

were found to be greater than Niini's measured values by 0.3 to 0.7 mm.

TABLE VII.

VAPOR PRESSURE AND EXCESS FREE ENERGY OF TERNARY MIXTURES

| $x_1$     | $x_2$  | $y_1$  | $y_2$  | Pres-<br>sure | $G_{123}^E$<br>(obsd.) | $\delta_{17}$ | $\delta_{18}$ |
|-----------|--------|--------|--------|---------------|------------------------|---------------|---------------|
| At 34.68° |        |        |        |               |                        |               |               |
| 0.2075    | 0.1900 | 0.4920 | 0.1472 | 291.11        | 248.3                  | 2.9           | 22.8          |
| .2110     | .3879  | .4864  | .2774  | 302.13        | 257.6                  | 2.1           | 29.3          |
| .1987     | .5876  | .4733  | .3999  | 308.63        | 253.6                  | 4.0           | 26.9          |
| .3781     | .3122  | .5043  | .2747  | 307.23        | 320.5                  | 3.4           | 18.7          |
| .5543     | .2078  | .5308  | .2501  | 308.13        | 314.3                  | 3.3           | 8.6           |
| .7599     | .1076  | .5903  | .2080  | 298.80        | 225.2                  | 2.6           | 2.4           |
| At 55.00° |        |        |        |               |                        |               |               |
| 0.1880    | 0.1960 | 0.5152 | 0.1387 | 665.26        | 235.3                  | -1.5          | 17.9          |
| .1983     | .3961  | .5130  | .2624  | 690.29        | 251.1                  | -2.6          | 24.2          |
| .1982     | .3963  | .5109  | .2628  | 689.67        | 252.3                  | -1.3          | 25.5          |
| .1945     | .5922  | .5068  | .3733  | 706.51        | 253.0                  | -1.3          | 20.9          |
| .3590     | .3230  | .5397  | .2539  | 711.17        | 324.6                  | 0.3           | 16.7          |
| .5557     | .2134  | .5672  | .2316  | 717.20        | 324.6                  | 1.8           | 6.4           |
| .7515     | .1115  | .6209  | .1925  | 703.34        | 238.0                  | 0.2           | -0.4          |
| .8433     | .0814  | .6736  | .1890  | 680.86        | 168.8                  | -0.9          | -1.8          |

The results of the measurements on the ternary mixtures are given in Table VII. We believe the uncertainty in the 35° ternary runs is greater than in the 55° runs and the true deviation values may be of the same magnitude. Hence we believe the 55° runs give a truer picture of the relative merits of the two estimation methods discussed below. An error of 100 ml./mole in  $\beta_{ij}$  would cause an error of about 0.5 and 1.0 calorie per mole at 35 and 55°, respectively. An error of 100 ml./mole in  $\beta_{ij}$  would give an error of about 0.3 and 0.6 cal. per mole at 35 and 55°. The limit of accuracy in

the composition measurements was 0.001, the accuracy of the temperature calibration was about 0.05 at 55°, and 0.1 at 35°, the pressure measurements were accurate to about 0.005 mm. Based upon these considerations our measured excess free energies are estimated to be accurate within two and four calories per mole at 55 and 35°, respectively. The excess free energy of ternary mixtures may be estimated from those of the component binary mixtures by equations corresponding to equation (1) or (9) of our previous paper.<sup>13</sup> The equation for the excess free energy of the ternary mixtures corresponding to equation (9) is

$$G_{123}^E = x_1x_2[-1715.8 - 6.453T \ln T + 46.77T - (237 - 0.185T)(2x_1 - 1) + 0.633T(2x_1 - 1)^2 - (383 - 0.692T)(2x_1 - 1)^3 + (346 - 0.587T)(2x_1 - 1)^4] + x_1x_3[-841.4 - 4.917T \ln T + 34.88T - (250 - 0.312T)(2x_1 - 1) + 0.640T(2x_1 - 1)^2 - (550 - 1.435T)(2x_1 - 1)^3 + (800 - 2.376T)(2x_1 - 1)^4] + x_2x_3[119.6 - 0.1375T - 0.85(x_2 - x_3)] \quad (17)$$

