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

The Liquid–Vapor Equilibrium of the System Tungsten Hexafluoride–Perfluoro–*n*-Pentane

BY E. J. BARBER AND G. H. CADY[1]

The system tungsten hexafluoride–perfluoro-*n*-pentane has been studied under conditions of a constant temperature of 25° and also under conditions of a constant pressure of 1.5 atmospheres. A positive deviation from Raoult's law was found, the system forming a minimum boiling mixture containing about 93 mole per cent. tungsten hexafluoride. The maximum observed excess free energy of mixing was about 60 cal./mole, obtained at 0.6 mole fraction tungsten hexafluoride. The solutions were not strictly "regular," and they were more nearly ideal than one would predict from the solubility theory developed by Hildebrand and Wood[2] and by Scatchard.[3] Consideration of the effect of the difference between molecular volumes of the components upon the entropy of mixing improved the agreement between the theoretical and experimental values but did not completely remove the discrepancy.

Grosse and Cady[4] have pointed out in a qualitative way the poor solvent properties of fluorocarbons, but have given few quantitative data and no theoretical treatments. Recently Scott,[5] and Hildebrand and co-workers[6–10] have presented data on the solubilities of several materials in fluorocarbons and have indicated the possible application of solubility theory developed for non-polar substances[2,3] to such systems. In a study of the liquid–vapor equilibrium of the system, *n*-pentane–perfluoro-*n*-pentane, Simons and Dunlap[11] found strong positive deviation from the simple theory, even after application of the corrections for the difference between the partial molar volumes and the molar volumes of the pure substances and for the change in entropy on mixing introduced by the unequal molar volumes.[12,13] This deviation they have ascribed to the properties of the hydrocarbon.

In this paper and the next, consideration is given to systems of another kind. Many of the remarkable properties of fluorocarbons including their poor solvent powers result from the low intermolecular forces which accompany the very low polarizability of the peripheral fluorine atoms.[14] For example, the volatility of a fluorocarbon is only slightly less than one would expect to find for a rare gas of the same molecular weight.[15] Another class of substances exhibiting very similar behavior for the same reason is the volatile metal fluorides exemplified by tungsten hexafluoride, molybdenum hexafluoride and osmium octafluoride. If one of these substances were mixed with a fluorocarbon, the solution formed might intuitively be expected to be nearly ideal. A different prediction is reached, however, when one applies the solubility theory which takes into account the energy of vaporization per milliliter of each component. Since this quantity is considerably larger for a volatile metal fluoride than for a fluorocarbon, the theory predicts that a system of two such substances should be far from ideal. These conflicting predictions suggest the desirability of studying systems of this kind.

Experimental

Preparation of Compounds.—Perfluoro-*n*-pentane was prepared and purified as described in the previous paper.[16] Tungsten hexafluoride was prepared in a Monel metal system from pure powdered tungsten and elementary fluorine under the conditions recommended by Ruff, *et al.*[17,18] The compound was freed from tungsten oxyfluoride (WOF_4) and hydrogen fluoride by triple vacuum distillation over anhydrous potassium fluoride.

Apparatus.—An all metal equilibrium still patterned after the high pressure still of Othmer and Morley[19] was used for this research.[20] Several different mixtures of the two components were allowed to come to equilibrium; then samples of the liquid and vapor were taken for analysis.

Analysis of Samples.—The method of analysis was based upon the following properties of the two components: (1) tungsten hexafluoride and perfluoro-*n*-pentane are volatile and can be transferred quantitatively from one vessel to another by distillation; (2) tungsten hexafluoride is hydrolyzed completely by a saturated solution of potassium hydroxide while the fluorocarbon remains unchanged.

