$$G^{E}_{x} = x_1x_3\Sigma\, G^{\nu}_{12}\,(2x_1 - 1)^{\nu} + x_1x_3\Sigma_{\nu}\, G^{\nu}_{13}(2x_1 - 1)^{\nu} + x_2x_3\Sigma_{\nu}\, G^{\nu}_{23}(x_2 - x_3)^{\nu} \quad (9)$$

Table II gives the measured heats of mixing for some ternary mixtures and the values calculated by equations (1) and (9) with the parameters given for the binary systems in Table I. Figure 2 shows the heat of mixing as a function of the mole fraction of methanol for mixtures of methanol with carbon tetrachloride, with benzene and with an equimolal mixture of carbon tetrachloride and benzene, with the pure liquid components as standard states. For the mixture, values from equation (1) are given as a broken line and from equation (9) as a full line. The experimental points are given only for the mixture.

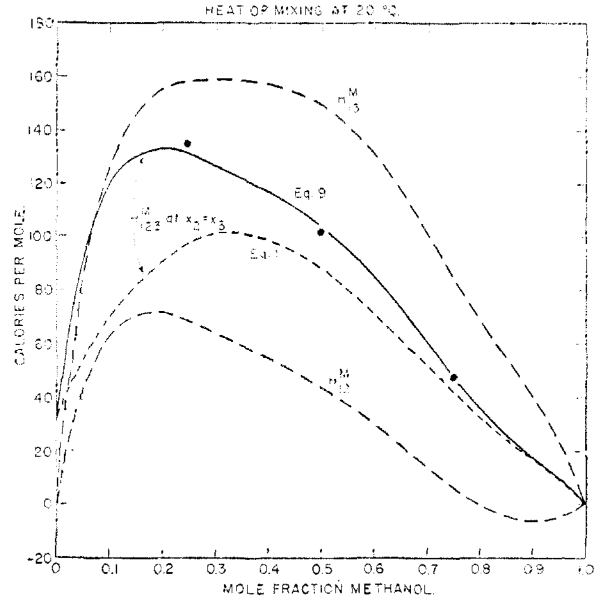

Fig. 2.

Table II

Heats of Mixing of Methanol–Carbon Tetrachloride–Benzene

x_1	x_2	x_1	Meas.	H^{M}_{x} (cal./mole) Eq. (1)	Eq. (9)
0.2460	0.3750	0.3790	136	95	131
.5198	.2444	.2358	97	84	100
.7494	.1319	.1187	47	39	46

For a mixture of 0.3340 ml. of carbon tetrachloride, 0.3091 ml. of benzene and 0.3569 ml. of cyclohexane, the measured heat was 1.22 cal./ml.; calculation on the basis of volume fractions instead of mole fractions gave 1.19 for equation (1) and 1.20 for equation (9) with carbon tetrachloride as component 1. Equation (1) fits the measurement with all non-polar components within the experimental error, but fails to fit those for mixtures containing methanol. Equation (9) fits either within the experimental error.

It is possible that for some mixtures with all non-polar components, one component is sufficiently different from the others so that equation (9) is preferable to equation (1). It is also possible that in some system there will be an advantage in also replacing $(x_2 - x_3)$ by $(2x_2 - 1)$. Certainly there are systems which cannot be described without the addition of terms with three different subscripts.

Cambridge, Massachusetts

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Vapor–Liquid Equilibrium. IX. The Methanol–Carbon Tetrachloride–Benzene System[1]

By George Scatchard and Leland B. Ticknor

Received February 28, 1952

The second virial coefficient of mixtures of methanol with benzene and with carbon tetrachloride is computed from the theory of polar–non-polar gas mixtures, and the thermodynamic properties of these mixtures are redetermined from the vapor liquid equilibrium measurements of Scatchard, Wood and Mochel. A new type of equilibrium still is described, which is more satisfactory for large differences between vapor and liquid compositions. The vapor–liquid equilibrium of the ternary system methanol–carbon tetrachloride–benzene is determined at 35° and 55°, and an equation for the excess free energy is presented which expresses these results and the enthalpy of mixing determined by Scatchard, Ticknor, Goates and McCartney.