The equation corresponding to equation (1) differs from equation (17) only in replacing  $(2x_1 - 1)$  by  $(x_1 - x_2)$  when multiplied by  $x_1x_2$ , and by  $(x_1 - x_3)$  when multiplied by  $x_1x_3$ . We will refer to it as equation (18). Table VII includes the deviations of the experimental  $G_x^E$  from that calculated by equations (17) and (18) as  $\delta_{17}$  and  $\delta_{18}$ , respectively. Although the advantage of grouping the non-polar components together is not so great as for the heats of mixing,<sup>13</sup> it is quite evident in the excess free energies for this system. The values calculated by equation (17) approximate the measured values closely enough to make unnecessary the use of terms in the excess free energy function involving all three components which can be obtained only from measurements on ternary mixtures.

CAMBRIDGE, MASS.

{CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY}

## The Volume of Mixing and the Thermodynamic Functions of Binary Mixtures. III. Cyclohexane-Carbon Tetrachloride<sup>1</sup>

BY SCOTT E. WOOD<sup>2</sup> AND JOHN A. GRAY, III

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The volume change on mixing carbon tetrachloride and cyclohexane at constant pressure has been determined over the entire composition range from 15 to 75°. From this the excess change over that of an ideal solution of the Helmholtz free energy, energy and entropy on mixing at constant volume have been calculated. The volume of mixing is positive and is essentially independent of the temperature while the excess energy and entropy of mixing at constant volume are both positive and appear to decrease with the temperature.

The vapor pressures of the three binary systems using benzene, cyclohexane and carbon tetrachloride have been determined<sup>3</sup> and from these data the change of the thermodynamic functions on forming the solutions from the components at constant pressure have been calculated. The volumes of mixing at constant pressure of the benzene-carbon tetrachloride<sup>4</sup> and benzene-cyclohexane<sup>5</sup> systems have been measured from which the changes of the thermodynamic functions on mixing at constant volume have been calculated. This paper reports the volume of mixing over the

temperature range of 15 to 75° and the changes of the thermodynamic functions on mixing at constant volume for the last system of this series, cyclohexane-carbon tetrachloride. The apparatus and procedure for the experimental measurements were identical to those described in the previous papers of this series.<sup>4,5</sup>

**Purification of Materials.**—The purification of the carbon tetrachloride<sup>4</sup> and the cyclohexane<sup>6</sup> was carried out as previously described. The density of the purified carbon tetrachloride was 1.57459 g. per cc. with dissolved air at 30°. Wood and Brusie<sup>4</sup> reported a value of 1.57682 g. per cc. at 30° with dissolved air and Gibson and Loeffler<sup>6</sup> have reported a value of 1.57484 g. per cc. at 30° without dissolved air. The dissolved air reduces the density 0.00019 g. per cc. The density of the cyclohexane at 30° was 0.76912 g. per cc. while Wood and Austin<sup>5</sup> reported a value of 0.76910 g. per cc. and Scatchard, Wood and Mochel<sup>3a</sup> give 0.76914 g. per cc. both values being at 30° and with dissolved air.

The water used for calibration was the laboratory distilled water, condensed from the steam system of the building, and was reboiled before use to remove air and carbon dioxide.

(1) This contribution contains material taken from a thesis by John A. Gray, III, presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois.

(3) G. Scatchard, S. E. Wood and J. M. Mochel, (a) *J. Phys. Chem.*, **43**, 119 (1939); (b) *THIS JOURNAL*, **61**, 3206 (1939); (c) *ibid.*, **62**, 712 (1940).

(4) S. E. Wood and J. P. Brusie, *ibid.*, **65**, 1891 (1943).

(5) S. E. Wood and A. E. Austin, *ibid.*, **67**, 480 (1945).

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

The mercury was cleaned by passing through a column of nitric acid, oxidation with air while covered with a layer of concentrated sulfuric acid, and finally by distillation.

