

On the Properties of Liquid Mixtures - Part II

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uniformly about the centre of the cylinder or sphere, the curves described by the trails of images will be equiangular spirals.

DISCUSSION.

Dr. S. P. THOMPSON said the method and the results obtained would find useful application in the solution of many allied problems.

XVI. *On the Properties of Liquid Mixtures.*—Part II. By R. A. LEHFELDT, *Professor of Physics at the E. London Technical College*.*.

IN a previous article (Phil. Mag. (5) vol. xl. p. 398) an attempt was made to follow out the consequences of a certain thermodynamic relation between the composition of a liquid mixture, and that of the vapour in equilibrium with it, and the saturation pressure of the system. Experiments were there described on mixtures of benzene with ethyl and methyl acetates in which a small fraction of each mixture was distilled, as nearly as possible at a constant temperature, and the distillate analysed; these led to an empirical expression connecting the composition of liquid and vapour. Experiments were afterwards made to determine the vapour-pressure of similar mixtures by the dynamic method, but they led to unsatisfactory results owing to decomposition of the esters on prolonged boiling. I was able to resume the work in 1897, and then chose more stable compounds to work on, viz., benzene and toluene mixed with carbon tetrachloride, as types of normal organic compounds, and benzene and toluene mixed with ethyl alcohol, as type of a so-called "associated" liquid. The experiments to be described here were carried out at the Davy-Faraday laboratory, which the managers of the Royal Institution very obligingly placed at my service.

Two other papers on the same subject, which appeared about the same time as my earlier one, call for some notice.

* Read March 11, 1898.

These are by C. E. Linebarger (*Journ. of Amer. Chem. Soc.* vol. xvii.) and by M. Margules (*Wien. Ber.* vol. civ.).

Linebarger made measurements of the vapour-pressures of certain liquid mixtures, and of the way in which the two components shared the pressure between them. He did not attempt to relate his results to the deductions of thermodynamics, but merely to obtain empirical generalizations. The method he adopted is at first sight a very promising one, as it allows of the determination of both total and partial pressures in the same experiment; it consisted in drawing a measured volume of air through the liquid mixture, and analysing by combustion the vapour which the air carried away with it. The method has been applied successfully to find the vapour-pressure of aqueous solutions of low volatility, but it is not so suitable to the present case, as in Linebarger's experiments the vapour-pressure was sometimes as high as 300 mm., and the inaccuracies of it appear to increase out of proportion to the pressure to be measured. Linebarger tested his apparatus by preliminary measurements of pure liquids: finding for instance, for ethyl iodide 199 mm. against Regnault's 206, and for chloroform 290.1 against 301.1. This he calls a "most excellent correspondence." I tried the method before reading the account of his results, and found similar discrepancies of one or two per cent., so that it can evidently not be regarded as satisfactorily worked out as yet. It has also the disadvantage of being so slow that it is impossible to get numerous data. I have, therefore, preferred to revert to the better known methods, and nearly all the observations mentioned below were taken by the "dynamic" method.

Linebarger gives an empirical result which may be considered along with the observations contained in this paper: that strictly normal liquids, such as benzene and toluene, have in mixtures a partial pressure simply proportional to the molecular percentage of them present in the liquid. It is important, as on it Linebarger bases a rule for determining the molecular complexity of liquids. To this point we shall have to revert.

Margules's paper consists only of deductions from the previous experiments of others; but it includes a theorem given

in my paper (*loc. cit.*) as well as several others; and in an appendix mentions that all these results have been forestalled in the very systematic thermodynamical studies of Duhem—a fact which I also had overlooked. Margules's chief new contribution is, therefore, the empirical formula he proposes for the relation between composition of liquid and vapour, as will be mentioned below.

Measurements of Vapour-Pressure.

The measurements made form two distinct groups, those of vapour-pressure and those of composition of vapour, which were carried out separately, but on material from the same source, and prepared in identical manner. The materials were as follows:—

Benzene.—Kahlbaum's thiophene-free: its boiling-point was nearly constant, but it was fractionated twice from calcium chloride, and then stood over sodium. B.p. (corrected and reduced to 760 mm.) = $80^{\circ}0$. Vapour-pressure at 50° = 270.9 mm. Density $\frac{18}{4} = 0.8803$. μ_D at 18° = 1.5024 by spectrometer.

Toluene.—Baird and Tatlock's purest. Fractionated from calcium chloride and stood over sodium. B.p. (corr. and red.) = $110^{\circ}0$. Vapour-pressure at 50° = 93.0 mm. Density $\frac{18}{4} = 0.8667$. μ_D at 18° = 1.4970.

Carbon Tetrachloride.—Baird and Tatlock. Slightly yellow when obtained; on fractional distillation it became colourless, and on redistilling the best fraction nearly the whole came over within $0^{\circ}1$. B.p. $76^{\circ}6$ (corr. and red.). Vapour-pressure at 50° = 310.2 mm. Density $\frac{18}{4} = 1.5979$. μ_D at 18° = 1.4618.

