x	mole fraction
z	compressibility factor

Greek Letters

Γ	potential energy, kJ/mol
δ	solubility parameter, $(kJ/m^3)^{1/2}$
ρ	density, kg/m^3
τ	constant (0.74)

Superscripts

$\sim$	reduced property
*	reducing property
G	gas phase
L	liquid phase
s	saturated

Subscripts

1	solvent
c	critical
fl	flask
pr	probe
s	sample
vap	vapor

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Temperature Dependence of Excess Thermodynamic Properties of Ethanol + *n*-Heptane and 2-Propanol + *n*-Heptane Solutions

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Heat capacities of *n*-heptane, ethanol, 2-propanol, and their binary mixtures have been measured by adiabatic calorimetry with an uncertainty of about 0.2%: *n*-heptane (184–302 K), ethanol (160–306 K), 2-propanol (188–304 K), five mixtures of ethanol + *n*-heptane (195–305 K), and five mixtures of 2-propanol + *n*-heptane (188–305 K). These data were used to obtain the excess heat capacity, C_p^E, for the solutions. The molar excess thermodynamic functions H^E, G^E, and S^E were computed by using these C_p^E values, together with values of G^E and H^E at 303.15 K, reported by others. The variation of G^E with composition and temperature was correlated by using two forms of the Redlich–Kister equation, the Wilson equation, and the Wiehe–Bagley equation. The composition and temperature dependence of G^E and H^E of the above systems and the ethanol–methylcyclohexane system were used to test variations of the theory of associated solutions based on volume fraction and mole fraction statistics.

Introduction

The theory of solutions of nonelectrolytes has been the subject of discussion and research for many years. In the past few decades concentrated study has been made of solutions in which specific strong interactions occur, especially solutions of alcohols with an inert solvent in which hydrogen bonding effects are present.

One method of studying such solutions experimentally is to determine the excess thermodynamic properties, C_p^E, H^E, G^E, and S^E, of the solution as a function of temperature and composition. Two different theoretical approaches have proven useful in analyzing these excess property data. One approach, developed by Barker (*1*, *2*) and Tompa (*3*), is based on a quasi-lattice model of the liquid, in which each molecule occupies a certain number of sites of the lattice. A second approach (the theory of associated solutions) is based on a chemical model first proposed by Dolezalek (*4*) and since modified by others (*5*–*11*). The chemical theory ascribes the major effect of chemical interaction to the alcohol molecules which form polymeric species having varying stabilities.

In the present work C_p^E has been determined experimentally as a function of temperature and composition for the ethanol–*n*-heptane and 2-propanol–*n*-heptane systems. The resulting C_p^E data were used to compute the temperature and composition dependence of the excess thermodynamic properties H^E, G^E, and S^E. These latter calculations made use of the experimental data for G^E and H^E as a function of composition at 303.15 K of Van Ness et al. (*12*) for the ethanol–*n*-heptane system and of Van ness et al. (*13*) for the 2-propanol–*n*-heptane system. The present studies, together with those of Van Ness et al. (*11*–*13*) from room temperature to 75 °C, provide a very wide temperature range for the excess thermodynamic properties of these systems.

The variation of G^E with composition and temperature was correlated by using the Redlich–Kister equation (*14*), the Wilson equation (*15*), and the Wiehe–Bagley equation (*16*, *17*). The composition and temperature dependence of G^E and H^E were also used to test several variations of the theory of associated solutions based on volume fraction and mole fraction statistics (*11*).

Experimental Section

Heat Capacity Measurements. The heat capacity measurements were carried out in a precision adiabatic-shield

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Table I. Melting Points and Purities of Materials

	present work			
	impurity mole fraction × 10^4	mp,[a] K	lit. mp,[a] K	ref
ethanol	6 ± 2	159.00 ± 0.03	159.02 ± 0.05	9
2-propanol	16 ± 3	185.25 ± 0.04	185.23	29
n-heptane	30 ± 8	182.59 ± 0.04	182.59 ± 0.01	25
			182.58 ± 0.05	26

[a] IPTS-68. Corrections from IPTS-48 to IPTS-68 were made by using Table 8 of Barber (*22*).

high-vacuum calorimeter similar in design to one described by Scott et al. (*18*). A detailed description of the apparatus has been given by McGee (*19*). A brief description has been given by Ziegler et al. (*20*). The calorimeter has been used for measurements similar to those described in the present work by Hwa and Ziegler (*9*) and Holzhauer and Ziegler (*21*). The calorimeter assembly made use of a constant-temperature bath. Depending upon the temperature range of measurement three different baths were used: liquid nitrogen up to about 201 K, ethanol–solid carbon dioxide from about 195 to 279 K, liquid water–ice from about 273 to 308 K. The sample temperature was measured with a capsule-type platinum resistance thermometer which has been calibrated by the U.S. National Bureau of Standards on the International Practical Temperature Scale of 1948 (IPTS-48). All IPTS-48 temperatures were converted to IPTS-68 by using the difference between the two temperature scales tabulated by Barber (*22*). In the case of the heat capacity measurements, this conversion to IPTS-68 was made before the temperature increment was computed.

For the heat capacity measurements the calorimeter can, which had a volume of about 160 cm^3, was filled with about 150 cm^3 of liquid using dry nitrogen gas. The liquid mixture was prepared by weighing. Calculations showed that the heat capacity of the gas phase and the effect of sample vaporization were both quite small. No corrections for these effects have been applied to the heat capacity data. Calculations also showed the effect of pressure on the heat capacity of the liquid to be negligible in the pressure and temperature range used. Consequently the heat capacity measurements are reported as C_p.

Materials. The chemicals as originally purchased had the following specifications: *n*-heptane, minimum purity 99 mol % (Phillips Petroleum Co.); 2-propanol, minimum purity 99 mol % (Fisher Scientific Co.); ethanol, reagent quality 200 proof (U.S. Industrial Chemicals Co.) The ethanol was further purified by a method described by Fieser (*23*) and redistilled at 1 atm pressure using a 60 in. long by 0.5 in. diameter vacuum-jacketed column packed with $^1/_8$-in. glass helices. The 2-propanol was dried over calcium hydride but was not purified further. The *n*-heptane was used as received.

The melting point of the pure substances and the mole fraction of impurity were determined calorimetrically by measuring the fraction melted as a function of temperature. The usual assumptions were made, that the impurity was insoluble in the solid phase and that the liquid phase was an ideal solution. The details of this method have been outlined by Rossini (*24*). The melting points of the pure substances and the mole fraction impurity found are given in Table I, together with values of melting points reported by other investigators.

Discussion of the Heat Capacity Measurements

The sample composition and temperature range of the heat capacity measurements are given in Table II. The temperature increments used were about 5 K. No corrections were applied for curvature. The molecular weights used in the calculations were (C-12 basis): *n*-heptane = 100.206, ethanol = 46.070, 2-propanol = 60.097. All sample weights were converted to an in vacuo basis. Conversion between the defined calorie and the joule was made by using the relation: 1 cal = 4.184 J.

Table II. Summary of Heat Capacity Measuremens

system	mole fraction of alcohol	temp range, K
n-heptane		mp-302
2-propanol		mp-304
ethanol		mp-306
ethanol + *n*-heptane	0.8107[a]	195-306
	0.6140	212-306
	0.2805	219-306
	0.1023	203-305
	0.4388	216-305
2-propanol + *n*-heptane	0.4219	188-305
	0.5993	188-305
	0.0809	188-304
	0.7984	188-305
	0.2492	188-304

[a] Compositions are given in chronological order of measurement.

The results of the individual heat capacity measurements for the pure substances and solutions are given in Tables XX–XXIV (supplementary material). These experimental values have been fitted by a least-squares procedure to polynomials in temperature of the form

$$Y = \sum_{i=0}^{5} A_i T^i \qquad (1)$$

where $Y = C_p$ (pure components) or C_p^{E} (mixtures) in J/(mol K) and T is in kelvin (IPTS-68). The coefficients of the resulting polynomials are given in Table III.

The experimental heat capacity data for the pure substances were also fitted to polynomials of the type given in eq 1 with the temperature expressed in the form $T = t$ °C(IPTS-48) + 273.15. This form was chosen to permit direct comparison with the data of other investigators who had used this temperature scale.

