$$\log p = -2892.3693/T - 2.892736 \log T -$$
$$4.9369728 \times 10^{-3}T + 5.606905 \times 10^{-6}T^2 -$$
$$4.645869 \times 10^{-9}T^3 + 3.7874 \times 10^{-12}T^4 + 19.3011421$$

converted from the thermodynamic to the International scale by the relation[9]

$$T - t = 273.16 + (t/100)(t/100 - 1)(0.04217 - 0.00007481t)$$

The average difference between the two temperatures in the two series was less than 0.01°, and the maximum difference less than 0.02°. The relation between temperature and e.m.f. was smoothed to the temperatures for the mixtures by plotting against the temperature the deviations of e.m.f. from a quadratic in the temperature. This plot gave an intercept of about −0.07° instead of zero at 0°, perhaps because the ice bath was rather shallow.

Three runs were made with water at the temperatures 5, 25, 45, 65, and 85°, two of them before the degassing technique had been developed so that the residual pressures were 0.200 and 0.340 mm. instead of the 0.023 and 0.044 in the third run and in the calibration. The average deviation of the values interpolated from the calibration, giving equal weights to the water and benzene series, was 0.015° from the first run and 0.006° from each of the others.

The potentiometer was set at exactly the same value for the measurements of the pressures of benzene and of water at about 7°, 19°, 35°, 50°, 65°, and 79°, and the vapor pressure of water was also measured at about 99°.

The water was conductivity water from the still in this Laboratory. The benzene was Mallinckrodt thiophene-free benzene fractionated in the 2.5-m. fractionating column in this Laboratory. Three top fractions of about 40 cc. each and two bottom fractions of 100 cc. each were discarded. The boiling points of the last bottom and the last top fractions differed by 0.01°.

Material Transport.—Since days of degassing at 85° are necessary after even a few minutes exposure to argon or air, the apparatus was opened only when necessary for repairs. The components are introduced into the cell and the mixture is removed after the measurements by distillation. The containers for the degassed components are a permanent part of the apparatus. The receiving flask for the solutions is in the argon side of the apparatus. The receivers are cooled in ice water except as noted, and the evaporating liquid is sometimes warmed with warm water.

The loading arm is connected to the equilibrium cell through seal 2 and to the vacuum-argon manifold through a metal valve. It consisted of the two component containers and a calibrated 10-cc. centrifuge tube into which the desired quantity of a component is condensed and then distilled into the equilibrium cell. The measuring tube is never exposed to permanent gas and is kept evacuated except when in use.

The collecting train is connected to the argon side of the null manometer through seal 3. There is a finger which can be cooled in liquid air to collect the last traces of vapor; seal 4; a cell of about 20-cc. capacity with a magnetic stirrer, a vertical tube at the top with a mercury-sealed ground-glass cap, and a small dimple in the bottom below the tube to permit nearly complete removal of the contents with a hypodermic syringe; and seal 5 leading to the main manometer and pressure reservoir.

Procedure.—After the apparatus was built foreign vapors and gases were excluded from the equilibrium cell and the loading

(9) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

arm, thus decreasing considerably the amount of degassing necessary with each solution. Initially the apparatus was degassed by first pumping overnight with a mercury diffusion pump. Then one of the components was introduced, the system was heated to the highest temperature of measurement and vapor was expanded off periodically. This method degasses about ten times as fast as heating while pumping with a diffusion pump.

For each solution the equilibrium cell is filled as described above, seal 1 is closed, and the rest of the system evacuated. The seal is opened with the cell still at 0°, closed again, and the evacuation repeated. The first two measurements with each system are made at room temperature and at 5°; the others are made with ascending temperatures with a final reading after return to room temperature. The difference between the two room temperature readings gives the permanent gas buildup, nearly all of which is attributed to the highest temperature.

During the temperature changes, care is taken to keep the equilibrium cell cooler than the rest of the apparatus, from which it is isolated by seal 1. The final adjustments of temperature and pressure are attained simultaneously.

After the null manometer reading has been taken, the equalizing coil is filled with vapor from the auxiliary cell to the proper pressure. After seal 3 has been closed, the coil is connected to the argon side through valve 5 and then to the vapor side for the few seconds necessary for the zero reading. Then the valves are closed and the coil is evacuated. The change in reading is usually 0.05 mm. or less, so the gain or loss of material is negligible. The length and shape of the equalization coil prevents contamination with argon by convection or diffusion.

