From 170 to 200°, as the critical region was approached, the logarithm of the vapor pressure no longer could be represented by a linear function of the reciprocal of the absolute temperature. The equation, derived by aid of a central difference table, was found to be

$$(4)\quad 170\text{–}200°: \log_{10} p\ (\text{mm.}) = -2089.553682 + 233{,}084.9289/T + 7034.8267 \times 10^{-3}\ T - 1049.16605 \times 10^{-5}\ T^2 + 5868.8889 \times 10^{-3}\ T^3$$

Equations (1) and (2) reproduce the data to within ±0.3%, while equations (3) and (4) are reliable to a mean deviation of ±0.1 per cent.

The vapor pressures calculated by means of these equations at a few selected rounded temperatures are given in Table I.

The latent heats of vaporization were calculated for 0 and 30.07° by means of the exact Clapeyron equation; the vapor volume was calculated by means of the van der Waals equation, the constants of which for pentene-1 were derived from critical data. These values are 6225 and 6117 calories per gram mole for 0 and 30.07°.

TABLE I

SOME VAPOR PRESSURES OF PENTENE-1 FROM 0 TO 200°

Temp., °C.	Vapor pressure, mm.	Temp., °C.	Vapor pressure, mm.
0	241.3	100	5.221
5	297.1	120	7.913
10	363.1	150	13.717
20	531.3	170	19.055
30.07[a]	760	180	22.233
40	1069	190	25.850
60	1933	195	27.902
80	3269	200	30.203

[a] Normal boiling point.

Summary

1. The densities of liquid pentene-1 under its vapor pressure were determined from 0 to 50°.
2. The vapor pressures of pentene-1 were determined from 0 to 200°;
3. Calculated heats of vaporization are reported at 0 and 30.07°.

AUSTIN, TEXAS RECEIVED JANUARY 14, 1948

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Densities and Liquid–Vapor Equilibria of the System Ethanol–Isoöctane (2,2,4-Trimethylpentane) between 0 and 50°

BY CARL B. KRETSCHMER, JANINA NOWAKOWSKA AND RICHARD WIEBE

The present investigation is part of a systematic program in progress at this Laboratory to determine certain physical properties of ethanol–hydrocarbon systems. A considerable amount of experimental and theoretical material on solutions of aliphatic alcohols in non-polar solvents has been published and will be referred to in its proper place.

Density Measurements

Commercial absolute ethanol was fractionated in a 5-foot column packed with glass helices and then treated with magnesium ethylate.[2] The final product of d^{25}_4 0.78506 was kept under its own vapor pressure in a sealed container over magnesium ethylate and samples were withdrawn by vacuum distillation. Certified isoöctane (2,2,4-trimethylpentane) was fractionated in the same column. The middle fraction taken was filtered through a column of silica gel to remove the small content of olefins.[3] The final density was found to be d^{25}_4 0.68777.

The 13-ml. pycnometer shown in Fig. 1A was used for measuring the densities of the air-saturated liquids and solutions at 25°. No noticeable loss of liquid through evaporation was experienced during weighing because of the smallness of the capillaries (0.3 mm.). By applying gentle suction at the top, filling was accomplished by means of a device shown in Fig. 1B, and the turned-down tip[4] greatly facilitated the adjustment of volume. The accuracy of measurement was estimated to be 2×10^{-5} g./ml. or better.

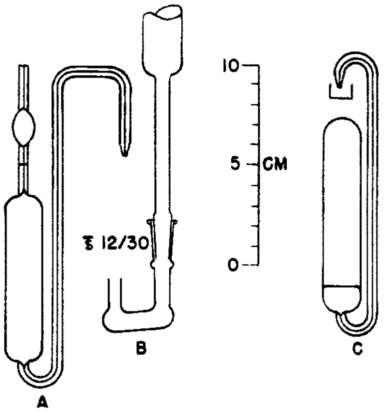

Fig. 1.—A. pycnometer; B, filling device; C. weight dilatometer.

The densities of the two pure liquids at 0 and 50° relative to their values at 25° were measured in a 14-ml. Pyrex weight dilatometer (Fig. 1C). Both apparatus and method were similar to those

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

[2] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[3] B. J. Mair and A. F. Forziati, *J. Research Nat. Bur. Standards*, **32**, 151, 165 (1944).

