[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Liquid–Vapor Equilibrium for the System: Perfluoro-*n*-hexane–*n*-Hexane[1]

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The total vapor pressure curves and the compositions of the equilibrated liquid and vapor phases were determined over the whole range of composition at 25, 35 and 45° for the system perfluoro-*n*-hexane–*n*-hexane. Three-parameter analytical expressions of the Guggenheim–Scatchard form were obtained for the excess thermodynamic functions. The values of the excess functions at 35° and $x = {}^1/_2$ are $F^E = 318$ cal. mole^{-1}, $H^E = 567$ cal. mole^{-1} and $S^E = 0.8$ e.u. The excess entropy can be accounted for reasonably well by considering the large volume expansion of 5.4 cm.^{3} mole^{-1} associated with this system. The shape and magnitude of the free energy functions are compared with those obtained for fluorocarbon–hydrocarbon systems previously studied and with the predictions of regular solution theory.

Introduction

Solutions of fluorocarbon and hydrocarbon liquids previously studied have large positive deviations from Raoult's law. Large volume and energy changes accompany mixing and the mutual solubilities are much lower than those predicted by the Hildebrand–Scatchard theory of regular solutions.[2] Scott,[3] in a recent review article, has assembled all of the available experimental data on these systems and has reviewed critically the various attempts to explain their anomalous behavior. The mutual solubility curve and the volume changes on mixing for the perfluoro-*n*-hexane–*n*-hexane system have been previously reported.[4] The present study of the liquid–vapor equilibrium is a continuation of our investigation of the detailed shapes of the excess thermodynamic functions near and above the critical solution temperature.

Experimental

Materials.—The *n*-hexane was Phillips Petroleum Company Pure Grade (99 mole %). The perfluoro-*n*-hexane was obtained through the courtesy of the Minnesota Mining and Manufacturing Company, refined by fractional crystallization and found to be 99.98 mole % pure by analysis of the freezing curve. The purification and physical properties of the materials used have been described.[4,5]

Equilibrator.—The equilibrator consisted of a copper vessel, 3 cm. in dia. by 15 cm. long, to contain the liquid, a 1-liter vapor space which could be isolated from the liquid by closing Hoke #462 stainless steel toggle valves, and an automatic vapor pump to circulate the vapor through the liquid. The copper vessel was immersed in a water-bath regulated to 0.01°, and the entire apparatus including the bath and manometer was enclosed in an insulated metal box with a double pane window for viewing the manometer. The air temperature in the box was maintained a few degrees above that of the bath to prevent condensation in the lines and manometer. The Hoke valves and thermoregulator could be operated from the outside of the box. The temperature of the water-bath was measured with a calibrated copper–constantan thermocouple. Vapor pressure was determined to 0.1 mm. using a Gaertner M-908 cathetometer to interpolate between the divisions of a calibrated meter bar mounted between the arms of the manometer. At least 2 hr. were allowed for the attainment of equilibrium, after which the vapor and liquid were isolated by closing the valves.

Analysis.—Liquid samples were withdrawn through #27 gauge hypodermic needle tubing in which they were flash boiled. The gas densities of both liquid and vapor samples were determined in a gas density balance described earlier.[5] At least two and usually three independent samples of liquid and vapor were analyzed at each temperature and composition. Analyses were reproducible to 0.1%. The second virial coefficients were determined for both the pure and mixed vapors for the purpose of calculating compositions from the gas densities determined at different pressures. For the mixtures it was found to be sufficiently accurate to use a linear combination of the virial coefficients previously reported for the pure components.[5] As an example, a mixture was prepared by weight whose composition was known to 1 part in 50,000. Its theoretical molecular weight was 234.3. The gas densities were then determined in the density balance at eight pressures between 75 and 255 mm. The molecular weight calculated from the limiting gas density was 234.3 ±0.2. The average of the values calculated from the gas densities using a linear combination of the pure component virial coefficients was 234.1 ±0.3.