The heat capacity of *n*-heptane has been measured by the U.S. National Bureau of Standards (*25*) and the U.S. Bureau of Mines (*26*). Both groups used *n*-heptane having a purity of 99.97%. McCullough and Messerly (*26*) made an analysis of five sets of measurements of the Bureau of Mines. From their analysis they selected what they considered to be the most probable values. They compared these selected heat capacities with the U.S. Bureau of Standards measurements, which they found to be consistently lower by an average of 0.04 cal/(mol K) or 0.1%. The smoothed heat capacities found from the present work are consistently lower than the selected U.S. Bureau Mines values by 0.09 cal/(mol K) (0.2%) on the average, with a maximum deviation of 0.24%. The agreement of the present values with those found by Holzhauer and Ziegler (*21*), who used the same calorimeter and a sample of *n*-heptane from the same lot, is within 0.2% except at room temperature where their values are somewhat more than 0.2% lower.

The heat capacity of ethanol has been measured by Hwa (*9*), Nikolaev et al. (*27*), and by Kelley (*28*). Kelley stated that above 200 K his heat capacities might be in error by as much as 1%. Nikolaev et al. gave the error of individual heat capacity to be about 0.2%. Both sets of measurements deviate from the present work with a maximum deviation slightly larger than 1%. The measurements of Hwa deviate from the present measurements by an average deviation of 0.16%. Hwa failed to make a buoyancy correction in the calculation of his sample weight. This discrepancy accounts for a systematic deviation of about 0.13%. Applying this correction to Hwa's data results

Table III. C_p and C_p^E Data in Polynomial Form[a]

	n-heptane	2-propanol	ethanol
A_0	1.884 434 77 (03)	5.382 064 47 (01)	1.276 165 05 (02)
A_1	−3.175 894 96 (01)	7.924 121 93 (−01)	−6.869 297 71 (−01)
A_2	2.396 563 90 (−01)	−4.560 172 18 (−03)	4.207 329 78 (−03)
A_3	−9.100 000 47 (−04)	1.018 876 19 (−05)	−1.186 367 54 (−05)
A_4	1.745 085 27 (−06)	0	1.642 160 24 (−08)
A_5	−1.343 892 53 (−09)	0	0
std dev	0.163	0.059	0.044
	2-Propanol (1) + *n*-Heptane (2)		
	$x_1 = 0.0809$	$x_1 = 0.2492$	$x_1 = 0.4219$
A_0	−2.811 778 63 (02)	−1.402 981 77 (02)	−2.870 237 93 (02)
A_1	4.925 548 08	2.273 815 86	4.870 005 64
A_2	−3.193 025 59 (−02)	−1.373 730 90 (−02)	−3.103 160 58 (−02)
A_3	9.021 470 92 (−05)	3.602 924 90 (−05)	8.701 804 99 (−05)
A_4	−9.227 748 16 (−08)	−3.257 547 88 (−08)	−8.825 954 22 (−08)
std dev	0.058	0.068	0.070
	$x_1 = 0.5993$	$x_1 = 0.7984$	
A_0	−3.627 202 21 (02)	−2.927 499 90 (02)	
A_1	6.131 898 26	4.823 761 73	
A_2	−3.884 390 89 (−02)	−2.973 011 11 (−02)	
A_3	1.081 113 47 (−04)	8.034 900 09 (−05)	
A_4	−1.093 592 08 (−07)	−7.891 318 08 (−08)	
std dev	0.054	0.054	
	Ethanol (1) + *n*-Heptane (2)		
	$x_1 = 0.1023$	$x_1 = 0.2805$	$x_1 = 0.4388$
A_0	−5.090 121 02 (01)	5.344 724 15 (02)	1.641 982 57 (02)
A_1	9.715 398 05 (−01)	−7.986 805 15	−2.439 515 43
A_2	−6.635 292 68 (−03)	4.475 919 47 (−02)	1.379 224 24 (−02)
A_3	1.871 868 16 (−05)	−1.125 105 24 (−04)	−3.617 230 22 (−05)
A_4	−1.707 079 10 (−08)	1.090 669 18 (−07)	3.886 032 91 (−08)
std dev	0.072	0.059	0.063
	$x_1 = 0.6140$	$x_1 = 0.8107$	
A_0	3.294 530 65 (02)	1.463 001 10 (02)	
A_1	−5.157 037 32	−2.437 266 49	
A_2	3.045 345 94 (−02)	1.517 000 60 (−02)	
A_3	−8.094 921 03 (−05)	−4.236 595 37 (−05)	
A_4	8.303 370 49 (−08)	4.548 908 81 (−08)	
std dev	0.053	0.064	

[a] Numbers in parentheses indicate multiplication by 10 raised to this power. Units are J/(mol K).

in agreement between these corrected data and the present results of about 0.05%.

The heat capacity of 2-propanol has been measured by Andon et al. (*29*). A comparison of the smoothed heat capacities of the present work with their experimental data gave an average deviation of 0.03 cal/(mol K) or 0.11% and a maximum deviation of 0.33%.

From consideration of the reproducibility of the heat capacities, the small average and maximum deviations from the smoothed data, and the good agreement with data available in the literature, it is concluded that the heat capacities of the pure components and mixtures are accurate to about 0.2%. The error in the excess heat capacity is related to the reproducibility of these measurements. If the reproducibility of the heat capacity is taken to be a random error, the error in C_p^E is the sum of the errors in the heat capacities of the solution and the pure components times $2^{1/2}$. On this basis C_p^E is estimated to be accurate to 0.15–0.07 J/(mol K) for $0 \leq x_1(n\text{-heptane}) \leq 1$.

The heat capacities of *n*-heptane, ethanol, and three of their solutions have been determined by Klesper (*30*) over the range 20–70 °C with an uncertainty of about 0.1%. A comparison of Klesper's heat capacity values in the range 20–30 °C with those of the present work showed agreement for *n*-heptane to within 0.03%, while the heat capacities of ethanol deviated by as much as 0.8%. The difference between the C_p^E values found in the present work and the C_p^E values of Klesper is about 0.5 J/(mol K) which is somewhat larger than the estimated uncertainty 0.07–0.15 J/(mol K) in the values reported in the present paper.

Fortier and Benson (*31*) have measured C_p^E for the ethanol-*n*-heptane system at 298.15 K. Their results are in good agreement with those found in the present work.

The excess heat capacity of the 2-propanol + *n*-heptane system has not been measured previously.

Derived Excess Thermodynamic Functions

The molar excess thermodynamic functions G^E, H^E, S^E, and C_p^E for a binary solution are defined by the relations

$$G^E = [G - (x_1G_1^\circ + x_2G_2^\circ) - RT(x_1 \ln x_1 + x_2 \ln x_2)]_{P,T} \tag{2}$$

$$H^E = [H - (x_1H_1^\circ + x_2H_2^\circ)]_{P,T} \tag{3}$$

$$S^E = [S - (x_1S_1^\circ + x_2S_2^\circ) + R(x_1 \ln x_1 + x_2 \ln x_2)]_{P,T} \tag{4}$$

$$C_p^E = [C_p - (x_1C_{p1}^\circ + x_2C_{p2}^\circ)]_{P,T} \tag{5}$$

These functions are related by the equations

$$\left(\frac{\partial H^E}{\partial T}\right)_{P,x} = C_p^{\,E} \tag{6}$$

$$\left(\frac{\partial S^E}{\partial T}\right)_{P,x} = \frac{C_p^{\,E}}{T} \tag{7}$$

$$TS^E = H^E - G^E \tag{8}$$

The $C_p^{\,E}$ data, as represented by the polynomials given in Table III, were used to integrate eq 6 and 7. The effect of pressure on the excess properties can be shown to be negligible for the pressure used in the measurements and has been neglected.

The integation constants needed to integrate eq 6 and 7 were taken from the literature. For the 2-propanol-*n*-heptane system the H^E and G^E data reported by Van Ness et al. (*13*, *32*) at 303.15 K were used. The ethanol-*n*-heptane system has been studied quite extensively near room temperature. The excess enthalpy has been measured by Van Ness et al. (*12*, *33*) from 283.15 to 348.15 K, by Grosse-Wortmann et al. (*34*) at 293.15 K, and by Ramalho and Ruel (*35*) from 293.15 to 303.15 K. Klesper (*30*) used his determination of $C_p^{\,E}$ from 293.15 to 343.15 K and H^E of Grosse-Wortmann to derive H^E at 303.15 K. The excess enthalpy data at 303.15 K from these several sources all agree within the estimated experimental error. The excess Gibbs free energy data for this system have been determined by Van Ness et al. (*12*, *33*) at 303.15 K and by Rothe (*36*) from 303.15 to 333.15 K from vapor-liquid equilibrium measurements. The smoothed G^E and H^E data of Van Ness et al. at 303.15 K have been used to provide the needed integration constants.

