measured at 0 and 25° by a new procedure, confirming prior findings. The equilibrium constant for the aquation of this ion at 25° has also been determined.

4. The carbonato pentammine cobalti ion appears to undergo a very slow but still perceptible direct aquation.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 26, 1944

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Volume of Mixing and the Thermodynamic Functions of Binary Mixtures. II. Benzene–Cyclohexane[1]

BY SCOTT E. WOOD AND ALFRED E. AUSTIN[2]

The changes of the thermodynamic functions on mixing at constant pressure have been determined for mixtures of benzene and cyclohexane.[3] It is of interest in the theory of solutions to determine the changes of these functions on mixing at constant volume. In this paper the relation between the density and the composition of mixtures of benzene and cyclohexane at 30° and the specific volumes of the solutions from 15 to 75° have been measured. From these the changes of the volume on mixing at constant pressure and the changes of the thermodynamic functions on mixing at constant volume have been calculated.

The apparatus and procedure were identical to that described in the first paper of this series.[4] It was found that more consistent results in the measurement of the coefficient of expansion could be obtained if the walls of the capillary tip are quite thick. This prevents too rapid cooling while exchanging the mercury cups. The tip of the better dilatometer used in this work had an outside diameter of 5 mm. with a 0.1 mm. bore.

Purification of Materials.—Synthetic thiophene-free benzene was fractionally frozen twice, discarding approximately one-fifth of the starting material each time. It was then fractionally distilled in a 3-m. column,[4] six low-boiling and four high-boiling fractions being removed. The product was still not pure as determined by the density and consequently was frozen three more times, removing one-tenth of the liquid each time. The benzene was again distilled removing one low-boiling and one high-boiling fraction. The density of the final product at 30.00 ± 0.01° was 0.86833 g. per cc. in comparison with 0.86836 given by Scatchard, Wood and Mochel[3] and 0.86839 determined by Wood and Brusie.[4]

A technical grade of cyclohexane was nitrated with a mixture of five parts of concentrated nitric acid and nine parts of concentrated sulfuric acid for six hours at 5 to 10°. The two layers were separated and the cyclohexane was successively washed with water, dilute sodium hydroxide, and water. It was dried over Hydralo for forty-eight hours. It was then fractionally distilled, six low-boiling and three high-boiling fractions being removed. The density of the product at 30.00 ± 0.01° was 0.76910 g. per cc. in comparison with 0.76914 given by Scatchard, Wood and Mochel.[3]

Density–Composition Curve at 30°.—Since the composition of the solutions used in the dilatometer could not be determined directly, it was necessary to establish a density–composition curve. The temperature used was 30.00 ± 0.01°. Determinations of the density of the solutions were made at approximately each eighth mole fraction. Duplicate measurements, in which the order of weighing the components was reversed, were made at each composition. The observed weights were corrected for the displacement of air by both the liquid and vapor and for the weight of each component in the vapor after mixing, assuming equilibrium to be obtained. The vapor pressure data were used for these calculations.[3]

Since the density–composition measurements were made with the liquids saturated with air and the coefficient of expansion data were determined with solutions free from air, a further correction was applied. The difference between the density observed in the dilatometer and that in the pycnometer at 30° was 0.00012 g. per cc. for benzene and −0.00002 g. per cc. for cyclohexane. The corrections necessary for the solutions were assumed to be additive in the volume fraction although the difference between using the volume fraction and mole fraction is negligible.

The mole fractions of the solutions used in the dilatometer were determined from the density at 30° by means of the equations

$$d = \frac{d_2 + (d_1 - d_2)z_1}{1 + V^M/V^0} \qquad (1)$$

$$100\,V^M/V^0 = z_1z_2(3.0129 - 0.7590z_1) \qquad (2)$$

V is the molal volume of the mixture, V^0 that of the unmixed components, and $V^M = V - V^0$, z_1 is the volume fraction of benzene; d_1 and d_2 are the corresponding densities of the two components. The mole fraction of benzene in the solutions, the density corrected for air, the difference of the observed density and that calculated from equations 1 and 2, and 100 V^M/V^0 calculated from

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[1] This contribution contains material taken from a thesis by Alfred E. Austin presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: Corning Glass Works, Corning, New York.

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

[4] S. E. Wood and J. P. Brusie, THIS JOURNAL, **65**, 1891 (1943).