The total volume of the equilibrium side of the apparatus is 113.5 ml., of which about 10 ml. is occupied by the liquid.[10] So at 5° the composition of the liquid is very close to the over-all composition. At only one point in our studies was the difference (0.0011) greater than 0.1%. Even at the highest temperature there was only one point at which the difference (0.0112) was greater than 1%. Calculating the free energy at the lowest temperature first and proceeding step by step to the highest eliminates any inconvenience of knowing the over-all composition rather than the liquid composition. The practical advantages are great. The two men required to operate the apparatus without undue tension can measure six equilibria at five different temperatures on a single sample every second day. The alternate days are used to analyze the sample, refill the apparatus, and other auxiliary tasks.

The apparatus can be used from −10 to 120° for pressures not greater than 1 atmosphere. The precision is about 0.01 mm. and about 0.01°. For pressures greater than about 20 mm., the precision of the pressure is better than that of the temperature. One common criterion for the choice of the two systems discussed in the following papers was that there should be very large differences between the vapor and liquid compositions since this condition leads to serious difficulties with "equilibrium stills."

Note Added in Proof.—Hermsen and Prausnitz[11] describe an apparatus embodying some of these characteristics. They compare it with our earlier apparatus,[2,3] but do not refer to the thesis of Wilson although they borrowed a copy of it in 1958.

(10) The volume of the equalizing coil is 23.6 ml., that of the argon side to seal 3 is 445 ml., and that between seals 3 and 5 is 80 ml.

(11) R. W. Hermsen and J. M. Prausnitz, *Chem. Eng. Sci.*, **18**, 485 (1963).

Vapor–Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing

By Grant M. Wilson[1]

Received September 3, 1963

An equation has been found which represents the excess free energy of mixing nonelectrolytes with two, or sometimes three, parameters for a binary mixture and no additional parameters for polycomponent systems. It is compared with the experimental values for several mixtures. The corresponding equations for the excess enthalpy and entropy of mixing are also derived. A semitheoretical interpretation is given. This equation should be particularly useful for large deviations from normality and for polycomponent mixtures.

A new expression has been found to represent the excess free energy of mixing which has the advantages that a system of any number, n, of components can probably be fitted with $n(n-1)$ parameters obtained from the binaries. This equation which leads to Raoult's law and Henry's law at the limits $x_i = 1$ and $x_i = 0$ is

(1) Based on the Ph.D. Thesis of Grant M. Wilson, M.I.T., 1958. Present address: Air Products and Chemicals, Inc., Allentown, Pa.

$$\bar{G}^E/RT = -\sum_i x_i \ln\left(1 - \sum_j x_j A_{j/i}\right) \qquad (1)$$

where x_i = mole fraction of component i and $A_{j/i}$ = adjustable parameters $(A_{i/i} = 0,\ A_{j/i} \neq A_{i/j})$.

The following equation results for a binary mixture.

$$\bar{G}^E/RT = -x_1 \ln(1 - A_{2/1}x_2) - x_2 \ln(1 - A_{1/2}x_1) \qquad (2)$$

The two parameters $A_{2/1}$ and $A_{1/2}$ of eq. 2 are positive if the deviation from ideality is positive, and the param-

eters are negative if the deviation from ideality is negative. In some case the parameters will have opposite signs. The deviation from ideality will then depend upon which has the greater effect and may also change sign. Values of the parameters equal to or greater than unity produce imaginary numbers for the excess free energy at certain compositions. Only values less than unity are required in actual use, however, since, as shown in the Appendix, a parameter of unity has the significance of zero interaction between two molecules.

There are numerous other equations which might be used to express the excess free energy of mixing[2-4]; a commonly used equation is the series expansion

$$\bar{G}^{E}/RT = x_1 x_2 \sum_n B_{12}{}^{(n)}(x_1 - x_2)^n \qquad (3)$$

where as many terms are used as are required to fit the data.

A comparison of eq. 1 and 3 follows in terms of the representation of binary data with only a few parameters and in terms of the prediction of ternary data from a representation of the binary data.

Methanol–Carbon Tetrachloride–Benzene Mixtures.
—The binary data of Scatchard and co-workers[5] involving the three components methanol (1), carbon tetrachloride (2), and benzene (3) at 35° were fitted; and then from the parameters obtained from the binary data the excess free energy of the ternary system was calculated and compared with measured values.

