tetrachlorides containing, respectively, a large and a small central atom. The test is insensitive, however, since the solubility characteristics of binary mixtures, according to the Hildebrand equations, depend upon the square of the difference of solubility parameters, and even if, for example, the tin (IV) chloride had an effective solubility parameter considerably different from the theoretical value, the effect on the behavior of the solution would be small.

A much better test for possible deviation from regular solution behavior is provided by the c.s.t. data for the system perfluoroheptane ($\delta = 5.7$)–tin(IV) chloride. The predicted (ref. (6), p. 253, equation (3)) c.s.t. of 115° and the observed value of 97° are felt to be in excellent agreement. Since the solubility parameters of the two compounds differ by 3 units, even a small deviation of the effective difference in solubility parameters from that calculated would result in considerable departure of the solution from predicted behavior. The fact that this is not observed is evidence for non-interpenetration in tin(IV) chloride.

The vapor–liquid equilibrium data for the system tin(IV) chloride–octane ($\delta = 7.6$) indicate a system slightly more nearly ideal than predicted by the Hildebrand equations. This is in accord with Hildebrand's and Simons and Dunlap's observation of an effective solubility parameter in excess of the calculated value for the hydrocarbon (making the difference in parameters less than calculated, and hence the behavior more nearly ideal) although the sensitivity is low because of the small difference in the two parameters.

The c.s.t. value for the system perfluoroheptane–tetrachloromethane (84° calculated, 58° found) is in fair agreement with the Hildebrand equation, and is consistent with the fact that the binary mixtures of each of the components of this system with tin(IV) chloride were essentially regular.

A difference of more than 170° between calculated (−106°) and found (68°) c.s.t. for the system: perfluoroheptane–octane corresponds to a solubility parameter for the hydrocarbon greater than that calculated as the square root of the quotient of energy of vaporization and molar volume, the behavior being less ideal than predicted since the fluorocarbon has a parameter lower than that of the hydrocarbon.

Within the accuracy of this work, no evidence has been found for assumption of interpenetration in tin(IV) chloride; this is entirely in accord with the warning of Simons and Dunlap against consideration of interpenetration wholly on the basis of a geometric model. The data obtained correspond with the viewpoint that the unmodified regular solution theory is not applicable to binary mixtures containing a hydrocarbon, regardless of the nature of the second (non-hydrocarbon) component.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Molecular Addition Compounds of Titanium Tetrachloride with Several Ethers[1]

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The compounds $TiCl_4 \cdot O(CH_2CH_2)_2O$, $TiCl_4 \cdot C_5H_{10}O$, $TiCl_4 \cdot 2C_5H_{10}O$, $TiCl_4 \cdot C_4H_8O$, $TiCl_4 \cdot 2C_4H_8O$ and $TiCl_4 \cdot CH_3OC_6H_5$ have been prepared by the direct combination of titanium tetrachloride with the corresponding ether in carbon tetrachloride solution. These are yellow crystalline solids at room temperature. With diisopropyl ether the compound $TiCl_3(OCH(CH_3)_2)$ is obtained. Titanium tetrachloride splits trioxane to yield formaldehyde and perhaps polymethylene oxide polymers. Molecular weight determinations showed that the molecular formula of $TiCl_4 \cdot 2C_5H_{10}O$ is the same as the empirical formula.

During the past few years several papers have been published from this Laboratory[2-4] dealing with the reactions of carbon, silicon, germanium and tin tetrachlorides and tin tetrabromides and iodides with various ethers. The work reported in these papers indicates that the tetrachlorides of silicon and germanium are sterically incapable of accepting pairs of electrons from oxygen bases. This is apparently due to the small size of the silicon and germanium atoms relative to the size of the chlorine atom. Tin tetrachloride does not appear to be so sterically hindered, but when the chlorine atoms are replaced by the larger bromine atoms, or by the still larger iodine atoms, an increasing amount of steric interference is obtained.[4]

Titanium tetrachloride, in many ways, has properties similar to the tetrachlorides of the carbon–silicon–germanium family. It differs from these, however, in the fact that it has an electronic configuration of the "transitional" type. Furthermore, the atomic and ionic radii of titanium are intermediate between the corresponding values for germanium and tin. We were, therefore, interested in studying the reaction of titanium tetrachloride with a variety of ethers. Numerous addition compounds of titanium tetrachloride with organic nitrogen and sulfur bases, and with oxygen compounds such as alcohols, ketones and esters have been reported. However, the only ether addition compounds with titanium tetrachloride

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[1] Presented at the Atlantic City meeting of the American Chemical Society, September, 1952. Based upon the theses submitted by P. M. Hamilton, and R. McBeth for the M.S. and B.S. degrees, respectively.

[2] H. H. Sisler, W. Wilson, B. Gibbins, H. H. Batey, B. Pfahler and R. Mattair, THIS JOURNAL, **70**, 3818 (1948).