TABLE I

DENSITY OF BENZENE–CYCLOHEXANE MIXTURES AT 30°

x_1	d	Δd	$100V^M/V^0$
0.0000	0.76908	....	0.000
.1286	.77762	−0.00001	.283
.1333	.77796	.00000	.292
.2521	.78682	− .00001	.484
.2548	.78703	− .00001	.488
.3803	.79755	− .00005	.615
.3832	.79777	+ .00002	.617
.5007	.80865	+ .00002	.661
.5084	.80938	.00000	.662
.6206	.82090	+ .00002	.631
.6290	.82182	+ .00003	.625
.7484	.83534	.00000	.510
.7511	.83567	.00000	.506
.8651	.84988	− .00002	.318
.8710	.85065	− .00002	.307
1.0000	.86845	....	.000

equation 2 are given in Table I. The standard deviation in the density is 2×10^{-5} g. per cc. The values of $100V^M/V^0$ are shown in Fig. 1; the open circles represent points obtained in this research and the filled circles represent the data of Scatchard, Wood and Mochel.[3]

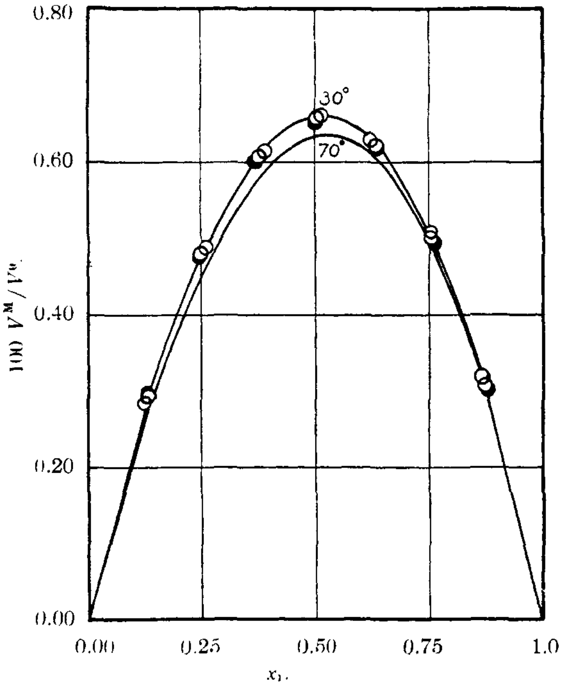

Fig. 1.—Percentage change of the volume on mixing at 30 and 70°

Coefficient of Expansion.—The specific volumes of the pure liquids were determined from 15 to 79° and those of the solutions from 15 to 75° at 10° intervals. The temperature was determined to ±0.01°. The weight of the dilatometer and the expelled mercury at the end of the experiment agreed within 0.5 mg. of the original weight. This would give a total error of 0.00004 cc. in the change of the specific volume from 15 to 75°. The specific volumes were fitted to a cubic equation in the temperature by the method of least squares. Table II gives the mole fraction of benzene, the coefficients for the type equation

$$v = a + bt + ct^2 + dt^3 \qquad (3)$$

and the standard deviations of the calculated specific volumes from the observed values. The densities of the solutions at 30° were calculated from these equations and the composition of the solutions in turn was calculated from equations 1 and 2.

TABLE II

COEFFICIENTS FOR THE EQUATION FOR THE SPECIFIC VOLUMES

x_1	a	$b \times 10^3$	$c \times 10^6$	$d \times 10^9$	$\Delta v \times 10$
0.0000	1.25439	1.4718	1.472	15.56	10
.1534	1.23784	1.4387	2.012	8.51	2
.2539	1.22567	1.4506	1.217	14.77	2
.3606	1.21223	1.4201	1.691	9.90	2
.5056	1.19198	1.4263	0.747	17.74	4
.6364	1.17295	1.3574	2.020	6.24	1
.7513	1.15407	1.3756	1.028	13.20	2
.8681	1.13448	1.3327	1.497	8.85	1
1.0000	1.11062	1.3105	1.477	7.65	4

The specific volume of benzene at 25° given by the equation is 1.14442 cc. per g. in comparison to 1.14443 given by Wood and Brusie,[4] 1.14434 given by Burlew,[5] 1.14456 given by Scatchard, Wood and Mochel,[6] and 1.14457 given by Timmermans and Martin.[7] The differences between the values of $(\partial v/\partial t)_p$ obtained by Wood and Brusie[4] and in this work are shown by the dotted line and the differences between the values of Burlew[5] and this work are shown by the solid line in Fig. 2.