**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  $30 \pm 0.01^\circ$ . Determinations of the density were made at approximately each eighth mole fraction. Duplicate measurements, in which the order of weighing the components in making up the solutions was reversed, were made at each composition. For each mixture a total of 20 to 25 cc. of solution was made by weight. All weighings were reproducible to within  $\pm 0.03$  mg. The observed weights were corrected for evaporation loss to the actual time of mixing, 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 last calculations.<sup>3b</sup> In making the buoyancy corrections the true density of the air was used and was determined by the equation<sup>7</sup>

$$\sigma = \frac{464.6}{10^6} \left( \frac{B - 0.3783e}{T} \right) \text{ g. per cc.}$$

where  $\sigma$  is the density of the air,  $B$  the barometric pressure in mm.,  $e$  the vapor pressure of water in mm. times the relative humidity, and  $T$  the balance temperature. The temperature at the balance case was measured to  $0.1^\circ$ , the relative humidity to 2%, and the barometric pressure to 0.1 mm. The air inside of the solution bottles and pycnometer was assumed to be dry air. In the actual determination of the density of the liquids it was found necessary to correct for the weight of vapor above the meniscus in the capillary. This correction amounted to 0.37 mg. of carbon tetrachloride and 0.17 mg. of cyclohexane. The pycnometers were calibrated by the use of water, the density of the water being calculated from Tilton and Taylor's equation.<sup>8</sup> The conversion factor used in order to convert the density to units of g. per cc. was 0.999972 ml. per cc.

Since the density-composition measurements were made with the liquids saturated with air and the coefficient of expansion was determined with solutions free from air, a correction to the density for the dissolved air is necessary in order to determine the composition of the solutions used in the dilatometer. The difference between the density observed in the dilatometer and that in the pycnometer at  $30^\circ$  was  $+0.00019$  g. per cc. for carbon tetrachloride and  $+0.00005$  g. per cc. for cyclohexane. Wood and Brusie<sup>4</sup> reported the value of 0.00021 for carbon tetrachloride and Wood and Austin<sup>5</sup> the value of 0.00002 for cyclohexane.

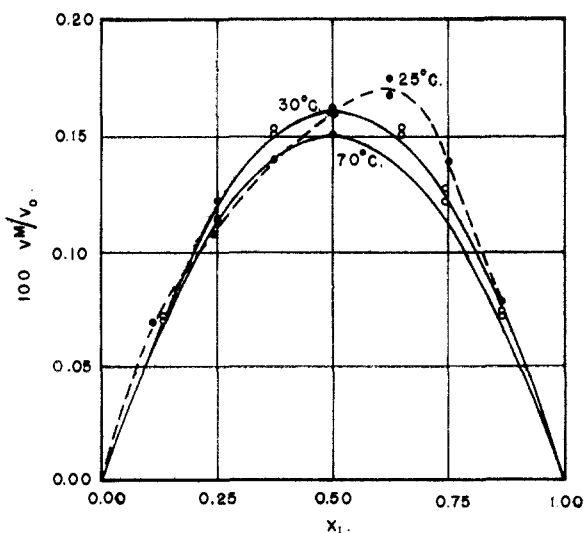


Fig. 1.—Percentage change of the volume on mixing.

(7) "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 71

(8) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **18**, 205 (1937).

The corrections necessary for the solutions were assumed to be linear in the volume fraction.

The mole fractions of the solutions used in the dilatometer were determined from the density at  $30^\circ$  by means of the equations

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

and

$$100 V^M/V^0 = z_1 z_2 (0.694 - 0.0917 z_1) \quad (2)$$

In these equations  $V^M$  equals  $V - V^0$  where  $V$  is the molal volume of the solutions and  $V^0$  the additive volume,  $z_1$  is the volume fraction of carbon tetrachloride, and  $d_1$  and  $d_2$  are the corresponding densities of the two pure components. The mole fraction of carbon tetrachloride, the density corrected for air, the difference of the observed density and that calculated from equations 1 and 2,  $100 V^M/V^0$  and the difference in  $100 V^M/V^0$  between the observed and calculated values are given in Table I. The standard deviation in the density is  $3 \times 10^{-5}$  g. per cc. and that in  $100 V^M/V^0$  is 0.002. The values of  $100 V^M/V^0$  are shown in Fig. 1; the open circles represent the points obtained in this research at  $30^\circ$  and the filled circles and the dotted line represent the data of Scatchard, Wood and Mochel<sup>3b</sup> at  $25^\circ$ . The solid curves represent the final smoothed values at  $30$  and  $70^\circ$  obtained from the results of the coefficient of expansion.

