[Contribution from the Department of Chemistry of Princeton University]

MOLECULAR ORIENTATION AND THE PARTIAL VAPOR PRESSURES OF BINARY MIXTURES.

I. SYSTEMS COMPOSED OF NORMAL LIQUIDS

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Although many measurements have been made of the vapor pressures of solutions containing but one volatile component and the total vapor pressures of great numbers of binary mixtures of volatile liquids have been determined, few experimental data are available on the partial pressures of binary liquid mixtures. Many partial pressures have been calculated from total pressures by means of equations, theoretical and empirical, the success of the calculations depending not only upon the nature of the equations but, unfortunately, upon that of the mixtures as well. An equation recently developed by Langmuir[1] seemed to offer a means not merely of calculating partial pressures but also of learning much about the molecular condition of liquids. In order to examine the applicability of this equation and in order to gain information which might be coördinated with the results of studies of the dielectric polarization of liquids, the measurement of partial vapor pressures was undertaken.

Apparatus and Procedure

The apparatus employed (Fig. 1) was similar in many respects to that used by Sameshima.[2] The vessel A, which had a capacity of 200 cc., contained the liquid mixture, the partial vapor pressures of which were to be measured. A was immersed to the level of the ground-glass stopper S in a carefully regulated thermostat, the temperature of which was approximately 2° above the temperature at which the pressures were to be measured. Superheating was prevented by stirring the liquid electrically by means of a current through platinum spiral B, which was carried by a tube entering the vessel through a ground joint with a mercury seal. The temperature of the boiling liquid was read on the thermometer T, which was suspended by a platinum wire from a hook on the stopper S. The thermometers used were of short range, calibrated in fifths of a degree and standardized at the U. S. Bureau of Standards. The large side tube C was wound with an electric heater, which prevented the condensation of any vapor in C and its subsequent direct return to A. The condensers, D and D′, were surrounded by insulated copper jackets, E and E′, which were filled with solid carbon dioxide in the form of "dry ice." The low temperature obtained with the solid carbon dioxide prevented the escape of vapor and consequent change in the composition of the liquid, which occurred in the preliminary experiments when ice was used for the condensation of the more volatile liquids. In the case of liquids of high freezing point, solidification in the condenser was prevented by inserting a thin sheet of asbestos between the condenser bulbs and the "dry ice." The vapor condensed in D flowed down into the bulb

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[1] Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, 1925, p. 3.

[2] Sameshima, This Journal, 40, 1482 (1918).

F, which had a capacity of about 4 cc. The bulb ordinarily filled within three minutes after the liquid had begun to boil in A and then overflowed through G back into A.

With the aid of the carboys, H and J, which functioned as stabilizers, the pressure was maintained constant during a run by means of the manometer K and a rotary oil pump. When the pressure had been lowered by the pump to a point where the liquid in A boiled at the desired temperature, the platinum wire L, sealed through a small glass tube and attached to a length of copper wire, was adjusted so that its end was at the top of the mercury column, the adjustment being made by sliding the copper wire through the soft wax seal X. This wire and the wire sealed into the manometer at K were connected through a relay, which turned the pump off and on as the mercury column made or broke contact with the wire L at its surface, the pressure thus being kept so constant that no variations could be observed on the manometer N.

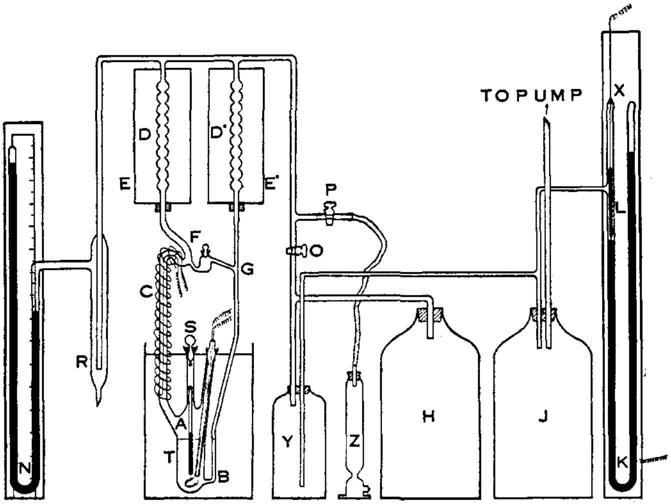

Fig. 1.—Apparatus for vapor pressure measurements.

In order to avoid pressure gradient between A and the manometer N, the tubing used was, for the most part, of 10-mm. internal diameter. The trap R was inserted to keep any liquid which might get into the upper part of the apparatus from running down into the manometer, but this precaution proved unnecessary. The stopcocks O and P were employed to open the main apparatus to atmospheric pressure, while maintaining low pressure in the carboys when desired. Bottles Y and Z contained calcium chloride.

A measurement was carried out in the following manner. About 100 cc. of a mixture, the composition of which was approximately that desired, was placed in Vessel A. The pressure was gradually reduced until, when the electrical stirrer was turned on, the liquid began to boil. The pressure was then regulated until the thermometer constantly indicated the desired temperature. The liquid was allowed to boil for some time, the temperature being kept under careful surveillance. It was found that five or ten minutes were normally sufficient for the attainment of equilibrium conditions, but, for the sake of safety, thirty or forty minutes were usually allowed. The liquid condensed in F now had the composition of the vapor in equilibrium with the liquid in A; 3- or 4-cc. samples were pipetted out of A and F and analyzed by the measurement of their refractive indices as was done by Zawidski.[3] If the mole fractions of the two components of the liquid in F were A and B and the total pressures read on Manometer N were P, the partial pressures of the liquid in Vessel A were AP and BP.

