less rich in chloroform. The loss through the condenser was, however, not more than 0.5 cc. per hour, and the deviations from the steady state compositions should be less than the experimental error.

When the steady state is reached, the manometer system is shut off from the still, the heater is extinguished and nitrogen is admitted to the still as rapidly as possible to a pressure of slightly more than one atmosphere. This gives a very rapid change from steady state boiling to none at all. The pressure is measured on the main manometer. Then samples of the liquids in the inner boiler and in the condensate trap are removed for analysis by means of ice-jacketed pipets.

As previously noted the temperature may be reproduced to 0.001° and the pressure may be measured to 0.01 mm. In favorable cases the compositions of the liquids in the inner boiler and in the condensate trap may be determined to less than 0.1%. However, the equilibrium compositions, temperature and pressure can certainly not be determined to this order of accuracy. Only a careful study of several systems can show how accurately the equilibrium properties may be determined by this method.

Summary

An equilibrium still is described with a Cottrell pump which is heated only by the equilibrium vapor.

Auxiliary apparatus for the precise measurement of temperature and pressure is also described, and the procedure for making measurements is given.

CAMBRIDGE, MASS. RECEIVED MARCH 8, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 400]

Vapor-Liquid Equilibrium. II. Chloroform-Ethanol Mixtures at 35, 45 and 55°

BY GEORGE SCATCHARD AND C. L. RAYMOND[1]

Many mixtures containing chloroform show interesting behavior. Mixtures with substances containing oxygen but no hydroxyl have large negative changes of heat content on mixing and negative non-ideal free energy changes, smaller in magnitude than the corresponding heat content changes. A plausible explanation is that two different dipoles can align themselves in the co-linear parallel position much more closely than can two like dipoles of either species. Mixtures with the lower aliphatic alcohols have negative changes of heat content when the alcohol is in excess but positive changes when the chloroform is in excess.[2] These measurements of the vapor-liquid equilibrium for chloroform-ethanol systems were undertaken in the hope of throwing light upon this very interesting phenomenon.

Equilibrium Measurements

The equilibrium measurements were carried out as described in Part I of this series except that the still was left connected to the barometer during the pressure measurements on the pure components. Fluctuations in the pressure due to the boiling were not greater than 0.02 mm. The compositions of the mixtures were determined from the densities.

Ethanol was purified as described by Harris[3] and kept in 100-cc. glass-stoppered bottles. Density measurements indicated the presence of 0.12–0.18% of water. The vapor pressures at 55° of the products of three purifications were 279.82, 279.90 and 279.81$_5$ mm. Chloroform was purified by the method of Timmermans and Martin.[4] The density and vapor pressures of the pure chloroform were determined immediately. The material used for mixtures was stored in ground-glass stoppered bottles in the dark after the addition of 1% ethanol as a stabilizer. The vapor pressures at 55° of the products of three different purifications were 617.77, 617.90 and 617.84 mm.

The vapor pressures of the pure components, measured at 5° intervals, are given in Table I. The measurements with alcohol agree excellently with most of those of Louder, Briggs and Browne, and below 60° are from 0.2 to 0.4% lower than those of Merriman. They are from 0.5 to 1.0% lower than the values of the "International Critical Tables.[5] The measurements with chloroform are in agreement with those of Beckmann and Leische and of Rex, and are about 5% lower than those of Herz and Rathmann. They are 1–2% lower than the values of the "International

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[1] Taken from the thesis submitted to the Massachusetts Institute of Technology by C. L. Raymond in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. Hirobe, *J. Fac. Sci. Tokyo*, [1] **1**, 155 (1925).

[3] L. Harris, THIS JOURNAL, **55**, 1940 (1933).

[4] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 763 (1926).

[5] "International Critical Tables," Vol. III, p. 215. The other literature references will be found there.

Critical Tables,[5] which appear to give too much weight to the measurements of Herz and Rathmann. Since chloroform forms minimum boiling mixtures with its most probable impurities, and since the products of its decomposition are very volatile, the lower values are probably to be preferred.

TABLE I

VAPOR PRESSURES OF CHLOROFORM AND OF ETHANOL

t, °C.	$P_{\text{mm.}}$ (ethanol)	$P_{\text{mm.}}$ (chloroform)
35	102.78	295.11
40	134.09	360.28
45	172.76	433.54
50	221.18	519.18
55	279.86	617.84
60	351.32	730.14
65	438.36	
70	542.09	
75	666.49	

The densities at 25° of the mixtures were determined in pycnometers which contain about 11 cc. and have wide tubes between the capillaries and the glass stoppers to allow for expansion. The results are given in Table II. To determine the compositions the mole fraction of ethanol, x, was expressed as a function of the specific volume, v (the reciprocal of the density), and the function $\delta = x + 3.43407 - 6.88931v + 2.67566v^2$ was plotted against v. δ varies from -0.04 to $+0.04$ and a smooth curve fits the points to 0.03% and fits the corresponding points from the density measurements of Hirobe[2] to 0.1%.

TABLE II

DENSITY OF ETHANOL–CHLOROFORM MIXTURES AT 25°

Weight fraction ethanol	Mole fraction ethanol	Density d^{25}_{4}	Specific volume
0.0000	0.0000	1.47955	0.67588
.0337	.0829	1.43640	.69619
.0658	.1544	1.39796	.71533
.0865	.1971	1.37477	.72739
.1483	.3111	1.30804	.76450
.1651	.3389	1.29163	.77422
.2714	.4912	1.19656	.83573
.3591	.5923	1.12584	.88823
.4130	.6459	1.08789	.91921
.5939	.7913	0.97374	1.02697
.6479	.8267	.94561	1.05752
.7276	.8733	.90360	1.10668
.7856	.9047	.87544	1.14228
.8480	.9352	.84774	1.17961
1.0000	1.0000	.78562	1.27288

The results of the equilibrium measurements are given in Tables III, IV and V. The first column is x, the mole fraction of alcohol in the liquid;

