Heats of Mixing in Some Non-electrolyte Solutions

BY GEORGE SCATCHARD, LELAND B. TICKNOR,[1a] J. REX GOATES[1b] AND ERIC R. MCCARTNEY[1c]

RECEIVED FEBRUARY 28, 1952

A simple calorimeter for determining the heat of mixing two liquids is described. With it the enthalpy of mixing of several binary and a few ternary mixtures have been determined. For non-polar mixtures there is good agreement with the values previously determined from the change of vapor–liquid equilibrium with temperature, and the enthalpy of ternary mixtures can be calculated from those of the component binaries by methods previously used. For mixtures containing methanol, the enthalpy of binary mixtures agrees with the revised values of Scatchard and Ticknor, and the enthalpy of ternary mixtures can be calculated from that of the component binaries only if the polar component is treated differently from the non-polar components.

The enthalpy and entropy of mixing of two volatile liquids have been calculated in this Laboratory from the free energy of mixing and its variation with the temperature.[2-4] The desirability of checking them with direct calorimetric measurements was made clearer when Williams, Rosenberg and Rothenberg[5] found by direct measurement 156 cal./mole, instead of the 268 cal./mole calculated by Scatchard, Wood and Mochel, for the maximum heat of mixing of methanol and benzene. The error in the latter calculation is explained in the following paper.[6]

Apparatus and Method

The discrepancies between heats of mixing measured by different observers are surprisingly large, and are probably caused by errors due to evaporation or condensation, which have large heat effects. The very simple apparatus described below makes this error negligible.

The liquids were mixed in an 18-mm. glass tube bent into an oval about 10 cm. in diameter, as in Fig. 1. The ends were drawn down to a 4-mm. diameter and closed with cork stoppers. The tube contained two glass wells of 8-mm. tubing; one held a three-junction copper–constantan thermocouple and the other was designed for a small heater, which was not used however. The reference junctions of the thermocouple were maintained at room temperature by immersion in water contained in a dewar flask. The e.m.f. was measured with an L and N Type K potentiometer and suitable galvanometer, which allowed observation of a temperature change of 0.01°.

The mixing tube was mounted on a wheel and suspended in a vertical plane in the center of a one-gallon dewar flask. The tube was filled by weighing about 14 ml. of mercury into the bottom, about 13 ml. of pure liquid A into one side and about 13 ml. of liquid B into the other side. This amount of mercury was sufficient to keep the liquids separated until the tube was rotated, and then it served to give quick and thorough mixing. In filling the tube the vapor space was kept at a minimum in order to reduce the errors which would result from evaporation or condensation.

It was necessary to have about the same volume of liquid in each arm of the tube. Therefore, in order to obtain mixtures with volume fraction equal to $^1/_4$, one arm was filled with the already measured mixture having volume fraction equal to $^1/_2$, and the other arm was filled with pure component. Thus, the composition range could be covered at volume fractions near $^1/_8$, $^1/_4$, $^3/_8$, $^1/_2$, etc. A similar procedure was used for the ternary mixtures. In these experi-

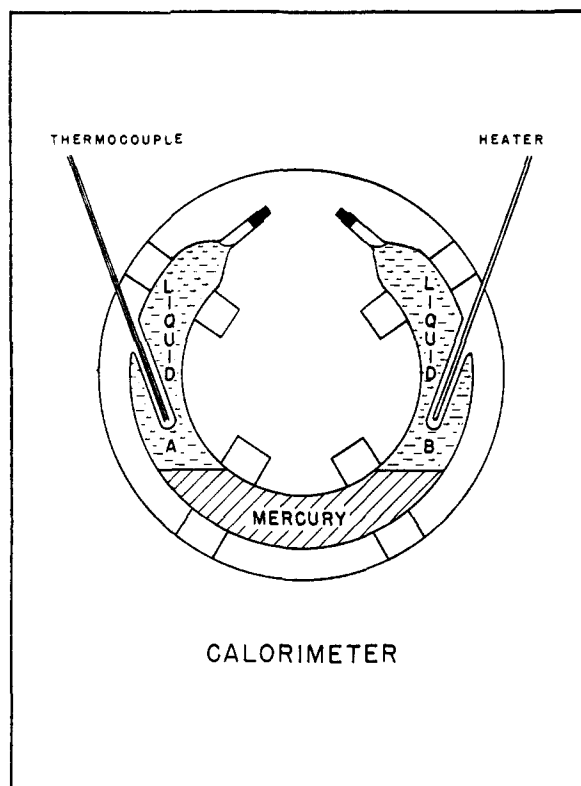THERMOCOUPLE   HEATER

MERCURY

CALORIMETER

Fig. 1.

ments the best quality commercial reagents were used without further purification.