Vapor-liquid equilibrium measurements furnish a method of measuring the activity coefficients or excess chemical potentials in a liquid mixture. The excess chemical potentials of each component in a mixture may be calculated from the relation

$$\mu^{E}_{i} = RT \ln \frac{Py_i}{P_{i_0}x_i} + (\beta_{ii} - V_i)(P - P_{i_0}) + P[\Sigma_j\delta_{ij}y_j(1 - y_i) - \Sigma_{jk}\delta_{jk}y_jy_k/2] + \Delta \quad (1)^{2}$$

in which P is the vapor pressure of the solution at the absolute temperature T, y_i and x_i are the mole fraction of the ith component in the vapor and liquid, respectively, $\delta_{ij} = 2\beta_{ij} - \beta_{ii} - \beta_{jj}$, and V_i is the liquid molal volume of component i, $i \neq i \neq k \neq i$, and Δ represents correction terms of higher orders of P. Equation 1 is valid for any number of components.

Deviations from Gas Laws.—In later work from this Laboratory it was assumed that the δ's and Δ were all zero, and the β's were calculated from those of water and the theory of corresponding states since there were no direct measurements for most of the substances studied. Recently Lam-

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(1) This paper is based on the Ph.D. thesis of L. B. Ticknor, 1950. Paper VIII in this series is G. Scatchard, G. M. Kavanagh and L. B. Ticknor, This Journal, **74**, 3715 (1952).

(2) G. Scatchard and C. L. Raymond, *ibid.*, **60**, 1278 (1938).

bert, Roberts, Rowlinson and Wilkinson[3] have made measurements with several of these substances below the normal boiling point. They found that the Berthelot equation

$$\beta = B - A/T^2 = 9RT_c/128\,p_c - 27RT_c^3/64p_cT^2 \quad (2)$$

agrees well with the experimental measurements in this range for most non-polar substances, and also with the Lennard-Jones expression[4] for a gas in which the mutual energy of two molecules, u, is given by the relation

$$u = \epsilon[(r_0/r)^{12} - 2(r_0/r)^6] \quad (3)$$

in which r is the distance of separation and r_0 is the distance at which u has its most negative value, $-\epsilon$. It is therefore convenient to base the discussion on the Berthelot equation. Baxendale, Enüstün and Stern[5] find that the second virial coefficient of benzene is 10% greater than that given by Lambert and co-workers at 80° and 50% greater at 40°. We retain these values, however, for consistency with those for the other components. The effect of deviations from the gas laws is much smaller when both components have nearly the same vapor pressure than when only one is volatile.

To determine β_{ij} for a non-polar mixture, we treat B and A of equation (2) as we would van der Waals b and a or the Beattie-Bridgeman B_0 and A_0

$$B_{ij} = (\sqrt[3]{B_{ii}} + \sqrt[3]{B_{jj}})^3/8 \quad (4)$$

$$A_{ij}/B^2_{ij} = \sqrt{A_{ii}A_{jj}/B^2_{ii}B^2_{jj}} \quad (5)$$

Equation (4) is the Lorentz combination which assumes approximately that r_0 is additive. Equation (5) corresponds to calculating the energy density of a liquid mixture[6] from

$$(E/V)_{ij} = \sqrt{(E/V)_{ii}(E/V)_{jj}} \quad (6)$$

in which E is the energy difference between the perfect gas and liquid state and V is the volume in the liquid. The justification is that the separation of molecules in the liquid is approximately proportional to r_0, and the energy of evaporation is approximately ϵ times half the number of nearest neighbors in the liquid. Other workers have used the corresponding quadratic combination of A, AB and A/B. Measurements with methane–butane mixtures,[7] for which the ratio of B's is great enough to show a difference, fall between A/B and A/B^2. Guggenheim and McGlashan,[8] however, obtain results which indicate that this relation may depend upon the different ranges of reduced temperature in which the constants for the two gases were determined. For the non-polar mixtures which we have studied, the differences are much too small to make the choice important. Indeed, for such mixtures, the differences between β_{ij} and $(\beta_{ii} + \beta_{jj})/2$ are so small that δ_{ij} may be taken as zero.

Polar Molecules.—The case is very different for a mixture of a polar and a non-polar gas. At any instant any molecule is anisotropic; a molecule which is isotropic on the average is called non-polar; one which is permanently anisotropic is called polar. The attraction of two non-polar molecules arises entirely from their instantaneous anisotropy. Two permanently anisotropic molecules have additional attraction because their relative orientation is more often such as to attract than it is to repel. This permanent anisotropy is usually important only in the case of a dipole, where the centroids of positive charges and of negative charges do not coincide, and is very important if one of the charges is very near the surface, as a hydrogen bond-forming proton. An anisotropic molecule also attracts any other molecule by polarizing it to give an induced charge. London[9] has shown that the induction effect is less than 6% of the total energy for many polar gases, and we will neglect it, although we recognize that the induction effect is a large part of the energy of a hydrogen bond.