Ethyl Alcohol.—Baird and Tatlock's "absolute." Digested on a water-bath with lime and baryta till a yellow colour appeared; then distilled with special care to avoid moisture. B.p. (corr. and red.) = $78^{\circ}3$. Vapour-pressure at 50° = 219.5 mm. Density $\frac{18}{4} = 0.7929$. μ_D at 18° = 1.3622.

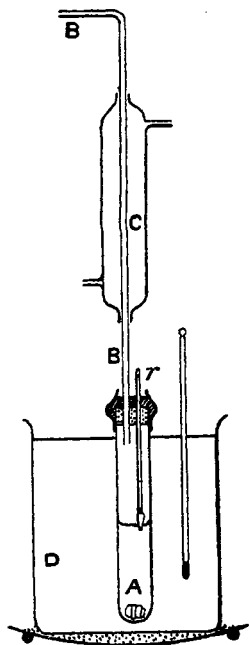
The density is not so low as it should be according to Mendeléef; but it is probable that if a purer alcohol had been

obtained it would have absorbed some moisture in the course of the inevitable manipulation of the mixtures. Distillation from sodium was also tried, but did not give any better results.

To measure the vapour-pressure of the mixtures, the dynamic method was adopted. The most interesting part of the apparatus is shown in the accompanying sketch (fig. 1); it consists of a boiling-tube A about 15 cm. \times 3, closed at the top by a cork with two holes. Through one passed the thermometer—a short one with milk glass scale 40° to 60° in $\frac{1}{2}$; its bulb was surrounded with a little cotton-wool, and an end of the wool hung down into the liquid, so that the bulb was always moist; if that is the case, and the stem does not touch the side of the boiling-tube, the readings are very trustworthy. Through the cork there passed also a tube B, about 9 mm. wide,

surrounded by a short condenser, bent at right angles above, and leading to (1) a mercury manometer, (2) a T-piece, of which the vertical limb passed into a Winchester, serving as a reservoir of air, and containing a little strong sulphuric acid; and the further limb a glass tap. The necks of the boiling-tube and of the winchester were surrounded by a short piece of wide rubber tubing each, and the corks drowned in mercury; the only other joints in the apparatus were the two rubber tubing joints of the manometer and the glass tap; it could be made absolutely air-tight without trouble. On

Fig. 1.



the far side of the glass tap was placed a T-piece leading to a hand air-pump on one side, and on the other into the atmosphere, through a long capillary glass tube which served to reduce the flow of air; the pressure in the apparatus could thus be adjusted with any degree of nicety. The boiling-tube

contained about 10 to 15 grams of liquid mixture, previously made up by weighing, and a piece of pumice-stone weighted with copper wire, to make the ebullition steady; although the thermometer was surrounded by vapour, its readings were never constant unless the liquid was boiling freely. Heat was applied by means of a water-bath, consisting of a two-litre beaker, heated over a sand-tray, with a small flame; this was provided with a stirrer and thermometer, and kept three or four degrees above the temperature at which the mixture boiled.

An experiment consisted in weighing out a mixture, taking its refractive index by the Pulfrich refractometer, placing in the boiling-tube, and after adjusting temperature and pressures, taking eight observations at temperatures rising from 45° to 55° , and then falling to 45° again, and taking the refractive index of the residue: the refractive index was throughout used as a means of analysis (as in the previous paper, *g. v.*), and it showed that no appreciable change of composition took place during the experiments.

The instruments used were the following:—(i.) A cathetometer (by Fuess) to read the manobарometer with. Its scale was taken as correct; and since readings were only taken to one-tenth of a millimetre, no difficulty was encountered. Pressures were in all cases corrected for temperature of the mercury, and reduced to sea-level in lat. 45° .

(ii.) Five thermometers, of which the most important were "A" of range 40° to 60° in $\frac{1}{5}$, used for the boiling-tube, and "B" of range -5° to $+35^{\circ}$ in $\frac{1}{5}$, used for the refractometer, both by C. E. Müller. Their errors, which were very small, were determined by comparison with the standards of the Reichsanstalt, nos. 7346 and 7347, belonging to the Davy-Faraday laboratory.

(iii.) Pulfrich refractometer of the old pattern (by Max Wolz). Measurements of the refractive indices of alcohol (1.36), carbon tetrachloride (1.46), and benzene (1.50) were taken by it and a small Schmidt and Haensch spectrometer. The values given by Pulfrich's table were thus found to be too low by 0.00620 for alcohol, 0.00613 for carbon tetrachloride, and 0.00615 for benzene. Accordingly 0.0062 was

added to the number from the table in each case. Measurements of the refractive index of the mixtures were always taken as near to 18° as possible (though unfortunately in the summer the room rose frequently to 21°): the temperature-coefficients were interpolated from the known coefficients of the pure substances (this involves very little error as the coefficients only vary from 0.00040 for alcohol to 0.00064 for benzene), and the readings reduced to the standard temperature.

