25° intervals from 100° to and including 275° at pressures ranging from one or two atmospheres above the vapor pressures to approximately 300 atmospheres.

2. The data are presented tabularly and graphically, the specific volumes in cc./g. being related to the pressures at different temperatures.

AUSTIN, TEXAS RECEIVED JUNE 15, 1943

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Volume of Mixing and the Thermodynamic Functions of Benzene–Carbon Tetrachloride Mixture[1]

BY SCOTT E. WOOD AND JAMES P. BRUSIE

The study of binary liquid mixtures by means of vapor pressures gives the change of the thermodynamic functions on mixing at constant pressure, whereas the theory gives the change of these functions on mixing at constant volume. The relationship between these functions for the two processes of mixing involves the volume of mixing.[2] It is therefore important to determine the volumes of mixing at several temperatures in order to determine how these functions change with temperature. This has been accomplished for benzene–carbon tetrachloride mixtures by measuring the volume of mixing at 30° and the coefficient of expansion from 15 to 75° over the whole range of composition.

Apparatus and Procedure.—The apparatus used for the expansion measurements is essentially that of Burlew.[3] The design of the dilatometer was changed to that in Fig. 1b for greater ease of filling. The volume was about 5 cc., approximately 3 cc. being allowed for the solutions and 2 cc. for the mercury. During operation the tip of the capillary was always immersed below the surface of the mercury contained in the small receiving cups. Great difficulty was encountered in removing the last bubble of air from the tip of the capillary when joining the mercury in the capillary and in the cup. Many times the bubble seemed to cling to the tip and reënter the capillary when the dilatometer was cooled. This was overcome by grinding one side of the tip at a 45° angle up to the edge of the bore, as shown in cross-section in Fig. 1b.

It was determined that noticeable amounts of mercury evaporated from the collecting cups during the course of a run. Therefore a second cup of approximately the same size was always placed beside the collecting cup in order to determine this loss. At the end of each run the dilatometer was again weighed which together with the weight of the mercury in the receiving cups gave a measure of the loss of mercury by evaporation. This loss agreed to about 10% of the loss of mercury from the control cups.

The dilatometers were filled at room temperature under vacuum in the same manner as described by Burlew.[3] However, since the density of the liquid mixtures was unknown, it was necessary to weigh both the mercury and solution in the dilatometer. All weights were recorded to ±0.01 mg. and were consistent to ±0.03 mg. They were corrected to vacuum. After the capillary had been dried the dilatometer was placed in the steel cylinder with a receiving cup in position. The mercury was then joined by gently heating the steel cylinder. Each series of measurements was started at 15°. The dilatometer was held at the desired temperature for one hour at the end of which time the two cups were replaced by another set and the temperature was raised. The temperature of the oil-bath was held to ±0.005°.

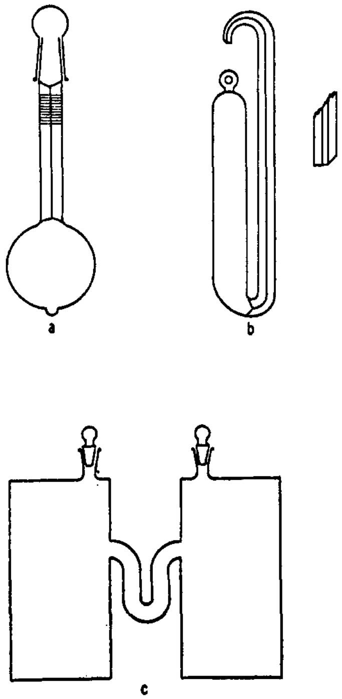

Fig. 1.—Apparatus.

The dilatometers were calibrated by a series of measurements with water at 10° intervals from 15 to 85°. The density of water in grams per cubic centimeter was com-

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[1] This contribution contains material taken from a thesis by James P. Brusie presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1943.

