[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 443]

Vapor–Liquid Equilibrium. V. Carbon Tetrachloride–Benzene Mixtures[1]

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These measurements on carbon tetrachloride–benzene mixtures complete the cycle of binary systems with the components: carbon tetrachloride, benzene and cyclohexane. They permit an interesting comparison of these three systems and a prediction of the behavior of ternary systems of these components.

The purification of materials was the same as in III and IV and the measurements were made as in IV, with nitrogen as the confining gas. The leakage through the stoppers was so reduced by moistening them with the liquid in the still and seating them very tightly that the temperature increase was only 0.0002–0.0004° per minute at 40° and not over 0.0001° per minute at 70°. The vapor pressures of the pure substances agreed with the equations given in IV as well as did the measurements from which the equations were obtained. Apparently no phosgene was formed during these measurements as not even its odor was detected.

The electrical heating permits a fairly precise measurement of the rate of boiling at atmospheric pressure and so makes possible an estimate of the difference in pressure necessary to keep the vapors streaming from the boiler and to the condenser, which is more accurate than the estimate made in I. Since the rate of heating is almost independent of the boiling temperature, the rate of boiling may be taken to be so, also. At atmospheric pressure 2–2.2 cc. of benzene distilled per minute. This corresponds to a pressure drop along a tube 9 cm. long and 0.5 cm. in diameter of 0.003 mm. at 760 mm. pressure, and of 0.013 mm. at 120 mm. pressure. These pressure drops are smaller than those estimated in I, because the rate of distillation is smaller than we estimated, and they are also much smaller than the errors in measuring the pressures.

The density measurements showed systematic errors of the same magnitude as those reported in IV, probably caused by the evaporation of the first component weighed out in the preparation of the standards. Since they correspond to less than 0.02% in the composition, the equation for the relation between density and composition was determined by applying an average correction to the measurements. Table I contains the uncorrected densities and their deviations from the equation

TABLE I

DENSITIES OF BENZENE–CARBON TETRACHLORIDE MIXTURES AT 25°

Wt. fract. CCl_4	Mole fract.	Density	Deviation	$100\ V^M/V^0$
0.0000	0.0000	0.87370	....	.....
.2189	.1246	0.96878	+0.00003	+0.004
.2488	.1440	0.98344	+ .00006	+ .002
.3838	.2402	1.05527	+ .00004	+ .008
.5383	.3719	1.15171	+ .00007	+ .009
.6572	.4932	1.23893	+ .00026	− .006
.6581	.4943	1.23963	+ .00023	− .003
.6593	.4956	1.24050	+ .00015	+ .003
.6601	.4965	1.24115	+ .00018	+ .001
.6642	.5011	1.24405	− .00020	+ .031
.6669	.5041	1.24614	− .00021	+ .032
.7780	.6403	1.34163	− .00020	+ .029
.8583	.7547	1.42024	− .00019	+ .024
.9302	.8712	1.49891	− .00013	+ .015
1.0000	1.0000	1.58426	....	.....

$$d = (0.87370 + 0.71056z_1)/(1 + 0.00061)z_1z_2 \quad (1)$$

$$z_1 = 1 - z_2 = 1/(1 + w_2d_1/w_1d_2) \quad (2)$$

in which d is the density of the solution, d_1 and d_2 the densities of the components, w_1 and w_2 their weights in the solution, and z_1 and z_2 their volume fractions. The last column gives $100V^M/V^0 = 100(V - V^0)/V^0$, in which V^0 is the volume of the unmixed components, V is the volume of the solution, and V^M is the increase of volume on mixing. From equation 1 it follows that

$$V^M/V^0 = 0.00061\ z_1z_2 \quad (3)$$

Vapor–liquid equilibrium measurements were made at intervals of approximately one-eighth in the mole fraction of the liquid at 40 and 70° and for an approximately equimolal mixture at 30, 50 and 60°. The measurements at 40° are shown in Fig. 1, in which the curves are determined from equations 4 and 5 and the circles are the individual experimental points. The top curve with the plain circles gives the equilibrium pressure as ordinate and the liquid composition, expressed as mole fraction of carbon tetrachloride, as abscissa. The curve just below it with the

(1) Paper IV in this series appeared in THIS JOURNAL, 61, 3206 (1939).