The apparatus was operated in an air-conditioned room regulated at 20°. After the tube was filled and placed in the dewar, about three hours were required for the thermocouple e.m.f. to become constant. It was assumed that the liquids in the tube were then at the same temperature and mixing was begun. The tube was rotated alternately in opposite directions through about 270° at a constant rate; this rotation was continued throughout the period of observation. About 1.5 minutes were sufficient for mixing and for the transfer of heat to the thermocouple.

During the period of mixing the temperature of the tube was different from that of the air in the dewar. Accordingly, a correction was made for the transfer of heat between the air and the tube. A correction was also made for the heat added to the tube by stirring. The stirring correction amounted to about 0.03 cal./ml. and the correction for the heat exchanged with the air varied from 8 to about 20% of the total heat of mixing; the total correction was usually less than 15%.

The observed change in heat content was calculated from the change in e.m.f., the temperature vs. e.m.f. relation for the thermocouple, and the heat capacity of the tube, mercury and mixed liquids. Values were obtained from the literature for the specific heats of mercury[7] and the pure

(1) (a) This paper is based on the Ph.D. Thesis of L. B. Ticknor, 1950. The measurements were made in the summer of 1948. (b) Brigham Young University. (c) New South Wales University.

(2) G. Scatchard and C. L. Raymond, THIS JOURNAL, 60, 1278 (1938).

(3) G. Scatchard, S. E. Wood and J. M. Mochel, J. Phys. Chem., 43, 119 (1939).

(4) (a) G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, 61, 3206 (1939); (b) 62, 712 (1940); (c) 68, 1957 (1946); (d) 68, 1960 (1946).

(5) G. C. Williams, S. Rosenberg and H. A. Rothenberg, Ind. Eng. Chem., 40, 1273 (1948).

(6) G. Scatchard and L. B. Ticknor, THIS JOURNAL, 74, 3724 (1952).

(7) "International Critical Tables," Vol. V.

liquids[5-11] and for the change of heat capacity on mixing for the benzene–carbon tetrachloride–methanol mixtures.[6,7,17] For the other mixtures the heat capacity of mixing was taken to be zero. The value of the heat capacity of mixing is relatively unimportant since it changes the values of the heat of mixing by only about 2% at the most.

The heat capacity of the tube was measured by diluting hydrochloric acid solutions, for which the heat was obtained from the data of Van Nuys.[13] Two runs gave values of 10.23 and 9.85 cal. per degree; and a weighted average of 10.0 was taken.

No correction was made for volatilization or condensation nor for the absorption of liquid into the cork stoppers. These errors are estimated to be less than 0.1 and 0.2 cal. per mole, respectively. The uncertainty in the galvanometer readings was about one microvolt, which corresponded to about 0.2 cal. for the apparatus (about one calorie per mole or one-hundredth of a calorie per milliliter). The uncertainty in the heat capacity of the tube is believed to be less than 0.3 cal., which corresponds to about 1.2% of the total heat capacity. The heat capacity of the mixed liquids may be in error by 1% of the total heat capacity. The error in the corrections applied is probably less than 10%, which corresponds to 1.5% error in the corrected values.

Results

The heats of mixing were measured at $20 \pm 2°$ for six binary and two ternary systems. The results are given in Table I and are expressed as the heat of mixing in calories per milliliter, H_z^M, as a function of volume fraction, z. The volume per mole, V_x, the enthalpy of mixing per mole, H_x^M, and the mole fraction, x, may be computed from the relations

$$V_x = 1/\Sigma_i z_i / V_i$$
$$H_x^M = H_z^M V_x$$
$$x_i = V_x z_i / V_i$$

and the following values of molal volumes, V; methanol, 40.49; carbon tetrachloride, 96.51; benzene, 88.89; cyclohexane, 108.04; n-hexane, 130.68; n-hexadecane, 292.79.