Results

The liquid–vapor equilibrium diagram at 35° shown in Fig. 1, is an example of the behavior of fluorocarbon–hydrocarbon mixtures. The experimental vapor pressures, vapor and liquid compositions, and calculated excess free energies are shown in Tables I, II and III. The excess free energies were calculated from the equation

$$\mu_i{}^E = RT \ln (py_i/P_i{}^0x_i) + (B_{ii} - V_i)(P - P_i{}^0) \quad (1)$$

where $P_i{}^0$ denotes the vapor pressure of the pure component, P is the total pressure, $\mu_i{}^E$ is the excess chemical potential, B and V are the second virial coefficient and molar liquid volume of the pure component and x and y are the compositions of the liquid and vapor, respectively. This treatment corresponds to the treatment originated by Scatchard and Raymond.[6] The rates of change of the virial coefficients with temperature were estimated from the Berthelot equation. The corrections due to gas law deviations and the effect of pressure on the vapor pressure at $x = 0.5$ amount to 8, 11 and 15 cal. mole^{-1} at 25, 35 and 45°, respectively. The seemingly large corrections are attributed in part to the large positive deviations from Raoult's law, and in part to the unusually large virial coefficient for perfluoro-*n*-hexane. The partial molal excess free energies were checked for internal consistency by graphical integration of the Gibbs–Duhem equation.

The calculated excess free energies were fitted by power series equations of the form suggested by Guggenheim[7] and Scatchard[8] using least squares. All points were assigned equal weight. The coefficients for the equation are shown in Table IV

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[1] Presented at the Division of Physical Chemistry, 133rd meeting of The American Chemical Society, San Francisco, California, April, 1958.

[2] J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

[3] R. L. Scott, *J. Phys. Chem.*, **62**, 136 (1958).

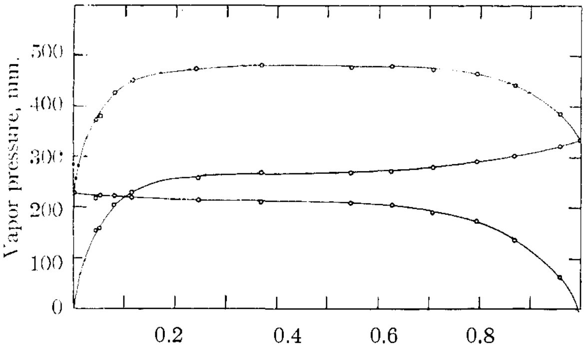
[4] R. G. Bedford and R. D. Dunlap, THIS JOURNAL, **80**, 282 (1958).

[5] R. D. Dunlap, C. J. Murphy and R. G. Bedford, *ibid.*, **80**, 83 (1958).

[6] G. Scatchard and C. L. Raymond, *ibid.*, **60**, 1278 (1938).

[7] E. A. Guggenheim, *Trans. Faraday Soc.*, **33**, 151 (1937).

[8] G. Scatchard, *Chem. Revs.*, **44**, 7 (1949).



Mole fraction of n-perfluorohexane.

Fig. 1.—Liquid–vapor equilibrium diagram at 35°.

together with the coefficients for corresponding functions for the enthalpy and excess entropy of mixing. The differences between the excess free energies and those calculated from the power series

$$F^E,\ \text{cal. mole}^{-1} = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 \ldots] \quad (2)$$

equation are shown in the fifth columns of Tables I, II and III. As in the case of the excess volume of mixing,[4] it was found that the use of three constants in the analytical expression is significantly better than two and that these data do not justify the use of four constants.

