

The System Germanium Tetrachloride-Methyl *o*-Cresyl Ether.—The data obtained for this system are illustrated graphically in curve A, Fig. 5. Curve A, Fig. 5 gives no indication of compound formation. An eutectic is obtained at about 73 mole per cent. of germanium tetrachloride and about -60° . A freezing point curve for only the metastable form of germanium tetrachloride was obtained.

The System Germanium Tetrachloride-*n*-Propyl Phenyl Ether.—The data for this system are recorded in curve B, Fig. 5. A freezing point curve was obtained for the metastable form only of germanium tetrachloride. Curve B, Fig. 5 gives no indication of compound formation between germanium tetrachloride and *n*-propyl phenyl ether. An eutectic was obtained at about 88.5 mole per cent. of the tetrachloride and -56.0° .

Conclusions

The results reported in this paper may be summarized as follows: (a) Carbon tetrachloride forms addition compounds with some aromatic ethers but not with others. In general these addition compounds are highly dissociated and difficult to crystallize. (b) Silicon and germanium tetrachlorides exhibit no more than a very slight tendency to form addition compounds with the aromatic ethers studied. (c) Tin tetrachloride forms addition compounds with all the aromatic ethers with which it was studied. These also do not appear to be very stable.

Since there are so many different factors involved in the formation of solid addition compounds, the formation of such compounds cannot be taken as evidence of any particular mechanism. However, the failure of silicon and germanium tetrachlorides to exhibit more than a slight tendency to form addition compounds with aromatic ethers does indicate that the oxygen atoms in these ethers probably do not readily share electron pairs with the silicon and germanium atoms in the respective tetrachlorides. It may, of course, be stated that

in those cases where carbon tetrachloride forms such addition compounds, some mechanism other than the acceptance of an electron pair from the oxygen by the carbon atom must be involved, for the valence shell of the carbon does not have an orbital available for accepting such an electron pair. Our results, with respect to silicon tetrachloride, are in accord with results obtained with this substance and dioxane.^{6,7,8}

The failure of oxygen atoms in aromatic ethers to share electron pairs with silicon and germanium in their respective tetrachlorides may result from one or more of the following factors: the electron withdrawing effect of the benzene ring reducing the electron density about the oxygen, the steric interference by the aromatic group, the steric interference of the halogen atoms on the silicon or germanium atom, or too high an electron density about the silicon and germanium atoms. The latter possibility can be eliminated in terms of known reactions of the tetrachlorides. The relative importance of the other three factors cannot be evaluated from the present data.

Summary

Freezing point curves for the binary systems of a variety of aromatic ethers with the tetrachlorides of the elements of group 4a have been constructed. Compound formation occurs in some of the carbon tetrachloride systems and in all the tin tetrachloride systems. Silicon and germanium tetrachloride exhibit little tendency to form addition compounds with aromatic ethers.

(6) Lane, McCusker and Curran, *THIS JOURNAL*, **64**, 2076 (1942).

(7) Kelley and McCusker, *ibid.*, **65**, 1307 (1943).

(8) Kennard and McCusker, *ibid.*, **70**, 1039 (1948).

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Phase Studies of Some Group 4a Tetrachloride-Aliphatic Ether Systems

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In the last publication¹ in this series it was shown that silicon and germanium tetrachlorides exhibit little tendency to form addition compounds with various aromatic ethers and, therefore, it was concluded that there is probably little tendency for the oxygen atom of the aromatic ether to share electrons with the silicon or germanium atoms in the respective tetrachloride. Tetrahydrofuran has been shown to have a strong tendency to form addition compounds with certain electron acceptor molecules.² It was considered desirable, therefore, to carry out phase studies of the systems of the four group 4a tetrachlorides with tetrahydrofuran. Since it was ex-

pected that tetrahydropyran would be similar to tetrahydrofuran in its ability to form addition compounds, it was decided that the germanium tetrachloride-tetrahydropyran and tin tetrachloride-tetrahydropyran systems should be studied.

