

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

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

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

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

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

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

If the following definition is made

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

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. SATKIEWICZ¹

RECEIVED SEPTEMBER 3, 1963

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, $x_B = (n_B + n'_B)/(n_A + n_B + n'_A + n'_B)$, 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).

TABLE I

x_B	VOLUME OF MIXING		
	d^{27}_A	\bar{V}^M , cc./mole	δv
0.0000	0.78345	0	0
.10195	.77810	0.27416	+0.00720
.20612	.77486	.43094	- .00072
.31404	.77273	.52169	+ .00109
.41569	.77140	.56464	+ .00432
.49729	.77072	.56957	\pm .00000
.53836	.77040	.57227	+ .00456
.60716	.77012	.55083	- .00357
.69580	.76994	.50476	- .00995
.79885	.77001	.41767	- .00585
.89642	.77038	.29339	+ .02347
.90211	.77043	.28214	+ .02382
.95347	.77089	.17790	+ .04033
1.00000	.77188	0	0

Equilibrium Phase Compositions.—The compositions of the liquid and vapor phases are calculated from the equations¹²

$$p = p_A^{(A)} x_A \exp(\bar{G}_A^E/RT + \delta_A) + p_B^{(B)} x_B \exp(\bar{G}_B^E/RT + \delta_B) \quad (8)$$

$$y_B = p_B^{(B)} x_B \exp(\bar{G}_B^E/RT + \delta_B)/p \quad (9)$$

in which p is the vapor pressure, $p_i^{(i)}$ is the vapor pressure of pure component i , x_i and y_i are its mole fractions in the liquid and vapor phase, \bar{G}_i^E is its excess molal chemical potential in the liquid or vapor phase, respectively.

$$-\delta_A = [(\beta_{AA} - \bar{V}_A)(p - p_A^{(A)}) + (2\beta_{AB} - \beta_{AA} - \beta_{BB})py^2_B]/RT \quad (10)$$

$$-\delta_B = [(\beta_{BB} - \bar{V}_B)(p - p_B^{(B)}) + (2\beta_{AB} - \beta_{AA} - \beta_{BB})py^2_A]/RT \quad (11)$$

The two excess chemical potentials must be consist-

TABLE II

z_B t , °C.	EQUILIBRIUM PRESSURES								
	0.0000	0.0919	0.2456	0.3933	0.5085	0.6140	0.7517	0.9030	1.0000
	16.798	36.772	46.229	48.324	48.752	48.915	48.960	48.482	36.457
5	43.990	83.536	103.281	107.827	108.847	109.918	109.172	107.463	77.511
20	103.210	174.829	212.348	227.324	223.231	223.815	223.264	217.968	150.641
35	221.200	340.289	405.908	421.889	425.117	425.810	423.418	408.416	271.960
50	437.724	623.068	729.931	756.346	761.130	760.846	753.048	713.491	461.259
					Δp				
5		-0.784	+0.021	+0.094	+0.016	-0.006	+0.001	-0.103	
20		-1.129	.030	.034	-.046	-.051	-.108	-0.614	
35		-0.798	.157	.255	+.050	+.058	-.075	-1.014	
50		-1.520	.040	.012	-.288	-.058	-.487	-0.468	
65		-1.402	.100	.125	+.255	-.066	-1.043	-1.702	

Virial Coefficients.—The interpretation of the measurements requires the virial coefficients of the vapors. Kretschmer and Wiebe⁹ have expressed their measurements of the second virial coefficient of ethanol by the three parameter equation

$$\beta_{AA} = -290 - 0.284 \exp(2730/T) \quad (2)$$

We have determined the parameters of an equation of the Berthelot type for cyclohexane from the measurements of Waelbrock¹⁰ as

$$\beta_{BB} = B_{BB} - A_{BB}/T^2 = 534 - 20.19 \times 10^7/T^2 \quad (3)$$

To determine the mixed coefficient, β_{AB} , we have used the method and constants of Scatchard and Ticknor¹¹ to determine first the parameters $B_{AA(n)}$ and $A_{AA(n)}$ for ethanol and then the interaction parameters by combining these with the parameters of cyclohexane

$$B_{AA(n)} = \bar{V}_A/1.360 = 4.34 \quad (4)$$

$$A_{AA(n)} = \bar{V}_A^2 r_A^s / 8.37 = 1.806 \times 10^7 \quad (5)$$

in which \bar{V}_A is the molal volume of liquid ethanol and r_A its refraction, $(n^2 - 1)/(n^2 + 2)$.

$$B_{AB} = (B_{AA}^{1/3(n)} + B_{BB}^{1/3})^3 / 8 = 59.3 \quad (6)$$

$$A_{AB}/B_{AB}^2 = (A_{AA(n)} A_{BB}/B_{AA(n)}^2 B_{BB}^2)^{1/2} = 5.193 \times 10^7 \quad (7)$$

The values of the second virial coefficients are listed in Table III.

