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Thermodynamic Excess Properties for Ethanol–*n*-Heptane

H. C. VAN NESS, C. A. SOCZEK[1], and N. K. KOCHAR[2]
Chemical Engineering Department, Rensselaer Polytechnic Institute, Troy, N. Y.

Thermodynamic property changes of mixing, both total and partial, are presented as functions of temperature and composition for the binary liquid system ethanol–*n*-heptane. Results are applied to the calculation of vapor-liquid equilibria at atmospheric pressure.

IN A RECENT paper (*14*) correlations were presented for the property changes of mixing ΔC_p, ΔH, ΔS^E, and ΔG^E as functions of temperature at a series of compositions for the ethanol-toluene, 1-propanol-*n*-heptane, and 2-propanol-*n*-heptane systems. This paper is devoted to a similar correlation of an extensive set of data for the binary liquid system ethanol-*n*-heptane. No attempt is made here to relate these data to any theory of molecular interactions. However, in another publication (*15*) the heat-of-mixing data reported are used in conjunction with infrared spectral data to determine the nature of ethanol association in hydrocarbon solutions.

It is assumed that the heat capacity change of mixing for a solution of given composition is given as a function of temperature by:

$$\frac{\Delta C_p}{x_1x_2R} = A + BT + DT^2 \qquad \text{(constant composition)} \qquad (1)$$

The following equations then result from basic thermodynamic relations (*12*):

$$\frac{\Delta H}{x_1x_2R} = AT + \frac{BT^2}{2} + \frac{DT^3}{3} + C \qquad (2)$$

$$\frac{\Delta G^E}{x_1x_2R} = -AT\ln T - \frac{BT^2}{2} - \frac{DT^3}{6} + C + IT \qquad (3)$$

$$\frac{\Delta S^E}{x_1x_2R} = A\ln T + BT + \frac{DT^2}{2} + (A - I) \qquad (4)$$

where T is the absolute temperature, and A, B, C, D, and I are constants. B has the dimensions of T^{-1}; D, the dimensions of T^{-2}; and C, the dimensions of T. A and I are dimensionless.

If the property changes of mixing ΔC_p, ΔH, ΔG^E, and ΔS^E of Equations 1 through 4 are each represented by ΔM, then the corresponding partial molar property changes of mixing are designated $\overline{\Delta M}_i$, where by definition

$$\overline{\Delta M}_i = \frac{\partial(n\Delta M)}{\partial n_i}$$

The temperature dependence of these partial molar property changes of mixing is given by equations analogous to Equations 1 through 4, namely:

$$\frac{\overline{\Delta C}_{p_i}}{R} = A_i + B_iT + D_iT^2 \qquad (5)$$

$$\frac{\overline{\Delta H}_i}{R} = A_iT + \frac{B_iT^2}{2} + \frac{D_iT^3}{3} + C_i \qquad (6)$$

$$\frac{\overline{\Delta G}_i^E}{R} = -A_iT\ln T - \frac{B_iT^2}{2} - \frac{D_iT^3}{6} + C_i + I_iT \qquad (7)$$

and

$$\frac{\overline{\Delta S}_i^E}{R} = A_i\ln T + B_iT + \frac{D_iT^2}{2} + (A_i - I_i) \qquad (8)$$

Since the total property changes of mixing for a binary system are obtained from partial molar values according to the relation:

$$\Delta M = x_1\overline{\Delta M}_1 + x_2\overline{\Delta M}_2$$

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[1] Present address: E. I. du Pont de Nemours and Co., Deep Water, N. J.
[2] Present address: The Lummus Co., Newark, N. J.

the five constants in Equations 1 through 4 are related to those in Equations 5 through 8 by equations of the form:

$$K = \frac{x_1K_1 + x_2K_2}{x_1x_2} \tag{9}$$

The constants in these equations have been determined for ethanol-*n*-heptane at a series of compositions from heat-of-mixing data as a function of temperature and from solution vapor pressure data at a single temperature. The ethanol used in this work was reagent quality, 200 proof, and was supplied by U. S. Industrial Chemicals. The *n*-heptane was the pure grade of Phillips Petroleum Co. Chromatographic analyses showed only trace impurities, and these materials were used without further purification.