TABLE III

35° ISOTHERM

x	y	$P_{\text{mm.}}$	Py
0	0	295.11	0
0.0384	0.0586	303.91	17.81
.0400	.0597	303.69	18.13
.0414	.0615	304.17	18.69
.0440	.0637	304.87	19.42
.0685	.0839	306.05	25.68
.1517	.1217	306.25	37.27
.1577	.1248	305.12	38.08
.1735	.1302	305.39	39.76
.2254	.1446	303.05	43.82
.3217	.1673	296.93	49.68
.3815	.1819	291.95	53.10
.5154	.2188	274.46	60.05
.5173	.2203	274.04	60.37
.5616	.2354	267.65	63.00
.6078	.2588	255.28	66.07
.6155	.2630	253.39	66.64
.6773	.2991	236.50	70.74
.6986	.3130	229.24	71.75
.7127	.3253	225.06	73.21
.7639	.3793	205.68	78.01
.8270	.4696	177.60	83.40
.8891	.6115	148.26	90.66
.9406	.7657	125.82	96.34
.9458	.7846	123.54	96.93
.9703	.8790	113.61	99.86
.9759	.9009	111.31	100.28
.9938	.9746	104.87	102.21
1	1	102.78	102.78

TABLE IV

45 ISOTHERM

x	y	$P_{\text{mm.}}$	Py
0	0	433.54	0
0.0134	0.0273	439.89	12.01
.0242	.0421	443.07	18.64
.0323	.0546	445.38	24.32
.0443	.0681	448.49	30.52
.0837	.1026	453.76	46.56
.0875	.1054	454.02	47.85
.0900	.1067	454.54	48.45
.1148	.1217	455.79	55.47
.1794	.1484	455.56	67.61
.2852	.1809	448.17	81.07
.3717	.2046	438.89	89.80
.4595	.2297	425.28	97.69
.4860	.2397	420.63	100.83
.5561	.2660	403.91	107.44
.5985	.2857	391.51	111.85
.6702	.3286	365.07	119.96
.6884	.3443	355.66	122.45
.7431	.3940	329.62	129.87
.7989	.4605	299.63	137.98
.8003	.4634	298.08	138.13
.8740	.6026	249.92	150.60
.9288	.7533	214.44	161.54
.9524	.8283	199.62	165.34
.9811	.9284	182.63	169.55
.9843	.9400	180.96	170.10
1	1	172.76	172.76

Table V

55° Isotherm

x	y	$P_{mm.}$	Py
0	0	617.84	0
0.0348	0.0592	626.79	37.71
.0570	.0850	644.24	54.79
.0963	.1202	650.38	78.18
.1610	.1583	653.11	103.39
.2236	.1819	650.96	118.41
.2731	.1990	646.79	128.71
.3149	.2143	641.49	137.47
.3789	.2361	632.14	149.25
.4270	.2473	623.67	154.23
.5206	.2839	599.03	170.06
.6035	.3240	569.02	184.36
.6096	.3280	566.74	185.89
.6233	.3359	560.25	188.19
.6555	.3581	545.72	195.42
.6588	.3593	543.53	195.29
.7194	.4058	508.78	206.46
.7799	.4729	469.41	221.98
.8131	.5205	441.04	229.56
.8521	.5965	407.90	243.31
.8971	.6877	367.01	252.40
.9198	.7467	346.89	259.02
.9288	.7698	339.89	261.65
.9669	.8838	306.38	270.78
1	1	279.86	279.86

the second column is y, the mole fraction in the vapor; and the third column is P, the equilibrium pressure. The partial pressure of ethanol is defined as Py and that of chloroform as $P(1-y)$. Py is given in the fourth column. The primary data are represented in Fig. 1. The ordinates are P and the abscissas are x for the plain circles and y for the flagged circles. This figure shows at a glance that with decreasing temperature the constant boiling mixture becomes richer in chloroform, the maximum difference between the vapor and liquid compositions increases, and an inflection appears in the P-x curve. Figure 2 shows the partial and total pressure curves at 45°, which are typical, and Fig. 3 shows the experimental points for $\log Py/P_1x$ and for $\log P(1-y)/P_2(1-x)$ which would be the logarithms of the activity coefficients of the two components and proportional to the excess chemical potentials if the vapors were very dilute perfect gases.

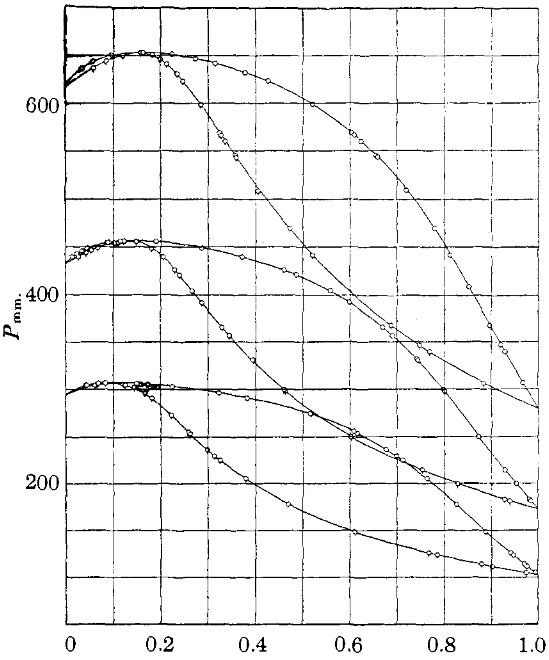

Fig. 1.—Pressure-composition equilibrium curves. Upper 55°, middle 45°, lower 35°; plain circles mole fraction of liquid; flagged circles mole fraction of vapor.

