1. Charcoal–Sulfur Process. Sulfur vapor reacts with charcoal at temperatures of 750–900°C to form carbon disulfide:

$$C + S_2 \longrightarrow CS_2 \tag{25}$$

Sulfur vapor is an equilibrium mixture of several molecular species, including S_8, S_6, and S_2. The equilibrium shifts toward S_2 at higher temperatures and lower pressures. The overall reaction is endothermic and theoretically consumes 1950 kJ/kg (466 kcal/kg) of carbon disulfide when the reactants are at 25°C and the products are at 750°C. Most of the heat input goes into dissociation of sulfur vapor to the reactive species, S_2. Equation 25 is slightly exothermic when the reactants are at a constant temperature of 750°C.

Charcoal–sulfur processes need low ash hardwood charcoal, prepared at 400–500°C under controlled conditions. At the carbon disulfide plant site, the charcoal is calcined before use to expel water and residual hydrogen and oxygen compounds. This precalcination step minimizes the undesirable formation of hydrogen sulfide and carbonyl sulfide. Although wood charcoal is preferred, other sources of carbon can be used including coal (30,31), lignite chars (32,33), and coke (34). Sulfur specifications are also important; low ash content is necessary to minimize fouling of the process equipment.

Various reactor designs have been proposed, including fluidized beds (35–37), a whirlpool-type system (38), and a moving refractory bed to superheat the sulfur (39).

Retort Process. Retorts for producing carbon disulfide are typically oval or cylindrical vessels approximately 1 m in diameter by 3 m high, constructed from chrome alloy steel or cast iron (40,41). Normally one to four retorts are installed in a single furnace, fired with coal, gas, or oil. Alternatively, external electric heaters can be used. The precalcined charcoal is intermittently charged to the top of the retort through a special valve arrangement. Sulfur is added continuously near the bottom of the retort. The sulfur may be first vaporized and superheated to about 700°C in a pipe-coil heat exchanger located in the furnace. Carbon disulfide forms as the sulfur vapor rises through the hot charcoal at 850–900°C. Carbon disulfide, excess sulfur, and other vapors exit from the top of the retort through a duct. Nonreactive ash consolidates with charcoal dust and sifts down to the bottom of the retort from where the residue is periodically removed. Depending on the quality of the raw materials, deposits on the inside walls of the retort must be scraped off approximately monthly. Retorts must be replaced every 1–2 years due primarily to corrosive attack from sulfur vapor. Production capacities are typically up to about 5 tons of carbon disulfide per day per retort with external sulfur vaporization, or 1–3 tons per day with liquid sulfur feed.

The vapor leaving the retort consists of carbon disulfide along with smaller amounts of free sulfur, hydrogen sulfide, and carbonyl sulfide. Sulfur is condensed and recycled. Carbon disulfide is next condensed and then distilled to yield a pure product. In some adaptations, gases leaving the primary condensation are treated by mineral oil absorption to remove residual carbon disulfide selectively, which is later recovered by stripping. The distilled carbon disulfide is treated with lime or dilute sodium hydroxide to neutralize any remaining hydrogen sulfide or other acidic impurities, and the product is finally washed with water. Depending on local circumstances, the tail gas, containing principally hydrogen sulfide, is either flared, incinerated, treated with caustic soda solution to make coproduct sodium hydrogen sulfide [16721-80-5], NaSH, or sent to a Claus sulfur recovery unit. Raw material and energy usages per kg of carbon disulfide product are approximately 0.92–0.95 kg sulfur, 0.22–0.25 kg charcoal, and 8.4–10.0 MJ (2000–2400 kcal) fuel.

