Summary

The vapor-liquid equilibrium pressures and compositions of benzene-methanol mixtures have been measured at approximately each eighth mole fraction at 35 and 55° and for approximately equimolal mixtures at 25 and 45°. The densities have been determined at 25°.

The excess change of the free energy, enthalpy, and entropy have been calculated and expressed analytically. The excess free energy change is positive over the entire range of composition and is quite symmetrical. The change of enthalpy is positive over the entire range of composition but is quite unsymmetrical, the maximum occurring at a mole fraction of about 0.3 in methanol. The excess entropy change is positive for solutions have a mole fraction up to about 0.3 in methanol and then becomes negative.

Cambridge, Mass. Received May 31, 1946

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Vapor-Liquid Equilibrium. VII. Carbon Tetrachloride-Methanol Mixtures[1]

By George Scatchard, Scott E. Wood[2] and John M. Mochel[3]

The present paper continues the measurement of the vapor-liquid equilibrium of solutions of methanol with the non-polar substances previously studied. The purification of the carbon tetrachloride was carried out as described in paper IV[4] of this series. The methanol was of the same material used for the measurements on the benzene-methanol system, VI.[5] The vapor pressure of carbon tetrachloride agreed with the values calculated by the equation given in IV within the experimental error.

Experimental

The apparatus and procedure for the density-composition measurements were the same as described in VI.[5] Due to the high molecular weight of carbon tetrachloride it was found necessary to correct the observed weight of the component first weighed in making up the solutions for the weight of the vapor displaced on addition of the second component. The results are shown in Table I in which are given the weight fraction and mole fraction of methanol, the observed density, δ, defined by equation VI-2,[6] and 100 V^M/V^0. The absolute values of V^M/V^0 for this system are somewhat larger in the methanol poor solutions and about five times larger in the methanol rich solutions than for the benzene-methanol system. The compositions of the vapor and liquid samples in the vapor pressure measurements were determined from their densities by Eq. VI-2, δ being read off from a large scale graph of the observed δ quantities *versus* the density.

Table I

Densities of Carbon Tetrachloride-Methanol Mixtures at 25°

Wt. fract. CH_3OH	Mole fract. CH_3OH	d	δ	$100V^M/V^0$
0.0000	0.0000	1.58452	....	.....
.0296	.1276	1.53764	+0.00032	+0.049
.0640	.2472	1.48731	+ .00026	+ .039
.1326	.4233	1.39691	− .00015	− .021
.1736	.5022	1.34781	− .00035	− .047
.2579	.6252	1.25715	− .00076	− .095
.2597	.6274	1.25526	− .00071	− .089
.3874	.7523	1.13928	− .00144	− .164
.3927	.7564	1.13472	− .00138	− .156
.5987	.8775	0.98697	− .00126	− .124
1.0000	1.0000	0.78654	....	.....

The vapor-liquid equilibrium measurements were made at intervals of approximately one-eighth mole fraction of the whole system at 35 and 55° and for approximately equi-molal mixtures at 25 and 45°, using the same apparatus and procedure described in the earlier papers.[5] As in the attain a steady state for those mixtures whose mole fraction of methanol in the whole system was 0.125 and 0.25 due to the extreme sensitivity of the boiling point to the composition of the liquid and the extreme sensitivity of this composition to the distribution of methanol in the various parts of the equilibrium still. For these mixtures the pressure was adjusted to maintain the temperature within 0.05° of the desired temperature for at least an hour.

The excess change in the free energy on mixing at constant pressure over that of an ideal solution of the same concentration was calculated from the observed vapor pressure and the equilibrium mole fractions of the vapor and liquid phases using the equations given in VI. The vapor pressures of carbon tetrachloride in mm. used in these calculations are 113.88, 174.47, 258.94 and 373.53 at 25, 35, 45 and 55°, respectively. The limits at zero pressure of the difference between the molal volume of the vapor and that of an ideal gas at the same temperature and pressure are −2290, −1992, −1749 and −1549 at 25, 35, 45 and 55°,

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Atlantic City, New Jersey, April 10, 1946.