To make an analysis the apparatus shown in Fig. 1 was evacuated and weighed. The sample was then condensed in bulb C by liquid air, held in cup B. Later the sample was admitted to cham-

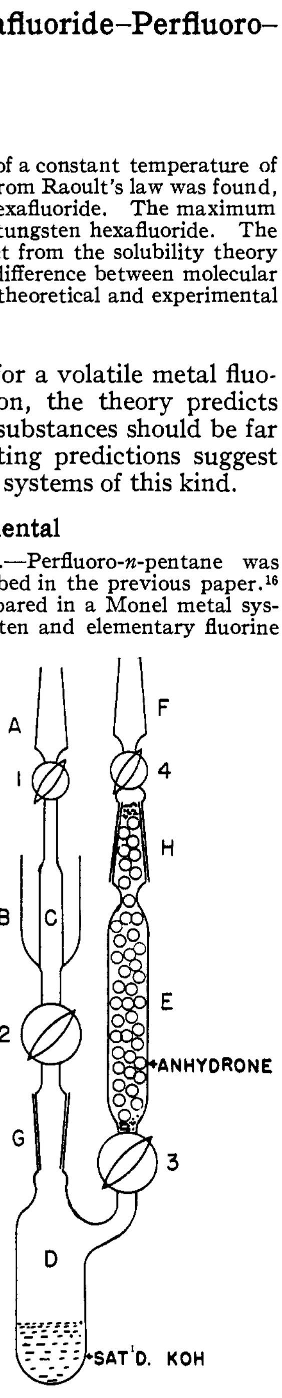

Fig. 1.—Analytical apparatus.

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[1] Senior author.

[2] J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

[3] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931).

[4] A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 369 (1947).

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[6] H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 3978 (1948).

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[9] J. Chr. Gjaldbaek and J. H. Hildebrand, *ibid.*, **72**, 609 (1950).

[10] J. H. Hildebrand, H. A. Benesi and L. M. Mower, *ibid.*, **72**, 1017 (1950).

[11] J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

[12] P. J. Flory, *ibid.*, **9**, 660 (1941); **10**, 51 (1942); **13**, 453 (1945).

[13] M. L. Huggins, *ibid.*, **9**, 440 (1941); *J. Phys. Chem.*, **46**, 151 (1942).

[14] G. H. Rohrback and G. H. Cady, THIS JOURNAL, **71**, 1938 (1949).

[15] J. H. Simons and L. Block, *ibid.*, **61**, 2962 (1939).

[16] E. J. Barber, L. L. Burger and G. H. Cady, *ibid.*, **73**, 4241 (1951).

[17] O. Ruff and F. Eisner, *Ber.*, **38**, 742 (1905).

[18] O. Ruff, F. Eisner and W. Heller, *Z. anorg. Chem.*, **52**, 256 (1907).

[19] D. F. Othmer and F. R. Morley, *Ind. Eng. Chem.*, **38**, 751 (1946).

[20] For a complete description of the still and its method of operation order Document 3253 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D .C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.20 for photocopies (6 × 8 inches) readable without optical aid.

ber D where the tungsten hexafluoride reacted with potassium hydroxide solution. After weighing the apparatus, the fluorocarbon was pumped away through tube E where water vapor was absorbed by "Anhydrone." The system was again weighed and the three weighings were used to obtain the amounts of tungsten hexafluoride and perfluoro-*n*-pentane in the original sample. Using samples weighing about 1 g. the method was found to give reproducible analyses. For example, a sample made up to contain 5% *n*-C_5F_{12} was found to contain 5.07, 5.06, 5.08, 5.05 and 5.06% *n*-C_5F_{12}.

Results.—Equilibrium studies were made under two sets of conditions: (1) when the system was at 25°, (2) when the total pressure of the vapor phase was 1140 mm. The data are presented in Table I and some of them are represented in Fig. 2.

TABLE I

LIQUID-VAPOR EQUILIBRIA OF THE SYSTEM WF_6-*n*-C_5F_{12}

At 25°			At 1140 mm. (0°) pressure		
Total pressure, mm. (0°)	Y_1	X_1	Temp., °C.	Y_1	X_1
1019.4	1.000	1.000	28.15	1.000	1.000
1021.3	0.946	0.948	28.11	0.946	0.947
1020.9	.903	.896	28.11	.947	.948
1012.9	.837	.818	28.14	.898	.891
1013.9	.841	.816	28.33	.838	.818
950.5	.681	.614	30.22	.662	.578
909.4	...	.476	31.52	.594	.477
902.2	.603	.458	31.74	...	.460
852.1	.487	.342	33.48	...	.355
842.6	.478	.332	33.77	.472	.320
790.4	.346	.222	35.54	...	.226
778.5	.325	.197	35.71	...	.220
706.8	.168	.093	36.01	.342	.218
709.6	.188	...	38.66	.153	.092
646.5	.000	.000	40.86	.000	.000

