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 Wiebe[14] 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

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

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

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

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.

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

BY GEORGE SCATCHARD AND GRANT M. WILSON[1]

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 Cretcher[2] 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 Treybal[4]; 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	$-\bar{V}^E_{measd}$	$(\bar{V}^E_{measd} - \bar{V}^E_{calcd})$
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

TABLE II

EQUILIBRIUM PRESSURES

z_1	0.0000	0.0743	0.1478	0.2140	0.3074	0.5072	0.6836	0.7885	0.8986	1.0000
t, °C.					p_{measd}					
5	0.161	1.399	2.432	3.285	4.243	5.641	6.173	6.357	6.436	6.537
25	0.852	5.404	9.225	12.338	15.909	20.996	23.092	23.568	23.965	23.743
45	3.455	17.219	28.880	38.253	49.324	64.984	70.211	72.476	72.887	71.858
65	11.511	46.671	76.757	101.136	130.20	171.86	188.22	191.46	(191.71)[a]	187.58
85	32.535	109.948	177.65	233.08	300.47	399.43	439.04	445.84	(446.14)[a]	433.57
Resid. press.	0.064	0.055	0.055	0.079	0.136	0.159	0.020	0.103	0.085	0.044
					$p_{measd} - p_{calcd}$					
5		+0.011	−0.014	+0.022	−0.001	+0.004	−0.034	+0.012	+0.046	
25		+ .041	− .029	+ .029	+ .002	− .067	− .073	± .000	+ .178	
45		+ .192	+ .023	+ .103	+ .180	+ .003	− .240	− .052	+ .509	
65		+ .42	+ .04	+ .14	+ .42	+ .21	− .38	− .09	.....	
85		+ .23	− .98	−1.23	− .26	+ .23	− .28	− .49	.....	

[a] Two liquid phases above 50.364°, where p is 95.648.

closed off. The line to the forepump was 4-mm. tubing to reduce loss of the glycol. The boiler was heated for 2 days in a water bath so as to give only surface evaporation. Degassing of either component was considered sufficient when the vapor which had been standing above it gave a pressure of 0.0001 mm. or less in the McLeod gage.

Compositions and Molal Volumes.—The compositions of the solutions from the cell were determined from the densities at 27°. Table I gives for the calibrating solutions, the mole fraction, density, excess molal volume, or volume change on mixing per mole, $\bar{V}^E$, and the difference between this volume and that calculated from the equation

$$\bar{V}^E = -x_1(1 - x_1)[2.828 + 2.435(x_1 - \tfrac{1}{2}) + 2.250(x_1 - \tfrac{1}{2})^2 + 2.125(x_1 - \tfrac{1}{2})^3] \quad (1)$$

Since the degassing decreased the density of the butyl glycol by 0.00014 and did not change that of water, the density of an unknown from the cell was corrected by adding 0.00014 times the weight fraction of butyl glycol.

Vapor Pressures.—The vapor pressures of the pure components and of eight mixtures at every 20° from 5 to 85° are given in Table II as functions of the over-all composition, z_1

$$z_1 = (n_1 + n_1')/(n_1 + n_1' + n_2 + n_2') \quad (2)$$

in which n_1 and n_2 are the numbers of moles of components 1 and 2 in the liquid and n_1' and n_2' the numbers 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.

Our vapor pressures of butyl glycol at 65 and 85° are 0.02 and 0.03% larger than those interpolated from the measurements of Rothe[8] at 60, 70, 80, and 90°. This difference corresponds to 0.05 and 0.09 mole % more water in our glycol than in his, and to density differences of 0.000014 and 0.000026. The average, 0.000020, is the difference between our density and Onken's. Although both differences are in the last place quoted, the agreement makes this explanation plausible. The 0.07 mole % is 0.01 weight %.

