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.

ITHACA, N. Y. RECEIVED APRIL 5, 1940

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

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).

that chlorine attached to carbon will denote a pair of electrons to free chlorine. The purpose of the current investigation was to determine whether or not chlorides, in which the chlorine was attached to a more electropositive element than carbon, would also form solvates with free chlorine.

In the present investigation of the freezing point *vs.* concentration equilibria in the system of hydrogen chloride–chlorine, the experimental procedure was substantially identical with that employed in the study of the system of methyl chloride–chlorine.[2] The data obtained are presented in Table I and are plotted in Fig. 1.

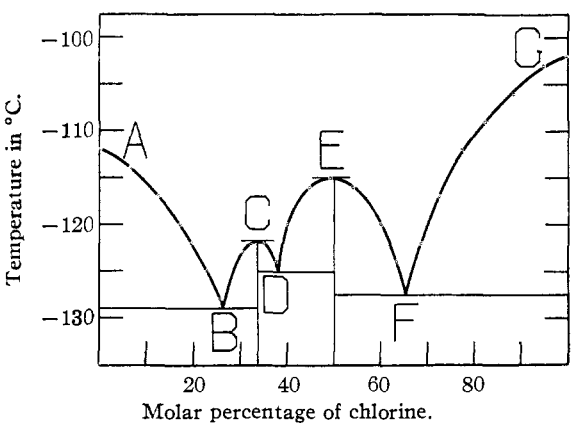

Fig. 1.—Freezing point *vs.* composition in system of hydrogen chloride–chlorine.

From the foregoing data it may be concluded that chlorine forms two solvates (chlorinates) with hydrogen chloride, whose empirical formulas and congruent melting points are as follows: (1) hydrogen chloride hemichlorinate, $(HCl)_2:Cl_2$, −121°; (2) hydrogen chloride monochlorinate, $HCl:Cl_2$, −115°.

Nothing concerning the structure of these compounds can be deduced from these data, but the authors venture the statement that it seems probable that hydrogen chloride should be combined with free chlorine by a coördinate covalent link. Since the hydrogen–chlorine link in hydrogen chloride is more polar than the chlorine–chlorine link in the free chlorine, the chlorine attached to hydrogen probably donates a pair of electrons which is accepted by the free chlorine. The structural formulas would therefore be

(1) H—Cl ⟶ Cl—Cl ⟵ Cl—H
(2) H—Cl ⟶ Cl—Cl

In conformity with the definition of perchlorides proposed in the second article of the current series,[2] the compounds identified during this investigation may be considered as perchlorides of hydrogen whose empirical formulas are H_2Cl_4 and HCl_3.

Summary

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

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Chlorides of Gallium

BY A. W. LAUBENGAYER AND F. B. SCHIRMER

The formation of compounds by gallium has been shown to present numerous interesting problems, both of valence state and of molecular configuration. While trivalency, which is to be expected for this atom, is well established, the molecular species and configuration of the compounds in this state have not been well understood. Gallium also has been reported[1] to show divalence, a condition which cannot be reconciled with its atomic structure, and univalence, which should be possible due to the use of only the 4*p* electron for bonding purposes. Very little work is available about these lower valence states.

The system gallium–chlorine is a favorable one to study because gallium–chlorine bonds are strong enough to ensure reasonably stable molecules and the volatility of the chlorides makes it possible to investigate them in the vapor phase.

Gallium trichloride has been shown[1] to resemble aluminum chloride closely, being associated at lower temperatures. While a recent vapor pressure and density investigation[2] of this compound has given considerable data, this work does not agree on a number of points with the reports of earlier investigators, the temperature range cov-

(1) L. de Boisbaudran, *Compt. rend.*, **93**, 294 (1881).

(2) Fischer and Jubermann, *Z. anorg. allgem. Chem.*, **227**, 227 (1936).