

Table V. Difference of Partial Molar Excess Entropies of Gas in Alcohols and in *n*-Hexane

Alcohol		$\bar{s}_{R,A}^E - \bar{s}_{R,B}^E$, cal/mol·K
	Hydrogen	Nitrogen
MeOH	-3.28	-3.66
EtOH	-2.78	-3.03
<i>n</i> -PrOH	-2.50	-2.93
<i>i</i> -PrOH	...	-2.54
<i>n</i> -BuOH	-2.41	-2.54

As Henry's constant is interrelated to the activity coefficient of solute, the theoretical expression for $\bar{s}_{R,A}^E - \bar{s}_{R,B}^E$ is given by means of suitable activity coefficient equations. Qualitative explanation of experimental values for $\bar{s}_{R,A}^E - \bar{s}_{R,B}^E$ is obtained when the Kretschmer-Wiebe equation (7) is assumed for component A and the Flory-Huggins equation with the Scatchard-Hildebrand equation for component B.

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Nomenclature

C = molar concentration, mol/cc

H = Henry's constant, atm

\bar{h} = partial molar enthalpy, cal/mol

L = Ostwald coefficient, —

P = total pressure, atm

p = partial pressure, atm

R = gas constant, cal/mol·K

\bar{s} = partial molar entropy, cal/mol·K

T = absolute temperature, K

x = mole fraction, —

Subscripts

A = alcohol

B = inert solvent (*n*-hexane)

R = gas component (H₂ or N₂)

R, α = refer to R in binary mixture of R and α

Superscripts

E = excess quantity

G = gas phase

L = liquid phase

s = quantity at saturation

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Isothermal Liquid-Vapor Equilibria for System Methanol-Water

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Gibbs free energies of mixing of methanol-water mixtures in the range of 35–65 °C and densities of the mixtures at 25 °C are measured. The enthalpies and free energies of mixing are thermodynamically consistent within the limits to which the gas imperfections are known. Earlier liquid-vapor equilibrium measurements are reanalyzed, using only total pressure and liquid composition data, and with corrections for gas imperfections. Of the previously reported free energies of mixing, only the single set of transpiration measurements at 25 °C by Butler et al. is to any degree consistent with our data.

The recent renewal of interest in alcohol-water systems prompts us to report measurements of free energies of mixing at 35, 50, and 65 °C and densities of mixtures at 25 °C, which we have hitherto hesitated to publish for lack of a detailed theoretical interpretation. Although there are some re-

cent isobaric studies at atmospheric pressure (8, 14, 15), there have been few new isothermal data (4, 22) reported in the past few years.

A precise evaluation of the free energy of mixing from vapor-pressure data requires a knowledge of the gas imperfections of both the pure components and of their mixtures. Second virial coefficients are known fairly precisely for water (9a), imprecisely for methanol (16, 17), and not at all for their mixtures. It is frequently assumed (13) that the cross term, B_{12} , is given by the arithmetic mean of the virial coefficients of the pure components. Such an approximation is, however, highly suspect for mixtures with strong interactions between the components. An alternative approach is to assume that the vapor pressures and phase compositions are consistent with the Gibbs-Duhem equation, which allows an estimate of B_{12} to be made (19). Both approaches are considered here.

Thermodynamic consistency between enthalpy and free energy measurements has often been tested by estimating the heat of mixing from the temperature coefficient of the

free energies of mixing. We have used a procedure involving the integration of the enthalpy data, according to the relation

$$\frac{G^E(T_2)}{T_2} - \frac{G^E(T_1)}{T_1} = \int_{T_1}^{T_2} -H^E/T^2 dT \quad (1)$$

Experimental

Density measurements. Accurate density-composition data were required for the analysis of liquid and vapor samples from the equilibrium still. The two sets of published measurements (11, 12) differ significantly, and it was therefore thought desirable to repeat the measurements. (Since these measurements were made, it has been widely recognized that it is more accurate and simpler experimentally to measure V^E directly and to deduce therefrom the densities of the mixtures. Such measurements have not yet been made on this system.) Mixtures were prepared by weighing each of the components in turn into a 50-ml stoppered flask. The calculated compositions were corrected for the amount of the first component expelled as vapor by the addition of the second component, and for the amounts of the two components present as vapor above the mixture. Densities were measured in duplicate, using single stem 18-ml pycnometers, at 25 ± 0.01 °C in a thermostat which was stable to ± 0.001 °C. Volume measurements were corrected for the meniscus volume, assuming the meniscus to be the cap of a sphere. The pycnometers were calibrated using pure water, the density of which was assumed to be 0.997075 g cm $^{-3}$ at 25 °C (9b). All weighings were corrected for air buoyancy. The duplicate measurements never differed from their mean by more than ± 0.00005 g cm $^{-3}$.