The experimental heat-of-mixing data, covering a temperature range from 10° to 75° C., were determined by isothermal calorimetry (*11*), and are given in Table I. A typical set of data is shown in Figure 1, and the correlation of data with temperature is illustrated in Figure 2. These data are sufficiently precise to allow reliable partial molar heats of mixing to be determined, and the temperature range is adequate to permit the least-square fitting of these partial molar values by Equation 6. The constants so derived, for ethanol and for *n*-heptane, are given in Table II.

The remaining constants I_1 and I_2 were determined from vapor-liquid equilibrium data at 30° C. Total solution vapor pressures were measured as a function of liquid composition (*7*), and are given in Table III. These isothermal *P-x* data were used for numerical integration of the coexistence equation (*12*). The resulting *P-x-y* data allowed calculation of the liquid-phase activity coefficients:

$$\begin{aligned} \ln \gamma_1 &= \ln \frac{y_1P}{x_1P_1} + \frac{(B_{11} - V_1^L)(P - P_1) + P\delta_{12}y_2^2}{RT} \\ \ln \gamma_2 &= \ln \frac{y_2P}{x_2P_2} + \frac{(B_{22} - V_2^L)(P - P_2) + P\delta_{12}y_1^2}{RT} \end{aligned} \tag{10}$$

Since $\ln \gamma_i = \overline{\Delta G_i^E}/RT$, values of I_1 and I_2 were then calculated by Equation 7, and are listed in Table II. For convenience, Table IV is included to give the constants for calculation of the total excess functions. These result from Equation 9.

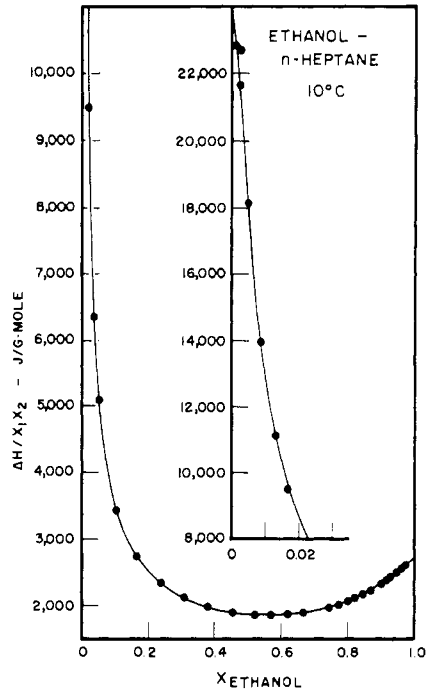


Figure 1. Heat-of-mixing data for ethanol–*n*-heptane at 10° C.

Klesper (*5*) has recently reported values of ΔC_p, ΔH, ΔS^E, and ΔG^E for ethanol-*n*-heptane at four compositions in the same temperature range covered by the present correlation. His results for ΔC_p and ΔH were determined from heat capacity measurements over the temperature range 20° to 70° C. and from heats of mixing at 20° C. His values for ΔG^E were calculated from solution vapor pressures over the temperature range 30° to 60° C., and his ΔS^E values were calculated from the equation $\Delta G^E = \Delta H - T\Delta S^E$.

