

and the perforated plate *b*. A 5-g. quantity of CaSi (see p. 946 for preparation) is poured from flask *m* (by rotating the flask in the joint) into 300 ml. of HCl-saturated absolute alcohol, which covers the glass filter plate *g*. The procedure must be carried out in an atmosphere of dry CO₂ with good agitation. The addition of CaSi takes about an hour. Good cooling must be provided. After standing overnight while the evolution of H₂ ceases, the brown precipitate is separated in a CO₂ atmosphere from the supernatant liquid. The precipitate is first washed with ice-cold absolute alcohol and then with absolute ether.

The preparation of the higher unsaturated Si hydrides may be accomplished by cleaving the saturated hydrides with electrical discharge.

PROPERTIES:

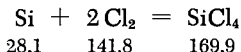
(SiH)_x: lemon-yellow substance. Hard, amorphous; oxidizes slowly in air.

(SiH₂)_x: brownish substance. The dry material ignites spontaneously in air, leaving a SiO₂ residue which may be gray because of the presence of iron silicide. Evolves H₂ with alkali hydroxides.

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Silicon Tetrachloride



Silicon (prepared as shown above) or coarsely ground ferro-silicon (which should contain as much Si as possible) is placed in a boat inserted into a Pyrex tube about 60 cm. long and 2-3 cm. in diameter, through which a stream of Cl₂ is passed (Fig. 223). The Cl₂ is predried over concentrated H₂SO₄. A condenser is attached to the other end of the tube by means of an adapter; the tube itself is heated in an electric furnace. The tube should incline toward the condenser to prevent the SiCl₄ from backing up.

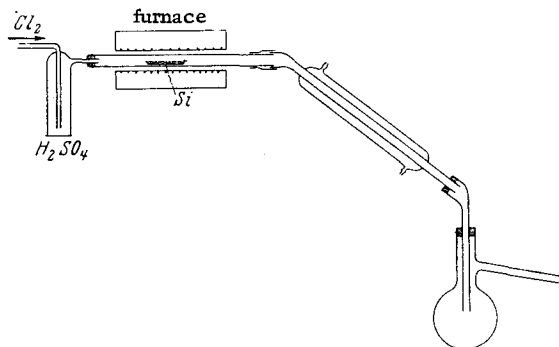


Fig. 223. Preparation of silicon tetrachloride.

The condenser end of the reaction tube should project out of the furnace for some distance so that the invariable byproduct FeCl_3 may deposit without plugging the condenser. The condenser discharges into a distilling flask which is set in an ice bath. All joints must be tight and the entire apparatus carefully dried before the start of the run. A CaCl_2 tube is attached at the end of the side arm of the distilling flask. If this precaution is overlooked, the side arm will immediately be plugged with silicic acid produced by reaction with atmospheric moisture. The reaction tube is heated to about 400°C and the Cl_2 flow is then started.

If, in addition to SiCl_4 , the higher Si chlorides are desired (Si_2Cl_6 and Si_3Cl_8), the temperature of the tube should be as low as possible, but no lower than just below 400°C . When the reaction is well established, heating may be sharply reduced since the reaction itself evolves considerable heat. The crude chloride, which is accumulated in the distilling flask, may be purified by fractional distillation. If an absolutely Cl-free preparation is desired, a second distillation over Cu turnings is performed. Both distillations must be run in absolutely dry equipment. The ampoules into which the SiCl_4 is distilled should be fused to the distillation apparatus, since it is impossible to obtain a non-turbid product if this is not done. Yield is quantitative.

PROPERTIES:

Clear, colorless liquid; fumes heavily upon exposure to air. Rapidly hydrolyzes in water to form a SiO_2 gel. Miscible with benzene, ether, chloroform and saturated hydrocarbons. Forms esters of silicic acid with alcohols. B.p. 57.5°C , m.p. -68°C ; d 1.52.

Higher Silicon Chlorides

If the preparation of SiCl_4 is carried out at temperatures below 400°C , it is possible to isolate very small quantities of Si_2Cl_6 and Si_3Cl_8 from the residue of the final distillation.