For analytical purposes, the compositions of unknown mixtures were obtained from the density measurements using a modification of the procedure described by Brown and Smith (6). The estimated accuracy of the mole fractions so determined is ± 0.0003 .

Liquid-vapor equilibrium measurements. Liquid-vapor equilibrium data were measured with an equilibrium still of the type described by Brown (5), pressures being measured to ± 0.04 mm Hg with a Precision Tool and Instrument Co. cathetometer and a precision manometer (2). Temperatures were measured to ± 0.001 °C with a 5 junction copper-constantan thermopile, which was calibrated at 35, 50, and 65 °C using vapor-pressure-temperature data for pure water (9c). Samples of the equilibrium liquid and vapor were analyzed by measurement of their densities, as described above.

Materials. Methanol was freed from aldehydes by treatment with AR silver nitrate and was fractionally distilled in a column of 27 theoretical plates. The middle fraction was dried by treatment with magnesium, redistilled, and stored under nitrogen. The density of the purified methanol is shown in Table I.

Water was purified by redistillation from alkaline potassium permanganate of once distilled tap water.

Results

Densities. Table I shows the densities of mixtures together with the density of pure methanol at 25 °C. In addition to their use for analytical purposes, the densities allow the calculation of the volume changes on mixing, V^E . [The values of V^E are also shown in Table I, and a comparison between our data and those of other workers is shown in Figure 1, where deviations of the V^E values from the parabola $4x(1-x)$ are plotted.] There is excellent agreement between the present measurements and those of Gibson (11), while the measurements of Griffiths (12) scatter badly and are obviously unreliable.

The volumes of mixing have been fitted by an equation of the type

$$V^E/\text{cm}^3 \text{ mol}^{-1} = x(1-x) \sum_0^{n-1} v_i(1-2x)^i \quad (2)$$

for various numbers of parameters. Although the numbers shown in Figure 1 suggest that both our measurements and those of Gibson (11) agree within $\delta V^E = \pm 0.005$ cm 3 mol $^{-1}$, we hesitate to quote the five-parameter fit for Equation 2 which is necessary to reproduce the data to this accuracy. The four-parameter equation with $v_0 = -4.033$, $v_1 =$

Table I. Densities of Methanol-Water at 25 °C

Methanol	$d, \text{ g ml}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$
0.04085	0.98472	-0.1173
0.06168	0.97919	-0.1845
0.11445	0.96649	-0.3613
0.15546	0.99730	-0.4950
0.19739	0.94796	-0.6171
0.24867	0.93658	-0.7449
0.34382	0.91534	-0.9085
0.49446	0.88242	-0.9996
0.61267	0.85790	-0.9380
0.69241	0.84210	-0.8351
0.78454	0.82458	-0.6565
0.89229	0.80510	-0.3698
1.00000	0.78663	...