The parameters obtained from the binaries are given in Table I and the deviations of calculated values from the binary data are given in Table II. Since there are only two parameters per binary in eq. 1, it is remarkable that so good a fit should be obtained to the methanol–benzene and methanol–carbon tetrachloride binaries which exhibit large deviations from ideality. Scatchard found that five parameters are necessary to obtain a similar fit when eq. 3 is used.

TABLE I
PARAMETERS OBTAINED FROM BINARY DATA: METHANOL (1), CARBON TETRACHLORIDE (2), BENZENE (3), $A_{j/i}{}^{35°}$

i/j	1	2	3
1	0.0000	0.95216	0.91226
2	.6782	.0000	.1250
3	.6579	.0000	.0000

TABLE II
DEVIATION OF ANALYTICAL EXPRESSIONS FROM BINARY DATA[5]

	MeOH–CCl₄, 35°			MeOH–C₆H₆, 35°	
	$\bar{G}_{12}{}^{E}$			$\bar{G}_{13}{}^{E}$	
	measd., cal./	(measd. − calcd.)		measd., cal./	(measd. − calcd.)
		Eq. 1	Eq. 3		Eq. 1	Eq. 3
x_1	mole	2 par.	5 par.	x_1 mole	2 par.	5 par.
0.0169	38.31	2.93	5.86	0.0242 47.15	4.85	7.00
.0189	43.10	3.88	7.00	.0254 40.67	−3.54	−1.29
.1349	194.17	0.03	1.69	.1302 173.40	0.06	2.43
.3500	316.03	.10	1.00	.3107 281.08	−3.79	−1.15
.4776	326.64	.30	−0.06	.4989 306.06	−2.43	0.05
.4939	325.61	.42	− .11	.5191 304.24	−2.15	.08
.6557	284.25	.81	− .25	.6305 278.46	−1.30	− .08
.7912	206.67	.00	− .43	.7965 192.65	0.12	.10
.9120	99.91	− .86	−1.72	.9197 89.15	0.69	.28
	Std. dev.	1.9	4.7	Std. dev.	3.0	3.4

	CCl₄–C₆H₆	
	$\bar{G}_{23}{}^{E}$ measd.,	$\bar{G}_{23}{}^{E} - \bar{G}_{23}{}^{E}{}_{calcd}$
x_2	cal./mole	Eq. 1
1/4	14.5	−0.08
3/4	14.0	−0.11

(2) G. Scatchard, *Chem. Rev.*, **44**, 7 (1949).

(3) K. Wohl, *Trans. Am. Inst. Chem. Engrs.*, **42**, 215 (1946).

(4) (a) E. Hala, *Russ. J. Phys. Chem.*, 463 (Nov., 1959) (English Translation); (b) E. Hala, J. Pick, V. Fried, and O. Vilim, "Vapour–Liquid Equilibrium," Pergamon Press, New York, N. Y., 1958, translated into English by G. Standart.

(5) G. Scatchard and L. B. Ticknor, *J. Am. Chem. Soc.*, **74**, 3724 (1952).

A comparison of calculated and measured values at individual points in the ternary system is given in Table III where it is seen that the agreement with measured values is as good as in the binaries. This result is quite significant since it was also found by Scatchard that there is some ambiguity as to how eq. 3 for the binary systems should be combined for the ternary system.

TABLE III
COMPARISON OF VALUES CALCULATED FROM BINARY DATA WITH MEASURED TERNARY VALUES: METHANOL (1), CARBON TETRACHLORIDE (2), BENZENE (3)[5]

		$\bar{G}_{123}{}^{E}$		
		measd., cal./	(measd. − calcd.)	
			Eq. 1	Ref. 1[a]	Ref. 1[a]
x_1	x_2	mole	6 par.	12 par.	12 par.
0.2075	0.1900	248.3	−0.5	22.8	2.9
.2110	.3879	257.6	−1.5	29.3	2.1
.1987	.5876	253.6	1.4	26.9	4.0
.3781	.3122	320.5	−0.9	18.7	3.4
.5543	.2078	314.3	0.5	8.6	3.3
.7599	.1076	225.2	1.6	2.4	2.6
		Std. dev.	1.2	20.5	3.1

[a] Binaries combined in two ways.