TABLE I  
DENSITY OF CARBON TETRACHLORIDE-CYCLOHEXANE MIXTURES AT  $30^\circ$

| $z_1$  | $d$     | $\Delta d$ | $100 V^M/V^0$ | $\Delta 100 V^M/V^0$ |
|--------|---------|------------|---------------|----------------------|
| 1.0000 | 1.57478 | .....      | 0.000         | .....                |
| 0.8725 | 1.46041 | +0.00003   | .074          | -0.002               |
| .8716  | 1.45957 | + .00001   | .075          | - .001               |
| .7485  | 1.35278 | - .00004   | .125          | + .003               |
| .7482  | 1.35262 | + .00003   | .125          | - .002               |
| .6511  | 1.27068 | - .00005   | .149          | + .004               |
| .6506  | 1.27034 | - .00003   | .149          | + .002               |
| .4978  | 1.14561 | + .00001   | .162          | - .001               |
| .4974  | 1.14527 | .00000     | .162          | .000                 |
| .3751  | 1.04872 | - .00001   | .150          | + .001               |
| .3743  | 1.04805 | - .00002   | .150          | + .002               |
| .2520  | 0.95430 | - .00002   | .120          | + .002               |
| .2517  | .95418  | + .00006   | .120          | - .006               |
| .1303  | .86364  | - .00001   | .071          | + .001               |
| .1294  | .86293  | + .00001   | .071          | - .001               |
| .0000  | .76918  | .....      | .000          | .....                |

**Coefficient of Expansion.**—The specific volumes of the pure liquids and solutions were determined from 15 to  $75^\circ$  using the dilatometers. These dilatometers were calibrated as formerly making use of water and mercury. The density of water up to  $45^\circ$  was determined by Tilton and Taylor's equation. White<sup>9</sup> has determined corrections to this equation to obtain more accurate values of the density of water above  $45^\circ$ . These corrections were fitted to the equation

$$10^{-6}(d - d') = -575.56 + 41.12t - 1.07055t^2 + 0.01176666t^3 - 4.3750 \times 10^{-5} t^4 \text{ g. per ml.}$$

to provide values of the density of water from  $45$  to  $85^\circ$ . In this equation  $d'$  refers to the value calculated by the Tilton and Taylor equation. The temperature was determined to  $\pm 0.01^\circ$ . The weight of the dilatometer and the expelled mercury at the end of each experiment agreed within 0.4 mg. of the original weight. This would give a total error of 0.00003 cc. in the change of the specific volume from  $15$  to  $75^\circ$ . 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 carbon tetrachloride, the coefficients of the type equation

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

and the standard deviations of the calculated values from the observed values. The densities of the solutions at  $30^\circ$

(9) J. White, Thesis, Yale University, 1944.

were calculated from these equations and the compositions of the solutions were calculated in turn from equations 1 and 2.

TABLE II  
COEFFICIENTS FOR THE EQUATION FOR THE SPECIFIC VOLUMES

| $x_1$  | $a$     | $b \times 10^{-3}$ | $c \times 10^{-5}$ | $d \times 10^{-9}$ | $\Delta v \times 10^{-5}$ |
|--------|---------|--------------------|--------------------|--------------------|---------------------------|
| 0.0000 | 1.25459 | 1.4362             | 2.529              | 5.37               | 2.6                       |
| .1289  | 1.11832 | 1.3106             | 1.568              | 9.62               | 1.0                       |
| .2512  | 1.01133 | 1.1940             | 1.205              | 10.15              | 1.5                       |
| .2514  | 1.01141 | 1.1803             | 1.471              | 8.31               | 0.9                       |
| .3720  | 0.92189 | 1.0855             | 1.171              | 8.57               | 1.2                       |
| .4978  | .84224  | 0.9768             | 1.381              | 5.81               | 0.8                       |
| .6506  | .75911  | .9080              | 0.687              | 8.74               | .7                        |
| .7482  | .71306  | .8456              | .777               | 7.68               | .5                        |
| .7475  | .71332  | .8479              | .790               | 7.12               | .9                        |
| .8716  | .66057  | .7946              | .528               | 7.92               | .9                        |
| 1.0000 | .61233  | .7294              | .722               | 5.52               | 1.4                       |