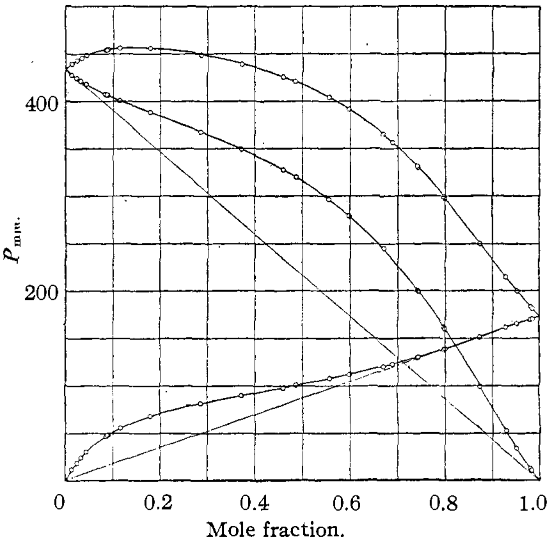

Fig. 2.—Total and partial pressures at 45°.

It is well to note that this system does not obey Henry's law so rigidly that the curve for $\log Py/P_1x$ has a horizontal asymptote at $x = 0$ and that for $\log P(1-y)/P_2(1-x)$ a horizontal asymptote at $x = 1$. That such horizontal asymptotes are rare exceptions in non-ideal mixtures is shown best by freezing point measurements, which may be carried out precisely to very low concentrations.

Deviations from the Gas Laws

If the vapors were perfect gases and the volume of the liquid were negligible relative to that of the vapor, the Duhem–Margules equation would give a relation between P, y and x by which one of these quantities could be determined from the other two and would thus give a check of the experimental accuracy. If the measurements were absolutely accurate, the corresponding exact equations would permit the determination of the deviations of the vapor from the perfect gas laws. Actually we must check the deviations from the gas laws and the experimental accuracy together.

We may assume that, at the low pressures of our experiments, the volume of the vapor, V', is given by

$$V'/(N_1 + N_2) = RT/P + \beta_1 y^2 + \beta_2(1 - y)^2 + 2\beta_{12}y(1 - y)$$
$$= RT/P + \beta_1 y + \beta_2(1 - y) + \delta y(1 - y) \quad (1)$$

if δ is defined as

$$\delta = 2\beta_{12} - \beta_1 - \beta_2 \quad (2)$$

in which N_1 and N_2 are the numbers of moles of the two components and the β's and δ are functions of the temperature characteristic of the gases. We may assume that the volume of the liquid, V, is given by the expression

$$V/(N_1 + N_2) = V_1 x + V_2(1 - x) \quad (3)$$

in which V_1 and V_2 are the molal volumes of the components and may be regarded for our purposes as independent of the pressure. Only if a more exact equation for the vapor volume is used is it necessary to consider the change of partial volumes in the liquid with pressure and composition. The equations which follow become more intricate though essentially no more difficult.

Then the chemical potentials of the components in a solution at the arbitrary pressure P_0 may be written

$$\mu_1 = F_{10} + RT \ln Py + \beta_1 P + \delta P(1 - y)^2 + V_1(P_0 - P) \quad (4)$$

$$\mu_2 = F_{20} + RT \ln P(1 - y) + \beta_2 P + \delta P y^2 + V_2(P_0 - P) \quad (5)$$

in which F_{10} and F_{20} are functions of the temperature only. We may write the "Gibbs–Duhem Equation" at constant temperature and pressure

$$x d\mu_1 + (1 - x)d\mu_2 = 0$$

Carrying out the differentiation of equations 4 and 5, and collecting terms yield

$$y - x = (1 + D)y(1 - y)\mathrm{d} \ln P/\mathrm{d}y \quad (6)$$

$$D = \frac{(P/RT)\{x(\beta_1 - V_1) + (1 - x)(\beta_2 - V_2) + \delta[x(1 - y)^2 + (1 - x)y^2 + 2y(1 - y)]\}}{1 - (P/RT)2\delta y(1 - y)} \quad (7)$$

If the vapor is a perfect gas and the volume of the liquid is negligible relative to that of the vapor, D is zero and equation 6 is the same as that derived by Lewis and Murphree,[6] as the Duhem–Margules equation in terms of the independently measured quantities instead of the calculated partial pressures. Therefore the variables may be separated, except in the small correcting term, so that P may be determined from x and y by integration, or x may be determined from P and y by differentiation. The calculation of the complete expression by successive approximations is not difficult. Unfortunately y cannot be calculated from P and x without some further assumption.

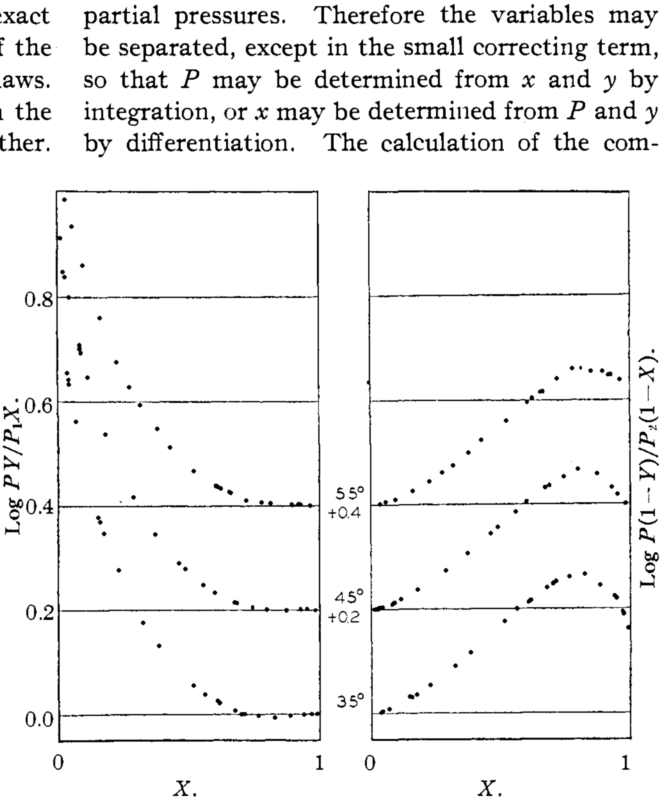

Fig. 3.—Logarithmic deviations from Raoult's law.