Because of deviations from the ideal gas laws, the partial pressures calculated in this manner are not identical with the pressures which the vapors of the components would exert if allowed to occupy the same volume separately.[4] The results of other investigators have shown that these deviations cause errors of less than 1% in the apparent molecular weights of a large number of vapors measured between 70 and 100°, and Sameshima[2] has found the deviations in mixtures of ether and acetone vapors at 25° to be so small as to be without appreciable effect upon the values of the partial pressures calculated upon the assumption of the applicability of Dalton's law. Even though the deviations may have an appreciable effect in some of the mixtures here studied, the effect should be too slight to impair the use of the results in the examination of Langmuir's theory.

The indices of refraction for the sodium D line were measured with a Pulfrich refractometer, a temperature of 20°, constant within 0.01°, being obtained by a flow of water from carefully adjusted thermostats. The probable error of a measurement was 0.00007. For a given system from twelve to fifteen mixtures of known composition were made up and measured. The molar composition of the mixture corresponding to the observed refractive index if the refractive index were a linear function of composition was calculated and subtracted from the known composition. The differences between the theoretical and the known mole fractions obtained in this way were plotted against the theoretical mole fractions to give a curve which was used to correct the theoretical composition of an unknown mixture of the two liquids calculated from the refractive index on the assumption that the latter was a linear function of the composition. The accuracy of this method of analysis depended upon the precision of the index measurements and upon the difference between the indices of the two components of the mixture. The probable error in the mole fraction was usually 0.001–0.003. The probable error of the partial pressure data was somewhat dependent upon the nature of the liquids under investigation and upon the temperature of the measurement, but was normally 2 ± 1 mm.

In order to ascertain whether or not the apparatus functioned properly, the system benzene–carbon tetrachloride was investigated, the partial pressures being found to duplicate the measurements of Zawidski within the experimental error.[3] The vapor pressure–temperature curves obtained for a number of the pure substances under investigation were found to agree well with the data in the literature.

Purification of Materials

The purification of the materials used is described below. Under each material are given the values of physical constants which serve as criteria of purity. In addition to the boiling point and the refractive index for the sodium D line at 20°, the melting point and the density were occasionally measured. The vapor pressures measured at several temperatures agree well with those given in Landolt-Börnstein, "Tabellen," 5th ed., Berlin, 1923, as previously remarked.

***n*-Hexane.**—A synthetic product obtained from the Eastman Kodak Company was washed repeatedly with slightly diluted sulfuric acid, then with alkaline permanganate solution, dried over sodium, and distilled; b. p. 68.8°; $d_4^{20} = 0.6600$; $n_D^{20} = 1.37508$.

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[3] Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

[4] Dolezalek and Schulze, *Verhandl. deut. physik. Ges.*, 14, 1091 (1912); Schulze, *ibid.*, **15**, **488** (1913); *Physik. Z.*, **14**, **922** (1913).

n-**Heptane.**—Material obtained from the Ethyl Gasoline Corporation was found to require no purification; m. p. −90.5°; b. p. 98.4°; d_4^{20} = 0.6838; n_D^{20} = 1.38767.

Carbon Tetrachloride.—The best product obtainable from Merck was dried over fused calcium chloride and distilled. A fraction boiling constantly at 76.4° was employed; b. p. 76.4°; n_D^{20} = 1.46026.

n-**Butyl Chloride.**—A material of good quality obtained from the Eastman Kodak Company was refluxed gently for half an hour over an equal volume of concentrated sulfuric acid, distilled, washed with water until free of sulfate, dried over fused calcium chloride and fractionated. A fraction boiling from 77.3 to 77.6° was employed; n_D^{20} = 1.40173.

Ethyl Bromide.—A material obtained from the Eastman Kodak Company was washed several times with cold, concentrated sulfuric acid, then with water until all sulfate was removed, dried over fused calcium chloride and fractionated. The fraction boiling at 38.3–38.4° was employed. Two lots thus prepared gave values of 1.42403 and 1.42408 for the refractive index; d_4^{20} = 1.4586; n_D^{20} = 1.42405.

Ethyl Iodide.—A material obtained from Merck was washed with a very dilute caustic potash solution until decolorized. Several drops of the caustic solution were added in excess and the material was then separated, thoroughly washed with water, dried over fused calcium chloride and fractionated. A fraction distilling without any perceptible change in temperature at 73.2° was employed. The vapor pressure of this material, 355.0 mm. at 50°, differs from Regnault's value 364.0 mm. given in Landolt-Börnstein, "Tabellen," but agrees satisfactorily with the more accurate value of Zawidski,[3] 353.4 mm.; b. p. 73.2°; d_4^{20} = 1.9292; n_D^{20} = 1.51330.

n-**Butyl Bromide.**—Material obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, then with sodium carbonate solution, dried over fused calcium chloride and fractionated. A fraction boiling from 100.4° to 100.6° was employed; n_D^{20} = 1.43984.

Ethyl Alcohol.—Ordinary 95% alcohol was refluxed over quicklime to which a small stick of sodium hydroxide was added. The refluxing was continued for 75–100

TABLE I

VAPOR PRESSURES OF PURE LIQUIDS (MM. OF HG)

t, °C.	Hexane	Ethyl iodide	Butyl chloride	Butyl bromide
20.0	...	...	31.3	82.3
30.0	186.1	162.6	51.0	130.2
40.0	275.7	244.8	52.2	198.5
50.0	400.6	355.0	126.7	295.8
60.0	568.0	505.9	189.6	420.7
70.0	...	...	271.3	591.4

t, °C.	Heptane	*t*, °C.	Carbon tetrachloride	*t*, °C.	Ethyl alcohol
22.7	41.4	19.2	88.0	22.7	51.8
30.0	58.2	32.4	156.0	32.6	90.1
30.3	58.8	41.2	222.8	35.7	105.6
38.4	86.0	50.0	312.0	41.8	145.1
50.0	141.1	60.8	452.8	57.2	306.8
51.2	150.0	68.7	586.4	59.6	342.7
61.2	220.0	76.4	760.0	69.4	531.1
69.5	297.8	..	...	78.1	747.6
70.0	301.4	..	...	78.4	760.0
79.5	419.7	..	...	..	...
98.4	760	..	...	..	...