Electric Furnace Process. In this process charcoal and sulfur continuously react in a resistance-type electric furnace (40,42–44). One such furnace described in the literature is a cylindrical, refractory-lined vessel roughly 5 m in diameter by 10 m high. Lump charcoal is fed at the top through a gas-lock valve. Electric current supplied to two or four electrodes in the base of the furnace generates heat in passing through the bed of charcoal between opposing electrodes. The electrodes may either be radially or axially placed in the cylindrical furnace. Liquid sulfur enters the furnace at multiple locations in the sidewall near the base, where it quickly vaporizes and heats to 800–1000°C. Carbon disulfide forms in the lower section of the furnace. As the vapors rise, heat is transferred to incoming charcoal in the upper section. Product purification is by methods similar to those used in the retort process, except that entrained dust is normally removed from the vapor prior to the sulfur condensation step. Because heat is formed internally instead of being conducted through a thick wall, large-capacity reactors are feasible. Vessels can last many years, depending largely on the integrity of the lining. Sulfur and charcoal usages are similar to those of the retort process. Electric power consumption is approximately 4.0–4.8 MJ (1.1 – 1.3 k/W · h) per kg of carbon disulfide, about half the external energy required for the retort process. Electric furnaces were first employed for carbon disulfide around 1900 but did not gain wide acceptance until the 1940s.

4.2. Hydrocarbon–Sulfur Process.

The principal commercial hydrocarbon is methane from natural gas, although ethane, and olefins such as propylene (45, 46), have also been used.

Methane [74-82-8] reacts with sulfur essentially without side reactions:

$$\mathrm{CH_4 + 2\,S_2 \longrightarrow CS_2 + 2\,H_2S} \tag{26}$$

At 400–700°C, equilibrium exceeds 99.9% (24). About 5–10% excess sulfur is usually maintained in the reaction mixture to promote high methane conversion and to minimize by-product yield. Carbon disulfide is also formed by the following reaction that is 80% complete at equilibrium at 700°C (47):

$$\mathrm{CH_4 + S_2 \longrightarrow CS_2 + 2\,H_2} \tag{27}$$

Reaction 27 is usually negligible in practice because of the less favorable equilibrium and the usual presence of excess sulfur, which favors reaction 26.

Other hydrocarbons can be used. Stoichiometrically, ethane [74-84-0] is preferable to methane since its lower hydrogen/carbon ratio results in a smaller yield of coproduct hydrogen sulfide:

$$\mathrm{2\,C_2H_6 + 7\,S_2 \longrightarrow 4\,CS_2 + 6\,H_2S} \tag{28}$$

Propane [74-98-6] and heavier paraffins tend to form undesired products, although reaction conditions can be controlled to minimize coke formation (48).

Propylene [115-07-1] can be used in a properly designed system (45,46):

$$\mathrm{2\,C_3H_6 + 9\,S_2 \longrightarrow 6\,CS_2 + 6\,H_2S} \tag{29}$$

Extensive research has been conducted on catalysts that promote the methane–sulfur reaction to carbon disulfide. Data are published for silica gel (49), alumina-based materials (50–59), magnesia (60,61), charcoal (62), various metal compounds (63,64), and metal salts, oxides, or sulfides (65–71). For a silica gel catalyst the rate constant for temperatures of 500–700°C and various space velocities is (72)

$$\log k_c = 10.9 - 131.4/[2.303(RT)] \tag{30}$$

The overall activation energy for equation 30 is 131.4 kJ (31.4 kcal) per mole. Without catalysts, high yields are claimed under certain conditions for using methane (73,74) or olefin (75–77) feedstocks.

For equation 26, starting with methane and solid sulfur at 25°C, and ending with gaseous products at 600°C, the reaction is endothermic and requires 2.95 MJ/kg (705 kcal/kg) of CS_2. The reaction of methane and sulfur vapor in the diatomic form is actually exothermic (23,78). Superheating of the sulfur is claimed to be preferable (79), and series operation of reactors offers a means of reducing process temperatures at which the sulfur dissociates (80).