Carbon Tetrachloride–Acetonitrile; Carbon Tetrachloride–Nitromethane Mixtures.—Further tests of eq. 1 to predict ternary systems have not been made; however, the equation has been tested in other binaries. In Table IV is a comparison of calculated and measured values at individual points in the two binary systems composed of carbon tetrachloride and acetonitrile measured by Brown and Smith[6] at 45° and of carbon tetrachloride and nitromethane measured by Brown and Smith[7] at 45°.

TABLE IV
DEVIATION OF ANALYTICAL EXPRESSIONS FROM BINARY DATA

	CCl₄–CH₃C≡N, 45°			CCl₄–CH₃NO₂, 45°		
		$\bar{G}_{24}{}^{E}$			$\bar{G}_{25}{}^{E}$	
	measd., cal./	(measd. − calcd.)		measd., cal./	(measd. − calcd.)	
		Eq. 1	Eq. 3		Eq. 1	Eq. 3
x_2	mole	2 par.	4 par.	x_2 mole	2 par.	3 par.
0.0347	37.6	0.2	1.3	0.0512 62.6	−1.7	−1.4
.0892	90.2	0.0	1.6	.0961 111.5	−1.8	−1.4
.1914	168.0	−1.9	2.1	.1957 200.1	−0.8	−0.2
.2887	226.9	−0.3	−0.1	.3165 273.3	.5	1.1
.3752	261.0	− .3	.0	.3935 301.2	.2	0.5
.4567	279.5	− .5	.3	.4634 317.0	1.8	1.6
.4790	282.4	− .4	.5	.5341 318.9	0.2	−0.6
.5060	284.3	− .5	.4	.6344 304.8	.6	−1.0
.6049	279.2	− .4	.2	.7171 273.3	− .7	−2.0
.7164	248.0	.3	− .7	.8046 221.1	− .7	−0.4
.8069	200.1	1.1	−1.1	.9082 125.9	− .9	2.2
.8959	129.2	2.7	0.5	.9541 69.4	− .3	2.8
.9609	56.7	2.7	1.9			
Std. dev.		1.4	1.3	Std. dev.	1.1	1.7

$A_{4/2}$ 0.6118 $A_{5/2}$ 0.7220
$A_{2/4}$ 0.8287 $A_{2/5}$ 0.8568

The agreement is again good; in this case four parameters of eq. 3 were used for the carbon tetrachloride–acetonitrile system and three parameters for the carbon tetrachloride–nitromethane system by Brown and Smith.

Chloroform–Acetone Mixtures.—Systems with negative deviations from ideality apparently are not represented as well as systems with positive deviations from ideality; the chloroform–acetone data of Röck and Schröder[8] is represented a little better by eq. 3 with

(6) I. Brown and F. Smith, *Australian J. Chem.*, **7**, 269 (1954).

(7) I. Brown and F. Smith, *ibid.*, **8**, 501 (1955).

(8) H. Röck and W. Schröder, *Z. physik. Chem.* (Frankfurt), **11**, 41 (1957).

three parameters than by eq. 1 with two parameters as is shown in Table V.

<div align="center">TABLE V</div>

DEVIATION OF ANALYTICAL EXPRESSION FROM CHLOROFORM
(6)–ACETONE (7) DATA[5]

		$\bar{G}_{67}{}^E$		
		(measd. − calcd.)		
	measd.,	Eq. 1	Eq. 3	
x_7	cal./mole	2 par.	3 par.	
0.104	−52.5	+6.2	+2.4	
.200	−95.7	+1.3	−0.7	
.301	−123.1	−0.2	+1.3	$A_{6/7} = -0.01$
.401	−140.5	−5.0	−0.8	$A_{7/6} = -1.13$
.503	−140.7	−4.2	+0.5	
.591	−128.8	−0.3	+2.9	
.695	−109.1	+0.3	−0.2	
.801	−76.4	+3.5	− .8	
.897	−39.9	+5.3	.0	
	Std. dev.	4.2	1.7	

Methanol–Benzene Vapor–Liquid Data.—The parameters may also be obtained from the partial pressures of one component or from the total vapor pressures of the mixtures. The latter procedure is shown in the following examples. From eq. 1 the activity coefficient of a component is determined as

$$\ln \gamma_i = -\ln \left(1 - \sum_j x_j A_{j/i}\right) + 1 -$$
$$\sum_j \left[x_j(1 - A_{i/j})/(1 - \sum_k x_k A_{k/j}) \right] \quad (4)$$