TABLE II

PARTIAL VAPOR PRESSURES OF BINARY MIXTURES (MM. OF HG)

(A) 50° (B)
Hexane–Heptane

B	p_A	p_B
0	400.6	0
0.1136	359.3	14.2
.2787	282.1	43.2
.3583	252.0	51.9
.4328	222.9	58.7
.5163	187.7	73.9
.6702	120.4	99.3
.8586	53.9	123.1
1.0000	0	141.1

(A) 50° (B)
Heptane–Butyl chloride

0	140.0	0
0.0496	135.2	17.2
.1128	129.4	37.8
.1580	118.9	63.9
.2870	105.5	96.2
.3853	93.9	123.7
.4462	85.6	143.4
.5273	72.4	167.2
.5955	63.8	184.4
.6386	57.6	197.6
.6979	50.4	212.1
.7797	39.5	231.7
.8645	25.2	255.0
.9565	11.5	277.3
1.0000	0	294.2

(A) 50° (B)
Carbon Tetrachloride–Heptane

0	308.5	0
0.0351	301.5	2.6
.1008	279.7	15.7
.1874	254.2	28.2
.2677	231.9	39.2
.3504	206.9	50.0
.4300	183.9	60.8
.4988	162.6	69.7
.5676	142.4	78.3
.6431	120.4	87.0
.6976	104.9	93.8
.8286	59.8	114.2
.9017	34.5	125.3
.9668	11.7	135.0
1.0000	0	140.5

(A) 50° (B)
Heptane–Ethyl iodide

B	p_A	p_B
0	141.1	0
0.0672	131.6	35.7
.1095	124.8	64.2
.1692	116.4	92.4
.2253	108.1	119.9
.3116	99.5	154.1
.3793	90.8	180.1
.4277	85.1	196.2
.4993	80.2	215.3
.5119	76.4	222.4
.5791	72.6	236.5
.6641	60.8	260.1
.7696	47.8	285.8
.8272	39.9	301.2
.8783	37.6	309.4
.9426	16.3	336.3
.9805	6.3	347.7
1.0000	0	354.1

(A) 50° (B)
Butyl chloride–Butyl bromide

0	295.8	0
0.0501	276.5	5.4
.1380	250.9	16.8
.2498	217.2	32.5
.3280	194.3	41.8
.4222	167.2	53.4
.4878	151.3	58.2
.5009	145.7	61.4
.5481	126.9	72.8
.6334	100.5	83.5
.7082	83.4	90.1
.7554	70.6	95.8
.8226	50.0	103.5
.8924	27.9	113.6
.9583	10.7	120.9
1.0000	0	126.7

(A) 30° (B)
Heptane–Ethyl iodide

B	p_A	p_B
0	58.2	0
0.0927	54.6	27.3
.1628	50.9	42.6
.2458	47.5	58.1
.2965	44.4	69.6
.3548	42.1	79.3
.4134	39.5	87.9
.4836	37.0	95.9
.5281	33.4	103.5
.5738	31.9	109.0
.6124	31.6	112.1
.7056	24.2	125.6
.7743	20.9	133.7
.8325	17.4	140.6
.8892	12.8	147.1
1.0000	0	161.8

(A) 30° (B)
Ethyl bromide–Ethyl iodide

0	560.9	0
0.0406	538.2	3.8
.0895	509.6	13.9
.1445	479.8	24.4
.2096	442.0	36.7
.2579	411.7	46.4
.3131	384.0	56.0
.3557	358.7	64.3
.3941	334.2	72.4
.4327	312.5	79.8
.4683	292.7	87.0
.4948	274.2	92.5
.5523	242.3	103.6
.5786	226.9	108.9
.6103	207.6	114.6
.6419	190.5	119.7
.6615	180.9	123.0
.7027	159.1	129.2
.7402	136.9	133.8
.8253	97.0	136.5
.8693	73.7	148.3
.9161	35.1	155.5
1.0000	0	161.8

TABLE II (*Concluded*)

(A) 50° (B)
Heptane–Butyl bromide

B	p_A	p_B
0	140.0	0
0.1171	125.8	19.6
.2362	110.6	37.8
.3329	98.4	51.1
.4323	86.1	62.8
.5182	74.8	72.6
.5836	66.4	80.0
.6333	59.6	85.9
.6588	57.3	87.5
.7123	49.0	94.5
.7935	37.2	102.6
.8805	23.3	112.2
.9521	9.6	121.2
0	0	127.0

(A) 30° (B)
Heptane–Ethyl bromide

B	p_A	p_B
0	58.0	0
0.0923	55.7	66.3
.2176	48.6	151.1
.2843	44.1	195.7
.3246	43.4	217.6
.4621	34.9	302.2
.4723	34.0	306.3
.6219	26.7	377.3
.7985	17.4	456.8
.9540	7.5	536.4
1.0000	0	567.8

(A) 30° (B)
Hexane—Heptane

B	p_B	p_B
0	186.1	0
0.1136	163.9	7.1
.2012	147.4	11.4
.3583	118.5	21.4
.4328	103.7	26.1
.5314	84.8	31.5
.6320	65.2	38.9
.6953	52.7	42.3
.8339	27.6	50.1
1.0000	0	58.0

hours, the lime being renewed four or five times. An exceptionally good quality of powdered lime was finally used and the material distilled off; b. p. 78.4–78.5°; n_D^{20} = 1.36130.

n-Butyl Alcohol.—Material obtained from the Commercial Solvent Corporation was refluxed over lime and twice fractionated. A fraction boiling between 117.1 and 117.2° was employed: n_D^{20} = 1.39942.