[4] G. F. Hennion, *Ind. Eng. Chem., Anal. Ed.*, **9**, 479 (1937).

described by Burlew.[5] Temperatures were measured by means of a standard platinum resistance thermometer and were not in error by more than 0.003°. The correction for the exposed portion of the capillary amounted to 5×10^{-6} g./ml.

The values obtained for ethanol are given in the last column of Table I. For isoöctane the values obtained were 0.708120, 0.687773 and 0.666855 g./ml. at 0, 25, and 50°, respectively. These values are the means of two or three determinations which differed by amounts indicating a precision of 4×10^{-6} g./ml. in the change of density over each 25° interval. In addition, the densities at all three temperatures are affected equally by the uncertainty of 2×10^{-5} g./ml. in the pycnometer measurements at 25° which were used to calculate the weight of liquid in the dilatometer. The densities given refer to liquids containing enough dissolved air to saturate them at 25°.

In Table I values recorded in the literature for the density of ethanol between 0° and 50° are compared with those obtained in this work. Osborne's[6] values from 10° to 40° are generally believed to be very reliable. At room temperature, our value and that of Riiber[7] are in good agreement with them. Tyrer's[8] densities are higher than the others, probably because of water in his sample. His value of thermal expansion from 0° to 25° is lower than ours, while the reverse is true for the interval 25–50°, the difference in each case being of the order of 10^{-4} ml./g. Our value of the density at 0° is slightly higher than those of Young,[9] Klason and Norlin,[10] and of Merriman,[11] while our value at 50° is appreciably lower than that of Young.

TABLE I

RECORDED VALUES FOR DENSITY OF ETHANOL, 0 TO 50°, G./ML.

Temp. °C.	Osborne[a]	Young[b]	Klason[c]	Tyrer[d]	Merriman[e] 0° Riiber[f] 20°	Authors' values obtained
0		0.80627	0.80628	0.80645	0.80628	0.806306
10	0.79784		.79792	.79803		
20	.78934	.7894	.78938		.78933	
25	.78506			.78532		0.785063
30	.78075		.78080			
40	.77203	.7722		.77224		
50		.7633		.76331		0.763137

[a] N. S. Osborne, E. C. McKelvy and H. W. Bearce.[6] [b] S. Young.[9] [c] P. Klason and E. Norlin.[10] [d] D. Tyrer.[8] [e] R. W. Merriman.[11] [f] C. N. Riiber.[7]

Brooks, Howard and Crafton[12] have measured the density of isoöctane at 20 and 25°, and our value at 25° is in excellent agreement with theirs.

The following equations fit the data for ethanol and isoöctane, respectively, for the range 0 to 50°

Ethanol

$$d^t_4 = 0.806306 - 8.4456 \times 10^{-4}t - 3.52 \times 10^{-8}t^2 - 6.82 \times 10^{-9}t^3$$

Isoöctane

$$d^t_4 = 0.708120 - 8.0481 \times 10^{-4}t - 3.168 \times 10^{-7}t^2 - 1.87 \times 10^{-9}t^3$$

The cubic terms were chosen to make the equation for ethanol agree with Osborne's figures, and to make the equation for isoöctane agree with Brooks, Howard and Crafton's value at 20°, all to within 1×10^{-5} g./ml.

Solutions were prepared by distilling the individual components into an evacuated bulb, and the amounts determined by weighing. In this way any loss, as well as any correction for the displacement of air, was avoided. Transfer to the pycnometer (Fig. 1A) was effected through displacement by mercury. The results shown in Table II were used in subsequent work for converting densities to compositions.

TABLE II

DENSITIES AT 25°

Ethanol Wt. fract.	Ethanol Mol. fract.[a]	d^{25}_4	$1000\ (V/V_0 - 1)$
0	0	0.68777	0
0.0130	0.0316	.68834	0.786
.0163	.0394	.68857	0.861
.0431	.1005	.69041	1.532
.0499	.1152	.69088	1.686
.1432	.2930	.69823	2.820
.2960	.5104	.71140	3.602
.4680	.6856	.72735	3.806
.6313	.8093	.74358	3.448
.8057	.9114	.76227	2.348
.8962	.9554	.77261	1.407
1	1	.78506	0

[a] Molecular weights: ethanol 46.07; isoöctane 114.22.