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

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

puted from the data given in the "International Critical Tables."[4] The density of mercury was obtained from the equation given by Scheel and Blankenstein.[5] Two dilatometers were used in the course of the work. The values of the volume of the dilatometer at different temperatures were fitted to a linear equation in t by the method of least squares. The resulting equations are

$$v_t = 0.0735560\ (1 + 1.8182 \times 10^{-4}\, t + 7.8 \times 10^{-9}\, t^2)$$

$$V_t = 5.39603 + 5.47 \times 10^{-5} t$$

and

$$V_t = 5.23939 + 5.61 \times 10^{-5} t$$

The standard deviation from the equation for the first dilatometer was 2.5×10^{-5} and the second dilatometer was 2.2×10^{-5}. However, there is a systematic error of approximately $\pm 1 \times 10^{-4}$ due to the uncertainty in the weight of water. The coefficient of expansion of the Pyrex glass determined from these equations is 1.01×10^{-5} for the first dilatometer and 1.07×10^{-5} for the second. This compares with 1.06×10^{-5} given by Burlew[3] and 0.985×10^{-5} given by Jones and Jelen.[6]

Since the composition of the solutions used in the dilatometers could not be determined directly it was necessary to establish a density–composition curve at some one temperature. The temperature used was 30.00 ± 0.01°. The pycnometers were of the design shown in Fig. 1a and had a volume of about 10 cc. The solutions were made up in vessels constructed as in Fig. 1c, each side having a volume of about 60 cc. The small U-tube was sealed with mercury and the individual components were weighed in the separate sides. The liquids were easily mixed by tipping the vessels back and forth.

The purification of the materials was carried out as described previously.[7] The distilling column was of similar design but had a length of about 3 meters and an internal diameter of 1.9 cm. Three heaters were wound on the shield around the column in such a way that five heating zones were obtained. The lowest fifth was held at the temperature of the pot, the middle fifth at the temperature of the middle part of the column, and highest fifth at the temperature of the head. The second and fourth fifths of the shield had an average temperature of the two sections on either side. The density of the purified carbon tetrachloride at 30° was 1.57482 g. per cc. in comparison with 1.57484 g. per cc. obtained by Gibson and Loeffler.[8] The sample used by Gibson, however, did not contain dissolved air. The density of the purified benzene at 30° was 0.86839 g. per cc. in comparison with 0.86836 g. per cc. given by Scatchard, Wood, and Mochel.[7a]

Density–Composition Curve at 30°.—Determinations of the density of the solutions were made at approximately each eighth mole fraction. Duplicate measurements were made at approximate mole fractions in carbon tetrachloride (x_1) of 0.5 and 0.625 reversing the order of weighing the pure liquids. It was found necessary to correct the observed weights of the liquids for the displacement of air by the vapor and for the weight of benzene and carbon tetrachloride in the vapor after mixing the liquids assuming equilibrium to be obtained. The vapor pressure data of Scatchard, Wood and Mochel[9] were used for these calculations.

Since the density–composition relationship was determined using the liquids saturated with air and the coefficient of expansion data were determined with the liquids free from air, a further correction must be applied to the density–composition data. The difference between the density observed in the dilatometer and in the pycnometer at 30° was 0.00021 g. per cc. for carbon tetrachloride and 0.00006 g. per cc. for benzene. The corrections necessary for the solutions were assumed to be additive in the volume fraction although the difference between the volume fraction and mole fraction is negligible.

The compositions of the solutions used in the dilatometers were determined from the density at 30° by means of the equations

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

$$100V^M/V^0 = z_1 z_2(0.2029 - 0.5200\, z_1 + 0.5448\, z_1^2) \qquad (2)$$

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 carbon tetrachloride and z_2 that of benzene; d_1 and d_2 are the corresponding densities. In Table I are given the density corrected for dissolved air, the deviations of the density calculated from equations 1 and 2, and $100V^M/V^0$ calculated from equation 2. The