The smoothed values of $C_p^{\,E}$ and the derived values of H^E, G^E, and S^E at 5 K intervals are given for the ethanol-*n*-heptane system (183.15-318.15 K) and the 2-propanol-*n*-heptane system (163.15-318.15 K) in Tables IV and V. The values of G^E and H^E at 303.15 K used as integration constants are also given in these tables. The excess functions at several constant temperatures over the experimental temperature range studied are shown in Figures 1-4. Values of the excess functions above 303.15 K and below 213.15 and 183.15 K for the ethanol and 2-propanol systems, respectively, were obtained by extrapolation of the experimental $C_p^{\,E}$ functions.

The error in the G^E, H^E, and S^E functions arises from two sources: the uncertainty in the integration constants used and the error which may arise from the error inherent in the $C_p^{\,E}$ data. The first error is a constant error; that is, an error of 10 J/mol in H^E or G^E at 303.15 K is transmitted as the same error to values at any other temperature. The second error is propagated with temperature and is related to the error in $C_p^{\,E}$ itself and the temperature range of the integration. The error in $C_p^{\,E}$ has been estimated to be 0.15-0.07 J/(mol K) from a concentration of pure *n*-heptane to pure alcohol. The uncertainty in the H^E and G^E values used as integration constants at 303.15 K are estimated to be 1-2 and 2%, respectively. By use of these error estimates an error analysis yielded an estimated uncertainty in H^E of 4-12 J/mol at 303.15 K, increasing to 17-26 J/mol at 183.15 K. The estimated uncertainty in G^E is 2-7 J/mol at 303.15 K, increasing to 6-13 J/mol at 183.15 K. The uncertainty in S^E was estimated to be 0.02-0.06 J/(mol K) at 303.15 K, increasing to 0.16 J/(mol K) at 183.15 K.

The H^E data for the ethanol + *n*-heptane found in the present work agree with the measurements of Grosse-Wortmann et al. (*34*) and Ramalho and Ruel (*35*) at 283.15 K and the measurements of Van Ness et al. (*12*, *33*) at 293.15 K within 2%. The $C_p^{\,E}$ data for the ethanol + *n*-heptane and 2-propanol + *n*-heptane systems were extrapolated to 318.15 K to derive H^E for both systems at this temperature. The values of H^E so found

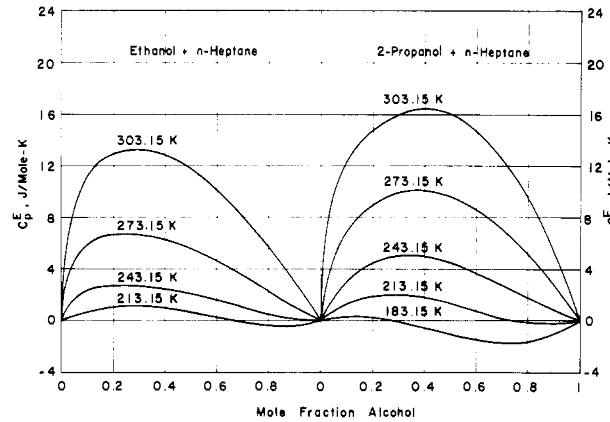

Figure 1. Excess heat capacity as a function of temperature and composition.

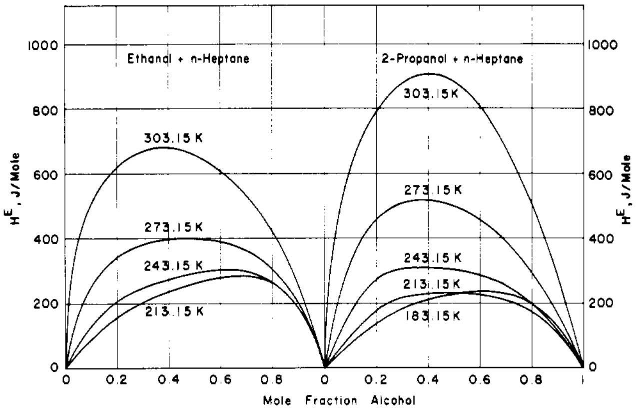

Figure 2. Excess enthalpy as a function of temperature and composition.

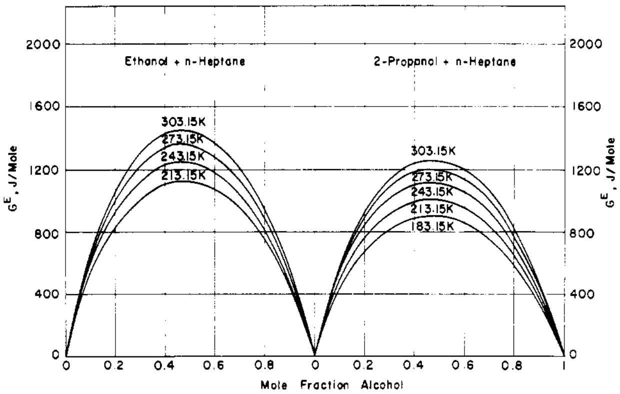

Figure 3. Excess Gibbs free energy as a function of temperature and composition.

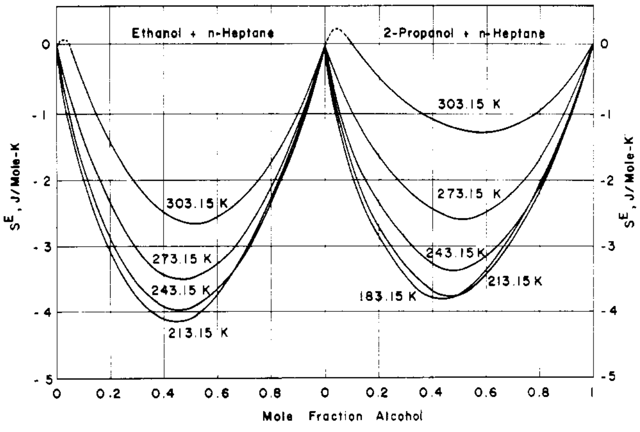

Figure 4. Excess entropy as a function of temperature and composition.