The solid lines of Figures 3 and 4 represent the present correlation, whereas the filled circles show the data reported

Table I. Experimental Heat-of-Mixing Data (Joules/Gram Mole) Ethanol(1)–*n*-Heptane(2)

10° C.		30° C.		45° C.		60° C.		75° C.	
x_1	$\Delta H/x_1x_2$	x_1	$\Delta H/x_1x_2$	x_1	$\Delta H/x_1x_2$	x_1	$\Delta H/x_1x_2$	x_1	$\Delta H/x_1x_2$
0.0000	(23800)[a]	0.0000	(23600)	0.0000	(23350)	0.0000	(22900)	0.0000	(22100)
0.0010	22830	0.0035	22420	0.0093	21020	0.0112	21720	0.0113	21540
0.0023	21650	0.0054	21510	0.0150	19220	0.0190	20300	0.0190	20900
0.0047	18150	0.0075	20280	0.0199	17670	0.0261	18750	0.0295	19690
0.0085	13950	0.0102	18500	0.0268	15620	0.0304	17840	0.0374	18680
0.0130	11120	0.0141	16210	0.0384	13080	0.0349	16950	0.0830	13950
0.0168	9490	0.0281	11440	0.0533	10900	0.0453	15190	0.1208	11650
0.0335	6350	0.0530	7940	0.0729	9160	0.0562	13630	0.1666	9893
0.0496	5077	0.0894	5880	0.0946	7915	0.0727	12030	0.2352	8309
0.1025	3430	0.1351	4686	0.1207	6908	0.0940	10480	0.3026	7336
0.1644	2737	0.1882	3947	0.1793	5569	0.1187	9260	0.3657	6706
0.2395	2329	0.2409	3498	0.2463	4727	0.1461	8293	0.4901	5906
0.3084	2116	0.2974	3175	0.3569	3959	0.1844	7316	0.5794	5552
0.3807	1980	0.4243	2752	0.4695	3536	0.2395	6395	0.6544	5354
0.4536	1897	0.5373	2569	0.5755	3315	0.3061	5658	0.7555	5184
0.5221	1862	0.6562	2508	0.6673	3225	0.3797	5113	0.8076	5153
0.5713	1857	0.7779	2568	0.7079	3210	0.4569	4722	0.8866	5186
0.6190	1869	0.8468	2682	0.7785	3234	0.5297	4463	0.9211	5226
0.7438	1973	0.9135	2852	0.8632	3335	0.5998	4291	1.0000	(5390)
0.8221	2111	0.9540	2998	0.9444	3532	0.6629	4188		
0.9170	2383	1.0000	(3180)	1.0000	(3730)	0.7475	4132		
0.9599	2560					0.8021	4134		
1.0000	(2730)					0.9065	4245		
						1.0000	(4470)		

[a] Values in parentheses are extrapolated.

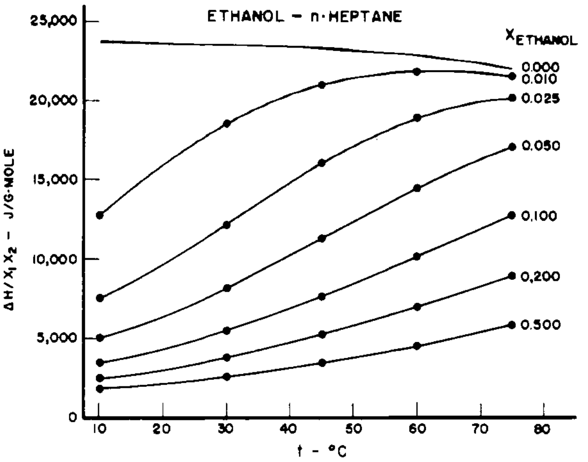


Figure 2. Heats of mixing for ethanol–*n*-heptane as a function of temperature

Table III. Experimental Vapor Pressures, Ethanol–*n*-Heptane at 30° C.