Results

The vapor pressures of several pure liquids are given in Table I and in Table II are the partial vapor pressures of the binary mixtures. In a system A–B the less polar liquid is, as a rule, designated as A, but where there is no polarity or little difference in polarity, other considerations may determine the order. For each system the column under B gives the mole fraction of component B in the mixture and the columns under p_A and p_B give the partial pressures of components A and B over the mixture.

Langmuir[1] has employed the principle of independent surface action to derive the following expressions for the partial vapor pressures of a mixture of two liquids, A and B

$$p_A = P_A A e^{S_A \varphi \beta^2/kT} \text{ and } p_B = P_B B e^{S_B \varphi \alpha^2/kT} \qquad (1)$$

in which p_A and p_B are partial pressures of Components A and B, respectively; P_A and P_B are vapor pressures of the pure liquids A and B, respectively; A and B are mole fractions of components A and B; S_A and S_B are surface areas of molecules of A and B; α and β are surface fractions of Components A and B

$$\alpha = \frac{S_A A}{S_A A + S_B B} \text{ and } \beta = \frac{S_B B}{S_A A + S_B B} \qquad (2)$$

k is the Boltzmann constant = 1.372×10^{-16}; T is the absolute temperature; and φ the "mixture energy," is a constant, dependent upon the molecular surface energies and independent of concentration.

For a mixture of two liquids, A and B, the molecules of one of which substances are enclosed by two kinds of surface, A and C, those of the other being enclosed by surfaces B and D

$$\varphi = ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd} - ac\gamma_{ac} - bd\gamma_{bd} \tag{3}$$

in which a and c are the fractions of the surface of molecule A which are A-surface and C-surface, respectively, and b and d are the fractions of the surface of molecule B which are B-surface and D-surface, while γ_{ab} is the energy per sq. cm. of interface between surfaces A and B, γ_{ad} is the energy per sq. cm. of interface between A and D, etc.; φ is shown to be the energy per sq. cm. of molecular surface required for the transfer of a molecule of A from pure liquid A to pure liquid B or for the transfer of a molecule of B from pure liquid B to pure liquid A. The somewhat hypothetical surface areas of the molecules, expressed in square Ångstroms (10^{-16} cm.^{2}) are calculated from the densities by supposing that the liquids consist of close-packed spheres and the fractions of molecular surface, a, b, c, etc., used in the present paper are estimated from a comparison of the values of $V^{2/3}$ for the different groups, where V is the molar volume of the group at the boiling point of the liquid. It is assumed that the areas of the different kinds of surfaces in contact with one another are proportional to the fractions of the molecular surfaces involved, thus being calculable on the basis of a random orientation of the molecules. The value of γ for a certain kind of surface in a molecule is regarded as independent of the nature of the rest of the molecule. Thus γ should be the same for a hydrocarbon surface whether it be that of the heptane molecule or of the ethyl group in the ethyl alcohol molecule or of the butyl group in butyl chloride. Similarly, the energy per sq. cm. at a chlorine–hydrocarbon interface should be the same whether the chlorine is in carbon tetrachloride or butyl chloride, and whether the hydrocarbon is in another butyl chloride molecule or an alcohol or a heptane molecule. For binary mixtures in which fewer kinds of surface are involved, Equation 3 is simplified by the elimination of some of the terms, as will appear when it is applied to the results of the present investigation, in which only two or three kinds of surface are generally involved. This makes it possible to calculate the values of γ when φ is obtained for different mixtures.

Equation 1 may be written in the form

$$\varphi = 2.303\,\frac{kT}{S_A\beta^2}\log\frac{p_A}{P_A A} \quad \text{and} \quad \varphi = 2.303\,\frac{kT}{S_B\alpha^2}\log\frac{p_B}{P_B B} \tag{4}$$

and used to calculate the value of φ, which, if the assumptions of the theory were rigidly correct, should be constant and the same for both partial pressure curves. Since the values of φ are greatly affected by experimental error, particularly at the ends of the partial pressure curves, it has seemed best to interpolate the values of p_A and p_B at intervals of 0.1 in the mole fraction and, for the sake of comparison, to designate the values of

φ calculated from the one partial pressure curve as φ_A and those from the other curve as φ_B. In Table III the first column gives the mole fractions of Component B from 0.1 to 0.9, and the succeeding columns give, for different systems, the values of p_A/p_AA and p_B/p_BB and the values of φ calculated from them. The deviations of p_A/p_AA and p_B/p_BB from 1 measure the deviations of the mixtures from Raoult's law.

TABLE III

VALUES OF p_A/P_AA, p_B/P_BB AND φ

	(A) 50° (B) Carbon tetrachloride–heptane P_A = 308.5 P_B = 140.5				(A) 50° (B) 50° Heptane–butyl chloride P_A = 140.0 P_B = 294.2			
B	p_A/P_AA	p_B/P_BB	φ_A	φ_B	p_A/P_AA	p_B/P_BB	φ_A	φ_B
0.1	1.008	1.068	1.89	0.25	1.032	1.156	1.15	0.57
.2	1.014	1.068	.86	.34	1.044	1.156	2.41	.71
.3	1.028	1.043	.81	.30	1.060	1.132	1.90	.77
.4	1.040	1.015	.68	.15	1.071	1.095	1.45	.75
.5	1.057	0.996	.65	−.01	1.092	1.074	1.17	.86
.6	1.077	.996	.64	−.02	1.124	1.053	1.05	.92
.7	1.107	.991	.68	−.08	1.178	1.055	1.05	1.05
.8	1.110	.992	.46	−.19	1.250	1.018	1.07	1.20
.9	1.151	.996	.64	−.32	1.358	1.012	1.05	2.94