An accuracy of the order 1 in 1000 was aimed at in the various measurements; but of course the final results are hardly reliable to that extent. To take a typical case, the saturation-pressure to be measured might be about 250 mm.: there is of course no difficulty whatever in reading the height of the mercury-column to one thousandth of that ($\frac{1}{4}$ mm.). The corresponding temperature needs to be known to about $\frac{1}{40}$ degree, since 1° would make about 10 mm. difference in pressure. The thermometer was read to $\frac{1}{50}$ by eye with certainty; and when the apparatus was in good working order, it kept constant to that extent. Again, to change the vapour-pressure by $\frac{1}{1000}$ (temperature constant) would need a change usually as great as $\frac{1}{500}$ or more in the composition; this would correspond to about $2'$ of arc on the refractometer—a quantity very easily observed. The composition of the mixture might alter by escape of the vapour past the condenser; this would be discovered by a comparison of the refractive index before and after the boiling—as a matter of fact, the change rarely exceeded $2'$: further, it would necessarily alter as some of the substance was present in the form of vapour, but the weight of vapour in the apparatus could not have exceeded $\frac{1}{250}$ of the weight of liquid, and as the composition of the vapour is never 30 per cent. different from that of the liquid, the evaporation of that quantity could not alter the composition of the remainder more than about $\frac{1}{800}$. The degree of accuracy thus anticipated appears to have been realized except in a few unfavourable cases, as will be seen from the following observation, which is given as a specimen, and to show the mode of reduction adopted.

Specimen Observation.

Weighing-bottle 11.3608 grms. }
 + toluene . . 17.1159 „ } 52.40 per cent. of CCl_4 .
 + CCl_4 . . 23.4510 „ }
 Refractometer before $40^\circ 16\frac{1}{2}'$ at $21^\circ.1$. Hence $\mu_{18} = 1.48817$.
 „ after $40^\circ 20\frac{1}{2}'$ at $21^\circ.8$. „ = 1.48809.

Height of		Pressure.	Obs. temp.	Corr. temp.	Log pressure.	Log p_{50} .
Barom.	Gauge.					
779.1	614.5	164.6	48.14	48.20	2.2164	2.2470
(779.4)	596.8	182.6	50.84	50.92	.2615	59
(779.6)	580.5	199.1	53.18	53.31	.2991	27
779.9	561.3	218.6	55.60	55.79	.3397	12
(779.6)	587.4	192.2	52.24	52.33	.2838	42
(779.4)	608.0	171.4	49.38	49.45	.2340	32
(779.2)	625.3	153.9	46.64	46.69	.1872	36
779.1	641.4	137.7	43.90	43.93	.1389	22
Mean =						2.2437

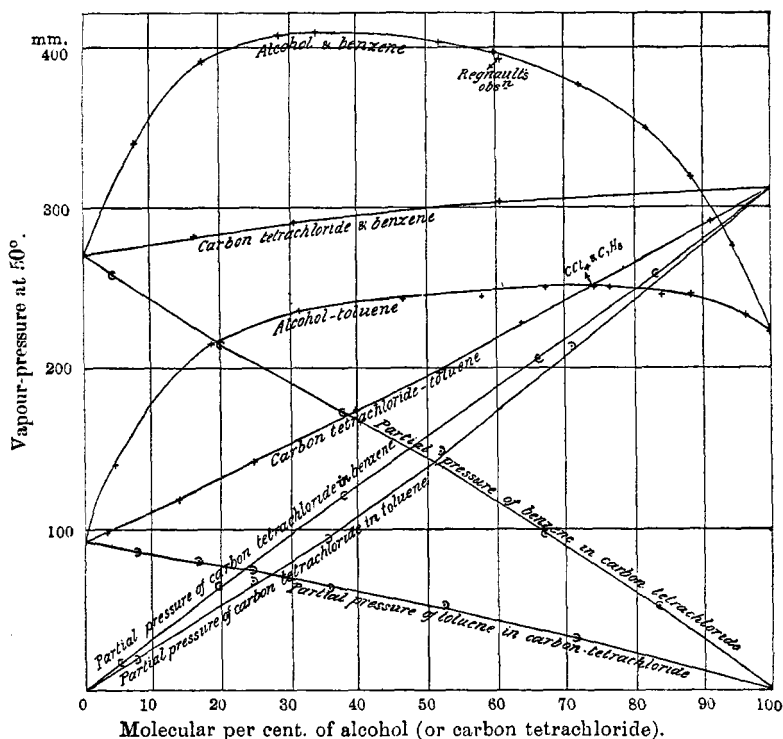
From curve $\frac{d(\log p)}{dt} = 0.01702$.