Table I

Vapor Pressures and Excess Free Energies at 25°

Mole fraction n-C_6F_{14} Liquid	Mole fraction n-C_6F_{14} Vapor	Vapor pressure std., mm.	F^E, cal./mole	$F^E_{eq(1)} - F^E_{eq(2)}$
0.0000		151.2		
.0512	0.4543	269.7	81.0	2.5
.0990	.5325	307.3	139.3	−0.8
.1831	.5476	319.4	226.8	2.5
.2800	.5543	322.5	286.7	−1.3
.3729	.5527	323.0	319.8	−0.9
.3888	.5579	323.3	321.3	−2.5
.5464	.5583	324.7	322.5	2.0
.7143	.5813	321.5	257.1	1.4
.7905	.6063	316.7	208.1	1.6
.8592	.6536	302.9	148.4	−2.4
.9497	.8064	261.4	57.3	−2.7
1.0000		220.3		$\sigma = \pm 2.1$

Table II

Vapor Pressures and Excess Free Energies at 35°

Mole fraction n-C_6F_{14} Liquid	Mole fraction n-C_6F_{14} Vapor	Vapor pressure std., mm.	F^E, cal./mole	$F^E_{eq(1)} - F^E_{eq(2)}$
0.0000		229.5		
.0436	0.4082	373.4	60.1	−6.5
.0452	.4118	377.1	64.9	−4.0
.0779	.4805	425.0	113.2	0.9
.1152	.5047	450.4	165.9	10.2
.2395	.5468	473.3	256.6	−2.4
.3677	.5599	477.9	307.0	−3.6
.5452	.5623	478.5	311.9	0.8
.6262	.5706	478.9	290.1	1.8
.7080	.5936	474.8	252.8	1.0
.7945	.6262	465.7	198.4	0.3
.8680	.6861	443.5	138.6	−0.9
.9577	.8322	386.0	45.6	−4.4
1.0000		335.1		$\sigma = \pm 4$

Table III

Vapor Pressures and Excess Free Energies at 45°

Mole fraction n-C_6F_{14} Liquid	Mole fraction n-C_6F_{14} Vapor	Vapor pressure	F^E, cal./mole	$F^E_{eq(1)} - F^E_{eq(2)}$
0.0000		337.7		
.0372	0.3471	507.3	57.5	4.7
.0502	.3963	541.8	71.8	1.9
.1478	.5206	652.3	175.3	−2.5
.2542	.5373	677.5	260.1	3.0
.3392	.5480	683.1	293.7	−1.2
.3415	.5504	682.7	292.7	−2.9
.5424	.5666	687.8	304.1	−1.2
.6536	.5873	688.7	273.1	3.7
.6560	.5813	686.2	268.8	0.4
.7088	.6024	682.9	245.2	3.3
.7806	.6242	670.8	197.4	0.4
.7973	.6282	665.2	181.8	−3.4
.8080	.6361	661.8	174.0	−3.3
.8815	.7115	628.0	117.6	0.2
.9597	.8592	555.0	43.9	1.1
1.0000		493.4		$\sigma = \pm 2.7$

Table IV

Excess Thermodynamic Functions for the System Perfluoro-n-hexane—n-Hexane

	A_0	A_1	A_2
$F^E_{25°}$, cal. mole^{-1}	1310	−200	156
$F^E_{35°}$	1271	−200	172
$F^E_{45°}$	1246	−199	50
H^M, cal. mole^{-1}	2255 ± 86	−215 ± 4	$1.7 \pm 0.8 \times 10^3$
S^E, cal. mole^{-1} deg.$^{-1}$	3.2	−0.05	5.3

The coefficients in the enthalpy and excess entropy functions were obtained from the coefficients in the free energy functions by least squares, assuming $(\partial F^E/\partial T)_P$ to be independent of T in this temperature interval. The excess free energy, the enthalpy and excess entropy of mixing are shown in Fig. 2. The vertical lines represent the uncertainty in the enthalpy due to the uncertainty in the free energy. The uncertainty is the same for the TS^E curve. The calculated heat of mixing at $x = {}^1/_2$ and at 35° is 567 ± 20 cal. mole^{-1}.