To determine P by integration $(x-y)/y(1-y)$ is plotted against y as in Fig. 4. These curves are irregular even for ideal solutions, and become indeterminate at either end. It is usually helpful to plot the logarithm of the "relative volatility," $\log \alpha = \log y(1-x)/x(1-y)$, against x. This curve is also indeterminate at both ends, but it is a horizontal line for ideal solutions and a straight line for any solution in which the excess chemical potential of one component is proportional to the square of the mole fraction of the other component, and it shows but little curvature for most solutions. The points of Fig. 4 are so closely spaced and so precise that there is no difficulty in drawing the curves without this aid. The comparison of the integrated values with the directly measured pressures at 45° is shown in Fig. 5, in which $\Delta \log P = \log P - y \log P_1 - (1-y) \log P_2$ is

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[6] W. K. Lewis and E. V. Murphree, THIS JOURNAL, **46**, 1 (1924).

plotted against y. This deviation curve is used to give a large enough scale to show the discrepancies. The broken line is the integrated curve with the integration constant chosen to give equal deviations at the two ends. The central set of circles represent the directly measured pressures. The corresponding curves at 35 and at 55° are omitted to leave the drawing clearer. The ratio of the directly measured log P_2/P_1 to that determined by integration is 1.026 at 35 and at 45° and 1.031 at 55°.

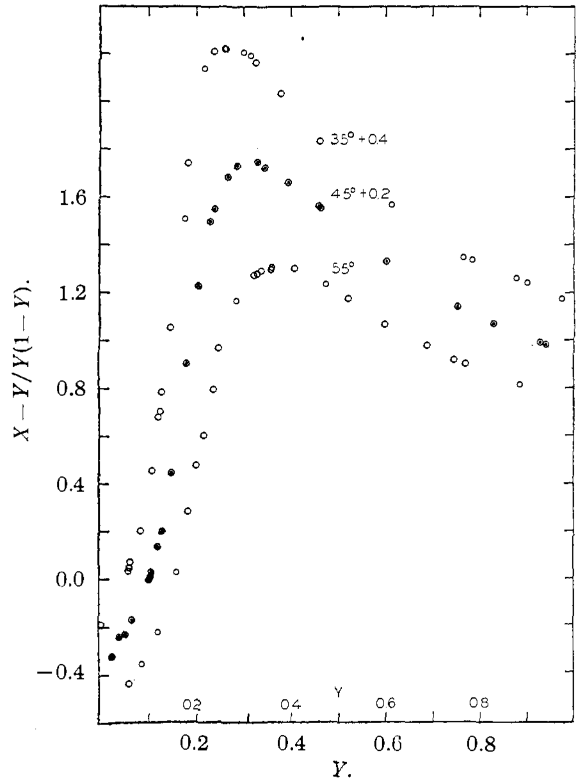

Fig. 4.—Basis of integration.

These ratios correspond to values of D too small for the precise determination of the three parameters upon which they depend. We have, therefore, made two simplifying assumptions so that only one parameter need be determined from the measurements. The first is the assumption usually made in the treatment of gaseous mixtures at moderate pressures, that δ is zero. This makes $D = (P/RT)\,[x(\beta_1 - V_1) + (1-x)\,(\beta_2 - V_2)]$. The second is the assumption that the ratio β_1/β_2 is that calculated by the theory of corresponding states.[7] According to this theory, the limit at zero pressure of $\beta P_c/T_c$ should be the same function of T_r for all gases, if P_c and T_c are the critical pressure and temperature and T_r is the reduced temperature T/T_c. The only measurements at so small values of T_r are those on water vapor. In terms of critical and reduced quantities, the equation of Smith, Keyes and Gerry[8] becomes $\beta P_c/T_c = 11.5 - (24.78/T_r) \times 10^{0.1930/T_r^2}$ when β is in cc./mole, P_c in atmospheres and T_c in centigrade degrees. This equation is determined from measurements with T_r between 0.5 and 1.1. The values of P_c, T_c and the β's and V's at the three temperatures are given in Table VI.

TABLE VI

DEVIATIONS ACCORDING TO CORRESPONDING STATES

	T_c	P_c	$-\beta_j$ (cc./mole)			V_j		
			35°	45°	55°	35°	45°	55°
Ethanol	516.3	63.1	1090	960	865	61.4	62.2	62.8
Chloroform	533.2	54.9	1470	1290	1150	81.7	82.7	83.8
$-\beta_{12}$			1930	1450	1170			
$-\delta$			1300	650	325			

The full curves in Fig. 5 show Δ log P calculated by these assumptions with the ratio of the β's to the corresponding states values chosen to give the proper vapor pressure ratio for the pure components. The corresponding states β's are given in Table VI. To give the full curves in Fig. 5 they must be multiplied by 2.2 at 35°, 1.65 at 45° and 1.5 at 55°. At 35° some of the directly measured circles lie slightly below the integrated curve; at 45° some of the circles are slightly above the curve, and at 55° it would be difficult to draw a smooth curve which fits the circles better than that determined quite independently of them by integration. So there is no trend with the temperature and all deviations are too small for an attempt to correct them by choosing a second parameter to fit the data. We may, however, choose the single parameter with other assumptions. We have also tried the assumption that β_1 and β_2 have the corresponding states values and determined the values of β_{12} necessary to fit our measurements. These values and the corresponding values of δ are given in the last two rows of Table VI. For two non-polar substances β_{12} should be approximately the geometric mean of β_1 and β_2, yielding small positive values for δ. For substances such as chloroform and alcohol it is not impossible that two unlike molecules should attract each other more strongly than two like molecules of either species. The very rapid

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(7) J. Q. Cope, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931); R. H. Newton, *ibid.*, **27**, 302 (1935); R. H. Newton and B. F. Dodge, *ibid.*, **27**, 577 (1935).

