compared with quantum mechanical calculations.

Melamine monohydrochloride hemihydrate has been briefly examined and found to be orthorhombic, $a = 16.75$ Å., $b = 12.29$ Å., $c = 6.93$ Å., space group, *Cmcm*, *Cmc* or *C2cm*.

PASADENA, CALIFORNIA RECEIVED MARCH 28, 1941

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

Vapor Pressures of Binary Liquid Mixtures*

BY J. R. LACHER AND ROY E. HUNT

A measurement of the total and partial pressures of a binary liquid mixture leads to information concerning the chemical potentials of the liquid phase components provided certain thermodynamic properties of the gaseous phase are known. A knowledge of these chemical potentials is important for the development of theories concerning the structure of liquids and liquid mixtures. In the present paper are reported measurements on mixtures of chlorobenzene–ethylene bromide and 1-nitropropane–ethylene bromide.

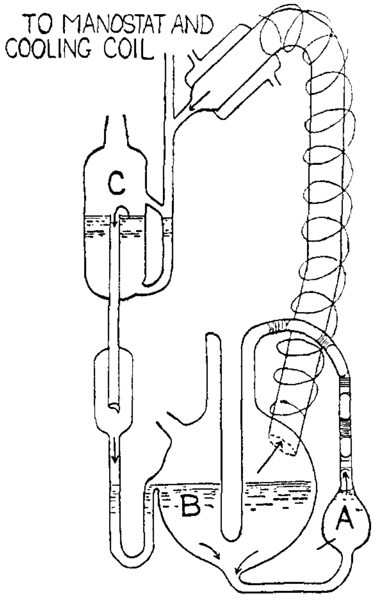


Fig. 1.

Experimental Details.—The apparatus, which is quite similar to that used by Sameshima,[1] is shown diagrammatically in Fig. 1. Instead of boiling the liquid in B by means of an electrically heated wire, a small pump A, of dimensions recommended by Swietoslawski[2] was used to force liquid and vapor over a thermometer well in B. This well was made quite long in order to permit the detection of any temperature gradients in B. A and B were heated electrically. The vapors in B passed up a heated tube of large diameter, condensed, and returned to the reservoir via a hold-up trap C. The drop counter below C indicated the speed of circulation of the vapor. The heated parts of the apparatus were insulated with asbestos and shielded with aluminum foil. C and B are fitted with mercury sealed ground glass caps and liquid samples were removed for analysis in ice-jacketed pipets.

A cooling coil connected the still to a manostat and pump. Most of the condensation occurred in the water cooled condenser, but the cooling coil was necessary to prevent a slow diffusion of vapor out of the still. The manostat had a 45 l. capacity and was thermally insulated. Dry air was used as the confining gas. Pressures were read with a mercury manometer using a calibrated paper scale. The individual pressure readings could be made to 0.2–0.3 mm. However, all the pressures reported in this paper represent the average of a large number of individual readings. The pressure in the apparatus did not drift provided the cooling coil was maintained at a sufficiently low temperature and that the temperature of the manostat did not change. A tenth degree mercury thermometer read with a good telescope permitted temperature measurements accurate to a few hundredths of a degree.

Experiments performed on pure liquids and mixtures of ethylene bromide–chlorobenzene and ethylene bromide–1-nitropropane (whose components have almost identical vapor pressures) showed that the boiling temperatures were independent of a three-fold variation in electrical energy supplied to pump A. There was a long region of constant temperature in the upper part of the thermometer well. The temperature at the bottom depended on the heating current supplied to B. For most runs this current was adjusted so that all temperature gradients along the well vanished. However, their presence has no effect on the final experimental data which, for the above mixtures, satisfy the Margules equation.