Stockmayer[10] has shown that the polar and non-polar parts of the energy of attraction must be combined separately. We cannot, however, use his method in detail. Our method uses the relations that B is approximately proportional to the liquid molal volume and that A/B^2, like the energy density, is proportional to the five-thirds power of the refraction,[11] $r = (n^2 - 1)/(n^2 + 2)$.

Table I contains the values of the liquid volume, V, the refraction, r, and B and A of equation (2) calculated from the critical constants for six non-polar and slightly polar substances. It also contains k_1 and k_2, calculated from the equations

TABLE I

VALUES OF k_1 AND k_2

Substance	V, ml./mole	r	B, ml./mole	$10^{-7} A$, ml./mole/°K.²	k_1	$10^4 k_2$	10μ, D
Carbon tetrachloride	97.35	0.2743	71.4	13.25	1.362	8.28	0
Benzene	88.89	.2948	67.9	12.85	1.310	8.04	0
Cyclohexane	107.95	.2567	78.8	14.52	1.371	8.33	0
n-Hexane	130.47	.2294	99.5	15.26	1.312	9.60	0
Chloroform	80.17	.2670	57.4	9.89	1.394	7.26	1.1
Diethyl ether	103.75	.2166	73.5	9.65	1.412	8.72	1.15
Average					1.360	8.37	
Ethyl bromide	74.8	.2515	47.3	7.23	1.58	7.77	2.02
Phenyl bromide	106.7	.3232	87.7	23.6	1.217	7.34	1.77
Methanol	40.44	.2035	37.6	5.945	1.078	1.94	1.66

$$B = V/k_1 \quad (7)$$

$$A = V^2r^{5/3}/k_2 \quad (8)$$

and their average values. Below, it gives the same values for three more highly polar substances, one of which, methanol, contains a bond-forming proton. The dipole moments of these substances are given in the last column.

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[3] J. D. Lambert, G. A. H. Roberts, J. S. Rowlinson and V. J. Wilkinson, *Proc. Roy. Soc.* (*London*), **196A**, 113 (1949).

[4] J. E. Lennard-Jones and A. F. Devonshire, *ibid.*, **163A**, 53 (1937).

[5] J. H. Baxendale, B. V. Enüstün and J. Stern, *ibid.*, **A243**, 169 (1951).

[6] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931).

[7] J. A. Beattie, W. H. Stockmayer and H. G. Ingersoll, *J. Chem. Phys.*, **9**, 871 (1941); J. A. Beattie and W. H. Stockmayer, *ibid.*, **10**, 473 (1942).

[8] E. A. Guggenheim and M. L. McGlashan, *Proc. Roy. Soc.* (*London*), **A206**, 448 (1951).

[9] F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

[10] W. H. Stockmayer, *J. Chem. Phys.*, **9**, 1863 (1941).

[11] G. Scatchard, *Chem. Revs.*, **44**, 7 (1949).

Polar–Non-polar Mixtures.—The average values of k_1 and k_2 and the values of V and r for methanol from Table I give $B_n = 29.8$ and $A_n = 1.378 \times 10^{-7}$, which accounts for less than a tenth of β for methanol. More than nine-tenths of the virial coefficient of methanol arises from its permanent asymmetry which gives little interaction with non-polar molecules. We assume that the interaction of methanol with carbon tetrachloride or with benzene is determined only by the non-polar repulsion and dispersion terms, and that these may be expressed by equation (2) with the parameters combined by equations (4) and (5) for B_n and A_n of methanol as given above for the B's and A's of the non-polar components given in Table I. The interaction of carbon tetrachloride and benzene is determined in the same way. These yield

$$\beta_{12} = 47.3 - 4.49 \times 10^{-7}/T^2$$
$$\beta_{13} = 46.2 - 4.43 \times 10^{-7}/T^2$$
$$\beta_{23} = 69.65 - 13.05 \times 10^{-7}/T^2$$
$$\delta_{23} = 0.00$$

in which the subscript $_1$ refers to methanol, $_2$ to carbon tetrachloride and $_3$ to benzene.