In a binary mixture this equation becomes, after rearrangement of terms

$$\ln \gamma_1 = -\ln (1 - A_{2/1}x_2) + x_2 \left[\frac{x_2 A_{1/2}}{1 - A_{1/2}x_1} - \frac{x_1 A_{2/1}}{1 - A_{2/1}x_2} \right] \quad (5)$$

$$\ln \gamma_2 = -\ln (1 - A_{1/2}x_1) - x_1 \left[\frac{x_2 A_{1/2}}{1 - A_{1/2}x_1} - \frac{x_1 A_{2/1}}{1 - A_{2/1}x_2} \right] \quad (6)$$

The total pressure data for the methanol–benzene system[1] was fitted in terms of the parameters of eq. 5 and 6 by methods similar to those of Scatchard and co-workers.[9] The vapor imperfection corrections that were made are the same as the corrections made by Scatchard. In Table VI is given a summary of the pressure deviations and a comparison of calculated and measured values for the vapor composition and the excess free energy. As can be seen, a good fit is obtained to the experimental pressures; also the agreement between calculated and measured vapor compositions is

<div align="center">TABLE VI</div>

TEST OF EQUATION 1 IN CORRELATING VAPOR–LIQUID
EQUILIBRIUM DATA, METHANOL–BENZENE, 35°[5]

x_1	p_{measd}, mm.	$p -$ p_{calcd}	$\bar{G}^E_{measd}$, cal./ mole	$\bar{G}^E -$ $\bar{G}^E_{calcd}{}^a$	γ_{1measd}	$\gamma_1 -$ γ_{calcd}
0.0242	203.29	−4.55	47.15	7.20	0.2733	−0.0251
.0254	211.10	1.12	40.67	−1.21	.3128	.0073
.1302	274.25	0.43	173.40	5.73	.4858	− .0042
.3107	288.47	.00	281.08	1.59	.5304	− .0016
.4987	292.50	.14	306.06	1.68	.5546	− .0017
.5191	292.70	.16	304.24	1.17	.5571	− .0022
.6305	292.49	.15	278.46	0.85	.5790	− .0016
.7965	283.58	.00	192.65	.76	.6421	− .0008
.9197	255.82	− .70	89.15	.70	.7688	.0020

$A_{3/1} = 0.89256$; $A_{1/3} = 0.66587$. Best fit to total pressure (compare with Table I)

^{a} Compare with Table II.

(9) G. Scatchard, G. M. Kavanagh, and L. B. Ticknor, J. Am. Chem. Soc., **74**, 3715 (1952).

not only a credit to the equation but also is indicative of the good thermodynamic consistency of the data. Deviations in the excess free energy can be compared with those in Table II where the parameters were determined directly from the excess free energy.

Heat of Mixing and Excess Entropy of Mixing.—The heat of mixing is given from eq. 1 as

$$\bar{H}^E/RT = -T \sum_i x_i \left[\left(\sum_j x_j dA_{j/i}/dT\right)/(1 - \sum_k x_k A_{k/i}) \right] \quad (7)$$

and the excess entropy of mixing is given as

$$\bar{S}^E/R = -T \sum_i x_i \left[\left(\sum_j x_j dA_{j/i}/dT\right)/(1 - \sum_k x_k A_{k/i}) \right] +$$
$$\sum_i x_i \ln \left(1 - \sum_j x_j A_{j/i}\right) \quad (8)$$

These equations do not have the same analytical form as that of eq. 1. This has been urged as a disadvantage in the application of eq. 1, since these properties all have the same analytical form when eq. 3 is used. However, the advantage of better representation of excess free energy data by eq. 1 than by eq. 3 should outweight this disadvantage.

No attempt has been made to correlate experimental heat of mixing data directly with eq. 7; thus the utility of this equation for this purpose is not known.

Immiscible Liquid Mixtures.—Although eq. 1 is found to fit quite well the data of liquid systems presented here, it is to be expected that there are systems for which a good fit will not be obtained since it cannot predict separation into two liquid phases no matter the values of the parameters. According to the equation a system will be close to separation into two phases when the parameters $A_{j/i}$ are close to unity. But in the limit as the parameters approach unity the excess free energy becomes equal and opposite in sign to the ideal free energy of mixing, and the free energy of mixing becomes identically zero at all compositions.

