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The Isolation of Chlorodiborane; Some Additions to the High-vacuum Technique for Chemical Work with Volatile Substances

BY ANTON B. BURG

In an earlier paper, published in collaboration with Professor H. I. Schlesinger,[1] it was shown that the reaction of hydrogen with boron trichloride in the electric discharge produces chlorodiborane (B_2H_5Cl), an extremely unstable substance which had not been isolated at that time. The present paper deals with the isolation of this compound, and also describes some developments and modifications of the high vacuum methods, originally developed by Stock,[2] for handling substances of that kind.

Apparatus for Fractional Condensation.—The apparatus used for isolating chlorodiborane also may be used for the fractionation of any separable mixture of volatile substances which do not react with glass or mercury, and which are completely condensable by the use of liquid nitrogen. This apparatus, shown in Fig. 1, is a part of a larger apparatus, some parts of which have been described in earlier publications.[3] The several parts of the complete apparatus are connected through mercury float-valves to a long "central tube," which serves as a means of communication between widely separated parts of the system. The U-tubes U1 and U2 are provided with closed-end U-manometers registering pressures as high as 1400 mm. They may be used for the measurement of gas volumes and vapor tensions.

The float-valves used in this apparatus differ somewhat from the original design by Stock.[4] They are made of 8 mm. (i. d.) Pyrex tubing, with float-plugs of ordinary "soft" soda-lime glass. In the opened valve each plug is supported by two horizontal knife-edge indentations. The high thermal expansion of the plugs makes it possible to open these valves under considerable differences of pressure; the top of the socket on the high-pressure side is warmed gently by a flame and then the mercury is lowered. The cool plug falls, while the warmed one remains in its socket until it has cooled enough to loosen its grip. Sometimes the rush of gas will lift the cool plug back into place. This is avoided in the valve V28 (Fig. 1), whose limbs are connected by a tube 1 cm. below the sockets. Such valves also allow faster evacuation at low pressures.

Gases are separated in this apparatus by a combined process of distillation and fractional condensation. The sample is condensed completely in U1, and then allowed to warm up until the most volatile component attains a vapor pressure of 1 or 2 mm. The vapor is allowed to pass in the direction of U1A, U2A and U2. U1A is immersed in a bath at a temperature such that all of the most volatile substance will pass through, whereas only very little of the less volatile material will escape condensation in that place.[5] U2A is immersed in a bath intended to trap out all except the most volatile substance, which is condensed in U2. If one operation does not give complete separation of the two most volatile components, the condensate in U1A is transferred to another part of the apparatus and the fraction condensed in U2A is subjected again to the process. This procedure is highly efficient because it minimizes the effect of solubility: the most volatile substance is safely out of the way before any large part of the less volatile material reaches the intermediate traps.

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(1) Schlesinger and Burg, THIS JOURNAL, **53**, 4321 (1931).

(2) Stock, *Ber.*, **54A**, 142 (1921). See also Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, 1933.

(3) Schlesinger and Burg, THIS JOURNAL, **53**, 4324 (1931); **55**, 4012 (1933).

(4) Stock, Z. *Elektrochem.*, **23**, 33 (1917).

(5) If the sample contains unknown substances, the suitable bath temperatures must be determined by a preliminary distillation.

Fractionating Columns.—Samples larger than 1 or 2 cc. of liquid may be fractionated still more effectively by the use of a fractionating column. The one shown in Fig. 2 was designed for separating the products of the reaction of hydrogen and boron trichloride in the electric discharge. It differs from other low-temperature fractionating columns[6] mainly in that the insulation, a large Dewar cylinder surrounding the whole instrument, may be removed easily to permit baking at high vacuum whenever necessary. The complete elimination of grease, rubber, air and moisture makes it applicable to many substances which could not well be handled by other types of apparatus.

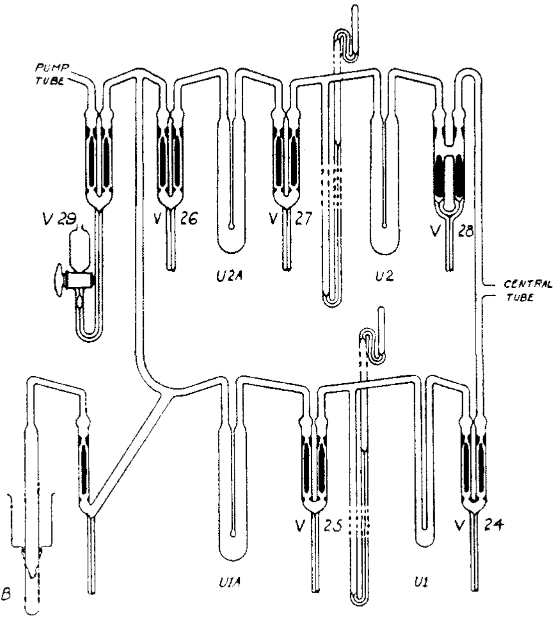

Fig. 1.