The observed temperatures and logarithms of the pressure were, in practice, plotted on a curve (which was approximately a straight line), and the values of $\log p_{50}$ and $d(\log p)/dt$ read off. Here the values of $\log p_{50}$ have been calculated from each observation and the assumed temperature-coefficient, in order to show the degree of concordance obtained. The probable error of $\log p_{50} = 0.0005$, whence $p_{50} = 175.3 \pm 0.1$. This reduced to 0° and sea-level in lat. 45° becomes $p_{50} = 174.8$ mm. The results are shown in the accompanying diagram (fig. 2) and in the tables below. I have only been able to find one earlier observation on the same mixtures: from Regnault's experiments* on mixtures of alcohol and benzene at higher and lower temperatures one finds by interpolation $p_{50} = 391$ mm. for a mixture in equal volumes of the liquids, whilst the value from my curve is 393 mm. It is satisfactory to find this confirmation, slight as it is, because the alcohol mixtures are

* Regnault, *Mém. de l'Acad.* xxvi.

the least certain, on account of the inevitable presence of traces of water.

Fig. 2.



The difference between the alcohol curves and those of the normal liquids is most marked; for while mixtures of carbon tetrachloride and benzene, or carbon tetrachloride and toluene, have a vapour-pressure never very different to that which would be obtained by interpolation from the pressures of the pure substances, both mixtures containing alcohol show a maximum—a very flat one. In the case of alcohol and benzene it occurs at about 40 per cent. (molecular) of alcohol, and is 406 mm., being $406/(271 + 220) = 83$ per cent. of the sum of the pressures of the pure substances; while for alcohol and toluene it is at about 74 per cent. of alcohol, and has the value 249 mm., which is $249/(93 + 220) = 80$ per cent. of the sum of the pressures.

With regard to the variation of pressure with temperature, we may, as already remarked, regard $\log p$ as linear in t over a few degrees. But the value of $\partial(\log p)/\partial t$ for the pure substances varies somewhat; this is partly due to the fact that 50° is a different fraction of the critical temperature in each case; it diminishes as the "reduced" temperature rises, and consequently has a higher value for toluene at 50° than for benzene or carbon tetrachloride at the same temperature. Alcohol, though its critical point is the lowest of the four, has the highest value of the coefficient—a marked instance of its exceptional behaviour. The numbers are:—

	$\partial(\log p)/\partial t$.
Toluene	0.0189
Benzene	0.0164
Carbon tetrachloride . . .	0.0156
Alcohol	0.0209

The coefficients found for the mixtures are necessarily (on account of the small range of temperature) less reliable than the vapour-pressures themselves: they are in all cases nearly those that would be calculated by interpolation from the coefficients of the pure substances, even when the vapour-pressure curve shows a maximum, *i. e.* they are additive. The differences from the additive values are not greater than the probable errors of experiment. I have included the values of the coefficients in the tables, but lay no stress on them.

Alcohol and Benzene : Vapour-pressures at 50° .

Per cent. alcohol.	Mol. per cent. alcohol.	Saturation-press. p_{50} .	$\frac{d(\log p)}{dt}$.
0	0	270.9	0.0164
4.32	7.11	339.8	
11.11	17.49	389.9	0.0172
18.87	28.28	404.3	179
23.20	33.87	406.4	179
38.81	51.80	400.3	178
46.75	59.80	394.0	188
60.33	72.05	375.3	182
72.37	81.61	345.8	184
81.32	88.07	318.8	175
90.61	94.24	274.3	193
100	100	219.5	209

Alcohol and Toluene.

Per cent. alcohol.	Mol. per cent. alcohol.	Saturation press. p_{50} .	$\frac{d(\log p)}{dt}$.
0	0	93.0	0.0189
2.14	4.20	141.2	
9.74	17.75	214.8	178
18.26	30.89	233.1	193
29.98	46.13	242.1	193
40.50	57.65	244.2	195
50.15	66.80	249.2	
61.65	76.27	248.2	
71.95	83.69	244.4	
78.60	88.02	243.0	
92.29	95.99	230.9	
100	100	219.5	200

In some of the above cases the temperature-coefficient was not found from experiment, but p_{50} derived from the additive value of it; therefore no number is recorded in the last column.

Carbon Tetrachloride and Benzene.

Per cent. CCl_4 .	Mol. per cent. CCl_4 .	p_{50} .	$\frac{d(\log p)}{dt}$.
0	0	270.9	0.0164
26.97	15.78	281.0	162
46.32	30.44	290.0	163
75.75	61.31	302.3	161
100	100	310.2	156

These two liquids have so nearly the same vapour-pressure, and the curve between them is so nearly straight, that three observations were considered enough.

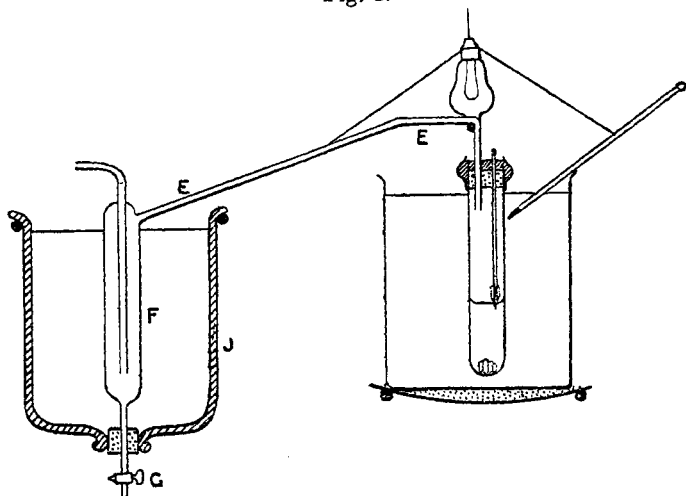
Carbon Tetrachloride and Toluene.

