[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Chlorinates. III. Temperature–Concentration Equilibria in the Systems Methylene Chloride–Chlorine and Methyl Chloride–Chlorine. The Perchlorides of Methylene and of Methyl[1,2]

BY J. ALLEN WHEAT, II, AND A. W. BROWNE

In determining temperature–concentration equilibria in the system methylene chloride–chlorine the experimental procedure was identical with that followed in the earlier work with chloroform and chlorine.[2] The data obtained are presented in Table I and are plotted in Fig. 1.

TABLE I

TEMPERATURE–CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM CH_2Cl_2–Cl_2

Temp., °C.	Concn., mole % Cl_2	Curve (Fig. 1)
− 97.0	0.0	A. (Solid CH_2Cl_2, liq., vapor)
− 98.0	1.5	
− 99.5	3.1	
−101.5	6.0	
−104.0	7.4	
−108.5	11.5	
−110.0	14.7	AB. (Solid CH_2Cl_2, satd. soln., vapor)
−113.0	16.8	
−116.5	20.5	
−119.5	22.9	
−120.5	23.8	
−122.5	25.1	
−124.5	26.5	
−128.0	27.7	B. (Eutectic: solid CH_2Cl_2, solid $(CH_2Cl_2)_2{\cdot}Cl_2$, satd. soln., vapor)
−127.0	28.5	
−126.0	29.4	
−125.5	30.8	
−125.0	32.2	
−125.0	34.8	BCD. (Solid $(CH_2Cl_2)_2{\cdot}Cl_2$, satd. soln., vapor)
−126.0	37.4	
−127.5	39.4	
−129.5	41.0	
−131.5	42.6	
−134.0	44.5	
−135.0	45.1	D. (Eutectic: solid $(CH_2Cl_2)_2{\cdot}Cl_2$, solid $CH_2Cl_2{\cdot}Cl_2$, satd. soln., vapor)
−130.5	46.6	
−127.0	48.9	
−126.5	50.5	DEF. (Solid $CH_2Cl_2{\cdot}Cl_2$, satd. soln., vapor)
−127.0	51.3	
−128.0	53.0	
−130.5	55.0	
−132.0	55.5	F. (Eutectic: solid $CH_2Cl_2{\cdot}Cl_2$, solid $CH_2Cl_2{\cdot}2Cl_2$, satd. soln., vapor)
−129.5	56.3	
−125.5	59.1	
−123.0	61.1	
−121.5	63.2	
−119.0	65.6	FGH. (Solid $CH_2Cl_2{\cdot}2Cl_2$, satd. soln., vapor)
−117.5	67.0	
−119.0	68.6	
−121.0	70.2	
−122.0	71.3	H. (Eutectic: solid $CH_2Cl_2{\cdot}2Cl_2$, solid Cl_2, satd. soln., vapor)
−120.0	72.5	
−119.0	74.8	
−117.5	76.2	
−115.5	79.8	HI. (Solid Cl_2, satd. soln., vapor)
−110.5	85.6	
−106.0	92.3	
−104.0	95.9	
−102.0	100.0	I. (Solid Cl_2, liquid, vapor)

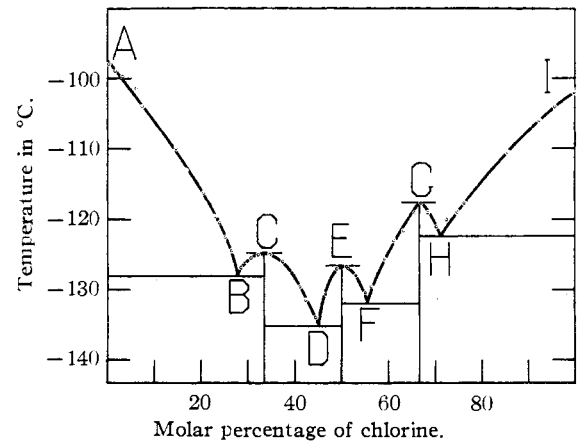

Fig. 1.—Freezing point *vs.* composition for system of methylene chloride–chlorine.

For the investigation of the system methyl chloride–chlorine, in which both components are vapors at ordinary temperatures, a special apparatus, shown in Fig. 3, was used. This consisted essentially of a closed reaction cell immersed in a pentane bath, the temperature of which could readily be controlled between −150° and +20° by means of liquid air. Accessory devices facilitated the introduction of measured amounts of either component into the cell. For

(1) This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allen Wheat, II, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) For the preceding articles in the current series, see Wheat and Browne, THIS JOURNAL, **58**, 2410 (1936); **60**, 371 (1938).