(8) F. G. Keyes, L. B. Smith and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **70**, 319 (1936).

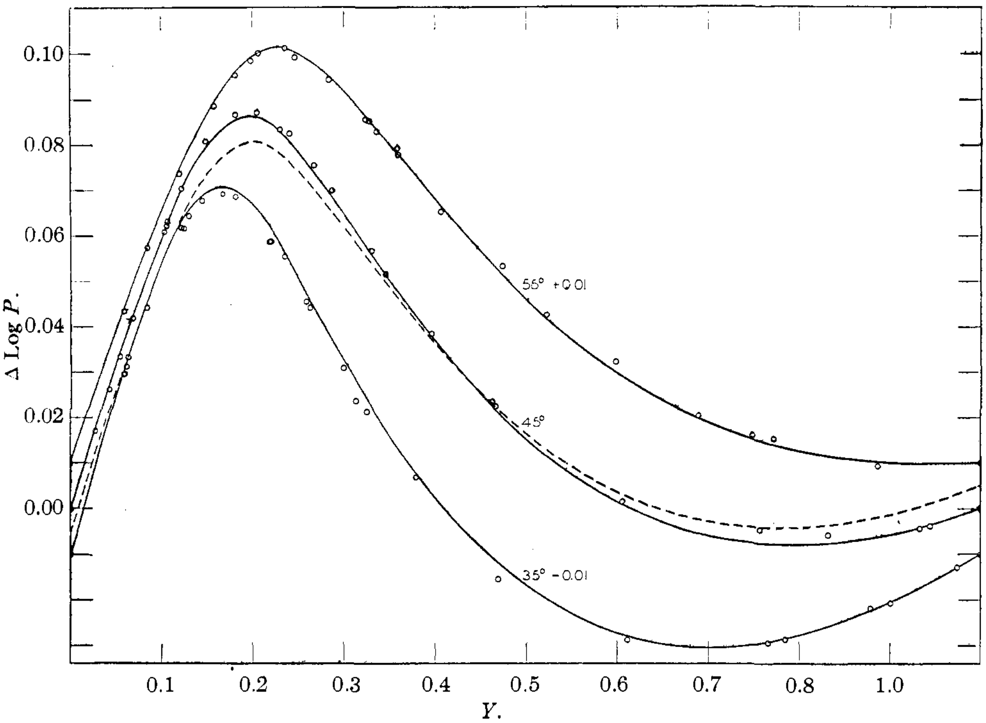

Fig. 5.—Comparison of integration with direct measurements.

temperature variation required by this assumption leads us to believe, however, that it is more probable that δ is very small than that the β's are exactly the corresponding states values.

We have also determined $(x - y)/y(1 - y)$, and therefore x, from d ln $P/\mathrm{d}y$. A smooth curve was drawn through each set of circles of Fig. 5. These curves were read at each 0.01 in y and smoothed through third differences. Then the slope was obtained at each 0.02 in y by the five point method of Rutledge.[9] The resulting curves need smoothing, and therefore have little or no advantage over the integrated curves in showing the magnitude of D at various values of y. The values of β_{12} and δ in Table VI were determined by this method rather than by integration.

The curves for chloroform–ethanol mixtures are more complicated than most, and it may well be that equally precise work on other mixtures will lead to more definite information about the behavior of vapors. For this mixture we have used the assumption that δ is zero in the calculation of the quantities listed in the next tables.

Chemical Potentials, Free Energy, Entropy and Heat Content

The derived functions of thermodynamic interest were calculated from smoothed values of P and y at round values of x, which are given in Table VII. The simplest expression of these functions is to take as standard state the unmixed liquid components at the same temperature and pressure as the mixture. The difference in any of these functions in the state under discussion and in the standard state will be designated by the symbol for that function with a superscript $^{\mathrm{M}}$ (mixing) and the difference between that function and one for an ideal solution of the same composition will be designated with a superscript $^{\mathrm{E}}$

TABLE VII

VAPOR COMPOSITIONS AND PRESSURES AT ROUNDED LIQUID COMPOSITIONS

	y			P		
x	35°	45°	55°	35°	45°	55°
0.00	0.0000	0.0000	0.0000	295.11	433.54	617.84
.01	.0196	.0206	.0200	298.29	438.59	624.02
.02	.0356	.0374	.0366	300.74	442.16	629.94
.05	.0696	.0746	.0774	304.89	449.38	642.22
.10	.1024	.1132	.1226	306.84	455.06	650.84
.20	.1382	.1552	.1736	304.22	454.53	652.23
.30	.1622	.1850	.2086	298.53	446.75	643.65
.40	.1864	.2126	.2402	290.20	435.19	628.77
.50	.2142	.2440	.2748	276.98	417.71	605.23
.60	.2554	.2862	.3226	257.17	391.04	570.62
.70	.3156	.3530	.3892	228.88	351.18	521.14
.80	.4246	.4640	.5012	190.19	298.18	452.00
.90	.6412	.6688	.6946	143.23	232.58	364.32
.95	.8000	.8202	.8306	121.58	200.81	320.64
.98	.9168	.9242	.9274	109.83	183.38	295.85
.99	.9586	.9610	.9628	106.20	177.95	287.85
1.00	1.0000	1.0000	1.0000	102.78	172.76	279.86

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(9) G. Rutledge, *Phys. Rev.*, **40**, 262 (1932).

(excess). Thus for the chemical potential $\mu_1^{\mathrm{M}} = RT \ln a_1$ and $\mu_1^{\mathrm{E}} = RT \ln \gamma_1$, in which a_1 and γ_1 are the activity and the activity coefficient of the first component. We know of no other simple expression for F^{M}, F^{E}, etc.