When mixtures of ethylene chloride–*sym*-tetrachloroethane were boiled in the still, the temperature of boiling increased with increasing pump speed and reliable measurements could not be made. The vapor pressures of the pure components differ by almost a factor of ten in this case. Ethylene bromide–*sym*-tetrachloroethane and chlorobenzene–*sym*-tetrachloroethane mixtures are made of components whose vapor pressures differ by a factor of two; their boiling temperatures were independent of the pumping speed. However, a comparison of the data with the requirements of the Margules equation showed that the mole fraction of the more volatile component in the vapor

---

* Original manuscript received December 6, 1939.

[1] J. Sameshima, THIS JOURNAL, **40**, 734 (1918).

[2] "Ebulliometry," W. Swietoslawski, Jagellonian University Press, 1936.

phase was too small, giving rise to errors of 1–2 in the per cent. deviations from Raoult's law as calculated by the method of Gilmann and Gross.[3]

The present apparatus will give reliable results for liquid mixtures whose components have almost identical vapor pressures. However, it is not effective in producing equilibrium between the liquid and gaseous phase when they differ considerably in composition. In such cases it is better to pass the vapor through a liquid mixture of the same components as suggested by Rosanoff, Lamb and Breithut[4] and as is done by Scatchard and his co-workers.[5]

Technical chlorobenzene, ethylene bromide, and 1-nitropropane were dried over calcium chloride and fractionated repeatedly in an efficient still. The densities of the liquid mixtures were determined in Weld specific gravity bottles having a capacity of 5 cc. The results, obtained at 30°, are expressed by the equations

$$d_1 = 1.0959 + 1.0635N_B - (0.174 + 0.042N_B)N_BN_C$$
$$d_2 = 0.9904 + 1.1693N_B - (0.0495 + 0.0080N_B)N_BN_N \tag{1}$$

d_1 and d_2 represent the density of mixtures of ethylene bromide with chlorobenzene and with 1-nitropropane, respectively. N_B, N_C, N_N give the mole fractions of ethylene bromide, chlorobenzene, and 1-nitropropane. Because of the large difference in density of the pure components and the low volatility of the mixtures at room temperature, the composition could be determined quite accurately.

Experimental Results.—Table I gives the data obtained by measuring pressure–composition isotherms at 75 and 100° for ethylene bromide–chlorobenzene mixtures. Such mixtures will be called system one. Table II gives similar results for ethylene bromide–1-nitropropane, system two, at 75 and 120°. Measurements at 100° for system two are not reported since they furnish no further information; except for this, all runs are included. N represents the mole fraction of the appropriate component in the liquid phase, Y the mole fraction in the gas phase, P is the total pressure in mm. mercury, and F^E represents the excess free energy of mixing in cal./mole.

TABLE I

ETHYLENE BROMIDE–CHLOROBENZENE

N_B	Y_B	P, mm.	F^E, cal.
(a) 75° isotherm			
1	1	119.9	0
0.9214	0.9034	122.3	11.4
.7895	.7633	125.6	28.2
.6443	.6268	127.7	38.6
.5132	.5101	128.4	41.4
.3576	.3707	128.0	37.2
.1684	.1882	125.4	20.3
0	0	121.9	0
(b) 100° isotherm			
1	1	295.3	0
0.9207	0.9053	300.3	11.0
.7901	.7695	306.4	25.6
.6434	.6306	310.0	34.4
.5129	.5130	311.2	37.2
.3568	.3707	309.5	32.5
.1693	.1881	304.4	19.5
0	0	296.1	0