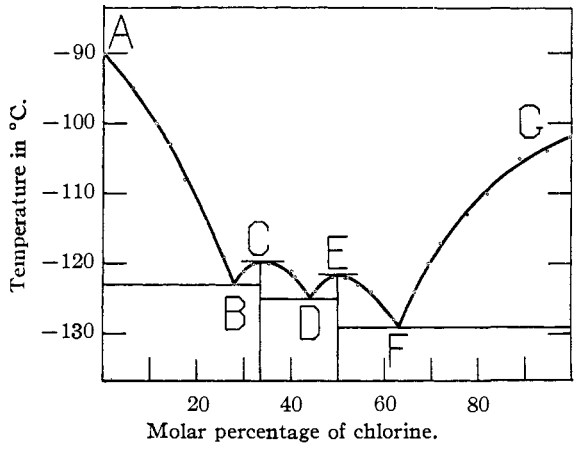

Fig. 2.—Freezing point *vs.* composition for system of methyl chloride–chlorine.

each concentration studied, the system was cooled well below the freezing point, with constant agitation, until solidification occurred. The bath was then allowed to warm slowly, with constant stirring, and the temperature of the bath at which the last trace of the solid phase disappeared, was taken as the freezing point. Possible error due to temperature lag between bath and cell was elimi-

TABLE II

TEMPERATURE-CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM CH_3Cl-Cl_2

Temp., °C.	Concn., mole % Cl_2	Curve (Fig. 2)
− 90	0.0	A. (Solid CH_3Cl, liq., vapor)
− 95	6.5	
−100	11.2	
−103	14.2	AB. (Solid CH_3Cl, satd. soln., vapor)
−108	17.5	
−114	21.6	
−119	25.8	
−124	27.8	B. (Eutectic: solid CH_3Cl, solid $(CH_3Cl)_2{\cdot}Cl_2$, satd. soln., vapor)
−123	28.3	
−121	30.0	
−120	34.6	
−120	35.1	BCD. (Solid $(CH_3Cl)_2{\cdot}Cl_2$, satd. soln., vapor)
−121	40.1	
−122	41.0	
−124	43.2	
−125	44.1	D. (Eutectic: solid $(CH_3Cl)_2{\cdot}Cl_2$, solid $CH_3Cl{\cdot}Cl_2$, satd. soln., vapor)
−124	45.2	
−122	49.0	
−122	51.6	DEF. (Solid $CH_3Cl{\cdot}Cl_2$, satd. soln., vapor)
−123	54.5	
−124	57.4	
−128	62.0	
−129	63.3	F. (Eutectic: solid $CH_3Cl{\cdot}Cl_2$, solid Cl_2, satd. soln., vapor)
−124	66.5	
−120	69.5	
−117	72.0	FG. (Solid Cl_2, satd. soln., vapor)
−113	78.0	
−110	82.0	
−105	89.6	
−104	95.0	
−102	100.0	G. (Solid Cl_2, liq., vapor)

