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).

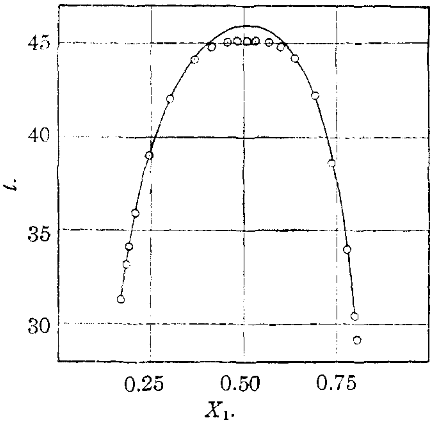

Fig. 1.—The liquid-liquid equilibria of cyclohexane–methanol mixtures.

liquid phase region would lie on a straight line connecting the end-points of the solid portions of the curves. The excess free energy change is of the same order of magnitude as that in the benzene–methanol and carbon tetrachloride–methanol systems and is also quite symmetrical. The heat of mixing appears to be several times larger than in the other two systems. However, it is quite unsymmetrical and shows characteristics similar to those in the other two systems. The excess change of the entropy also appears to be several times larger than in the other two systems but again it has similar characteristics. All the quantities are positive over the whole range of composition except the excess entropy change which appears to become slightly negative at 31° for solutions very rich in methanol. At 40° it is also positive over the whole range of composition.

TABLE I

THE THERMODYNAMIC QUANTITIES AT 31 AND 40° IN CALORIES PER MOLE

x_1	F_x^E	H_x^M	TS_x^E
		31°	
0.1	130	349	219
.2	230	603	374
.3	300	757	457
.4	341	810	468
.5	353	768	416
.6	335	650	315
.7	290	478	188
.8	218	285	67
.9	121	109	−11
		40°	
0.1	122	464	342
.2	216	809	593
.3	283	1027	743
.4	323	1117	794
.5	336	1087	752
.6	322	955	636
.7	281	744	463
.8	213	486	273
.9	119	222	102

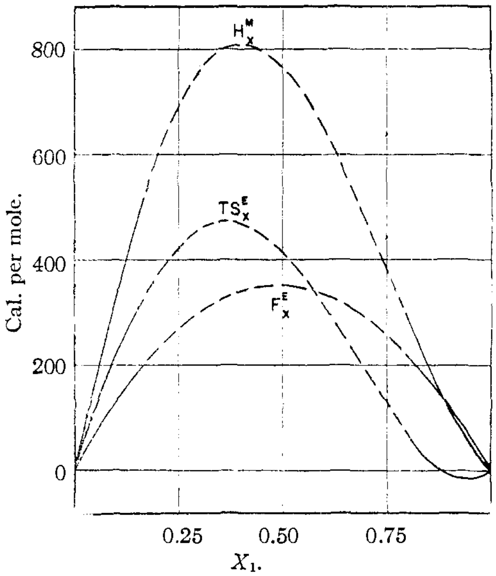

Fig. 2.—Various thermodynamic functions of cyclohexane–methanol mixtures at 31°.

Wolf[7] and Mondain-Monval[8] have both reported the heats of mixing for this system. Wolf's results are at 20° and Mondain-Monval's are over a range of temperature from 18 to 52°. These values at the conjugate solutions are of the order of 100 to 200 cal. It is estimated that the uncertainty in F_x^E due to uncertainties in the composition alone is about 5 cal. at 31° and 1 cal. at 40° at a mole fraction of methanol of 0.8. This would cause an uncertainty of about 200 cal. in H_x^M and TS_x^E, assuming a linear change in F_x^E with the temperature. At a mole fraction of 0.2, the uncertainties in F_x^E at 31° and 40° are about 2 cal., resulting in an uncertainty of about 150 cal. in H_x^M and TS_x^E. The uncertainty in F_x^E at both 31 and 40° due to an uncertainty of 0.01° in the temperature are estimated to be less than one calorie with a corresponding smaller uncertainty in both H_x^M and TS_x^E. The values of H_x^M calculated in this paper then agree with the experimental values within these estimated uncertainties. In spite of these large uncertainties the quantities in Table I are given to 1 cal. in order to obtain the curves shown in Fig. 2. The limitations of expressing the excess change of free energy as a somewhat arbitrary function of the composition containing only two parameters and of determining the values of these parameters from only two points may well transpose a dependency on composition into a dependency on temperature. This may result in considerable uncertainty in both the heat of mixing and the excess change of entropy on mixing and it is believed that these calculated results are too large if anything. It should be noted that any lowering of the entropy values would result in these values becoming negative

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[7] K. L. Wolf, *Trans. Faraday Soc.*, **33**, 179 (1937).