The specific volume of carbon tetrachloride at 25° given by the equation is 0.63110 cc. per g. in comparison to 0.63100 reported by Wood and Brusie,<sup>4</sup> 0.63108 reported by Gibson and Loeffler,<sup>6</sup> 0.63111 reported by Timmermans and Martin,<sup>10</sup> and 0.63126 reported by Scatchard, Wood and Moche.<sup>3b</sup> The density of cyclohexane at 20° was calculated to be 0.77859 g. per cc. in comparison to 0.77849 given by the equation of Wood and Austin,<sup>9</sup> 0.77860 given by Pavlov,<sup>11</sup> and 0.77857 given by Forziati, Glasgow, Willingham and Rossini.<sup>12</sup> The density at 25° was found to be 0.77390 g. per cc. while Forziati, Glasgow, Willingham and Rossini<sup>12</sup> report 0.77391. The differences between the values of  $(\partial v/\partial T)_p$  for carbon tetrachloride obtained by Wood and Brusie and in this work are shown by the curve represented by the filled circles in Fig. 2, those between the values given by Gibson and Loeffler<sup>6</sup> and this work by the curve represented by the open circles, and those between the values of Gibson and Loeffler and Wood and Brusie by the curve represented by the crosses. The differences in the same quantity for cyclohexane between the values of Wood and Austin<sup>9</sup> and this work are shown in Fig. 3.

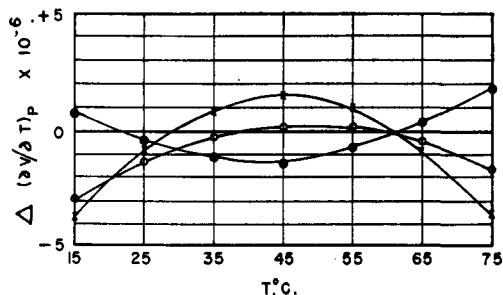


Fig. 2.—Deviations of  $(\partial V/\partial T)_P$  for carbon tetrachloride.

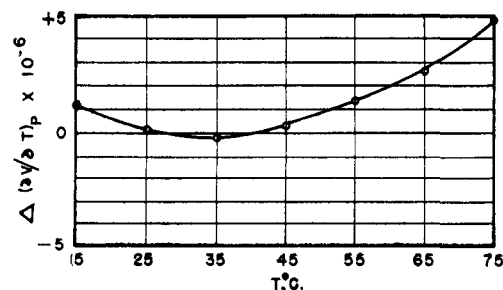


Fig. 3.—Deviations of  $(\partial V/\partial T)_P$  for cyclohexane.

The values of  $V^M/V^0$  have been calculated from equation (3) at 5° intervals. The equation

$$100V^M/V^0 = z_1z_2[0.6763 - (0.04362 + 0.001335t)z_1] \quad (4)$$

has been obtained from these values by the use of the method of least squares. It is estimated that the uncertainty in  $100V^M/V^0$  is less than  $\pm 0.003$ . The deviations of the densities calculated from equations 1 and 4 from the densities observed in the expansion measurements are shown in Fig. 4. The standard deviation of all the densities is  $3.8 \times 10^{-5}$ . The curves for  $100V^M/V^0$  at 30 and 70° are shown in Fig. 1. The temperature dependency of  $100V^M/V^0$  appears only in the asymmetric term of equation (4). Consequently both  $100V^M/V^0$  and  $V^M$  are almost constant in respect to temperature. The quantity  $100V^M/V^0$  decreases slightly with increase in temperature at all concentrations while  $V^M$  increases slightly with increase of temperature up to a mole fraction of carbon tetrachloride of about 0.65 and then decreases slightly.