TABLE I

DENSITY OF CARBON TETRACHLORIDE–BENZENE MIXTURES AT 30°

x_1	d	$d_{obs.} - d_{calcd.}$	$100V^M/V^0$
0.00000	0.86845	....	0.000
.12370	.96221	0.00000	.016
.24604	1.05313	.00000	.020
.36752	1.14160	− .00001	.020
.49810	1.23475	+ .00003	.020
.50271	1.23793	− .00004	.020
.61685	1.31771	+ .00005	.021
.61734	1.31795	− .00005	.021
.74427	1.40492	+ .00002	.022
.86739	1.48756	− .00001	.018
1.00000	1.57503	....	.000

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[4] "International Critical Tables," Vol. III, pp. 25–26.

[5] K. Scheel and F. Blankenstein, *Z. Physik*, **31**, 202 (1925).

[6] G. Jones and F. C. Jelen, THIS JOURNAL, **57**, 2532 (1935).

[7] (a) G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939); (b) THIS JOURNAL, **61**, 3206 (1939).

[8] R. E. Gibson and O. H. Loeffler, *ibid.*, **63**, 898 (1941).

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

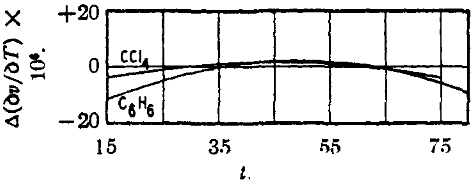

Fig. 2.—Deviations of $(\partial v/\partial T)_P$ for benzene and carbon tetrachloride.

estimated maximum error in $100V^M/V^0$ at half mole fraction is ±0.005. The values of $100V^M/V^0$ are shown graphically in Fig. 3, where the circles represent the experimental points and the solid curve the calculated results. The first three points and the two lower ones at approximate mole fraction 0.50 and 0.62 were obtained by weighing benzene first and the others by weighing carbon tetrachloride first. There is evidence of a slight minimum in $100V^M/V^0$ but it is within the estimated experimental accuracy.

The form of equation 2 is not justified by the density–composition data alone and the values of $100V^M/V^0$ calculated by means of this equation are more accurate than is warranted. The equation, $100V^M/V^0 = 0.001z_1z_2$, would fit the results at 30° to about the estimated accuracy. However, the deviations would be positive at each end and negative in the middle. Moreover, if $100V^M/V^0$ is calculated at 15° using this equation as discussed in the next section, an inflection or a maximum in the benzene-rich solutions is indicated along with a definite minimum. Furthermore even if a symmetrical equation is used at 30°, V^M/V^0 does not remain symmetrical at the other temperatures. Due to these considerations it was decided to use the more complex equation.

Coefficient of Expansion.—The specific volumes of the pure liquids were determined at 10° intervals from 15° up to about 0.5° within their normal boiling points; those of the solutions were determined at 10° intervals from 15 to 75°. These specific volumes were fitted to a cubic equation in t by the method of least squares. Table II gives the mole fraction of carbon tetrachloride, the constants for the type equation

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

and the standard deviation of the calculated specific volumes from the observed values. The densities of the solutions at 30° were calculated from these equations in order to determine the composition.

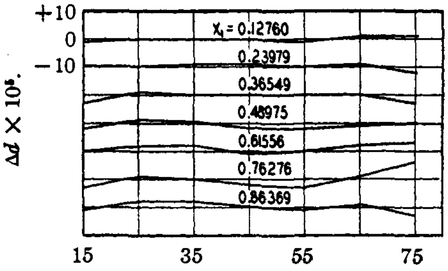

Fig. 3.—Difference between the observed density and that calculated by equations 1, 4, and 5.