flagged circles gives the equilibrium pressure *versus* the vapor composition, and the two lower curves are the derived partial pressures. The broken lines represent the Raoult's law total and partial pressures *versus* the liquid composition. The measurements are reported in detail in Table II as mole

TABLE II

VAPOR PRESSURES OF BENZENE–CARBON TETRACHLORIDE MIXTURES

x_{CCl_4}	y_{CCl_4}	Dev. in y_1	P	Dev. in P	F^E_x	Dev. in F^E_x
			40°			
0.1398	0.1703	−0.0009	190.18	−0.06	9.11	−0.06
.2378	.2774	− .0018	194.70	− .06	13.85	+ .04
.3735	.4159	− .0012	200.07	− .05	17.78	− .01
.4919	.5295	− .0008	204.02	± .00	19.06	+ .08
.4986	.5359	− .0006	204.20	− .01	18.99	+ .02
.6201	.6475	− .0010	207.44	− .04	17.82	− .03
.7585	.7739	− .0005	210.37	± .00	13.86	+ .02
.8718	.8783	− .0002	211.97	− .13	8.06	− .37
			70°			
.1428	.1666	− .0003	568.89	+ .01	8.86	+ .05
.2394	.2702	− .0004	579.13	± .00	13.13	+ .04
.3791	.4105	− .0007	591.62	+ .02	16.98	+ .09
(.4930)	(.5204)	(− .0002)	(600.77)	(+ .85)	(18.92)	(+1.01)
.4939	.5215	± .0000	599.67	− .24	17.63	−0.27
.6224	.6411	− .0007	607.22	− .07	16.76	− .04
.7624	.7719	− .0002	613.08	+ .01	12.93	+ .01
.8750	.8780	− .0003	616.02	+ .01	7.80	+ .02
			30°			
.4865	.5298	+ .0002	134.40	+ .03	19.46	+ .14
			50°			
.4926	.5265	− .0005	300.20	+ .04	18.74	+ .12
			60°			
.4907	.5210	− .0007	429.52	+ .02	18.35	+ .09

fraction of carbon tetrachloride in the liquid, and in the vapor, equilibrium pressure, and the derived excess free energy of mixing. After each of the last three is given the deviation of the corresponding quantity from that calculated by the following equations together with these vapor pressures of the pure components at 30, 40, 50, 60 and 70° from IV: benzene—119.16, 182.70, 271.34, 391.66, 551.03; carbon tetrachloride—141.55, 213.34, 312.04, 444.28, 617.43.

$$\mu^E_1 = RT \ln Py_1/P_1x_1 + (\beta_1 - V_1)(P - P_1) = (1.25141 - 0.0014837\ T)(1 + 0.14z_1)V_1z_2^2 \quad (4)$$

$$\mu^E_2 = RT \ln Py_2/P_2x_2 + (\beta_2 - V_2)(P - P_2) = (1.25141 - 0.0014837T)(0.93 + 0.14z_1)V_2z_1^2 \quad (5)$$

$$F^E_x = (1.25141 - 0.0014837T)(1 + 0.07z_1)V^0_xz_1z_2 \quad (6)$$

$$H^M_x = 1.25141\ (1 + 0.07z_1)V^0_xz_1z_2 \quad (7)$$

$$S^E_x = 0.0014837\ (1 + 0.07z_1)V^0_xz_1z_2 \quad (8)$$

in which $V^0_x = x_1V_1 + x_2V_2 = V^0/(N_1 + N_2)$, x is the mole fraction in the liquid, y is that in the vapor, and the subscript $_1$ refers to carbon tetrachloride, V_1 and V_2 are the molal volumes at