Densities of solutions at 0 and 50°, referred to the density of air-saturated solutions at 25°, were measured with a pycnometer similar to the one

TABLE III

DENSITIES OF SOLUTIONS AT 0 AND 50°

Ethanol Wt. fract.	Ethanol Mol. fract.	d^0_4	d^{50}_4	$1000\ (V/V_0 - 1)$ 0°	$1000\ (V/V_0 - 1)$ 50°
0	0	0.70812	0.66686	0	0
0.0544	0.1248	.71207	.66959	1.09	2.81
.1120	.2382	.71676	.67378	1.60	3.92
.2332	.4299	.72705	.68368	2.43	4.96
.3232	.5421	.73508	.69158	2.79	5.25
.4166	.6390	.74371	.70018	3.03	5.25
.5307	.7371	.75464	.71119	3.18	4.95
.5397	.7440	.75554	.71212	3.17	4.86
.6409	.8157	.76573	.72243	3.05	4.28
.6968	.8507	.77160	.72831	2.83	3.87
.8042	.9106	.78330	.74009	2.16	2.80
.9195	.9659	.79658	.75342	1.04	1.26
.9332	.9719	.79823	.75503	0.85	1.08
1	1	.80631	.76314	0	0

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(5) J. S. Burlew, THIS JOURNAL, **62**, 690 (1940).

(6) N. S. Osborne, E. C. McKelvy and H. W. Bearce, *Bull. Bur. Standards*, **9**, 327 (1913).

(7) C. N. Riiber, *Z. Elektrochem.*, **29**, 335 (1923).

(8) D. Tyrer, *J. Chem. Soc.*, 2534 (1914).

(9) S. Young, *ibid.*, 707 (1902); *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

(10) P. Klason and E. Norlin, *Arkiv Kemi Mineral. Geol.*, **2**, No. 24, 1 (1906).

(11) R. W. Merriman, *J. Chem. Soc.*, 628 (1913).

(12) D. B. Brooks, F. L. Howard and H. C. Crafton, *J. Research Nat. Bur. Standards*, **24**, 33 (1940).

shown in Fig. 1A, with an estimated accuracy of 7×10^{-5} g./ml. Results are given in Table III.

Discussion

Data of relative expansion of mixing, $(V/V_0) - 1$, where V is the volume of the solution and V_0 the sum of the volumes of the components, given in Tables II and III, are plotted in Fig. 2. Harms,[13] using the mass law, calculated this volume increase on mixing for several aliphatic alcohols in cyclohexane on the basis of dissociation of complexes containing from two to an infinite number of alcohol molecules. On this basis he obtained excellent agreement between experimental and calculated values for ethanol–cyclohexane solutions, whose volumetric behavior closely resembles that of the system ethanol–isoöctane. We feel, however, that the discussion is based on an oversimplified physical picture, and that the agreement is partly due to the fact that Harms' treatment contains two adjustable constants.

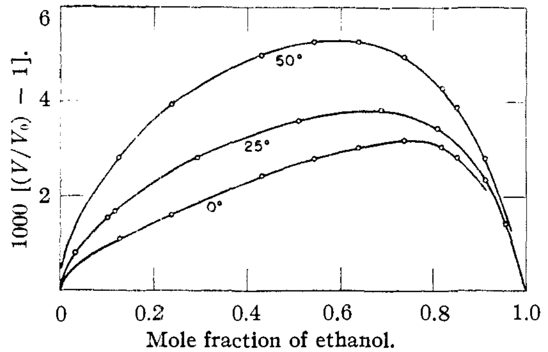

Fig. 2.—Relative expansion of mixing.

Liquid–Vapor Equilibrium Measurements

After a thorough consideration of existing methods, including actual trials, which emphasized the desirability of generating vapor in a separate boiler rather than depending on the boiling process itself to give equilibrium, the equilibrium still of Scatchard and co-workers[14] was selected as a basis.

Purification and density of the ethanol and isooctane used have been described previously. Figure 3 shows the equilibrium still. A water-bath was substituted for the vapor jacket used by Scatchard, which simplified construction and tended to maintain A at a more uniform temperature. Vapor was generated in boiler D and passed into the vapor-lift tube B where liquid was entrained and lifted to the top of chamber A. The mixture of liquid and vapor descended through the annular space packed with 3-mm. glass helices surrounding the thermometer well, and the vapor which separated passed through tube E to a condenser and finally to trap F. A heater located at the bend prevented any condensation during the passage. Bulb J was used to remove any possible traces of water as the ternary azeotrope. When a steady state was reached, the composition of the vapor in A was the same as that of the liquid in F, and the liquid and vapor samples were taken by means of evacuated sampling containers G. The tubes connecting the sampling containers G to the apparatus were full of air for all practical purposes and the error due to liquid holdup from this cause was negligible. No trouble was experienced using Apiezon grease L on stopcocks and joints when suitable precautions were taken.