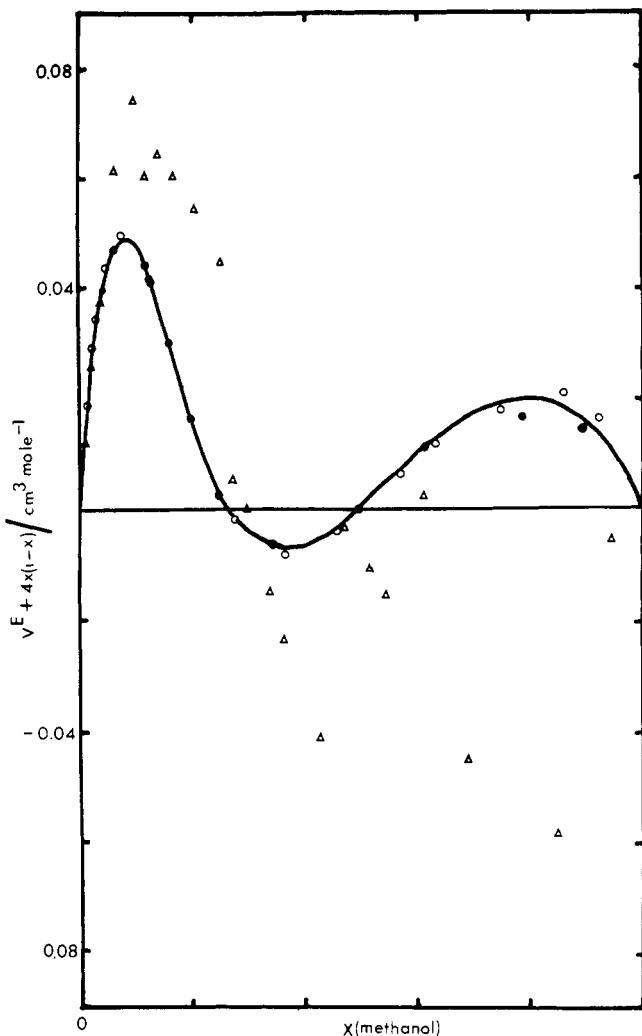


Figure 1. Comparison of density measurements for methanol-water in terms of V^E
● This work; ○ Gibson (11); △ Griffiths (12)

-0.294 , $v_2 = 0.478$, $v_3 = 0.851$ fits the data within ± 0.01 $\text{cm}^3 \text{mol}^{-1}$ at any point. The value of

$$\sigma = (\sum (V^E(\text{exp}) - V^E(\text{calc}))^2 / (m - n))^{1/2} \quad (3)$$

where m is the number of points and n is the number of parameters is $\sigma = 8 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ for $n = 4$.

Free energies of mixing. Table II shows the mole fractions x_1 and y_1 of methanol in the liquid and vapor phases, respectively, in equilibrium at pressure p and the excess Gibbs free energies calculated according to the expression

$$G^E = x_1 RT \ln p y_1 / p_1^\circ x_1 + x_2 RT \ln p y_2 / p_2^\circ x_2 + x_1 (B_{11} - V_1^\circ) (p - p_1^\circ) + x_2 (B_{22} - V_2^\circ) (p - p_2^\circ) \quad (4)$$

where p_1° , p_2° are the vapor pressures, B_{11} , B_{22} are the second virial coefficients, and V_1° , V_2° are the liquid molar vol-

umes of methanol and water, respectively. The pure component properties (8, 16) are shown in Table III.

A more complete expression for the Gibbs free energy of mixing would include the term $+(x_1 y_2^\circ + x_2 y_1^\circ)p(2B_{12} - B_{11} - B_{22})$ on the right-hand side. However, in the absence of data on the second virial coefficients of mixtures, we have used the crude assumption

$$B_{12} = (B_{11} + B_{22})/2 \quad (5)$$

Discussion

Correlation of enthalpy and free energy measurements. The enthalpy and free energy data, if precise, must obey Equation 1. Integration of Equation 1 using the enthalpies of mixing of McGlashan and Morcom (18) gives

$$G^E/T = F(T, x) + \phi(x) \quad (6)$$

$$\begin{aligned} \text{where } F(T, x) &= x(1-x)(11808 \text{ deg}/T + \\ &\quad 118.5 \ln(T/\text{deg}) - 8.2285 T/\text{deg}) \\ &\quad + x(1-x)(1-2x)[-7438 \text{ deg}/T - 19.67 \ln(T/\text{deg})] \\ &\quad + x(1-x)(1-2x)^2[-8524 \text{ deg}/T - 21.71 \ln(T/\text{deg})] \\ &\quad + x(1-x)(1-2x)^3[-3342 \text{ deg}/T - 8.29 \ln(T/\text{deg})] \end{aligned} \quad (7)$$

and $\phi(x)$ depends only on composition. Values of $\phi(x)$ calculated from Equations 6 and 7 using the experimental G^E data at the three temperatures should lie on a single curve. For convenience, we have in fact calculated values of the quantity