Except in mixtures containing methanol the results are at least as symmetrical on the volume fraction basis as on the mole fraction basis. Analytic equations are given with the results for each system. The first three parameters were found to be insufficient to represent our results within our estimated uncertainty for the methanol–carbon tetrachloride and methanol–benzene systems.

The benzene–carbon tetrachloride system has been measured several times previously.[4b,12,14-17] The results at 20° range from 20 to 30 cal. per mole for an equal molal mixture with most values near 25 cal. per mole. Our value of 31 cal. per mole agrees more closely with the vapor–liquid equilibrium result[4b] of 30 cal. per mole.

In the methanol–benzene system the maximum occurs at about 0.3 mole-fraction methanol. At

(8) D. R. Douslin and H. M. Huffman, THIS JOURNAL, **68**, 1704 (1946).

(9) J. F. G. Hicks, J. G. Hooley and C. C. Stephenson, *ibid.*, **66**, 1064 (1944).

(10) G. D. Oliver, M. Eaton and H. M. Huffman, *ibid.*, **70**, 1502 (1948).

(11) R. A. Ruehrwein and H. M. Huffman, *ibid.*, **65**, 1620 (1943).

(12) Ch. G. Boissonnas and M. Cruchaud, *Helv. Chim. Acta*, **27**, 994 (1944).

(13) C. C. Van Nuys, *Trans. Am. Inst. Chem. Engrs.*, **39**, 663 (1943).

(14) E. Baud, *Bull. soc. chim.*, [IV] **17**, 329 (1915).

(15) H. Hirobe, *J. Faculty Sci. Imp. Univ. Tokyo*, **1**, 155 (1925).

(16) G. C. Schmidt, *Z. physik. Chim.*, **121**, 221 (1926).

(17) R. D. Vold, THIS JOURNAL, **59**, 1515 (1937).

TABLE I
CALORIMETRIC HEATS OF MIXING
Methanol (1)–Carbon tetrachloride (2)

$$H_z^M = x_1 x_2 [176 - 237(x_1 - x_2) - 383(x_1 - x_2^3) + 346(x_1 - x_2)^4)]$$

z_1	H_z^M	z_1	H_z^M
0.0564	0.78	0.2243	0.74
.0654	.78	.4740	.28
.0993	.85	.4900	.25
.1133	.83	.7465	−.11
.2164	.70	.7545	−.17

Methanol (1)–Benzene (2)

$$H_z^M = x_1 x_2 [600 - 250(x_1 - x_2) - 550(x_1 - x_2)^3 + 800(x_1 - x_2)^4]$$

0.0559	1.64	0.4766	1.93
.1134	2.02	.4828	1.86
.1162	2.05	.4918	1.97
.2485	2.17		

Carbon tetrachloride (1)–Benzene (2)

$$H_z^M = x_1 x_2 [123 - 35(x_1 - x_2)^2]$$
$$H_z^M = z_1 z_2 [1.25 + 0.08(z_1 - z_2)]$$

0.2416	0.22	0.7686	0.23
.5250	.31		

Carbon tetrachloride (1)–Cyclohexane (2)

$$H_z^M = z_1 z_2 [1.49 + 0.49(z_1 - z_2)^2]$$

0.2476	0.30	0.7738	0.29
.4988	.37		

Benzene (1)–Cyclohexane (2)

$$H_z^M = z_1 z_2 [8.00 - 0.59(z_1 - z_2)]$$

0.2659	1.58	0.5195	1.98
.4759	2.02	.7761	1.36

n-Hexane (1)–n-Hexadecane (2)

$$H_z^M = z_1 z_2 [0.67 - 0.18(z_1 - z_2)]$$

0.2246	0.13	0.5093	0.17
.4864	.17	.7928	.09

Methanol (1)–Carbon tetrachloride (2)–Benzene (3)

z_1	z_2	z_3	H_z^M
0.1247	0.4533	0.4220	1.71
.3208	.3596	.3196	1.48
.5658	.2374	.1968	0.88

Carbon tetrachloride (1)–Benzene (2)–Cyclohexane(3)

0.3340	0.3091	0.3569	1.22

this composition the heat of mixing in calories per mole was found by Wolfe, Pahlke and Wehage[18] to be about 195 at 20°, by Williams, *et al.*,[5] to be 156 and by this research to be 159. The values of Scatchard, Wood and Mochel[4c] are changed by the corrections given in the following paper[6] and now are in essential agreement with our calorimetric heats of mixing. The asymmetry of our curve is similar to that of Williams, *et al.*[5]