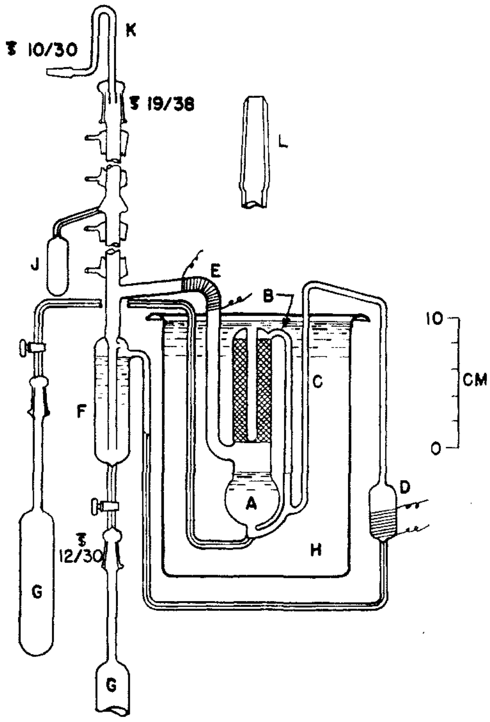

Fig. 3.—Equilibrium still: L, detail of sample bulb.

A platinum resistance thermometer and Mueller bridge, both recently calibrated, were used for temperature measurement. The condenser above trap F was connected to a 20-liter ballast and a manometer through trap K, an inverted U-tube surrounded by solid carbon dioxide. The manometer of 12 mm. i. d. tubing had provision for evacuating the vacuum arm when necessary. It was read with a Gaertner cathetometer (model M901) at a distance of 250 mm. Readings could easily be estimated to 0.02 mm., and no errors of this magnitude were found when the cathetometer was checked at the same working distance against a Gaertner standard meter calibrated by the Bureau of Standards. The vapor pressures are given in International mm. of mercury and have an estimated accuracy of 0.05 mm.

After complete evacuation, dry air was admitted and approximately 52 ml. of solution was introduced into the apparatus. Distillation rates were about 35 ml./hr. at 25° and 100 ml./hr. at

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(13) H. Harms, *Z. physik. Chem.*, **53B**, 280 (1943).

(14) G. Scatchard, *et al.*, THIS JOURNAL, **60**, 1275, 1278 (1938); **61**, 3206 (1939); **62**, 712 (1940); and **68**, 1957, 1960 (1946).

50°. The pressure was regulated manually to keep the resistance thermometer reading exactly at 25.00° or 50.00°. The bath temperature was regulated to keep a constant amount of liquid (about 3 ml.) in boiler D, which required that the bath be several hundredths of a degree above the temperature in A. During initial operation a small amount was distilled into J to eliminate any possible traces of water, as explained previously. The steady state was maintained for considerable time after which temperature and pressure were measured in quick succession, heaters turned off, the apparatus was brought to atmospheric pressure, and samples were taken.

In addition, static measurements were made of the total vapor pressure of the solutions at 0 and 25°, by use of a vapor-pressure cell equipped with a magnetic stirrer and connected directly to the manometer. The solutions were freed of dissolved gases and traces of water by slowly distilling off part of the sample while the stirrer was in operation. This process was continued until McLeod gage readings on the portion of distillate uncondensed at −78° showed no more gases were being evolved. Vapor pressure and density of the remaining solution were then measured.

Results

Static vapor pressures at 0 and 25° and liquid-vapor equilibrium measurements at 25 and 50° are presented in Tables IV and V, respectively. The good agreement between static and dynamic vapor pressure measurements at 25° is indicated in Fig. 4; the actual agreement is within 0.2 mm.

