[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Addition Compounds of the Group 4a Tetrachlorides with Arsenic Trichloride

BY HARRY H. SISLER, BARBARA PFAHLER[1] AND WILBUR J. WILSON[2]

As a part of an extended program of phase studies of binary systems involving, as one component, a group 4a tetrachloride, it was decided to investigate the systems of arsenic trichloride with carbon, silicon, germanium and tin tetrachlorides, respectively. As in previous studies in this series[3,4] the systems were studied by the freezing point method.

Experimental

Preparation of Materials.—The tetrachlorides of carbon, silicon, germanium and tin were obtained from the same sources and purified in the same manner as the same materials used in previous studies.[3] Arsenic trichloride was obtained from Baker and Adamson and purified by careful fractionation at atmospheric pressure, using a five-foot column packed with glass helices, and using a reflux ratio greater than 20:1. A freezing point of −18.0° was obtained for the purified product. This agrees with values cited in the literature.

Method.—The solid–liquid equilibrium curves were obtained by the method of taking cooling curves of synthetic mixtures of the two components. The cooling curves were automatically recorded by means of a Leeds and Northrup Micromax self-recording potentiometer using a copper–constantan thermocouple. The closed cell which was used has been previously described,[5] as has also the method of interpreting the curves.[3] The points obtained in these studies are believed accurate to within ±1.5°. Considerable variation of the rate of cooling did not change the indicated freezing point for various synthetic mixtures, so it is believed that equilibrium was attained. No system was completed from a single batch of material, and, in most of the systems, the data were obtained using materials from several different batches.

Results

It is apparent from the data in curve A, Fig. 1, that carbon tetrachloride and arsenic trichloride do not form addition compounds with each other under the conditions of the experiment. The break in the freezing point curve of carbon tetrachloride at about −48.0° corresponds to a previously recorded transition temperature of carbon tetrachloride. The eutectic between arsenic trichloride and the β-form of carbon tetrachloride occurs at about 77 mole per cent. of carbon tetrachloride and −50°.

The data for the silicon tetrachloride system (curve B, Fig. 1) indicate that the compound $SiCl_4 \cdot AsCl_3$ melting at about −29.5° is formed. The flat nature of the maximum suggests that this compound is not very stable. Further breaks in the freezing point curve indicate the possible formation of 1:2 and 1:3 compounds; these breaks are so slight, however, that one cannot accept the existence of these compounds without further proof, which is, at present, unavailable. An eutectic at −69.5° and 92 to 93 mole per cent. silicon tetrachloride was obtained.

Though there is a slight inflection in the curve for the germanium tetrachloride system (curve C, Fig. 1), there is no definite evidence of compound formation. An eutectic with the β- form of germanium tetrachloride was obtained at −55.5° and about −89.0 mole per cent. germanium tetrachloride. An eutectic with the α- form at about −55.0° and 88.5 mole per cent. tetrachloride is indicated.

The system arsenic trichloride–tin tetrachloride (curve D, Fig. 1) gives no evidence of compound formation. An eutectic was obtained at −48.0° and 69. mole per cent. tin tetrachloride.

There is, at present, no theoretical basis for interpreting the results of these experiments except to say that it is apparent that no very strong interaction occurs in these systems. Even in the arsenic trichloride–silicon tetrachloride system, where compound formation was observed, the compounds formed are apparently not very stable.

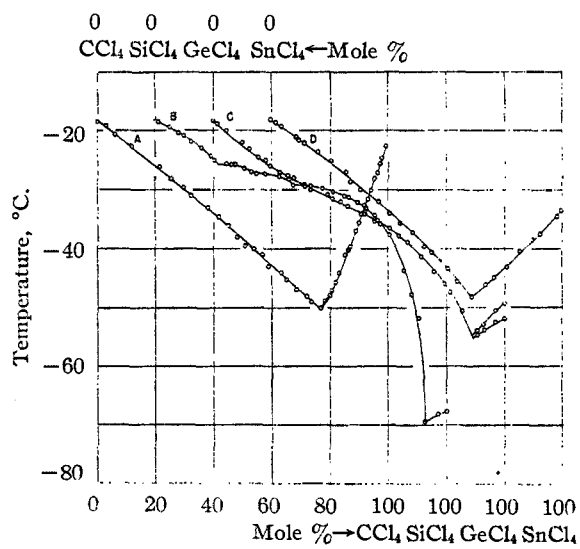

Fig. 1.

Summary

The binary systems of arsenic trichloride with the four tetrachlorides of group 4a, respectively, have been investigated by the freezing point method. Compound formation was observed only in the system $AsCl_3$–$SiCl_4$. In this system positive evidence for the existence of the compound $SiCl_4 \cdot AsCl_3$ melting at −29.5° was obtained. Less positive indications of a 1:2 and a 1:3 compound in this system were observed.

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(1) Present address: Shell Development Co., Emeryville, California.

(2) Present address: Wilmington College, Wilmington, Ohio.

(3) Sisler, Wilson, Gibbins, Batey, Pfahler and Mattair, THIS JOURNAL, **70**, 3818 (1948).

(4) Sisler, Batey, Pfahler and Mattair, *ibid.*, **70**, 3821 (1948).

(5) Sisler and Cory, *ibid.*, **69**, 1515 (1947).