Per cent. CCl_4 .	Mol. per cent. CCl_4 .	p_{50} .	$\frac{d(\log p)}{dt}$.
0	0	93.0	0.0189
6.52	3.99	99.0	183
20.75	13.51	117.9	174
34.61	24.01	140.8	173
52.40	39.70	174.8	170
63.93	51.42	197.7	167
74.47	63.51	226.5	169
82.64	73.98	248.5	163
94.44	90.99	288.8	156
100	100	310.2	156

Composition of the Vapour over Liquid-Mixtures.

The method used was essentially the same as that described in the previous paper, to distil a little of a mixture and analyse the distillate. The apparatus was, however, arranged so that the distillate could be drawn off by a tap as required ; it is shown in fig. 3. It consisted of a boiling-tube, fitted

Fig. 3.



and heated as before ; but with the delivery-tube *EE* bent round to a condenser *F*. The condenser was provided with a tap *G* for drawing off the distillate, and a tube which connected to the pressure-gauge, reservoir, and air-pump arranged as before. The condenser was designed so as to permit of the use of a freezing-mixture in the bell-jar *J* by which it was surrounded ; a good many experiments showed, however, that it made no difference to the result whether ice and salt or only cold water was used in *J* ; so water was used for greater convenience. To make the apparatus air-tight, a crucible full of mercury was placed round *G*, since obviously it was not permissible to lubricate that tap. It is essential to the success of the experiment that no back-condensation should occur, but that the vapour should be collected exactly in the condition it is produced ; so the delivery-tube before

the bend must be at least 50° , if the evaporation is taking place at that temperature. This condition was secured by a very simple device : an incandescent lamp with the ordinary conical shade was lowered as close as possible over the water-bath, and a cloth hung round the whole ; the electrical heating was then sufficient to keep the top of the apparatus at least as hot as the small flame kept the bottom, and at the same time provided an excellent light to read the thermometers by. About 30 c.c. of mixture was placed in the tube ; the temperature of the bath adjusted to between 51° and 52° , and then the pressure lowered till the liquid boiled tranquilly at as near as possible 50° ; as the distillation proceeded, the thermometer of course tended to rise ; this was corrected by an occasional stroke of the pump as required. Three lots of about 1 c.c. each were usually distilled, and examined separately by the Pulfrich refractometer ; from 5 to 10 minutes being required to distil 1 c.c.

In order to interpret the results it was first needful to construct tables of the refractive index of the mixtures used ; the refractive index is far from additive in any of the four cases, and cannot be satisfactorily expressed by the parabolic formula used in Part I. for mixtures of benzene with methyl and ethyl acetates ; it is therefore worth while to record the results by a short extract from the tables used, which were themselves derived from a smoothed curve based on experiment.

Refractive Indices (at 18° for sodium light).

Per cent. of alcohol (or CCl_4).	Alcohol- benzene.	Alcohol- toluene.	Carbon tetrachloride- benzene.	Carbon tetrachloride- toluene.
0	1.5024	1.4970	1.5024	1.4970
10	1.4869	1.4823	1.5008	1.4956
20	1.4716	1.4680	1.4985	1.4937
30	1.4568	1.4539	1.4958	1.4914
40	1.4425	1.4401	1.4929	1.4889
50	1.4283	1.4265	1.4894	1.4860
60	1.4146	1.4131	1.4853	1.4827
70	1.4011	1.4000	1.4807	1.4787
80	1.3878	1.3873	1.4755	1.4742
90	1.3749	1.3747	1.4692	1.4685
100	1.3622	1.3622	1.4618	1.4618

The numbers recorded in an experiment on the composition of the vapour were (1) the refractometer reading, with the corresponding temperature for the liquid before distillation; (2) that for each of the distillates; (3) that of the residue. From them were calculated the refractive indices, reduced to 18° , and then, from the tables quoted above, the percentage composition of the liquid (mean between the reading before and after), and of the vapour (mean of the three distillates). The results are shown in the following tables:—

Composition of Vapours.

A, B = molecular weights of the two components.

z = fractional composition of liquid.

y = " " vapour.

ζ = molecular fractional composition of liquid.

η = " " " vapour.

q = ratio of masses of substances A and B present in liquid.

t = " " " " vapour.

χ = ratio of number of molecules of A and B present in liquid.

s = " " " " vapour.

p = total vapour-pressure.

p_A = partial pressure due to A.

p_B = " " B.

Alcohol-Benzene.