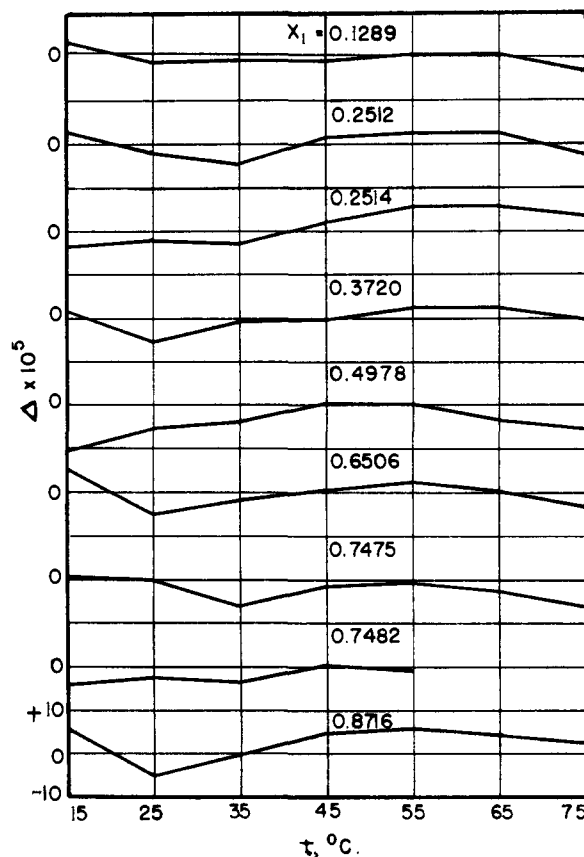


Fig. 4.

**Thermodynamic Functions.**—The excess change of the molal free energy above that of an ideal solution on mixing at constant pressure,  $F_{P,x}^E$ , the molal heat of mixing at constant pressure,  $H_{P,x}^M$ , and the excess change of the molal entropy on mixing at constant pressure,  $S_{P,x}^E$ , have been determined from the measured vapor pressures.<sup>3c</sup> The excess free energy could only be expressed as a linear function of the temperature within the experimental accuracy, resulting in values of the heat of mixing and excess entropy of mixing at constant pressure independent of the temperature. However, Scatchard, *et al.*,<sup>13</sup> have measured the heat

(13) G. Scatchard, L. B. Ticknor, J. R. Goates and E. R. McCartney, THIS JOURNAL, **74**, 3721 (1952).

(10) J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 750 (1926).  
 (11) G. S. Pavlov, *J. soc. phys. chim. russe*, **58**, 1902 (1926).  
 (12) A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 129 (1946).

of mixing of this system at 20° and has expressed the results by the equation

$$H_{P_x}^M = z_1 z_2 V^0 [1.49 + 0.49 (z_1 - z_2)^2] \quad (5)$$

The corresponding equation determined from the vapor pressure data is

$$H_{P_x}^M = 1.3335 z_1 z_2 V^0 \quad (6)$$

There is sufficient difference in these two equations to necessitate a re-evaluation of the thermodynamic functions of this system. Unfortunately equation 5 is not parabolic whereas the vapor pressure data yields a parabolic equation for the excess free energy. Two choices are available: one to carry the additional term in equation 5 throughout the calculations assuming it to be independent of the temperature and the other to omit it. The latter choice has been made in this paper. The results of these two choices agree at half-volume fraction but diverge to a maximum of 34% at the limits of the composition range. This error amounts to approximately 2 cal. per mole in the excess free energy, less than 5 cal. per mole in the heat of mixing and about 0.01 cal. per mole degree in the excess entropy.

Making this choice it is then possible to set

$$F_x^E / z_1 z_2 V^0 = a + bT + cT^2 \quad (7)$$

from which

$$H_x^M / z_1 z_2 V^0 = a - cT^2 \quad (8)$$

Knowing the value<sup>3c</sup> of equation 7 at 40°, that of equation 8 at 20° and that<sup>3c</sup>

$$(F_x^E)_{40^\circ} - (F_x^E)_{70^\circ} = 30 S_x^E \quad (9)$$

three equations are obtained from which the values of  $a$ ,  $b$  and  $c$  may be determined. The result is

$$F_x^E = z_1 z_2 V^0 (2.27 - 0.0080T + 0.000087T^2) \quad (10)$$

where in this equation  $z_1 z_2 V^0$  is evaluated at 25°. This equation yields values for the excess free energy that agree with the older values within 0.1 cal. per mole. At half mole fraction the heat of mixing decreases from 38 cal. per mole at 25° to 32 cal. per mole at 70° and the excess entropy decreases from 0.07 cal. per mole degree at 25° to 0.05 cal. per mole degree at 70°.