Virial Coefficients.—The second virial coefficient, β_{11}, of water was calculated from the equation of Keyes, Smith, and Gerry[10]

$$\beta = (T_c/p_c)\left[11.5 - \frac{42.70}{T/T_b} 10^{0.5813/(T/T_b)^2}\right] \quad (3)$$

$$\beta_{11} = 18\left[1.89 - \frac{2641.62}{T} 10^{80870/T^2}\right] \quad (4)$$

in which T_c and p_c are the critical temperature and pressure, and T_b is the boiling point.

(10) F. G. Keyes, L. B. Smith, and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **70**, 319 (1936).

No direct measurements were available for butyl glycol. We therefore used eq. 3 for it also. This equation agrees moderately well with the measurements on the alcohols,[11–13] and the agreement is better as T/T_b approaches the range of our measurements. The boiling points of methyl, ethyl, and butyl glycol (124.5, 135, 171°) are nearly the same as those of the corresponding alcohols with CH_2 replacing the ether O (118, 138, and 175°). The critical temperature and pressure of butyl glycol were unknown at the time of our measurements. Since $V/(T_c/p_c)$ in cc. atm./°K. is 6.05 for water, 6.18 for methanol, 7.13 for ethanol, 8.07 for isopropyl alcohol, and 7.93 for 1-butanol, we assumed that it is 8 for butyl glycol. So we used 16.4 for T_c/P_c and 444° for T_b in eq. 3. Schneider and Wilhelm later published $T_c = 643 \pm 5°$, $p_c = 38 \pm 0.5$ atm., which corresponds to 16.7 for T_c/p_c. The resulting difference in the virial coefficient would be well within the error of estimation.

The mixed coefficient β_{12} was calculated by assuming first that the polar and nonpolar parts of β_{11} and β_{22} are in the same ratio as in the energy of vaporization per unit volume as calculated by the method of Scatchard,[14] $(E/V)_{nonpolar} = 614 r^{5/3}$ cal./cc., in which $r = (n^2 - 1)/(n^2 + 1)$ and n is the index of refraction for the sodium D line. The nonpolar fraction was found to be 0.078 for water and 0.603 for butyl glycol.

The constant b_{12} was calculated from the relation

$$b_{12} = (b_{11}^{1/3} + b_{22}^{1/3})^3/8 \quad (5)$$

and the polar and nonpolar parts of $(\beta_{12} - b_{12})$ by the relation

$$(\beta_{12} - b_{12}) = [(\beta_{11} - b_{11})(\beta_{22} - b_{22})/\bar{V}_1\bar{V}_2]^{1/2}(\bar{V}_1\bar{V}_2) \quad (6)$$

The values of the virial coefficients at the temperatures of our measurements are given in Table III.

TABLE III

VIRIAL COEFFICIENTS (L./MOLE)

t, °C.	$-\beta_{11}$	$-\beta_{22}$	$-\beta_{12}$
5	1.860	33.40	7.65
25	1.260	19.90	4.78
45	0.907	12.90	3.30
65	.683	8.95	2.38
85	.533	6.53	1.80

Equilibrium Phase Compositions.—As in paper XII,[15] the equilibrium compositions of the liquid and vapor

