

polations have been revised by Dr. Parks and Dr. K. K. Kelley in view of recent data to lower temperatures, including those of this paper. Thus these somewhat arbitrary steps in the calculations have been carried out in a completely impartial manner. At best, however, these values are still uncertain and have been arbitrarily assigned the error of 1 cal. per degree. The other experimental values are from this and the preceding research for the two trimethylpentanes, and from the work of Aston and associates for isobutane⁶ and tetramethylmethane.⁷ It appears that in the heptane-octane range equation (1) gives as good results as the more complex statistical equations, although possibly the average of the two results would be better. The accuracy seems to be to about 1 cal. per degree. For the simpler molecules the statistical treatment is to be preferred.

In connection with equation (1) it may be convenient to note that the entropies at 298.1°K. of the gaseous normal paraffins above butane can be represented by the simple equation

$$S_n = 9.13n + 37.62 \text{ cal. per degree mole} \quad (2)$$

where n is the number of carbon atoms. This equation fits both the experimental entropies and the statistical formulas within about 0.1 cal. per degree.

The combination of these two equations for entropies and the equation given in the accompanying paper for heat capacities should make pos-

(6) J. G. Aston, R. M. Kennedy and S. C. Schumann, *THIS JOURNAL*, **62**, 2059 (1940).

(7) J. G. Aston and G. H. Messerly, *ibid.*, **58**, 2354 (1936).

sible very convenient and reasonably accurate calculations of the various thermodynamic properties of the paraffins in the perfect gas stage, provided of course that heat of formation values are available where needed. Although experimental data on additional substances are desirable, it appears that considerable confidence can be placed in these results.

Summary

The following results were obtained for 2,3,4-trimethylpentane: melting point, $163.63 \pm 0.1^\circ\text{K.}$; heat of fusion, 2215 ± 5 cal. per mole; heat of vaporization, 7810 ± 30 cal. per mole; entropy of liquid at 298.1°K. , 78.71 ± 0.2 cal. per degree mole; entropy of the real gas at the boiling point 386.5°K. , 115.78 ± 0.3 cal. per degree mole. Heat capacities of the solid, liquid, or gas are given covering most of the range 15 to 417°K. This entropy is shown to be in reasonable agreement with a value calculated from approximate statistical formulas.

A simple semi-empirical formula is suggested for calculating entropies of the heavier branched-chain paraffins. It is shown to give results in agreement with the available experimental data, and with the values calculated from the more complex statistical formulas. The combination of this formula for entropies with the simple formula for heat capacities, given in the accompanying paper, should constitute a convenient method for thermodynamic calculations.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

Vapor Pressure Studies. II. Chlorobenzene-1-Nitropropane¹

By J. R. LACHER, W. B. BUCK AND W. H. PARRY

The present paper reports on vapor pressure measurements of chlorobenzene-1-nitropropane mixtures. It also includes some data on the heats of mixing of ethylene bromide, chlorobenzene and 1-nitropropane. The results make possible a fairly accurate comparison of the thermodynamic properties of the three possible binary mixtures of these liquids.

Experimental Details.—The apparatus employed in the vapor pressure measurements was practically identical to that designed by Sames-

hima² and differs from that used in the previous research¹ in that the liquid was boiled directly by means of an electrically heated wire. The experimental procedure was the same in both cases. The composition of the liquid and condensed vapor was determined by measuring densities at 30° . The densities of known mixtures could be fitted to the equation

$$d_m = 0.9901 + 0.1058N_C + [0.0192 - 0.0040N_C]N_CN_N \quad (1)$$

(1) Paper I appeared in *THIS JOURNAL*, **63**, 1752 (1941).

(2) J. Sameshima, *ibid.*, **40**, 734 (1918).

N_C and N_N give the mole fractions of chlorobenzene and 1-nitropropane, respectively.

The calorimeter used in the heat measurements was modified after that of Zellhoefer and Copley.³ A cylindrical Pyrex mixing chamber of about 275 cc. capacity was furnished with a tight fitting bakelite cap. Holes drilled in the latter accommodated the pipet tip, Beckmann thermometer, stirrer, and leads from a heating coil. The pipet had a capacity of 109.0 cc. Thorough mixing of the liquids was effected by a hand-operated ring-type stirrer made of thin Pyrex tubing. The heating coil, which was suspended in the mixing chamber, contained 10.50 ohms of no. 28 constantan wire and had no. 18 copper leads. The resistance of the heater remained constant to $\pm 0.2\%$ throughout all the runs.