It has long been known that tin tetrachloride forms stable addition compounds of the formula $\text{SnCl}_4 \cdot 2\text{R}_2\text{O}$, which are solid at room temperature, with a number of aliphatic ethers including diethyl ether.³ It has also been shown that carbon tetrachloride forms the addition compound $\text{CCl}_4 \cdot 2\text{Et}_2\text{O}$ ⁴ which is, however, much less stable and of much lower melting point than the tin compounds. It was decided to complete the diethyl ether series by investigating the systems silicon tetrachloride-

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

(2) Brown, unpublished.

(3) Pfeiffer and Halperin, *Z. anorg. Chem.*, **87**, 335 (1914).

(4) Wyatt, *Trans. Faraday Soc.*, **25**, 43 (1929).

diethyl ether and germanium tetrachloride-diethyl ether.

Experimental Method

Preparation of Materials.—The sources and methods of purification of the group 4a tetrachlorides were outlined in a previous publication¹ from this Laboratory. The tetrahydrofuran and tetrahydropyran for use in this work were contributed by the Electro-Chemicals Division of the E. I. du Pont de Nemours Co., and, after standing over sodium, were fractionated using a packed column. In each case a constant boiling middle fraction was used. Diethyl ether, C.P. grade, obtained from Merck and Co., was purified in the same manner. No system was completed from a single batch of material, and, in most systems, the data were obtained using materials from several different batches.

Procedure.—The freezing points in these systems were obtained by means of cooling curves, recorded automatically by a Leeds-Northrup Micromax temperature recorder with a copper-constantan thermocouple. The method is discussed in detail in a previous publication.¹ The data are believed to have an accuracy of $\pm 1.5^\circ$.

It will be noted that, in certain cases, freezing points for only the lower melting forms of germanium tetrachloride and diethyl ether were obtained. No explanation can be given for this, and, because of the low temperatures involved and the necessity for working in a closed system, attempts to obtain the higher melting forms by such methods as seeding were deemed unfeasible. Attempts to obtain these forms by varying the rate of cooling and by cooling far below the freezing points were not successful.

The tin tetrachloride-tetrahydrofuran and the tin tetrachloride-tetrahydropyran compounds were prepared by adding, in an atmosphere of dry nitrogen, either component to an excess of the other component dissolved in dry Skellysolve B, and cooled in an ice-bath. The solid which precipitated in each case was washed repeatedly with Skellysolve B and filtered under a positive pressure of dry nitro-

gen. The product was then dried in a stream of nitrogen and transferred to a weighing bottle and placed in a desiccator over phosphorus pentoxide.

Method of Analysis of the Tin Tetrachloride-Diethyl Ether Compounds.—Samples, weighed by difference, were added to 100-ml. portions of water, to which suspensions were then added 50-ml. portions of concentrated, silica-free, ammonia solution. The suspensions were digested until solution was complete. At this time 1 g. of ammonium nitrate was added to each solution and digestion continued until hydrous stannic oxide had precipitated and coagulated. After filtration the stannic oxide precipitates were ignited at 1000° and weighed.

Results

The Tetrahydrofuran Systems.—Data for tetrahydrofuran-carbon tetrachloride, -silicon tetrachloride, and -germanium tetrachloride systems are recorded graphically in Fig. 1, curves A, B and C. The freezing point obtained for pure tetrahydrofuran was -108.5° , in good agreement with the results obtained by the American Petroleum Institute.⁵

The flat portion of curve A between 61 and 71 mole per cent. of carbon tetrachloride results from the fact that, in this composition range, the solid is freezing out of a two-phase liquid system. The separation of the liquid mixture in this composition range into two liquid phases could be observed visually before freezing occurred. However, the boundaries of the area of immiscibility were not determined. A break in the freezing point curve at about -81° and 39 mole per cent. carbon tetrachloride may be considered to be evidence of some sort of compound formation. However, since the compound melts incongruently and the potential maximum in the curve is almost completely obscured no statement concerning the composition of this compound can be made. If, like diethyl ether, tetrahydrofuran forms a 2:1 compound with carbon tetrachloride, the melting point of the compound is probably between -70° and -80° . An eutectic is obtained at about 12 mole per cent. and -113.5° . No indication of the phase transition in carbon tetrachloride at -48° was observed in this system.