In the methanol–carbon tetrachloride system also a large discrepancy was found to exist between our calorimetric heats of mixing and those reported by Scatchard, Wood and Mochel,[4d] which were obtained from vapor–liquid equilibrium measurements. The corrections to the latter[6] bring them into essential agreement with our calorimetric values. The measurements of Roth as

(18) K. L. Wolfe, H. Pahlke and K. Wehage, *Z. physik. Chem.*, **B28**, 1 (1935).

reported by Mecke[19] give values which are greater than those from our equation for mole fractions of methanol less than 0.1, and lower than ours for mole fractions from 0.1 to 0.17, the limit of his measurements.

In the carbon tetrachloride–cyclohexane system the vapor–liquid equilibrium results between 30 and 70° of Scatchard, Wood and Mochel[4a] are about 11% or 0.04 cal. per ml. lower than our results. For the system benzene–cyclohexane Baud[16] obtained results which are within 1% of our results. The vapor–liquid equilibrium results between 30 and 70° of Scatchard, Wood and Mochel[3] are about 12% or 0.25 cal. per ml. lower. These differences may well be due to a decrease in the enthalpy of mixing with increasing temperature, due to the increase in volume.

The measurements with n-hexane-n-hexadecane were undertaken to correlate the enthalpy of mixing with the free energy determined by Brønsted and Koefoed[20] in order to compare the entropy with that calculated by Flory[21] and Huggins.[22] Recently van der Waals and Hermans[23,24] have made a very thorough study of several mixtures of aliphatic hydrocarbons. Their measurements on hexane–hexadecane appear to be the least precise. They obtain the equation $H_x^M = 120\ x_1x_2$ cal./mole, which gives a maximum of 0.14 cal./ml., where we obtain 0.17 cal./ml. The combination of our results with those of Brønsted and Koefoed yields an entropy of mixing approximately equal to that calculated by the equation of Flory and Huggins. Since the Flory–Huggins result should apply at constant total volume and ours at constant pressure, we should expect our value of TS^E to be greater than the Flory–Huggins value by about one-fourth of the heat of mixing.[25] The absolute values of the deviations from ideal solutions for this system are so small that these discrepancies are all about the magnitude of our experimental uncertainty.

Scatchard, Wood and Mochel[4b] proposed that for nearly symmetrical solutions, the excess free energy of a ternary solution may be expressed as the sum of the expressions for the three binary systems which make it up, provided that the higher terms are expressed symmetrically or antisymmetrically. They used volume fractions. Redlich and Kister[26] made the same proposal in terms of mole fractions, and expressed it much more elegantly as

$$G_x^M = x_1x_2\Sigma_\nu\ G_{12}^\nu(x_1 - x_2)^\nu + x_1x_3\Sigma_\nu\ G_{13}^\nu(x_1 - x_3)^\nu + $$
$$x_2x_3\Sigma_\nu\ G_{23}^\nu(x_2 - x_3)^\nu \quad (1)$$

If the parameters G_{12}, etc., are expressed as functions

(19) R. Mecke, Z. Elektrochem., **52**, 107 (1948).

(20) J. N. Brønsted and J. Koefoed, Det Kgl. Danske Videnkabernes Selskab, XXII, Nr. 17 (1946).

(21) P. J. Flory, J. Chem. Phys., **9**, 660 (1941); **10**, 51 (1942); **12**, 425 (1944); **13**, 453 (1945).

(22) M. L. Huggins, ibid., **9**, 440 (1941); J. Phys. Chem., **46**, 151 (1942); Ann. N. Y. Acad. Sci., **41**, 11 (1942); THIS JOURNAL, **64**, 1712 (1942).

(23) J. H. van der Waals and J. J. Hermans, Rec. trav. chim., **69**, 949, 971 (1950).

(24) J. H. van der Waals, ibid., **70**, 101 (1951).

(25) G. Scatchard, Trans. Faraday Soc., **33**, 160 (1937).

(26) O. Redlich and A. T. Kister, Ind. Eng. Chem., **40**, 341 (1948).

of T and P, this is a fundamental equation and any other thermodynamic function may be obtained by differentiation. The heat of mixing will have the same form but different values of the parameters. Furthermore, the expression may obviously be extended to any number of components. The justification suggested by Scatchard, Wood and Mochel was that if there is only a small effect of triple interactions when two of the three molecules are alike, we may expect a small effect from triple interactions when all the molecules are different.