$$\phi(x) + F(323.16, x)$$

that is, the values of G^E/T at 50 °C were calculated from those at 35 and 65 °C using the enthalpy data. Figure 2 shows that the values of $\phi(x) + F(323.16, x)$ do indeed lie close to a common curve over most of the composition range but that there are systematic deviations of up to 0.1 J $\text{mol}^{-1} \text{deg}^{-1}$ in the range $0.15 < x < 0.4$. These deviations may arise from any of the following causes: experimental errors in the vapor-pressure measurements; experimental errors in the enthalpies of mixing; errors introduced in expressing H^E as a function of x and T ; errors in the values of B_{11} and B_{22} ; and errors introduced in the assumption $B_{12} = (B_{11} + B_{22})$. We believe that the sum of the errors from the first four sources does not exceed $\pm 0.03 \text{ J mol}^{-1} \text{ K}^{-1}$ and that the deviations from a common curve in Figure 2 are mainly due to the factor (3) above.

Reanalysis of earlier data. Since some of the earlier measurements have been shown to be inconsistent (21) with the

Table II. Mole Fractions of Methanol in Liquid and Vapor Phases in Equilibrium and Excess Gibbs Free Energies

x_1	y_1	$P, \text{mm Hg}$	$G^E (\delta = 0), \text{J mol}^{-1}$
35 °C			
0	0	42.16	0
0.0408	0.2490	55.00	101
0.0553	0.4343	70.33	200
0.1387	0.5274	81.55	268
0.2488	0.6738	105.09	344
0.3603	0.7559	122.99	364
0.4694	0.8084	137.61	368
0.6012	0.8611	154.36	327
0.7239	0.9071	170.12	244
0.7951	0.9316	179.87	193
0.8880	0.9636	193.20	110
0.9005	0.9683	193.96	82
0.9406	0.9815	201.05	57
1	1	210.09	0
50 °C			
0	0	92.50	0
0.0453	0.2661	122.73	116
0.0863	0.4057	146.74	192
0.1387	0.5227	174.21	266
0.1854	0.5898	194.62	321
0.3137	0.7087	239.97	397
0.4177	0.7684	266.99	399
0.5411	0.8212	298.44	402
0.6166	0.8520	316.58	367
0.7598	0.9090	352.21	258
0.8525	0.9455	376.44	164
0.9514	0.9817	403.33	58
1	1	417.40	0
65 °C			
0	0	187.54	0
0.0854	0.3926	292.72	223
0.0874	0.4018	294.04	205
0.1328	0.4963	337.21	285
0.1816	0.5718	377.29	334
0.2586	0.6512	429.60	397
0.4920	0.7842	544.83	460
0.5815	0.8242	583.87	426
0.7043	0.8747	634.71	378
0.8028	0.9180	680.39	240
0.9030	0.9605	727.27	122
1	1	774.95	0

Table III. Second Virial Coefficients and Molar Volumes

$T, \text{°C}$	$-B_{22}, \text{cm}^3 \text{mol}^{-1}$	$V_2^\circ, \text{cm}^3 \text{mol}^{-1}$	$-B_{11}, \text{cm}^3 \text{mol}^{-1}$	$V_1^\circ, \text{cm}^3 \text{mol}^{-1}$
35	1062	18.1	1500	41.2
50	842	18.2	1375	42.0
65	683	18.4	1200	42.8

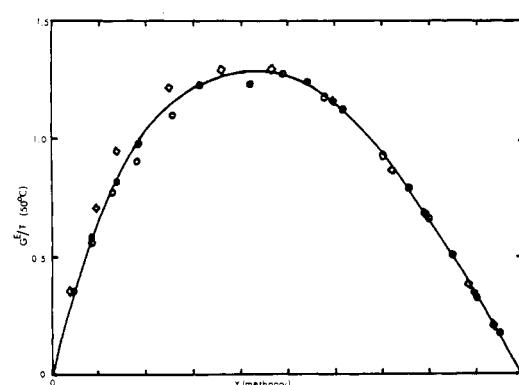


Figure 2. Consistency of excess Gibbs free energies of mixing with heats of mixing