Though there is a slight inflection in the freezing point curve of silicon tetrachloride (curve B) the results of the study of the system silicon tetrachloride-tetrahydrofuran may be considered negative as far as any indication of compound formation is concerned. An eutectic at about 17 mole per cent. silicon tetrachloride and -113.0° was obtained.

As is shown in curve C, Fig. 1, the results of the study of the germanium tetrachloride-tetrahydrofuran system give no indication of compound formation. No freezing point curve for the β -form of the tetrachloride was obtained. An eutectic was obtained at about 28 mole per cent. of the tetrachloride and -117.5° .

Whenever tin tetrachloride and tetrahydrofuran are mixed in any proportion, a vigorous reaction

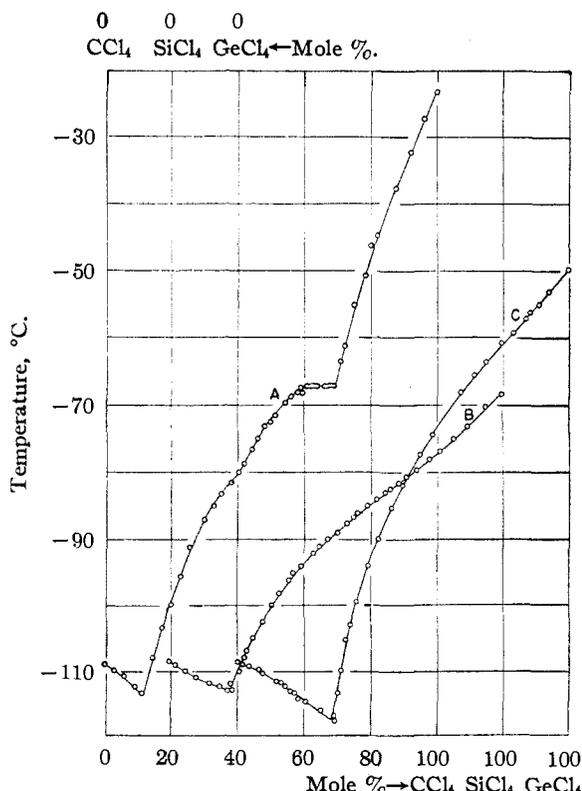


Fig. 1.—Tetrahydrofuran systems.

(5) Ninth Annual Report American Petroleum Institute Project No. 45. The Ohio State University Research Foundation.

occurs and a white precipitate is obtained. The reaction between tin tetrachloride and tetrahydrofuran was, therefore, studied directly by the method already described in this paper, *viz.*, that of allowing the two components to react in an inert solvent. The reaction was carried out both by adding tin tetrachloride to a solution of an excess of the ether and by adding tetrahydrofuran to a solution of an excess of the tetrachloride, with apparently the same reaction in each case. The precipitates, after washing and drying in the manner described above, were analyzed for tin tetrachloride with the following results: Product obtained with excess ether: SnCl_4 , 63.94, 63.85; product obtained with excess tetrachloride: SnCl_4 , 64.40, 63.51. Calculated for $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$: 64.37. Thus, in both instances, the compound $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$ is obtained. This is a gray-white, crystalline, very hygroscopic substance; it sublimes at temperatures above 160° . When heated in a closed tube it melts with decomposition and charring at about 180° .