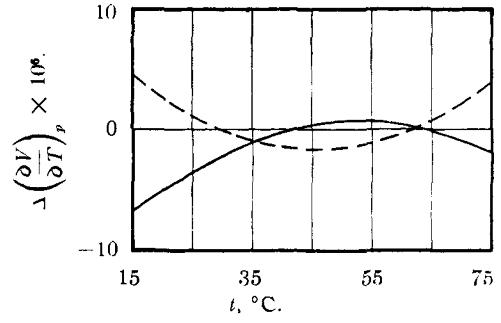

Fig. 2.—Deviations of $(\partial V/\partial T)_p$ for benzene.

The values of V^M/V^0 have been calculated from equations 3 at 5° intervals and fitted to an equation of the form

$$100V^M/V^0 = z_1z_2(A - Bz_1) \qquad (4)$$

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[5] J. S. Burlew, THIS JOURNAL, **62**, 690 (1940).

[6] G. Scatchard, S. E. Wood and J. M. Mochel, *ibid.*, **62**, 712 (1940).

[7] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926).

in which the coefficients are the following functions of the temperature

$$
\begin{aligned}
A &= 2.9818 - 1.845 \times 10^{-3}t + \\
&\quad 1.338 \times 10^{-4}t^2 - 2.065 \times 10^{-6}t^3 \\
B &= 0.6640 - 5.072 \times 10^{-4}t + \\
&\quad 1.833 \times 10^{-4}t^2 - 2.874 \times 10^{-6}t^3.
\end{aligned} \qquad (5)
$$

The deviations of the densities calculated from equations 1, 4 and 5 from the densities observed in the expansion measurements are shown in Fig. 3. The standard deviation of the densities at each composition is 3 × 10^{-5}. The curves for $100V^{\mathrm{M}}/V^0$ at 30 and 70° are shown in Fig. 1. In Fig. 4, $100V^{\mathrm{M}}/V^0$ is shown as a function of the temperature by the solid lines and V^{M} by the dotted lines. While $100V^{\mathrm{M}}/V^0$ is asymmetric toward the solutions richer in benzene, V^{M} is asymmetric toward the solutions richer in cyclohexane. This reversal is due to the large differences in the molal volumes of the pure components which are about 20%. $100V^{\mathrm{M}}/V^0$ decreases with the temperature. V^{M}, on the other hand, passes through a maximum in solutions having a mole fraction of benzene of 0.6364 or less and increases continuously in the range of the temperature studied for the solutions having a mole fraction of 0.7513 and 0.8681. The data of Pavlow[8] at 20° are in reasonable agreement with the present results. Dunken[9] gives a maximum of 0.65 cc. at 20° for V^{M} for equal molal mixtures in comparison to 0.66 obtained in this work.

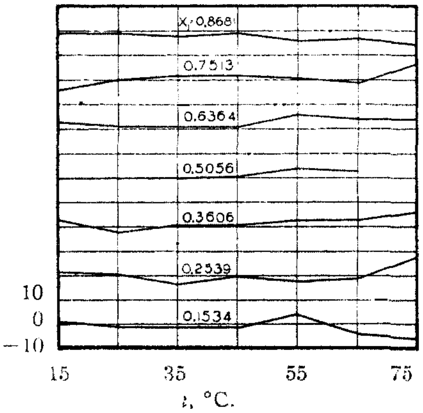

Fig. 3.—Difference between the observed density and that calculated by equations 1, 4 and 5.

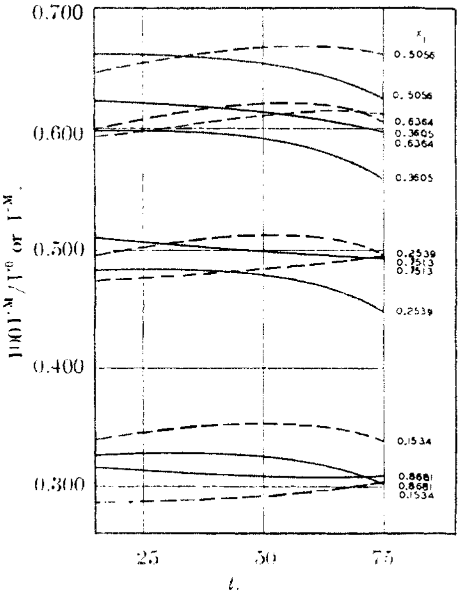

Fig. 4.—Variation of $100V^{\mathrm{M}}/V^0$ (solid lines) and V^{M} (dotted lines) with the temperature.