Table IV. Derived Excess Thermodynamic Properties of Ethanol + *n*-Heptane

	x_a						x_a				
T, K	0.1023	0.2805	0.4388	0.6140	0.8107	T, K	0.1023	0.2805	0.4388	0.6140	0.8107
	C_p^E, Excess Heat Capacity, J/(mol K)						G^E, Excess Gibbs Free Energy, J/mol				
318.15	14.47	18.23	17.39	14.13	8.13	318.15	673	1283	1481	1387	938
313.15	13.32	16.43	15.67	12.54	7.13	313.15	672	1276	1471	1376	931
308.15	12.22	14.79	14.08	11.12	6.25	308.15	671	1268	1460	1365	923
303.15^a	11.16	13.29	12.62	9.84	5.45	303.15^a	(669)^c	(1259)^c	(1448)^c	(1353)^c	(915)^c
298.15	10.15	11.92	11.28	8.69	4.75	298.15	666	1249	1435	1340	906
293.15	9.19	10.67	10.04	7.66	4.12	293.15	662	1237	1420	1326	897
288.15	8.28	9.52	8.90	6.73	3.56	288.15	657	1225	1405	1312	888
283.15	7.42	8.47	7.86	5.89	3.06	283.15	652	1212	1389	1297	878
278.15	6.62	7.49	6.91	5.14	2.62	278.15	646	1198	1373	1282	869
273.15	5.87	6.59	6.03	4.46	2.22	273.15	639	1184	1355	1266	858
268.15	5.17	5.76	5.24	3.84	1.86	268.15	632	1169	1338	1250	848
263.15	4.52	5.00	4.52	3.28	1.54	263.15	624	1153	1319	1233	838
258.15	3.93	4.30	3.86	2.78	1.25	258.15	616	1137	1301	1216	827
253.15	3.39	3.66	3.28	2.32	0.99	253.15	607	1120	1282	1199	816
248.15	2.90	3.08	2.75	1.91	0.75	248.15	598	1103	1262	1181	805
243.15	2.46	2.57	2.29	1.54	0.53	243.15	589	1086	1243	1164	794
238.15	2.07	2.13	1.89	1.21	0.33	238.15	580	1069	1223	1146	783
233.15	1.72	1.76	1.54	0.93	0.16	233.15	570	1051	1203	1128	772
228.15	1.42	1.47	1.26	0.69	−0.00	228.15	560	1033	1182	1110	761
223.15	1.16	1.28	1.03	0.51	−0.14	223.15	550	1015	1162	1092	750
218.15	0.94	1.18	0.86	0.37	−0.26	218.15	540	997	1141	1074	739
213.15^b	0.76	1.20	0.76	0.30	−0.36	213.15^b	530	978	1121	1055	728
208.15	0.61	1.35	0.71	0.29	−0.44	208.15	519	960	1100	1037	717
203.15	0.49	1.64	0.73	0.36	−0.48	203.15	509	941	1079	1019	706
198.15	0.40	2.09	0.82	0.51	−0.50	198.15	499	923	1058	1001	695
193.15	0.33	2.72	0.99	0.76	−0.48	193.15	488	903	1037	982	684
188.15	0.29	3.54	1.23	1.11	−0.42	188.15	478	884	1016	964	674
183.15	0.25	4.59	1.55	1.58	−0.32	183.15	467	864	995	945	663
	H^E, Excess Enthalpy, J/mol						S^E, Excess Entropy, J/(mol K)				
318.15	699	899	894	771	509	318.15	0.082	−1.208	−1.847	−1.935	−1.349
313.15	629	812	811	704	471	313.15	−0.138	−1.482	−2.108	−2.146	−1.469
308.15	565	734	737	645	437	308.15	−0.343	−1.733	−2.348	−2.336	−1.577
303.15^a	(507)^c	(664)^c	(670)^c	(593)^c	(408)^c	303.15^a	−0.534	−1.963	−2.566	−2.507	−1.672
298.15	454	601	610	547	383	298.15	−0.711	−2.172	−2.765	−2.661	−1.757
293.15	405	545	557	506	360	293.15	−0.875	−2.363	−2.945	−2.799	−1.832
288.15	362	494	510	470	341	288.15	−1.025	−2.537	−3.108	−2.922	−1.898
283.15	323	449	468	439	325	283.15	−1.162	−2.694	−3.254	−3.033	−1.956
278.15	287	409	431	411	310	278.15	−1.287	−2.836	−3.386	−3.131	−2.007
273.15	256	374	399	387	298	273.15	−1.400	−2.964	−3.503	−3.217	−2.050
268.15	229	343	371	366	288	268.15	−1.502	−3.078	−3.607	−3.294	−2.088
263.15	205	316	346	348	280	263.15	−1.593	−3.179	−3.699	−3.361	−2.120
258.15	183	293	325	333	273	258.15	−1.674	−3.268	−3.779	−3.419	−2.147
253.15	165	273	307	321	267	253.15	−1.746	−3.345	−3.849	−3.469	−2.168
248.15	149	257	292	310	263	248.15	−1.808	−3.413	−3.909	−3.511	−2.186
243.15	136	242	280	302	260	243.15	−1.863	−3.470	−3.960	−3.546	−2.199
238.15	125	231	269	294	257	238.15	−1.910	−3.519	−4.003	−3.574	−2.208
233.15	115	221	261	289	256	233.15	−1.950	−3.560	−4.039	−3.597	−2.213
228.15	108	213	254	285	256	228.15	−1.984	−3.594	−4.070	−3.615	−2.214
223.15	101	206	248	282	256	223.15	−2.012	−3.625	−4.095	−3.628	−2.213
218.15	95.9	200	243	280	257	218.15	−2.036	−3.652	−4.116	−3.638	−2.208
213.15^b	91.6	194	239	278	259	213.15^b	−2.056	−3.680	−4.135	−3.645	−2.201
208.15	88.2	188	236	277	261	208.15	−2.071	−3.710	−4.152	−3.652	−2.191
203.15	85.4	180	232	275	263	203.15	−2.085	−3.746	−4.170	−3.660	−2.180
198.15	83.3	171	228	273	266	198.15	−2.096	−3.792	−4.190	−3.671	−2.168
193.15	81.4	159	223	270	268	193.15	−2.105	−3.853	−4.212	−3.687	−2.155
188.15	79.9	144	218	266	270	188.15	−2.113	−3.935	−4.241	−3.711	−2.143
183.15	78.5	123	211	259	272	183.15	−2.121	−4.044	−4.278	−3.747	−2.133

^{a} Values above this temperature obtained by extrapolating the polynomials given in Table III. ^{b} Values below this temperature obtained by extrapolating the polynomials given in Table III. ^{c} Integration constants.

for both systems agree with the measurements of Van Ness et al. (*12*, *33*) to within 2%.

At the outset of the experimental measurements the possibility of phase separation in the system under study was examined. Rough quantitative measurements viewed visually showed that no phase separation occurred in an equimolar 2-propanol–*n*-heptane solution down to 170 K. The lowest temperature used in the heat capacity measurements for the 2-propanol–*n*-heptane system was about 187 K. For the ethanol–*n*-heptane system cloud point experiments showed phase separation for x_a = 0.43 at 207.6 ± 0.5 K. The lowest temperature used in the heat capacity measurements of the ethanol–*n*-heptane system in the alcohol composition range 0.28 ≤ x_a ≤ 0.61 was about 211 K. Hence no phase separation is believed to have occurred during these measurements. The Gibbs free energy of mixing data obtained from the heat capacity measurements are in general agreement with these observations. Thus the ΔG^M vs. x_a curve for the 2-propanol–*n*-heptane system shows no clear evidence for phase separation at 163.15 K, whereas the corresponding curve for the ethanol–*n*-heptane system at

