The Variation of Molecular Surface-Energy with Temperature

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XIII. *The Variation of Molecular Surface-Energy with Temperature.*

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[PLATES 24, 25.]

INTRODUCTION.

1. The well-known relation of volume-energy to temperature, expressed by the equation

$$pv = \mathrm{RT},$$

and the simple relations between p, v, and T when the substance examined is in the state of gas, together with the constancy in the value of R, if the weights of unit volumes of gases taken are proportional to their molecular weights, have led us to make experiments on the surface-tension of liquids in the hope of discovering relations as direct and simple. We were guided to this research by experiments by EÖTVÖS, which shall be discussed later.* We have not been disappointed; it appears that a similar formula expresses with moderate accuracy the variation of surface-energy with temperature; it may be stated in similar terms, using the symbols γ for surface-tension, *i.e.*, the force exerted along a linear centimetre of the liquid; s for a surface over which are distributed a number of molecules the same for all liquids; κ for a constant analogous to R in the gaseous equation; and τ for temperature measured in Centigrade degrees downwards, the critical temperature being taken at zero. An equation completely analogous to the gaseous equation, $pv = \mathrm{RT}$, should therefore be $\gamma s = \kappa \tau$.

That this is reasonable follows from the following consideration :—In the gas equation, $pv = \mathrm{RT}$, if v be kept constant, p decreases with fall of T, until where $p = 0$, $\mathrm{T} = -273°$, or absolute zero; the origin of the scale of absolute temperature is also the origin of the scale of pressure.

Correspondingly, in the liquid surface equation, if s be kept constant, γ decreases with τ, until where $\gamma = 0$, a condition of affairs which takes place at the critical

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* OSTWALD ('Lehrbuch der Allgemeinen Chemie,' p. 1130) has also pointed out the bearings of the experiments of EÖTVÖS in this direction, and has indicated the possibility of determining the molecular weights of liquids by investigation of this " colligative " property.

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temperature, τ is zero; hence the origin of the temperature-scale (τ) is also the origin of the scale of tension.

But the above equation, unmodified, represents facts with only approximate accuracy, for reasons which will now be adduced.

Let γs and τ be the axes of the curve AO, showing the relation between γs and τ. At O, the critical temperature, $\tau = 0$, and the value of γs is also 0. With rise of τ, i.e., with fall of temperature, γs increases slowly at first, but soon attains a nearly steady rate of increase, pictured by the nearly straight line CA. The origin of the

Fig. 1.
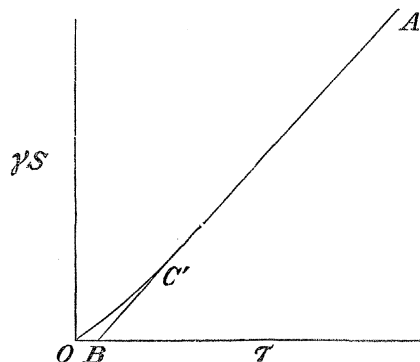
line CA, which may be regarded as a tangent to a curve at some point intermediate between A and C, is not O, but B, a temperature some degrees on the ordinary scale below O, the critical temperature. Hence, in representing the slope of the line CA by an equation, τ cannot be one of the factors, but τ diminished by the number of degrees between O and B. The equation then becomes, where d represents that number,

$$\gamma s = \kappa \, (\tau - d).$$

A similar correction might possibly be applicable to the gaseous equation, if we wish to exhibit the behaviour of gases at ordinary temperatures, which are far above the absolute zero of the thermo-dynamic scale. Were such a correction applicable, it would have the effect of merely altering the zero-point on the gas thermometer by some degrees.

That $d\,(\gamma s/dt)$ is a constant has been shown to be approximately true by Eötvös ('Wied. Ann.,' 27, 452); he also points out that s may be taken as equal to $(Mv)^{\frac{2}{3}}$, where v is the molecular volume of the liquid under investigation, i.e., the volume in cub. centims. occupied by molecular weight of the compound taken in grammes. He deduces from the constancy of the differential the equation $\gamma\,(Mv)^{\frac{2}{3}} = \kappa\,(T - T')$, where T is the critical temperature of the liquid, and T' the temperature at which γ and $(Mv)^{\frac{2}{3}}$ are observed, i.e. $(T - T') = \tau$. But, as we shall show, such an equation leads to erroneous results.