The values of β for the components were read graphically from the curves of Lambert and his co-workers,[3] with a slight extrapolation when necessary. The values of β's and of δ's are listed in Table II.

TABLE II

VALUES OF β AND δ

Temp., °C.	β_{11}	β_{22}	β_{33}	δ_{12}	δ_{13}	δ_{23}
25	−1830	−1630	−1390	2540	2314	0
35	−1620	−1510	−1290	2278	2066	0
45	−1460	−1390	−1210	2054	1886	0
55	−1300	−1270	−1130	1834	1698	0

Corrections to Published Excess Free Energies.—The excess free energies of the binary systems methanol–carbon tetrachloride, methanol–benzene and carbon tetrachloride–benzene have been recalculated from the measurements of Scatchard, Wood and Mochel[12] using the β's and δ's of Table II. The values of G^E_x are given in Table III. The maximum change from the values previously calculated is 6.65 cal./mole at 35° and 11.61 at 55° for methanol–carbon tetrachloride, 6.48 at 35° and 11.62 at 55° for methanol–benzene, 0.14 at 40° and 0.16 at 70° for carbon tetrachloride–benzene. Most of the change arises from the δ terms which were not considered in the earlier calculations.

Analytical Expressions.—We have expressed the excess free energy per mole in the form[11]

$$G^E_x = x_ix_j[G^0_{ij} + G'_{ij}(x_i - x_j) + G''_{ij}(x_i - x_j)^2 + \ldots]$$
$$= x_ix_j\Sigma_\nu G^\nu_{ij}(x_i - x_j)^\nu \qquad (9)$$

in which G^0_{ij}, G'_{ij}, etc., are functions of the temperature. From this expression may be calculated the excess entropy and the change of enthalpy and heat capacity on mixing, all of which have the same form as equation (9), but different parameters. If we had also expressed the G'_{ij}'s as functions of the pressure, we would have included the change in volume on mixing. The excess chemical potentials may also be calculated by the relations

$$\bar{G}^E_i = x_j^2[G^0_{ij} + G'_{ij}(3x_i - x_j) + G''_{ij}(5x_i - x_j)(x_i - x_j) + \ldots]$$
$$= x_j^2\Sigma_\nu G_{ij}^\nu[(x_i - x_j)^\nu + 2\nu x_i(x_i - x_j)^{\nu-1}] \qquad (10)$$
$$\bar{G}^E_j = x_i^2[G^0_{ij} + G'_{ij}(x_i - 3x_j) + G''_{ij}(x_i - 5x_j)(x_i - x_j) + \ldots]$$
$$= x_i^2\Sigma_\nu G_{ij}^\nu[(x_i - x_j)^\nu - 2\nu x_j(x_i - x_j)^{\nu-1}] \qquad (11)$$

The larger values of the revised excess free energies make it even more difficult than before to obtain expressions which do not indicate separation into two phases for the mixtures containing methanol. We were unable to achieve this with less than five terms at each temperature. The temperature functions are chosen to fit our results at all temperatures and also to give the same expressions for the heats of mixing as in our previous paper.[13]

TABLE III

CORRECTED VALUES OF THE EXCESS FREE ENERGY

t, °C.	X_1	G^E_{12}	Dev. in G^E_{12}
	Methanol–Carbon tetrachloride		
25	0.4880	317.42	−0.20
35	.0169	38.31	5.86
	.0189	43.10	7.00
	.1349	194.17	1.69
	.3560	316.03	1.00
	.4776	326.64	−0.06
	.4939	325.61	− .11
	.6557	284.25	− .25
	.7912	205.67	− .43
	.9120	99.91	−1.72
45	.4866	334.41	0.05
55	.0254	52.90	4.00
	.0579	111.16	8.44
	.1493	214.61	1.12
	.3647	332.28	0.89
	.4893	341.66	− .04
	.4946	341.29	− .04
	.6448	304.17	.36
	.7903	218.83	.04
	.9087	112.74	1.42
	Methanol–Benzene		
25	0.4742	301.38	−1.31
35	.0242	47.15	7.00
	.0254	40.67	−1.29
	.1302	173.40	2.43
	.3107	281.08	−1.15
	.4989	306.06	0.05
	.5191	304.24	.08
	.6305	278.46	− .08
	.7965	192.65	.10
	.9197	89.15	.28
	Methanol–Benzene (Contd.)		
45	0.5234	309.49	1.57
55	.0304	56.70	7.73
	.0493	71.05	−5.39
	.1031	140.52	−3.11
	.3297	296.09	1.10
	.4874	314.67	−0.23
	.4984	314.09	− .18
	.6076	294.04	− .10
	.7898	203.93	.00
	.9014	111.24	.94
	Carbon tetrachloride–Benzene		
30	0.4865	19.59	0.12
40	.1398	9.19	− .09
	.2378	13.97	.02
	.3735	17.92	− .04
	.4919	19.20	.07
	.4986	19.13	.00
	.6201	17.95	− .03
	.7585	13.96	.02
	.8718	8.12	− .36
50	.4926	18.89	.10
60	.4907	18.51	.06
70	.1428	8.95	.07
	.2394	13.26	− .01
	.3791	17.14	.04
	.4930	19.08	1.02
	.4939	17.79	−0.31
	.6224	16.90	.07
	.7624	13.04	.00
	.8750	7.86	.01

