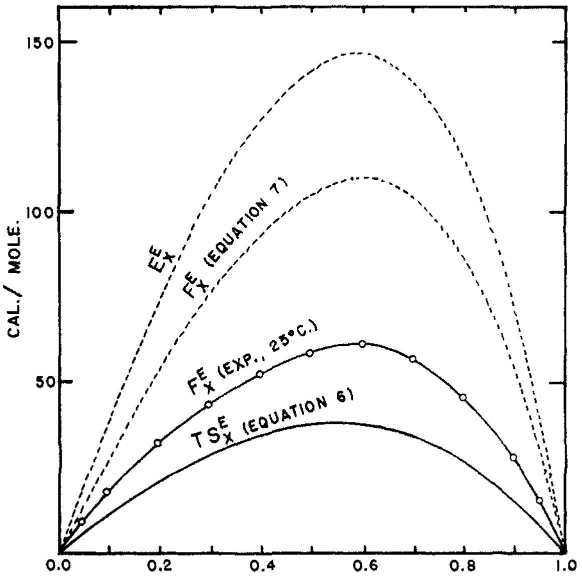

Fig. 4.—Excess thermodynamic functions.

In many systems, for example: benzene–cyclohexane, benzene–carbon tetrachloride, cyclohexane–carbon tetrachloride[27,29] and others, the observed values of $E^{\mathrm{E}}_{\mathrm{X}}$ are greater than those predicted from equation (10). Until recently the opinion had been held[30] that $E^{\mathrm{E}}_{\mathrm{X}}$, calculated from equation (10) in the manner mentioned above, constituted the minimum value which one might expect to find. If observed values smaller than those expected from the theory had been found they would have been explained as due to "chemical combination" of the two components. Such an explanation seems unreasonable in the case of the system discussed in this paper.

Recently, Gjaldbaek and Hildebrand[8] have found that nitrogen is more soluble in fluorocarbons than one would expect from the theory expressed in equation (4). They have interpreted this high solubility to result from the entropy of mixing of molecules of different sizes rather than from "chemical combination" of solute with solvent. Their work, together with that of Benesi and Hildebrand[6] and that reported in this paper, shows clearly that the Flory–Huggins[12,13] kind of entropy of mixing should be considered when one interprets the behavior of a system of substances whose molar volumes differ greatly.

Acknowledgments.—This work was done under contract with the Office of Naval Research. The authors wish to express their appreciation to Professor J. H. Hildebrand of the University of California for his helpful suggestions.

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(29) G. Scatchard, S. E. Wood and J. M. Mochel, *Trans. Faraday Soc.*, **35**, 993 (1939).

(30) J. H. Hildebrand, "Solubility of Non-electrolytes," 2nd ed., A. C. S. Monograph Series 17, Reinhold Publishing Corp., New York, N. Y., 1936, p. 73.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

The Liquid–Vapor Equilibrium of the System Tungsten Hexafluoride–Perfluorocycyclopentane[1]

BY GILSON H. ROHRBACK AND GEORGE H. CADY[2]

The liquid–vapor equilibrium of the system tungsten hexafluoride–perfluorocyclopentane has been studied at 25° and at 45°. This system, like that described in the preceding paper is more nearly ideal than one would predict from the solubility theory expressed in equation (4). The deviation from that theory can be largely attributed to a greater than ideal entropy of mixing caused by the difference in size of molecules of the two components.

In a previous paper, Barber and Cady[3] have given reasons for being interested in liquid–vapor equilibria of systems of volatile fluorides and have reported the results of a study for the system tungsten hexafluoride–perfluoro-*n*-pentane. The present paper describes a similar system which has been studied over a wider temperature range and interpreted somewhat more fully.

Experimental

The apparatus and experimental method used in this research were the same as those employed by Barber and Cady.[3] Both of the fluorides were available as the result of earlier work.[3,4]

The liquid–vapor equilibrium data are recorded in Table I. The total pressure is given; X_1 is the mole per cent. of tungsten hexafluoride in the liquid; Y_1 is the mole per cent. of tungsten hexafluoride in the vapor. The data at 25° are represented in Fig. 1.

TABLE I

LIQUID–VAPOR EQUILIBRIUM, WF_6–CYCLO-C_5F_{10}

At 25°			At 45°		
Press., mm. at 0°	X_1 mole %	Y_1 mole %	Pressure, mm. at 0°	X_1 mole %	Y_1 mole %
1019.4	100.0	100.0	1982.4	100.0	100.0
1030.3	93.9	93.2	1998.0	94.4	93.9
1035.0	89.6	88.9	2000.5	93.7	...
1034.4	82.4	82.6	2008.8	89.7	89.5
1030.7	75.1	75.8	2009.0	...	83.1
1004.4	52.5	57.6	2010.3	82.6	82.7
978.1	40.0	45.5	2004.4	75.2	76.6
944.3	25.9	34.3	1967.1	57.3	60.6
919.2	17.9	25.5	1899.1	40.5	44.6
896.9	11.7	18.0	1834.9	26.2	33.0
833.4	0.0	0.0	1788.3	17.9	23.9
			1757.8	12.9	17.5
			1642.3	0.0	0.0

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(1) Presented on September 20, 1949, at the Meeting of the American Chemical Society in Atlantic City, New Jersey.

(2) Senior Author.

(3) E. J. Barber and G. H. Cady, THIS JOURNAL, **73**, 4247 (1951).

(4) E. J. Barber, L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4241 (1951).