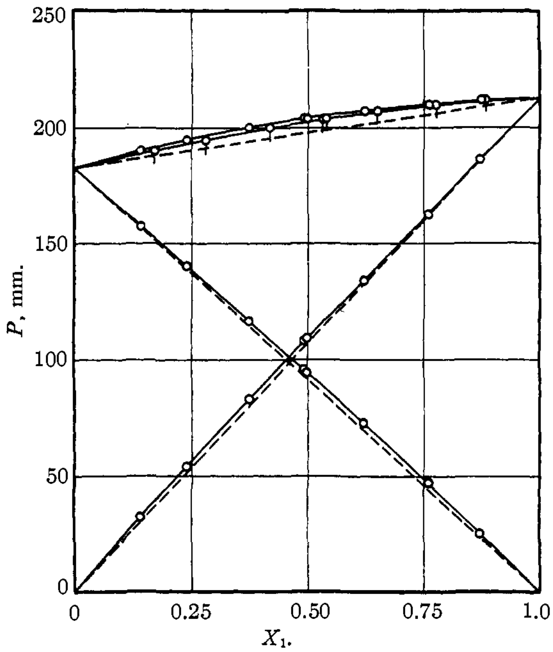

Fig. 1.—Vapor pressure *vs.* mole fraction for carbon tetrachloride-benzene at 40°.

25°, and β_1 and β_2 are the limits at zero pressure of the differences between the molal volumes of the vapors and those of perfect gases at the same temperature and pressure. The values of β used for benzene, carbon tetrachloride and cyclohexane, respectively, are −1839, −1864 and −2031 cc. per mole at 40° and −1287, −1310 and −1426 cc. per mole at 70°. The calculated results from which the curves in Fig. 1 and the deviations in Table II are calculated are from equation 6 for F^E_x and from the combined equations 4 and 5 for P and y. The constants are chosen to give the average of F^E_x at 40 and 70° and a linear variation of F^E_x with temperature. The average deviation is 0.06% in y and 0.015% in P, which is about the same as for carbon tetrachloride-cyclohexane mixtures.

To calculate the thermodynamic functions for mixing at constant total volume, we have made use of the following expressions for the coefficients of thermal expansion and compressibility in reciprocal degrees centigrade or reciprocal atmospheres

$$\alpha_0 = 1.228 \times 10^{-3}(1 - 0.0024z_2)$$
$$\beta_0 = 1.10 \times 10^{-4}(1 - 0.1z_2)$$
$$\alpha_0/\beta_0 = 11.16(1 + 0.108z_2)$$
$$d \ln \beta/dT = 0.0076$$

and $V_0 = 97.104/(1 + 0.086z_2)$. Then

$$(A^E_v - F^E_p)_x = 4.05 \times 10^{-5}(97.104)z_1^2z_2^2/(1 - 0.1z_2)(1 + 0.086z_2) \quad (9)$$

$$(S^E_v - S^E_p)_x = -(16.40 \times 10^{-5})(97.104)(1 + 0.108z_2)z_1z_2/(1 + 0.086z_2) + 0.0076(A^E_v - F^E_p)_x \quad (10)$$

$$(E^M_v - H^M_p)_x = T(S^E_v - S^E_p)_x + (A^E_v - F^E_p)_x \quad (11)$$

In Fig. 2 are shown F^E_{px} at 25 and at 70° from equation 6, H^M_{px} from equation 7, and E^M_{vx} from H^M_{px} and equation 11. The value for A^E_{vx} at 25° is so near that of F^E_{px} that they could not be distinguished on a scale many times as large as this one. For the equimolal mixture at 25°, F^E_{px} (or A^E_{vx}) is 19.5, H^M_{px} is 30.2 and E^M_{vx} is 29.0 cal./mole. The correction to $(E^M_{vx} - A^E_{vx})$ caused by deviations from random distribution is calculated from Kirkwood's equation[1] as -0.18 cal./mole, which is very small relative to the measured $+9.5$ cal./mole. V^M_x/β is 3.27 cal./mole, which is scarcely more than a tenth of E^M_{vx}.

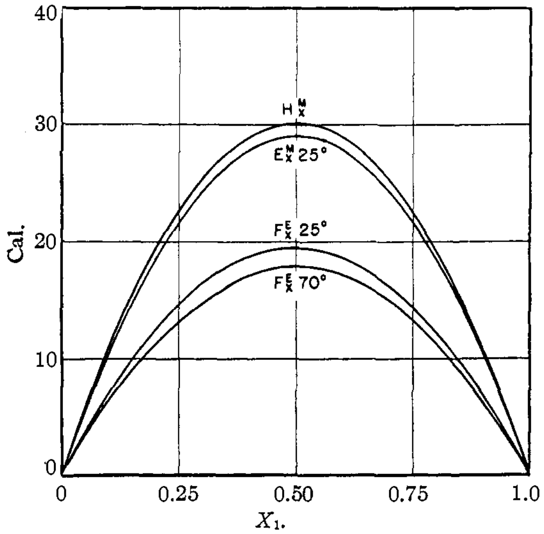

Fig. 2.—Various thermodynamic functions for carbon tetrachloride–benzene.