Mixtures containing a polar component have large higher terms and require a more thorough analysis. We use g_{ij} to represent the contribution to any property of a binary interaction and g_{ijk} for the contribution of a ternary interaction. If no higher interactions need be considered we have for the binary mixture of 2 and 3

$$G_x = g_{22}x_2^2 + 2g_{23}x_2x_3 + g_{33}x_2^2 + g_{222}x_2^3 + 3g_{223}x_2^2x_3$$
$$+ 3g_{233}x_2x_3^2 + g_{333}x_3^3 \quad (2)$$
$$G_x^M = G_x - G_2x_2 - G_3x_3$$
$$= G_x - x_2(x_2 + x_3)g_{22} - x_2(x_2 + x_3)^2g_{222} -$$
$$x_3(x_2 + x_3)g_{33} - x_3(x_2 + x_3)^2g_{333}$$
$$= (2g_{23} - g_{22} - g_{33})x_2x_3 + (3g_{223} - 2g_{222} - g_{333})x_2^2x_3$$
$$+ (3g_{233} - g_{222} - 2g_{333})x_2x_3^2 \quad (3)$$

In a ternary mixture we have the sum of 3 sets corresponding to equation (3) with interchanged subscripts and in addition the term

$$(6g_{123} - 2g_{111} - 2g_{222} - 2g_{333})x_1x_2x_3$$

It is not possible to separate the interactions in the pure components except arbitrarily. Equation (1) for a binary system corresponds to choosing them such that

$$3g_{223} - 2g_{222} - g_{333} + 3g_{233} - g_{222} - 2g_{333} = 0$$

or

$$g_{223} + g_{233} = g_{222} + g_{333} \quad (4)$$

Equation (1) for a ternary system assumes that if this is true

$$6g_{123} = 2g_{111} + 2g_{222} + 2g_{333} = g_{112} + g_{122} + g_{113} +$$
$$g_{133} + g_{223} + g_{233} \quad (5)$$

Equations (4) and (5) are reasonable enough for non-polar mixtures, but in mixtures containing alcohol and two non-polar components, equation (5) does not seem probable. If interactions between alcohol molecules are more important than any others, we might expect rather that

$$2g_{123} = g_{122} + g_{133} \quad (6)$$

This will result in the replacement of $(x_1 - x_2)$ and $(x_1 - x_3)$ in the second term of equation (1) by $(2x_1 - 1)$, which causes no change in the equations for binary systems. The same replacement in the third term requires that

$$2g_{1123} = g_{1122} + g_{1133} \quad (7)$$

and

$$g_{1223} + g_{1233} = g_{1222} + g_{1333} \quad (8)$$

which are equivalent to equations (6) and (4) with a subscript 1 added to each g. The requirements for the higher terms need not be written out. We may then replace equation (1) for the first component polar, the second and third non-polar, by

$$G_Y^V = x_1 x_2 \Sigma \, G_{12}^v \, (2x_1 - 1)^v + x_1 x_3 \Sigma_v \, G_{13}^v (2x_1 - 1)^v +$$
$$x_2 x_3 \Sigma_v \, G_{23}^v (x_2 - x_3)^v \quad (9)$$

Table II gives the measured heats of mixing for some ternary mixtures and the values calculated by equations (1) and (9) with the parameters given for the binary systems in Table I. Figure 2 shows the heat of mixing as a function of the mole fraction of methanol for mixtures of methanol with carbon tetrachloride, with benzene and with an equimolal mixture of carbon tetrachloride and benzene, with
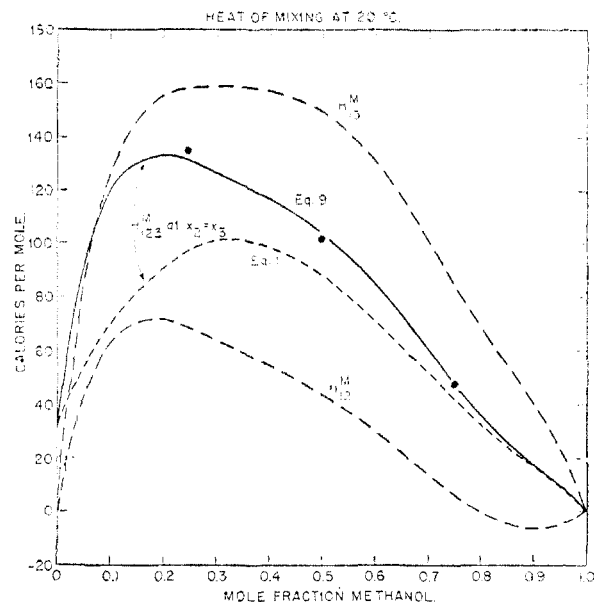