The modification to be introduced into the equation $\gamma \, (\mathrm{M}v)^{\frac{2}{3}} = \kappa \, (\tau - d)$ in order to secure concordance at temperatures (or values of τ) higher than those represented by the point C on the figure will be considered later.

In calculating the results of experiment, we have assumed with EÖTVÖS that $(\mathrm{M}v)^{\frac{2}{3}} = s$; for the surface of a liquid conceived to be contained in a cubical vessel is obviously a square on the line representing the cube-root of its volume. Such an assumption, if molecular volumes be employed, gives a comparison of surfaces on which are distributed equal numbers of molecules, and permits of comparison between different liquids. *

2. *Proof of the Validity of the Equation* $\gamma \, (\mathrm{M}v)^{\frac{2}{3}} = \kappa \, (\tau - d)$.

The data necessary in order to calculate the molecular surface-energy of a liquid are : (1) the height to which the liquid rises in a capillary tube of known diameter ; (2) the density of the liquid at the temperature of observation ; (3) the molecular weight of the liquid examined. These data will be found on p. 667, *et. seq.*

The liquids examined were : (1) ethyl oxide or ether ; (2) methyl alcohol ; (3) ethyl alcohol ; the specific orthobaric volumes of these liquids at temperatures from that of the atmosphere to their critical temperatures were determined by RAMSAY and YOUNG ('Phil. Trans.,' 1887, A., 87 ; 313 ; 1886, A., 313) ; (4) methyl formate ; and (5) ethyl acetate ; the constants for these two liquids were kindly communicated to us by YOUNG, as they are not yet published ; (6) carbon tetrachloride ; (7) benzene ; and (8) chlorobenzene, examined by YOUNG ('Trans. Chem. Soc.,' 1891, p. 932 ; 1889, p. 504 ; and 1891, p. 134) ; and acetic acid (*ibid.*, 1886, p. 790 ; and 1891, p. 909). These are at present the only liquids for which such data are available, and therefore they are the only ones of which the surface-energy and its variation with temperature can be determined.

They divide into two groups ; to the first group belong ether, methyl formate, and ethyl acetate, carbon tetrachloride, benzene, and chlorobenzene. These liquids may be termed normal liquids, inasmuch as their behaviour resembles that of a normal gas. The second group comprises acetic acid and the alcohols ; and these display properties which, as will afterwards be shown, make it more than likely that their molecules coalesce to form aggregates, as temperature falls, as indeed is known to be the case with acetic acid, even in the state of gas.

The first of these groups has the advantage of comprising liquids differing widely from each other chemically ; they are therefore specially suitable for testing the truth

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* It has been assumed that the distribution of molecules on the surface of a liquid is such that the average distance between any two molecules on the surface is equal to that in the interior. We can give no proof of the correctness of this assumption, save to refer to the results of this investigation which appear to justify it.

of a physical law.   They will be first considered, leaving till later the "associating" liquids, acetic acid and the alcohols.

The following table contains numerical data regarding the variation of the molecular surface-energy of the "normal" liquids with temperature, and a comparison with numbers calculated by means of the equation $\gamma (Mv)^{\frac{2}{3}} = \kappa (\tau - d)$:—

TABLE I.