This inadequacy of the equation to predict immiscibility can be removed if the equation is multiplied by a constant to be determined empirically; thus

$$\bar{G}^E/RT = -C \sum_i x_i \ln \sum_j x_j A_{j/i} \quad (9)$$

where the parameter C may in many cases equal unity, although to predict phase separation it must be greater than unity. An example of the use of this equation is given in an accompanying paper.[10]

<div align="center">Summary</div>

A new equation has been found for the representation of excess free energy of mixing data. The advantages of this equation are: (a) accurate representation of data with only a few parameters; (b) accurate prediction of multicomponent properties from binary data; (c) a semitheoretical interpretation of the parameters is obtained.

<div align="center">Appendix</div>

Equation 1 may be derived from the following assumptions: a. The free energy of mixing is assumed to be given by a relation similar to the Flory–Huggins equation

$$\bar{G}^M/RT = \sum_i x_i \ln \xi_i \quad (10)$$

where ξ_i is the "local" volume fraction of component i about a central molecule of the same type.

b. The distribution of molecules about a central molecule is assumed to be given by the relation

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j e^{-\varepsilon_{ji}/kT}}{x_k e^{-\varepsilon_{ki}/kT}} \quad (11)$$

(10) G. Scatchard and G. M. Wilson, ibid., **86**, 133 (1964).

where x_{ji} is the "local" mole fraction of j around i and g_{ji} is proportional to the interaction energy between molecules j and i.

According to assumption b the "local" volume fraction of component i in the neighborhood of a central molecule of the same type is calculated to be

$$\xi_i = \frac{x_i \bar{V}_i e^{-g_{ii}/kT}}{\sum_j x_j \bar{V}_j e^{-g_{ii}/kT}} \quad (12)$$

where $\bar{V}_j$ is the molar volume of component j. It is seen from this equation that if $g_{ii} = g_{ij}$ for all values of j, the "local" volume fraction is equivalent to the average volume fraction and eq. 10 reduces to the Flory–Huggins equation. Substitution of eq. 12 into eq. 10 gives

the relation

$$\bar{G}^M/RT = \sum_i x_i \ln \frac{x_i \bar{V}_i e^{-g_{ii}/kT}}{\sum_j x_j \bar{V}_j e^{-g_{ii}/kT}} \quad (13)$$

from which the excess free energy of mixing is calculated to be

$$\tilde{G}^E/RT = -\sum_i x_i \ln \sum_j x_j (\bar{V}_j/\bar{V}_i) e^{-(g_{ij} - g_{ii})/kT} \quad (14)$$

If the following definition is made

$$A_{j/i} = 1 - (\bar{V}_j/\bar{V}_i) e^{-(g_{ii}-g_{ji})/kT} \quad (15)$$

where $A_{j/i}$ does not equal $A_{i/j}$ although g_{ji} does equal g_{ij}, then eq. 14 becomes equivalent to eq. 1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Vapor–Liquid Equilibrium. XII. The System Ethanol–Cyclohexane from 5 to 65°

BY GEORGE SCATCHARD AND FRANK G. SATKIEWICZ[1]

The vapor pressures of the system ethanol–cyclohexane have been measured by a static method for seven mixtures and five temperatures from 5 to 65°. They agree very well with the equation of Wilson with one parameter a linear function of the temperature and the other a quadratic. The corresponding values of the liquid and vapor compositions, and the excess free energy, enthalpy, entropy, and volume are tabulated and discussed.

Although the vapor–liquid equilibrium of the ethanol–cyclohexane system at 25° has been measured by Washburn and Handorf,[2] this system has not been studied with the same thoroughness and precision as similar mixtures of an alcohol and a nonpolar liquid. The deviations from ideality are large so that the differences in composition of liquid and vapor are sometimes very large, which makes this an excellent system to test both the method and the equation described in the previous papers.[3,4]

Materials.—Eastman Kodak cyclohexane (catalog No. 702) was purified in the 2.5-m. fractionating column in this Laboratory. Six top fractions of about 40 ml. each and two bottom fractions of about 100 ml. each were removed. The boiling point of the last top was 0.015° lower than that of the product; that of the last bottom was 0.003° higher.