(11) C. B. Kretschmer and R. Wiebe, *J. Am. Chem. Soc.*, **76**, 2579 (1954).
(12) O. R. Foz, J. Moicello, and A. Mendez, *Ann. R. Soc. Exp. F. S. Quim.*, **50B**, 17 (1954).
(13) J. Russell and O. Maas, *Can. J. Res.*, **5**, 436 (1931).
(14) G. Scatchard, *Chem. Rev.*, **44**, 7 (1949).
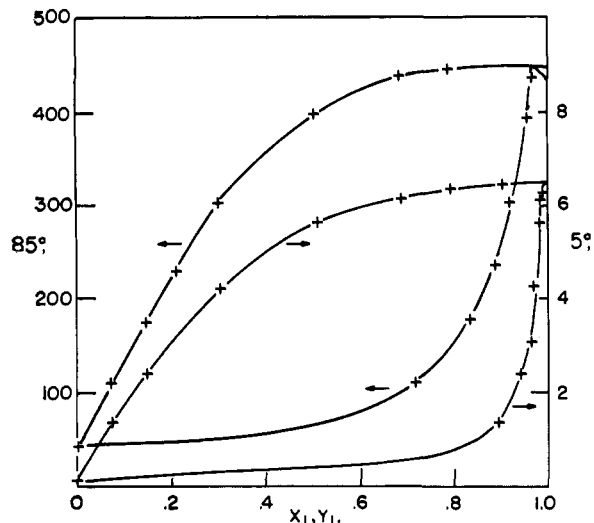(15) G. Scatchard and F. G. Satkiewicz, *J. Am. Chem. Soc.*, **86**, 130 (1964).

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

phases are calculated from the equations[16]

$$p = p_1{}^0 x_1 \exp(\bar{G}^E{}_1/RT + \delta_1) + p_2{}^0 x_2 \exp(\bar{G}^E{}_2/RT + \delta_2) \quad (7)$$

$$y_2 = p_2{}^0 x_2 \exp(\bar{G}^E{}_2/RT + \delta_2)/p \quad (8)$$

in which p is the vapor pressure, $p_i{}^0$ is the vapor pressure of pure component i, x_i and y_i are its mole fractions in the liquid and vapor phase, respectively, and $\bar{G}^E{}_i$ is its excess molal chemical potential (in either phase)

$$-\delta_1 = [(\beta_{11} - \bar{V}_1)(p - p_1{}^0) + (2\beta_{12} - \beta_{11} - \beta_{22})py_2{}^2]/RT \quad (9)$$

$$-\delta_2 = [(\beta_{22} - \bar{V}_2)(p - p_2{}^0) + (2\beta_{12} - \beta_{11} - \beta_{22})py_1{}^2]/RT \quad (10)$$

The two excess chemical potentials must be consistent and are most conveniently analytical functions. We have chosen the form discussed in paper XI[17]

$$\bar{G}^E/RT = -c[x_1 \ln (1 - ax_2) + x_2 \ln (1 - bx_1)] \quad (11)$$

$$\bar{G}^E{}_1/RT = -c\left[\ln (1 - ax_2) - x_2 \left(\frac{bx_2}{1 - bx_1} - \frac{ax_1}{1 - ax_2}\right)\right] \quad (12)$$

$$\bar{G}^E{}_2/RT = -c\left[\ln (1 - bx_1) + x_1 \left(\frac{bx_2}{1 - bx_1} - \frac{ax_1}{1 - ax_2}\right)\right] \quad (13)$$

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

The quantities x_2, y_2, a, b, and c must be determined from the measurements of p and z_2. We started at the lowest temperature where the pressures are so low that $x_2 \simeq z_2$ and $\delta_1 \simeq 0 \simeq \delta_2$. The pressure of butyl glycol is so much smaller than that of water that it is convenient for desk computations to start with py_2 and to determine py_1 by difference. It is not necessary to be so considerate of the time of an electronic computer. When approximate values of the parameters had been obtained for each temperature, they were smoothed for temperature to give

$$a = -0.4087 + 42.5/T \quad (14)$$

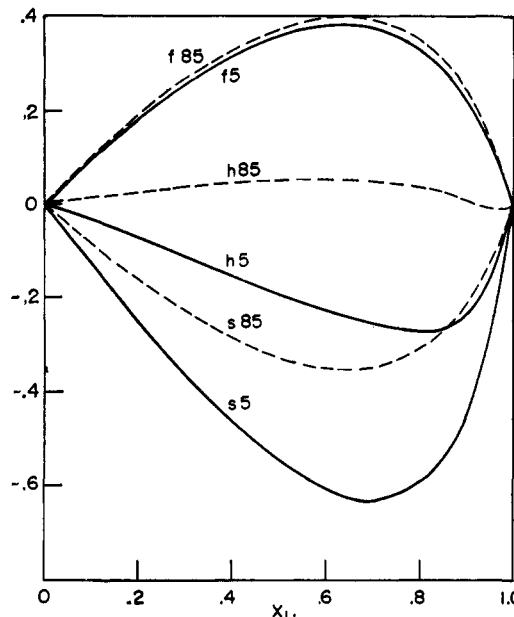$$b = 0.4335 + 364.7/T - 6.44 \times 10^4/T^2 \quad (15)$$