The mixing chamber and pipet were mounted in a gallon dewar flask and covered with an insulating lid. In order to make a run, 109.0 cc. of one liquid was placed in the mixing chamber and the pipet filled with the other. The apparatus was assembled in a large air-bath and let stand overnight to ensure thermal equilibrium. The pipet was emptied into the mixing chamber, the liquids mixed thoroughly and the temperature change determined. The heat capacities of the mixing chamber and contents were determined electrically. This gives enough information to calculate the heat absorbed on mixing. When identical liquids were mixed, the heat effect was 2 cal. or less per mole.

The liquids used were purified as described previously.

Vapor Pressures.—The vapor pressures of pure liquids and of liquid mixtures measured in the present apparatus increase slightly with increasing rate of boiling due to superheating. The magnitude of the variation can be seen from Table I which gives the vapor pressures of the pure components at 75 and 120° measured with two heating currents. The vapor pressures measured in the former apparatus are also included.

TABLE I

	Pressure, mm.		Current, amperes
	75°	120°	
Chlorobenzene	118.5	543.8	1.01
	120.8	545.2	1.41
	121.9	...	Ref. 1
1-Nitropropane	111.4	543.5	1.01
	112.6	546.3	1.41
	115.0	550.2	Ref. 1

(3) Zellhoefer and Copley, THIS JOURNAL, 60, 1343 (1938).

They are somewhat higher since superheating did not occur. We have ascertained that the ratio P_Y/P^0N is independent of the speed of boiling. Here Y and N represent the mole fraction of a given component in the gaseous and liquid phase; P and P^0 the pressures of the solution and pure component measured under identical conditions. This is no doubt due to the fact that, for this mixture, the superheating is the same for the components and solution. The primary data obtained at 75 and 120° are given in Table II. Subscripts C and N refer to chlorobenzene and 1-nitropropane, respectively.

TABLE II

N_C	Y_C	P , mm.	$\log \frac{PY_C}{P^0CNC}$	$\log \frac{PY_N}{P^0NNC}$	F^E , cal.
(a) 75° isotherm					
0.119	0.159	119.4	0.121	0.005	31
.132	.174	119.6	.115	.005	30
.187	.233	121.6	.098	.008	39
.289	.335	125.2	.079	.017	55
.460	.484	128.9	.039	.050	69
.472	.493	129.8	.050	.044	73
.583	.587	129.5	.033	.057	67
.691*	.680	127.1	.024	.073	61
.771	.745	129.5	.015	.107	57
(b) 120° isotherm					
.096	.118	565.2	.105	.004	24
.282	.314	590.2	.081	.014	58
.282*	.319	586.1	.086	.010	55
.454*	.471	597.2	.057	.027	71
.507*	.512	597.6	.045	.037	72
.675	.652	596.6	.024	.068	67
.765	.730	589.4	.014	.093	56
.844	.804	579.9	.006	.125	42

The data marked with an asterisk were obtained using a heating current of 1.01 amperes and the remainder at a current of 1.41 amperes. The excess free energy of mixing in cal./mole, F^E , was calculated from equation 4 of reference 1. The logarithms of the activity coefficients can be reproduced by the equations

$$\begin{aligned} \log \gamma_C &= 0.180N_N^2; \log \gamma_N = 0.180N_C^2; 75^\circ \\ \log \gamma_C &= 0.166N_N^2; \log \gamma_N = 0.166N_C^2; 120^\circ \quad (2) \end{aligned}$$

At 120° the data suggest that a term in N^3 might be included; however, the deviations from the above equations are hardly greater than the experimental errors.

In Fig. 1 we have graphed the experimental values of F^E against the mole fraction of chlorobenzene. The open circles refer to 120 and the closed circles to 75° data; the continuous curves were calculated by using equations 2. It is evident that the excess free energy of mixing is fairly large

and positive and that the excess entropy of mixing is not determined.

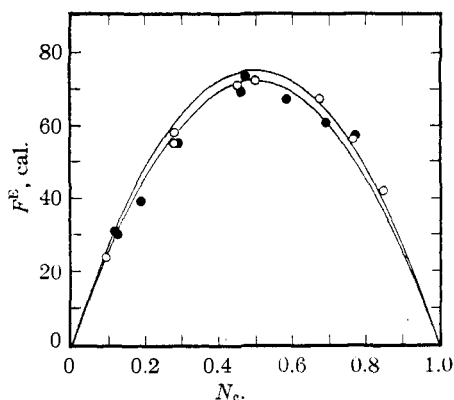


Fig. 1.—Excess free energy of mixing *versus* mole fraction of chlorobenzene; O and upper curve represent 120° data; ● and lower curve represent 75° data.