Thermodynamic Functions.—The excess change of the molal free energy above that of an ideal solution on mixing at constant pressure, $F^{\mathrm{E}}{}_{\mathrm{px}}$, the molal heat of mixing at constant pressure $H^{\mathrm{M}}{}_{\mathrm{px}}$, and the excess change of the molal entropy on mixing at constant pressure, $S^{\mathrm{E}}{}_{\mathrm{px}}$, have been determined from the vapor pressure.[3] By use of the equations given by Scatchard[10] and the results of this research the excess change at constant volume of the molal work content and entropy, $A^{\mathrm{E}}{}_{\mathrm{vx}}$ and $S^{\mathrm{E}}{}_{\mathrm{vx}}$, and the molal energy of mixing at constant volume, $E^{\mathrm{M}}{}_{\mathrm{vx}}$, have been calculated at 25, 30, 40 and 70°. The variation of the free energy of mixing with the temperature, as determined from the vapor pressure measurements, is uncertain. Consequently the variation of the heat of mixing and entropy of mixing with the temperature is quite indefinite. Scatchard, Wood and Mochel[3] give two equations for the excess free energy change. These are

$$F^{\mathrm{E}}{}_{\mathrm{px}} = (6.943 - 0.0132337T)\,V^0{}_{\mathrm{x}}z_1z_2(1 + 0.084z_2{}^2) \qquad (6)$$

and

$$
\begin{aligned}
F^{\mathrm{E}}{}_{\mathrm{px}} = (13.154 - 0.0511587T &+ \\
0.00005777T^2)\,V^0{}_{\mathrm{x}}z_1z_2&(1 + 0.084z_2{}^2)
\end{aligned} \qquad (7)
$$

Preference was given to the simpler equation since the accuracy of the experimental data did not warrant the more complicated equation. Both equations have been used in this research but no further conclusion as to the preference between them can be given.

For these calculations the values of the coefficient of expansion in reciprocal degrees and of the coefficient of compressibility in reciprocal atmospheres are given in Table III. α_0, β_0,[11,12] and α_0/β_0 are additive in the volume fraction. It is assumed that d ln $\beta/\mathrm{d}T$ is also additive in the volume fraction. The errors in this assumption and the assumption that β equals β_0 for the solutions are negligible. The values of z based on the values of V_1 and V_2 at 25° are identical within 1 × 10^{-4} to those based on V_1 and V_2 at the separate temperatures.

The curves of $H^{\mathrm{M}}{}_{\mathrm{px}}$, and $F^{\mathrm{E}}{}_{\mathrm{px}}$ and $E^{\mathrm{M}}{}_{\mathrm{vx}}$ at 30

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[8] G. S. Pavlow, *J. soc. phys.-chim. russe*, **58**, 1302 (1926).

[9] H. Dunken, *Z. physik. Chem.*, **B53**, 264 (1943).

[10] G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

[11] "International Critical Tables," Vol. III, p. 38.

[12] "Tables Annuelles de Constantes et Données Numériques," VI, 16 (1923-1924).

TABLE III

	25°	30°	40°	70°
	Benzene			
$\alpha_0 \times 10^3$	1.222	1.233	1.257	1.344
$\beta_0 \times 10^6$	99	103	111	143
α_0/β_0	12.34	11.97	11.32	9.40
$d \ln \beta/dT$	0.0078	0.0079	0.0081	0.0087
	Cyclohexane			
$\alpha_0 \times 10^3$	1.218	1.232	1.264	1.392
$\beta_0 \times 10^6$	110	116	129	170
α_0/β_0	11.07	10.62	9.80	8.19
$d \ln \beta/dT$	0.0110	0.0107	0.0101	0.0084

and 70° shown in Fig. 5 are obtained by the use of equation 6. The values of A^{E}_{vx} differ from those of F^{E}_{px} by less than 0.5 calorie and consequently the two curves coincide in the figure. The circles represent the values of H^{M}_{px} given by Baud[13] between 15 and 20°. Table IV gives a summary of the various quantities of equimolal mixtures at 25, 30, 40, and 70°. The numbers 6 and 7 in parentheses refer to the use of either equation 6 or 7 as a basic equation. Using equation 6, H^{M}_{px} and S^{E}_{px} are constant in respect to the temperature and both E^{M}_{vx} and S^{E}_{vx} increase with the temperature. When equation 7 is used, all the quantities H^{M}_{px}, E^{M}_{vx}, S^{E}_{px} and S^{E}_{vx} show rather large decreases as the temperature increases. The values of E^{M}_{vx} at the different temperatures are calculated on the basis that the volume of the solution is the same as the additive volume of the pure components measured at the corresponding temperature and one atmosphere pressure. However, these quantities should be compared at the various temperatures under such conditions that the volume is the same at all temperatures. Very accurate measurements of the compressibilities of these solutions are needed for such calculations. S^{E}_{vx}, using either equation, is always greater than zero while in the simple theory it is assumed to be zero.