TABLE III

t , °C.	SECOND VIRIAL COEFFICIENTS (L./MOLE)			
	$-\beta_{AA}$	$-\beta_{BB}$	$(2\beta_{AB} - \beta_{AA} - \beta_{BB})$	
5	5.48	2.07	6.33	
20	3.43	1.80	4.14	
35	2.28	1.59	2.90	
50	1.61	1.40	2.13	
65	1.20	1.23	1.64	

(9) C. B. Kretschmer and R. Wiebe, *J. Am. Chem. Soc.*, **76**, 2579 (1954).

(10) F. G. Waelbrock, *J. Chem. Phys.*, **23**, 749 (1955).

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

ent and are most conveniently analytical functions. We have chosen the form discussed in the previous paper⁴

$$\bar{G}^E/RT = -x_A \ln(1 - ax_B) - x_B \ln(1 - bx_A) \quad (12)$$

$$\bar{G}_A^E/RT = -\ln(1 - ax_B) + x_B \left[\frac{bx_B}{1 - bx_A} - \frac{ax_A}{1 - ax_B} \right] \quad (13)$$

$$\bar{G}_B^E/RT = -\ln(1 - bx_A) - x_A \left[\frac{bx_B}{1 - bx_A} - \frac{ax_A}{1 - ax_B} \right] \quad (14)$$

in which \bar{G}^E is the excess free energy per mole of liquid and a and b are functions of the temperature, but not of the composition.

The quantities x_B , y_B , a , and b must be determined from the measurements of z_B and p . We start at the lowest temperature where the pressures are so low that $x_B \simeq z_B$ and $\delta_A \simeq 0 \simeq \delta_B$, so

$$p = p_A^{(A)} x_A \exp(\bar{G}_A^E/RT) + p_B^{(B)} x_B \exp(\bar{G}_B^E/RT) \quad (15)$$

which gives a good first approximation. After the best values at the lowest temperature are determined, they serve as first approximations for the next higher temperature, etc. After this method has been applied at all the temperatures, it is repeated to give a and b as smooth functions of the temperature. We obtained

$$a = 0.0757 - 532.0/T + 6.71 \times 10^4/T^2 \quad (16)$$

$$b = -0.3420 - 120.71/T \quad (17)$$

The deviations of the measured pressures from those calculated are included in Table II. Except at the extreme concentrations the average deviation is less than one part per thousand. The 9 and 90% cyclohexane solutions show negative deviations at all temperatures. For the former at 5°, where the cyclohexane fraction in the vapor is six times that in the liquid, the discrepancy is 0.8 mm. or 2%. The fact that all deviations are

(12) G. Scatchard, G. Kavanagh, and L. B. Ticknor, *ibid.*, **74**, 3715 (1952).

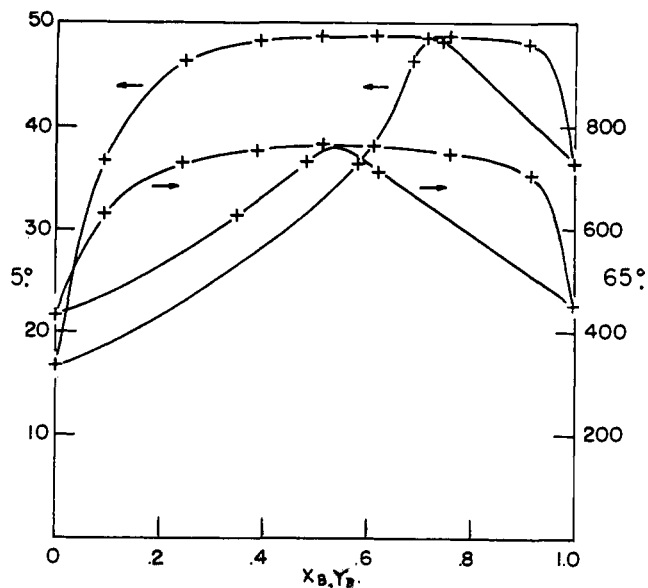


Fig. 1.—Vapor pressures vs. liquid and vapor compositions.