[3] H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, *ibid.*, **70**, 3821 (1948).

[4] H. H. Sisler, E. E. Schilling and W. O. Groves, *ibid.*, **73**, 426 (1951).

recorded in the literature are those with dimethyl, diethyl and di-*n*-butyl ethers, and the cyclic ether piperonal.

Experimental

Preparation of Materials.—Titanium tetrachloride obtained from the Fisher Scientific Company was purified by fractional distillation at atmospheric pressure using a five-foot column packed with glass helices, and protected from moisture by drying tubes filled with calcium chloride. The middle fraction boiling at 136°[5] was collected. The ethers were dried for several days over calcium chloride and distilled over sodium using another five-foot fractionation column under an atmosphere of dry nitrogen. In each case the constant boiling middle fraction was taken, stored over sodium wire, and a piece of iron wire added to retard peroxide formation. Trioxane obtained from the Heyden Chemical Corporation, melting at 61–62°,[6] was used without further purification.

Experimental Procedure.—Because of the vigorous reaction between titanium tetrachloride and some of the ethers, the reactions were carried out in carbon tetrachloride solution. One hundred ml. of carbon tetrachloride was first added to a 250-ml. reaction flask, through a side arm. Through an adjacent side arm dry nitrogen was passed into the flask to exclude moist air. A weighed portion of the reagent to be in excess was then added to the solvent by means of a Lunge pipet. After starting a magnetic stirrer, a weighed portion of the other reagent was added slowly from a Lunge pipet. Finally the flask was attached to a vacuum system consisting of two traps immersed in a Dry Ice freezing mixture and a vacuum pump. After turning off the dry nitrogen supply, the pressure was reduced until the solution just began to boil. When the solvent and excess reagent had been distilled off dry nitrogen was again admitted, the precipitate broken up, and another 25 ml. of the solvent added. This procedure was repeated twice in order to remove the excess titanium tetrachloride or ether. The product was stored in a closed container in a desiccator containing phosphorus pentoxide.

Essentially the same apparatus was used for thermal studies on several of the compounds. In these experiments the compounds were heated in the reaction flask, under a vacuum (0.1 mm.), by means of an oil-bath.

Method of Analysis.—The compounds were analyzed for chlorine by the Volhard method, the sample being weighed by difference into a glass stoppered erlenmeyer flask and hydrolyzed by adding distilled water. The titanium content was determined by adding a few drops of water to a weighed sample, drying slowly on a hot plate, igniting the sample at 1000° and weighing as TiO_2.

Reaction with Dioxane.—The compound $TiCl_4 \cdot O(CH_2CH_2)_2O$ is formed when titanium tetrachloride and dioxane are mixed regardless of which reagent is in excess. This compound appears to be the most stable of the compounds obtained in this study with respect to hydrolysis and thermal decomposition. It is a light yellow, crystalline substance which changes from a yellow to a white solid at 180° and is completely charred at 201°. It is insoluble in carbon tetrachloride, benzene, petroleum ether, dioxane and diethyl ether, but dissolves in acetone, yielding a light yellow colored solution which gradually turns red on standing. The compound did not show any evidence of decomposition after being stored for several months in a closed container.

Reaction with Tetrahydropyran.—In an excess of titanium tetrachloride, tetrahydropyran forms the yellow colored compound $TiCl_4 \cdot C_5H_{10}O$. At 124° this yellow solid changes to a black solid which liquefies at 125°. When tetrahydropyran is in excess the compound $TiCl_4 \cdot 2C_5H_{10}O$ is formed. This substance decomposes in a similar manner at 145–148°. The 1:1 compound has a slightly deeper yellow color and is less soluble in tetrahydropyran than is the 1:2 compound. Both addition compounds are insoluble in carbon tetrachloride, petroleum ether and diethyl ether, are slightly soluble in benzene, and are soluble in acetone imparting a yellow color to the solution. Neither compound showed evidence of decomposition after standing for several months in closed containers.

Reaction with Tetrahydrofuran.—The compound $TiCl_4 \cdot C_4H_8O$, which forms when tetrahydrofuran is added to an excess of titanium tetrachloride, decomposes at 138–139°. The compound $TiCl_4 \cdot 2C_4H_8O$ which forms in an excess of tetrahydrofuran changes from a yellow solid to a black liquid at 122–124°. As is the case with the tetrahydropyran compounds, the 1:1 compound has a slightly deeper yellow color than does the 1:2 compound. The solubilities and stabilities of the tetrahydrofuran compounds resemble those of the compounds formed with tetrahydropyran.