A disadvantage of the hydrocarbon–sulfur process is the formation of one mole of hydrogen sulfide by-product for every two atoms of hydrogen in the hydrocarbon. Technology for efficient recovery of sulfur values in hydrogen sulfide became commercially available at about the same time that the methane–sulfur process was developed. With an efficient Claus sulfur recovery unit, the hydrocarbon–sulfur process is economically attractive.

In a modern carbon disulfide plant, all operations are continuous and under automatic control. On-stream times in excess of 90% are obtainable. The process is in three steps: melting and purification of sulfur; production and purification of carbon disulfide; and recovery of sulfur from by-product hydrogen sulfide (50).

High purity sulfur with low ash and organic content is desirable. If the raw sulfur is in solid form, it is first melted and filtered or otherwise treated for purification. Liquid sulfur must be handled between the melting point (132°C) and about 150°C to avoid its peculiar high viscosity range (see SULFUR).

The hydrocarbon gas feedstock and liquid sulfur are separately preheated in an externally fired tubular heater. When the gas reaches 480–650°C, it joins the vaporized sulfur. A special venturi nozzle can be used for mixing the two streams (81). The mixed stream flows through a radiantly-heated pipe coil, where some reaction takes place, before entering an adiabatic catalytic reactor. In the adiabatic reactor, the reaction goes to over 90% completion at a temperature of 580–635°C and a pressure of approximately 250–500 kPa (2.5–5.0 atm). Heater tubes are constructed from high alloy stainless steel and reportedly must be replaced every 2–3 years (79, 82–84). Furnaces are generally fired with natural gas or refinery gas, and heat transfer to the tube coil occurs primarily by radiation with no direct contact of the flames on the tubes. Design of the furnace is critical to achieve uniform heat around the tubes to avoid rapid corrosion at "hot spots."

The reaction products are cooled to about 132°C in a waste-heat boiler before going to a sulfur separator where recirculating liquid sulfur scrubs the incoming gases (85). The collected sulfur is recycled to the reactor heater. The sulfur-free process stream is cooled to about 38°C prior to entering a counter-current column where carbon disulfide is absorbed in a circulating oil stream and hydrogen sulfide goes overhead. Carbon disulfide is recovered from the oil in a separate stripping tower, and the lean oil is cooled and recycled. The carbon disulfide stream from the top of the stripping tower contains hydrogen sulfide and oil, which are removed in a series of two fractional distillation towers to produce the final carbon disulfide product. The liquid CS_2 product is sometimes washed with water or dilute alkali to neutralize traces of hydrogen sulfide, but in a well-controlled plant this precautionary step can often be omitted.

The gas leaving the absorber contains mainly hydrogen sulfide with small amounts of methane, carbon disulfide, and inerts (nitrogen). That stream is sent to a Claus sulfur recovery unit (see SULFUR REMOVAL AND RECOVERY). In the Claus unit, part of the hydrogen sulfide is burned in air to form sulfur dioxide and water. The sulfur dioxide and the remaining hydrogen sulfide are then catalytically converted to elemental sulfur and water. Sulfur is condensed in one or more waste-heat boilers and recycled as liquid. The Claus unit must be specially designed to handle high concentration (90+%) of hydrogen sulfide. Gas leaving the Claus unit may be incinerated or subjected to tail gas treatment, depending on the desired efficiency or local environmental conditions.

Water that has been in contact with carbon disulfide can be steam-stripped to 5 ppm or less carbon disulfide before discharge (86). Safety release vents throughout the process are routed to a flare. Gas displaced from vessels and other equipment containing carbon disulfide can be incinerated, or the carbon disulfide can be collected by oil absorption or active carbon adsorption. Mechanical safety features in sections of the plant handling liquid carbon disulfide can include centrifugal pumps having double mechanical seals with oil seal fluid, or long-shaft vertical pumps. Special canned pumps have also been used. Oversized electrical equipment can be used to minimize hot surfaces that could ignite carbon disulfide vapor (86).