	(A) 30° (B) Heptane–ethyl bromide P_A = 58.0 P_B = 567.8				(A) 50° (B) Heptane–butyl bromide P_A = 140.0 P_B = 127.0			
0.1	1.034	1.285	5.22	1.21	1.014	1.402	5.80	1.42
.2	1.078	1.221	4.64	1.08	1.028	1.299	2.79	1.34
.3	1.132	1.196	4.06	1.22	1.047	1.237	1.98	1.38
.4	1.149	1.180	3.48	1.42	1.072	1.165	1.58	1.29
.5	1.241	1.133	2.90	1.41	1.103	1.114	1.41	1.27
.6	1.293	1.080	2.32	1.24	1.143	1.075	1.28	1.27
.7	1.322	1.039	1.74	1.00	1.214	1.048	1.31	1.41
.8	1.379	1.009	1.16	0.49	1.300	1.016	1.29	1.03
.9	1.550	0.990	0.58	−1.94	1.428	0.998	1.33	−0.12

	(A) 50° (B) Heptane—ethyl iodide P_A = 141.1 P_B = 354.1				(A) 30° (B) Ethyl bromide—ethyl iodide P_A = 560.9 P_B = 161.8			
0.10	.984	1.680	−1.79	2.54	0.9964	1.051	−1.37	0.25
.2	.997	1.524	−0.09	2.42	.9962	1.082	−0.37	.50
.3	1.019	1.413	1.08	2.42	.9933	1.092	−.29	.75
.4	1.063	1.313	1.82	2.40	.9806	1.128	−.43	1.39
.5	1.119	1.220	1.99	2.34	.9627	1.162	−.61	2.52
.6	1.204	1.139	2.10	2.19	.9538	1.149	−.53	3.66
.7	1.345	1.082	2.28	2.17	.9508	1.130	−.42	5.82
.8	1.506	1.034	2.18	1.90	.9538	1.097	−.30	10.1
.9	1.758	1.008	2.17	1.66	.9449	1.058	−.28	24.1

The hexane–heptane mixtures are not included in Table III, because the linearity of the partial pressure curves shows that φ is 0. This supports the assumption involved in Langmuir's treatment that the energy, γ, between like surfaces, such as R–R, Br–Br, etc., is 0, since, for this system, Equation 3 simplifies to $\varphi = \gamma_{R-R}$ and $\varphi = 0$. The butyl chloride–butyl bromide mixtures are omitted from Table III because of the approximation of their curves to linearity and the heptane–ethyl iodide results at 30° are

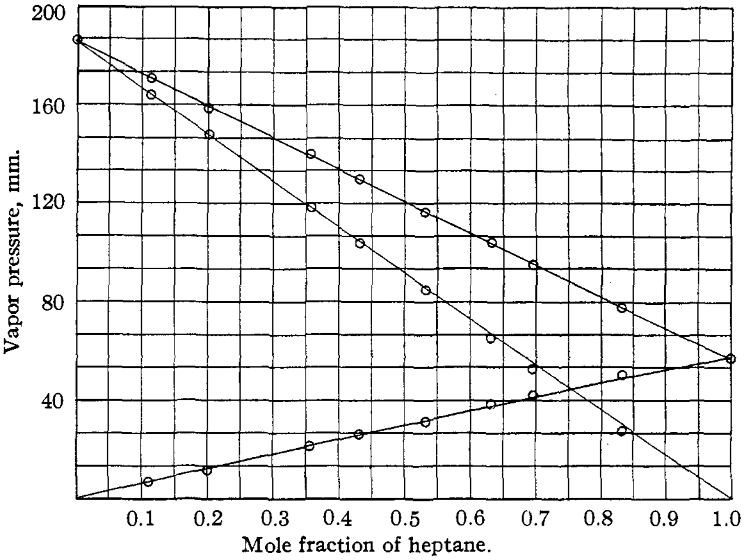

Fig. 2.—Hexane (A)–heptane (B) at 30°.

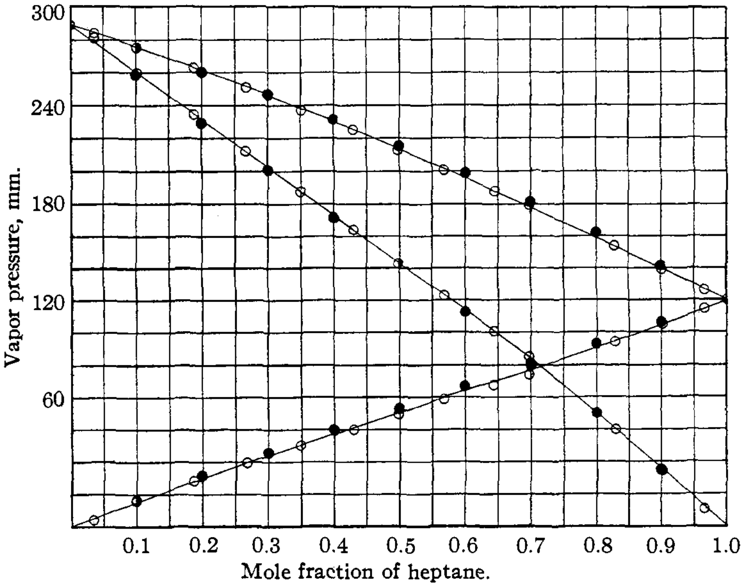

Fig. 3.—Carbon tetrachloride (A)–heptane (B) at 50°.