[2] Present address: Yale University, New Haven, Connecticut.

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[4] G. Scatchard, S. E. Wood and J. M. Mochel, This Journal, **61**, 3206 (1939).

[5] G. Scatchard, S. E. Wood and J. M. Mochel, *ibid.*, **68**, 1957 (1946).

[6] Equation numbers beginning with VI refer to the preceding paper.

respectively. The molal volumes of the liquid were determined from the density equations given in the "International Critical Tables."

The analytical expression of these results led to difficulties similar to those with the benzene–methanol system, and they were met in the same way. The parameters determined for equation VI-9 are

$$A_{1112} = -66.55 + 1.224T \quad (1)$$
$$A_{1122} = 307.97 + 0.215T \quad (2)$$
$$A_{1222} = 300.65 + 0.365T \quad (3)$$

The experimental measurements are given in Table II in the order of the mole fraction of methanol in the liquid phase, the mole fraction of methanol in the vapor phase, the vapor pressure of the solution in mm., and the excess change of the free energy on mixing in cal. per mole. Adjacent to the last three columns the deviations of the corresponding quantities, calculated by equations 3, 4 and 9 of paper VI and equations 1, 2 and 3 of this paper, are also listed.

TABLE II

VAPOR PRESSURE OF CARBON TETRACHLORIDE–METHANOL MIXTURES

x_{CH_3OH}	y_{CH_3OH}	Dev. in y	Press., mm.	Dev. in P	F_x^E	Dev. in F_x^E
			35°			
0.0169	0.3297	+0.118	259.13	+39.3	34.90	+ 7.7
.0189	.3374	+ .112	262.31	+39.0	39.51	+ 9.2
.1349	.4630	− .027	315.12	− 6.5	187.52	+10.0
.3560	.4915	− .007	324.64	− 2.1	309.71	+ 9.6
.4776	.5030	+ .003	325.71	− 1.0	320.87	− 2.1
.4939	.5056	+ .005	325.71	− 2.0	319.92	− 1.9
.6557	.5302	+ .003	323.81	− 0.2	279.62	+ 0.4
.7912	.5792	− .004	312.61	+ 1.4	202.46	+ 0.8
.9120	.7024	− .004	277.37	+ 1.8	98.80	+ 0.4
			55°			
.0254	.3619	+0.087	580.66	+68.9	46.46	+ 5.5
.0579	.3639	− .044	591.16	−24.9	104.32	+15.9
.1493	.4981	− .013	716.95	− 5.6	202.21	+ 7.2
.3647	.5284	− .003	741.36	− 1.3	320.67	+ 0.2
.4893	.5431	+ .002	745.60	+ 0.1	331.22	− .4
.4946	.5438	+ .002	745.72	+ 0.2	330.90	− .4
.6448	.5686	− .001	744.54	+ 0.8	295.74	+ .4
.7903	.6187	− .005	724.28	+ 2.6	213.21	− .2
.9087	.7337	+ .004	658.37	+ 2.2	110.72	+ 2.1
			25°			
.4880	.4838	− .016	205.30	+ 7.3	312.91	− 4.8
			45°			
.4866	.5231	+ .002	500.13	− 0.3	326.57	− 0.5

The results at 35° are shown in Fig. 1 in which the total pressure and partial pressures plotted against the mole fraction of the liquid phase are represented by circles and the total pressures plotted against the mole fraction of the vapor phase are represented by the flagged circles. The solid lines give the corresponding calculated values and the dotted lines show the behavior of the system according to Raoult's law.