Heats of Mixing.—A calculation of the excess entropy of mixing from a knowledge of pressure-composition isotherms at several temperatures requires quite accurate data. Direct measurements of heats of mixing give a simple means for obtaining S^E and serve also as a check on the reliability of vapor pressure measurements. Accordingly we have determined the heats of solution of the three possible binary mixtures from ethylene bromide, chlorobenzene, and 1-nitropropane. In order to test the accuracy of the apparatus used, we have studied the systems benzene-carbon tetrachloride and benzene-cyclohexane. The results obtained at 30° are given in Table III.

TABLE III
HEATS OF MIXING

Liquids mixed	H , cal./mole	Mole fraction	H , cal./mole 0.5 mole fraction
$C_6H_6-CCl_4$	29	0.521 C_6H_6	29
$C_6H_6-CCl_4$	29	.521 C_6H_6	29
$C_6H_6-CCl_4$	28	.521 C_6H_6	28
$C_6H_6-CCl_4$	26*	.521 C_6H_6	26
$C_6H_6-CCl_4$	27*	.521 C_6H_6	27
$C_6H_6-C_6H_{12}$	181*	.547 C_6H_6	183
$C_6H_6-C_6H_{12}$	180	.547 C_6H_6	182
$C_6H_5Cl-C_3H_7NO_2$	29*	.467 C_6H_5Cl	29
$C_6H_5Cl-C_3H_7NO_2$	28	.467 C_6H_5Cl	28
$C_6H_5Cl-C_2H_4Br_2$	93	.541 $C_2H_4Br_2$	94
$C_2H_4Br_2-C_3H_7NO_2$	122	.508 $C_2H_4Br_2$	122

Equal volumes of liquids were used. The first column gives the heat absorbed in cal. per mole of solution, the second column the mole fraction of the resulting solution, and the third gives the calculated heat absorbed for a solution having a mole

fraction of one-half. The calculation assumed that $H = \text{const. } N_1N_2$ which is very nearly true for these mixtures. The data marked with an asterisk were obtained by emptying the lighter liquid from the pipet onto the heavier liquid in the mixing chamber. For the liquid pairs benzene-cyclohexane and chlorobenzene-1-nitropropane where very little density difference exists, the heat absorbed is independent of the order of mixing. The slightly higher values obtained when carbon tetrachloride was emptied onto benzene are due to the fact that thorough mixing is easily obtained; whereas, if they are mixed in the reverse order, such is not the case. The higher values are probably the more reliable.

The heat of mixing of carbon tetrachloride and benzene at a mole fraction of 0.5 is given as 20 cal. by Vold,⁴ 25.5 cal. by Hirobe,⁵ and 30 cal. by Scatchard and co-workers.⁶ For benzene and cyclohexane Scatchard and co-workers⁷ find 175 cal. at a volume fraction of 0.5 and quote Wolf, Frahm and Harms⁸ as giving 198 cal. for mixtures of the same composition at 30°. The present experiments are in better agreement with the calculated heats of mixing given by Scatchard than with the direct measurements of others. We had planned to extend our measurements over the whole range of composition, but the work was interrupted before that was accomplished.

Discussion.—In Table IV we have summarized the thermodynamic properties for the three possible binary mixtures from ethylene bromide, chlorobenzene, and 1-nitropropane. The data are for 30° and refer to equimolar mixtures. The percentage volume change for chlorobenzene-1-nitropropane mixtures was calculated from equation 1. The calculation of F^E at 30° from the measured values at higher temperatures was based on the assumption that the heats of mixing could be treated as constant for the purpose of calculating $(\partial F^E/\partial T)_{P,N}$. TS^E was then calculated from $F^E = H - TS^E$.

TABLE IV
PROPERTIES OF EQUIMOLAR MIXTURES AT 30°

$V^M 100/V_0$	F^E , cal.	H , cal.	TS^E , cal.	Mixture
+0.31	48	94	46	$C_2H_4Br_2-C_6H_5Cl$
+ .10	92	122	30	$C_2H_4Br_2-C_3H_7NO_2$
- .08	65	29	-36	$C_6H_5Cl-C_3H_7NO_2$

(4) R. D. Vold, *THIS JOURNAL*, **59**, 1515 (1937).