Table V. Derived Excess Thermodynamic Properties of 2-Propanol + *n*-Heptane

	x_a						x_a				
T, K	0.0809	0.2492	0.4219	0.5993	0.7984	T, K	0.0809	0.2492	0.4219	0.5993	0.7984
	C_p^E, Excess Heat Capacity, J/(mol K)						G^E, Excess Gibbs Free Energy, J/mol				
318.15	13.69	19.13	19.35	17.46	11.65	318.15	504	1048	1262	1215	823
313.15	13.06	17.77	18.42	16.63	10.92	313.15	507	1048	1259	1211	820
308.15	12.36	16.45	17.43	15.71	10.17	308.15	510	1047	1256	1207	817
303.15[a]	11.61	15.19	16.38	14.73	9.39	303.15[a]	(511)[c]	(1044)[c]	(1251)[c]	(1201)[c]	(812)[c]
298.15	10.82	13.97	15.32	13.71	8.60	298.15	511	1040	1245	1194	807
293.15	10.00	12.82	14.24	12.67	7.82	293.15	511	1035	1237	1186	800
288.15	9.18	11.72	13.16	11.62	7.05	288.15	509	1029	1228	1176	794
283.15	8.36	10.68	12.09	10.58	6.30	283.15	507	1022	1218	1166	786
278.15	7.55	9.70	11.04	9.55	5.58	278.15	504	1013	1207	1155	778
273.15	6.77	8.78	10.02	8.55	4.89	273.15	500	1004	1195	1143	770
268.15	6.03	7.92	9.04	7.60	4.24	268.15	496	995	1183	1130	761
263.15	5.33	7.11	8.11	6.69	3.63	263.15	491	984	1169	1116	751
258.15	4.67	6.37	7.22	5.83	3.07	258.15	486	973	1154	1102	742
253.15	4.07	5.69	6.39	5.04	2.56	253.15	480	961	1139	1087	732
248.15	3.52	5.06	5.61	4.30	2.09	248.15	474	949	1123	1072	722
243.15	3.03	4.48	4.89	3.62	1.67	243.15	467	936	1107	1056	711
238.15	2.59	3.95	4.23	3.01	1.29	238.15	460	922	1090	1040	701
233.15	2.21	3.47	3.62	2.45	0.96	233.15	453	909	1072	1024	690
228.15	1.89	3.03	3.07	1.95	0.66	228.15	446	894	1055	1007	679
223.15	1.61	2.62	2.56	1.50	0.39	223.15	438	880	1037	990	668
218.15	1.38	2.25	2.10	1.09	0.15	218.15	430	865	1018	973	657
213.15	1.18	1.91	1.67	0.72	−0.08	213.15	423	850	1000	956	646
208.15	1.02	1.58	1.26	0.37	−0.30	208.15	414	835	981	939	635
203.15	0.88	1.28	0.88	0.03	−0.52	203.15	406	819	962	922	624
198.15	0.74	0.98	0.50	−0.31	−0.76	198.15	398	804	943	904	613
193.15	0.62	0.67	0.12	−0.67	−1.03	193.15	390	788	924	887	603
188.15	0.46	0.37	−0.28	−1.06	−1.34	188.15	381	772	904	870	592
183.15[b]	0.28	0.04	−0.71	−1.50	−1.71	183.15[b]	373	756	885	853	582
178.15	0.05	−0.31	−1.19	−2.02	−2.15	178.15	364	740	866	836	571
173.15	−0.24	−0.69	−1.74	−2.63	−2.68	173.15	355	725	848	819	561
168.15	−0.62	−1.11	−2.38	−3.36	−3.32	168.15	347	709	829	803	552
163.15	−1.09	−1.60	−3.12	−4.23	−4.09	163.15	338	693	811	787	543
	H^E, Excess Enthalpy, J/mol						S^E, Excess Entropy, J/(mol K)				
318.15	748	1101	1179	1051	664	318.15	0.768	0.167	−0.260	−0.514	−0.501
313.15	682	1009	1084	966	608	313.15	0.556	−0.126	−0.560	−0.784	−0.680
308.15	618	923	995	885	555	308.15	0.351	−0.401	−0.848	−1.044	−0.849
303.15[a]	(558)[c]	(844)[c]	(910)[c]	(809)[c]	(506)[c]	303.15[a]	0.155	−0.660	−1.125	−1.293	−1.009
298.15	502	771	831	738	461	298.15	−0.031	−0.902	−1.389	−1.530	−1.159
293.15	450	704	757	672	420	293.15	−0.207	−1.129	−1.639	−1.753	−1.298
288.15	402	643	688	611	383	288.15	−0.372	−1.340	−1.874	−1.962	−1.426
283.15	358	587	625	556	349	283.15	−0.526	−1.535	−2.095	−2.156	−1.542
278.15	318	536	567	505	320	278.15	−0.668	−1.717	−2.301	−2.335	−1.648
273.15	283	490	515	460	294	273.15	−0.797	−1.884	−2.492	−2.499	−1.743
268.15	251	448	467	420	271	268.15	−0.916	−2.038	−2.668	−2.648	−1.827
263.15	222	411	424	384	251	263.15	−1.022	−2.180	−2.830	−2.783	−1.901
258.15	197	377	386	353	234	258.15	−1.118	−2.309	−2.977	−2.903	−1.965
253.15	175	347	352	326	220	253.15	−1.203	−2.427	−3.110	−3.009	−2.020
248.15	156	320	322	302	209	248.15	−1.279	−2.534	−3.229	−3.102	−2.067
243.15	140	296	296	283	199	243.15	−1.345	−2.631	−3.336	−3.182	−2.105
238.15	126	275	273	266	192	238.15	−1.404	−2.718	−3.431	−3.251	−2.135
233.15	114	257	253	252	186	233.15	−1.455	−2.797	−3.514	−3.309	−2.159
228.15	104	240	236	241	182	228.15	−1.499	−2.867	−3.586	−3.357	−2.177
223.15	95.2	226	222	233	180	223.15	−1.537	−2.929	−3.649	−3.395	−2.188
218.15	87.7	214	211	226	178	218.15	−1.571	−2.985	−3.701	−3.424	−2.194
213.15	81.3	204	201	222	178	213.15	−1.601	−3.033	−3.745	−3.445	−2.195
208.15	75.8	195	194	219	179	208.15	−1.627	−3.074	-3.779	−3.458	−2.191
203.15	71.1	188	189	218	181	203.15	−1.650	−3.109	−3.805	−3.463	−2.181
198.15	67.0	182	185	219	184	198.15	−1.670	−3.137	−3.823	−3.460	−2.165
193.15	63.6	178	184	221	189	193.15	−1.688	−3.158	−3.831	−3.447	−2.142
188.15	60.9	175	184	225	195	188.15	−1.702	−3.172	−3.829	−3.425	−2.111
183.15[b]	59.1	174	187	232	202	183.15[b]	−1.712	−3.177	−3.815	−3.390	−2.070
178.15	58.2	175	191	241	212	178.15	−1.717	−3.173	−3.789	−3.342	−2.017
173.15	58.6	178	199	252	224	173.15	−1.714	−3.159	−3.747	−3.276	−1.949
168.15	60.7	182	209	267	239	168.15	−1.702	−3.133	−3.687	−3.188	−1.861
163.15	65.0	189	223	286	257	163.15	−1.676	−3.092	−3.604	−3.074	−1.750

[a] Values above this temperature obtained by extrapolating the polynomials given in Table III. [b] Values below this temperature obtained by extrapolating the polynomials given in Table III. [c] Integration constants.

183.15 K suggests phase separation at this temperature.

Representation of Derived G^E Data Using Various Solution Models

The smoothed G^E data given in Tables IV and V at several constant temperatures have been used to examine a number of solution models. The temperatures used for the ethanol + *n*-heptane system were 213.15, 243.15, 273.15, 283.15, and 303.15 K; for the 2-propanol + *n*-heptane system the temperatures were 183.15, 213.15, 243.15, and 303.15 K. The

Table VI. Coefficients, Y_i, of the Redlich-Kister Equation

T, K	Y_0	Y_1	Y_2	Y_3
		Ethanol + n-Heptane		
213.15	2.513 771 52	−0.149 683 85	0.787 577 98	−0.217 399 49
243.15	2.442 799 41	−0.175 239 76	0.718 569 15	−0.234 807 45
273.15	2.371 987 76	−0.189 540 58	0.658 295 21	−0.210 115 23
283.15	2.346 406 95	−0.185 617 36	0.633 148 65	−0.203 303 24
303.15	2.287 411 79	−0.179 629 56	0.576 397 37	−0.156 091 69
		2-Propanol + n-Heptane		
183.15	2.340 078 86	−0.144 067 08	0.681 442 65	−0.587 750 74
213.15	2.262 863 53	−0.153 590 15	0.622 993 44	−0.613 592 51
243.15	2.193 909 53	−0.143 239 38	0.576 500 83	−0.619 904 38
273.15	2.111 148 23	−0.115 516 26	0.529 196 83	−0.606 419 19
303.15	1.995 851 36	−0.097 111 33	0.471 213 89	−0.504 835 79

Table VII. Coefficients, Z_i, of the Modified Redlich-Kister Equation

T, K	Z_0	Z_1	Z_2	Z_3
		Ethanol + n-Heptane		
213.15	0.396 996 23	0.027 970 73	−0.104 911 55	0
243.15	0.408 622 11	0.034 406 57	−0.101 105 56	0
273.15	0.420 877 57	0.037 957 18	−0.098 190 76	0
283.15	0.425 511 49	0.038 055 84	−0.096 883 90	0
303.15	0.436 542 03	0.037 154 37	−0.093 552 30	0
		2-Propanol + n-Heptane		
183.15	0.426 268 31	0.034 967 83	−0.099 252 97	0.043 877 24
213.15	0.440 781 44	0.039 962 62	−0.095 104 30	0.049 949 07
243.15	0.454 633 21	0.040 731 57	−0.092 981 21	0.055 609 78
273.15	0.472 495 31	0.037 292 21	−0.092 847 02	0.063 183 43
303.15	0.499 980 91	0.034 558 78	−0.095 088 54	0.061 498 11

Table VIII. Comparison of G^E Calculated from Empirical Equations with G^E Derived from ${C_p}^E$ for Ethanol + n-Heptane[a]

T, K	${x_a}^b$	G^E derived	G^E R-K	G^E M-R-K	G^E Wilson	G^E W-B
303.15	0.1023	669	665	666	668	679
	0.2805	1259	1267	1265	1258	1259
	0.4388	1448	1439	1441	1445	1443
	0.6140	1353	1359	1357	1363	1364
	0.8107	915	913	913	909	914
273.15	0.1023	639	635	635	639	665
	0.2805	1184	1192	1190	1181	1195
	0.4388	1355	1345	1348	1351	1355
	0.6140	1266	1270	1268	1275	1271
	0.8107	858	857	857	855	847
243.15	0.1023	589	586	585	590	620
	0.2805	1086	1093	1091	1082	1098
	0.4388	1243	1232	1236	1238	1241
	0.6140	1164	1168	1165	1172	1164
	0.8107	794	793	794	794	778
213.15	0.1023	530	527	528	532	560
	0.2805	978	983	981	972	990
	0.4388	1121	1110	1113	1115	1123
	0.6140	1055	1058	1056	1062	1061
	0.8107	728	727	727	730	720

[a] Units of G^E are J/mol. [b] x_a = mole fraction of alcohol.