We obtain the expressions

Methanol–carbon tetrachloride

$$G^E_x = x_1x_2[-1715.8 - 6.453T\ln T + 46.77T - (237 - 0.185T)(x_1 - x_2) + 0.633T(x_1 - x_2)^2 - (383 - 0.092T)(x_1 - x_2)^3 + (346 - 0.587T)(x_1 - x_2)^4] \qquad (12)$$

Methanol–benzene

$$G^E_x = x_1x_3[-841.4 - 4.917T\ln T + 34.88T - (250 - 0.312T)(x_1 - x_3) + 0.640T(x_1 - x_3)^2 - (550 - 1.435T)(x_1 - x_3)^3 + (800 - 2.376T)(x_1 - x_3)^4] \qquad (13)$$

Carbon tetrachloride–benzene

$$G^E_x = x_2x_3[119.6 - 0.1375T - 0.85(x_2 - x_3)] \qquad (14)$$

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[12] G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **66**, 1960, 1957 (1946); *J. Phys. Chem.*, **43**, 119 (1939).

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

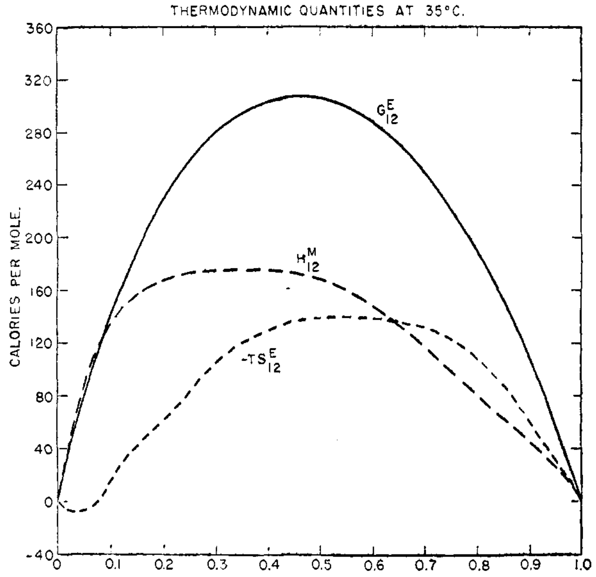

Fig. 1.

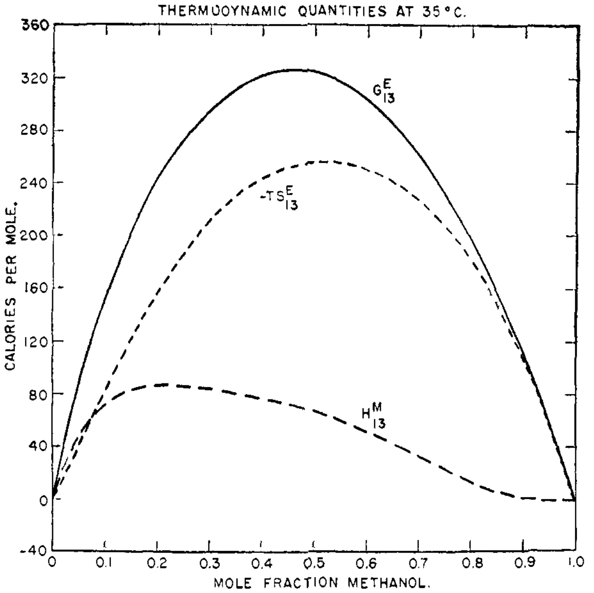

Fig. 2.

