PROPERTIES:

Formula weight 52.04. Colorless, poisonous, lachrymatory gas with a stifling odor. M.p. −27.83°C, b.p. −21.15°C; crit. t. 218.30°C; crit. p. 59.75 atm.

Burns with a peach-blossom-colored, blue-edged flame; mixtures containing 14 vol.% O_2 are explosive.

Soluble in H_2O, alcohol and ether. The solutions quickly decompose. Polymerizes to solid, brown-black paracyanogen on heating or even in sunlight. Forms HCN and HNCO ("pseudohalogen") with water.

d (b.p.) 0.954. Heat of formation 62.0 kcal./mole.

REFERENCES:

I. J. McMorris and R. M. Badger. J. Amer. Chem. Soc. 55, 1954 (1933).

II. R. P. Cook and P. L. Robinson. J. Chem. Soc. (London) 1935, 1001.

Cyanogen Chloride

$CNCl$

I.

$$\underset{247.6}{K_2[Zn(CN)_4]} + 4\,\underset{283.6}{Cl_2} = 4\,\underset{245.8}{CNCl} + 2\,\underset{149.1}{KCl} + \underset{136.3}{ZnCl_2}$$

A solution of 130 g. of KCN in 200 ml. of water is added to a solution of 145 g. of $ZnSO_4 \cdot 7\ H_2O$ in 200 ml. of water held in flask *a* (see Fig. 213). This results in a suspension of $K_2[Zn(CN)_4]$ in 400 ml. of water. The suspension is vigorously stirred with a ground glass stirrer, the apparatus is purged with N_2, and Cl_2 is introduced through a fritted glass filter. At a Cl_2 rate of 8 to 10 bubbles per second, a steady, fast stream of CNCl is produced 1-1.5 hours after the start of the run. Prior to gas generation the mixture evolves some heat. This is removed by cooling with running water so as to keep the temperature below 20°C. Foam is broken up by the stirrer in the broad upper section of the reaction flask. The product is dried over $CaCl_2$ and is frozen out in a receiver cooled with an ice-salt mixture or, even better, with Dry Ice-acetone. After one half of the required quantity has

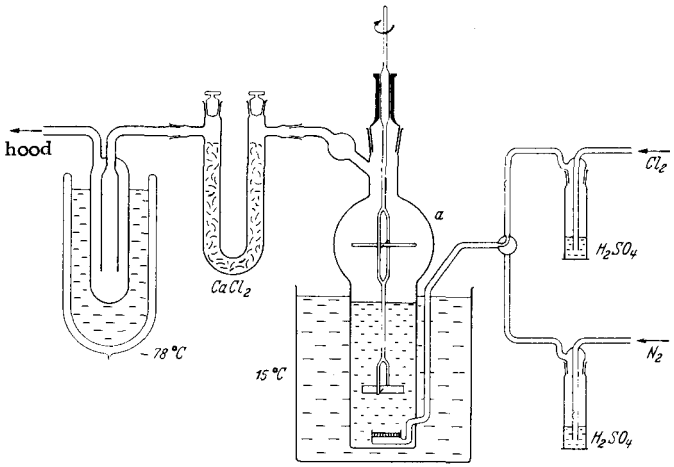

Fig. 213. Preparation of cyanogen chloride.

been introduced the Cl_2 stream rate is reduced every hour by 2 to 3 bubbles per second, so that no unreacted Cl_2 can contaminate the product. After five hours the reaction mixture clears up. The Cl_2 flow is interrupted and the residual CNCl is driven off with N_2.

The yield of pure CNCl is 98%, based on KCN, and 85% based on Cl_2. The product requires no further purification. It is entirely free of chlorine. The content of possible impurities other than chlorine is less than 0.1%. The cation bound to the $[Zn(CN_4)]^{2-}$ complex is not important. Experiments with $Na_2[Zn(CN)_4]$ and $Ca[Zn(CN)_4]$ result in equally satisfactory yields and equally pure products.