The smooth values of the excess change of the free energy on mixing at 35°, the heat of mixing, and 308.16 times the excess change of the entropy on mixing, all expressed in cal. per mole are given in Table III. The uncertainty in F_x^E at half mole fraction at 35 and 55° is estimated to be about 1 cal. This would cause uncertainties of about 0.1 cal. per deg. in S_x^E and about 31 to 33 cal. in TS_x^E and H_x^M. The uncertainties in these quantities for solutions richer in methanol are probably smaller than these estimates. It is for this reason that the values of the latter two quantities are given to 1 cal. in Table III and the deviations in F_x^E listed in Table II are given to 0.1 cal. The change of the volume on mixing at constant pressure is again quite small and consequently the difference in the change of the thermodynamic functions on mixing at constant pressure and on mixing at constant volume may be neglected.[7] However the values of 308.16 $(S_v^E - S_p^E)$ and $E_v^M - H_p^M$ are given in Table III.

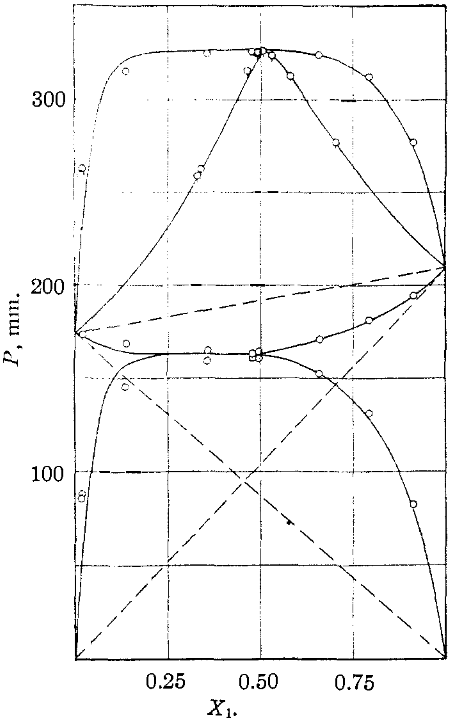

Fig. 1.—Vapor pressure *vs.* mole fraction for carbon tetrachloride–methanol at 35°.

TABLE III

SMOOTH VALUES OF THE THERMODYNAMIC FUNCTIONS IN CAL.

x_1	F_{x35}^E	H_x^M	308.16 S_x^E	308.16 $(S_v^E - S_p^E)$	$E_v^M - H_p^M$
0.1	140	102	− 37	−3	−3
.2	235	169	− 66	−3	−3
.3	293	200	− 92	−2	−2
.4	320	200	−120	+1	+1
.5	321	174	−147	+2	+2
.6	300	130	−171	+6	+5
.7	258	77	−181	+7	+7
.8	195	28	−168	+8	+7
.9	110	−3	−114	+5	+5

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

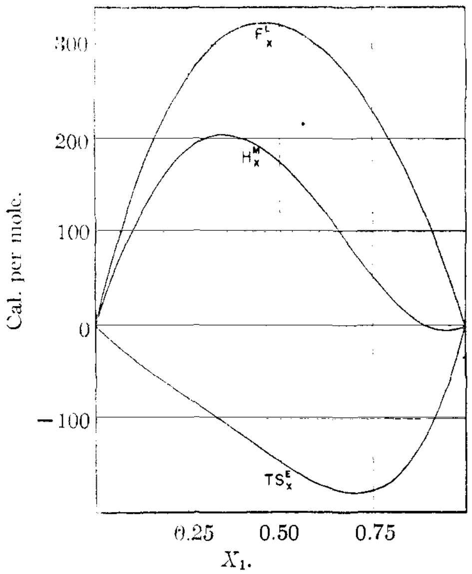

Fig. 2.—Various thermodynamic functions for carbon tetrachloride–methanol at 35°.

The smoothed values of F_x^E and TS_x^E at 35° and H_x^M are shown in Fig. 2. The excess change of the free energy on mixing is positive over the whole range of composition and is fairly symmetrical. The heat of mixing is quite unsymmetrical and apparently becomes negative in the solutions extremely rich in methanol. The minimum value is about −7 cal. per mole which may be about the uncertainty in this range of composition. Timofeev[8] has reported positive and negative values of the heat of mixing. Further the simple measurements of the heat of mixing of carbon tetrachloride and ethanol reported by Scatchard and Raymond[9] indicate both positive and negative values. It is therefore believed that although the uncertainties in the heat of mixing are somewhat large the general behavior is that shown by the curve. The excess change of the entropy on mixing appears to be negative over the whole range of composition, though much less so in the methanol poor solutions than in the methanol rich.