The deviations of the experimental results from these expressions are given in Table III.

Figures 1 and 2 show the values of the thermodynamic functions at 35° for the methanol–carbon tetrachloride and methanol–benzene systems. The functions for the carbon tetrachloride–benzene system are essentially unchanged from those originally published.[10]

The methanol–benzene and methanol–carbon tetrachloride systems show large unsymmetrical excess functions, while the benzene–carbon tetrachloride system has relatively small nearly symmetrical functions. These facts indicated that measurements of the vapor–liquid equilibrium for ternary mixtures of benzene–carbon tetrachloride–methanol should be of interest.

New Measurements.—The equilibrium still used in this research is essentially different from those stills previously used in this Laboratory. The previous stills were the double boiler type; *i.e.*, vapors from the boiling liquid in the outer boiler passed through the liquid in the inner boiler, thus heating it and pumping it over the thermocouple well. This type of still has the advantage of not superheating the liquid, but it has the disadvantage of allowing a variation in the composition and the amount of the liquid in the inner boiler. Kavanagh's still[1] was designed to control these variations. Part of the difficulties, however, are inherent in the double boiler still. They are particularly troublesome when the compositions of the equilibrium vapor and liquid are very different. Since the pressures are different in the outer and inner boilers, the temperatures are also different, so there is a tendency for condensation in the inner boiler. Unless this is compensated very exactly, the quantity of liquid in the inner boiler changes and its composition also changes. It is very difficult to control the quantity of liquid accurately enough to avoid error due to this change.

In an attempt to eliminate the difficulties of double boiler stills, a single boiler still was designed, Figs. 3 and 4. It is similar to one used by Redlich and Kister.[14] Since this still contains only one boiler, fluctuations in the rate of heating should not cause a change in composition, but only a change in rate of boiling. In this still the vapor chamber is surrounded by a silvered evacuated jacket which, in turn, is surrounded by an adiabatic shield.

The still operates as follows: Dowtherm heating oil flows into the heating chamber H through the tube U. On top of the heating chamber, at I, was fused some powdered glass. It was hoped that this would create active spots for the formation of bubbles of vapor, but it was found insufficiently effective. This corresponds with Marboe's findings.[15] Accordingly, a spirally wound Chromel-A heating wire, W, was inserted in the boiling chamber to create bubbles. The bubbles of vapor force liquid up the tube J and onto the thermocouple well K where the liquid and vapor equilibrate; L is a spiral of glass wound around the thermocouple well to ensure an even coating of liquid on the well. When the liquid drops off the thermocouple well, it passes through the tube M and through the cooler D, which is cooled with ice-water. After passing through the liquid trap E, the liquid returns to the boiling chamber through S. The condensed vapor, after passing through the vapor trap C, is mixed with the liquid in S where the mixture is heated to just below the boiling point by a small electrical heater before returning to the boiling chamber. The caps F and G allow the removal of samples of liquid and of condensed vapor from the traps by means of a long hypodermic needle and syringe

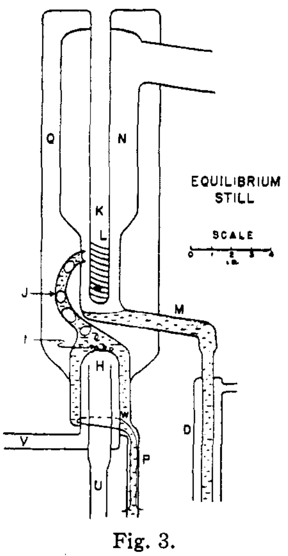

Fig. 3.

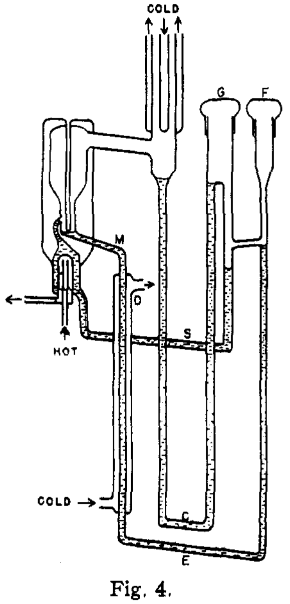

Fig. 4.