The column consists of a Dufton spiral,[7] with a liquid air-cooled aluminum cylinder for maintaining a suitable reflux temperature. The boiler tube is heated from below by an electric heating coil. An aluminum shield protects the column against stray heat. During operation, a small part of the most volatile substance bubbles through the pressure-controlling half-valve V19, and is condensed in C. In most fractionations the operating pressure will be less than 100 mm., and the final condensing agent may be liquid air or nitrogen. Substances having a high vapor tension at the melting point (for example, hydrogen chloride) must be handled at higher pressure. In such cases the distillate is condensed by a bath only a few degrees colder than the reflux temperature.

This column is designed to fractionate as much as fifty liters (gas) of the hydrogen chloride–chlorodiborane–boron trichloride mixture in one operation. Approximately 99% of the hydrogen chloride is removed in a state of purity above 99.95%, as determined from the quantity of hydrogen produced by absorption in water. The intermediate fraction, containing chlorodiborane, is easily separated by the method of fractional condensation.

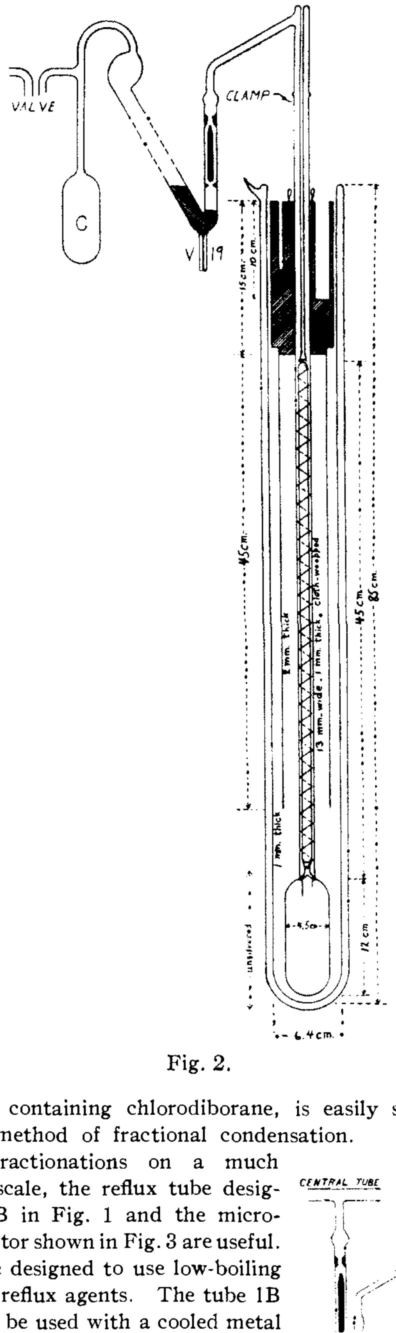

Fig. 2.

For fractionations on a much smaller scale, the reflux tube designated 1B in Fig. 1 and the microfractionator shown in Fig. 3 are useful. Both are designed to use low-boiling gases as reflux agents. The tube 1B also may be used with a cooled metal block, as in the large fractionating column. The microfractionator may be used also for measuring vapor tensions of extremely small samples.

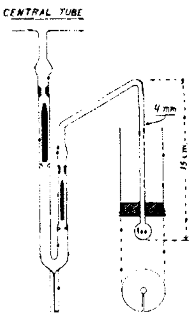

Fig. 3.

The Isolation of Chlorodiborane.—A sample of diborane (about 400 cc. of gas), containing a quantity of combined chlorine equivalent to a 2% concentration of chlorodiborane, was allowed to stand longer than a week at room temperature. Thus the equilib-

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[6] Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929); Schaufelberger, *Oil Gas J.*, **29**, 46 (1930); Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931); **5**, 119 (1933); Ebrey and Engelder, *ibid.*, **23**, 1034 (1931); McGillivray, *J. Chem. Soc.*, 941 (1932).