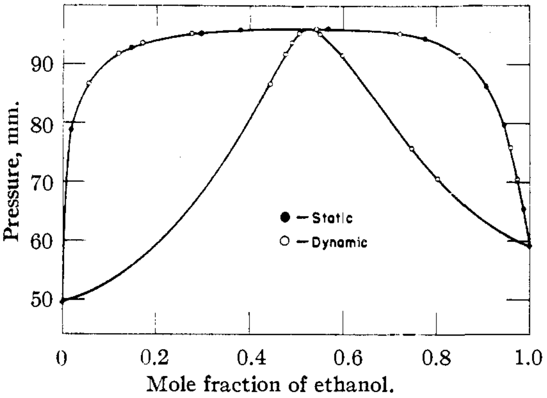

Fig. 4.—Vapor pressure at 25°.

The vapor curve below 0.4 mole fraction ethanol is conjectural. The data for 50° give curves of similar shape The azeotropic mole fraction of ethanol at 25° is 0.5270 and at 50° is 0.5941; the corresponding vapor pressures are 96.1 and 318.8 mm.

Vapor pressures for isoöctane reported here are in good agreement with the ones calculated from the equation published by Willingham and coworkers,[15] as shown in the following comparison at 0, 25 and 50° with their values in parentheses: 13.04 (12.99), 49.31 (49.34) and 146.47 (146.51). Since the value quoted by Willingham, *et al.*, for 0° represents an extrapolation from their lowest experimental point of nearly 25°, the agreement demonstrates the suitability of the Antoine equation used by them.

TABLE IV

STATIC VAPOR PRESSURE MEASUREMENTS

Mole fract. C_2H_5OH	*P*, mm. 0°	*P*, mm. 25°	Mole fract. C_2H_5OH	*P*, mm. 0°	*P*, mm. 25°
0.0000	13.03	49.29	0.5684	22.65	96.05
.0000	13.06	49.33	.7749	22.18	94.41
.0000 Av.	13.04	49.31	.9077	19.94	86.31
.0186	19.95	78.83	.9458	17.99	79.64
.1470	22.30	92.81	.9882	13.81	65.28
.2967	22.61	95.32	1.0000	11.96	59.01
.3795	22.68	95.83	1.0000	11.94	59.04
			1.0000 Av.	11.95	59.02

TABLE V

EQUILIBRIUM-STILL MEASUREMENTS

Liquid. mole fract. C_2H_5OH	Vapor. mole fract. C_2H_5OH	*P*, mm.	10^4 Δ log *P*
		25°	
0.0000	0.0000	49.31[a]	0
.0565	.4441	86.56	− 34
.1182	.4762	91.81	10
.1700	.4910	93.57	4
.2748	.5073	95.22	1
.3773	.5153	95.85	2
.5416	.5285	96.14	6
.7225	.5501	95.25	6
.8511	.5994	91.49	27
.9603	.7471	75.71	− 70
.9757	.8023	70.41	−120
1.0000	1.0000	59.03[a]	− 16
		50°	
0.0000	0.0000	146.47	0
.0113	.2938	207.31	32
.0340	.4238	250.15	16
.0579	.4752	271.87	13
.1240	.5254	296.29	21
.3428	.5701	315.21	21
.5176	.5863	318.26	27
.5943	.5941	318.75	29
.6144	.5969	318.82	29
.7713	.6279	315.10	30
.8799	.6881	301.38	43
.9319	.7526	282.86	30
.9516	.7942	271.27	22
.9829	.9008	242.85	− 23
1.0000	1.0000	220.94	− 50

[a] Static measurements.

A comparison of the vapor pressures of ethanol at 0, 25 and 50° reported here with those of Merriman[11] in parentheses: 11.95 (12.0), 59.02 (59.0) and 220.94 (222.2) shows a good agreement except at 50°. Recorded values for the vapor pressure at 50° range from 219.8 mm.[16] to Merriman's

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

(16) W. Ramsay and S. Young, *Phil. Trans. Roy. Soc. London*, **A177**, 123 (1886).

222.2 mm. and the value given here is in reasonable agreement with the one of Scatchard and Raymond,[17] *viz.*, 221.17 mm.