A (Alcohol) = 45.70. B (Benzene) = 77.46.

z .	y .	ζ .	η .	$\log q$.	$\log t$.	p (from curve).	p_A p_B (from p & η).
0.05.4	0.18.7	0.08.8	0.28.1	2.7566	1.3617	350.4	98.5 251.9
0.07.5	0.21.0	0.12.1	0.32.2	2.9090	1.4478	369.0	118.8 250.2
0.13.9	0.24.7	0.21.5	0.35.7	1.2079	1.5159	397.0	141.6 255.3
0.24.5	0.27.5	0.35.5	0.39.1	1.5112	1.5790	406.0	158.7 247.2
0.32.0	0.29.7	0.44.4	0.41.7	1.6727	1.6258	404.4	168.6 235.8
0.43.0	0.32.6	0.56.1	0.45.1	1.8776	1.6846	397.6	179.3 218.3
0.58.0	0.38.3	0.69.7	0.51.3	0.1326	1.7929	378.4	194.1 184.3
0.82.1	0.54.3	0.88.6	0.66.8	0.6615	0.0748	315.0	210.4 104.6

Alcohol-Toluene.

A=45.70. B(Toluene)=91.37.

z .	y .	ζ .	η .	$\log q$.	$\log t$.	p .	p_A .	p_B .
0.074	0.419	0.138	0.591	2.9025	1.8581	119.5	117.9	81.6
.20.0	.49.1	.33.4	.65.9	1.3989	1.9843	235.0	154.8	80.2
.28.0	.51.6	.43.7	.68.1	1.5898	0.0278	241.0	164.1	76.9
.36.3	.54.4	.53.3	.70.5	1.7558	0.0766	245.0	172.8	72.2
.46.4	.55.4	.63.4	.71.3	1.9374	0.0941	247.0	176.1	70.9
.58.2	.58.6	.73.6	.73.9	0.1436	0.1508	249.0	184.0	65.0
.67.5	.62.1	.80.6	.76.6	0.3174	0.2146	246.5	188.8	57.7
.79.3	.72.3	.88.5	.83.9	0.5833	0.4163	241.5	202.6	38.9
.89.8	.82.1	.94.6	.90.2	0.9447	0.6615	233.5	210.6	22.9

Carbon tetrachloride-Benzene.

A (Carbon tetrachloride)=152.70. B=77.46.

z .	y .	ζ .	η .	$\log q$.	$\log t$.	p .	p_A .	p_B .
0.181	.10.1	.04.3	.05.4	2.9450	1.0508	273.6	14.7	258.9
.32.6	.37.4	.19.7	.23.3	1.6846	1.7763	280.0	65.2	214.8
.54.3	.58.0	.37.6	.41.2	0.0748	0.1402	294.0	121.1	172.9
.79.3	.80.5	.66.0	.67.7	0.5833	0.6157	303.4	205.3	98.1
.90.6	.90.9	.83.0	.83.5	0.9840	0.9995	306.5	255.8	50.7

Carbon tetrachloride-Toluene.

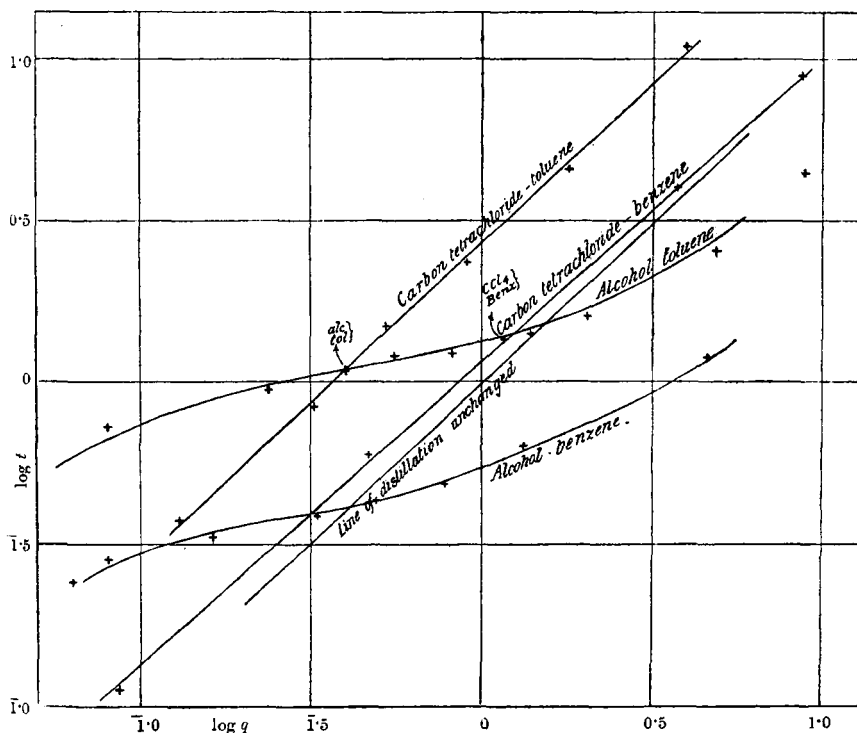
A=152.70. B=91.37.