The still holds about 42 ml. of liquid, 12 ml. in the vapor trap, 13 ml. in the liquid trap, and about 17 ml. in the boiling

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[14] O. Redlich and A. T. Kister, *ibid.*, **71**, 505 (1949).

[15] E. C. Marboe, *Chem. Eng. News*, **27**, 2198 (1949).

chamber. The distillation rate is about 1 ml. per minute. It is estimated that the liquid in the liquid trap circulates at about 5 ml. per minute. It usually takes about three hours for the still to reach equilibrium and it will accomplish this starting from unmixed liquids.

The pressure control and measurement equipment were the same as those used previously.[1] The twenty-junction thermocouple was recalibrated in the new still by boiling conductivity water and purified benzene.

Mallinckrodt Reagent Grade benzene, carbon tetrachloride and methanol were purified by distillation in the fractionating column previously used here.[13] Water vapor was excluded from the column and the purified liquids were stored in a dried atmosphere. The normal boiling point on the International Scale, densities at 25° and refractive indices for the D line at 25° for the purified liquids are given in Table IV.

TABLE IV

PROPERTIES OF COMPONENTS

	Methanol	Benzene	Carbon tetrachloride
Boiling point, °C.	64.509	80.093	76.669
Literature	64.511[12]	80.103[16]	76.687[12]
Density	0.78653	0.87351	1.58437
Ref. 12	.78654	.87368	1.58452
I.C.T.	.78660	.87341	1.58435
Refractive index	1.3267	1.4979	1.4572
I.C.T.	1.3266	1.4979	1.4573

In order to determine the composition of a ternary mixture it is necessary to measure two properties. In our system the density is largely a measure of the fraction of carbon tetrachloride and the refractive index measures essentially the fraction of methanol. These measurements were made at 25°. The refractive indices limited the accuracy of our composition determinations to about one part in a thousand.

In order to determine the density and refractive index as functions of composition these properties were measured for solutions of known compositions. From the measurements on the pure liquids and the binary mixtures the parameters in equations (15) and (16) were obtained. The molecular weights used for methanol, carbon tetrachloride and benzene were, respectively, 32.04, 153.84 and 78.11. These gave molar volumes at 25° in the same order of 40.74, 97.10 and 89.42. In the following equations n is the refractive index, d is the density and z is the volume fraction which equals $V_i/\Sigma V_i$ where V_i is the volume of the unmixed component. n_1, n_2, n_3, d_1, d_2 and d_3 are the measured values of the refractive index and density given in Table IV.

$$n = n_1z_1 + n_2z_2 + n_3z_3 - 0.0004z_1z_2 - 0.0048z_1z_3 + 0.0032z_2z_3 \quad (15)$$

$$d = d_1z_1 + d_2z_2 + d_3z_3 - 0.00060z_2z_3 + z_1z_2[0.00636 + 0.00341(2z_1 - 1) - 0.00667\,(2z_1 - 1)^2] + z_1z_3[0.00114 + 0.00198\,(2z_1 - 1) - 0.00110\,(2z_1 - 1)^2] \quad (16)$$

Table V gives the experimental and calculated values of density and refractive index for the solutions of known compositions. Since the difference between the observed and calculated densities in the ternary mixtures is small compared to the uncertainty in the determination of the refractive index, it was unnecessary to include more parameters in equation (16).

The behavior of an equilibrium still varies greatly with the substance boiled and the pressure of operation. It was found that the order of increasing ease of cavitation was water, methanol, benzene and carbon tetrachloride. Marboe[15] has suggested that cavitation is hindered by hydrogen bonding between the liquid and the glass. This is consistent with our observations.

In the measurements on mixtures the temperature did not vary at constant heating rate, but, in contrast with the pure liquids, a change in heating rate caused a change in temperature. This change in temperature might arise from a change in composition due to a change in the distribution of material in the different parts of the apparatus, even though the vapor and liquid leaving the thermometer remain in equilibrium. Hence, liquid mixtures were boiled under the same conditions as were found best for the pure liquids.