Raw material usages per ton of carbon disulfide are approximately 310 m^3 of methane, or equivalent volume of other hydrocarbon gas, and 0.86–0.92 ton of sulfur (87,88), which includes typical Claus sulfur recovery efficiency. Fuel usage, as natural gas, is about 180 m^3/ton carbon disulfide excluding the fuel gas assist for the incinerator or flare. The process is a net generator of steam; the amount depends on process design considerations.

Several variations of the basic process are possible (89–91). One proposed simplification is elimination of the oil absorption and stripping steps by operating the reactor at a higher pressure of 1000–2000 kPa (10–20 atm) and with a reaction zone space velocity of about 1000 h^{-1} (92). Gas leaving the reactor sulfur separator goes directly to the distillation columns where hydrogen sulfide and other light-boiling compounds are taken overhead in the first tower, and carbon disulfide bottoms are then distilled in the second column. Alternatively, the reactor can be operated at lower pressure with the product gas compressed prior to entering the recovery section (93).

4.3. Other Processes. Sulfur vapor reacts with other hydrocarbon gases, such as acetylene [74-86-2] (94) or ethylene [74-85-1] (95), to form carbon disulfide. Higher hydrocarbons can produce mercaptan, sulfide, and thiophene intermediates along with carbon disulfide, and the quantity of intermediates increases if insufficient sulfur is added (96). Light gas oil was reported to be successful on a semiworks scale (97). In the reaction with hydrocarbons or carbon, pyrites can be the sulfur source. With methane and iron pyrite the reaction products are carbon disulfide, hydrogen sulfide, and iron or iron sulfide. Pyrite can be reduced with carbon monoxide to produce carbon disulfide.

The reaction of hydrogen sulfide and methane has a calculated equilibrium of 67% at 1100°C and 86.5% at 1288°C (47,98):

$$CH_4 + 2\,H_2S \rightleftarrows CS_2 + 4\,H_2 \tag{31}$$

Side reactions reduce the yield (99). Proposed processes for obtaining carbon disulfide from hydrogen sulfide and methane include a high temperature plasma (100) and low temperature operation with a catalyst and oxygen (101).

Hydrogen sulfide and carbon react at 900°C to give a 70% yield of carbon disulfide (102,103). A process for reaction of coke and hydrogen sulfide or sulfur in an electric-resistance-heated fluidized bed has been demonstrated on a laboratory scale (104). Hydrogen sulfide also forms carbon disulfide in reactions with carbon monoxide at 600−1125°C (105) or carbon dioxide at 350−450°C in the presence of catalysts (106).

Sulfur dioxide [7446-09-5] and methane react to form carbon disulfide in a yield of 84% at 850°C in the presence of certain catalysts (107). Sulfur dioxide and anthracite at 900−1000°C produce very high yields (108).

Carbonyl sulfide can be either a starting or intermediate material (108–110), or it can be used as a fluidizing gas in a carbon fluid-bed process (111). Making carbon disulfide from boiler flue gas by catalytically reducing SO_2 with CO to COS, and then converting COS to CS_2 over an alumina catalyst has been proposed (112).

5. Handling, Shipment, and Storage

Transportation of carbon disulfide is controlled by federal regulations (113). Acceptable shipping containers include drums, tank trucks, special portable tanks, and rail tank cars. Barges have been used in the past. The United States Department of Transportation classifies carbon disulfide as a flammable liquid and a poison. For ship transport, carbon disulfide must be marked as a marine pollutant (114). All air transport, cargo, or passenger, is forbidden (115).

Carbon disulfide is normally stored and handled in mild steel equipment. Tanks and pipes are usually made from steel. Valves are typically cast-steel bodies with chrome steel trim. Lead is sometimes used, particularly for pressure relief disks. Copper and copper alloys are attacked by carbon disulfide and must be avoided. Carbon disulfide liquid and vapor become very corrosive to iron and steel at temperatures above about 250°C. High chromium stainless steels, glass, and ceramics may be suitable at elevated temperatures.