TABLE II

x_1	a	$b \times 10^4$	$c \times 10^6$	$d \times 10^9$	$\Delta v \times 10^5$
0.00000	1.11047	13.2258	1.1786	9.82	1
.12760	0.99900	11.9365	1.2240	7.62	0
.23979	.91929	11.1228	0.9257	8.62	0
.36549	.84533	10.2449	.9145	7.47	0
.48975	.78426	9.5237	.8552	6.90	0
.61556	.73179	8.9646	.5891	8.16	1
.76276	.68001	8.2292	.7053	6.70	0
.86369	.64902	7.9019	.4430	8.49	1
1.00000	.61220	7.3275	.6130	6.39	1

The specific volume of carbon tetrachloride at 25° given by the equation is 0.63100 cc. per g. in comparison to 0.63108 given by Gibson and Loeffler,[8] 0.63111 given by Timmermans and Martin,[10] and 0.63126 given by Scatchard, Wood and Mochel.[9] The difference of $(\partial v/\partial T)_P$ given by Gibson and Loeffler[8] and that found in this work is shown in Fig. 2. The specific volume of benzene at 25° given by the equation is 1.14443 cc. per g. in comparison to 1.14434 given by Burlew,[8] 1.14456 given by Scatchard, Wood and Mochel,[9] and 1.14457 given by Timmermans and Martin.[11] The difference of $(\partial v/\partial T)_P$ given by Burlew[8] and that obtained in this work is shown in Fig. 2.

For the purposes of this work it is necessary to know V^M/V^0 at several temperatures and it is more convenient if the constants of the equation are functions of the temperature rather than of the composition. Therefore the values of $100V^M/V^0$ were calculated from equation 3 for every 5° interval and fitted by the method of least squares to an equation of the form

$$100V^M/V^0 = z_1z_2(A - Bz_1 + Cz_1^2) \qquad (4)$$

The constants of this equation are expressed as functions of t as follows

$$\begin{aligned} A &= 0.0204 + 5.005 \times 10^{-3}t + 4.674 \times 10^{-6}t^2 - 3.008 \times 10^{-7}t^3 \\ B &= 0.6984 - 7.024 \times 10^{-3}t - 0.921 \times 10^{-5}t^2 + 15.989 \times 10^{-7}t^3 \qquad (5) \\ C &= 0.5438 + 6.678 \times 10^{-3}t - 35.470 \times 10^{-5}t^2 + 45.272 \times 10^{-7}t^3 \end{aligned}$$

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(10) J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926).

(11) J. Timmermans and F. Martin, *ibid.*, **23**, 750 (1926).

Figure 3 shows the deviation of the densities calculated by equations 1, 4, and 5 from the densities observed in the expansion measurements for each solution. The values of $100V^{\mathrm{M}}/V^0$ at even 10° and at 25° are shown in Fig. 4. The dotted line is that given by Scatchard, Wood and Mochel[9] at 25°. The curves become more unsymmetrical toward carbon tetrachloride as the temperature is increased. The values determined by Hubbard[12] at 25° and at 50° are of the same magnitude as given here.

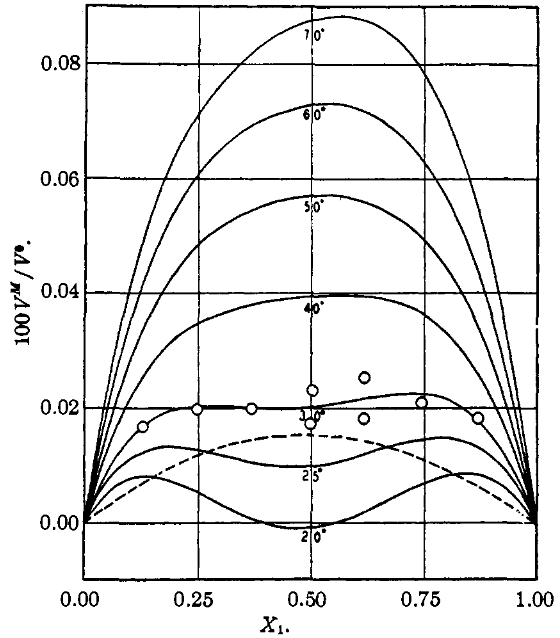

Fig. 4.—Percentage change of the volume on mixing.