negative indicates that the error is not in the reading of pressure. It may be in failure to attain the equilibrium

TABLE IV
EQUILIBRIUM PHASE COMPOSITIONS

x_B	0.0919	0.2456	0.3933	0.5085	0.6140	0.7517	0.9030
$t, ^\circ\text{C.}$	x_B						
5	0.0918	0.2452	0.3929	0.5080	0.6142	0.7519	0.9041
20	.0910	.2441	.3920	.5077	.6138	.7524	.9045
35	.0899	.2429	.3912	.5075	.6175	.7534	.9061
50	.0886	.2413	.3903	.5072	.6148	.7555	.9094
65	.0874	.2395	.3894	.5076	.6166	.7589	.9142
	y_B						
5	0.5821	0.6811	0.7048	0.7131	0.7178	0.7222	0.7299
20	.5148	.6287	.6580	.6688	.6749	.6814	.6960
35	.4513	.5784	.6127	.6257	.6338	.6442	.6646
50	.3956	.5293	.5690	.5844	.5942	.6061	.6419
65	.3447	.4838	.5276	.5454	.5569	.5726	.6209
	$\log \alpha$						
5	1.1392	0.8179	0.5669	0.3815	0.2035	-0.0666	-0.5427
20	1.0253	.7196	.4748	.2919	.1160	-.1524	-.6167
35	0.9123	.6311	.3914	.2102	.0303	-.2272	-.6874
50	.8283	.5845	.3143	.1355	-.0375	-.3027	-.7483
65	.7398	.4737	.2434	.0659	-.1071	-.3710	-.8133

TABLE V
EXCESS QUANTITIES AT ROUND MOLE FRACTIONS

x_B	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95
$t, ^\circ\text{C.}$	\bar{G}^E/RT									
5	0.2118	0.3666	0.4757	0.5453	0.5770	0.5715	0.5261	0.4338	0.2788	0.1640
20	.2040	.3548	.4624	.5307	.5628	.5575	.5130	.4216	.2692	.1573
35	.1973	.3442	.4492	.5395	.5478	.5427	.4985	.4085	.2581	.1492
50	.1911	.3343	.4368	.5024	.5333	.5278	.4835	.3949	.2473	.1411
65	.1851	.3247	.4251	.4891	.5188	.5130	.4690	.3811	.2367	.1340
	\bar{H}^E/RT									
5	0.1472	0.2184	0.2522	0.2647	0.2637	0.2508	0.2351	0.2092	0.1681	0.1286
20	.1404	.2161	.2573	.2790	.2868	.2845	.2733	.2512	.2058	.1546
35	.1349	.2135	.2609	.2887	.3030	.3065	.2994	.2786	.2256	.1636
50	.1302	.2107	.2622	.2945	.3138	.3211	.3163	.2940	.2334	.1633
65	.1262	.2078	.2623	.2985	.3207	.3305	.3265	.3009	.2341	.1585
	$-\bar{S}^E/RT$									
5	0.0646	0.1482	0.2235	0.2806	0.3133	0.3207	0.2910	0.2346	0.1105	0.0354
20	.0636	.1387	.2051	.2517	.2760	.2730	.2397	.1704	.0634	.0027
35	.0624	.1307	.1883	.2508	.2448	.2362	.2091	.1299	.0325	-.0144
50	.0609	.1236	.1746	.2075	.2195	.2057	.1672	.1009	.0139	-.0222
65	.0590	.1169	.1628	.1906	.1981	.1825	.1425	.0802	.0026	-.0245

pressure, but reaching only the pressure corresponding to liquid composition a few tenths of a per cent further from that of the vapor. This is the direction to be ex-