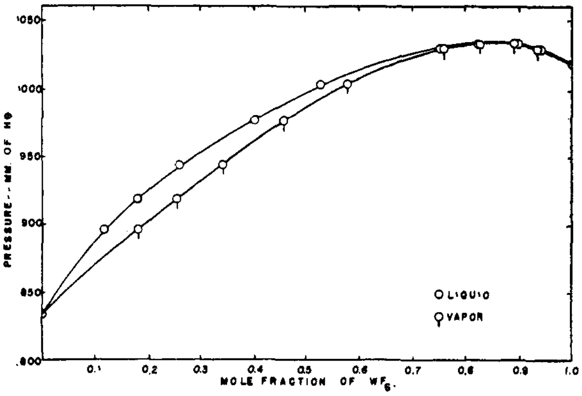

Fig. 1.—Pressure *vs.* composition at 25°.

Discussion

The data for this system have been used to make calculations like those described by Barber and Cady.[3] Their equation numbers are used in this paper.

Activity coefficients calculated from equation (1) using values taken from smoothed curves drawn through plots of X_1 *vs.* Y_1 data are represented in Fig. 2. These may be compared in the same figure with theoretical activity coefficients calculated from equation (4) and also from equation (7) for a temperature of 25°.[5] It is apparent that this system, like the system tungsten hexafluoride–perfluoro-*n*-pentane, is more nearly ideal than would be predicted from either of the theoretical equations. However, the fact that equation (7) gives better agreement with experiment than equation (4) constitutes additional evidence that the excess entropy of mixing resulting from the differences in sizes of molecules of the components is an important factor to be considered in theories of solutions.

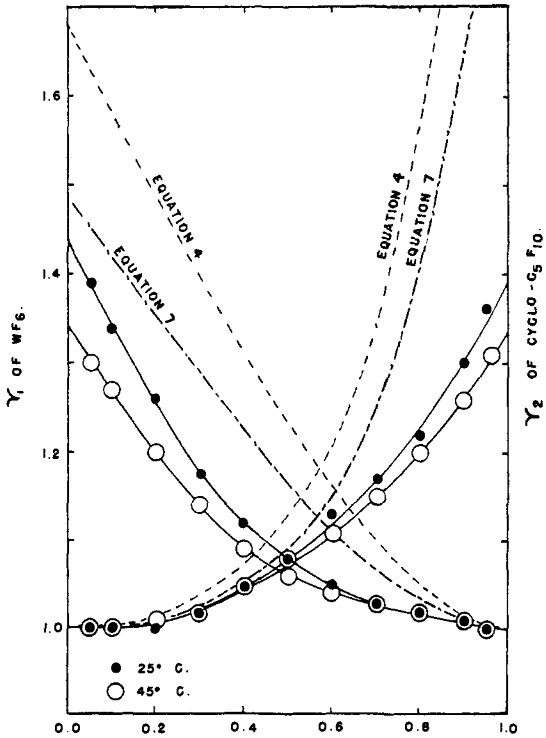

Fig. 2.—Activity coefficients.

Several thermodynamic properties of the system at 25° are plotted in Fig. 3. These are: (1) F^E, the experimental free energy in excess of that for an ideal system per total mole of mixture, (2) H^E, the heat content in excess of that for an ideal system (this quantity was determined from the temperature dependence of the experimental activity coefficients), (3) TS^E, a quantity obtained by subtracting F^E from H^E, (4) TS^E (theoretical) a quantity calculated from equation (6) as given in the paper of Barber and Cady,[3] (5) H^E (theoretical), a quantity assumed to be equal to E^E (theoretical). H^E is equal to E^E if there is no change in volume upon mixing the two components. In the case of this system the change in volume must be small, for a mixture in which the mole fraction of WF_6 was 0.752 had a density of 2.78 g./cc. at 25°. With no volume change the density should have been 2.75 g./cc. For explanation of the method used to calculate E^E refer to equation (10).[3]

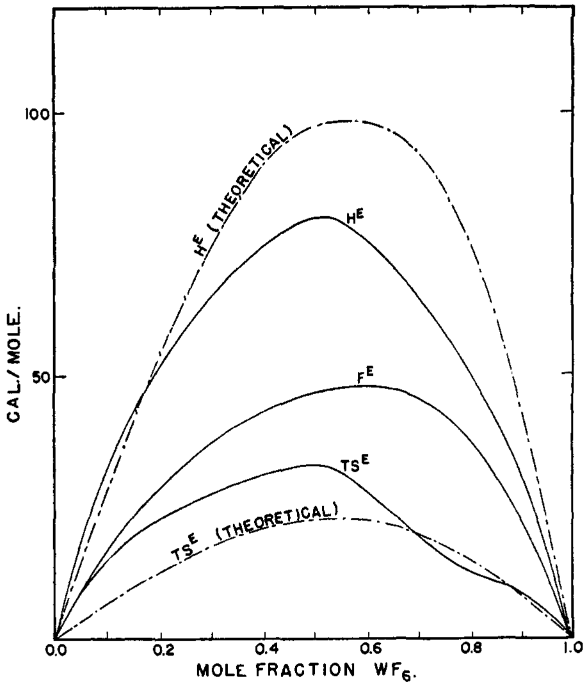

Fig. 3.—Excess thermodynamic functions.

While the agreement between experiment and theory in the case of this system is not perfect, it is nevertheless to be regarded as unusually good. It appears desirable that other systems of volatile fluorides be studied in order that further evidence regarding the effect of molecular size (and perhaps shape) may be obtained.

Acknowledgment.—This work was done under contract with the office of Naval Research, U. S. Navy Department.

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[5] When making these calculations the following data were used:

Substance	ΔE vaporization, cal.	Density, g./cc.
Cyclo-C_5F_{10}	5695	1.6292
WF_6	5575	3.386