Thermodynamic Functions.—The change of the thermodynamic functions on mixing at constant volume have been calculated from those on mixing at constant pressure[9] at 25, 40 and 70° by means of the equations developed by Scatchard.[2] It is to be noted that the values of V^0 and z used in the previous work[9] are calculated from the values of V_1 and V_2 at 25° whereas in this work they are based on the values of V_1 and V_2 at the corresponding temperatures. The coefficients of expansion in reciprocal degrees and the coefficients of compressibility[13] in reciprocal atmospheres together with d ln β/dT for the pure components used in the calculations are given in Table III. The values α_0, β_0, and α_0/β_0 for the mixed components are additive in the volume fraction. It was assumed that d ln β/dT was also additive in the volume fractions for the solutions. The error in this assumption and the assumption that β equals β_0 for the solutions are negligible. In Fig. 5, F^{E}_{px}, and E^{M}_{vx} at 25° and 70° together with H^{M}_{px} are shown.[14] The values of A^{E}_{vx} are practically identical with those of F^{E}_{px}. The properties of equimolal mixtures at the three temperatures are given in Table IV.

TABLE III

	25°	40°	70°
		CARBON TETRACHLORIDE	
α_0	1.229×10^{-3}	1.264×10^{-3}	1.365×10^{-3}
β_0	1.10×10^{-4}	1.24×10^{-4}	1.60×10^{-4}
α_0/β_0	11.13	10.22	8.52
d ln β/dT	0.0076	0.0077	0.0079
		BENZENE	
α_0	1.223×10^{-3}	1.256×10^{-3}	1.346×10^{-3}
β_0	0.99×10^{-4}	1.11×10^{-4}	1.43×10^{-4}
α_0/β_0	12.32	11.31	9.42
d ln β/dT	0.0078	0.0081	0.0087

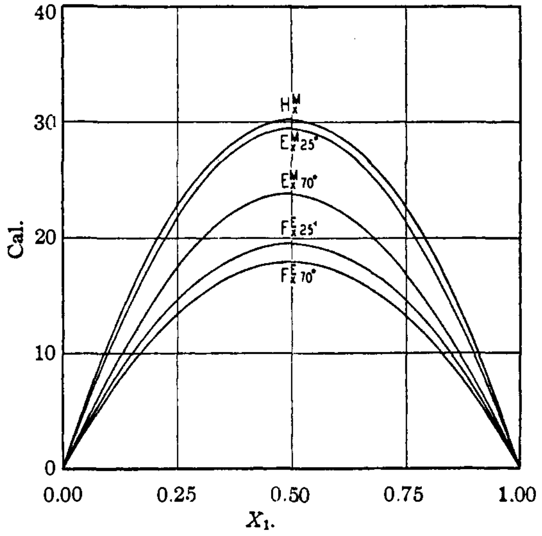

Fig. 5.—Various thermodynamic functions of benzene–carbon tetrachloride mixtures at 25 and 70°.

Between 25 and 70°, $100V^{\mathrm{M}}/V^0$ increases almost ninefold and S^{E}_{vx} decreases by about one-half. At 70° S^{E}_{vx} is still positive. However, the value of S^{E}_{vx} depends on H^{M}_{px}. Hirobe's[15] value of the heat of mixing at 25° at half mole fraction is 4.6 cal. per mole lower than the value used here and Vold's[16] value is 9.4 cal. per mole lower. The

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(12) J. C. Hubbard, *Z. physik. Chem.*, **74**, 207 (1910).

(13) "International Critical Tables," Vol. III, p. 38.

(14) The symbols used here follow those used by Scatchard. The superscript M indicates the change of the thermodynamic functions on mixing and the superscript E indicates the excess change of the functions on mixing above that of an ideal solution of the same composition. The subscript v or p indicates whether the mixing is done at constant volume or constant pressure. The subscript x indicates molal quantities.