Contact of carbon disulfide with air should be avoided because the combination of high volatility, wide flammability range, and low ignition temperature results in a readily combustible mixture (116). Carbon disulfide must be stored in inert-blanketed, closed tanks. Normally carbon disulfide is transferred from vessels or tank cars through a downpipe by displacement with an inert material such as water or nitrogen (8,117). Direct pumping requires special equipment and precautions, hence that method of transfer is less common. Carbon disulfide is normally padded with water in storage tanks and bulk containers. Nitrogen blanketing has been used in cold climates. A combination of water with nitrogen above it can also be used, but in any case the total space not occupied by liquid carbon disulfide must be filled with inert material. The tanks themselves should be underwater or surrounded by dikes capable of holding the total tank contents. All equipment containing carbon disulfide should be located well away from potential sources of ignition, which include open flames, frictional heat, sparks, exposed electric light bulbs, and bare steam pipes. Good ground or floor-level ventilation should be provided because carbon disulfide vapor is heavier than air and can accumulate in low areas. Each piece of stationary equipment should be individually grounded by easily-visible conductors. Automatic monitoring of grounding continuity, with electrical detection and alarms, is recommended.

Temporary grounding connections should be provided for movable equipment, such as drums or tank cars. Drums should be kept in a shaded but ventilated area with provision for cooling by water spray or other means if temperature exceeds ca 30°C. All of the equipment and operations preferably should be outdoors.

Small carbon disulfide fires can be smothered with carbon dioxide. Large fires can be controlled with certain types of foams or by a fog or spray of water with attention to proper impoundment of the contaminated water runoff. Without containment, the runoff may transport toxic fumes and fire or explosion hazards to other areas, such as sewers. Caution should be used in fighting a carbon disulfide fire because the flame is nearly invisible and a product of combustion is toxic sulfur dioxide. Special fire-fighting procedures have been published (118,119). Guidelines for emergency response to leaks, spills, and fires are available from the Department of Transportation (120). Cleanup of spills or disposal of wastes containing carbon disulfide must be managed in accordance with government regulations (22,121,122).

6. Economic Aspects

Depending on energy and raw material costs, the minimum economic carbon disulfide plant size is generally in the range of about 2000–5000 tons per year for an electric furnace process and 15,000–20,000 tons per year for a hydrocarbon-based process. A typical charcoal–sulfur facility produces approximately 5000 tons per year. Hydrocarbon–sulfur plants tend be on the scale of 50,000–200,000 tons per year. The production capacities of known U.S. hydrocarbon–sulfur based plants are listed in Table 2 (123).

Demand for carbon disulfide was 71×10^3 t in 2001. Projected demand for 2005 is 71×10^3 t, ie, 0% growth is expected. Demand equals production plus imports (in 2001, 0.9×10^3 t) less exports (in 2001, 6.8×10^3 t). For the period 1996–2001, prices range from \$465/t to \$485/t (123).

Production of carbon disulfide expanded rapidly after World War II to supply the growing needs of the viscose rayon industry, which consumes about 0.31 ton CS_2 per ton rayon. The high plant capacities obtainable with the methane–sulfur route resulted in consolidation of the carbon disulfide industries in the United States and Western Europe, where a few producers now account for the bulk of the capacity. Some rayon manufacturers produce their own carbon disulfide. Rayon enjoys an extensive international market that can affect local

Table 2. **U.S. Manufacturers of Carbon Disulfide**[a]

Producer	Location	Estimated annual capacity, 10^3 t
Akzo Noble Chemicals	Axis, Ala.	113
PPG Industries	Natrium, W. Va.	27
Auto Fina Chemicals	Houston, Texas	18
Total		*158*

[a] Ref. 123.

CS_2 manufacturers. Competition from noncellulosic synthetic fibers has caused a drop in rayon production in the United States since the mid-1960s. One rayon plant in the United States closed in 1989 as a result of environmental concerns. This pattern of modern viscose rayon plants replacing aging facilities that cannot be economically upgraded is apt to be repeated in other parts of the world. In a development that could have far-ranging implications, a viscose rayon producer is constructing a solvent spun cellulosic fiber plant using an amine oxide solvent rather than carbon disulfide (124,125).