Ethyl oxide. (Crit. temp., 194°·5 C.) $\gamma (Mv)^{\frac{2}{3}} = 2\cdot1716 (\tau - 8\cdot5)$.				Methyl formate. (Crit. temp., 214° C.) $\gamma (Mv)^{\frac{2}{3}} = 2\cdot0419 (\tau - 5\cdot9)$.				Ethyl acetate. (Crit. temp., 251° C.) $\gamma (Mv)^{\frac{2}{3}} = 2\cdot2256 (\tau - 6\cdot7)$.			
t (cent.).	τ.	$\gamma (Mv)$.		t (cent.).	τ.	$\gamma (Mv)^{\frac{2}{3}}$.		t (cent.).	τ.	$\gamma (Mv)^{\frac{2}{3}}$.	
		Found.	Cal.			Found.	Cal.			Found.	Cal.
°	°	Ergs.	Ergs.	°	°	Ergs.	Ergs.	°	°	Ergs.	Ergs.
20	174·5	363·7	360·5	20	194	383·9	384·1	20	231	500·7	499·2
40	154·5	317·4	317·1	30	184	363·7	363·7	80	171	367·2	365·7
50	144·5	296·0	295·3	40	174	343·2	343·2	90	161	344·4	343·9
60	134·5	272·8	273·6	50	164	322·6	322·8	100	151	321·7	321·2
70	124·5	251·0	251·9	60	154	302·5	302·4	110	141	299·0	298·9
80	114·5	229·5	230·2	70	144	282·7	282·0	120	131	277·1	276·6
90	104·5	208·1	208·4	80	134	262·0	261·6	130	121	254·7	254·4
100	94·5	186·9	186·8	90	124	241·5	241·1	140	111	231·9	232·1
110	84·5	165·3	165·0	100	114	221·2	220·7	150	101	209·6	209·9
120	74·5	143·6	143·3	110	104	200·5	200·2	160	91	187·1	187·6
130	64·5	122·0	121·6	120	94	180·0	179·9	170	81	164·8	165·4
140	54·5	100·4	99·9	130	84	159·4	159·5	180	71	143·0	143·1
150*	44·5	78·7	78·2	140	74	138·3	139·1	190	61	120·4	120·8
160	34·5	58·6	56·5	150	64	118·0	118·6	200	51	98·9	98·6
170	24·5	39·0	34·8	160	54	97·1	98·2	210*	41	78·4	76·3
180	14·5	19·9	13·0	170	44	76·9	77·8	220	31	56·8	54·1
185	9·5	12·3	2·2	180	34	57·3	57·4	230	21	35·7	31·8
190	4·5	5·5	— 8·7	190	24	37·7	37·0	240	11	15·9	9·6
194·5	0·0	0·0		200*	14	19·2	16·5	245	6	7·2	— 1·6
				210	4	4·0	— 3·9	251	0	0·0	
				214	0	0·0					

TABLE I—(continued).

Carbon tetrachloride. (Crit. temp., 283° C.) $\gamma (Mv)^{\frac{2}{3}} = 2{\cdot}1052\,(\tau - 6{\cdot}0)$.				Benzene. (Crit. temp., 288°·5 C.) $\gamma (Mv)^{\frac{2}{3}} = 2{\cdot}1043\,(\tau - 6{\cdot}5)$.				Chlorobenzene. (Crit. temp., 360° C.) $\gamma (Mv)^{\frac{2}{3}} = 2{\cdot}0770\,(\tau - 6{\cdot}3)$.			
t (cent.).	τ.	$\gamma (Mv)^{\frac{2}{3}}$.		t (cent.).	τ.	$\gamma (Mv)^{\frac{2}{3}}$.		t (cent.).	τ.	$\gamma (Mv)^{\frac{2}{3}}$.	
		Found.	Cal.			Found.	Cal.			Found.	Cal.
°	°	Ergs.	Ergs.	°	°	Ergs.	Ergs.	°	°	Ergs.	Ergs.
80	203	414·6	414·7	80	208·5	425·1	425·1	150	210	423·2	423·1
90	193	393·7	393·7	90	198·5	404·5	404·0	160	200	401·3	402·3
100	183	372·3	372·6	110	188·5	384·0	383·0	170	190	381·8	381·5
110	173	351·7	351·6	110	178·5	362·9	361·9	180	180	360·5	360·8
120	163	330·3	330·5	120	168·5	341·6	340·9	190	170	340·0	340·0
130	153	309·4	309·5	130	158·5	320·3	319·8	200	160	319·1	319·2
140	143	288·1	288·4	140	148·5	299·0	298·8	210	150	298·2	298·5
150	133	267·4	267·4	150	138·5	278·1	277·8	220	140	277·0	277·7
160	123	246·7	246·3	160	128·5	256·9	256·7	230	130	256·2	256·9
170	113	226·0	225·3	170	118·5	235·2	235·7	240	120	234·9	236·2
180	103	204·8	204·2	180	108·5	213·8	214·6	250	110	213·9	215·4
190	93	183·3	183·2	190	98·5	193·4	193·6	260	100	192·8	194·6
200	83	162·3	162·1	200	88·5	172·5	172·5	270	90	171·9	173·9
210	73	140·8	141·1	210	78·5	151·9	151·5	280	80	150·6	153·1
220	63	118·9	120·0	220	68·5	131·0	130·5	290	70	128·9	132·3
230	53	96·8	99·0	230	58·5	110·1	109·4	300	60	109·7	111·5
240	43	76·5	77·9	240	48·5	89·0	88·4	310	50	90·3	90·8
250	33	55·5	56·8	250*	38·5	68·7	67·3	320*	40	71·5	70·0
260	23	35·9	35·8	260	28·5	48·6	46·3	333	27	46·7	43.0
270*	13	21·7	14·7	270	18·5	28·8	25·3	360	0	0·0	
283	0	0·0		275	13·5	19·9	14·8				
				280	8·5	9·0	4·2				
				288·5	0·0	0·0					