In this table and in calculations made from the data, the following conventions have been adopted: (1) The subscript 1 refers to the more volatile product, tungsten hexafluoride. (2) X_i and Y_i refer to the mole fraction of the i^{th} component in the liquid and vapor phases, respectively. (3) P is the total pressure on the system. (4) P_i^0 refers to the vapor pressure of the i^{th} component in the standard state which is taken to be that of the pure liquid at the temperature of the measurement. (5) γ_i is the activity coefficient of the i^{th} component.

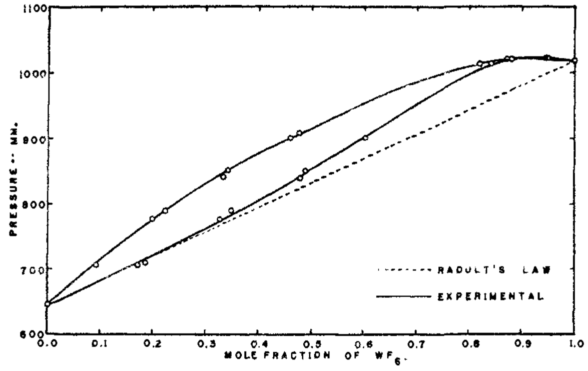

Fig. 2.—Pressure *vs.* composition at 25°.

The activity coefficients were calculated using the relationship

$$\gamma_i = \frac{Y_i P}{X_i P_i^0} \tag{1}$$

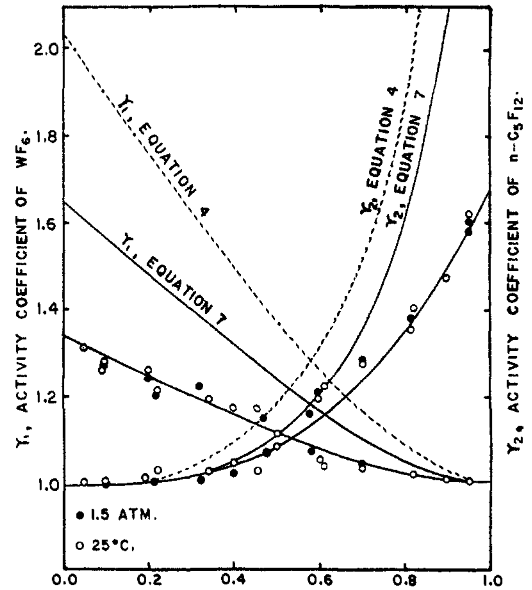

Fig. 3.—Activity coefficients.

and the assumption that the vapors behave as ideal gases. Values so obtained are shown in Fig. 3. Solid lines in this figure drawn through the points for the activity coefficients of the two components satisfy the Gibbs–Duhem relationship

$$X_1\left(\frac{\partial \ln \gamma_1}{\partial X_1}\right)_{P,T} = X_2\left(\frac{\partial \ln \gamma_2}{\partial X_2}\right)_{P,T} \tag{2}$$

which may be more easily applied in the form

$$\frac{X_1}{\gamma_1}\left(\frac{\partial \gamma_1}{X_1}\right)_{P,T} = \frac{X_2}{\gamma_2}\left(\frac{\partial \gamma_2}{\partial X_2}\right)_{P,T} \tag{3}$$

Discussion

Tungsten hexafluoride mixes in all proportions with perfluoro-*n*-pentane forming solutions which differ appreciably from ideal behavior. A comparison of the actual nature of the system with that predicted by theory is of interest. In the presentation of the discussion the differences between actual and ideal thermodynamic properties of the system are termed "excess thermodynamic properties" and after the manner of Scatchard[21] are designated by a superscript E.