Table IX. Comparison of G^E Calculated from Empirical Equations with G^E Derived from ${C_p}^E$ for 2-Propanol + n-Heptane[a]

T, K	x_a	G^E derived	G^E R-K	G^E M-R-K	G^E Wilson	G^E W-B
303.15	0.0809	511	507	509	497	515
	0.2492	1044	1050	1046	1062	1074
	0.4219	1251	1244	1249	1268	1279
	0.5993	1201	1205	1202	1191	1204
	0.7984	812	811	812	785	800
273.15	0.0809	500	496	498	490	524
	0.2492	1004	1011	1006	1019	1045
	0.4219	1195	1188	1193	1208	1223
	0.5993	1143	1148	1144	1133	1140
	0.7984	770	768	769	751	751
243.15	0.0809	467	464	466	461	500
	0.2492	936	941	937	944	970
	0.4219	1107	1101	1106	1116	1127
	0.5993	1056	1060	1057	1050	1046
	0.7984	711	710	711	699	688
213.15	0.0809	423	420	424	419	456
	0.2492	850	853	849	852	881
	0.4219	1000	996	1000	1008	1025
	0.5993	956	958	956	952	958
	0.7984	646	645	646	640	637
183.15	0.0809	373	372	376	371	401
	0.2492	756	757	753	753	775
	0.4219	885	884	888	895	907
	0.5993	853	853	851	850	854
	0.7984	582	581	582	579	575

[a] Units of G^E are J/mol.

Table X. Coefficients of the Wilson G^E Equation

T, K	D	C
	Ethanol + n-Heptane	
303.15[a]	0.064 61	0.189 21
273.15	0.042 03	0.163 94
243.15	0.030 65	0.135 78
213.15	0.024 05	0.102 43
	2-Propanol + n-Heptane	
303.15[b]	0.088 47	0.344 26
273.15	0.057 73	0.307 33
243.15	0.041 22	0.274 56
213.15	0.032 20	0.241 54
183.15	0.026 23	0.199 46

[a] Using G^E data of Van Ness et al. (*12*) at 303.15 K over the complete composition range gave $D = 0.04405$ and $C = 0.21669$. [b] Using G^E data of Van Ness et al. (*13*) at 303.15 K over the complete composition range gave $D = 0.05467$ and $C = 0.40169$.

G^E values were fitted to the various models by a least-squares technique.

Redlich-Kister and Wilson Equations. The G^E values derived from the experimental ${C_p}^E$ data were fitted to the Redlich-Kister (R-K) model (*14*) in the four-parameter form

$$G^E/(x_a x_h RT) = \sum_{i=0}^{i=3} Y_i (x_a - x_h)^i \tag{9}$$

and a modified Redlich-Kister (M-R-K) model (*42*) in the three-parameter form

$$x_a x_h RT/G^E = \sum_{i=0}^{i=2} Z_i (x_a - x_h)^i \tag{10}$$

A least-squares procedure using orthogonal polynomials was employed to obtain the fits. The constants obtained for these fits at the several constant temperatures given above are shown in Tables VI and VII. Tables VIII and IX give a comparison of the values for G^E computed from these fits obtained with the input values for G^E given in Tables IV and V.

The derived G^E data for the two systems given in Table IV and V have also been fitted by an iterative least-squares procedure to the Wilson two-parameter model (*15*) in the form

$$G^E/(RT) = -x_a \ln (x_a + Dx_h) - x_h \ln (x_h + Cx_a) \tag{11}$$

Table XI. Coefficients of the Wiehe–Bagley Equation

T, K	H_A, J/mol	S_A, J/(mol K)	K_A	ρ	$d\rho/dT$, K^{-1}
		Ethanol + n-Heptane			
303.15[a]	−24 686	−4.94	348.6	5.709	0.002 16
273.15	−24 686	−4.94	1022.1	5.743	−0.008 00
243.15	−24 686	−4.94	3907.9	6.304	−0.029 76
213.15	−24 686	−4.94	21794	8.402	−0.113 13
		2-Propanol + n-Heptane			
303.15[b]	−24 686	−5.93	129.5	3.187	−0.000 10
273.15	−24 686	−5.93	379.8	3.203	−0.001 49
243.15	−24 686	−5.93	1452.1	3.299	−0.010 65
213.15	−24 686	−5.93	8098	3.858	−0.022 50
183.15	−24 686	−5.93	79301	4.625	−0.029 50

[a] Using G^E data of Van Ness et al. (*12*) at 303.15 K over the complete composition range gave $\rho = 5.703$. [b] Using G^E data of Van Ness et al. (*13*) at 303.15 K over the complete composition range gave $\rho = 3.193$.

Table XII. Excess Enthalpy Predicted by the Wiehe–Bagley Model for Ethanol + n-Heptane

	$T = 303.15$ K		$T = 273.15$ K	
x_a	H^E(W-B)	H^E_{der}[a]	H^E(W-B)	H^E_{der}[a]
0.1023	723	507	371	256
0.2805	859	664	424	374
0.4388	778	670	397	399
0.6140	596	593	329	387
0.8107	316	408	207	298

	$T = 243.15$ K		$T = 213.15$ K	
x_a	H^E(W-B)	H^E_{der}[a]	H^E(W-B)	H^E_{der}[a]
0.1023	172	136	99	91.6
0.2805	233	242	199	194
0.4388	260	280	274	239
0.6140	267	302	335	278
0.8107	223	260	337	259

[a] Values of H^E_{der} from Table IV. Units are in J/mol.

Table XIII. Excess Enthalpy Predicted by the Wiehe–Bagley Model for 2-Propanol + n-Heptane

	$T = 303.15$ K		$T = 273.15$ K	
x_a	H^E(W-B)	H^E_{der}[a]	H^E(W-B)	H^E_{der}[a]
0.0809	785	558	445	283
0.2492	1069	844	539	490
0.4219	1001	910	493	515
0.5993	785	809	388	460
0.7984	438	506	224	294

	$T = 243.15$ K		$T = 213.15$ K	
x_a	H^E(W-B)	H^E_{der}[a]	H^E(W-B)	H^E_{der}[a]
0.0809	209	140	95	81.3
0.2492	292	296	181	204
0.4219	323	296	245	201
0.5993	315	283	277	222
0.7984	237	199	241	178

	$T = 183.15$ K	
x_a	H^E(W-B)	H^E_{der}
0.0809	39	59.1
0.2492	98	174
0.4219	147	187
0.5993	179	232
0.7984	168	202

[a] Values of H^E_{der} from Table V. Units are in J/mol.

Table XIV. Parameters of the Volume Fraction Associated Model

T, K	$H°$, J/mol	K	β, J/cm³	β', J/cm³
		Ethanol + n-Heptane		
303.15	−25 104	352	11.20	6.12
273.15	−25 104	1051	10.99	4.55
243.15	−25 104	4110	10.81	7.14
213.15	−25 104	23598	10.92	10.70
		2-Propanol + n-Heptane		
303.15	−25 104	111	8.11	5.37
273.15	−25 104	332	7.92	1.76
243.15	−25 104	1298	7.58	2.70
213.15	−25 104	7452	7.43	2.53
183.15	−25 104	75854	7.77	8.73
		Ethanol + Methylcyclohexane		
303.15	−25 104	352	10.99	5.83
273.15	−25 104	1051	10.70	3.98
243.15	−25 104	4110	10.44	6.73
213.15	−25 104	23598	10.56	10.73

The values of the parameters obtained are given in Table X. The G^E values obtained for this fit are compared with the imput data in Tables VIII and IX.

The two-parameter Wilson model was found to fit the G^E data for the ethanol–n-heptane system about as well as the M-R-K and R-K models using three and four parameters, respectively. The agreement between the Wilson and the M-R-K and R-K models was not quite so good for the 2-propanol–n-heptane system.