These results clearly show the validity of the equation $\gamma (Mv)^{\frac{2}{3}} = \kappa\,(\tau - d)$ over a very long range of temperature ; from 20° C., in most cases, to within 20 or 30 degrees below the critical temperature. Deviation becomes apparent where an asterisk has been placed opposite the temperature. A complete formula, representing all the results with fair accuracy, will afterwards be adduced, but several important deductions may be drawn from the simpler one.

3. *Confirmation of these results at* − 89°·8.

Ethyl oxide, methyl formate, and ethyl acetate remain liquid, even when cooled to the boiling-point of nitrous oxide under atmospheric pressure. This temperature, which we have carefully determined by means of a thermometer filled with pure dry hydrogen ('Trans. Chem. Soc.,' 1893, p. 833), is − 89°·8. It was thought advisable to measure the surface-energy, and to find out whether the linear relation between molecular surface-energy and temperature persists even at that low temperature. The

results are given in the Table which follows; the method of experiment is described on p. 671.

TABLE II.—Surface-energy at $-89°\cdot8$ C.

Substance.	$\gamma (Mv)^{\frac{2}{3}}.$		Percentage deviation.
	Found.	Calculated.	
Ethyl oxide . . .	611·2	599·4	+ 2·0
Methyl formate . .	557·0	608·7	— 8·5
Ethyl acetate . .	761·5	744·0	+ 2·4

The agreement is good except in the case of methyl formate; here, however, the negative value, judging from experiments with acetic acid and with the alcohols, may be due to molecular association.   The positive value of the other two substances may be due to the fact that measurements were made in a different tube of wider capillary bore, and that the arrangements were necessarily less perfect than in determinations at higher temperatures.

We consider, therefore, that we are justified in stating that the linear relation between molecular surface-energy and temperature holds for ether within a range of 240°; approximately for methyl formate, of 270°; and for ethyl acetate, of 290°.

4. *Molecular Surface-energy of Acetic Acid and of Methyl and Ethyl Alcohols.*

The behaviour of acetic acid, and of methyl and ethyl alcohols, is exceptional; the surface-energy no longer shows a linear relation to temperature.   Surface-energy, as has been stated, is the product of $v^{\frac{2}{3}}$ and γ, where $v^{\frac{2}{3}}$ represents one-sixth of the surface of a cube containing one gramme of liquid, and γ, the surface tension.   It has been assumed, with Eötvös, that the molecular volume raised to the two-thirds power $(Mv)^{\frac{2}{3}}$, gives a comparison of surfaces on which equal numbers of molecules lie.   It is fair to assume that we have proved a linear relation to hold for "normal" liquids between $\gamma (Mv)^{\frac{2}{3}}$ and temperature.   The question now arises—if certain liquids fail to show a linear relation, to what factor must the variation be ascribed?