Chlorides up to $\text{Si}_5\text{Cl}_{14}$ are best prepared by chlorination of calcium silicide. The procedure is as follows: Cl_2 , dried over concentrated H_2SO_4 , is passed through a vertical glass tube (34-mm. diameter, about one meter long), half filled with bean-size lumps of Ca silicide (about 30–35% Ca). The tube should not be too full, for then it might plug during the run; about 200–250 g. is used. The tube is placed inside a short, movable electric heating coil. It is important that the reaction take place at the lowest possible temperature and that only a short section of the tube be heated at any time. The reaction starts at 250°C . The temperature must then be immediately lowered to 150°C . The Cl_2 flow should not exceed 100 bubbles/minute. The reaction products are accumulated in a cooled receiver via an attached condenser. After 12 to 14 days, during which the heating coil is slowly moved along the entire length of the tube, all the silicide is reacted, and about 700 ml. of chloride mixture is collected. The higher chlorides are obtained from this mixture by fractionation. If a low temperature and a slow flow rate of Cl_2 are used, then about 35% of the product mixture boils at a higher temperature than SiCl_4 . About 30% of this is Si_2Cl_6 , 4%, Si_3Cl_8 , and 1% represents chlorides up to $\text{Si}_5\text{Cl}_{14}$. After evaporation of the SiCl_4 , the residue is fractionated at reduced pressure. Addition of 2 to 5% of an alkali chloride, alkaline earth chloride or ammonium chloride or dilution of the chlorides (e.g., with SiCl_4) should improve the yield.

PROPERTIES:

B.p.: Si_2Cl_6 , 147°C ; Si_3Cl_8 , 216°C ; $\text{Si}_4\text{Cl}_{10}$, 150°C (at 15 mm.); $\text{Si}_5\text{Cl}_{12}$, 190°C (15 mm.); $\text{Si}_6\text{Cl}_{14}$ sublimes in vacuum at 200°C .

According to R. Schwarz, the higher Si chlorides, such as $\text{Si}_{10}\text{Cl}_{22}$, can be prepared by treatment of SiCl_4 in the apparatus illustrated in Fig. 224, which the author calls a "quenching tube." The procedure is as follows.

A silicon carbide rod, held in place by two electrode connector clamps, is fitted into a Liebig condenser. The electrode clamps are sealed into Pyrex caps, which fit over the ground-glass male joints of the condenser.

If the electrical terminals of these clamps consist of water-cooled copper tubing, then the seal to the glass caps is made with rubber tubing. A clamp is made by closing one end of the copper tube, welding on a piece of thin wall stainless steel tube and

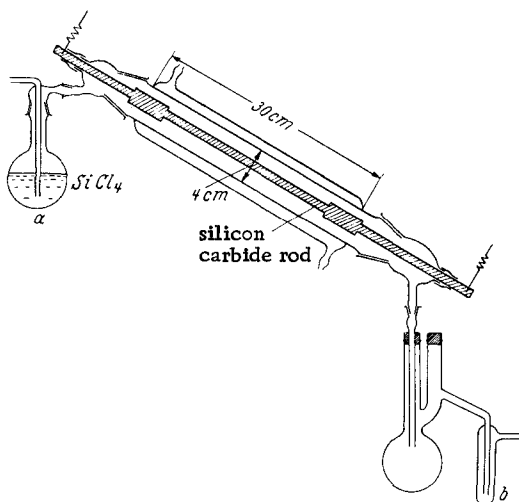


Fig. 224. Preparation of the higher silicon chlorides.

splitting the end of the latter with two lengthwise saw cuts. The SiC rod fits into that end. The open end of the copper tube is closed with a cap which carries the inlet and outlet tubes for the cooling water (the inlet tube extends well inside the closed tube).

Alternatively, iron electrode clamps, sealed to the Pyrex caps with asbestos-waterglass mixture, are used with no cooling. In that case, the Pyrex caps may have to be wound with cotton string, wetted with water to remove the heat.