x_{EtOH}	P, Mm. of Hg.
0.000	58.7
0.0156	94.2
0.0187	98.6
0.0216	101.0
0.0388	105.4
0.0518	108.4
0.0953	114.6
0.1464	117.6
0.3095	121.2
0.5260	122.1
0.6542	121.9
0.7203	121.1
0.7662	120.1
0.8072	118.9
0.8710	115.4
0.9265	107.4
0.9303	106.8
0.9630	98.2
0.9860	88.0
1.0000	78.8

by Klesper. The agreement shown is on the whole very good, being best in the case of ΔG^E and, as would be expected, poorest for ΔC_p. The ΔC_p values reported here result from differentiation of heat-of-mixing data with respect to temperature, and an order-of-magnitude loss of accuracy results from the differentiation. On the other hand, determination of ΔC_p from heat capacity measurements requires the subtraction of two relatively large numbers to give a small difference:

$$\Delta C_p = C_p - (x_1 C_{p_1} + x_2 C_{p_2})$$

Accuracy in the C_p measurements to an order of 0.1%, as claimed by Klesper, can lead to errors in ΔC_p of as much as 20%. Only at low ethanol concentrations does the discrepancy between the two sets of ΔC_p data approach this value. At this end of the composition range, $x_{EtOH} < 0.05$, the heats of mixing change at an extraordinary rate with composition, and this makes accurate experimental measurements most difficult. Thus, the ΔH values reported here for this composition range may well be less accurate than the 1% figure generally claimed for the calorimeter used. Nevertheless, correlation of ΔH values with temperature leads to smooth curves, as shown in Figure 2. This figure also indicates that ΔC_p becomes negative at very low ethanol concentrations, and increasingly so at higher temperatures. Direct experimental confirmation of this tentative conclusion will not be easy.

Calculation of isothermal vapor-liquid equilibria from Equations 7 and 10 is straight-forward because the ln γ_i

Table II. Constants in Equations 5 through 8 Ethanol(1)–*n*-Heptane(2)

For Ethanol

x_1	A_1	B_1, °K.$^{-1}$	C_1, °K.	D_1, °K.$^{-2}$	I_1,
0.000	29.7352	−0.103832	−1397.43	0.0	162.6251
0.010	−1460.0895	10.255466	135407.63	−0.017498354	−7499.9473
0.025	−1435.7320	8.982016	150802.74	−0.013744496	−7547.5500
0.050	501.2963	−3.481182	−48574.06	0.006131569	2593.5697
0.075	−58.6638	0.217463	8070.93	0.0	−326.6494
0.100	−45.9030	0.169127	6376.98	0.0	−255.7116
0.200	−21.4042	0.079078	2999.10	0.0	−118.8226
0.300	−12.9738	0.047992	1830.84	0.0	−71.8810
0.400	−8.5010	0.031390	1211.10	0.0	−47.0671
0.500	−6.3378	0.022851	928.63	0.0	−35.2773
0.600	−4.1832	0.014887	626.95	0.0	−23.3573
0.700	−2.7783	0.009748	423.83	0.0	−15.5707
0.800	−0.7827	0.002780	127.63	0.0	−4.3533
0.900	−0.2274	0.000764	40.24	0.0	−1.2794
0.950	−0.0455	0.000150	8.86	0.0	−0.2551
0.975	−0.0064	0.000023	1.41	0.0	−0.0347

For *n*-Heptane

x_1	A_2	B_2, °K.$^{-1}$	C_2, °K.	D_2, °K.$^{-2}$	I_2
0.01	17.3068	−0.111185	−1772.20	0.000176751	90.5966
0.025	−4.0949	0.043075	170.06	−0.000095603	−18.8856
0.050	−68.9655	0.456387	6910.95	−0.000747907	−359.1318
0.075	2.2272	−0.004866	−414.37	0.0	13.4063
0.100	0.8560	0.000159	−225.32	0.0	5.7321
0.200	−3.5929	0.016265	398.22	0.0	−19.2040
0.300	−5.9022	0.024973	712.20	0.0	−31.992
0.400	−8.3280	0.033955	1049.10	0.0	−45.4577
0.500	−10.1054	0.040962	1281.51	0.0	−55.1484
0.600	−12.6150	0.050297	1630.99	0.0	−69.0048
0.700	−14.7086	0.058139	1930.47	0.0	−80.5214
0.800	−19.6627	0.075656	2662.92	0.0	−108.2672
0.900	−22.8113	0.087117	3159.08	0.0	−125.6902
0.950	−24.9383	0.094282	3531.54	0.0	−137.6653
0.975	−25.9017	0.097428	3716.19	0.0	−143.0834
1.000	−26.2433	0.098736	3801.13	0.0	−144.8681