also omitted because of their resemblance to those at 50°, the values of φ at 30 and 50° differing by no more than the probable error. The results are represented graphically in Figs. 2–9, in which the vapor pressures in mm. of mercury are plotted as ordinates against the mole fractions of

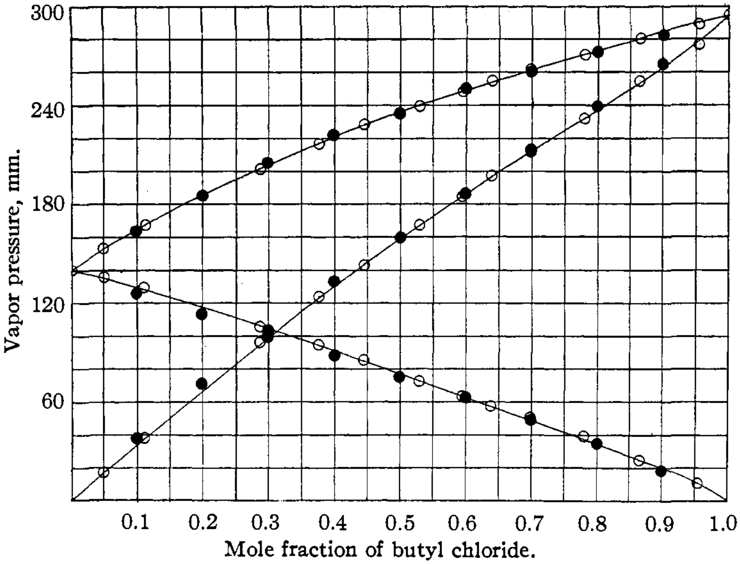

Fig. 4.—Heptane (A)–butyl chloride (B) at 50°.

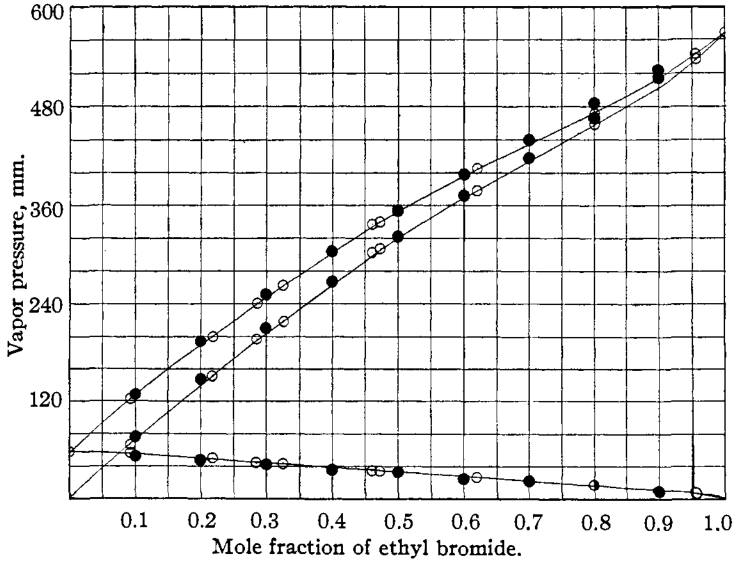

Fig. 5.—Heptane (A)–ethyl bromide (B) at 30°.

Component B as abscissas. The total pressure curve is, of course, uppermost and the partial pressure curve of Component B starts at the lower left-hand corner, while that of A starts at the lower right-hand corner. The experimental points are shown as hollow circles and the points calculated from φ as filled circles. Where the vapor pressure curves are straight, φ being 0, no calculated points are shown as they would obviously fall on the straight experimental lines. In the ethyl bromide–ethyl iodide system (Fig. 9) the departure from linearity is so slight as to render uncertain the value of φ, which is small in most of the mixtures and dependent upon concentration, as indicated by the curve in which the values of φ obtained from the pressures of the ethyl iodide are plotted as ordinates, shown at the right of the diagram, against the mole fractions of ethyl iodide as abscissas. In spite of the smoothness of this curve, great importance cannot be attached to it because φ is calculated from such small deviations.

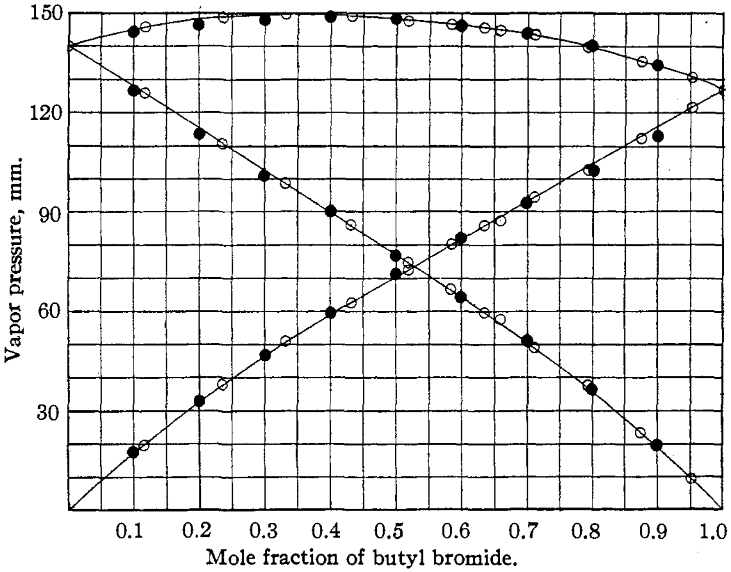

Fig. 6.—Heptane (A)–butyl bromide (B) at 50°.