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

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

TABLE IV

PROPERTIES OF EQUIMOLAL MIXTURES

	25°	40°	70°
$100 V^M/V^0$	0.010	0.039	0.088
F^E_{px} cal./mole	19.5	19.0	17.9
H^M_{px} cal./mole	30.2	30.2	30.2
E^M_{vx} cal./mole	29.4	27.1	23.8
V^M_x/β cal./mole	2.1	7.7	13.8
S^E_{px} cal./deg.	0.036	0.036	0.036
S^E_{vx} cal./deg.	0.033	0.026	0.017
a_{12}	−78.38	−74.06	−67.66
$\sqrt{a_{11}a_{22}}$	−78.84	−74.48	−68.01
$(100(a_{12} - \sqrt{a_{11}a_{22}}))/a_{12}$	0.58	0.56	0.52

free energy data are not sufficiently accurate and the heat capacity data are not consistent enough to determine H^M_{px} as a function of the temperature. Using Hirobe's value and assuming C^M_p to be zero, S^E_{vx} would be 0.004 cal. per deg. at 70°. Vold's results would make S^E_{vx} about zero at 25° and negative at 70° assuming C^M_p to be zero. V^M_x/β shows better agreement with E^M_{vx} with increasing temperature but still is only 58% of E^M_{vx} at 70°. There is a definite decrease of E^M_{vx} with temperature. In this calculation, however, the molal volume of the pure components and of the solution have increased with the temperature. The comparison with temperature should be made under conditions such that the molal volume of the components and of the solution remain identical to those at some arbitrarily chosen temperature.

The cohesive energy densities, a_{11} and a_{22}, at 25, 40, and 70° were calculated to be −73.88, −69.86, −63.86 cal. per cc. for carbon tetrachloride and −84.14, −79.40, and −72.42 cal. per cc. for benzene. The values of β in the equation of state, $V - RT/p = \beta$, at 25, 40, and 70° used in the calculation of the cohesive energy densities are −2544, −2071, and −1455 cc. for carbon tetrachloride and −2526, −2051, and −1436 cc. for benzene. The quantity a_{12} calculated from the equation

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

is always less than $\sqrt{a_{11}a_{22}}$, but it is interesting to note that the percentage difference is about the same at the three temperatures.

Summary

The increase of the volume on mixing benzene and carbon tetrachloride at constant pressure has been measured from 15 to 75°. From this the change of the thermodynamic functions on mixing at constant volume have been calculated from the change on mixing at constant pressure at 25, 40, and 70°. The volume of mixing increases approximately 9 fold; the excess entropy of mixing at constant volume decreases by about one-half from 25 to 70°.

NEW HAVEN, CONNECTICUT RECEIVED APRIL 15, 1943

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Revision of the Oxidation Potentials of the Orthophenanthroline- and Dipyridyl-Ferrous Complexes

BY DAVID N. HUME AND I. M. KOLTHOFF

Walden, Hammett and Chapman[1] described the properties of the orthophenanthroline-ferrous complex as an oxidation–reduction indicator, and reported the potential of the couple to be 1.14 v. with the pronounced color change taking place at 1.20 v. An indicator with such a potential permits a very accurate titration of ferrous ions with ceric sulfate in sulfuric acid. In the presence of hydrochloric acid, however, there should be a serious titration error due to the great decrease in the cerous-ceric potential under these conditions. The oxidation potential of the cerous–ceric couple is only 1.28 v. in 1 *M* hydrochloric acid[2] which with an indicator changing color at 1.14 or 1.20 v. would result in errors of +0.4 and +2.3%, respectively. The titration of ferrous iron is frequently performed in hydrochloric acid; we have verified the accuracy of the procedure, as shown by the results in Table I. The titrations were carried out under conditions which allowed a precision of better than 0.1 of one per cent. The color change at the end-point in the hydrochloric acid medium was as sharp as that in sulfuric acid.

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[1] (a) G. H. Walden, L. P. Hammett and R. P. Chapman, THIS JOURNAL, **53**, 3908 (1931); (b) **55**, 2649 (1933).

[2] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).