(5) H. Hirobe, *J. Faculty Sci. Imp. Univ. Tokyo*, **1**, 155 (1925).

(6) Scatchard, Wood and Mochel, *THIS JOURNAL*, **62**, 712 (1940).

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

(8) Wolf, *Trans. Faraday Soc.*, **33**, 179 (1937); Wolf, Frahm and Harms, *Z. physik. Chem.*, **B36**, 260 (1937).

The positive excess entropies of mixing shown by mixtures of ethylene bromide with chlorobenzene and 1-nitropropane confirm very nicely our previous free energy measurements on these mixtures. The present free energy measurements on mixtures of chlorobenzene-1-nitropropane suggest only slightly that the excess entropy is negative; the heats of mixing prove definitely that this is so.

In our previous communication, we pointed out that there was no simple relation between the excess free energy and entropy of mixing, but that the percentage volume change and the entropy change always possessed the same sign. Mixtures of chlorobenzene-1-nitropropane conform to this rule as both quantities are negative. In Fig. 2 we have graphed the percentage volume change against TS^E for the present mixtures and for the three possible binary systems from carbon tetrachloride, benzene and cyclohexane studied by Scatchard and co-workers.⁶ A fairly good straight line passing through the origin is obtained. Mixtures of chloroform and ethanol⁹ satisfy the above rule, but a very small volume change is accompanied by a relatively large entropy change. As far as the present comparison is concerned, the latter mixture is abnormal.

(9) G. Scatchard and C. L. Raymond, *THIS JOURNAL*, **60**, 1278 (1938).

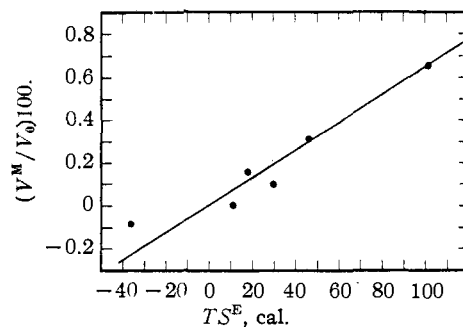


Fig. 2.—Percentage volume change *versus* TS^E at 30° for the possible binary mixtures from CCl_4 , C_6H_6 , C_6H_{12} and from $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_4\text{Br}_2$, $\text{C}_3\text{H}_7\text{NO}_2$. Mole fraction is 0.5.

Summary

The excess free energy of mixing for the system chlorobenzene-1-nitropropane has been measured at 75 and 120° . The heats of mixing of the three possible binary systems from ethylene bromide, chlorobenzene and 1-nitropropane have been determined for approximately equimolar mixtures. The data now on hand indicate that the excess entropy of mixing is approximately a linear function of the per cent. volume change for a considerable variety of liquid mixtures.

PROVIDENCE, R. I.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

The Densities and Surface Tensions of *cis*- and *trans*-Decahydronaphthalene between -30 and 180° ¹

BY W. F. SEYER AND CHARLES H. DAVENPORT

This is the second of a series of papers dealing with the physical-chemical properties of the *cis* and *trans* isomers of decahydronaphthalene. The method employed in obtaining these compounds in a high state of purity has been described already in a previous article.² In view of Wightman's deductions from specially constructed spatial models that the *cis* and *trans* forms might be only the limiting stable forms of a series of unstable ones, it became of interest to investigate the variation of certain of their physical properties with temperature.³ The properties selected for the work, described below, were the densities

(1) Original manuscript received July 12, 1939.

(2) Seyer, *THIS JOURNAL*, **60**, 2125 (1938).

(3) W. A. Wightman, *J. Chem. Soc.*, **127**, 1421 (1925).

and surface tensions of the hydrocarbons between -30 and 180° .

Materials.—The materials were part of the lots already described which had the freezing points -43.26 and -31.47° for the *cis* and *trans* forms, respectively.

Procedure.—The density was measured by finding the loss in weight of a quartz sinker, when immersed in the liquid hydrocarbon. From its weight in air, 31.0059 g., and in water 22.5162 g., its volume at 20° was calculated to be 8.5150 cc., after all corrections for buoyancy had been made. The sinker was suspended from the bottom of a balance pan by means of a fine platinum wire which had been platinized over the region where the wire came in contact with the surface of the liquid in order to minimize the surface tension forces. Much care was taken to see that the sinker was always immersed to the same depth before taking a weighing and by using the figure 0.000038 for the coefficient of cubical expansion of quartz it was