$$c = 1.465 \quad (16)$$

with $T = t + 273.16$.

The values of a and b at the temperatures of our experiments are given in Table IV.

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

(17) G. M. Wilson, ibid., 86, 127 (1964).

Fig. 2.—Thermodynamic functions at 5 and 85°: $f = \bar{F}^E/RT$, $h = \bar{H}^E/RT$, $s = \bar{S}^E/R$.

The deviations of the measured pressures from those calculated with these parameters are included in Table II. The agreement is good and no trends are apparent.

The corresponding values of x_1, y_1, and $\log \alpha_{12}p_2{}^0/p_1{}^0 = \log x_2 y_1/x_1 y_2 - \log p_1{}^0/p_2{}^0$ are given in Table V. The vapor pressures at 5 and at 85° are plotted in Fig. 1 vs. the liquid and vapor compositions. We see that the difference between the compositions of the liquid and vapor phases is sometimes more than 0.8. The chief differences between the results at the two temperatures arise from the facts that the ratio of the vapor pressure of pure butyl glycol to that of pure water increases from 0.025 at 5° to 0.075 at 85° and that at 85° there is separation into two liquid phases with x_1 equal to 0.81 and 0.98.

TABLE IV

PARAMETERS OF EQUATIONS 14 AND 15

t, °C.	5	25	45	65	85
$-a$	0.2559	0.2662	0.2751	0.2830	0.2900
b	0.91238	0.93235	0.94364	0.94883	0.94981

Thermodynamic Functions.—The values of $\bar{G}^E/RT$ calculated from eq. 11, of $\bar{H}^E/RT$ calculated from the corresponding equation

$$\bar{H}^E/RT = cx(1 - x) \left\{ \frac{da/d(1/T)}{1 - a(1 - x)} + \frac{db/d(1/T)}{1 - bx} \right\} \quad (17)$$

and those of

$$-\bar{S}^E/R = (\bar{G}^E - \bar{H}^E)/RT \quad (18)$$

are given in Table VI at rounded values of the mole fractions and at the five temperatures. The values at 5 and 85° are plotted in Fig. 2.

Discussion

Figure 1 shows the important characteristics of the vapor composition and equilibrium pressure as functions of the liquid composition. The details are shown in Tables II and III. The separation into two liquid phases shown in the 85° curve continues below 65° and the maximum pressure azeotrope persists below 25°. The wide spread between the vapor and liquid compositions is shown so clearly in the figure that only the non-ideal part of $\log \alpha_{12} = \log y_1 x_2/x_1 y_2$ is tabulated. The ideal part, $\log p_1{}^0/p_2{}^0$, varies from 1.6086 at 5° to 1.1247 at 85°. Like the thermodynamic function $\bar{G}^E/RT$ shown in Fig. 2 and Table IV, $\log \alpha_{12}p_2{}^0/p_1{}^0$