TABLE V

DENSITIES AND INDICES OF SOLUTIONS OF KNOWN COMPOSITION

z_1	z_2	z_1	$d_{\text{obsd.}}$	$d_{\text{calcd.}}$	$n_{\text{obsd.}}$	$n_{\text{calcd.}}$
0.26886	0.73114		1.37052	1.37052	1.4221	1.4221
.51242	.48758		1.17715	1.17715	1.3903	1.3903
.73074	.26926		1.00264	1.00264	1.3620	1.3618
0.25186		0.74814	0.85158	0.85160	1.4539	1.4538
.49387		.50613	.83083	.83083	1.4121	1.4121
.72871		.27129	.81049	.81048	1.3721	1.3722
	0.25264	0.74736	1.05311	1.05299	1.4882	1.4882
	.53429	.46571	1.25318	1.25317	1.4770	1.4770
	.73757	.26243	1.39763	1.39770	1.4686	1.4685
0.34235	0.33429	0.32336	1.08161	1.08188	1.4254	1.4255
.16917	.18390	.64693	0.98935	0.98942	1.4612	1.4613
.16867	.64931	.18202	1.32005	1.32044	1.4427	1.4428
.65468	.19001	.15531	0.95243	0.95262	1.3777	1.3776

This still was found considerably easier to operate than the previous (double boiler) still[1] because it has fewer and less sensitive controls. The thermocouple e.m.f. did not vacillate more than 0.002°, except in runs made on solutions that were very dilute in methanol. This still did reach a steady state. It appears that the single boiler still has the advantage in ease of operation and gives better results in mixtures with high relative volatility.

TABLE VI

VAPOR PRESSURE OF BINARY MIXTURES AT 55°

x	y	P	$G^E_{x\text{(calcd.)}}$	$G^E_{x\text{(obsd.)}}$	Dev.
		Methanol–Carbon tetrachloride			
0.5587[a]	0.5140	325.68	316.0	316.1	− 0.1
.0234	.3692	568.91	29.5	45.3	−15.8
.0343	.3926	592.60	52.5	64.6	−12.1
.0525	.4326	644.13	95.5	94.4	1.1
.1734	.5084	721.56	231.0	234.9	− 3.9
.5450	.5535	746.30	334.3	334.6	− 0.3
.8699	.6724	687.30	144.4	150.5	− 6.1
		Methanol–Benzene			
0.0405	0.3518	493.58	65.3	63.9	1.4
.0638	.4210	545.73	97.2	96.1	1.1
.0771	.4462	565.10	112.0	113.1	− 1.1
.2298	.5422	647.85	243.1	249.9	− 6.8
.5988	.6056	678.27	296.2	296.7	− 0.5
		Carbon tetrachloride–Benzene			
0.4542	0.4932	358.25	17.68	18.44	− 0.76

[a] At 35°.

Experimental Results.—Several runs were made on binary mixtures. The results of these are given in Table VI. x and y are the mole fraction of methanol in mixtures containing methanol, and the mole fraction of carbon tetrachloride in the carbon tetrachloride–benzene mixtures. The purposes of these runs were to compare the results in our still with others,[12] and to check operation of our still on solutions of low methanol content. The deviations from equations (2), (3) and (4) are given in Table VI. The deviations in dilute solutions are somewhat larger than those in concentrated solutions, but this may be expected from the large difference in composition between the liquid and vapor. A comparison of the vapor pressure as a function of liquid or vapor composition between our dilute runs and those of the earlier work (with a double boiler still) showed the present results to be more consistent.

The vapor pressures of methanol–carbon tetrachloride and methanol–benzene mixtures at 20° were calculated from equations (12) and (13) for mixtures of the same composition as reported by Niini.[17] Our calculated vapor pressures

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(16) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(17) A. Niini, *Ann. Acad. Sci. Fennicae*, **A55**, No. 8 (1940).

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	Pressure	G^E_{123} (obsd.)	δ_{17}	δ_{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 β_{ii} 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 β_{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.[13] The equation for the excess free energy of the ternary mixtures corresponding to equation (9) is

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

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^E_x from that calculated by equations (17) and (18) as δ_{17} and δ_{18}, respectively. Although the advantage of grouping the non-polar components together is not so great as for the heats of mixing,[13] 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.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Volume of Mixing and the Thermodynamic Functions of Binary Mixtures. III. Cyclohexane–Carbon Tetrachloride[1]

BY SCOTT E. WOOD[2] 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[3] 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[4] and benzene–cyclohexane[5] 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.[4,5]

Purification of Materials.—The purification of the carbon tetrachloride[4] and the cyclohexane[5] 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[4] reported a value of 1.57682 g. per cc. at 30° with dissolved air and Gibson and Loeffler[6] 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[5] reported a value of 0.76910 g. per cc. and Scatchard, Wood and Mochel[3a] 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.

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[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.

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[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).