Wiehe–Bagley Model. The Wiehe–Bagley model (*16*, *17*) is based on the chemical association theory using the Flory–Huggins athermal solution model for which G^E is expressed in terms of the volume fractions of the inert solvent and the alcohol complex species. The alcohol species are assumed to be related to each other by the chemical equilibria

$$A_i + A_1 = A_{i+1} \qquad (12)$$

and involve the formation of a hydrogen bond. The resulting expression for G^E is

$$\frac{G^E}{RT} = x_A \ln\left[\frac{1 + K_A}{\rho x_{A_B} + (1 + K_A)x_A}\right] + x_B \ln\left[\frac{\rho}{\rho x_B + x_A}\right] + \frac{1}{K_A}[x_A \ln(1 + K_A)] - \frac{(x_A + \rho x_B)}{K_A} \ln\left[\frac{x_A K_A}{\rho x_B + x_A} + 1\right] \qquad (13)$$

where the subscripts A and B refer to the alcohol and inert solvent, respectively. Expressions for the activity coefficients of the alcohol and solvent are also given by Wiehe and Bagley (*16*). The model makes use of a single equilibrium constant K_A for all reactions of eq 12, the temperature dependence of which is given by

$$K_A = \exp(S_A + 1 - H_A/RT) \qquad (14)$$

The parameter H_A, the standard enthalpy of formation of the hydrogen bond, is assumed to be independent of the alcohol for inert solvent–alcohol systems. The dimensionless temperature-independent parameter S_A, which is related to the standard entropy of formation of the hydrogen bond, depends upon the particular binary system.

From studies of alcohol–inert solvent systems near and above room temperatures Wiehe and Bagley (*16*, *17*) found values of S_A of −4.94 and −5.93 for the ethanol + n-heptane and 2-propanol + n-heptane systems, respectively. For H_A they used −5900 cal/mol. These same values were used in the present calculations.

Equation 13 contains the dimensionless parameter ρ defined as the ratio of the molar volume of the pure inert solvent to that

Table XV. Comparison of G^E from the Volume Fraction Associated Theory of Solutions with G^E Derived from C_p^E [a]

Ethanol + *n*-Heptane

	$T = 303.15$ K				$T = 273.15$ K			
x_a	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}
0.1023	635	65	700	669	607	61	668	639
0.2805	1111	160	1271	1259	1045	152	1197	1184
0.4388	1226	221	1447	1448	1148	210	1358	1355
0.6140	1108	248	1356	1353	1032	236	1268	1266
0.8107	694	198	892	915	644	188	832	858

	$T = 243.15$ K				$T = 213.15$ K			
x_a	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}
0.1023	562	59	621	589	505	57	562	530
0.2805	958	145	1103	1086	855	142	997	978
0.4388	1048	200	1248	1243	933	196	1129	1121
0.6140	940	225	1165	1164	835	220	1055	1055
0.8107	585	179	764	794	519	175	694	728

2-Propanol + *n*-Heptane

	$T = 303.15$ K				$T = 273.15$ K			
x_a	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}
0.0809	477	48	525	511	474	46	520	500
0.2492	938	133	1071	1044	907	126	1033	1004
0.4219	1076	192	1268	1251	1030	181	1211	1195
0.5993	977	211	1188	1201	930	199	1129	1143
0.7984	619	163	782	812	585	154	739	770

	$T = 243.15$ K				$T = 213.15$ K			
x_a	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}
0.0809	451	43	494	467	411	41	452	423
0.2492	847	117	964	936	763	111	874	850
0.4219	955	168	1123	1107	856	160	1016	1000
0.5993	857	185	1042	1056	766	176	942	956
0.7984	537	143	680	711	480	136	616	646

	$T = 183.15$ K			
x_a	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}
0.0809	359	42	401	373
0.2492	662	115	777	756
0.4219	739	165	904	885
0.5993	660	180	840	853
0.7984	412	138	550	582

Ethanol + Methylcyclohexane

	$T = 303.15$ K				$T = 273.15$ K			
x_a	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}
0.0742	504	46	550	542	482	44	526	516
0.1979	930	115	1045	1029	877	109	986	969
0.3456	1156	180	1336	1325	1082	170	1252	1238
0.5324	1151	227	1378	1374	1072	214	1286	1284
0.8004	686	183	869	897	636	173	809	839

	$T = 243.15$ K				$T = 213.15$ K			
x_a	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}	G_c^E	G_p^E	G^E_{calcd}	G^E_{der}
0.0742	447	42	489	474	402	41	443	427
0.1979	806	103	909	888	719	101	820	798
0.3456	989	161	1150	1133	881	158	1039	1019
0.5324	976	203	1179	1178	868	198	1066	1066
0.8004	577	163	740	775	512	160	672	708

[a] Units of G^E are J/mol.

of the pure alcohol. In the present use of the W-B model ρ has been treated as an empirical composition-independent parameter, which was evaluated for a fixed temperature, by using the experimental values of G^E given in Tables IV and V. The values of ρ and its temperature derivative at several fixed temperatures are given in Table XI.

The values of G^E calculated by using these parameters are given in Tables VIII and IX. Examination of these tables show that the Wiehe-Bagley model (W-B) provides a somewhat poorer fit of the derived G^E values for these systems than do the more empirical Redlish-Kister and Wilson models considered above.

Wiehe and Bagley (*16*) have given an expression for H^E in terms of the parameters of their model. This expression was derived from the thermodynamic relation

$$H^E = \left[\frac{\partial(G^E/T)}{\partial(1/T)}\right]_{P,x} \qquad (15)$$

Table XVI. Comparison of H^E Calculated from the Volume Associated Theory of Solutions with H^E Derived from C_p^E [a]

Ethanol + *n*-Heptane

	$T = 303.15$ K				$T = 273.15$ K			
x_a	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}
0.1023	446	35	481	507	275	25	300	256
0.2805	588	87	675	664	353	63	416	374
0.4388	570	121	691	670	340	87	427	399
0.6140	465	136	601	593	276	97	373	387
0.8107	266	108	374	408	157	78	235	298

	$T = 243.15$ K				$T = 213.15$ K			
x_a	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}
0.1023	145	39	184	136	62	56	118	91.6
0.2805	183	96	279	242	78	139	217	194
0.4388	175	132	307	280	74	192	266	239
0.6140	142	148	290	302	60	215	275	278
0.8107	80	118	198	260	34	171	205	259

2-Propanol + *n*-Heptane

	$T = 303.15$ K				$T = 273.15$ K			
x_a	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}
0.0809	551	32	583	558	358	10	368	283
0.2492	801	88	889	844	497	28	525	490
0.4219	791	127	918	910	484	40	524	515
0.5993	647	140	787	809	392	44	436	460
0.7984	373	108	481	506	225	34	259	294

	$T = 243.15$ K				$T = 213.15$ K			
x_a	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}
0.0809	195	15	210	140	85	30	115	81.3
0.2492	263	42	305	296	113	83	196	204
0.4219	253	60	313	296	108	119	227	201
0.5993	204	66	270	283	87	131	218	222
0.7984	117	51	168	199	49	101	150	178

	$T = 183.15$ K			
x_a	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}
0.0809	27	47	74	59.1
0.2492	35	129	164	174
0.4219	34	185	219	187
0.5993	27	203	230	232
0.7984	15	155	170	202

Ethanol + Methylcyclohexane

	$T = 303.15$ K				$T = 273.15$ K			
x_a	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}
0.0742	362	25	387	403	225	16	241	190
0.1979	508	61	569	563	308	40	348	303
0.3456	538	96	634	607	322	63	385	346
0.5324	470	120	590	587	280	80	360	373
0.8004	246	97	343	373	146	64	210	273

	$T = 243.15$ K				$T = 213.15$ K			
x_a	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}	H_c^E	H_p^E	H^E_{calcd}	H^E_{der}
0.0742	119	27	146	89	51	41	92	54
0.1979	160	67	227	187	68	102	170	149
0.3456	167	104	271	232	71	160	231	197
0.5324	144	131	275	288	61	202	263	268
0.8004	75	105	180	241	32	162	194	244

[a] Units of H^E are J/mol.