Reaction with Anisole.—In the reaction of anisole and titanium tetrachloride only the 1:1 compound $TiCl_4 \cdot CH_3OC_6H_5$ was isolated. This substance is formed in an excess of titanium tetrachloride. The freshly prepared orange colored compound melts at 44–45°, probably with decomposition. It is noticeably soluble in carbon tetrachloride, petroleum ether, anisole and benzene to give light orange colored solutions. The compound gradually decomposes upon standing in a sealed container, changing from an orange color to a blood red color with some sublimation to the upper part of the container. No definite compound could be formulated from the titanium and chlorine analysis of the residue. Several attempts were made to prepare an addition compound in an excess of anisole both at room temperature and lower temperatures. However, in every case, it was impossible to obtain a completely solid precipitate at room temperature.

Reaction with Diisopropyl Ether.—Several attempts were made to prepare an addition compound with diisopropyl ether, but without success. In each case an analysis of the light yellow precipitate obtained indicated that a substitution compound, namely, $TiCl_3(OCH(CH_3)_2)$ (calcd., Cl, 49.8; Ti, 22.4; found, Cl, 48.8; Ti, 22.4) had been formed. This substance changes from a light yellow solid to a white solid at 84–89° and finally chars at 96°. It gradually decomposes upon standing in a sealed container, changing from light yellow to brown in color over a period of a few weeks. No simple formula could be derived from the chlorine and titanium analysis of the residue.

Reaction with Trioxane.—When titanium tetrachloride is added to a solution of trioxane a white precipitate is formed which has a strong odor of formaldehyde. The chlorine analyses obtained for various experiments vary from 21 to 46%. It is believed that titanium tetrachloride splits the trioxane ring yielding formaldehyde and, perhaps, polymethylene oxide polymers.

Thermal Decomposition.—When the compounds $TiCl_4 \cdot 2C_4H_8O$ and $TiCl_4 \cdot 2C_5H_{10}O$ were heated under a vacuum, analysis of the sublimate obtained indicated that some decomposition of the original product had occurred. When the compound $TiCl_4 \cdot C_4H_8O$ was heated in a similar manner the yellow solid melted to form a dark liquid and finally a black tar. However, the compound $TiCl_4 \cdot 2C_5H_{10}O$ (calcd., Cl, 39.2; Ti, 13.2; found, Cl, 39.5; Ti, 13.1) collected on the upper walls of the container when the compound $TiCl_4 \cdot C_5H_{10}O$ was heated under a vacuum. A sample of the liquid in the trap boiled at 136° and fumed when exposed to air. This indicated that the liquid in the trap was titanium tetrachloride, and that the reaction $2TiCl_4 \cdot C_5H_{10}O \rightarrow TiCl_4 \cdot 2C_5H_{10}O + TiCl_4$ had occurred.

Results.—The new compounds prepared are listed with their analyses in Table I.

TABLE I

Compound	Yield, %	Cl, % Calcd.	Cl, % Found[b]	Ti, % Calcd.	Ti, % Found[b]
$TiCl_4 \cdot O(CH_2CH_2)_2O$	97.6	51.0	50.5	17.2	17.1
$TiCl_4 \cdot C_5H_{10}O$	100	51.3	51.4	17.4	17.5
$TiCl_4 \cdot 2C_5H_{10}O$	99.3	39.2	39.4	13.2	13.6
$TiCl_4 \cdot C_4H_8O$	97.5	54.2	54.6	18.3	18.2
$TiCl_4 \cdot 2C_4H_8O$	98.3	42.6	41.9	14.3	14.3
$TiCl_4 \cdot CH_3OC_6H_5$	86.0[a]	47.6	48.2	16.1	16.1

[a] Some of the product distilled over into trap. [b] Average results.

Molecular Weight Determinations.—In order to obtain information concerning the molecular formulas of these addition compounds, cryoscopic measurements on solutions of one of them, $TiCl_4 \cdot 2C_5H_{10}O$, in benzene were carried out. A freezing point cell which was completely isolated from the atmosphere and provided with continuous stirring was used

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(5) J. Barksdale, "Titanium: Occurrence, Chemistry and Technology," The Roland Press Co., New York, N. Y., 1949, p. 78.

(6) Walker and Carlisle, *Chem. Eng. News*, **21**, 1250 (1943).

and temperatures for the freezing point curves were measured by means of a G-2 Mueller bridge and a platinum resistance thermometer. In each case, the freezing point cell was first charged with carefully purified benzene, the freezing point determined, a sample of the addition compound added, the mixture stirred until complete solution had been obtained, and the freezing point of the solution determined. An atmosphere of dry nitrogen was maintained in the cell at all times. Results of a series of four determinations in the concentration range of 0.0168 to 0.0375 *m* gave values of 313, 320, 324 and 355 for the molecular weight. Since the theoretical value for the formula $TiCl_4 \cdot 2C_5H_{10}O$ is 314.09, these results indicate that this is the molecular formula for the compound.