II.

$$\underset{49.0}{NaCN} + \underset{70.9}{Cl_2} = \underset{58.4}{NaCl} + \underset{61.5}{CNCl}$$

Pulverized NaCN (49 g.) and 170 ml. of CCl_4 are charged into a 500-ml. three-neck flask (see Fig. 214), provided with a mercury seal stirrer and gas inlet and outlet tubes. The flask is cooled to —5 to —10°C in an ice-salt mixture, and the air is displaced with N_2. Now 2 ml. of glacial acetic acid is added to the reaction mixture, the stirrer is started, and Cl_2 is introduced. The Cl_2 flow rate is adjusted to assure its complete absorption. No gas bubbles

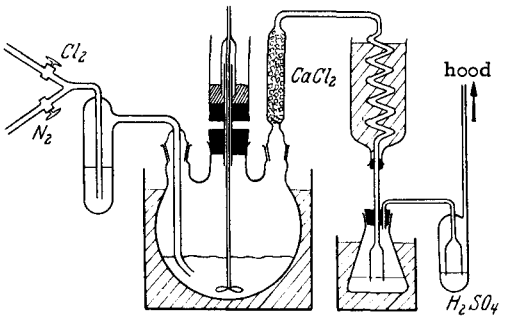

Fig. 214. Preparation of cyanogen chloride.

should form in the wash bottle attached in series with the apparatus. The temperature must be rigorously held at —5°C or less, since otherwise CNCl reacts with NaCN to form $(CN)_x$. The reaction ends after about 4.5 hours. The chlorine flow is stopped, the receiver is cooled to —40°C with Dry Ice-acetone, the spiral condenser is encased in an ice-salt mixture, and a slow N_2 stream is passed through the apparatus. The temperature of the three-neck flask is allowed to rise to 60-65°C over a period of 1-1.5 hours, so that all the CNCl distills. The Cl_2 dissolved in the CNCl can be removed either by placing a distillation column cooled with a —25°C bath over the Erlenmeyer flask containing the distillate, the CNCl being permitted to reflux while gaseous Cl_2 escapes; or by freezing the product at —79°C, removing the Cl_2 in a vacuum apparatus, and fractionating the residue. The yield is 44-47 g. (72-77%).

PROPERTIES:

Colorless liquid or colorless, lachrymatory gas. M.p. —6.5°C, b.p. 13°C; d (4°C) 1.218. Vapor pressure (0°C) 445 mm. Attacks Hg slightly. Pure CNCl does not polymerize. Exceptionally poisonous. Therefore, all work must be done under a good hood. The experimenter is strongly advised to protect himself with a gas mask when working with CNCl. Solubility: 2.5 liters in 100 ml. of water (20°C); 10 liters in 100 ml. of alcohol (20°C); 5 liters in 100 ml. of ether (20°C).

REFERENCES:

I. H. Schröder. Z. anorg. allg. Chem. 297, 296 (1958); A. Klemenc and G. Wagner. Z. anorg. allg. Chem. 235, 427 (1938).

II. W. L. Jennings and W. B. Scott. J. Amer. Chem. Soc. 41, 1241 (1919); G. H. Coleman, R. W. Leeper and C. C. Schulze in: W. C. Fernelius, Inorganic Syntheses, Vol. II, p. 90, New York—London, 1946.

Cyanogen Bromide

CNBr

I.

$$\underset{159.8}{Br_2} + \underset{49.0}{NaCN} = \underset{102.9}{NaBr} + \underset{105.9}{CNBr}$$

One kilogram of Br_2 (320 ml.) is covered with 150 ml. of water in a two-liter ground joint flask placed under a good hood. The stirrer is then turned on and a solution of 420 g. of NaCN (i.e., one third excess) in 850 ml. of water is added at the rate of 1 drop per second. The temperature of the mixture must be kept below 20°C. Any local excess of cyanide is carefully avoided because it leads to formation of $(CN)_x$. The last 150 ml. of the NaCN solution is diluted with twice that amount of water. Further dropwise addition of the solution is best performed manually, and the flask should be vigorously shaken by hand after each addition. When a persistent brown tint appears the rest of the NaCN solution is discarded. The addition of NaCN takes about five hours.

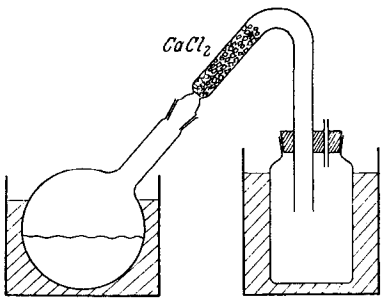

Fig. 215. Preparation of cyanogen bromide.

As shown in Fig. 215, a large diameter tube bent into a V is attached to the round-bottom flask. The shorter arm of the tube is filled with granular $CaCl_2$. The flask is placed on a water bath and the CNBr is distilled. It is collected in a 750-ml. powder bottle serving as receiver. The yield of snow-white crystals is 590 g. or 90% of theoretical, based on Br. The material can be stored in this form for a long time. Brownish CNBr is not stable.