Fig. 2.

the pure liquid components as standard states. For the mixture, values from equation (1) are given as a broken line and from equation (9) as a full line. The experimental points are given only for the mixture.

TABLE II

HEATS OF MIXING OF METHANOL–CARBON TETRACHLORIDE–BENZENE

| | | | | H_2^M (cal./mole) | |
x_1	x_2	x_3	Meas.	Eq. (1)	Eq. (9)
0.2460	0.3750	0.3790	136	95	131
.5198	.2444	.2358	97	84	100
.7494	.1319	.1187	47	39	46

For a mixture of 0.3340 ml. of carbon tetrachloride, 0.3091 ml. of benzene and 0.3569 ml. of cyclohexane, the measured heat was 1.22 cal./ml.; calculation on the basis of volume fractions instead of mole fractions gave 1.19 for equation (1) and 1.20 for equation (9) with carbon tetrachloride as component 1. Equation (1) fits the measurement with all non-polar components within the experimental error, but fails to fit those for mixtures containing methanol. Equation (9) fits either within the experimental error.

It is possible that for some mixtures with all non-polar components, one component is sufficiently different from the others so that equation (9) is preferable to equation (1). It is also possible that in some system there will be an advantage in also replacing $(x_2 - x_3)$ by $(2x_2 - 1)$. Certainly there are systems which cannot be described without the addition of terms with three different subscripts.

CAMBRIDGE, MASSACHUSETTS

Vapor–Liquid Equilibrium. IX. The Methanol–Carbon Tetrachloride–Benzene System[1]

BY GEORGE SCATCHARD AND LELAND B. TICKNOR

The second virial coefficient of mixtures of methanol with benzene and with carbon tetrachloride is computed from the theory of polar–non-polar gas mixtures, and the thermodynamic properties of these mixtures are redetermined from the vapor liquid equilibrium measurements of Scatchard, Wood and Mochel. A new type of equilibrium still is described, which is more satisfactory for large differences between vapor and liquid compositions. The vapor–liquid equilibrium of the ternary system methanol–carbon tetrachloride–benzene is determined at 35° and 55°, and an equation for the excess free energy is presented which expresses these results and the enthalpy of mixing determined by Scatchard, Ticknor, Goates and McCartney.

Vapor-liquid equilibrium measurements furnish a method of measuring the activity coefficients or excess chemical potentials in a liquid mixture. The excess chemical potentials of each component in a mixture may be calculated from the relation

$$\mu_i^E = RT \ln \frac{P y_i}{P_{i_0} x_i} + (\beta_{ii} - V_i)(P - P_{i_0}) +$$
$$P[\Sigma_j \delta_{ij} y_j (1 - y_i) - \Sigma_{jk} \delta_{jk} y_j y_k / 2] + \Delta \quad (1)^2$$

in which P is the vapor pressure of the solution at

(1) This paper is based on the Ph.D. thesis of L. B. Ticknor, 1950. Paper VIII in this series is G. Scatchard, G. M. Kavanagh and L. B. Ticknor, THIS JOURNAL, 74, 3715 (1952).

(2) G. Scatchard and C. L. Raymond, ibid., 60, 1278 (1938).

the absolute temperature T, y_i and x_i are the mole fraction of the ith component in the vapor and liquid, respectively, $\delta_{ij} = 2\beta_{ij} - \beta_{ii} - \beta_{jj}$, and V_i is the liquid molal volume of component i, $i \neq i \neq k \neq i$, and Δ represents correction terms of higher orders of P. Equation 1 is valid for any number of components.

Deviations from Gas Laws.—In later work from this Laboratory it was assumed that the δ's and Δ were all zero, and the β's were calculated from those of water and the theory of corresponding states since there were no direct measurements for most of the substances studied. Recently Lam-