Two of these factors, viz., γ and $(v)^{\frac{2}{3}}$, are deduced from actual measurements, viz., of the height of ascent in a capillary tube, and of the volume of one gramme of the substance.   But M has been taken as the molecular weight of the simple molecules, $C_2H_4O_2$, CH_4O, and C_2H_6O.   For acetic acid, at least, this assumption is acknowledgedly wrong, for it is well-known that its molecular weight, as determined from its gaseous density, is not a constant, but decreases with rise of temperature and fall of pressure.   It has been shown by RAMSAY and YOUNG ('Phil. Mag.,' 1887, p. 206),

that the volume of one gramme of the vapour of acetic acid at 50°, the lowest temperature at which measurements were possible, and at a pressure nearly that of the saturated vapour (51·35 millims., instead of 56·56) is 3567 cub. centims., corresponding to the molecular weight, 109·6, instead of 60, the molecular weight of $C_2H_4O_2$, or 120, that of $C_4H_8O_4$.

The alcohols show no such deviation in their vapour densities at any observed temperatures and pressures; but that does not preclude the occurrence of association between simple molecules to form more complex molecular groups in the liquid substances. It is known that if the molecules in the gaseous state be caused to recede, dissociation takes place; for instance, at the same temperature, 50°, but at a pressure of 13·4 millims., one gramme of acetic acid gas occupied no less than 15,100 cub. centims., implying a molecular weight of 99·2, considerably greater than that of $C_2H_4O_2$ (60), but not so great as that of $C_4H_8O_4$ (120). And many other similar instances could be given.

Now, since association is promoted by the approach of molecules, it is clear that as molecules in the liquid state are much nearer each other than in the gaseous state, it is not unreasonable to suppose that some liquids may consist in whole or part of associated molecules, even although their gases show no signs of abnormal density.

These observations are illustrated by the following tables, which show the variation with temperature of the molecular surface-energy of acetic acid, and of methyl and ethyl alcohols, assuming that the molecular weight in each case is that of the simple molecule, $C_2H_4O_2$, CH_4O, or C_2H_6O. By choosing suitable molecular weights, implying a mixture of simple and complex molecules, the relation can, of course, be made a linear one.

TABLE III.—Surface-energy of acetic acid and of methyl and ethyl alcohols.

Acetic acid (Crit. temp., 321·5° C.).			Methyl alcohol (Crit. temp., 240·0° C.).			Ethyl alcohol (Crit. temp., 243·1° C.).		
$t°$ C.	τ.	$\gamma (Mv)^{\frac{2}{3}}$.	$t°$ C.	τ.	$\gamma (Mv)^{\frac{2}{3}}$.	$t°$ C.	τ.	$\gamma (Mv)^{\frac{2}{3}}$.
		Ergs.			Ergs.			Ergs.
20	301·5	371·2	20	220	271·4	20	223·1	331·0
130	191·5	261·5	70	170	216·2	40	203·1	307·3
140	181·5	250·2	80	160	206·6	60	183·1	284·8
150	171·5	238·4	90	150	196·3	80	163·1	261·2
160	161·5	226·3	100	140	186·7	90	153·1	247·1
170	151·5	213·9	110	130	176·7	100	143·1	235·0
180	141·5	200·2	120	120	166·3	110	133·1	221·7
190	131·5	187·9	130	110	154·8	120	123·1	208·0
200	121·5	174·9	140	100	142·9	130	113·1	193·3
210	111·5	160·5	150	90	131·3	140	103·1	178·8
220	101·5	146·9	160	80	118·1	150	93·1	163·0
230	91·5	132·1	170	70	104·8	160	83·1	147·2
240	81·5	117·5	180	60	91·0	170	73·1	130·1
250	71·5	101·5	190	50	76·1	180	63·1	112·6
260	61·5	86·0	200	40	60·6	190	53·1	94·9
270	51·5	71·6	210	30	45·4	200	43·1	75·7
280	41·5	54·8	220	20	29·2	210	33·1	57·1
290	31·5	39·9	230	10	13·4	220	23·1	39·2
300	21·5	25·1	234	6	7·6	230	13·1	19·8
310	11·5	11·3	240	0	0·0	234	9·1	13·3
320	1·5	0·82				236	7·1	9·9
321·5	0·0	0·0				240	3·1	3·7
						243·1	0·0	0·0

Observations of the rise in a capillary tube were made at — 89°·8 with methyl and ethyl alcohols in contact with their own vapours only.