[7] Dufton, *Chem. and Ind.*, **46T** (1919); in this case a 45 cm. × 10 mm. closed tube, wrapped with a thirty-turn spiral of 0.8-mm. copper wire, is supported within the column by two small glass legs resting upon the inner-seal.

rium $5B_2H_6 + 2BCl_3 \rightleftarrows 6B_2H_5Cl$ was established, very much in favor of chlorodiborane. Then the sample was distilled through a U-tube at −150°, in which all substances less volatile than diborane were trapped. The chlorodiborane was freed from pentaborane, tetraborane and the probable constant-boiling mixture of boron trichloride and chlorodiborane, by several slow distillations through a U-tube at −120°. After each distillation it was necessary to heat and evacuate the tubes in which the boron trichloride was condensed, in order to remove adsorbed traces of this impurity. The diborane was entirely removed by distillation through a U-tube at −140°, in which nearly all of the chlorodiborane was condensed. At length there was obtained a 4-cc. (gas) sample having a vapor tension of 18 mm. at −78.5°; further repetition of the process of distillation gave the same result, and the value was also found to be independent of the volume of the measuring tube. The compound was so unstable that the vapor tension measurement had to be made within a period of twenty seconds.[8] During the measurement, enough decomposition occurred that a repetition of the measurement after complete recondensation showed an increase to 19 mm. The fact that the increase was observed only after complete recondensation shows that the decomposition occurred mainly in the vapor phase, part of which was at room temperature. It was not found possible to obtain a trustworthy set of vapor tensions at temperatures other than −78.5°. The melting point was measured by the use of the magnetic device of Stock[9] and the ethylene vapor tension thermometer.[10] It was found to be sharp, at −142.0°. The combined evidence of the recurring 18 mm. vapor tension and the sharp, reproducible melting point, is sufficient to establish, beyond reasonable doubt, the uniformity of the substance.

The substance was analyzed by passing the measured sample (3.68 cc. of gas) through a hot quartz tube, measuring the volumes of the resulting hydrogen, boron trichloride, and hydrogen chloride, and weighing the boron. The resulting analytical formula was $B_{1.8}H_{6.1}Cl_{0.95}$. A low value for boron was to be expected.

Summary

The isolation of the exceedingly unstable substance chlorodiborane (m. p. −142°; vapor tension at −78.5°, 18 mm.) is described.

Some modifications and additions to the high vacuum methods developed by Stock for handling highly volatile substances are given. These include a simplified technique of fractional condensation, new designs for the float valves and the application of fractionating columns.

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[8] *This time was ample, because of the thin, flat bottom of the* tube, and the extremely small liquid volume of the sample (about 0.01 cc.). Measurements on similar quantities of stable substances have shown that equilibrium actually is reached in ten seconds if the bath used is an ether suspension of solid carbon dioxide in equilibrium with its vapor at one atmosphere pressure.

(9) Stock, *Ber.*, **50**, 156 (1917).

(10) Stock, *Z. Elektrochem.*, **29**, 354 (1923).

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The Oxidation of Carbon Monoxide with a Silver Catalyst

BY ARTHUR F. BENTON AND RICHMOND T. BELL

The myriad studies of kinetics in contact catalysis have thrown much light on the problem but have so far failed to furnish an adequate picture of the processes involved. Kinetics have almost invariably been interpreted in terms of arbitrarily assumed adsorptions—a method which is notoriously fallible. Examples of the progress that may be anticipated from parallel studies of adsorption and catalysis on the same material are furnished by the investigations of Pease and coworkers[1] on the ethylene-hydrogen combination in contact with copper and other metals, and of Benton and Elgin[2] on the synthesis of water with silver and gold catalysts. The methods employed by the latter have now been applied to the oxidation of carbon monoxide in presence of finely-divided silver. This reaction has proved to be unusually simple, since it is not retarded by the reaction product and since only one of the reactants, oxygen, is much adsorbed by the catalyst.

The union of carbon monoxide and oxygen has been studied in numerous previous investigations, particularly with oxide catalysts and with platinum. Bone and Andrew[3] used several other metals, including gold gauze. No previous parallel study of adsorption and catalytic activity for this reaction has been made under conditions which permit a quantitative examination of its molecular statistics.

Method and Materials

Apparatus.—The "flow" method, essentially as described by Benton and Elgin,[2a] was employed. Measured propor-

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(1) Pease, THIS JOURNAL, **45**, 1196, 2235, 2296 (1923); Pease and Stewart, *ibid.*, **47**, 1235 (1925); **49**, 2783 (1927); Pease and Harris, *ibid.*, **49**, 2503 (1927).

(2) Benton and Elgin, (a) *ibid.*, **48**, 3027 (1926); (b) *ibid.*, **49**, 2426 (1927); (c) *ibid.*, **51**, 7 (1929).

(3) Bone and Andrew, *Proc. Roy. Soc.* (London), **A109**, 459 (1925); **A110**, 16 (1926).