[8] P. Mondain-Monval, *Compt. rend.*, **183**, 1104 (1926).

over a considerable range of composition for solutions rich in methanol.

Harms[9] has determined the change of volume on mixing at 30° for the homogeneous phases. The differences between the changes of the thermodynamic functions on mixing at constant volume and on mixing at constant pressure can thus be calculated. The greatest differences occur in the methanol rich solutions and for $A_V^E - F_p^E$ are about 0.6 cal. per mole and for $E_V^M - H_p^M$ and $T(S_V^E - S_p^E)$ are about 50 cal. per mole. These quantities are thus less than the estimated uncertainties.

The similarity of this system to the other systems containing an alcohol, which have been studied, has already been mentioned. The asymmetrical nature of both the heat of mixing and the excess change of entropy again suggest that the attractive forces operating between the unlike molecules are of considerable magnitude, leading to the formation of clusters[10] containing unlike molecules. It would appear, however, within the accuracy of these results, that this formation of clusters proceeds to a lesser extent than in the other systems.

The similar behavior of all four systems is further emphasized in Fig. 3 where the heats of mixing are plotted against the mole fraction of alcohol and in Fig. 4 where the excess changes of the entropy are also plotted against the mole fraction of alcohol. The values used for these two figures are at 31° for the cyclohexane–methanol system, at 35° for the benzene–methanol and carbon tetrachloride–methanol systems, and at 45° for the chloroform–ethanol system. The differences in the excess free energy change for the three systems containing methanol are very small; for example, the molal values at half mole fraction are 300 cal. for benzene–methanol at 35°, 321 cal. for carbon tetrachloride–methanol at 35°, and 353 cal. for cyclohexane–methanol at 31°. It is thus evident that, while the molecular structures of the components other than alcohol are very different, any explanation of the behavior of all four of these systems must be the same. While a possible explanation has been outlined in the previous pages, no completely satisfactory explanation is possible at the present time. Certain qualitative relationships between the intermolecular forces operating between the unlike molecules may be obtained, however.

The cohesive energy densities at 25° of the four components, cyclohexane, carbon tetrachloride, benzene and methanol, are −67.32, −73.88, −84.18 and −209.7 cal. per cc. mole, respectively. Then, according to the simple theory, the order of decrease of the energy of mixing at constant volume, which is approximated by the heat of mixing at constant pressure, should be cyclohexane, carbon tetrachloride and benzene for the three systems containing methanol. Actually the heat of mixing decreases in the order cyclohexane, benzene and carbon tetrachloride, indicating stronger attractive forces between methanol and carbon tetrachloride molecules than might be expected from the simple theory. It may be pointed out that the excess changes of the free energy fall in the order predicted by this theory.

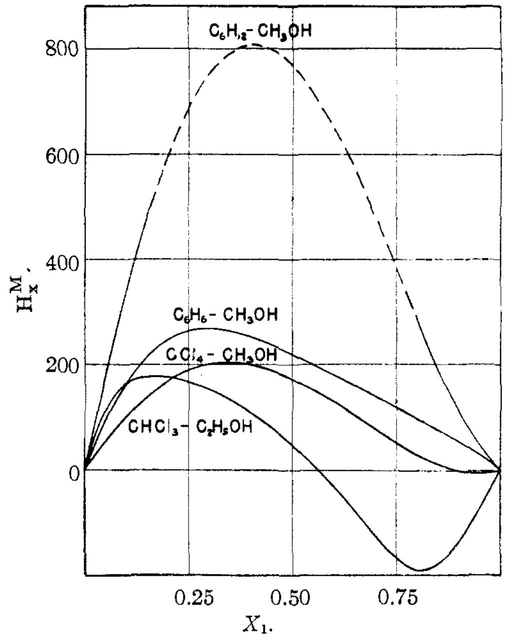

Fig. 3.—Heats of mixing *vs.* the mole fraction of alcohol.

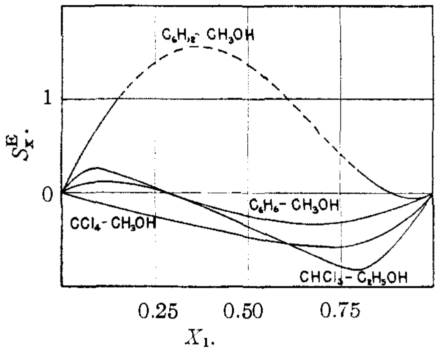

Fig. 4.—Excess entropy changes on mixing *vs.* the mole fraction of alcohol.

Scatchard and Raymond[11] suggested an explanation of the behavior of the chloroform–ethanol system based on very large attractions between the two unlike molecules when the net dipoles are parallel and colinear, with the hydroxyl group near the chloroform hydrogen, and on large attractions due to the parallel colinear dipoles formed by the four atoms C–Cl H–O. Similarly in the carbon tetrachloride–methanol system four such parallel colinear dipoles may exist resulting in large at-

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[9] H. Harms, *Z. physik. Chem.*, **B53**, 280 (1943).