Since the values of φ calculated from individual vapor pressures are subject to a considerable variation, φ may advantageously be obtained by plotting the values of $\log p_A/p_AA$ in Equation 4 as ordinates against those of β^2 as abscissas, or of $\log p_B/p_BB$ against those of α^2. If φ is constant, a straight line is thus obtained, the slope of which, when divided by $S_A/2.303kT$ or $S_B/2.303kT$, as the case may be, gives φ. The curves thus obtained for the heptane–ethyl iodide system show a tendency toward a slight deviation from linearity to give a curve with a point of inflection.

This deviation from linearity tends to increase with increasing difference in the polarity of the components. However, the curves are approximately linear for the systems heptane–butyl bromide, heptane–butyl chloride and heptane–carbon tetrachloride, and show no great deviation for heptane–ethyl bromide, although here the curvature is more pronounced. The curves for the ethyl bromide–ethyl iodide system show no approach to linearity, so that no constant value of φ can be obtained to use in calculating γ. The value of φ for hexane–heptane is 0 and for butyl chloride–butyl bromide so small as to be indistinguishable from 0. These values of φ are used to calculate the values of γ shown in Table IV, in which the

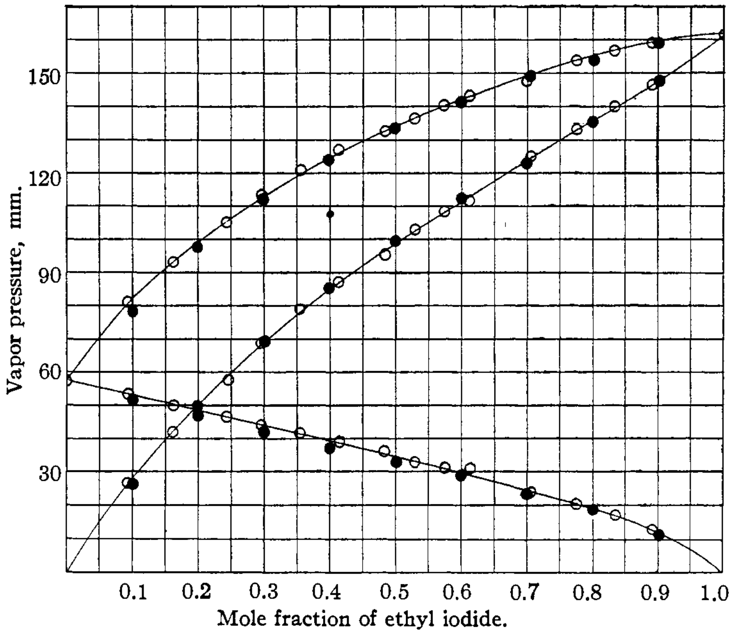

Fig. 7.—Heptane (A)–ethyl iodide (B) at 30°.

TABLE IV

VALUES OF SURFACE ENERGY, γ

Substance	Surface area (A^2)	Inter-face	System	φ	γ (ergs./cm.^{2})	γ (ergs./cm.^{2}) Langmuir
C_7H_{16}	154	R-Cl	C_7H_{16}-CCl_4	0.6	0.6	4.1
C_4H_9Cl	123	R-Cl	C_7H_{16}-C_4H_9Cl	1.14	10.0	
C_2H_5Br	99	R-Br	C_7H_{16}-C_2H_5Br	1.6	6.8	10.0
C_4H_9Br	125	R-Br	C_7H_{16}-C_4H_9Br	1.36	9.2	
C_2H_5I	104	R-I	C_7H_{16}-C_2H_5I (30°)	2.52	7.9	13.7
Cl	41.5	R-I	C_7H_{16}-C_2H_5I (50°)	2.29	7.2	
Br	48.1	Cl-Br	C_4H_9Cl-C_4H_9Br	0+	0+	
I	58.8	Cl-I		..	..	4.1

last column gives, for comparison, the values estimated by Langmuir. The molecules or radicals and their areas used in the calculation of the sixth column are shown in the first two columns. The calculation of the areas is, at best, a rough approximation, but, when the arbitrary character of the whole method of employing the molecular areas is considered, it becomes evident that the values assigned can have little significance as absolute quantities.

The value of $\gamma_{R\text{-}Cl}$ determined from the heptane–carbon tetrachloride system should be the most accurate value in Table IV, for only two kinds of surface being involved in the system, Equation 3 simplifies to $\varphi = \gamma_{R\text{-}Cl}$, thus eliminating the doubtful fractions of surfaces. The value of $\gamma_{R\text{-}Cl}$ determined from the heptane–butyl chloride system is very dependent upon the surface areas used, as shown by the fact that, when surface areas consistent with those of Langmuir are taken, a value of 37.0 is obtained instead of 10.0. It is certain that the great difference between the value of $\gamma_{R\text{-}Cl}$ obtained from the carbon tetrachloride–heptane system and that from the heptane–butyl chloride system can be due only in part to experimental error or the use of incorrect surface areas, and must, therefore, be attributed to a more fundamental cause. The values of $\gamma_{R\text{-}I}$ obtained from the heptane–ethyl iodide system, because of the different surface areas used, differ from Langmuir's figure which, in this one case, could be calculated directly from experimental data. When the values of the surface areas used by Langmuir are employed, good agreement is obtained at

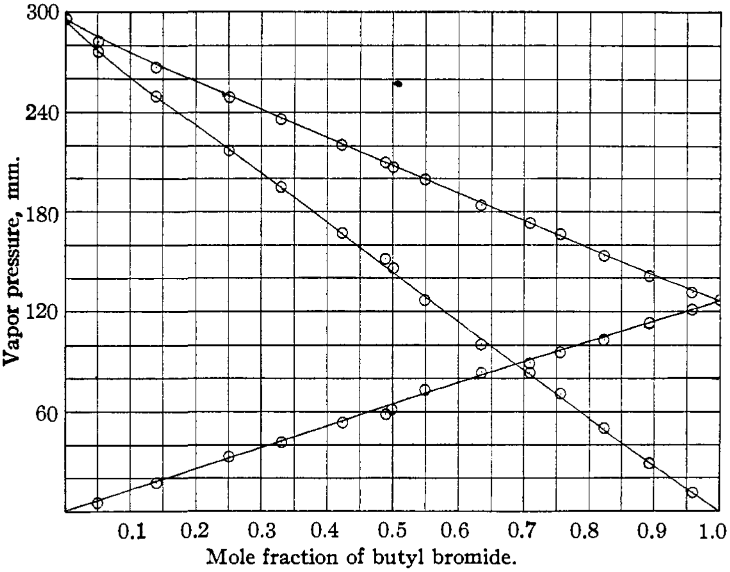

Fig. 8.—Butyl chloride (A)–butyl bromide (B) at 50°.