The results are made a little clearer if they are translated back to the measured pressure, for the effect on the vapor composition is very small. For equimolal solutions we find a pressure 2.75% greater than the average of the pressures of the components at 70°, and 3.15% greater at 40°. This decrease of 0.40% would be only 0.22% if the solutions were regular and 0.24% if the entropy of mixing at constant total volume were zero. A decrease of 0.16% in 30° is left unexplained. The deviations from random distribution, calculated by Kirkwood's equation, increase the unexplained deviations by 0.003%.

The cohesive energy densities at 25°, a_{11} and a_{22}, are calculated as -72.96 cal./mole for carbon tetrachloride and -84.11 for benzene. By quadratic combination they lead to 9.21 cal./mole for E^M_{vx}, or about one-third of the measured 29.0. However, the mutual energy per unit volume

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

is -77.91, which is only 0.54% less than $\sqrt{a_{11}a_{22}}$. As in the other systems, the quadratic combination of constants leads to fairly good agreement in the calculation of a_{12}, but the percentage error in $(2a_{12} - a_{11} - a_{22})$ is very large.

This system has been studied by many observers, but we shall compare our measurements with only a few. Hubbard[2] found values of V^M/V^0 at 25° which correspond very closely to ours. At 50° he finds V^M/V^0 about four times as great as calculated by our equation for 25°, which indicates that the discrepancy between V^M/β and E^M decreases rapidly as the temperature increases. Hirobe's measurements[3] of the heat of mixing at 25° are about 15% smaller, and those of Vold[4] are about 30% smaller than those we calculate from our equilibrium measurements. Vold's measurements are also higher in benzene-rich solutions and lower in benzene-poor solutions than a symmetrical curve. The curvature in F^E *versus* T necessary to give agreement with either set of the heat measurements is probably within the error of our measurements, but we see no basis for a choice between the two sets. The measurements by Zawidski[5] of the vapor pressure at 49.99° are 2–5 mm. lower than those calculated from our equations. The vapor pressures of the pure components are also lower, and his ratio of pressure to ideal pressure agrees very well with ours in solutions rich in benzene, and is higher than ours for solutions poor in benzene. His vapor compositions differ from ours on the average by 0.2%, which is about the spread in his measurements, and his vapor is always richer in that component which is in excess in the liquid. The vapor pressure measurements at 50.15° by Tahvonen[6] are in excellent agreement with ours.

Table III contains various properties of equimolal mixtures of each of the three systems of this cycle. If the deviations from ideality are measured by the percentage increase in pressure, $100(P - P_{\mathrm{I}})/P_{\mathrm{I}}$, the benzene–cyclohexane system shows much the largest deviation, and carbon tetrachloride mixtures with benzene deviate a little more than those with cyclohexane. The

(2) J. C. Hubbard, *Z. physik. Chem.*, **74**, 207 (1910).
(3) H. Hirobe, *J. Faculty Sci. Imp. Univ. Tokyo*, **1**, 155 (1925).
(4) R. D. Vold, This Journal, **59**, 1515 (1937).
(5) J. von Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).
(6) P. E. Tahvonen, *Finska-Vetenskaps Societeten, Comm. Phys. Mat.*, **10**, 1 (1938).

TABLE III

PROPERTIES OF EQUIMOLAL MIXTURES

	C_6H_6–C_6H_{12}	C_6H_{12}–CCl_4	C_6H_6–CCl_4
$100V^M/V^0$	0.65	0.16	0.003
$100(P - P_I)/P_I$ at 70°	9.73	2.17	2.75
$100(P - P_I)/P_I$ at 40°	12.32	2.63	3.15
Difference	2.59	0.46	0.40
Diff. from regular solution	1.77	0.28	0.18
Diff. from vol. regular solution	0.88	0.06	0.16
H^E_x (cal./mole)	175.8	34.2	30.2
F^E_x	74.4	16.7	19.5
TS^E_{xp}	101.4	17.5	10.7
E^E_x	120.0	20.7	29.0
TS^E_{xv}	50.0	4.0	9.5
E^E_x (calcd. quadratic combination)	26.0	3.8	9.2
$100(a_{12} - \sqrt{a_{11}a_{22}})/a_{12}$	2.5	0.5	0.5
TS^E_{xv} calculated Kirkwood	−3.6	−0.09	−0.18
Ratio to TS^E_{xv}	−0.07	−0.02	−0.02