TABLE V
EQUILIBRIUM COMPOSITIONS

z_1	0.0743	0.1478	0.2140	0.3074	0.5072	0.6836	0.7885	0.8986
t, °C.					x_1			
5	0.0742	0.1477	0.2139	0.3073	0.5072	0.6836	0.7885	0.8986
25	.0741	.1473	.2135	.3069	.5068	.6834	.7884	.8986
45	.0734	.1465	.2125	.3058	.5061	.6833	.7882	.8985
65	.0724	.1446	.2105	.3036	.5046	.6822	.7878	....
85	.0703	.1413	.2067	.2992	.5016	.6806	.7870	....
					y_1			
5	0.8923	0.9432	0.9603	0.9721	0.9827	0.9864	0.9874	0.9880
25	.8526	.9206	.9441	.9606	.9755	.9806	.9819	.9819
45	.8103	.8957	.9261	.9477	.9673	.9742	.9757	.9752
65	.7665	.8684	.9061	.9332	.9583	.9670	.9690	....
85	.7193	.8380	.8836	.9168	.9481	.9591	.9616	....
				$-\log \alpha_{12} p_2^0/p_1^0$				
5	0.4057	0.3729	0.3404	0.2866	0.1335	−0.0828	−0.2862	−0.6400
25	.4140	.3816	.3491	.2960	.1402	− .0756	− .2818	− .6582
45	.4138	.3812	.3489	.2961	.1423	− .0751	− .2851	− .6708
65	.4115	.3792	.3463	.2936	.1412	− .0771	− .2869	....
85	.4054	.3728	.3396	.2871	.1342	− .0833	− .2986	....

shows very little change with temperature in the range of our measurements. Its maximum (most positive value) occurs at a lower temperature than that of $\bar{G}^E/RT$. This fact together with the fact that it becomes more positive rather than becoming larger in absolute value shows that the deviations from ideality in the vapor are making an important contribution.
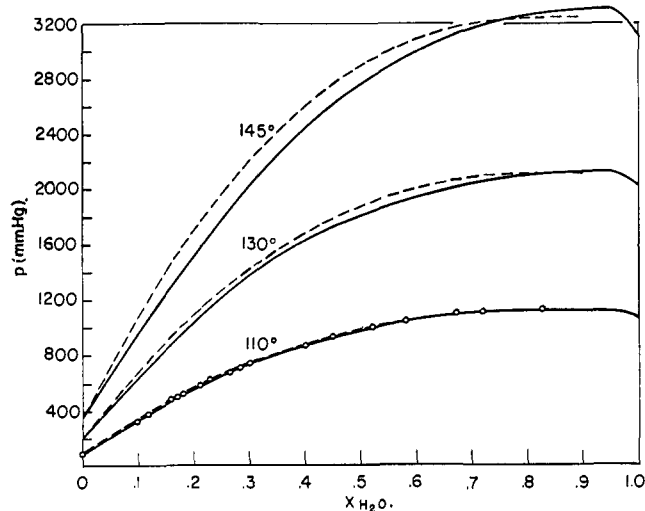

Fig. 3.—Total pressure at higher temperatures: ———, measured, Schneider and Wilhelm; − − − −, calculated, this paper.
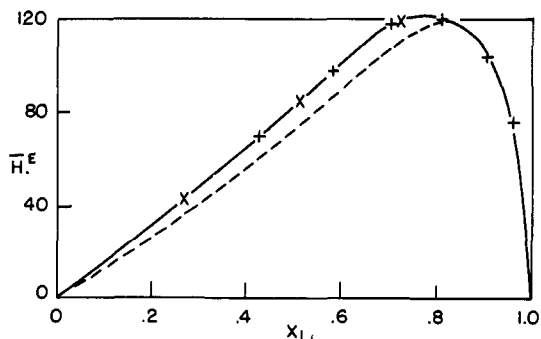

Fig. 4.—Excess enthalpy at 20°: +, measured; ×, interpolated, Onken; − − − −, calculated, this paper.

The behavior of the thermodynamic properties of the liquid is shown best by that of $\bar{H}^E/RT$ in Fig. 2 and Table IV. At 45° and lower temperatures $\bar{H}^E/RT$ is negative with a minimum near $x_1 = 0.8$. At 65° it is

positive for x_1 less than 0.6, and at 85° it is positive to about 0.92, but it is not yet very large.