TABLE II

ETHYLENE BROMIDE–1-NITROPROPANE

N_B	Y_B	P mm.	F^E, cal.
(a) 75° isotherm			
1	1	119.7	0
0.9431	0.9137	123.9	20.9
.8801	.8367	127.4	41.0
.7648	.7254	130.9	65.0
.6562	.6352	133.0	80.8
.5085	.5219	133.0	85.0
.3995	.4380	132.0	80.9
.2698	.3259	128.9	65.4
.1580	.2133	124.4	42.6
.0575	.0873	119.8	21.5
.0352	.0539	117.6	11.7
.0298	.0468	116.7	6.4
0	0	115.0	0
(b) 120° isotherm			
1	1	549.5	0
0.8842	0.8435	581.0	37.3
.7622	.7220	599.8	63.7
.6627	.6365	609.5	77.9
.4726	.4829	612.7	82.7
.2754	.3153	600.3	64.3
.1650	.2054	586.1	44.6
.0906	.1228	571.5	25.3
.0295	.0419	557.4	8.2
0	0	550.2	0

In order to compute activity coefficients from the experimentally measured quantities, it is necessary to take into account the deviations from the gas laws. The equations used are given by Scatchard and co-workers[5,6] and are for the system ethylene bromide–chlorobenzene

$$\begin{aligned}\log \gamma_B &= \log \frac{PY_B}{P^0_BN_B} + \frac{(\beta_B - V_B)(P - P^0_B)}{2.303RT}\\ \log \gamma_C &= \log \frac{PY_C}{P^0_CN_C} + \frac{(\beta_C - V_C)(P - P^0_C)}{2.303RT}\end{aligned} \tag{2}$$

P^0 and V refer to the vapor pressure and molar volume of the liquid component. The β's are constants depending only on temperature and express the fact that the vapors do not obey the ideal gas law. β_C was calculated from the theory of corresponding states using the critical temperature and pressure listed in the "International Critical Tables."[7] β_N was taken equal

---

[3] H. H. Gilmann and P. Gross, THIS JOURNAL, **60**, 1525 (1938).

[4] Rosanoff, Lamb and Breithut, *ibid.*, **31**, 448 (1909).

[5] Scatchard, Raymond and Gilmann, *ibid.*, **60**, 1275 (1938).

[6] Scatchard, Wood and Mochel, *J. Phys. Chem.*, **43**, 119 (1939).

[7] "International Critical Tables," Vol. III, p. 245.

to the measured value for nitromethane.[8] β_B was estimated to be one-half as large as β_C by comparing van der Waals constants for ethylene bromide and chlorobenzene. Since $P - P^0$ for these systems is quite small, the uncertainties in the β's have very little effect on the values of log γ. The maximum correction in log γ was 0.0005 for the ethylene bromide–chlorobenzene system and 0.0011 for the other mixture.

If the experimental data satisfy the requirements of the Margules equation, the activity coefficients should be expressible by equations of the form[9]

$$\begin{aligned} \log \gamma_C &= \frac{\alpha_2}{2} N_B{}^2 + \frac{\alpha_3}{3} N_B{}^3 \\ \log \gamma_B &= \frac{\alpha_2 + \alpha_3}{2} N_C{}^2 - \frac{\alpha_3}{3} N_C{}^3 \end{aligned} \tag{3}$$

The values of α_2 and α_3 which will reproduce the activity coefficients are listed in Table III.

TABLE III

Temp., °C.	α_2	α_3
(a) ETHYLENE BROMIDE–CHLOROBENZENE		
75	0.1598	0.0993
100	.1115	.1250
(b) Ethylene Bromide–1-Nitropropane		
75	0.2795	0.3000
120	.2315	.2834

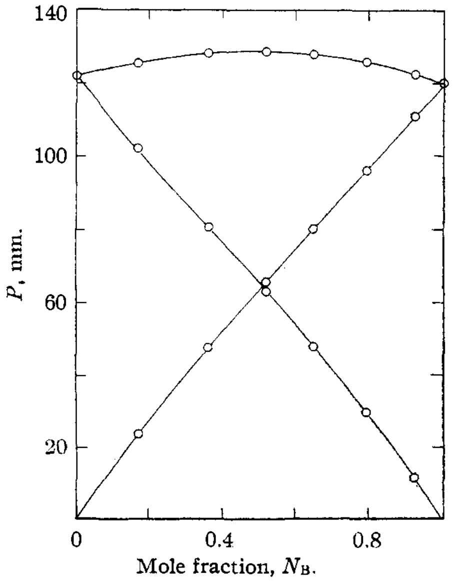


Fig. 2.—The 75° isotherm for ethylene bromide–chlorobenzene. Points represent measured total and partial pressures; continuous curves satisfy the Margules equation.