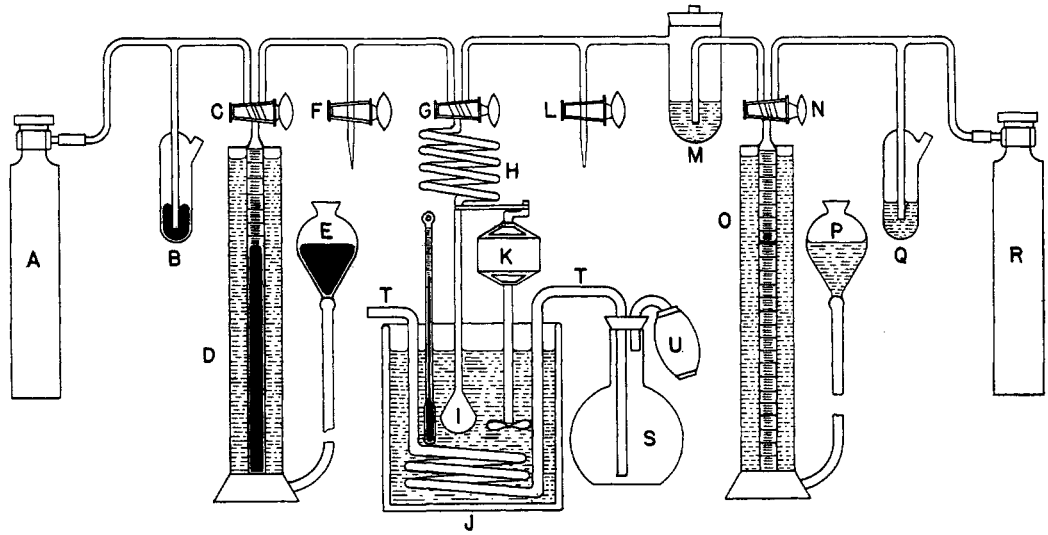

Fig. 3.—A, Cylinder of CH_3Cl; B, gas trap (mercury); C, double stopcock; D, E, water-jacketed gas buret and leveling bulb (mercury); F, exhaust stopcock; G, double stopcock; H, glass spiral; I, reaction cell; J, pentane-bath; K, electric motor; L, exhaust stopcock; M, gas drying bottle (concentrated sulfuric acid); N, double stopcock; O, P, water-jacketed gas buret and leveling bulb (saturated NaCl in water); Q, gas trap (saturated aqueous solution of sodium chloride); R, cylinder of chlorine; S, liquid air supply; T, copper tubing; U, aspirator pump.

nated by special calibration of the pentane thermometer with the aid of several pure gases whose (known) melting points were determined in the same way. The data are submitted in Table II, and are plotted in Fig. 2.

The data in the foregoing tables clearly indicate the formation of three chlorinates of methylene chloride, and two chlorinates of methyl chloride, all with congruent melting points, as follows

(1) methylene chloride hemichlorinate, $(CH_2Cl_2)_2 \cdot Cl_2$, −124.5°
(2) methylene chloride monochlorinate, $CH_2Cl_2 \cdot Cl_2$, −126.5°
(3) methylene chloride dichlorinate, $CH_2Cl_2 \cdot 2Cl_2$, −117.5°
(4) methyl chloride hemichlorinate, $(CH_3Cl)_2 \cdot Cl_2$, −120°
(5) methyl chloride monochlorinate, $CH_3Cl \cdot Cl_2$, −122°

While no evidence concerning the structure of these compounds has been obtained as yet, it is possible to write their formulas in the manner tentatively suggested for the chlorinates of chloroform and of carbon tetrachloride in the earlier articles of the current series. The fact that the maximum number of chlorine molecules held in combination by any of the chloromethanes is equal to the number of chlorine atoms in the chloromethane molecule tends, in the opinion of the authors, to confirm the idea that the solvates under investigation are coördination compounds.

In conformity with the definition of perchlorides proposed in the second article of this series, the three chlorinates of methylene chloride and the two of methyl chloride may be regarded as perchlorides of methylene, and of methyl, respectively. Their empirical composition could therefore be expressed by the formulas $(CH_2)_2Cl_6$, CH_2Cl_4, CH_2Cl_6, $(CH_3)_2Cl_4$ and CH_3Cl_3.

Summary

Two chlorinates of methyl chloride, or perchlorides of methyl, and three chlorinates of methylene chloride, or perchlorides of methylene, have been identified and their congruent melting points determined.

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The Chlorinates. IV. Temperature–Concentration Equilibria in the System Hydrogen Chloride–Chlorine. The Hydrogen Perchlorides[1,2]

BY J. ALLEN WHEAT, II, AND A. W. BROWNE

Since chlorine readily forms solvates with the chloromethanes[2] it has been suggested tentatively

TABLE I

TEMPERATURE–CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM HCl–Cl_2

Temp., °C.	Concn., mole % Cl_2	Curve (Fig. 1)
−112	0.0	A. (Solid HCl, liquid, vapor)
−114	6.7	AB. (Solid HCl, saturated solution, vapor)
−117	12.5	
−120	17.0	
−122	19.6	
−125	23.0	
−128	25.6	
−129	26.3	B. (Eutectic: Solid HCl, solid $(HCl)_2:Cl_2$, saturated solution, vapor)
−123	30.6	BCD. (Solid $(HCl)_2:Cl_2$, saturated solution, vapor)
−122	32.2	
−122	35.0	
−124	37.6	
−125	38.0	D. (Eutectic: Solid $(HCl)_2:Cl_2$, solid HCl:Cl_2, saturated solution, vapor)
−120	40.4	DEF. (Solid HCl:Cl_2, saturated solution, vapor)
−116	44.8	
−115	49.4	
−116	54.0	
−117	57.3	
−120	60.0	
−124	63.5	
−128	66.0	F. (Eutectic: Solid HCl:Cl_2, solid Cl_2, saturated solution, vapor)
−122	68.7	FG. (Solid Cl_2, saturated solution, vapor)
−117	72.6	
−112	77.5	
−109	82.5	
−106	88.9	
−103	95.0	
−102	100.0	G. (Solid Cl_2, liquid, vapor)

(1) This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allen Wheat, II, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) For the preceding articles in the current series, see Wheat and Browne, THIS JOURNAL, **58**, 2410 (1936); **60**, 371 (1938); **62**, 1575 (1940).