thermodynamic functions show the same relations, except that the heat of mixing and the excess entropy at constant pressure interchange the last two systems. This indicates that that property which determines these deviations is intermediate for carbon tetrachloride between the values for the two hydrocarbons and nearer to that for cyclohexane. We also see that the value for benzene–cyclohexane is much greater than the sum of the other two. The square roots of these deviation measures are, however, approximately additive. This relation between the square roots is that predicted by quadratic combination, and the cohesive energy density of carbon tetrachloride does lie between those of the two hydrocarbons and nearer to that of cyclohexane than to that of benzene. The simple theory of non-polar mixtures states that it is the square of the difference between the square roots of the cohesive energy densities which determines the deviations from ideality rather than any difference in molecular structure or nature of the atoms. So it should be quite possible for substances which are very different chemically to give nearly ideal solutions. The quantitative calculations for the energy densities give, however, only about a fifth of the measured values.

The volume increase on mixing is greater than that calculated from the energy of mixing by simple theory for the mixtures containing cyclohexane, but it is very much smaller for carbon tetrachloride–benzene mixtures. However, the measurements of Hubbard indicate that the volume increase becomes rapidly larger as the temperature increases.

For the two systems with large increase of volume, the excess entropy of mixing at constant total volume is considerably smaller than that at constant pressure, but it is still important in all three cases. It was suggested in III[7] that the entropy increase in the benzene–cyclohexane system might be due to an abnormally small entropy in one of the liquids, probably caused by incomplete randomness of orientation which becomes complete in the mixtures. If this explanation were correct, the excess entropy of the first system should equal the sum of that for the other two if there were no lack of randomness in the more symmetrical carbon tetrachloride, and would in general be less than this sum by twice the effect for carbon tetrachloride. From Table III we see that the excess entropy for benzene–cyclohexane is almost four times as great as the sum for the other two systems. Barring the very improbable case of a large negative entropy in one of the mixtures giving compensation, the study of the two systems with carbon tetrachloride shows that most of the excess entropy cannot arise from an abnormally low entropy in either of the components.

To consider ternary mixtures we will assign the subscripts $_1$ to benzene, $_2$ to cyclohexane, and $_3$ to carbon tetrachloride. If the excess free energies of the binary mixtures are given by expressions of the type $F^E_{12} = V^0B_{12}z_1z_2$, the expression for the free energies of ternary systems should be the sum of those for the binary systems: $F^E = V^0(B_{12}z_1z_2 + B_{13}z_1z_3 + B_{23}z_2z_3)$. If the expression for binary systems contains a triple product of the type $C_{112}z_1^2z_2$, however, we may expect for ternary mixtures a term $C_{123}z_1z_2z_3$ which cannot be determined by measurements on binary mixtures. Of the three systems under discussion, benzene–cyclohexane mixtures deviate from the symmetrical expression only enough to give a maximum discrepancy of about 0.4% in the pressure; benzene–carbon tetrachloride mixtures give a maximum discrepancy of about 0.1%, and cyclohexane–carbon tetrachloride mixtures give none within the accuracy of our measurements. We may then expect an error of about the average, which is less than two parts per thousand, if we ignore the term in $z_1z_2z_3$ and adjust our expression to merge into each of those for a binary liquid as the third component

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

disappears. Our expressions for the binary mixtures are

$$F_{12}/V^0 = z_1z_2(B_{12} + D_{12}z_2^2)$$
$$F_{23}/V^0 = z_1z_3(B_{13} + C_{13}z_3)$$
$$F_{23}/V^0 = z_2z_3B_{23}$$

For ternary mixtures we must eliminate the unsymmetrical method of writing the first two by replacing z_2 by its equivalent $(1 - z_1 + z_2)/2 = (2z_2 + z_3)/2$ and z_3 by $(z_2 + 2z_3)/2$. This gives the following expressions, in which the volume fraction of each component is eliminated in the expression for the potential of that component.