z .	y .	ζ .	η .	$\log q$.	$\log t$.	p .	p_A .	p_B .
0.117	0.27.0	0.07.3	0.18.1	1.1222	1.5681	105.4	19.0	86.4
.24.6	.46.7	.16.3	.34.4	1.5136	1.9426	122.8	42.2	80.6
.34.5	.59.7	.24.0	.47.0	1.7216	0.1706	140.0	65.8	74.2
.47.4	.71.2	.35.0	.59.7	1.9548	0.2930	158.0	94.3	63.7
.64.1	.82.8	.51.7	.74.2	0.2519	0.6825	198.9	147.6	51.3
.80.2	.91.9	.70.8	.87.2	0.6076	1.0550	242.0	211.0	31.0

It is difficult to say what is the degree of accuracy of these results, but certainly less than the accuracy of the vapour-pressure measurements, chiefly because some of the condensed vapour clings to the condensing-tube, and it is not certain that what is collected quite fairly represents the whole.

These results are also expressed by the curves on fig. 4. Considering first, then, two pairs of normal liquids, we see that the relation $\log t = \log k + r \log q$, where k and r are

Fig. 4.



constants, satisfactorily represents the phenomena. That is the relation proposed in the previous paper for mixtures of benzene with methyl and ethyl acetates, and in all these cases it appears to be correct within the limits of error of experiment. But Margules has quite rightly pointed out (*loc. cit.* p. 1266) that when $r < 1$ (as it usually is) the equation leads to infinite values of $\partial p / \partial \xi$ when $\xi = 0$ or $\xi = 1$, i. e., the

vapour-pressure curve would start and end vertically. That deduction I had overlooked, and it is obvious from the curves on fig. 2 that the vapour-pressure curve does not behave in that way. The relation given cannot therefore hold throughout; still the experiments show it to be a remarkably good empirical rule for mixtures which do not contain a very small proportion of either component, extending in the case of carbon tetrachloride-benzene mixtures from 8 to 91 per cent.

The empirical linear relations are then :—

For carbon tetrachloride-benzene ... $\log t = 0.065 + 0.947 \log q$,
 ,, carbon tetrachloride-toluene ... $\log t = 0.440 + 1.0 \log q$.

These relations are intended as a solution of the differential equation (11) in the foregoing paper. Margules proposes a more complicated solution, which satisfies the condition that for dilute solutions the lowering of the vapour-pressure of the other component (the solvent) should be normal, *i. e.* according to van't Hoff and Raoult's rule. It is doubtless possible to represent the experimental results that way by using a sufficient number of arbitrary constants; but I have not thought it worth while to do so, as it is complicated, and seems to go rather beyond what the experimental data justify.

With regard to the other mixtures, alcohol with benzene and toluene, the diagram shows the relations between $\log t$ and $\log q$ to be very far from linear. I have not attempted to find an equation to these curves, and will only make one or two remarks as to their character. They are not drawn directly from the experimental results on the composition of the distillate, because when the percentage of alcohol is very great or very small the observations lose considerably in accuracy; but on calculating the partial pressures, from the observed composition of the vapour, and the total pressure, smoothed curves could be drawn, the reliability of which is enhanced by the fact that their end points (vapour-pressure of the pure substances) are fixed. From these smoothed curves of partial pressure the compositions were calculated afresh, and it is the numbers so obtained that are represented by the curves on fig. 4. The crosses on that figure stand for the immediate results of observation, and it will be

noticed that they are regular enough in the middle parts of the curves but not at the ends.

At the maxima of vapour-pressure the composition of the liquid and the vapour must be the same. That is shown, consequently, by the intersection of the curves with the line $\log q = \log t$. The points of intersection form the most reliable measure of the position of the maxima. They give

	$\log q$.	z .	ξ .
Alcohol-benzene	1.605	0.28.7	0.40.6
Alcohol-toluene	0.170	0.59.7	0.74.7

It will be seen that these results agree well with the maxima shown in the vapour-pressure curves (fig. 2).

The differential equation referred to above is

$$\left(\frac{Bq}{Bq+A} - \frac{s}{s+1} \right) \frac{1}{s} \frac{\partial s}{\partial q} + \frac{1}{p} \frac{\partial p}{\partial q} = 0,$$

or, as it may be written,

$$(\eta - \xi) \frac{\partial \log s}{\partial \log q} = \frac{\xi(1-\xi)}{p} \frac{\partial p}{\partial \xi}.$$

For some purposes it is more convenient to express it in terms of the partial pressures, when it assumes the more symmetrical form adopted by Margules (*loc. cit.*) :

$$\xi \frac{\partial \log p_A}{\partial \xi} + (1-\xi) \frac{\partial \log p_B}{\partial \xi} = 0.$$