In order to illustrate the accuracy with which these α's will reproduce the experimental data, we have listed in Table IV the observed and calculated partial pressures, PY, at 75°. The data together with the total pressures, are graphed as a function of N_B in Figs. 2 and 3. The dots represent experimental and the continuous curves calculated pressures. The agreement is excellent.

TABLE IV

EXPERIMENTAL AND CALCULATED PARTIAL PRESSURES AT 75° IN MM.

N_B	PY_B Calcd.	PY_B Exptl.	PY_C Calcd.	PY_C Exptl.
(a) Ethylene Bromide–Chlorobenzene				
0.9214	110.7	110.5	11.9	11.8
.7895	95.9	95.9	29.9	29.7
.6443	80.0	80.0	47.8	47.7
.5132	65.5	65.5	63.0	62.9
.3576	47.6	47.4	80.5	80.6
.1684	23.8	23.6	102.0	101.8
(b) Ethylene Bromide–1-Nitropropane				
0.9431	113.1	113.2	10.6	10.7
.8801	106.4	106.6	20.7	20.8
.7648	94.8	95.0	36.3	36.0
.6562	84.3	84.5	48.6	48.5
.5085	69.6	69.4	63.5	63.6
.3995	57.9	57.8	74.0	74.2
.2698	42.2	42.0	86.5	86.9
.1580	26.5	26.5	97.8	97.9
.0575	10.3	10.5	108.6	109.3
.0352	6.4	6.3	111.1	111.3
.0298	5.4	5.5	111.6	111.2

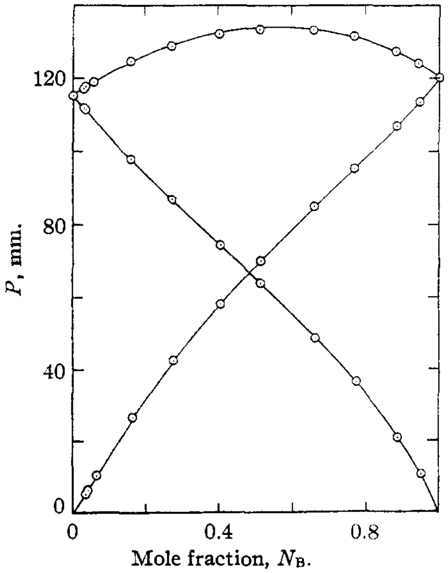


Fig. 3.—The 75° isotherm for ethylene bromide–1-nitropropane. Points represent measured total and partial pressures; continuous curves satisfy the Margules equation.

---

[8] Eucken and Meyer, *Z. physik Chem.*, **B5**, 452 (1929).

[9] Hildebrand, "Solubility," Reinhold Publishing Corp., New York, N. Y., 1936.

The excess free energy of mixing was calculated from the equation

$$F^E = 2.303RT[N_{\mathrm{B}} \log \gamma_{\mathrm{B}} + N_{\mathrm{C}} \log \gamma_{\mathrm{C}}] = 2.303RTN_{\mathrm{B}}N_{\mathrm{C}}\left[\frac{\alpha_2}{2} + \frac{\alpha_3}{6}(2 - N_{\mathrm{C}})\right] \quad (4)$$

The values of F^E calculated from the directly measured γ's are given in Tables I and II and graphed as points in Fig. 4. The continuous curves represent the values of F^E calculated from the α's given in Table III. The maximum correction to F^E due to gas imperfection was 0.7 and 1.5 cal. for systems one and two, respectively. For both mixtures F^E is slightly larger at 75° than it is at the higher temperatures. The maximum difference of 4.6 cal. for system one is, we believe, experimentally significant; the difference of 1.6 cal. shown by the other system is not larger than the experimental errors.