The Tetrahydropyran Systems.—The data obtained for the germanium tetrachloride-tetrahydropyran system are recorded graphically in Fig. 2. The freezing point, -49.2° , obtained for tetrahydropyran is in good agreement with the value reported in the literature.⁵ The region from 15 to 35 mole of germanium tetrachloride was very difficult to study because of a strong tendency to supercool. All the tetrahydropyran side was difficult because the very low heat of fusion of tetra-

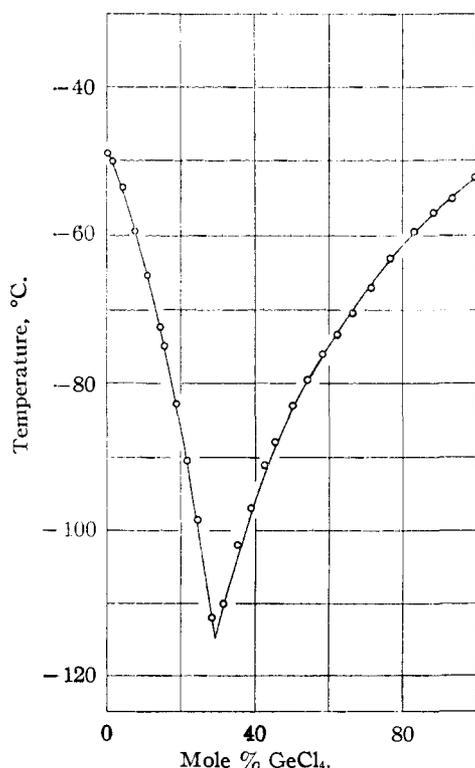


Fig. 2.— GeCl_4 -tetrahydropyran system.

hydropyran caused the break in the cooling curves produced by the crystallization of this substance to be very slight. No freezing point curve was obtained for the α -form of germanium chloride. It is apparent that Fig. 2 gives no indication of compound formation between germanium tetrachloride and tetrahydropyran. An eutectic was obtained at about 30 mole per cent. of germanium tetrachloride and -115.0° .

The reaction of tin tetrachloride with tetrahydropyran was, in every way, analogous to the corresponding reaction with tetrahydrofuran and was carried out in exactly the same manner. The product obtained by this reaction was physically and chemically very similar to the tetrahydrofuran compound with tin tetrachloride. The following analytical data were obtained: Product obtained with an excess of tetrahydropyran: SnCl_4 , 60.80, 61.13, 60.68. Product obtained with excess tin tetrachloride: SnCl_4 , 60.87, 61.87, 60.79. Calculated for $\text{SnCl}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$: 60.20 SnCl_4 . Thus, the compound $\text{SnCl}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$ is obtained either in excess ether or in excess tetrachloride.

The Diethyl Ether Systems.—The data obtained for the silicon tetrachloride-diethyl ether and the germanium tetrachloride-diethyl ether systems are recorded graphically in Fig. 3, curves A and B. A freezing point of -123.5° in good agreement with that listed in the literature⁶

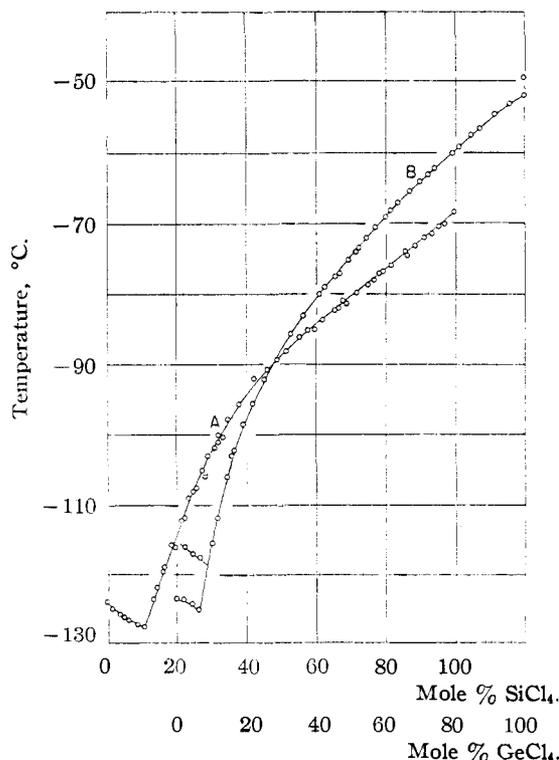


Fig. 3.—Diethyl ether systems.