Table IV. Constants in Equations 1 through 4 Ethanol(1)–*n*-Heptane(2)

x_1	A	B, ° K.$^{-1}$	C, ° K.	D, ° K.$^{-2}$	I
0.000	29.7352	−0.103832	−1397.43	0.0	162.6251
0.010	255.8388	−0.759415	−40444.83	0.0	1483.9559
0.025	−1636.3429	10.935328	161472.22	−0.017921030	−8496.4992
0.050	−851.6306	5.463329	87088.34	−0.008503864	−4452.5624
0.075	−33.7240	0.170209	3200.42	0.0	−174.3832
0.100	−42.4430	0.189512	4832.35	0.0	−226.8033
0.200	−44.7196	0.180174	5739.96	0.0	−244.5481
0.300	−38.2080	0.151804	4989.50	0.0	−209.3280
0.400	−34.9884	0.137205	4641.25	0.0	−192.0894
0.500	−32.8866	0.127625	4420.30	0.0	−180.8514
0.600	−31.4829	0.121048	4285.68	0.0	−173.4012
0.700	−30.2733	0.115551	4170.59	0.0	−166.9331
0.800	−28.4917	0.108472	3966.83	0.0	−157.1004
0.900	−27.6195	0.104442	3912.52	0.0	−152.4498
0.950	−27.1612	0.102244	3894.66	0.0	−150.0124
0.975	−26.8208	0.100832	3867.85	0.0	−148.1416
1.000	−26.2433	0.098736	3801.13	0.0	−144.8681

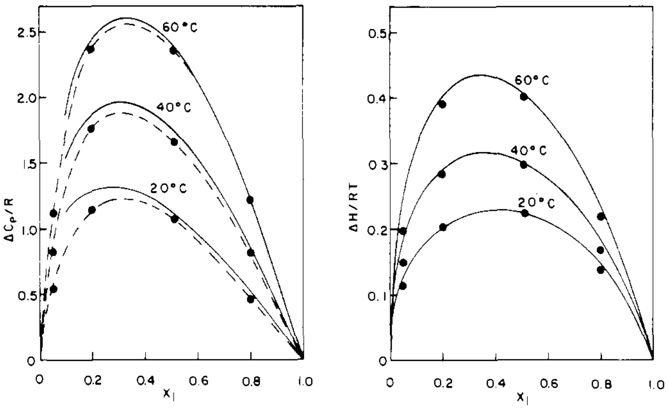


Figure 3. Heat capacity and enthalpy changes of mixing for ethanol–*n*-heptane

— Present correlation

● Data of Klesper (5)

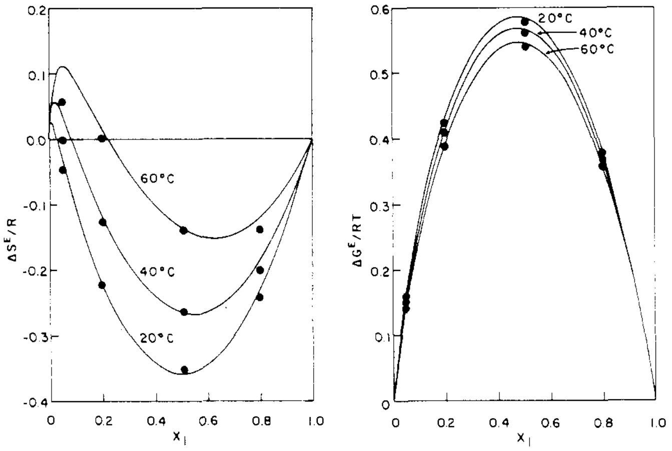


Figure 4. Excess entropies and Gibbs functions of mixing for ethanol–*n*-heptane

— Present correlation

● Data of Klesper (5)