TABLE IV

PROPERTIES OF EQUIMOLAL MIXTURES

		25°	30°	40°	70°
V^{M}		0.653	0.656	0.662	0.665
$100V^{M}/V^0$		0.659	0.658	0.656	0.633
F^{E}_{px} cal./mole	(6)	75.9	74.2	70.8	60.8
F^{E}_{px} cal./mole	(7)	76.8	74.8	70.8	60.8
H^{M}_{px} cal./mole	(6)	175.7	175.7	175.7	175.7
H^{M}_{px} cal./mole	(7)	202.9	198.5	189.5	160.7
E^{M}_{vx} cal./mole	(6)	122.7	123.5	124.8	128.7
E^{M}_{vx} cal./mole	(7)	150.0	146.3	138.6	113.7
S^{E}_{px} cal./deg.	(6)	0.335	0.335	0.335	0.335
S^{E}_{px} cal./deg.	(7)	0.423	0.408	0.379	0.291
S^{E}_{vx} cal./deg.	(6)	0.156	0.161	0.171	0.197
S^{E}_{vx} cal./deg.	(7)	0.244	0.234	0.215	0.153
a_{12}	(6)	−73.25	−72.02	−69.62	−62.87
a_{12}	(7)	−72.70	−71.56	−69.35	−63.16
$\sqrt{a_{11}a_{22}}$		−75.28	−74.07	−71.67	−64.95
$100\,(a_{12} - \sqrt{a_{11}a_{22}})/a_{12}$	(6)	2.77	2.85	2.94	3.31
	(7)	3.55	3.51	3.35	2.83

The cohesive energy density between the unlike molecules can be obtained by the equation

$$a_{12} = (a_{11} + a_{22} + E^{M}_{vx}/V^0 z_1 z_2)/2 \qquad (8)$$

The absolute values of a_{12} are always less than the geometrical mean of a_{11} and a_{22} in agreement with the prediction of the quantum mechanical treatment of intermolecular forces.[14] The per cent. decrease of a_{12} from $\sqrt{a_{11}a_{22}}$ increases with the temperature when equation 6 is used and decreases when equation 7 is used. The values of a_{11} and a_{22} at 25, 30, 40 and 70° were calculated to be −84.18, −82.80, −80.13, −72.54 cal. per cc. for benzene and −67.32, −66.25, −64.11, −58.15 cal. per cc. for cyclohexane. The values of β in the equation of state for the vapor, $V - RT/P = \beta$, at 25, 30, 40 and 70° used in these calculations are −2264, −2107, −1839, −1287 for benzene and −2488, −2318, −2028, −1427 for cyclohexane.

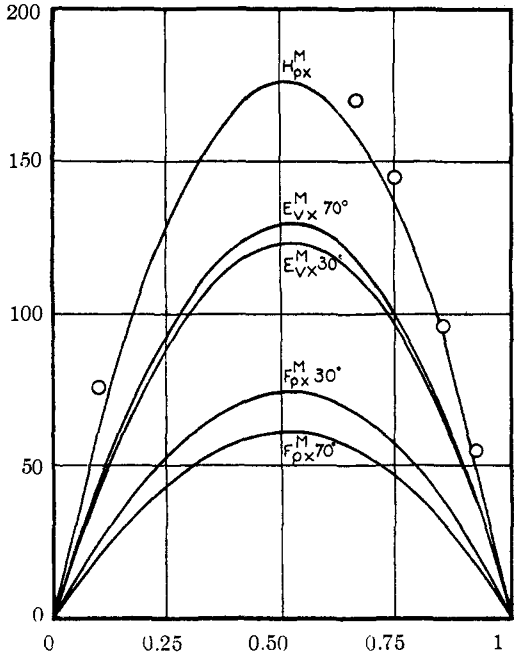

Fig. 5.—Various thermodynamic functions of benzene–cyclohexane mixtures at 30 and 70°.

Summary

The volume change on mixing benzene and cyclohexane at constant pressure has been determined over the entire composition range from 15 to 75°. From this the excess change of the work content, energy, and entropy on mixing at constant volume over that of an ideal solution has been calculated. The volume of mixing is positive and in general increases with the temperature and the excess entropy on mixing at constant volume is also positive over this temperature range.

NEW HAVEN, CONNECTICUT

RECEIVED DECEMBER 28, 1944

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

(14) F. London, *Z. physik. Chem.*, **B11**, 222 (1930).