Discussion

The partial molal free energy equation for binary solutions

$$x_1 \frac{d\bar{F}_1}{dx_1} + x_2 \frac{d\bar{F}_2}{dx_1} = 0$$

has been used extensively in the form of the Duhem–Margules equation

$$x_1 \frac{d \ln P_1}{dx_1} + x_2 \frac{d \ln P_2}{dx_1} = 0$$

or substituting total pressure times the corresponding mole fraction in the vapor phase Py and $P\ (1-y)$ for the partial pressures, the equation becomes[18]

$$d \ln P = \frac{y - x}{1 - y} d \ln y,$$

where deviations from ideal behavior of the vapor phase are neglected. This equation was integrated numerically, using our experimental values of mole fraction of ethanol in the liquid, x, and in the vapor, y. The differences $\Delta \log P$ between observed values of $\log P$ and those resulting from the integration are given in Table V. These deviations are made up of the experimental error plus the correction for vapor imperfections. The latter correction is proportional to the vapor pressure; at the low pressures involved in this work it is comparable in magnitude to the contribution of experimental errors to the integral. Hence, no significant evaluation of the parameters in the equation of state of the vapor can be obtained from the listed values of $\Delta \log P$. The agreement between calculated and observed pressures is reasonably satisfactory, however, since only two values of $\Delta \log P$ exceed 0.005.

TABLE VI

CALCULATED LIQUID–VAPOR EQUILIBRIUM AT 0°

Mole fraction ethanol			
Liquid	Vapor	Liquid	Vapor
0.01	0.2673	0.40	0.4491
.025	.3626	.50	.4527
.05	.4062	.60	.4592
.10	.4219	.70	.4698
.15	.4291	.80	.4952
.20	.4374	.90	.5511
.30	.4447	.95	.6206
		Azeotrope	.451

TABLE VII

SMOOTHED VALUES OF THERMODYNAMIC FUNCTIONS IN CAL./MOLE AT 25°

Mole fract. ethanol	F^E	$-TS^E$	H^M
0.05	93	28	65
.1	159	53	106
.2	250	100	150
.3	307	138	169
.4	335	166	169
.5	342	183	159
.6	325	183	142
.7	287	168	119
.8	225	138	87
.9	136	87	49
.95	76	49	27

Liquid–vapor compositions at 0° given in Table VI were calculated from the data in Table V on the assumption of additive specific heats. Using the same assumption, the differences $F - F_i = F^E$ and $S - S_i = S^E$ as well as H^M were computed, where F^E and S^E are the amounts of free energy and entropy above that of the ideal solution as indicated and H^M is the heat of mixing. They are shown in Table VII and Fig. 5. Detailed exposition of the method is given by Scatchard.[14] No correction was made for the imperfection of the vapor since it was found insignificant. The system carbon tetrachloride–methanol[14] shows a practically identical shape of curve for S^E *vs.* x as well as negative values for TS^E over the entire range. As pointed out, this must be due, in part at least, to the strong interaction of the two components. The entropy of mixing was discussed recently by Wood[19] at some length and it was stated that the orientational distribution is the principal factor. The negative values of S^E obtained in this investigation, as well as those obtained by Scatchard and co-workers for solutions of methanol in carbon tetrachloride and benzene,[14] would then be explained by increased orientation of the non-polar solvent molecules caused by the presence of alcohol molecules. Such an interaction is fairly plausible for carbon tetrachloride which contains chlorine atoms that can interact with the hydroxyl hydrogen, but it is somewhat surprising for the hydrocarbons, benzene and isooctane.

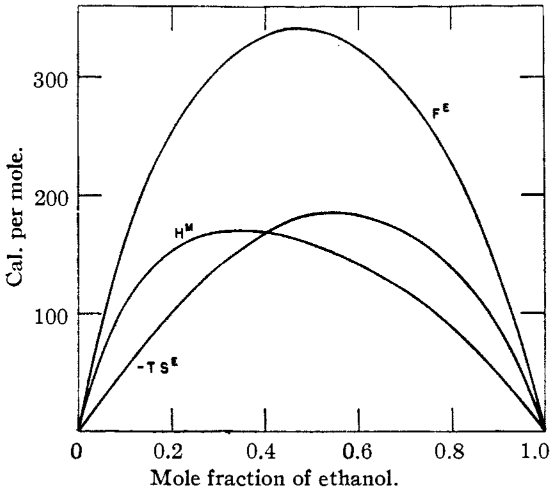

Fig. 5.—Thermodynamic functions at 25°.

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[17] G. Scatchard and C. L. Raymond, THIS JOURNAL, **60**, 3099 (1938).

[18] W. K. Lewis and E. V. Murphree, *ibid.*, **46**, 1 (1924).

[19] S. E. Wood, *J. Chem. Phys.*, **15**, 358 (1947).