values are given in this case by Equation 7. Such calculations have been made and the results are reported by Kochar (*6*) at 30°, 40°, 50°, and 60° C. Moreover, he compared computed results with the raw *P-x* data, and found good agreement, demonstrating the thermodynamic consistency of all data.

With $\ln \gamma_i = \overline{\Delta G_i^E}/RT$ expressed directly as a function of temperature by Equation 7, it becomes practical to compute isobaric *T-x-y* data by means of Equation 10. One must also express the virial coefficients and the pure-component vapor pressures as functions of *T*. The Antoine equation was used in this work for representing vapor pressures: $\log_{10} P = a - b/(t + c)$ where $t =$ ° C. and $P =$ mm. of Hg. The constants used are

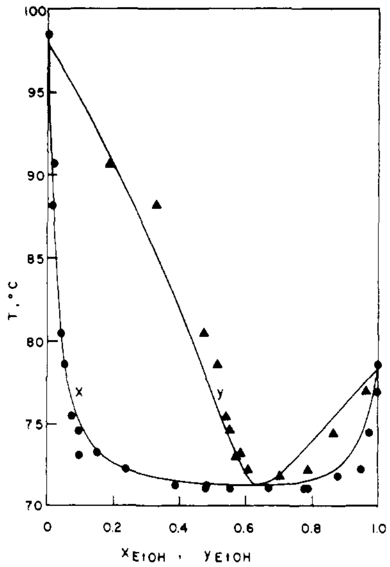
	a	b	c
Ethanol(1)	8.295981	1699.501	235.539
n-Heptane(2)	7.080171	1363.355	226.669

The virial coefficients, which appear only in small correction terms, were interpolated numerically from sets of values based on the data of McGlashan and Potter (*8*) for heptane and on generalized correlations for ethanol and the cross coefficient (*1, 2, 10*). The solution of Equation 10 is best carried out by an iterative procedure (*6*) with a computer. Results so determined for the ethanol–*n*-heptane system at 760 mm. of Hg are given in Table V and in Figures 5 and 6, where the experimental data of Katz and Newman (*4*) are included for comparison.

In the region where the greatest extrapolation of the present data is required ($x_{\text{EtOH}} < 0.1$ and $T > 75°$ C.), the comparison of results is at least as good as where no extrapolation is necessary. The little hook at the left end

Table V. Phase Equilibria at 760 Mm. of Hg. Ethanol(1)–*n*-Heptane(2)

x_1	y_1	T, ° C.	$\ln \gamma_1$	$\ln \gamma_2$
0.000	0.0000	98.0	(2.29)	0.0000
0.010	0.1669	92.07	2.321	0.0000
0.025	0.3371	85.04	2.364	0.0013
0.050	0.4667	78.81	2.226	0.0105
0.075	0.5110	76.30	2.007	0.0275
0.100	0.5396	75.01	1.818	0.0474
0.200	0.5853	72.62	1.304	0.1391
0.300	0.6029	71.84	0.9601	0.2541
0.400	0.6140	71.49	0.7050	0.3916
0.500	0.6250	71.28	0.5083	0.5527
0.600	0.6302	71.22	0.3370	0.7642
0.700	0.6495	71.25	0.2116	0.9971
0.800	0.6834	71.57	0.1109	1.3015
0.900	0.7449	72.65	0.0342	1.7345
0.950	0.8214	74.31	0.0106	2.024
0.975	0.8869	75.78	0.0028	2.220
1.000	1.0000	78.3	0.0000	(2.45)