Demand for carbon disulfide has apparently bottomed out at approx. 72.5×10^3 t over the last few years. Rayon is CS's largest market, but represents only 4% of the synthetic fiber market. This usage seems to stable.

Carbon disulfide is used in the manufacture of rubber vulcanization accelerators. Production of these accelerators required 12.7×10^3 t in 2001. Demand in agricultural chemicals is increasing slightly because of the use of Metam sodium as a replacement for methyl bromide.

Use of carbon disulfide for manufacture of cellophane [9005-81-6] had dropped dramatically because of competition from plastic films. The decline has stabilized. Cellophane remains strong in speciality applications like hard candy and cigar wrappings.

Carbon disulfide for manufacture of carbon tetrachloride increased in the 1950s and 1960s to supply the key raw material for chlorofluorocarbon refrigerants and aerosol propellants. Because of ecological and health concerns, carbon tetrachloride consumption began to decline in the mid-1970s. That use for carbon disulfide will suffer under a United Nations proposal to phase out carbon tetrachloride and chlorofluorocarbons to protect the earth's ozone layer (126). During 1991 the only remaining carbon tetrachloride plant in the United States that employed the carbon disulfide route was permanently shut down.

7. Specifications and Quality Control

Modern plants generally produce carbon disulfide of about 99.99% purity. High product quality is ensured by closely controlled continuous fractional distillation. Reagent and U.S. Federal specifications, and typical commercial-grade quality are listed in Table 3.

8. Health, and Safety Factors

Care must be exercised in handling carbon disulfide because of both health concerns and the danger of fire or explosions. Occupational exposure potentially may involve as many as 20,000 workers in the United States (129). Ingestion is rare, but a 10 mL dose can prove fatal (130). Contact usually occurs by inhalation of vapor. However, vapor and liquid can be absorbed through intact skin and poisoning may occur by the dermal route. Repeated contact of liquid carbon disulfide with the skin can cause inflammation and cracking because carbon disulfide removes protective waxes and oils. Extended skin contact results in blistering and possibly second- and third-degree burns. Precautions should be taken to

Table 3. **Carbon Disulfide Specifications**

Property	Method	Technical industry, typical	Technical, U.S. Federal[a]	Reagent, ACS[b]
specific gravity	pycnometer	1.270–1.272[c]	1.262–1.267[d]	
residue	dry at 60°C	0.002% max	10 mg/100 mL	0.002% max
color	APHA, Pt–Co 500 std	<20[e]	special test	10 max
boiling range, °C	ACS distillation	45.5–47.5	45.5–47.5	1°C incl. 46.3±0.1°C
foreign sulfide	lead acetate test	negative		
foreign sulfide	special tests		no discoloration of copper	
H_2S and SO_2	iodine color test			passes
water, %	Karl Fischer		no turbidity	0.05% max

[a] Ref. 127.

[b] Ref. 128. USP specifies ACS reagent-grade.

[c] 15/4°C.

[d] 20/20°C.

[e] Light transmission vs water = 98% minimum is sometimes used as a specification.

avoid breathing of vapors or mists that may contain carbon disulfide. Contact with skin or eyes should also be avoided, and adequate safety gear should be worn, including goggles, impervious gloves, and appropriate clothing. Contact lenses should be removed before going into any area where exposure to carbon disulfide might occur. A chemical cartridge respirator with an organic vapor cartridge can offer protection up to 50 ppm carbon disulfide in air. Above that level or in entering areas of unknown vapor concentrations, a self-contained breathing apparatus should be worn, with careful attention given to possible explosion hazards (131).

The odor threshold of carbon disulfide is about 1 ppm in air but varies widely depending on individual sensitivity and purity of the carbon disulfide. However, using the sense of smell to detect excessive concentrations of carbon disulfide is unreliable because of the frequent co-presence of hydrogen sulfide that dulls the olfactory sense.