— $\phi(x, T) = x(1-x)[1650 + 350(1-2x) + 234(1-2x)^2 + 675(1-2x)^3]$

◊ Calculated from G^E at 35 °C

○ Calculated from G^E at 65 °C

× Data for 50 °C

Table IV. Constants in Equation 7

Source of data	Temp, °C	$g_0, \text{J mol}^{-1}$	$g_1, \text{J mol}^{-1}$	$g_2, \text{J mol}^{-1}$	$g_3, \text{J mol}^{-1}$
This work P, x, y	65	0.6512	0.1458	0.0893	0.2333
	50	0.6122	0.1303	0.0670	0.2233
	35	0.5610	0.1081	0.0373	0.2102
This work P, x	65	0.6465	0.1530	-0.0382	
	50	0.6031	0.1366	-0.0492	
	35	0.5541	0.1122	-0.0953	
Butler et al. (7)	39.70	0.5069	0.0771	-0.1649	
		0.4912	0.0559	-0.1296	-0.1554
Vrewski (23)	39.90	0.5462	0.0970	-0.0639	
Bredig and Bayer (3)	49.76	0.5382	0.1107	-0.1904	

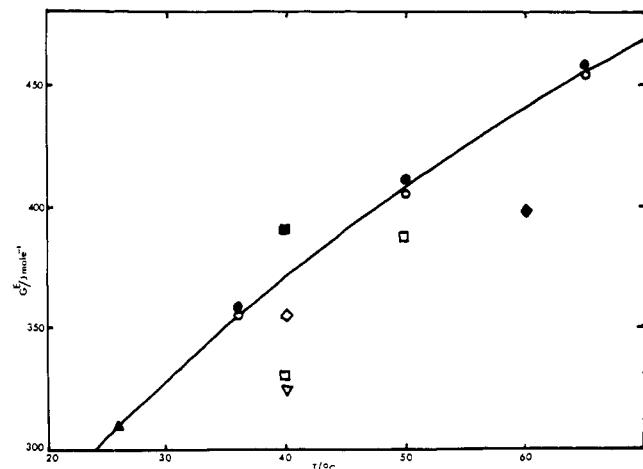


Figure 3. $G^{\circ f}$ at $x = 0.5$

- This work. Four-parameter equation using P, x, y
- This work. Three-parameter equation using P, x
- Bredig and Bayer (3) using P, x
- ◊ Vrewski (23) using P, x
- △ Butler et al. (7) using P, x
- ▽ Ferguson and Funnel (10) interpolated
- ◆ Broul et al. (4) using p, x, y ; no gas imperfection corrections
- Ratcliff and Chao (22) using p, x, y ; no gas imperfection corrections

Gibbs-Duhem relation and since it is our experience that the most probable source of experimental error in liquid-vapor equilibrium measurements is the vapor compositions, we have reanalyzed a number of them using the method described by Barker (1) which uses only the total pressure and liquid compositions and in which consistency with the Gibbs-Duhem relation is imposed on the results. The calculations were carried out with the assumption $\delta = 0$, and using the program devised by Myers and Scott (20) which leads to the parameters, g_n , in the equation

$$\frac{G^{\circ f}}{T} = x(1-x) \sum_{n=0}^m g_n(1-2x)^n \quad (8)$$

where x is the mole fraction of methanol. The results of these calculations are shown in Table IV. The values of g_n calculated in this way from our p, x data, together with the

values of g_n required to fit the $G^{\circ f}$ values calculated from our P, x, y data are also shown. (The differences in sign of g_2 arise from the method used to fit Equation 7 to the $G^{\circ f}$ values calculated from the P, x, y data. The graphical technique used in this case leads to alternate terms having the same sign, and since the first term is positive, the third term is also positive. The computer method used for the analysis of P, x data does not impose this restriction.) For all but the data of Butler et al., there is no justification for using more than three parameters. This method of imposing consistency with the Gibbs-Duhem relation makes only a small change in the values of $G^{\circ f}(x = 0.5)$ calculated from our experimental results. The values of $G^{\circ f}(x = 0.5)$ for the various studies are shown in Figure 3 from which only the data of Butler et al. are consistent with our own measurements.

We believe that this analysis of the available measurements is as far as one can go without experimental values of B_{12} for methanol-water mixtures.

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