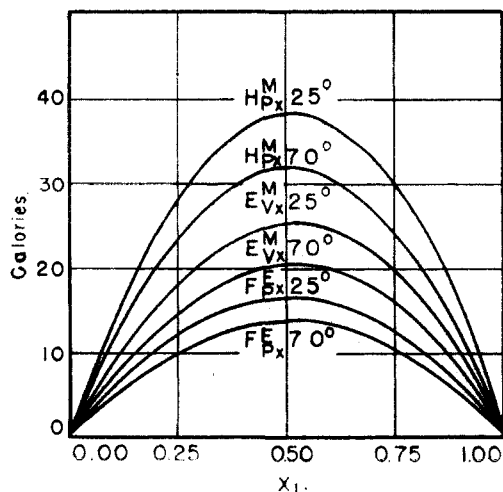


Fig. 5.

By use of these results the molal excess change of the Helmholtz free energy and the entropy on mixing at constant volume,  $A_{V_x}^E$  and  $S_{V_x}^E$ , and the molal energy of mixing at constant volume,  $E_{V_x}^M$ , have been calculated at 25, 40 and 70° using the results of this research and the equations given by Scatchard.<sup>14</sup> The values of the coefficient of expansion in reciprocal degrees,  $\alpha_0$ , and of the coefficient of compressibility in reciprocal atmospheres,  $\beta_0$ , used in these calculations are given in Table III.  $\alpha_0$ ,  $\beta_0$ ,<sup>15,16</sup> and  $\alpha_0/\beta_0$  are additive in the volume fraction. It is assumed that  $d \ln \beta/dT$  is also additive in the volume fraction. The errors in this assumption and the assumption that  $\beta$  equals  $\beta_0$  for the solutions are negligible.

TABLE III

|                        | 25°    | 40°    | 70°    |
|------------------------|--------|--------|--------|
| Cyclohexane            |        |        |        |
| $\alpha_0 \times 10^3$ | 1.217  | 1.264  | 1.365  |
| $\beta_0 \times 10^6$  | 110    | 129    | 170    |
| $\alpha_0/\beta_0$     | 11.06  | 9.80   | 8.03   |
| $d \ln \beta/dT$       | 0.0110 | 0.0101 | 0.0084 |
| Carbon tetrachloride   |        |        |        |
| $\alpha_0 \times 10^3$ | 1.229  | 1.265  | 1.363  |
| $\beta_0 \times 10^6$  | 110    | 124    | 160    |
| $\alpha_0/\beta_0$     | 11.17  | 10.20  | 8.52   |
| $d \ln \beta/dT$       | 0.0076 | 0.0077 | 0.0079 |

The values of  $F_{P_x}^E$ ,  $A_{V_x}^E$ ,  $H_{P_x}^M$  and  $E_{V_x}^M$  at 25 and 70° are shown in Fig. 5. The values of  $A_{V_x}^E$  differ from those of  $F_{P_x}^E$  by about 0.03 cal. per mole at half-mole fraction and consequently the two sets of values are identical in the graph. On the basis of equation 10, both  $E_{V_x}^M$  and  $S_{V_x}^E$  decrease with increase of temperature whereas using the simpler equation both would have increased. Table IV gives a summary of the various quantities for equimolar mixtures at 25, 40 and 70°. It should be pointed out that the values of  $E_{V_x}^M$  and  $S_{V_x}^E$  at the various temperatures have been 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

TABLE IV  
PROPERTIES OF EQUIMOLAL MIXTURES

|  | 25°   | 40°   | 70°   |
|--|-------|-------|-------|
| $V^M$                                      | 0.164 | 0.165 | 0.166 |
| $100 V^M/V^0$                              | 0.159 | 0.157 | 0.152 |
| $F_{P_x}^E$                                | 16.82 | 15.80 | 14.03 |
| $H_{P_x}^M$                                | 38.37 | 36.32 | 31.90 |
| $E_{V_x}^M$                                | 25.31 | 23.94 | 20.60 |
| $S_x^E$                                    | 0.072 | 0.066 | 0.052 |
| $S_{V_x}^E$                                | 0.028 | 0.026 | 0.019 |
| $a_{12}$                                   | 70.10 | 66.52 | 60.62 |
| $\sqrt{a_{11}a_{22}}$                      | 70.52 | 66.92 | 60.94 |
| $100(a_{12} - \sqrt{a_{11}a_{22}})/a_{12}$ | 0.60  | 0.60  | 0.53  |

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

(15) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., p. 38.

(16) "Tables Annuelles de Constantes et Données Numériques," Vol. VI, p. 16 (1923-1924).

various temperatures under such conditions of pressure that the volume is constant at all temperatures. This problem is treated in the following paper.