The theory easiest to apply is expressed in an equation derived independently by Scatchard[3] and Hildebrand and Wood[2] giving the activity coefficients of a binary mixture in terms of the molal volumes, volume fractions, and energies of vaporization per milliliter as

$$RT \ln \gamma_1 = V_1\phi_2^2\left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2 \tag{4}$$

γ_1 is the activity coefficient of component 1, V_1 and V_2 are the molar volumes of the components, ϕ_2 is the volume fraction of component 2, ΔE_1 and ΔE_2 are the molar energies of vaporization at temperature T for components 1 and 2, and $\Delta E_1/V_1$ (which is a measure of the intermolecular force field of component 1) is the "cohesive energy density" or the "internal pressure."

A similar equation holds for component 2.

No high degree of accuracy is claimed for the re-

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(21) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

lationship, but it is generally recognized as the best existing simple theory of the solubility of non-electrolytes. Actually equation (4) was originally derived as an expression for the partial molar excess energy of mixing, the direct substitution of $RT \ln \gamma_1$ being possible on the basis of the assumptions: (1) that the partial molar volumes were equal to the molar volumes, and (2) that the partial molal excess entropy of mixing was zero.

The energies of vaporization at 25° of tungsten hexafluoride and perfluoro-*n*-pentane were estimated by means of the Clapeyron equation using the vapor pressure curves and the liquid and vapor densities[22] to be 5575 and 5985 calories per mole, respectively.

The vapor density of n-C_5F_{12} was estimated from a generalized equation for the perfluoropentanes[22], $PV = RT(1 - 0.01848\ P)$, and that of tungsten hexafluoride from the data of Ruff, Eisner and Heller.[18] The liquid density of n-C_5F_{12} was estimated from data of Burger and Cady,[23] to be 1.6035 g./cc., while a value of 3.386 g./cc. for WF_6 at 25° was obtained by extrapolation of the data of Ruff and Ascher.[24] An article reporting vapor pressures of the pure fluorides is being prepared by the authors. The theoretical activity coefficients calculated at 25° by means of equation (4) are compared with the experimental values in Fig. 3. Obviously the system approaches ideality to a greater extent than is indicated by the theoretical activity coefficients calculated in this way. Thus the deviation found is in the direction anticipated by virtue of the similarity of the molecules, but the system is definitely not ideal.

To find out whether the solutions were "regular," *e.g.*, having entropies of mixing equal to those of ideal solutions, plots of $RT \ln \gamma_1/V_1$ and $RT \ln \gamma_2/V_2$ *versus* ϕ_2^2 and ϕ_1^2, respectively, were made. With this plot a regular system would yield two coincident straight lines with slope $[(\Delta E_1/V_1)^{1/2} - (\Delta E_2{}^{1/2}/V_2]^2$. Actually two slightly curved lines deviating almost symmetrically about a straight line were obtained, indicating that the system deviated somewhat from "regular" behavior.

A correction to equation (4) for deviations from "regularity" may be made by considering it to be, as originally derived, an expression for the partial molar excess energy of mixing and making a correction derived independently by Flory[12] and Huggins[13] for the partial molar excess entropy of mixing for binary mixtures having unequal molar volumes. Although these treatments were made specifically for solutions of a long chain polymer, Hildebrand[25] later obtained the same results from a generalized treatment by making certain simplifying assumptions which were equivalent to those used by Flory and Huggins. These equations for the partial molar excess entropy of mixing, $\bar{S}_2^E$, and total molar excess entropy of mixing, S_X^E, are

$$\bar{S}_1^E = -R\left[\ln \frac{\phi_1}{X_1} - \phi_2\left(\frac{V_1}{V_2} - 1\right)\right] \qquad (5)$$

$$S_X^E = -R\left[X_1 \ln \frac{\phi_1}{X_1} + X_2 \ln \frac{\phi_2}{X_2}\right] \qquad (6)$$

where X_1 and X_2 are the mole fractions of component 1 and component 2, respectively.