U.S.I. absolute ethanol was purified in the 2.5-m. column and one top and one bottom fraction removed. The middle fraction was dehydrated by distilling under nitrogen from magnesium alcoholate in an all-glass apparatus according to the method of Lund and Bjerrum.[5]

The densities at 27°, d^{27}_4, were 0.77188 for cyclohexane and 0.78345 for ethanol to be compared with 0.77203, obtained by linear extrapolation from the measurements of Forziati, et al.,[6] at 20 and 25° for cyclohexane and 0.78334 measured by Osborne, et al.,[7] for ethanol.

For the vapor pressure measurements the components were degassed in the apparatus described by Taylor,[8] two of which were attached to the vapor pressure apparatus and operated continuously during the measurements, serving as reservoirs.

Densities and Differential Refractions.—The small difference between the densities of the components and the existence of a mixture of minimum density preclude the use of density measurements to determine the composition. So we used the indices of refraction determined interferometrically. The interferometer

readings and the densities were determined on the same mixtures of known composition.

The mixtures were prepared by introducing a predetermined volume of one component into a previously weighed 14-ml. flask fitted with a capillary stopcock. The flask was vented at a known temperature and weighed. The second component was added in the same way, the solutions were mixed thoroughly, and the flask was weighed again. Corrections were made for the loss of liquid to the vapor phase and for the displacement of vapor on addition of the second component, as well as the usual corrections for precise weighings.

The interferometric measurements were made in a Zeiss portable interferometer. Matched 4-mm. glass plates were inserted in the 5-mm. cells so that the optical path was 2×1 mm. More efficient clamps were designed to hold the covers tight and prevent evaporation and the temperature was regulated to 0.1° by circulating thermostated water through a flattened $1/8$-in. copper coil on the bottom of the water bath.

One component, usually that with index of refraction nearer that of the mixture, was introduced into one cell and then the mixture into the other. The zero-order (blackest) bands were lined up and drum readings taken. Readings were also taken for the neighboring bands along with a description of the chromatic fringes in order to help fix the zero-order bands. Readings could be made to 0.1 division or about 1/150 of a band width. The difference between ethanol and cyclohexane corresponded to 3520 scale divisions, which could not be read directly, but mixtures from 0.3 to 0.6 mole fraction could be read against either component.

Measurements were made at approximately 0.1 steps in mole fraction and for 0.05 ethanol. No attempt was made to determine the index of refraction itself, but the mole fraction was expressed directly in terms of scale divisions by a deviation curve from a cubic equation. For readings smaller than 2000 divisions the largest deviation in mole fraction from the curve is 0.0017 and the average is 0.0007.

The densities of these same solutions were measured in a 7-ml. pycnometer with a single capillary stem. In Table I are given the mole fraction, density, d^{27}_4, the molal volume change on mixing, $\bar{V}^M$, and the deviations, δ_v, from the equation

$$\bar{V}^M = \bar{V} - (58.7759 + 50.1737x_B) = x_B(1 - x_B)[2.278 + (1 - 2x_B)^2] \quad (1)$$

Vapor Pressures.—The vapor pressures were measured at five temperatures for the pure components and for seven mixtures in the apparatus described in paper X.[3] The vapor pressure is given in Table II as a function of the temperature and over-all composition, $z_B = (n_B + n'_B)/(n_A + n_B + n'_A + n'_B)$, in which n_i is the number of moles of component i in the liquid and n'_i the number in the vapor. The small correction for the number of moles of each component in the vapor phase of the recovery flask was made by the method of subsequent sections.

(1) Condensed from the Ph.D. Thesis of Frank G. Satkiewicz, M.I.T., 1958. See G. Scatchard, G. M. Wilson, and F. G. Satkiewicz, J. Am. Chem. Soc., **86**, 125 (1964), footnote 1.

(2) E. R. Washburn and B. H. Handorf, ibid., **57**, 441 (1935).

(3) G. Scatchard, G. M. Wilson, and F. G. Satkiewicz, ibid., **86**, 125 (1964).

(4) G. M. Wilson, ibid., **86**, 127 (1964).

(5) H. Lund and N. J. Bjerrum, Ber., **64**, 210 (1931).

(6) A. F. Forziati, A. R. Glasgow, E. B. Willingham, and F. G. Rossini, J. Research Natl. Bur. Standards, **36**, 129 (1946).

(7) N. S. Osborne, E. C. McKelvy, and H. W. Bearce, Bull. U. S. Bur. Standards, **9**, 328 (1913).

(8) R. K. Taylor, J. Am. Chem. Soc., **52**, 3577 (1930).