From equations 4 and 5

$$\mu_1^{\mathrm{M}} = F_{10} + RT \ln Py + \beta_1 P + \delta P(1 - y)^2 + V_1(P_0 - P) - [F_{10} + RT \ln P_1 + \beta_1 P_1 + V_1(P_0 - P_1)] = RT \ln Py/P_1 + (\beta_1 - V_1)(P - P_1) + \delta P(1 - y)^2 \quad (8)$$

$$\mu_2^{\mathrm{M}} = RT \ln P(1 - y)/P_2 + (\beta_2 - V_2)(P - P_2) + \delta Py \quad (9)$$

in which P_1 and P_2 are the vapor pressures of the pure components.

$$\mu_1^{\mathrm{E}} = \mu_1^{\mathrm{M}} - RT \ln x = RT \ln Py/P_1x + (\beta_1 - V_1)(P - P_1) + \delta P(1 - y)^2 \quad (10)$$

$$\mu_2^{\mathrm{E}} = RT \ln P(1 - y)/P_1(1 - x) + (\beta_2 - V_2)(P - P_2) + \delta Py^2 \quad (11)$$

$$F_x^{\mathrm{E}} = F^{\mathrm{E}}/(N_1 + N_2) = x\mu_1^{\mathrm{E}} + (1 - x)\mu_2^{\mathrm{E}} \quad (12)$$

$$S_x^{\mathrm{E}} = -(\partial F_x^{\mathrm{E}}/\partial T)_{p,N} \quad (13)$$

$$H_x^{\mathrm{M}} = H_x^{\mathrm{E}} = F_x^{\mathrm{E}} + TS_x^{\mathrm{E}} \quad (14)$$

The subscript x is used to indicate the value per one total mole as shown in equation 12. The values of the entropy, listed as $-TS_x^{\mathrm{E}}$, and the heat content were calculated only at 45°. The equation actually used in place of 13 was

$$S_{x(45)}^{\mathrm{E}} = [F_{x(35)}^{\mathrm{E}} - F_{x(55)}^{\mathrm{E}}]/20 \quad (15)$$

Table VIII contains the values of the excess chemical potentials in joules per mole, and Table IX contains the corresponding free energy at the three temperatures, and the temperature–entropy product and heat content at 45°, calculated on the assumptions that $\delta = 0$ and that the ratio β_1/β_2 is given by the theory of corresponding states. The correction for the β's changes no point in Fig. 3 by a tenth of a division, so that this figure represents also the excess chemical potentials except for the difference in scale. The excess free energy, heat content and temperature entropy product are shown in Fig. 6.

TABLE VIII

EXCESS CHEMICAL POTENTIALS (JOULES PER MOLE)

Mole fraction ethanol	Excess chemical potentials Ethanol 35°	45°	55°	Chloroform 35°	45°	55°
0.01	4370	4298	4008	2	1	−2
.02	4144	4051	3791	6	3	4
.05	3556	3515	3390	28	22	21
.1	2788	2819	2790	90	85	67
.2	1762	1821	1898	266	264	221
.3	1090	1171	1218	488	478	441
.4	641	713	758	736	727	689
.5	312	383	417	997	996	958
.6	113	155	203	1245	1263	1225
.7	−28	28	57	1472	1487	1488
.8	−70	−22	6	1599	1637	1663
.9	−28	− 9	1	1442	1548	1639
.95	−14	5	− 1	1302	1380	1571
.98	− 2	1	− 1	1144	1281	1550
.99	1	− 1	0	1046	1247	1543

Discussion

The peculiarities of this system are brought out progressively in Figs. 1, 2, 3 and 6. Figure 1 shows an inflection near the alcohol end of the $P - x$ curve which Fig. 2 shows to be repeated in the curve for the partial pressure of chloroform and to be accompanied by a crossing of the Raoult's law line by the ethanol partial pressure curve. The inflection in Fig. 2 becomes a maximum in the right-hand side of Fig. 3, which becomes more marked as the temperature decreases, and the crossing of the Raoult's law line is shown clearly in the left-hand diagram at 35°. These peculiarities lead to only a moderate asymmetry in the curve for F_x^{E} in Fig. 6, in which a slight inflection near the alcohol end corresponds to the maximum in Fig. 3. For the heat content and for the entropy this inflection has shifted toward the chloroform end and has become so marked that each curve has a minimum and a maximum whose heights are of the same order of magnitude. The circles in Fig. 6 are Hirobe's directly measured values of H_x^{E} at 25°. The difference from our values might be accounted for by the difference in temperature.

TABLE IX

EXCESS FREE ENERGY, HEAT CONTENT AND TEMPERATURE ENTROPY PRODUCT (JOULES PER MOLE)

Mole fraction ethanol	F_x^{E} 35°	F_x^{E} 45°	F_x^{E} 55°	TS_x^{E} 45°	H_x^{E} 45°
0.01	45	44	38	106	150
.02	88	83	79	136	219
.05	203	196	188	228	424
.1	358	357	337	340	697
.2	564	575	554	162	737
.3	669	686	672	− 50	636
.4	699	722	716	− 256	466
.5	657	691	686	− 486	205
.6	568	600	611	− 678	− 78
.7	425	468	485	− 953	−485
.8	265	311	335	−1115	−804
.9	120	147	164	− 701	−554
.95	52	74	77	− 399	−325
.98	21	27	30	− 141	−114
.99	11	12	15	− 63	− 51

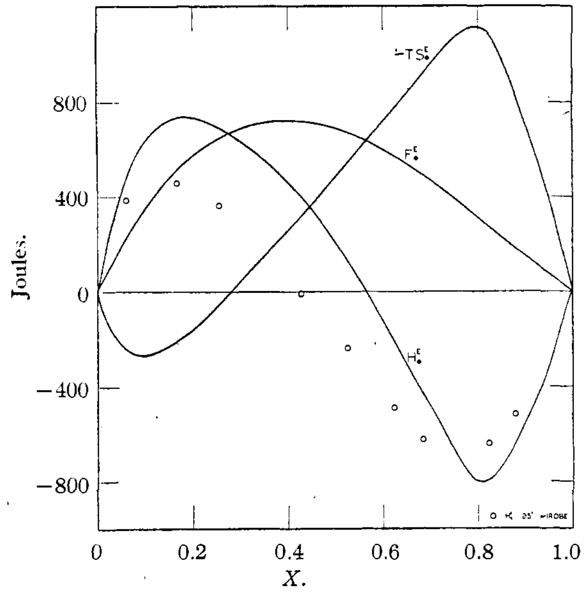

Fig. 6.—Excess free energy, heat content and temperature-entropy product at 45°.