◄ Figure 5. Phase equilibria for ethanol-*n*-heptane at 760 mm. of Hg

Curves computed from the present correlation, points from Katz and Newman (*4*)

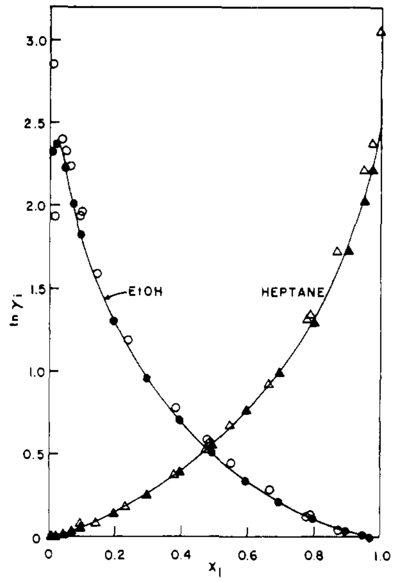


Figure 6. Activity coefficients for ethanol-*n*-heptane at 760 mm. of Hg

● ▲ Present correlation

○ △ Reported by Katz and Newman (*4*)

Table VI. Data for the Calculation of ϵ at 760 Mm. of Hg

x_1	t, ° C.	$\Delta H/RT$	$d\ln T/dx_1$	ϵ
0.00	98.00	0.00	−1.99	0.000
0.01	92.07	0.07	−1.54	+0.108
0.025	85.04	0.17	−1.00	+0.170
0.05	78.81	0.29	−0.45	+0.130
0.075	76.30	0.35	−0.18	+0.063
0.10	75.01	0.40	−0.09	+0.045
0.20	72.62	0.48	−0.03	+0.014
0.30	71.84	0.51	−0.02	+0.010
0.40	71.49	0.51	−0.01	+0.005
0.50	71.28	0.48	0.00	0.00
0.60	71.22	0.43	0.00	0.00
0.70	71.25	0.36	0.00	0.00
0.80	71.57	0.27	0.01	−0.003
0.90	72.65	0.16	0.07	−0.011
0.95	74.31	0.09	0.13	−0.012
0.975	75.78	0.05	0.21	−0.010
1.000	78.30	0.00	0.38	−0.000

Table VII. Volume Changes of Mixing, Ethanol(1)-*n*-Heptane(2)

	$\Delta V/x_1x_2$, Cc. per Gram Mole	
x_1	25° C.	45° C.
0.000	(8.6)[a]	(11.8)
0.010	6.50	9.65
0.025	4.69	7.64
0.050	3.63	5.61
0.075	3.13	4.71
0.100	2.84	4.19
0.150	2.50	3.60
0.200	2.28	3.25
0.300	2.01	2.83
0.400	1.89	2.60
0.500	1.86	2.47
0.600	1.88	2.45
0.700	1.97	2.49
0.800	2.12	2.60
0.900	2.39	2.83
1.000	(2.90)	(3.32)

[a] Extrapolated values.

of the activity coefficient curve for ethanol at 760 mm. of Hg seen in Figure 6 does not appear in similar figures where temperature rather than pressure is held constant. The activity coefficient is a function of both temperature and composition. In this region, as the ethanol concentration increases, the temperature drops very rapidly, and its influence is to increase γ_1 more than can be compensated by the decrease caused by increasing ethanol concentration.