(6) "International Critical Tables," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1928, p. 61.

for the lower melting form of diethyl ether, was obtained.

Curve A, Fig. 3, gives no indication whatsoever of compound formation between silicon tetrachloride and diethyl ether. An eutectic with the lower melting form of diethyl ether was obtained at about 10 mole per cent. of silicon tetrachloride and about -128° . No freezing point curve for the higher melting form was obtained in this system.

As is indicated by curve B, Fig. 3, a freezing point curve for only the lower form of germanium tetrachloride was obtained in the germanium tetrachloride-diethyl ether system. There is no indication whatsoever of compound formation between diethyl ether and germanium tetrachloride. An eutectic with the higher melting form of diethyl ether was obtained at about 8 mole per cent. of germanium tetrachloride and -118.5° . An eutectic with the lower melting form of the ether was found at about 7 mole per cent. of the tetrachloride and -125.5° .

Discussion

Summarizing the results of the experiments reported in this paper, the following statements may be made: (a) tin tetrachloride reacts vigorously with tetrahydropyran and with tetrahydrofuran to form very stable compounds of the formulas $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$ and $\text{SnCl}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$. (b) Silicon tetrachloride and germanium tetrachloride form no addition compounds with tetrahydrofuran, tetrahydropyran, or diethyl ether. (c) Carbon tetrachloride shows a weak indication of compound formation with tetrahydrofuran.

The fact that silicon tetrachloride and germanium tetrachloride do not form addition compounds with such strongly basic ethers as tetrahydrofuran, tetrahydropyran, or diethyl ether is an indication that the oxygen atoms of these ethers probably do not share electrons readily with the silicon or germanium atoms in the tetrachloride molecules, for it may be presumed that such

electron sharing would result in compound formation and, hence, in a maximum in the freezing point curve. One may suggest tentatively that the reason for this result is that the four chlorine atoms grouped about a silicon or germanium atom leave insufficient space for an oxygen atom or atoms to approach the silicon or germanium atom.

In conclusion, let us state that whereas failure to form addition compounds indicates that there is probably little, if any, coordination, the formation of addition compounds does not necessarily indicate that coordination, particularly coordination between two specific types of atoms, does take place. The authors, however, know of no other structure that can account for the *very stable* 1:2 addition compounds of tin tetrachloride with aliphatic ethers, than that of definite bond formation by coordination of the ether with the tin through the oxygen atoms. The fact that the 1:2 ratio leads to the customary coordination number of six for tin lends plausibility to this structure. The formation of weak addition compounds between carbon tetrachloride and certain ethers lacks satisfactory explanation. Since the addition compounds of tin tetrachloride with aromatic ethers reported in the previous paper¹ are apparently of the same order of stability as the carbon tetrachloride compounds, we are not justified in extending the structure suggested for the tin tetrachloride-aliphatic ether compounds to a consideration of the tin tetrachloride-aromatic ether compounds.

Summary

Freezing point curves for the systems $\text{CCl}_4\text{-C}_4\text{H}_8\text{O}$, $\text{SiCl}_4\text{-C}_4\text{H}_8\text{O}$, $\text{GeCl}_4\text{-C}_4\text{H}_8\text{O}$, $\text{GeCl}_4\text{-C}_5\text{H}_{10}\text{O}$, $\text{SiCl}_4\text{-(C}_2\text{H}_5)_2\text{O}$ and $\text{GeCl}_4\text{-(C}_2\text{H}_5)_2\text{O}$ have been constructed.

It has been shown that tin tetrachloride reacts with tetrahydrofuran and tetrahydropyran to produce the very stable compounds $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$ and $\text{SnCl}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$.

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