Schneider and Wilhelm[7] present the vapor pressure as a function of liquid composition from 0 to 65° for seven mixtures with $x_1 = 0.7 - 1.0$, p and α_{12} over the whole composition range at 110° and p, by graph only, at 130 and 145°. Rothe[8] gives the total pressure and
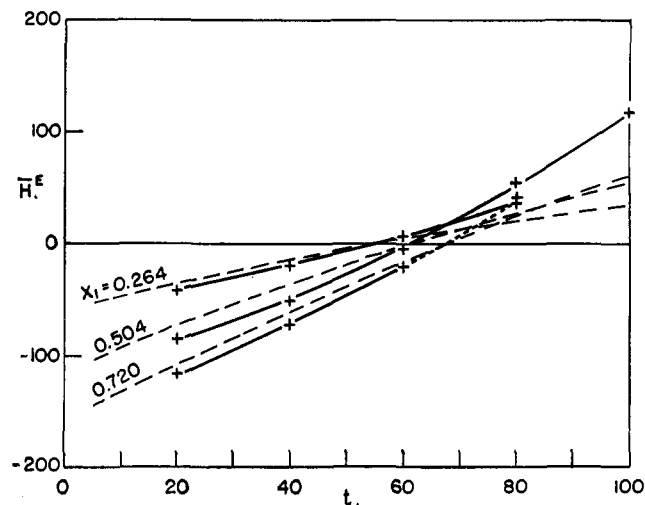

Fig. 5.—Excess enthalpy as function of temperature: ———, measured, : : : :, extrapolated, Onken; − − − −, calculated, this paper.

α_{12} over the whole composition range at 60, 70, 80, 90, and 100°, and some measurements at higher temperatures. The measurements at the lower temperatures agree with calculations from our equation within their apparent precision except for Rothe's α_{12} at 90°, which is inconsistent with their other measurements. A more interesting comparison is that of the measurements at higher temperatures with extrapolated values from our equation shown in Fig. 3. At 110° the agreement is very good, but our equations give results in the glycol-rich region about 5% too high at 130° and 10% high at 145°. Part of the discrepancy may arise from the calculation of the second virial coefficient of glycol, β_{22}, or even from the assumption that the higher coefficients may be neglected at pressures near four atmospheres.[18]

(18) In calculating thermodynamic quantities, Schneider and Wilhelm use values of β_{22} much smaller than ours. They also take $\beta_{12} = (\beta_{11} + \beta_{22})/2$. We believe that our values for β_{22} and β_{12} are both much more probable than theirs.

TABLE VI

EXCESS QUANTITIES AT ROUND MOLE FRACTIONS

x_1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
t, °C.					$\bar{G}^E/RT$				
5	0.0958	0.1815	0.2555	0.3154	0.3576	0.3789	0.3715	0.3250	0.2190
25	.0976	.1853	.2613	.3234	.3682	.3916	.3859	.3406	.2330
45	.0983	.1868	.2639	.3270	.3731	.3976	.3935	.3431	.2414
65	.0982	.1866	.2641	.3276	.3742	.3993	.3960	.3524	.2450
85	.0976	.1858	.2627	.3260	.3731	.3979	.3949	.3518	.2450
					$\bar{H}^E/RT$				
5	−0.0349	−0.0716	−0.1098	−0.1534	−0.1884	−0.2258	−0.2573	−0.2726	−0.2409
25	− .0176	− .0374	− .0598	− .0833	− .1044	− .1347	− .1592	− .1763	− .1666
45	− .0043	− .0108	− .0196	− .0309	− .0444	− .0598	− .0763	− .0909	− .0931
65	.0063	.0104	.0117	.0107	.0070	− .0007	− .0082	− .0187	− .0270
85	.0145	.0267	.0365	.0436	.0479	.0491	.0467	.0402	.0028
					$-S^E/R$				
5	0.1307	0.2531	0.3653	0.4688	0.5460	0.6047	0.6288	0.5976	0.4599
25	.1156	.2227	.3211	.4067	.4726	.5263	.5451	.5169	.3996
45	.1026	.1976	.2835	.3579	.4175	.4574	.4698	.4340	.3345
65	.0919	.1762	.2524	.3169	.3672	.3986	.4042	.3711	.2720
85	.0831	.1591	.2262	.2824	.3752	.3488	.3482	.3116	.2169