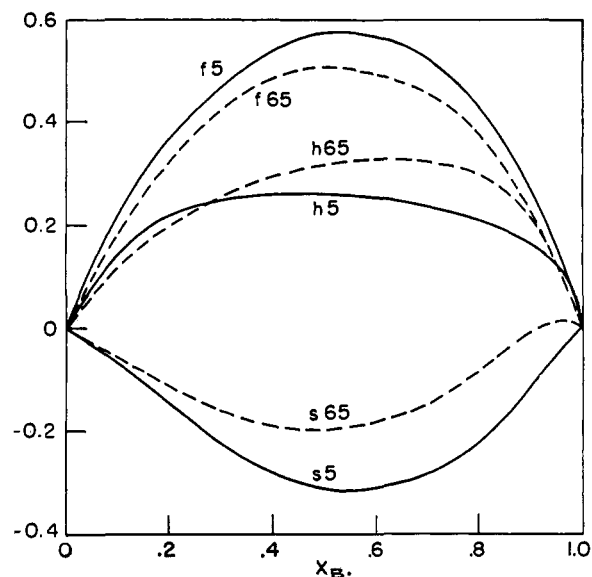


Fig. 2.—Thermodynamic functions at 5 and 65°C: $f = \bar{F}^E/RT$, $h = \bar{S}^E/RT$, $s = \bar{S}^E/R$.

pected of a systematic error. It may, of course, be partly due to the failure of a two-parameter equation to represent precisely the behavior of a system so near to separation into two phases. Vold and Washburn¹³ say that the critical mixing temperature is -15° , but we are unable to find their authority. The over-all agreement seems to us excellent.

The corresponding values of $x_B, y_B, \log \alpha = \log x_B y_A / x_A y_B$ are given in Table IV. The vapor pressures at 5 and at 65°C are plotted in Fig. 1 vs. the liquid and vapor compositions. This shows that the largest difference between the vapor and liquid composition is about 0.5, that at both temperatures the system very nearly separates into two liquid phases, and that the greatest change in this temperature range is in the ratio of the vapor pressures of the two components, which changes from 2.2 to 1.1.

Thermodynamic Functions.—The values of the excess functions per mole, $\bar{G}^E/RT, \bar{H}^E/RT$, and $-\bar{S}^E/R$, at even mole fractions are given at the five temperatures

in Table V, and the values at 5 and 65°C are plotted against the mole fraction in Fig. 2. Although \bar{G}^E/RT

(13) R. E. Vold and E. R. Washburn, *J. Am. Chem. Soc.*, **84**, 4217 (1932).

decreases slightly with increasing temperature, \bar{G}^E itself increases with the temperature except for very small concentrations of alcohol at the higher temperatures.

On the other hand, \bar{H}^E/RT increases with increasing temperature through most of the range.

These results may be compared with those for ethanol-methylcyclohexane mixtures. The excess free energy at 35° is almost identical with that measured by Kretschmer and Wiebe¹⁴ and the excess enthalpy lies between their value, calculated from vapor liquid equilibrium at 35 and 55°, and the presumably more accurate value determined calorimetrically by Brown, Fock, and Smith,¹⁵ which is approximately 30% lower than the earlier results. The enthalpies for cyclohexane mixtures are more symmetrical than those for methylcyclohexane and are closer to the calorimetric values

(14) C. B. Kretschmer and R. Wiebe, *J. Am. Chem. Soc.*, **71**, 3176 (1949).

(15) I. Brown, W. Fock, and F. Smith, *Australian J. Chem.*, **9**, 364 (1956).

for x_B greater than 0.4. It should be noted that the results for ethanol-isooctane^{16,17} at 25° are almost the same as for ethanol-methylcyclohexane, but in this case the two enthalpies agree well. The difference between the cyclohexane enthalpies and the others may be due to the absence of a methyl group.

If it is desired to determine the coefficients of the more usual expression obtained by expansion around the midpoint

$$\bar{F} = x(1-x)\Sigma F^{(n)}(2x-1)^n \quad (18)$$

in which \bar{F} is any excess molal quantity, the coefficients may be determined from the relation

$$[d^n[\bar{F}/x(1-x)]/dx^n]_{x=0.5} = n! 2^n F^{(n)} \quad (19)$$

Our expression gives an infinite series, and care must be taken to include enough terms so that the expression does not indicate separation into two phases.

(16) C. B. Kretschmer, J. Novakosvska, and R. Wiebe, *J. Am. Chem. Soc.*, **70**, 1785 (1948).

(17) I. Brown and W. Fock, *Australian J. Chem.*, **8**, 361 (1955). The values they calculate from the measurement of ref. 16 are very different.