Table XVII. Parameters of the Mole Fraction Associated Theory Model

T, K	K_2	H_2, J/mol	K_3	H_3, J/mol
303.15	25.20	−36 558	47.63	−23 252
288.15	53.88	−37 028	76.80	−23 012
273.15	126.60	−34 499	129.78	−22 772
243.15	997.04	−38 440	441.17	−22 291
213.15	14991	−39 382	2046	−21 810

Their expressions, eq 29 and 30, contain two misprints. In eq 29 RT should be RT^2; in eq 30 the numeral 1 in the first ln term should be followed by a + sign. The corrected expression was used, together with the parameters given in Table XI, to calculate H^E. These H^E values are compared with the values of H^E derived from the experimental C_p^E data (Tables IV and V) in Tables XII and XIII. The agreement between the H^E values predicted by the W-B model and the H^E values derived from the experimental C_p^E values is only fair. However, the predicted H^E values agree qualitatively with the derived values in that H^E is large and positive at room temperature, decreases with decreasing temperature, and has a maximum in the dilute alcohol

Table XVIII. Comparison of G^E Calculated from the Mole Fraction Associated Theory of Solutions with G^E Derived from C_p^E [a] for Ethanol + *n*-Heptane

	303.15 K		273.15 K		243.15 K		213.15 K	
x_a	G^E_{calcd}	G^E_{der}	G^E_{calcd}	G^E_{der}	G^E_{calcd}	G^E_{der}	G^E_{calcd}	G^E_{der}
0.1023	668	669	638	639	589	589	528	530
0.2805	1255	1259	1179	1184	1079	1086	963	978
0.4388	1465	1448	1370	1355	1251	1243	1116	1121
0.6140	1426	1353	1331	1266	1215	1164	1084	1055
0.8107	1024	915	955	858	874	794	781	728

[a] Units of G^E are J/mol.

Table XIX. Comparison of H^E Calculated from the Mole Fraction Associated Theory of Solutions with H^E Derived from C_p^E [a] for Ethanol + *n*-Heptane

	303.15 K		273.15 K		243.15 K		213.15 K	
x_a	H^E_{calcd}	H^E_{der}	H^E_{calcd}	H^E_{der}	H^E_{calcd}	H^E_{der}	H^E_{calcd}	H^E_{der}
0.1023	507	507	264	256	133	136	67	91.6
0.2805	653	664	358	374	195	242	103	194
0.4388	665	670	377	399	212	280	116	239
0.6140	603	593	354	387	205	302	114	278
0.8107	438	408	233	298	160	260	91	259

[a] Units of H^E are J/mol.

region near room temperature which shifts to the alcohol-rich region at lower temperatures.

Comparison with Theory of Associated Solutions. Two variations of the theory of associated solution based on the cell model were considered to describe the temperature and composition behavior of alcohol-hydrocarbon solutions. The volume fraction model, which is derived from volume fraction statistics, was applied to the ethanol + *n*-heptane and 2-propanol + *n*-heptane solutions reported here and to the data of Hwa and Ziegler (*9*) for ethanol-methylcyclohexane. A mole fraction model, which is derived from mole fraction statistics, was applied to ethanol + *n*-heptane. A discussion of the differences between these two models is given by Haskell et al. (*11*).

The volume fraction model used is that described by Renon and Prausnitz (*10*), as modified by them (*37*). The model made use of the following parameters: $H° = -6000$ cal/mol (independent of the alcohol); a K at 50 °C of 190 for the ethanol systems and 60 for the 2-propanol system. The parameters β and β' appearing in this model, given in Table XIV, were derived from the experimental G^E and H^E values, respectively, given in Tables IV and V, by using a least-squares procedure. The volume fractions were calculated on the assumption that the volume change on mixing is zero. Smoothed density data were used for *n*-heptane (*38*) and methylcyclohexane (*39*), for ethanol the values of Körber (40) were used, and for 2-propanol the data of Costello and Bowden (*41*) were used.

The values of G^E and H^E calculated by using these values of K, β, and β' are compared with the corresponding experimental values from Table IV and V and with the data of Hwa and Ziegler (*9*) for the ethanol-methylcyclohexane system in Tables XV and XVI. In these tables the quantities G_c^E and H_c^E (the "chemical" contribution) depend only upon the values chosen for $H°$ and K. The quantities G_p^E and H_p^E may be viewed as the contribution due to "physical" interactions such as the van der Waals forces. These latter quantities are dependent upon the empirically fitted values of β and β', respectively.

The mole fraction model used is that described by Haskell et al. (*11*). This model was applied only to the ethanol-*n*-heptane system. The parameters used are given in Table XVII. The values of the parameters at 288.15 K were taken from Haskell et al. (*11*). Values of K_2, K_3, H_2 and H_3 at other temperatures were compared by using the methods given by Haskell et al. (*11*). The values of G^E and H^E computed from this model are compared with the corresponding experimental values in Tables XVIII and XIX.

A comparison of the results obtained for the ethanol-*n*-heptane system (Tables XV, XVI, XVIII, and XIX) shows that G^E and H^E computed from the volume fraction model give somewhat better agreement with the smoothed experimental data than for the mole fraction model.

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Gas–Liquid Equilibrium for the Helium–Ethylene and Helium–Propylene Systems below 260 K and 120 Atm

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Gas–liquid phase equilibrium measurements are reported for the helium–ethylene and helium–propylene systems for a series of isotherms below 260 K up to pressures of 120 atm. Gas-phase compositions expressed in terms of the enhancement factor have been computed for several models by using thermodynamic relations and have been compared with the experimental results. The interaction parameter K_{12} has been computed from experimental values of the second virial interaction coefficient.

This work is a continuation of phase equilibrium studies made in this laboratory on binary systems involving helium and hydrogen gases as one component of the system. The present work is concerned with gas–liquid phase equilibrium measurements for the helium–ethylene and helium–propylene systems (*1*) below 260 K and up to pressures of approximately 120 atm. Other helium systems which have been studied by using techniques similar to those used in this work are He–Ar (*2*, *3*), He–CO_2 (*4*), and He–CF_4 and He–$CClF_3$ (*5*–*7*).

In all instances the experimental results have been compared with gas-phase equilibrium values computed from various models by appropriate thermodynamic relations.

Experimental Section

All phase equilibrium measurements have been made by using a single-pass flow-type apparatus described by Kirk (*8*) and Kirk and Ziegler (*9*). In this apparatus which consists of a thermostated copper equilibrium cell in which the pure liquid condensable component (in this instance ethylene or propylene) can be condensed, after which the pure helium gas is bubbled through the liquid until the composition of the exit helium gas mixture becomes constant at which time the liquid phase is sampled to determine its composition. The detailed operating procedures used were similar to those described by Kirk and Ziegler (*9*). Equilibrium was considered to have been reached when three successive gas-phase samples taken at approximately 10-min intervals showed the same composition within the experimental uncertainty of the measurements (approximately ±3% of the determined composition in mole fraction). When this state was reached for a fixed pressure and temperature of the equilibrium cell, liquid samples were taken from the cell and analyzed for helium.

The composition analyses were made by using two separate gas chromatographs (Perkin-Elmer 154 vapor fractometers). Analyses of the gas-phase samples to determine the hydrocarbon content made use of an activated silica gel column for ethylene and a dimethylsulforlane on fire-brick column for propylene with helium as the carrier gas. The liquid phase was analyzed for helium by using a molecular sieve column (Linde 5A) with argon as the carrier gas. The chromatographs were calibrated on a peak height basis as described by Kirk (*8*, *9*). The experimental phase equilibrium measurements made consisted of five or six isotherms at five to six different pressures in the range up to approximately 120 atm. The experimental results are given for the helium–ethylene system in Table I and for the helium–propylene system in Table II. The temperature of the equilibrium cell could be controlled to approximately ±0.03 K. All temperatures were measured with a capsule-type platinum resistance thermometer calibrated by the U.S. National Bureau of Standards on the International Practical Temperature Scale of 1948 (IPTS-48). All temperature in Tables I and II are given on the International Practical Temperature Scale of 1968 (IPTS-68), the conversion of Barber (*10*) having been used to convert the IPTS-48 to IPTS-68.

The two Bourdon gages used to measure the pressures (one for lower pressures and the second for the higher pressures) have been calibrated by Kirk (*8*, *9*). The calibration was verified by measuring the vapor pressures of pure argon and carbon dioxide. The uncertainty in the pressure reported in Tables I and II is estimated to be $\pm^1/_2$% of the indicated pressure.

From a consideration of the uncertainty in the temperature and pressure measurements and the scatter of the data in preparing the calibration curves for the chromatographs, the overall uncertainty of the gas-phase composition for the helium–ethylene system is estimated to be $\pm 4^1/_2$% of the reported values for the 129.98 and 150.00 K isotherms and ±3% of the quoted values for the higher temperature isotherms. For the helium–propylene gas-phase data y_1 is estimated to be uncertain to $\pm 4^1/_2$% for the 200.00 and 212.49 K isotherms and ±3% for the higher temperature isotherms.

One of the questions which arises with the use of the flow-through type of cell is whether or not equilibrium has been reached, as contrasted with a steady state which may or may not represent a true equilibrium state. In the present experi-

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