In Table V we have summarized some thermodynamic properties for these mixtures at the mean temperature of our experiments.

TABLE V

PROPERTIES OF EQUIMOLAL MIXTURES

	Ethylene bromide–chlorobenzene	Ethylene bromide–1-nitropropane
$(V^M/V_0)100$	0.31	0.10
F^E, cal.	39.4	85
H, cal.	105.6	98
TS^E, cal.	66.2	13

$(V^M/V_0)100$ is the per cent. volume change on mixing, V_0 being the volume of the unmixed components and V^M the difference between the volume of the mixture and V^0. TS^E was calculated from $(\partial F^E/\partial T)_p = -S^E$ and H from $F^E = H - TS^E$.

Discussion.—Both these systems show positive volume changes on mixing, system one expanding to a greater extent than system two. The excess free energy change, however, is twice as great for system two. Our experiments show, we believe, that TS^E is greater for system one. There appears to be a qualitative correlation between the volume and excess entropy change on mixing. The accurate measurements of Scatchard and his co-workers on chloroform–ethanol[10] and the three possible binary mixtures from benzene, cyclohexane, and carbon tetrachloride[6,11,12] lead to the same conclusion. In Table VI we have listed the relevant data which they have obtained.

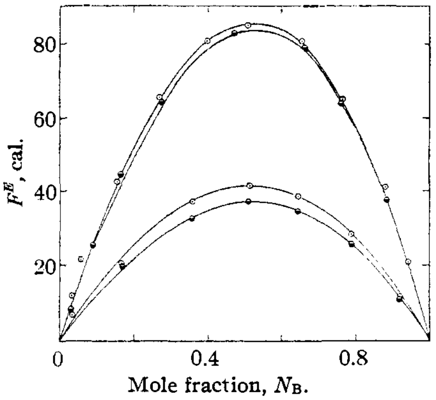


Fig. 4.—Excess free energy of mixing *versus* mole fraction of ethylene bromide. Upper curves are for mixtures with 1-nitropropane; lower curves for mixtures with chlorobenzene. ○, represent 75° data; ◒, represent 100° and 120° data.

The system chloroform–ethanol is particularly interesting in that it shows a reversal of sign in the volume and excess entropy change; the excess free energy is positive for all compositions of the mixture. It would be necessary, in order to make a quantitative comparison, to have direct measurements of the heat of mixing for the systems listed in Table V and also, perhaps, for benzene–carbon tetrachloride mixtures. If one uses the measured value for F^E for the latter mixture and Vold's[13] value of H, then TS^E becomes about 2 instead of 10.7 cal.

TABLE VI[a]

System	$(VM/V_0)100$	TSE, cal.	Mole fraction
C_6H_6–C_6H_{12}	0.65	101.4	0.5
C_6H_{12}–CCl_4	.16	17.5	.5
C_6H_6–CCl_4	.003	10.7	.5
$CHCl_3$–C_2H_5OH	.03	80	.12 (C_2H_5OH)
	.00	0	.28 (C_2H_5OH)
	− .39	−266	.80 (C_2H_5OH)

[a] We wish to thank Mr. W. B. Buck for making the calculations necessary for the preparation of this table.

The experimental data now available show that no simple relation exists between F^E and TS^E but that TS^E and $(V^M/V_0)100$ always possess the same sign. A possible explanation for the latter correlation can be given in terms of the probability function W, of Menke.[14,15] If two liquids contract on mixing, W must change so as to reproduce the more closely packed arrangement of the molecules and the excess entropy will be negative. The reverse will be true if the

---

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

(11) Scatchard, Wood and Mochel, *ibid.*, **61**, 3206 (1939).