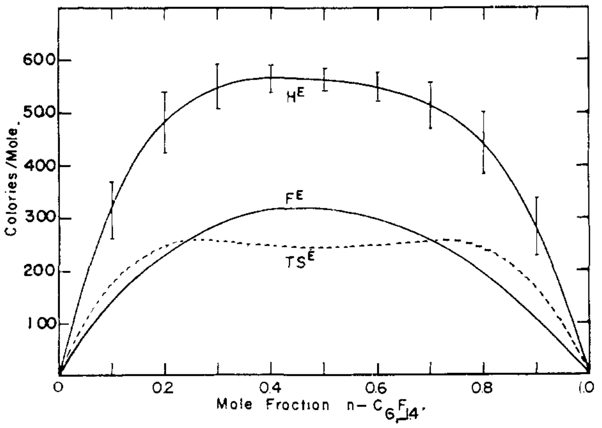


Fig. 2.—Excess thermodynamic functions at 35°.

For comparison, the values of the excess thermodynamic functions at $x = {}^1/_2$ for the systems containing fluorocarbons and hydrocarbons which have been previously studied are shown in Table V. For the systems perfluoro-n-butane–n-butane and perfluoro-n-pentane–n-pentane, the excess free energies were recalculated from Mausteller's data[9] and from the data of Simons and Dunlap,[10] using equation 1. In the earlier work corrections for gas imperfection and for the effect of pressure on the vapor pressure were not applied. In the case of the perfluoro-*n*-heptane–isoöctane system, the excess free energies were calculated from the fugacities reported by Mueller and Lewis.[11,12] The enthalpy of mixing at $x = {}^1/_2$ and 323°K. calculated from the temperature dependence of the excess free energy is 545 ± 115 cal. mole^{-1}. Mueller and Lewis[13] have also measured the heat of mixing calorimetrically and have reported a value of 420.7 cal. mole^{-1} at 30° and 0.507 mole fraction of isoöctane. Williamson, Scott and Dunlap report values of 493 cal. mole^{-1} at $x = 0.586$, and 498 cal. mole^{-1} at $x = 0.536$ mole fraction of isoöctane. From these data the value at $x = {}^1/_2$ is estimated to be 505 ± 5 cal. mole^{-1}. All values are shown in Table V. With the exception of the calorimetric heat reported by Mueller and Lewis, all of the data are consistent.

TABLE V

VALUES OF THE THERMODYNAMIC FUNCTIONS AT $x = {}^1/_2$ FOR FLUOROCARBON–HYDROCARBON SYSTEMS

System	Temp., °K.	F^E, cal. mole^{-1}	H^E, cal. mole^{-1}	S^E, cal. mole^{-1} deg.$^{-1}$
n-C_4F_{10} + *n*-C_4H_{10}	245	243	415	0.7
n-C_5F_{12} + *n*-C_5H_{12}	285	281	480	.7
n-C_6F_{14} + *n*-C_6H_{14}	308	328	567	.8
n-C_7F_{16} + iso-C_8H_{18}	323	310	545[a]	.7
	303	330	420[b]	.30
	303	330	505[c]	.58

[a] From liquid–vapor equilibrium data, ref. 11, 12. [b] From calorimetric measurement, ref. 13. [c] From calorimetric measurement. ref. 12.

Discussion

It is desired that a theory of solutions predict the magnitude and the functional form of the thermodynamic functions of mixing. The excess free energy, 318 cal. mole^{-1} at 35° and $x = {}^1/_2$ is considerably larger than 85 cal. mole^{-1} calculated from regular solution theory.[2] Reed[14,15] has suggested that the geometric mean approximation be refined to account for the differences in size and in ionization potentials of the molecules. If one uses Reed's method to estimate the ionization potential of perfluoro-*n*-hexane, this refinement brings the calculated excess free energy up to 185 cal. mole^{-1}. Recent measurements[16] of the internal pressures of mixtures of perfluoro-*n*-hexane with *n*-hexane lend support to Scott's argument[3] that failure of elementary theory to account for the large excess free energy is principally due to the failure of the geometric mean assumption rather than the assumption of random mixing. We have found that $(\partial P/\partial T)_V = 5.762$ atm. deg.$^{-1}$ at 35° and $x = 0.5409$ mole fraction of perfluoro-*n*-hexane. The corresponding increase in volume attending mixing[4] was found to be 5.38 cm.^{3}. If one assumes that the entropy of expansion is a linear function of the volume, the entropy of expansion is

$$S_{(V+\Delta V)} - S_V = \int_V^{V+\Delta V} (\partial S/\partial V)_T \mathrm{d}v = \int_V^{V+\Delta V} (\partial P/\partial T)_V \mathrm{d}v = 0.75 \text{ e.u.}$$