The cohesive energy density between the unlike molecules has been estimated by the equation

$$a_{12} = (a_{11} + a_{22} + E_{V_{12}}^M / V_{12}^0) / 2 \quad (11)$$

The absolute values of  $a_{12}$  are always less than the geometrical mean of  $a_{11}$  and  $a_{22}$  in agreement with the prediction given by London.<sup>17</sup> The per cent.

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

decrease increases with the temperature. The values of  $a_{11}$  and  $a_{22}$  at 25, 40 and 70° used in these equations are -73.88, -69.86 and -63.86 cal. per cc. for carbon tetrachloride and -67.32, -64.11 and -58.15 cal. per cc. for cyclohexane. The values of  $\beta$  in the equation of state for the vapor,  $V = (RT/p) + \beta$  at the same temperatures are -2544, -2071 and -1455 cc. for carbon tetrachloride and -2488, -2028 and -1427 cc. for cyclohexane.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

## The Effect of Volume and Temperature on the Energy and Entropy of Mixing at Constant Volume<sup>1,2</sup>

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The energy of mixing at constant volume and the excess entropy of mixing at constant volume for the benzene-carbon tetrachloride, benzene-cyclohexane and carbon tetrachloride-cyclohexane systems have been calculated at 70° but at the molal volume at 25° and one atmosphere pressure from previously reported data making use of the Tait equation. It is thus possible to compare the effect of temperature at constant volume and the effect of volume at constant temperature on these mixing quantities. It appears that these functions are only slowly varying functions of the temperature but are definitely dependent upon the volume.

In the development of the theory of solutions of non-polar liquids, it was necessary to assume the energy of mixing at constant volume to be independent of the temperature and the excess entropy of mixing, that is, the difference between the entropy of mixing of the solution and that of an ideal solution of the same concentration, under conditions of mixing at constant volume to be zero. However, experimental determinations of the excess entropy of mixing<sup>4</sup> for the three possible binary systems composed of benzene, cyclohexane and carbon tetrachloride have shown that the excess entropy of mixing at constant volume was positive over the entire range of composition. Measurements on the volume of mixing at various temperatures<sup>5</sup> have shown that both the energy of mixing at constant volume and the excess entropy of mixing at constant volume appear to be functions of the temperature.

However, it is important to realize that the change of these functions with the temperature has actually been determined under conditions of changing volume. While the process of mixing has taken place under conditions of constant volume, the comparisons with temperature are made

at volumes equal to the additive volumes of the pure components at one atmosphere pressure and the temperature in question. Consequently the volumes of the solution and of the components are changing with the temperature and these two effects actually enter into the apparent change of these thermodynamic quantities with temperature. It is therefore necessary to separate the effects of each of these variables keeping the other constant. This can be accomplished if the volumes of the solutions and of the components are known as a function of the pressure and of the temperature. These data are not available for the solutions but it is possible to estimate the necessary quantities from the data available in order to make the calculations and to obtain an approximate value of the energy of mixing and the excess entropy of mixing, both at constant volume at various temperatures referred to some reference volume independent of the temperature. In particular, the energy of mixing and the excess entropy of mixing at 70° at a constant volume equal to that of the components at 25° and one atmosphere pressure have been calculated from the values of these functions for the process of mixing at a constant volume equal to the additive volume of the components at 70° and one atmosphere pressure. These values are compared to the energy of mixing and the excess entropy of mixing at 25° and one atmosphere pressure. The necessary corrections are small and are somewhat uncertain. However, the results are indicative that the energy of mixing at constant volume and the excess entropy of mixing at constant volume are approximately independent of the temperature or at least slowly varying functions of the temperature for the three systems studied when referred to the same reference

(1) Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1949.

(2) This contribution contains material taken from a thesis by John A. Gray, III, presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(4) (a) G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939); (b) *THIS JOURNAL*, **61**, 3206 (1939); (c) *ibid.*, **62**, 712 (1940).

(5) (a) S. E. Wood and J. P. Brusie, *ibid.*, **65**, 1891 (1943); (b) S. E. Wood and A. E. Austin, *ibid.*, **67**, 480 (1945); (c) S. E. Wood and J. A. Gray, III, *ibid.*, **74**, 3729 (1952).