Immediate effects of overexposure to carbon disulfide vapors range from headache, dizziness, nausea, and vomiting to life-threatening convulsions, unconsciousness, and respiratory paralysis. For an exposure time of 30 min, 1150 ppm carbon disulfide in air results in serious symptoms, 3210 ppm is dangerous to life, and 4815 ppm is fatal (132). Prolonged and repeated exposure to carbon disulfide vapor can affect both the central and peripheral nervous systems. Manifestations of long-term overexposure may include headache, vertigo, irritability, nervousness, depression, mental derangement, memory loss, muscular weakness, fatigue, insomnia, eating disorders, gastrointestinal disturbances, impaired vision, diminished reflexes, numbness, and difficulty walking. Certain workers exposed to a time-weighted average of 11 ppm experienced headaches and dizziness, and those with an average of 186 ppm had additional complaints of nervousness, fatigue, sleep problems, and weight loss (133). Repeated exposure to relatively high concentrations of carbon disulfide has long been known to cause serious neurological and psychological impairments. In recent years, previously unrecognized and more subtle toxic effects of repeated lower level exposures became evident. This led OSHA in 1989 to reduce permissible concentration limits to 4 ppm (12 mg/m^3) maximum time-weighted average for 8-h exposure and 12 ppm (36 mg/m^3) maximum for 15 min short-term exposure (130). Compliance with both limits is preferably achieved by engineering and work practice controls, although respirators are acceptable in certain specific operations. OSHA states the new limits should substantially reduce the risk of both cardiovascular disease and adverse reproductive effects associated with carbon disulfide. Analysis of urine specimens for carbon disulfide metabolites by an iodine–azide test (134) and other methods (135) can indicate overexposure.

Health hazards linked to carbon disulfide are extensively covered (128). Also available are epidemiological studies (136–138), general reviews containing many references (139–142), and a Material Safety Data Sheet (143).

A method for the remediation of soil containing carbon disulfide via oxidation has been reported (144).

9. Uses

United States applications of carbon disulfide are rayon production (44%), agriculture and other chemicals (35%), rubber chemicals (18%), cellophane and other regenerated cellulosics (3%) (123).

Carbon disulfide is used to make intermediates in the manufacture of rubber vulcanization accelerators, including MTB (2-mercaptobenzothiazole [149-30-4]), thiocarbanilide, and dimethyl dithiocarbamate salts (see RUBBER CHEMICALS). Thiocarbanilide is also used in dyes. Thiophosgene (thiocarbonyl chloride), made from carbon disulfide, is a useful intermediate in the synthesis of many organic sulfur compounds. Xanthates (dithiocarbonates) produced from carbon disulfide are widely employed as flotation chemicals for metal sulfide ores in the mining industry. The solvent properties of carbon disulfide find a wide range of industrial uses, including various dehydration, extraction, reaction, and separation applications. A useful laboratory chemical, carbon disulfide is a reactant in the synthesis of many compounds and a solvent in Friedel-Crafts reactions. Its solvent properties are useful in spectroscopy and in solubilizing phosphorus and sulfur.

Pharmaceutical intermediates, such as thiocarbanilide and thiocyanates, are prepared from carbon disulfide. Methionine [59-51-8], an essential amino acid, is manufactured from carbon disulfide intermediates. At one time carbon disulfide was commonly used in combination with chlorinated hydrocarbons as a grain fumigant, but that application was suspended in 1985 by the United States Environmental Protection Agency. Carbon disulfide is a starting material for several fungicides, soil fumigants, and insecticides or their intermediates, such as trichloromethanesulfenyl chloride, disodium ethylenebis(dithiocarbamate), sodium methyldithiocarbamate, ammonium dithiocarbamate, and thiocyanate salts. The thiocyanates also have many nonagricultural uses.

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