The excess entropy calculated from the rate of change of the excess free energy with temperature is 0.80 ± 0.08 e.u. at $x = 0.5$. More accurate data on the heat of mixing are needed to obtain a more complete answer to the problem of the entropy of mixing.

The curves for the excess free energies are skewed toward the hydrocarbon, *i.e.*, toward the component with the smaller volume, as predicted by the regular solution theory. The degree of skewness, however, is less than predicted. For comparison with regular solution theory, the Hildebrand–Scatchard equation is written in the form[17]

$$F^E = \frac{2x_1x_2V_1V_2(\delta_2 - \delta_1)^2}{V_1 + V_2}\left[1 - \left(\frac{V_1 - V_2}{V_1 + V_2}\right)(x_1 - x_2) + \left(\frac{V_1 - V_2}{V_1 + V_2}\right)^2 (x_1 - x_2)^2 \ldots\right] \quad (3)$$

The ratios of the coefficients in the analytical expressions for the free energies, *viz.*, A_1/A_0, and A_2/A_0 can be compared with $(V_1 - V_2)/(V_1 + V_2)$ and $[(V_1 - V_2)/(V_1 + V_2)]^2$, respectively. The results are shown in Table VI together with comparisons for other fluorocarbon–hydrocarbon systems. In the case of the perfluoro-*n*-heptane + isoöctane system, the ratios shown in parentheses were calculated from the fugacities reported by Mueller and Lewis,[11] and the other numbers obtained by Barker's method[12,18] using only the total pressure and liquid composition.

TABLE VI

System	Temp., °K.	$-\frac{A_1}{A_0}\Big/\left(\frac{V_1 - V_2}{V_1 + V_2}\right)$	$\frac{A_2}{A_0}\Big/\left(\frac{V_1 - V_2}{V_1 + V_2}\right)^2$
n-C_4F_{10}–*n*-C_4H_{10}	259	0.82	1.0
	233	.64	2.0
n-C_5F_{12}–*n*-C_5H_{12}	293	.70	2.5
	278	.70	4.8
n-C_6F_{14}–*n*-C_6H_{14}	318	.69	0.9
	298	.72	2.6
n-C_7F_{16}–*iso*-C_8H_{18}	368	.74 (1.09)	3.1 (20)
	318	.58 (0.81)	3.3 (12)

Values of the quantity

$$-\frac{A_1}{A_0}\Big/\left(\frac{V_1 - V_2}{V_1 + V_2}\right)$$

shown in column 3 of Table VI are less than unity indicating that the degree of skewness toward the component of smaller volume is less than that predicted by regular solution theory and are somewhat independent of temperature. The ratio

$$-\frac{A_1}{A_0}\Big/\frac{V_1^{2/3} - V_2^{2/3}}{V_1^{2/3} + V_2^{2/3}}$$

is very nearly equal to unity for these systems, in-

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(11) C. R. Mueller and J. E. Lewis, *ibid.*, **26**, 286 (1957).

(12) A. G. Williamson, R. L. Scott and R. D. Dunlap, *ibid.*, **30**, 325 (1959).

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(14) T. M. Reed, III, *J. Phys. Chem.*, **59**, 425 (1955).

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(16) R. D. Dunlap and R. L. Scott, "Internal Pressures of Perfluoro-*n*-hexane, *n*-Hexane and Their Mixtures," to be published.

(17) Equation 3 is given in a slightly different form in reference 8.