This system is obviously very far from regular, for a regular solution is defined as one in which S^E_x is zero. Since there is an increase of excess entropy when a small amount of alcohol is added to a large amount of chloroform and a decrease when the quantities are reversed, the explanation must be complicated. It is very difficult to discuss it without using terms which imply chemical reactions, and we shall find it convenient to assume temporarily that the solutions are quasi-ideal, that is, that the activity of each species (rather than component) is proportional to its mole fraction. We believe, however, that there is no evidence for any chemical reaction and that there is the strongest evidence against these solutions being quasi-ideal.

The entropy of vaporization of chloroform is normal, while that of alcohol is large, indicating association which may be chemical or physical. The positive excess entropy of mixing should correspond to the destruction of this association of the alcohol, and the negative excess entropy should mean an association of chloroform and alcohol. The fact that the negative excess entropy prevails in the alcohol rich solutions should indicate that the number of alcohol molecules in a cluster is greater if the cluster also contains a chloroform molecule, but that each molecule is held less tightly in the latter clusters.

To show that such an explanation is adequate we assume quasi-ideal solutions containing chloroform, B, alcohol, A and A_2, and the compound A_3B. If the activity of the alcohol be taken as the independent variable, the computations are simple.[10] Assuming $x_A' = 0.2a_1$, $x_B' = a_2$, $x_{A_2}' = 0.8a_1^2$, $x_{A_3B}' = 0.4\,a_1^3a_2$ (x' being the number of moles of a species divided by the total number of moles of all species), and that the heat of formation of A_2 is $12RT$ and that of A_3B is $24RT$, the curves are given in Fig. 7 which reproduce the peculiarities of those in Figs. 3 and 6. The agreement could be made better by varying the constants and particularly by increasing the number of assumed species, but such agreement can never show that the solutions are quasi-ideal or that the assumed species correspond to those actually existing in the mixture. However, we are probably safe in concluding that the mixed clusters contain more than two alcohol molecules for each chloroform molecule.

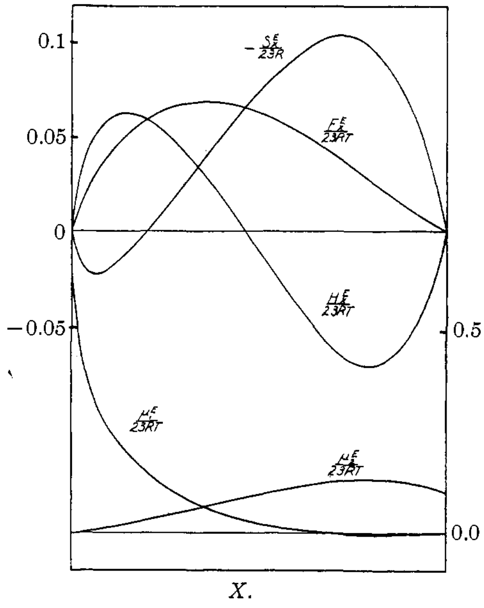

Fig. 7.—Excess functions calculated for quasi-ideal solutions.

A number of explanations of the behavior of chloroform with ethers, ketones and esters were offered at a recent discussion of the Faraday Society.[11] As stated by one of us there, we believe that these substances are "normal" when pure because the molecules are so large that two cannot approach closely when their dipoles are co-linear and parallel. However, it is probable that the positive end of the chloroform dipole

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[10] G. Scatchard, THIS JOURNAL, **43**, 2406 (1921); J. H. Hildebrand and H. E. Bent, *ibid.*, **49**, 3025 (1927).

[11] *Trans. Faraday Soc.*, **33**, 156, 165, 200–214 (1937).

and the negative end of the dipole in acetone, for example, are fairly near the surface, so that a chloroform and an acetone molecule may approach much more closely with parallel co-linear dipoles. This would lead to a cluster containing one molecule of each kind. Any effect of polarization or of resonance would be added to this dipole–dipole interaction, probably as a relatively small increment.

In hydroxyl compounds the minuteness of hydrogen makes it necessary to consider the individual dipoles at the O–H and O–R bonds and not merely their vector sum. The "association" of such compounds is probably largely due to the fact that the positive end of the O–H dipole can approach other molecules very closely—so closely that instead of two parallel colinear dipoles the stable structure may be three molecules with tetrahedral angles between their dipoles. The electrostatic effect is very much larger than that calculated for spherical molecules with short dipoles at their centers, and it is probably the chief effect even though polarization and quantum-mechanical resonance are more important than in the case considered above.[12] The essential characteristic of such clusters is that there is no limit to the number of molecules in a cluster.

In chloroform–alcohol mixtures we should expect a colinear parallel dipole effect of about the same magnitude as in chloroform–acetone mixtures, and we should expect further complications due to the exposed O–H dipoles, first, as an association of the alcohol, and, second, as the interaction of these dipoles with the chloroform. If the four atoms C–Cl H–O are in a straight line, the parallel colinear dipoles may approach so closely that their attraction is not nearly compensated by the repulsion of the other C–Cl dipoles. The stability of such an arrangement will probably be increased by deformation of the easily polarizable chlorines. From one to three molecules of alcohol might cluster about one chloroform molecule in this way in addition to the one held as in chloroform–acetone mixtures.

If this is the proper explanation, the same effect should be shown by alcohol–carbon tetrachloride mixtures. The measurements in the literature give little information,[13] so very simple measurements were made of the temperature change on mixing ethanol and carbon tetrachloride initially at 25° by pouring one into the other in a Dewar flask immersed in a 25° thermostat.