Discussion and Conclusions

The addition compounds of titanium tetrachloride with the ethers studied appear to have decreasing stabilities in the order: dioxane > (tetrahydrofuran, tetrahydropyran) > anisole > diisopropyl ether. Titanium tetrachloride reacts vigorously with these ethers to form crystalline solids which hydrolyze rapidly at room temperature. Though it is possible that an addition compound is first formed with diisopropyl ether, only the substitution product $TiCl_3(OCH(CH_3)_2)$ was isolated. Both this compound and the addition compound $TiCl_4 \cdot CH_3OC_6H_5$ gradually decompose at room temperature. At higher temperatures the compound $TiCl_4 \cdot C_5H_{10}O$ breaks down to yield the compound $TiCl_4 \cdot 2C_5H_{10}O$ and titanium tetrachloride. Failure of the compound $TiCl_4 \cdot C_4H_8O$ to react in a similar manner can possibly be attributed to the lower decomposition temperature of the compound $TiCl_4 \cdot 2C_4H_8O$. However, it is difficult to explain the apparent reversals of the decomposition temperatures of the tetrahydrofuran and tetrahydropyran addition compounds.

The fact, demonstrated by this research, that titanium tetrachloride forms stable addition compounds with a variety of ethers whereas germanium tetrachloride does not, is undoubtedly at least partially the result of the somewhat larger size of the titanium atom. However, it is quite likely that the "transitional" character of the electronic configuration of the titanium atom which enables it to form very stable octahedral orbitals (d^2sp^3 type) also contributes to this phenomenon; *i.e.*, the very strong bond forming character of d^2sp^3 orbitals may promote bond formation in spite of a certain amount of steric interference.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Ion Exchanger Electrodes

BY GEORGE SCATCHARD

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The equations for the electromotive force of ion exchanger electrodes are developed from the general equation for the electromotive force of a cell with transference. The most important difference from earlier results is in the effect of the transfer of water or other solvent, which gives the largest of the deviations from ideal electrode behavior. The discussion includes also: hydrolysis, the transition layers between membrane and solutions, diffusion, hydrolytic diffusion and biionic potentials.

The electromotive force of a galvanic cell containing a membrane with a fixed ionic charge was calculated independently by Teorell[1] and by Meyer and Sievers[2] for membranes in which the ions behave as ideal solutes and through which no water or other non-electrolyte is transferred by the electrical current. Neither of these conditions is satisfied in a high capacity ion exchanger. The differential equation for the electromotive force at such a membrane[3] may be obtained from the general thermodynamic equation for the electromotive force of a voltaic cell with the assumption that the laws of reversible thermodynamics apply in terms of the instantaneous values of the concentrations and activities, even though these values are changing due to the irreversible process of diffusion. This assumption is common to all thermodynamic treatments of voltaic cells, and will be made here without discussion. The integrated equation requires the assumption that the changes in activity in the transition layers between membranes and solutions are negligible relative to the changes within the membrane. This assumption will be discussed later.

Voltaic Cells in General.—The electromotive force, E, of a voltaic cell may be expressed as

$$E\mathfrak{F}/RT = E_{0\alpha}\mathfrak{F}/RT - \Sigma_i \nu_{i\alpha} \ln a_{i\alpha} - \int_{\alpha}^{\omega} \Sigma_i t_i \mathrm{d} \ln a_i - \Sigma_i \nu_{i\omega} \ln a_i - E_{0\omega}\mathfrak{F}/RT \qquad (1)$$

in which $\mathfrak{F}$ is the faraday, R and T have their usual significance, $E_{0\alpha}$ and $E_{0\omega}$ are the standard potentials of the two electrodes, $\nu_{i\alpha}$ and $\nu_{i\omega}$ are the numbers of moles of species i formed at the respective electrodes when one faraday of electricity goes through the cell from left to right, t_i is the number of moles of species i transferred in the direction of positive current for one faraday,[4] and a_i is the activity of species i. The transference number of an anion is therefore negative. It is also convenient to take the mobility, u_i, and the valence, z_i, as negative for an anion. The fraction of the current carried by the species i, its transport number, T_i, is $t_i z_i$, which is positive. The transference num-

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[1] T. Teorell, *Proc. Soc. Exp. Biol. Med.*, **33**, 382 (1935); *Proc. Nat. Acad. Sci. Wash.*, **21**, 152 (1935); *J. Biol. Chem.*, **113**, 735 (1936).

[2] K. H. Meyer and J. V. Sievers, *Helv. Chem. Acta*, **19**, 649 (1936).

[3] Although the electromotive force can be measured only for the whole cell, the associated change of state can be located, and it is sometimes convenient to talk of the electromotive force of a part of the cell in this sense, even though it involves single ion activities which cannot be determined.

[4] G. Scatchard in Cohn and Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943.