[10] This formation of clusters might also be considered as an ordering of both the orientational distribution and spatial distribution of molecules about a given center molecule.

[11] G. Scatchard and C. L. Raymond, THIS JOURNAL, **60**, 1278 (1938).

tractive forces. These forces may be further enhanced by electronic polarization of the two groups and to a much smaller extent by atomic polarization. However, in the benzene–methanol and cyclohexane–methanol systems no such parallel colinear dipoles can be formed. The attractive forces between the unlike molecules must be due primarily to electronic polarization of the benzene or cyclohexane in the field of the oxygen–hydrogen dipole.[1] Atomic polarization may also occur to some extent. A relative comparison of the magnitudes of these forces may be obtained from the differences of the energy of evaporation of methanol to an ideal gas and the partial molal heat of mixing of methanol at infinite dilution in the non-polar solvents. These differences would then give the change of energy on transferring one mole of methanol from the ideal gas state to an infinitely dilute solution of methanol in the non-polar substances. Such differences are −7200 cal. for carbon tetrachloride–methanol, and −6200 cal. for benzene–methanol, and −4600 cal. for cyclohexane–methanol. Due to the uncertainties in the heats of mixing, especially in the cyclohexane–methanol system, too great an emphasis should not be placed on the numerical value. It seems quite certain, however, that they are of this order of magnitude. It is striking in view of the different molecular structures of the three non-polar substances that these energies are so much the same.

The author wishes to thank Professor George Scatchard for his helpful criticisms of this paper.

Summary

The changes of the free energy, enthalpy and entropy on mixing at constant pressure for the cyclohexane–methanol system have been calculated from the measurements of the liquid–liquid equilibria reported by Eckfeldt and Lucasse. The excess changes of these functions over those of an ideal solution are all positive over the entire range of composition except the entropy which appears to become slightly negative in the very rich methanol solution at 31°.

The thermodynamic functions of the four systems, benzene–methanol, carbon tetrachloride–methanol, cyclohexane–methanol and chloroform–ethanol, are very similar. The behavior of these systems is considered to be due to rather strong attractive forces operating between the unlike molecules. A relative estimate of these attractive forces between methanol and carbon tetrachloride, benzene or cyclohexane shows that they decrease in this order but that they are of the same magnitude.

NEW HAVEN, CONN. RECEIVED MAY 31, 1946

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF VERMONT]

The Conductance of Iodine in Liquid Hydrogen Sulfide

BY EDGAR E. LINEKEN[1]

Iodine dissolves in liquid hydrogen sulfide to form a solution which conducts the electric current. Quam and Wilkinson[2] report the specific conductance of the saturated solution. They suggest that iodine forms both positive and negative ions and they cite a transference experiment in support of that explanation. Walden[3] has similarly explained the conductivity of iodine solutions. Chipman and McIntosh[4] have measured the conductance of solutions of iodine in liquid hydrogen sulfide throughout a range of concentration. They found no evidence of a reaction between liquid hydrogen sulfide and iodine.

It seemed worth while to repeat the work of Chipman and McIntosh using modern bridge technique and making measurements on solutions more dilute than those prepared by the above authors.

Experimental

Apparatus.—The measuring bridge differed in no essential from that described by Lineken and Wilkinson[5] which in turn was very like that described by Shedlovsky.[6] A direct balance was permitted up to 10^6 ohms. Resistances higher than 10^6 ohms were calculated from the measured parallel resistance of the solution and a 10^6-ohm resistor.

A one-tube oscillator employing a conventional circuit was used. The oscillator coil was a Western Electric 211B input transformer which was electrostatically and electromagnetically shielded. By changing the capacitance of the circuit the the frequency could be varied from 470 to 2640 cycles per second.[7] Power was taken from the oscillator directly from the plate and the oscillator

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[1] Present address: Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

[2] Quam and Wilkinson, THIS JOURNAL, **47**, 989–994 (1925).

[3] Walden, *Z. physik. Chem.*, **43**, 358 (1903).

[4] Chipman and McIntosh, *Proc. Trans. Nova Scotian Inst. Sci.*, **16**, (pt. 4), 189–195 (1926).

[5] Lineken and Wilkinson, THIS JOURNAL, **62**, 251–256 (1940).

[6] Shedlovsky, *ibid.*, **52**, 1793–1805 (1930).

[7] The author is indebted to Professor E. R. McKee of the Department of Electrical Engineering at the University of Vermont for the loan of the coil and the condensers used in constructing the oscillator, for suggesting the circuit to be employed, and for his help in constructing and in calibrating the oscillator.