For comparison the same experiment was carried out with ethanol and chloroform (containing about 1% ethanol). The approximate proportions are given in volumes of ethanol to volumes of tetrachloride or chloroform.

System	Vol. ratio	Temp. change, °C.		H^M_x (approximate)
EtOH–CCl_4	1:3	−2.32	−2.27	+400
EtOH–CCl_4	3:1	+0.32	+0.27	− 50
EtOH–$CHCl_3$	1:3	−1.88	−1.90	+300 (290)
EtOH–$CHCl_3$	3:1	+4.20	+4.15	−630 (650)

The values of H^M_x (approximate) are calculated on the assumptions of additive heat capacities and volumes and a value for the heat capacity of the calorimeter chosen to make equal the percentage deviations of the two chloroform determinations from those of Hirobe, which are given in parentheses, and neglecting any cooling by evaporation.[14] The effect for carbon tetrachloride is large enough to change the sign of the heat of mixing and to give a difference between the heats at these two ratios about half as great as that for chloroform. This indicates that in the case of chloroform–ethanol the interaction at the Cl–C sides of chloroform, although smaller, is of the same order of magnitude as that at the H–C side.

Summary

The vapor and liquid compositions and the pressures at equilibrium have been determined at 35, 45, and 55° for the system chloroform—ethanol in the apparatus described in the preceding paper.

Application of the "Gibbs–Duhem" equation shows the measurements to be very consistent and indicates deviations from the perfect gas laws somewhat larger than those calculated from the theory of corresponding states.

The excess chemical potentials, free energy, heat content and entropy of mixing are calculated from these results. Each of the last two passes through a maximum and minimum.

An explanation of the behavior of this system is suggested which includes very large attraction between two unlike molecules when the net dipoles are parallel and colinear with the hydroxyl near the chloroform hydrogen, and large attrac-

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[12] If so, the terms "hydrogen bond" and "hydroxyl bond" are particularly misleading.

[13] Smyth and Engel, THIS JOURNAL, **51**, 2660 (1929), shows the partial pressure of butyl alcohol crossing the Raoult's law line for mixtures with carbon tetrachloride, but it does not approach this line at high alcohol contents.

[14] These experiments were carried out by L. F. Epstein as part of a N. Y. A. project.

tions when the hydroxyl hydrogen is between its oxygen and a chlorine on the line of the carbon–chlorine bond.

Crude experiments show that the excess heat content of mixing of carbon tetrachloride–ethanol systems also passes through a maximum and a minimum.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 8, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

On the Adsorption of Gases by Graphite

BY ARTHUR B. LAMB AND EDWIN N. OHL

Careful measurements by Magnus and Kratz[1] have shown that both natural and artificial graphite adsorb carbon dioxide in modest amounts at 0°. This observation runs counter to current views as to the adsorptive properties of graphite, and indeed is somewhat surprising in view of the nearly complete saturation of the carbon atoms within the individual basal planes of the graphite crystal as evidenced on the one hand by their extreme involatility and on the other by the very weak cohesion between adjacent basal planes. Moreover, there is no evidence that the samples of graphite used by Magnus and Kratz were unusually finely ground or had any very considerable exterior surface.

A possible explanation of this unexpected behavior would be that the adsorption of the carbon dioxide takes place not only on the exterior surface of the graphite but also *within* the channels separating the basal layers of the carbon atoms in the crystal lattice. In this way a relatively huge inner surface would become available for adsorption, supplementing the relatively small outer surface of the powdered graphite.

Is such an invasion of gaseous molecules into the crystal lattice of graphite geometrically possible? On the basis of the recognized crystal structure of graphite the distance between the center of an atom in one basal plane and that of the nearest atom in the next adjacent plane is 3.40 Å. The distance between two carbon atoms linked together within the same molecule of aliphatic carbon compounds is about 1.5 Å. The difference, 1.9 Å., would represent the width of a channel in which repulsive forces would be relatively small and into which gaseous molecules, if they were small enough, might conceivably squeeze.

The smallest limiting diameter of the linear carbon dioxide molecule is certainly that of its oxygen atoms measured perpendicularly to the axis of the molecule. This is presumably not greatly different from the corresponding diameter of an oxygen atom in an oxygen molecule, and this in turn may be guessed as two thirds of the mean diameter of the molecule. This latter value, computed from the viscosity, is 2.9 and from the molecular refraction, 2.4 Å.; which would give 1.9 or 1.6 Å., respectively, as the smallest diameter of the oxygen molecule and hence also of the carbon dioxide molecule.[2] On this basis, these molecules might, therefore, conceivably make their way into the basal channels. With hydrogen the situation is more favorable; its mean diameter by the same methods of measurement is 2.3 and 2.0 Å., which would correspond to a smallest diameter of about 1.5 or 1.3 Å. If carbon dioxide could in any way invade the basal channels, hydrogen should do so much more freely.

Against the likelihood of any invasion of the basal planes, even if the molecules were small enough, is the consideration that the very forces of repulsion around the carbon atoms which prevent the closer approach of the basal planes to each other would prevent the ingress of other atoms. In rebuttal to this is the fact mentioned at the outset that the cohesive force between the basal planes is very weak, from which it follows that the repulsive force which balances it must be correspondingly weak. A further unfavorable consideration is the fact that the distance between the basal planes of graphite (3.40 Å.) is also the distance between contiguous carbon atoms of separate molecules of crystalline organic substances.[3] There is no evidence, so far as we are aware, that such substances display any adsorptive capacity for gases with small molecules, but it may be that this has never been adequately tested.

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[1] A. Magnus and H. Kratz, *Z. anorg. Chem.*, **184**, 241 (1929).

[2] Landolt–Börnstein, "Tabellen," 3rd Supplement, 1935, p. 105.

[3] W. L. Bragg, "Atomic Structure of Minerals," Cornell Univ. Press., Ithaca, N. Y., 1937, p. 54.