Discussion

The unusual behavior of the ethanol–chloroform system was attributed[9] to the interactions between the hydrogens of the hydroxyl and of chloroform with the oxygen of ethanol and the chlorine of chloroform. The positive enthalpy and excess entropy of mixing in solutions dilute in ethanol were attributed to dissociation of the aggregates of alcohol molecules, and the negative values in solutions rich in alcohol were attributed to an interaction between alcohol and chloroform to give aggregates each of which contains more molecules of alcohol than does an aggregate without chloroform. Since interaction of the chloroform hydrogen with the alcohol oxygen cannot account for this excess, it was assumed that the alcohol hydrogens react with the chloroform chlorines. This interaction seems to be the only explanation for the negative enthalpy change in ethanol–carbon tetrachloride mixtures rich in ethanol.

We expected in methanol–carbon tetrachloride mixtures a similar tendency to negative excess entropies and enthalpies in solutions rich in methanol, without being able to predict that the effect would be so different on the two functions that the enthalpy becomes negative only in mixtures very rich in methanol while the excess entropy is negative for all mixtures.

We were surprised, however, to find a similar asymmetry with methanol–benzene mixtures, although it is less marked than with carbon tetrachloride. Thus the enthalpy, though less positive in alcohol rich mixtures, is never negative, and the entropy changes from negative to positive as the methanol fraction becomes less than thirty per cent. In these mixtures there can be no parallel colinear dipoles such as that formed in methanol–carbon tetrachloride by the four atoms C–Cl H–O. There is a possibility of interaction between the hydrogen of benzene and the oxygen of methanol, but it does not seem probable that this can involve much energy and we know no other cases of strong interaction of aromatic hydrogen with oxygen. We believe that the most probable interaction is that of the hydroxyl hydrogen with the electrons within, and on both sides of, the benzene ring. These electrons should be easily polarizable, but we know no other examples of this type of interaction.

The mutual energy of unit volumes of the components may be calculated from the equation

$$a_{12} = \left(\frac{E_x^M}{z_1 z_2 V^0} + a_{11} + a_{22}\right)\Big/2$$

by approximating the value of E_x^M by H_x^M at half mole fraction and 35°. The absolute value of a_{12} is 5% greater than $\sqrt{a_{11}a_{22}}$ for benzene–methanol and about 8% greater than $\sqrt{a_{11}a_{22}}$ for carbon tetrachloride–methanol. This shows that there must be a strong interaction between molecules of the two components corresponding to the association of the alcohol molecules.

Summary

The vapor–liquid equilibrium pressures and compositions of carbon tetrachloride–methanol mixtures have been measured at approximately each eighth mole fraction at 35 and 55° and for approximately equimolal mixtures at 25 and 45°. The densities have been determined at 25°.

The excess change of the free energy, enthalpy and entropy have been calculated and expressed analytically. The excess free energy change is positive over the entire range of composition and is quite symmetrical. The change of enthalpy is positive over most of the range of composition

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[8] Timmermans, "Les Solutions Concentrées," Masson et Cie, Paris, 1936, p. 430.

[9] G. Scatchard and C. L. Raymond, This Journal, **60**, 1278 (1938).

apparently becoming negative for solutions extremely rich in methanol. The excess entropy change is negative over the whole range of composition and is also quite unsymmetrical.

The behavior of this system and that of benzene–methanol are discussed and explained by the strong and highly localized attractive forces.

