8. A preferential adsorption of $D_2$ was observed at low temperatures and was explained on the basis of van der Waals adsorption.

9. Ortho–para hydrogen conversion was noted below 140°K.

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

# The Chlorinates. II. Temperature–Concentration Equilibria in the System Alpha-Carbon Tetrachloride–Chlorine. The Carbon Perchlorides[1]

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Since chloroform has been found to form four solvates, the hemi-, mono-, di-, and trichlorinates, at low temperatures in liquid chlorine solution,[1] it is to be expected that carbon tetrachloride should form five solvates of this type.

The system carbon tetrachloride–chlorine already has been studied by Biltz and Meinecke[2] who found, at −48°, a sharp break in the otherwise smooth melting point curve. This point was construed as an inversion point at which, on cooling, α-carbon tetrachloride undergoes transformation into β-carbon tetrachloride. The polymorphism of carbon tetrachloride had already been established.[3] No conclusive evidence of the formation of solvates was obtained, although some indication that β-carbon tetrachloride may form a very unstable compound with chlorine was noted.[4]

In the present investigation of the temperature-concentration equilibria in the system carbon tetrachloride–chlorine the experimental procedure was substantially identical with that described in the preceding article.[1] The results obtained are presented in Table I and are plotted in Fig. 1.

TABLE I

TEMPERATURE–CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM $CCl_4$–$Cl_2$

Temperatures designated with an *asterisk* represent the congruent melting points of the respective solvates. If enclosed in parentheses they have been determined by graphic interpolation.

| Temp., °C. | Concn., mole % $Cl_2$ | Curve (Fig. 1) |
|---|---|---|
| − 22.5 | 0.0 | A. (Solid $CCl_4$, liq., vapor) |
| − 26.0 | 2.5 | |
| − 33.5 | 6.8 | |
| − 35.5 | 9.3 | |
| − 42.0 | 12.1 | |
| − 48.5 | 17.3 | AB. (Solid $CCl_4$, satd. soln., vapor) |
| − 57.5 | 20.6 | |
| − 61.5 | 23.0 | |
| − 72.0 | 25.8 | |
| − 75.0 | 27.0 | |
| (− 81.0) | 28.3 | B. (Eutectic: solid $CCl_4$, solid $(CCl_4)_2 \cdot Cl_2$, satd. soln., vapor) |
| − 77.5 | 29.4 | |
| − 72.0 | 30.8 | |
| − 68.5 | 32.3 | |
| (− 67.0)* | 33.3 | |
| − 67.5 | 33.9 | |
| − 71.0 | 35.3 | BCD. (Solid $(CCl_4)_2 \cdot Cl_2$, satd. soln., vapor) |
| − 76.0 | 37.7 | |
| − 79.5 | 38.8 | |
| − 84.0 | 40.6 | |
| − 88.5 | 42.5 | |
| − 94.0 | 44.5 | |
| (− 98.0) | 45.6 | D. (Eutectic: solid $(CCl_4)_2 \cdot Cl_2$, solid $CCl_4 \cdot Cl_2$, satd. soln., vapor) |
| − 97.0 | 46.2 | |
| − 93.0 | 48.1 | |
| − 90.5* | 50.0 | |
| − 92.0 | 52.0 | |
| − 94.0 | 54.5 | DEF. (Solid $CCl_4 \cdot Cl_2$, satd. soln., vapor) |
| − 97.5 | 57.0 | |
| 102.0 | 59.9 | |
| −106.5 | 61.5 | |
| −108.5 | 62.6 | |
| −116.5 | 63.6 | |
| (−122.0) | 64.4 | F. (Eutectic: solid $CCl_4 \cdot Cl_2$, solid $CCl_4 \cdot 2Cl_2$, satd. soln., vapor) |
| −119.0 | 64.7 | |
| −115.0 | 65.9 | |
| (−112.5)* | 66.7 | |
| −113.0 | 67.0 | FGH. (Solid $CCl_4 \cdot 2Cl_2$, satd. soln., vapor) |
| −114.0 | 68.3 | |
| −115.5 | 69.4 | |
| −117.5 | 70.7 | |
| −122.0 | 71.9 | |
| (−124.0) | 72.5 | H. (Eutectic: solid $CCl_4 \cdot 2Cl$, solid $CCl_4 \cdot 3Cl_2$, satd. soln., vapor) |
| −122.0 | 73.2 | |
| −117.5 | 74.0 | |

(1) For the first article of this series see THIS JOURNAL, **58**, 2410 (1936).

(2) Biltz and Meinecke, *Z. anorg. allgem. Chem.*, **131**, 1 (1923).

(3) Tammann, *Wied. Ann.*, **66**, 490 (1898); "Kristallisieren und Schmelzen," Barth, Leipzig, 1903, p. 222.

(4) Since the system at the inversion point contains carbon tetrachloride and chlorine in the molecular ratio of approximately 6:1, it is apparent that any solvate formed at this point (or to the left of it on the diagram) would contain *at least* 6 moles of carbon tetrachloride to one of chlorine.