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

Vapor-Liquid Equilibrium. XIII. The System Water-Butyl Glycol from 5 to 85°

BY GEORGE SCATCHARD AND GRANT M. WILSON¹

RECEIVED SEPTEMBER 3, 1963

The vapor pressures of the system water-butyl glycol have been measured by a static method for eight mixtures at five temperatures from 5 to 85°. They agree very well with the three-parameter equation of Wilson with one parameter a linear function of the reciprocal temperature, one a quadratic, and the third independent of the temperature. The corresponding values of the liquid and vapor compositions, and the excess free energy, enthalpy, and entropy are tabulated and discussed. Values in the literature of the vapor pressures at higher temperatures, of the directly measured excess enthalpy and heat capacity, and of the compositions of two liquid phases in equilibrium are compared with those calculated from our measurements.

The system water-*n*-butyl glycol (2-*n*-butoxyethanol-1, Butyl Cellosolve) has a particular interest because it has a closed miscibility gap. It is well suited to test our apparatus because the vapor pressure of *n*-butyl glycol is only 2.5 to 7.5% that of water so that the difference between the vapor and liquid compositions is sometimes very large.

Before our work started, the two-phase equilibrium had been studied by Cox and Cretcher² and by Poppe,³ by the latter also under high pressures; the vapor-liquid equilibrium under atmospheric pressure had been studied by Newman, Hayworth, and Treybal⁴; and some physical properties were given by Carbide and Carbon Chemicals Co.⁵ After our work had been completed, we learned that this system had been very thoroughly studied at the same time in the laboratory of Professor W. Jost, Göttingen.⁶⁻⁸ These studies give a much more rigorous test of our method.

We have measured the vapor-liquid equilibrium for eight mixtures of this system at 5, 25, 45, 65, and 85° in the apparatus described in paper X.⁹

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

(2) H. L. Cox and L. H. Cretcher, *ibid.*, **48**, 451 (1926).

(3) G. Poppe, *Bull. soc. chim. Belges*, **44**, 640 (1935).

(4) M. Newman, C. B. Hayworth, and R. E. Treybal, *Ind. Eng. Chem.*, **41**, 2039 (1949).

(5) "Cellosolve and Carbitol Solvents," Carbide and Carbons Chemicals Co., 1956.

(6) U. Onken, *Z. Elektrochem.*, **63**, 321 (1959).

(7) G. Schneider and G. Wilhelm, *Z. physik. Chem.*, **20**, 219 (1959).

(8) Diplomarbeiten of R. Rothe (1956) and of G. Schneider (1956).

We are very grateful to Professor Jost for sending us photostats of excerpts of the Dissertation of Onken (1958) and the Diplomarbeit of Rothe.

(9) G. Scatchard, G. M. Wilson, and F. G. Satkiewicz, *J. Am. Chem. Soc.*, **86**, 125 (1964).

TABLE I
DENSITIES AND MOLAL VOLUMES AT 27°

x_1	ρ	$-\bar{V}^E_{\text{measd}}$	$(\bar{V}^E_{\text{measd}} - \bar{V}^E_{\text{calcd}})$
0.0000	0.894735	0.0000	0.0000
.0762	.896915	.1435	.0000
.1300	.898621	.2408	+ .0004
.2126	.901528	.3785	- .0005
.3232	.906135	.5417	+ .0048
.3235	.906109	.5379	+ .0005
.4126	.910522	.6404	+ .0024
.5247	.917273	.7226	+ .0021
.6178	.924311	.7424	- .0011
.6190	.924400	.7415	- .0022
.7115	.933353	.7057	- .0054
.7119	.933406	.7059	- .0056
.8082	.946085	.5957	- .0017
.8121	.946747	.5912	+ .0003
.8990	.964336	.4200	+ .0302
.8991	.964393	.4207	+ .0313
.9377	.975652	.3194	+ .0594
.9785	.991303	.1831	+ .0835
.9896	.996433	.0997	+ .0502
1.0000	.996540	.0000	.0000

Materials.—The butyl glycol was prepared from the commercial material of Carbide and Carbon Chemicals Co. by repeated distillation at 45 mm. in a 4-ft. column packed with glass helices with dry nitrogen bubbling through the boiler. The midfraction of the fourth distillation was used. Its density, d_{27}^4 , was 0.89473 as distilled and 0.89460 after degassing. Linear interpolation of the measurements of Onken at 20 and 30° gives 0.89458.⁶

The water was collected hot under nitrogen from the still in this Laboratory.

The water was degassed in the storage bulb sealed into the apparatus by repeated expansion of the vapor into the vacuum manifold over a period of a month. The butyl glycol was evacuated in a Langmuir type diffusion pump with the intake end