(12) Scatchard, Wood and Mochel, *ibid.*, **62**, 712 (1940).

(13) R. D. Vold, *ibid.*, **59**, 1515 (1937).

(14) H. Menke, *Physik. Z.*, **33**, 593 (1932).

(15) J. H. Hildebrand and S. E. Wood, *J. Phys. Chem.*, **1**, 817 (1933).

liquids expand on mixing. It does not necessarily follow that TS^E will be zero if the liquids are mixed at constant volume, though this might be the case if W had spherical symmetry.

We wish to thank Dr. H. C. Eckstrom of this Laboratory for the opportunity of discussing this paper with him.

Summary

An apparatus is described for use in making vapor–liquid equilibrium measurements and the conditions under which it gives accurate results have been ascertained. The excess thermodynamic functions for mixtures of ethylene bromide with (1) chlorobenzene and (2) 1-nitropropane have been measured. Experimental data now available indicate that the excess entropy change and the volume change on mixing possess the same sign. A possible explanation for this is given.

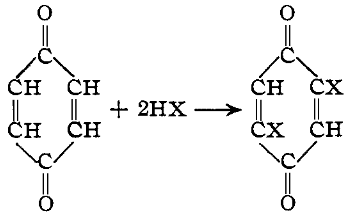
PROVIDENCE, RHODE ISLAND RECEIVED APRIL 12, 1941

NOTES

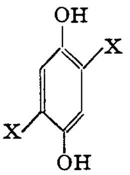
The Mechanism of the Addition of Hydrogen Cyanide to Benzoquinone

BY C. F. H. ALLEN AND C. V. WILSON

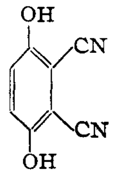
The addition of two molecules of unsymmetrical reagents to benzoquinone almost always gives rise to a substituted quinone (I) in which the new groups are on opposite sides of the benzene ring and in the 2,5-positions.



I



II

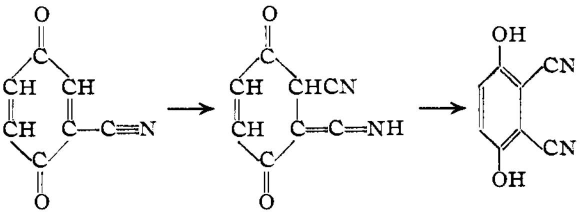


III

Sometimes the corresponding hydroquinone (II) results. The commonly accepted mechanism[1] accounts for the formation of this type of product by assuming consecutively 1,4-addition, enolization, and oxidation, the processes being repeated one or more times, depending upon the nature of the reactants.

An exception is encountered when hydrogen cyanide is the reagent of the type HX, used as an addend. In this instance, two molecules add; the product is a dicyanohydroquinone (III),[2] in which both CN groups are adjacent and on the same side of the molecule, *i. e.*, unsymmetrical addition has occurred. No intermediates can be isolated; the only other product of the reaction is hydroquinone. The mechanism cannot be the same, therefore, when this reagent is employed.

However, an explanation becomes evident when the available unsaturated systems are examined. Addition of the first molecule of hydrogen cyanide takes place as with all HX-type reagents,[1] and the cyanohydroquinone is oxidized by the excess quinone to form a monocyanoquinone (IV). This cyanoquinone now contains an alternate conjugated system involving the nitrile group, to which hydrogen cyanide would be expected to add more readily than to the system $C{=}C{-}C{=}C{=}O$.[3] The resulting substance would be 2,3-dicyanohydroquinone (III), which is actually obtained. This suggested mechanism is, thus, in accord with the known facts about the behavior of conjugated systems. It successfully accounts for the nature of the product and eliminates the apparent ex-



IV III

---

(1) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 600.

(2) Thiele and Meisenheimer, *Ber.*, **33**, 675 (1900).

(3) Duff and Ingold, *J. Chem. Soc.*, 87 (1934).