The "quenching tube" itself can be made of copper. In this case, the glass caps are sealed on with rubber tubing (pieces of bicycle inner tube).

The apparatus is first thoroughly dried by heating in a stream of inert gas, with the cooling water off. After brief cooling, a stream of hydrogen is introduced at *a* and the air is displaced. Then 25 ml. of SiCl_4 is placed in flask *a*, the hydrogen saturated with the SiCl_4 and the heating resumed [the hydrogen is first passed over Pd asbestos to remove O_2 and over P_2O_5 for drying (see section on Hydrogen)].

The first run in a new tube should be made with H_2 ; $\text{Si}_{10}\text{Cl}_{20}\text{H}_2$ is formed under these conditions. If oxygen-free argon and SiCl_4 are used in a later run, $\text{Si}_{10}\text{Cl}_{22}$ is formed. The temperature of the SiC rod should be between 1000°C and 1100°C . A trap *b*, cooled with liquid nitrogen, is connected to the distilling flask which serves as the receiver.

It happens occasionally that the reaction fails to start. In that case, the gas is either not completely water-free or it contains

oxygen. Whenever a new SiC rod is used, the first run should be made with H_2 as the carrier gas, for otherwise the reaction will not start. From 112 g. of $SiCl_4$ the yield is about 35 g. crude product, from which the lower boiling fractions are stripped off. The $Si_{10}Cl_{20}H_2$ cannot be distilled without decomposing. The product prepared with argon is fractionated under high vacuum. The $Si_{10}Cl_{22}$ comes over as a highly viscous oil between 215 and 220°C.

The preparation of the higher Si chlorides by passage of $SiCl_4$ over Si at 1000°C is described by Rochow and Didschenko; the preparation by means of a glow discharge is described by Hertwig and Wiberg.

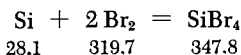
PROPERTIES:

Viscous, with a consistency ranging from oily to honeylike. Flammable. Hydrolyzed by water.

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A. Besson and L. Fournier, *Comptes Rendus Hebd. Séances Acad. Sci.*, **152**, 603 (1911); C. Friedel, *Comptes Rendus Hebd. Séances Acad. Sci.*, **73**, 1011 (1871); C. Friedel and A. Ladenburg, *Liebigs Ann. Chem.*, **203**, 253 (1880); L. Gatterman and E. Ellery, *Ber. dtsch. chem. Ges.*, **32**, 1114 (1899); L. Gatterman and K. Weinlig, *Ber. dtsch. chem. Ges.*, **27**, 1943 (1894); J. W. Mellor, *Comprehensive Treatise on Inorg. Chem.*, VI, p. 971; *Int. Crit. Tabl.*, Vol. I, p. 162; G. Martin, *J. Chem. Soc. (London)*, **105**, 2836, 2860 (1914); *Ber. dtsch. chem. Ges.*, **45**, 2097 (1912); **46**, 2442, 3289 (1913); L. Troost and P. Hautefeuille, *Ann. Chim. Phys.* (5) **7**, 459 (1871); R. Schwarz and H. Meckbach, *Z. anorg. allg. Chem.*, **232**, 241 (1937); E. G. Rochow and R. Didschenko, *J. Amer. Chem. Soc.*, **74**, 5545 (1952); H. S. Gutowski and E. O. Stejskal, *J. Chem. Phys.*, **22**, 939 (1954); D. F. Stedmann, U.S. Patent 2,621,111; W. J. Walton, U.S. Patent 2,602,728 (1952); H. Schaefer, *Z. anorg. allg. Chem.*, **274**, 265 (1953); C. F. Wilkins, *J. Chem. Soc. (London)*, **1953**, 3409; K. A. Hertwig and E. Wiberg, *Z. Naturforsch.*, **6b**, 336 (1951); W. C. Schumb and E. L. Gamble in H. S. Booth, *Inorg. Syntheses* New York and London, 1939, Vol. I, p. 42.

Silicon Tetrabromide



A boat, placed in a Vycor tube, is heated in an electric furnace to about 600°C. The boat contains finely powdered Si (which is