Since, however, the relation between q and s (or between ξ and η) has not so far been expressed successfully by an equation, it is not possible to integrate the differential equation in order to compare it with experiment. This is true even for the mixtures of benzene and toluene with carbon tetrachloride, since the empirical equations, quoted above, do not extend through the whole range of q , and therefore the arbitrary constant in the integral equation cannot be determined. We are reduced therefore to the very rough process of comparing the differential equation itself with

experiment, by measuring the slope of the vapour-pressure curves at various points. The relation $\log t = \log k + r \log q$ or $\log s = \log Bk/A + r \log q$ gives $\partial(\log s)/\partial(\log q) = r$, and hence

$$\eta - \zeta = \frac{\zeta(1-\zeta)}{rp} \frac{\partial p}{\partial \zeta}.$$

The agreement shown between the two sides of this equation is very rough. Thus :

Carbon tetrachloride and Toluene.

ζ .	0.073	0.163	0.240	0.350	0.517	0.708
$\eta - \zeta$	0.105	0.181	0.230	0.247	0.225	0.164
$\frac{\zeta(1-\zeta)}{rp} \frac{\partial p}{\partial \zeta}$	0.123	0.233	0.276	0.311	0.278	0.198

Carbon tetrachloride and Benzene.

ζ .	0.043	0.197	0.376	0.660	0.830
$\eta - \zeta$	0.011	0.036	0.036	0.017	0.005
$\frac{\zeta(1-\zeta)}{rp} \frac{\partial p}{\partial \zeta}$	0.010	0.037	0.040	0.017	0.009

Whether the disagreement is due to the difficulty of treating the differential equation directly, to errors of experiment, or to the approximations in the theory, I am at present unable to say.

In the case of the alcohol mixtures Margules's form of the equation was adopted, and the differential coefficients measured from the smoothed curves. The results following show, it will be seen, the kind of agreement that might be expected in the middle of the range, but in the case of alcohol and benzene disagree totally at the extreme percentages.

Alcohol and Benzene.

ζ .	0.10	0.30	0.50	0.70	0.90
$\frac{\zeta}{p_A} \frac{\partial p_A}{\partial \zeta} \dots\dots$	0.67	0.19	0.27	0.34	0.40
$\frac{1-\zeta}{p_B} \frac{\partial p_B}{\partial \zeta} \dots\dots$	0.31	0.16	0.34	0.46	0.82

Alcohol and Toluene.

ζ .	0.10	0.30	0.50	0.70	0.90
$\frac{\zeta}{p_A} \frac{\partial p_A}{\partial \zeta} \dots\dots$	0.61	0.23	0.21	0.27	0.62
$\frac{1-\zeta}{p_B} \frac{\partial p_B}{\partial \zeta} \dots\dots$	0.54	0.22	0.25	0.27	0.70

It has already been mentioned that Linebarger states the conclusion that the partial pressure of benzene and toluene in mixtures is simply proportional to the molecular percentage present; this conclusion appears to be only roughly true. According to the results expressed by the curves on fig. 2 no such simple relation holds; the partial pressures of these hydrocarbons being as far from linear as that of the carbon tetrachloride with which they are mixed.

Linebarger proceeds to apply his conclusion to determine the molecular weight of acetic acid, in mixtures of the acid with benzene and toluene.

For in any mixture the partial pressure of the hydrocarbon p_B divided by the pressure of the pure liquid π_B gives, according to this rule, the true molecular fraction of hydrocarbon present, say $1-\zeta'$, whilst $1-\zeta$ is that calculated from the formulæ C_6H_6 (or C_7H_8) and CH_3COOH , or

$$1-\zeta = p_B/\pi_B,$$

whence

$$\chi' = \zeta'/(1-\zeta') = (\pi_B - p_B)/p_B,$$

where χ' is the true ratio of the number of molecules of acetic

acid to molecules of hydrocarbon. If this be divided into the ratio χ calculated from the formulæ, the quotient will give the degree of aggregation of the molecules of acetic acid in the solution. In this way Linebarger found molecular weights which steadily increased with the concentration of the acid, and by extrapolation found 240 for the molecular weight of the pure liquid at 35°. My results for alcohol do not, however, at all confirm the accuracy of the method. On drawing smooth curves of partial pressure from the observations given in the tables above, and treating them in the way just indicated, we get

Molecules of Alcohol.	Aggregation of the Alcohol Molecules in	
	Benzene.	Toluene.
10	6.0	2.0
30	5.7	2.6
50	5.3	4.2
70	5.0	5.7
90	4.9	6.0

It will be seen that the two series disagree altogether, and that neither leads to any reasonable value for the aggregation of pure alcohol. I can only conclude that the partial pressure of the hydrocarbon vapour is not necessarily linear in mixtures, and that therefore the rule proposed by Linebarger for determining the molecular weight of liquids is not correct.

Further theoretical conclusions would not, I think, be justified at the present time on account of the small amount of material accumulated by experiment.

Davy-Faraday Laboratory of the Royal Institution,
London, December 1897.