(18) J. A. Barker, *Aust. J. Chem.*, **6**, 207 (1953).

dicating that the skewness is more nearly related to the surface areas of the molecules than their volumes. Such a treatment has been proposed by Langmuir.[19] Values of

$$-\frac{A_2}{A_0}\Big/\left(\frac{V_1 - V_2}{V_1 + V_2}\right)^2$$

appear to be highly temperature dependent, increasing rapidly near the temperatures corresponding to phase separation. This is a measure of the flattening of the free energy function and may be attributed to clustering. In the case of the quasichemical model of solutions,[20] the first-order correction to the free energy due to non-random mixing introduces a term in $(x_1x_2)^2$.

In the earlier studies,[10,21] the volume of mixing functions were found to be virtually symmetrical. Careful analysis[4] of the perfluoro-*n*-hexane–*n*-hexane system has shown them to be slightly skewed toward the fluorocarbon axis, the maximum occurring at $x = 0.524$ at 25°. This can be at least qualitatively explained by the relationship first proposed by Scatchard[22] and later by others,[23,24]

$$\Delta V = \frac{\alpha T F^{E}}{\delta^2}$$

where α and δ are the thermal coefficient of expansion and solubility parameter of the isolated components. The excess free energy functions are skewed toward the hydrocarbon axis, but the larger thermal coefficients of expansion and lower solubility parameters of the fluorocarbons combine to produce a coefficient which is concentration dependent in such a way that the excess volume function is nearly symmetrical. This was not the case for the perfluoromethane–methane system recently studied by Croll and Scott,[25] where the thermal coefficient of expansion of perfluoromethane was found to be smaller than that of methane and the solubility parameter larger.

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[19] I. Langmuir, "Colloid Symposium Monograph," Vol. III, The Chemical Catalogue Co., Inc., New York, N. Y., 1925.

[20] See ref. 2, p. 146, also E. A. Guggenheim, "Mixtures," The Clarendon Press, Oxford, 1952, p. 64; Prigogine, "The Molecular Theory of Solutions," North-Holland Publ. Co., Amsterdam, 1957, p. 63.

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[23] See ref. 2, p. 138.

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The Decomposition of Formic Acid Vapor on Nickel Surfaces[1]

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A study of the decomposition rate of formic acid in a flow system is combined with an examination of the nickel surfaces used as catalysts. Electron microscopy, electron diffraction and vacuum microweighing techniques are applied. Reproducible rates and activation energies are attained with specimens of different crystallographic and physical structure when careful attention is given to the pre-treatment of the surfaces and specially purified formic acid is used. An initially high decomposition rate declines to a steady state. The rate of this decline is a function of the pre-treatment of the nickel. Nickel formate films were detected only under special conditions and do not play a part in the decomposition under conditions for which the reaction has usually been studied.

The kinetics of the decomposition of formic acid vapor over hot nickel surfaces have been studied by several investigators. However, little is known concerning the role of the nickel surface in the reaction.

The present study was undertaken to correlate kinetics measurements with an examination of the surface of the nickel catalyst, using the techniques of electron microscopy, diffraction and vacuum microweighing.

Formic acid decomposes by two important processes at pressures near 1 atmosphere and temperatures between 25 and 500°

$$\mathrm{HCOOH} \longrightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad (1)$$

$$\mathrm{HCOOH} \longrightarrow \mathrm{CO} + \mathrm{H_2O} \qquad (2)$$

Both reactions are catalyzed by glass.[3] Nickel is reported[4,5] to catalyze the first reaction predominantly. Studies of the kinetics of the nickel-catalyzed reaction have given widely differing results.

Rienäcker,[5] using a static system, reports that the nickel-catalyzed decomposition follows zero-order kinetics. Wide variations are reported for both the decomposition rate and the activation energy of the reaction, activation energies between 12 and 30 kcal./mole having been reported by various investigators for different nickel preparations. Some investigators report a dependence of activation energy on the physical state of the nickel. For example, Rienäcker[6] reports an acti-

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[1] A portion of this work is taken from the Ph.D. dissertation of Roswell J. Ruka, The University of Michigan, Ann Arbor, Michigan, 1954.

[2] Department of Chemistry, The University of Texas, Austin 12, Texas.

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