30°. For the system butyl chloride–butyl bromide, φ is only approximately 0 and one can, therefore, say only that $\gamma_{\text{Cl-Br}}$ is small, presumably lower than Langmuir's value of 4.1 for $\gamma_{\text{Cl-I}}$, as the surface energy between chlorine and bromine might be expected to be less than that between chlorine and iodine.

These systems show linearity, in some cases very approximate, when log p_A/p_AA is plotted against β^2 and log p_B/p_BB against α^2, and the experimentally determined vapor pressures may be satisfactorily reproduced by the use of a single value of φ, in spite of the considerable variation shown by the individual values of φ in Table III. The definitely established difference between the value of $\gamma_{\text{R-Cl}}$ obtained from the heptane–carbon tetrachloride system and that from the heptane–butyl chloride system is significant since it indicates that the energy between surfaces is not always dependent only upon the kinds of surface involved, thus showing that the principle of independent surface action is limited in its applicability. The carbon tetrachloride molecule has no electric moment, while the butyl chloride molecule contains a large dipole.[5] The superposition of the forces of the dipole upon those of the chlorine surface presumably causes $\gamma_{\text{R-Cl}}$ as measured for the heptane–butyl chloride mixtures to be different from the energy between hydrocarbon and chlorine surfaces where no dipole is present. As these are dipoles of the same order of magnitude present in the other alkyl halides here studied, it is probable

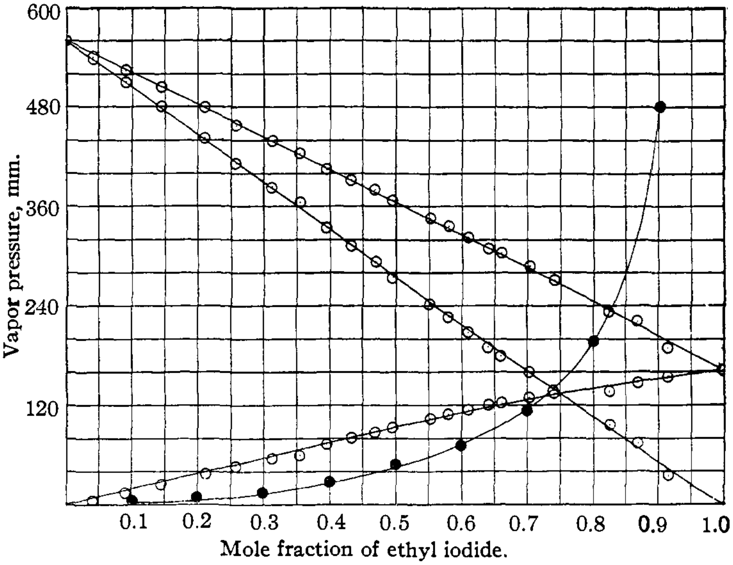

Fig. 9.—Ethyl bromide (A)-ethyl iodide (B) at 30°.

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[5] Smyth, *Chem. Reviews* (1929).

that the values of γ obtained from these systems are all influenced more or less by the fields due to these dipoles, which may also affect the results by bringing about molecular orientation. It is apparent that the lack of generality of the principle of independent surface action and the frequent absence of random orientation, as well as the uncertainty in estimating surface areas, prevent the accurate determination of absolute values for the surface energies and limit the applicability of the theory. These results will be further discussed in a subsequent paper, where they will be contrasted with the behavior of systems containing an alcohol as one component.

Summary

An apparatus is described for the measurement of the partial vapor pressures of binary liquid mixtures by a dynamic method. The pressures of eight different combinations of supposedly normal liquids and of several of the pure components are tabulated.

The data are used to examine Langmuir's theory of molecular surface energies, which is found to have an approximate applicability. Deviations from the theoretical behavior are ascribed to the presence of electric doublets in the molecules.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

MOLECULAR ORIENTATION AND THE PARTIAL VAPOR PRESSURES OF BINARY LIQUID MIXTURES.
II. SYSTEMS CONTAINING AN ALCOHOL

BY C. P. SMYTH AND E. W. ENGEL

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The apparatus described in Part I was used to determine the partial pressures of six different binary systems containing an alcohol as one of the components. The purification of the materials and the values of the physical constants used as criteria of their purity have been given in Part I.[1] Because of the somewhat different behavior of these systems containing an alcohol, it has been deemed advisable to treat them in a separate paper and contrast the results with those given by the supposedly normal liquids discussed in Part I. The experimentally determined partial pressures, p_A and p_B, of the components A and B are recorded in Table I, the composition of the mixtures being given in terms of the mole fraction B of the alcohol. The values of the partial pressures are interpolated graphically at intervals of 0.1 in the mole fraction of B and used to calculate the values of p_A/p_AA, p_B/p_BB, φ_A and φ_B, as was done in Part I,[2] the results

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[1] Smyth and Engel, THIS JOURNAL, 51, 2646 (1929).

[2] See Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, 1925, p. 3.