Our calculation of the temperature variation of $\bar{G}^E/RT$ may be tested more directly by the calorimetric measurements of Onken,[6] who measured the excess enthalpy at 20° over the whole composition range and the excess heat capacity over a considerable temperature range for mixtures with x_1 about 0.25, 0.5, and 0.75. His values for $\bar{H}^E$ at 25° and the curve calculated from our equation are shown in Fig. 4, and the values at the three compositions over a temperature range are given in Fig. 5. For x_1 equal to 0.8 or larger the agreement in $\bar{H}^E$ is excellent, but at smaller values our calculations are about 10% smaller. Figure 5 shows that this 10% difference is also in $\bar{C}^E{}_p$, for each of the three calculated curves of $\bar{H}^E$ intercepts the zero axis at the same temperature as the corresponding curve from the measurements. There is no obvious reason why the absolute value of the calculated $\bar{H}^E$ should be more accurate when it is zero than at any other temperature, except that it is not far from the middle of our temperature range.

One of the most severe tests of an analytical expression for the free energy is the prediction of separation into two liquid phases, which requires an inflection in the curve for free energy of mixing, $\bar{G}^M$, vs. mole fraction. The difficulty is especially great if both phases are rich in the same component, as in this system. Figure 6 shows the closed miscibility gap calculated from our equation and the measurements of Cox and Cretcher,[2] of Poppe,[3] and the limits of the gap given by Schneider and Wilhelm.[7] The quantitative agreement is not good, but considering that the equation is derived from an entirely different equilibrium, we find very satisfying the prediction of a closed immiscibility gap in approximately the right region.

The apparatus described in paper X[9] has enabled us to measure the vapor pressure of water–butyl glycol

solutions with considerable precision and without significant systematic error. The equation presented in paper XI[17] represents these results precisely and gives
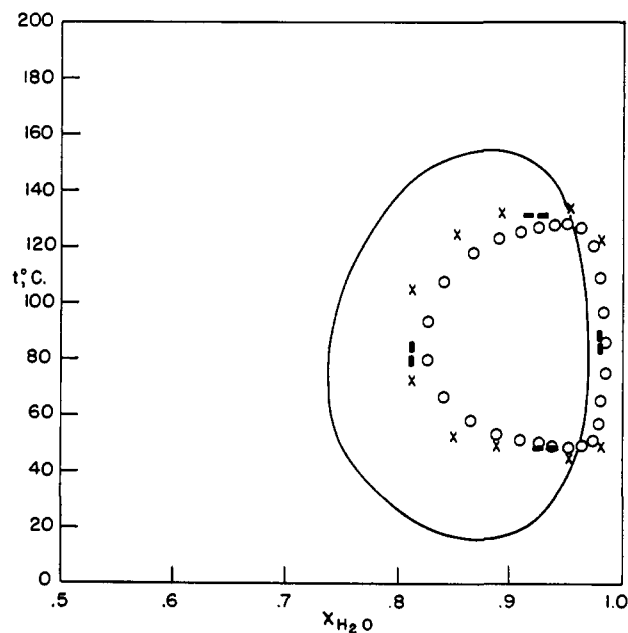

Fig. 6.—Immiscibility gap: comparison of experiments with calculations from vapor–liquid equilibrium: ■ ■, ref. 7; ✕, ref. 3; O, ref. 2; ———, calculated from vapor–liquid equilibrium.

the heat of mixing and even the range of the closed immiscibility gap to a satisfying approximation.