$$F^E/V^0 = B_{12}z_1z_2 + D_{12}(z_1z_2^3 + z_1z_2^2z_3 + z_1z_2z_3^2/4) + B_{13}z_1z_3 + C_{13}(z_1z_2z_3/2 + z_1z_3^2) + B_{23}z_2z_3$$

$$\mu^E{}_1/V_1 = B_{12}(z_2^2 + z_2z_3) + B_{13}(z_2z_3 + z_3^2) - B_{23}z_2z_3 + D_{12}(3z_2^4 - 2z_2^3 + 6z_2^3z_3 - 2z_2^2z_3 + 15z_2^2z_3^2/4 - z_2z_3^2/2 + 3\,z_2z_3^3/4) + C_{13}(z_2^2z_3 - z_2z_3/2 + 3z_2z_3^2 - z_3^2 + 2z_3^3)$$

$$\mu^E{}_2/V_2 = B_{12}(z_1^2 + z_1z_3) - B_{13}z_1z_3 + B_{23}(z_1z_3 + z_3^2) + D_{12}(3z_1^4 - 6z_1^3 + 6z_1^3z_3 + 3z_1^2 - 8z_1^2z_3 + 15z_1^2z_3^2/4 + 2z_1z_3 - 5z_1z_3^2/2 + 3z_1z_3^3/4) + C_{13}(z_1^2z_3 - z_1z_3/2 - z_1z_3^2)$$

$$\mu^E{}_3/V_3 = -B_{12}z_1z_2 + B_{13}(z_1^2 + z_1z_2) + B_{23}(z_1z_2 + z_2^2) + D_{12}(-3z_1^3z_2/4 + z_1^2z_2 + 3z_1^2z_2^2/2 - z_1z_2/4 - z_1z_2^2 - 3z_1z_2^3/4) + C_{13}(-2z_1^3 + 2z_1^2 - 3z_1^2z_2 + 3z_1z_2/2 - z_1z_2^2).$$

These equations readily may be extended to include the cases where any or all of the constants C_{12}, C_{13}, C_{23}, D_{12}, D_{13}, D_{23} are not zero by the appropriate interchange of coefficients, and to H^E or S^E instead of F^E. The values of the parameters for our system are: $V_1 = 89.400$, $V_2 = 108.754$, $V_3 = 97.104$, $B_{12} = (6.943 - 0.013233\ T)$, $B_{13} = (1.3335 - 0.0022916\ T)$, $B_{23} = (1.25141 - 0.0014837\ T)$, $D_{12} = 0.084\ B_{12}$, $C_{13} = 0.07\ B_{13}$. The units are cc./mole for the volumes and cal./cc. for the other parameters.

Applying these expressions to mixtures containing equal mole fractions of benzene and cyclohexane at 25° we find that, as the fraction of carbon tetrachloride increases from zero to unity, $\log Py_i/P_ix_i$ increases by 0.009 for benzene, decreases by 0.011 for cyclohexane and increases by 0.002 for carbon tetrachloride. As a result the total pressure is almost linear, and it varies only from 109.1 to 113.8 mm. The vapor pressures of benzene and cyclohexane are 94.98 and 97.45 mm., respectively, and the pressures of equimolal binary mixtures with carbon tetrachloride deviate 3.35 and 2.86% from Raoult's law. Therefore, the cross sections at constant mole fraction of carbon tetrachloride are nearly symmetrical and flatten out rapidly as the fraction of carbon tetrachloride increases. At one half mole fraction carbon tetrachloride, the excess over the average of the end-points has already decreased from 12.9 to 3.1 mm.

Summary

The vapor–liquid equilibrium pressure and compositions of benzene–carbon tetrachloride mixtures have been measured at 40 and 70° over the whole composition range, and at 30, 50 and 60° for approximately equimolal mixtures. The densities have been determined at 25°.

These measurements have been expressed analytically, and corresponding equations have been derived for the thermodynamic functions, including the energy and entropy of mixing at constant total volume.

These equations show a slight asymmetry, and a moderate deviation from regularity, which, on account of the nearly additive volumes, is almost the same at constant total volume as at constant pressure.

These results are compared with those obtained previously for mixtures of each of the components with cyclohexane, and approximate equations are derived for the ternary system: benzene–cyclohexane–carbon tetrachloride.

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RECEIVED JANUARY 15, 1940