CAMBRIDGE, MASS. RECEIVED MAY 31, 1946

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Thermodynamic Functions of Cyclohexane–Methanol Mixtures

BY SCOTT E. WOOD

The thermodynamic functions of benzene–methanol and carbon tetrachloride–methanol mixtures have been determined by vapor pressure measurements as described in the two preceding papers.[1] The same measurements have been obtained for the three possible binary systems using as components benzene, carbon tetrachloride, and cyclohexane.[2] The one remaining binary system of these four components, cyclohexane–methanol, is partially immiscible. Eckfeldt and Lucasse[3] have measured the liquid–liquid equilibria of this system. For the present paper the thermodynamic functions of the cyclohexane–methanol system have been calculated from these data by the method described by Scatchard and Hamer.[4] Also certain relationships between the three systems containing methanol are discussed.

Since the chemical potential of a component must be identical in the two liquid phases and since there are two components, analytical expressions containing two parameters can be set up for the chemical potentials in terms of the compositions. The basic equation[5] used in these calculations is

$$F_x^E = x_1x_2(A + Bx_1^2) \qquad (1)$$

where F_x^E is the excess change of the free energy per mole of solution on mixing at constant pressure over that of an ideal solution of the same concentration. The corresponding equations for the excess change in the chemical potentials are

$$\mu_1^E = x_2^2(A + Bx_1^2) \qquad (2)$$

and

$$\mu_2^E = x_1^2[A - Bx_1(3x_2 - 1)] \qquad (3)$$

This particular choice of expressing F_x^E as a function of the mole fraction was made since the equation yields reasonable values of both the excess change of free energy and the heat of mixing. This was not true of other two-parameter equations which were tried. However there is nothing in the data of the liquid–liquid equilibria to show whether this equation will represent the behavior of the homogeneous phases with changing composition. This can only be assumed.

In order to obtain values of A and B the compositions of the conjugate solutions at a given temperature must be known. However Eckfeldt and Lucasse report the solution temperatures from 31° to the critical solution temperature of 45.14° for various compositions. No simple equation for the solution temperature as a function of the composition nor of the composition as a function of the temperature could be found to fit the data. Consequently the deviations of the composition at various solution temperatures from the equation, $t = 11.76 + 131.04\,x_1 - 127.37\,x_1^2$, were plotted on a large scale. The deviations at each degree from 31 to 44° were then read off. The deviation at 45° could not be read accurately from the large scale plot. From these deviations the equilibrium concentrations were calculated and in turn the values of A and B. The values thus obtained were fitted to equations in the temperature by the method of least squares. The resulting equations are

$$A = 1563.3 - 1.852t + 3.3 \times 10^{-4}t^2 - 2.174 \times 10^{-3}t^3 \qquad (4)$$

$$B = -442.9 + 10.00t + 8.1 \times 10^{-3}t^2 \qquad (5)$$

The critical solution temperature and the mole fraction of cyclohexane in the critical solution were calculated to be 45.98 and 0.4895 in comparison to the observed values of 45.14° and 0.489. The compositions of the conjugate solutions were also calculated from these equations at every two degrees from 31 to 45° by the method described by Scatchard.[6] The curve in Fig. 1 represents the calculated liquid–liquid equilibria and the circles indicate the experimental points. The agreement between the calculated concentrations and those obtained by the use of the deviation curve is within 0.7%.

The excess change of the free energy, the heat of mixing, and the product of the temperature and the excess change of the entropy have been calculated at 31 and 40° and are given in Table I. These quantities at 31° plotted against the mole fraction of methanol are shown in Fig. 2. The solid portions of the curves are physically realizable whereas the dotted portions are not. The actual values of these quantities in the two-

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[1] G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **68**, 1957 (1946); *ibid.*, **68**, 1960 (1946).

[2] G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939); THIS JOURNAL, **61**, 3206 (1939); **62**, 712 (1940).

[3] E. L. Eckfeldt and W. W. Lucasse, *J. Phys. Chem.*, **47**, 164 (1943).

[4] G. Scatchard and W. J. Hamer, THIS JOURNAL, **57**, 1805 (1935).

[5] The subscript 1 is used to denote methanol.

[6] G. Scatchard, THIS JOURNAL, **62**, 2426 (1940).