TABLE I (*Concluded*)

| Temp., °C. | Concn., mole % $Cl_2$ | Curve (Fig. 1) |
|---|---|---|
| −115.5 | 74.8 | HIJ. (Solid $CCl_4 \cdot 3Cl_2$, satd. soln., |
| (−115.5)* | 75.0 | vapor) |
| −116.5 | 76.3 | |
| −118.5 | 76.8 | |
| (−122.0) | 77.2 | J. (Eutectic: solid $CCl_4 \cdot 3Cl_2$, solid $CCl_4 \cdot 4Cl_2$, satd. soln., vapor) |
| −116.0 | 78.3 | |
| −114.5 | 79.5 | |
| −114.0 | 79.9 | JKL. (Solid $CCl_4 \cdot 4Cl_2$, satd. |
| (−114.0)* | 80.0 | soln., vapor) |
| −114.5 | 80.5 | |
| −117.0 | 81.5 | |
| (−118.0) | 81.7 | L. (Eutectic: solid $CCl_4 \cdot 4Cl_2$, solid $Cl_2$, satd. soln., vapor) |
| −113.0 | 83.2 | |
| −111.5 | 85.0 | |
| −110.0 | 86.9 | LM. (Solid $Cl_2$, satd. soln., |
| −108.0 | 90.9 | vapor) |
| −106.0 | 95.2 | |
| −102.0 | 100.0 | M. (Solid $Cl_2$, liquid, vapor) |

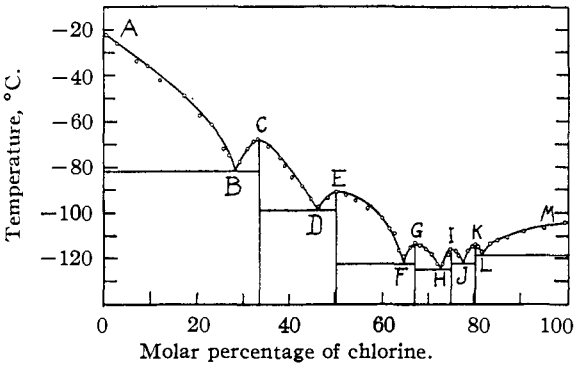
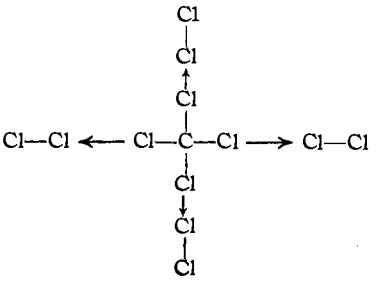



Fig. 1.—Freezing point *vs.* concentration: system of α-carbon tetrachloride–chlorine.

The foregoing data indicate the existence of five solvates, with congruent melting points, as follows:

(1) carbon tetrachloride hemichlorinate, $2(CCl_4)_2 \cdot Cl_2$, −67.0°
(2) carbon tetrachloride monochlorinate, $CCl_4 \cdot Cl_2$, −90.5°
(3) carbon tetrachloride dichlorinate, $CCl_4 \cdot 2Cl_2$, −112.5°
(4) carbon tetrachloride trichlorinate, $CCl_4 \cdot 3Cl_2$, −115.5°
(5) carbon tetrachloride tetrachlorinate, $CCl_4 \cdot 4Cl_2$, −114.0°

It seems probable that the "free" chlorine may act as acceptor of electron pairs from the chlorine of the carbon tetrachloride, as illustrated by the following tentative structural formula for the tetrachlorinate.




If "perchlorides" be defined as compounds of chlorine in which there is chlorine to chlorine linkage, the five chlorinates of carbon tetrachloride may be regarded as perchlorides of carbon with empirical composition expressed, respectively, by the formulas $C_2Cl_{10}$, $CCl_6$, $CCl_8$, $CCl_{10}$, and $CCl_{12}$. The previously described chlorinates of chloroform may similarly be regarded as methine perchlorides.

Comparison of the foregoing data with those published by Biltz and Meinecke reveals substantial agreement as to the form of curve over the range −22.5 to −48°.[5] At lower temperatures (and higher concentrations of chlorine), the present curve lies entirely below that of Biltz and Meinecke, and shows no inversion point in the neighborhood of −48°. It seems reasonable, therefore, to conclude that the solvates obtained during the present investigation are addition products of chlorine with metastable α-carbon tetrachloride.

## Summary

Five chlorinates of carbon tetrachloride, or perchlorides of carbon, have been identified during the current investigation, and their six eutectic points have been located.

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(5) That the authors' curve lies slightly above that of B. and M., however, is probably due to some difference in experimental procedure. For example, the pentane thermometer used by the authors was immersed directly in the system, while the resistance thermometer employed by B. and M. was surrounded by a protecting glass tube containing glycerol.