In the application of thermodynamics to constant-pressure vapor-liquid equilibria, the Gibbs-Duhem equation and other equations which result from it include a term ϵ, where (*13*):

$$\epsilon = -\frac{\Delta H}{RT^2}\left(\frac{dT}{dx_1}\right) = \left(\frac{-\Delta H}{RT}\right)\left(\frac{d\ln T}{dx_1}\right)$$

All data necessary for the direct evaluation of this term as a function of x_1 at 760 mm. of Hg are included in this paper. Table VI summarizes the results and shows that at ethanol mole fractions below 0.10 ϵ attains significant values. Thus the conclusion reached by Francesconi and Trevissoi (*3*) that ϵ is a superfluous term is not valid for this system, and is probably not valid for a number of alcohol-aliphatic hydrocarbon systems. The reason is the extraordinary steepness of the T-x plot at low ethanol concentrations and the marked skewness of the ΔH curves in the same direction.

Volume changes of mixing, also measured during the course of this work (*9*), are presented in Table VII.

Table VIII. Effect of Pressure on the Excess Functions for Ethanol-*n*-Heptane at 45° C.

Mole fraction ethanol	0.2	0.5	0.8
ΔV, cc./gram mole	0.520	0.617	0.416
$\partial\Delta V/\partial T$, cc./gram mole-° K.	0.0078	0.0077	0.0038
ΔH, cal./gram mole	201	207	124
$\partial\Delta H/\partial P$, cal./gram mole-atm.	−0.047	−0.044	−0.019
ΔS^E, cal./gram mole-° K.	−0.174	−0.469	−0.340
$\partial\Delta S^E/\partial P$, cal./gram mole-° K.-atm.	−0.00019	−0.00019	−0.00009
ΔG^E, cal./gram mole	257	356	233
$\partial\Delta G^E/\partial P$, cal./gram mole-atm.	0.0126	0.0150	0.0101

Table IX. Effect of Pressure on the Partial Molar Excess Properties of Ethanol at Infinite Dilution in *n*-Heptane at 45° C.

$\overline{\Delta V}$, cc./gram mole	11.8
$\partial\overline{\Delta V}/\partial T$, cc./gram mole-° K.	0.16
$\overline{\Delta H}$, cal./gram mole	5585
$\partial\overline{\Delta H}/\partial P$, cal./gram mole-atm.	−0.95
$\overline{\Delta S}^E$, cal./gram mole-° K.	10.67
$\partial\overline{\Delta S}^E/\partial P$, cal./gram mole-° K.-atm.	−0.0039
$\overline{\Delta G}^E$, cal./gram mole	2190
$\partial\overline{\Delta G}^E/\partial P$, cal./gram mole-atm.	0.286

These data are useful for showing the effect of pressure on the other excess functions. Thus at constant composition and temperature:

$$\frac{\partial \Delta G^E}{\Delta P} = \Delta V$$

$$\frac{\partial \Delta S^E}{\partial P} = \frac{\partial \Delta V}{\partial T}$$

and

$$\frac{\partial \Delta H}{\partial P} = \Delta V - T(\partial \Delta V/\partial T)$$

Analogous equations apply to the partial molar properties. Results of the application of these equations at 45° C. are shown in Tables VIII and IX.

The maximum effect of pressure amounts to no more than several hundredths of a per cent per atmosphere. The values of $\partial\Delta V/\partial T$ used in preparation of these tables assume a linear relation of ΔV to T between 25° and 45° C.

NOMENCLATURE

A = constant
B = constant
B_{ii} = second virial coefficient for pure i
B_{ij} = second cross virial coefficient
C = constant
C_p = molar heat capacity at constant pressure
D = constant
E = as superscript, designation of an excess function
G = molar Gibbs function or free energy
H = molar enthalpy
I = constant
K = constant representing A, B, C, D, or I
M = a molar thermodynamic property in general
P = vapor pressure
R = universal gas constant
S = molar entropy
T = absolute temperature
V = molar volume
a, b, c = constants in Antoine equation
n = number of moles
t = Celsius temperature
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = activity coefficient in liquid phase
δ_{12} = $2B_{12} - B_{11} - B_{22}$
1, 2 = as subscripts, designation of ethanol and *n*-heptane, respectively
$\overline{\ }$ = designation of partial molar property when placed over a symbol

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