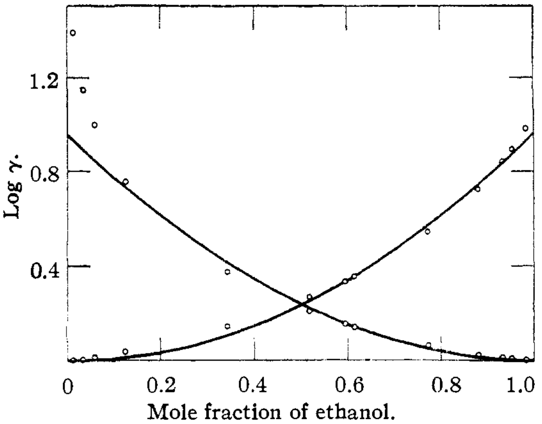

Fig. 6.—Logarithms of activity coefficients at 50°: circles, experimental values; curves, calculated from Van Laar equations.

Figure 6 shows the experimental activity coefficients at 50° compared with curves calculated from the Van Laar equations[20] fitted to the azeotropic composition and pressure. The two-constant Margules equations would give nearly identical curves since the terminal activity coefficients are nearly equal.[20] The agreement is seen to be fairly close except below 0.1 mole fraction where the equations fail to reproduce the rapidly increasing activity coefficient of ethanol. A better fit can be obtained only by using equations with more than two adjustable constants. However, the Van Laar equations would be useful in extending data on other hydrocarbon–alcohol systems, provided the peculiar behavior at low alcohol concentrations were kept in mind.

Summary

Densities of ethanol, isoöctane and of isoöctane–ethanol solutions were measured at 0, 25 and 50°. Equations giving the density of ethanol and isoöctane as a function of temperature are presented. The volume expansion on mixing increases rapidly with temperature.

Static vapor pressures at 0 and 25° and liquid–vapor equilibria at 25 and 50° were determined. Good agreement was obtained between the two sets of measurements at 25°. Satisfactory agreement was also obtained when calculating vapor pressures by means of the Duhem–Margules equation without corrections for imperfection of the vapor.

The excess thermodynamic functions F^E, TS^E and H^M were computed. Activity coefficients were calculated using the Van Laar equation and approximate reproduction of the experimental data were obtained.

PEORIA 5, ILLINOIS RECEIVED NOVEMBER 13, 1947

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[20] H. C. Carlson and A. P. Colburn, *Ind. Eng. Chem.*, **34**, 581 (1942).

[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

Melting Point Curves of Optical Isomers

BY CHARLES L. BICKEL AND ALFRED T. PEASLEE, JR.[1]

The problem of the melting points of mixtures of optical isomers was placed on a sound theoretical basis by Roozeboom[2] who showed that three types of melting point curves might be expected. Several of the substances studied[3,4] give the mixed-crystal curve predicted by Roozeboom, a continuous curve joining the melting points of the two optical isomers and a straight line in its simplest form. Most of the compounds investigated[3,4,5] give a curve with two minima and a maximum, indicating the formation of a racemic compound. Ross and Somerville[4] reported that pinene gave the third type of curve, characteristic of a simple mixture and consisting of two parts with a minimum at the point of intersection. However, Timmermans[6] stated that the "dextro" pinene used by Ross and Somerville was a mixture of the two isomers of α-pinene, so that these investigators were working with a ternary mixture and not with optical opposites.

The present study of the dextro and levo forms of β-benzoylhydratropic acid indicates that these optical opposites give a simple mixture. The identity of the isomers appears to be definitely established[7,8,9] so that the question involved in the case of pinene should not be raised in this case.[10] The experimental data for the acids are presented graphically in Fig. 1.

This study has been extended to include the methyl esters of the above acids. Figure 2 indicates that a racemic compound is formed. The behavior of the methyl esters therefore resembles that of most of the acids and esters previously investigated.

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[1] A senior in the Phillips Exeter Academy during the school year, 1947–1948.

[2] Roozeboom, *Z. physik. Chem.*, **28**, 494 (1899).

[3] Adriani, *ibid.*, **33**, 467 (1900).

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[10] Since the submission of this manuscript the observations of Singh and Tewari [*Proc. Indian Acad. Sci.*, **26A**, 389 (1947)] regarding 3-nitro-p-toluidinomethylenecamphor have come to our attention. The d and l isomers of this substance appear to form a simple mixture, the melting point of the eutectic being only 1.8° below the melting point of each pure isomer.