Assuming that there is no change in volume on mixing and incorporating equation (5) above, equation (4) may be written

$$RT \ln \gamma_1 = V_1\,\phi_2^2\left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2 + RT\left[\ln \frac{\phi_1}{X_1} - \phi_2\left(\frac{V_1}{V_2} - 1\right)\right] \qquad (7)$$

A corresponding equation holds for component 2. The activity coefficients calculated from equation (7) are shown as a solid line in Fig. 3 labeled γ, equation 7. Although this is an improvement, the actual system is still somewhat more ideal than equation (7) predicts.

Further comparisons were made between the thermodynamic properties of the system and those of an ideal solution. The excess partial molar free energy of component i is given by the expression

$$\bar{U}_i^E = RT \ln \gamma_i \qquad (8)$$

and the total excess free energy per one total mole for a binary mixture is

$$F_X^E = X_1\bar{U}_1^E + X_2\bar{U}_2^E \qquad (9)$$

The experimental total excess free energy at 25°, calculated employing equations (8) and (9) and the smoothed experimental values of the activity coefficient obtained from the curves in Fig. 3 is shown in Fig. 4. The curve for the values thus obtained is labeled F_X^E exp. 25°.

Using the Flory–Huggins equation (6), and the assumption that there is no change in volume on mixing, the quantity TS_X^E at 25° may be evaluated. This is plotted in Fig. 4 and labeled TS_X^E eq. (6).

Now Scatchard has demonstrated theoretically[21] and practically[26,27] that the experimental excess free energy of mixing, F_X^E, measured at constant pressure is not significantly different from A_X^E, the excess work function. This means that the excess free energy of mixing may be calculated as the difference between the excess energy of mixing and the quantity TS_X^E.[28] This is shown as a dashed line labeled F_X^E in Fig. 4. The value of the excess free energy of mixing so obtained is about twice the experimental value calculated using equations (8) and (9).

The dotted line labeled E_X^E represents the excess energy of mixing of one total mole calculated using equation (10) or the excess free energy of mixing of one total mole calculated using equations (4) and (8).

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(22) E. J. Barber, Thesis, University of Washington, 1948.

(23) L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1951).

(24) O. Ruff and E. Ascher, *Z. anorg. allgem. Chem.*, **196**, 413 (1931).

(25) J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947).

(26) G. Scatchard and C. L. Raymond, THIS JOURNAL, **60**, 1278 (1938).

(27) G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939).

(28) The theoretical expression for the partial molar excess energy of mixing is

$$\bar{E}_1^E = V_1\,\phi_1^2\left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2 \qquad (10)$$

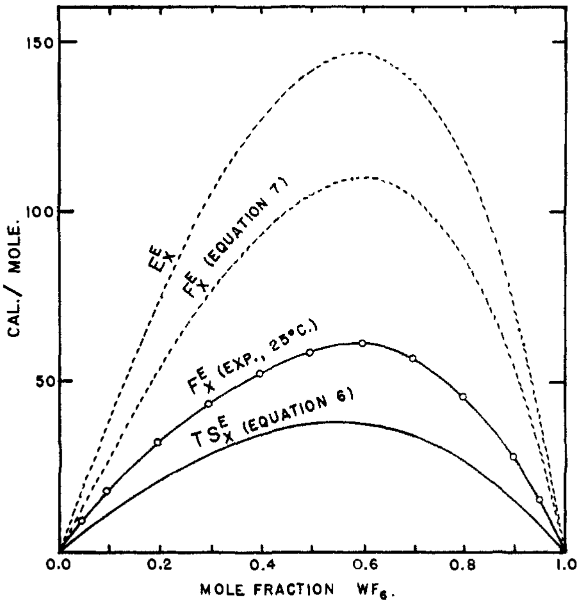

Fig. 4.—Excess thermodynamic functions.

In many systems, for example: benzene–cyclohexane, benzene–carbon tetrachloride, cyclohexane–carbon tetrachloride[27,29] and others, the observed values of E^E_X are greater than those predicted from equation (10). Until recently the opinion had been held[30] that E^E_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.

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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.

[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]

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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).