The results were :—

	$\gamma (Mv)^{\frac{2}{3}}$.
Methyl alcohol	361·8 ergs.
Ethyl alcohol.	436·1 „

These numbers appear to lie concordantly on prolongations of the respective curves representing the surface-energy of the alcohols in relation to temperature. (See Plate 25.)

Now it is possible to calculate the amount of association at any temperature for acetic acid and the alcohols, on the assumption that κ is a constant, which is approximately true for the normal liquids examined, and that if no association occurred with the anomalous liquids, the value of κ would be similar to that which it possesses for the normal liquids.

The following values of κ were found :—

	$\kappa.$
Ethyl oxide	2·1716
Methyl formate	2·0419
Ethyl acetate	2·2256
Carbon tetrachloride	2·1052
Benzene	2·1043
Chlorobenzene	2·0770
Mean value of κ	2·1209

Suppose acetic acid gas, consisting of molecules of $C_2H_4O_2$, to undergo molecular condensation, so that $2C_2H_4O_2 = C_4H_8O_4$, the pressure of the gas would fall to half of the original pressure, provided volume were kept constant; *i.e.*, unit volume would contain only half the original number of molecules. How would this affect the number of molecules on the surface of a cube representing unit volume? Clearly, if the number of molecules in unit volume is halved, the number of molecules on unit surface will be altered to $(\frac{1}{2})^{\frac{2}{3}}$; and a similar change will take place in the surface energy, one of the factors of which is molecular surface, or $(Mv)^{\frac{2}{3}}$. The value of the differential of surface-energy with temperature will be similarly altered; the amount of association can, therefore, be calculated by the equation

$$\frac{2\cdot12}{k} = x^{\frac{2}{3}},$$

where k is the differential found for the dissociating liquid at the temperature chosen, and x the unknown factor of association.

For example, calculating for acetic acid, and for methyl and ethyl alcohols the amount of association at $-89°\cdot8$, $20°$, $100°$, and $150°$, we obtain the following numbers :—

Acetic acid.				Methyl alcohol.				Ethyl alcohol.			
$t.$	$k.$	$x.$	$x \times 60$ $= $ M.W.	$t.$	$k.$	$x.$	$x \times 32$ $= $ M.W.	$t.$	$k.$	$x.$	$x \times 46$ $= $ M.W.
$\overset{\circ}{20}$	0·8815	3·73	223·9	$- \overset{\circ}{89}\cdot8$	0·868	3·82	122·2	$- \overset{\circ}{89}\cdot8$	0·949	3·34	153·6
100	1·058	2·84	170·3	$+ \ 20$	0·932	3·43	109·8	$+ \ 20$	1·070	2·79	128·3
150	1·198	2·36	140·3	150	1·236	2·25	72·0	150	1·569	1·57	72 2

From these numbers it would appear that the limit to the amount of possible association is 4. With acetic acid at $20°$ the molecule is chiefly $(C_2H_4O_2)_4$; with methyl alcohol at $-89°\cdot8$ $(CH_4O)_4$ is approached; ethyl alcohol has not reached so great a degree of association at such a temperature.

In seeking for other evidence pointing to similar conclusions, attention is naturally drawn to deductions of molecular weight from the depression in freezing-point of a solvent. But, in such cases, the concentration of the dissolved substance is comparatively small. Data by E. BECKMANN are available for ethyl alcohol dissolved in acetic acid and in benzene, and for acetic acid dissolved in benzene (' Zeitschr. Phys. Chem.,' vol. 2, p. 728). The molecular weight of C_2H_6O is 46, but BECKMANN found that a solution of alcohol in benzene, containing 32·45 per cent. of alcohol, froze at a temperature which implied a molecular weight of 318; i.e., 6·9 simple molecules of C_2H_6O had coalesced to form complex molecules. Here, however, it was not proved that the crystals separating from the solution consisted of pure benzene, and not of a compound. The same solvent gave a molecular depression, when it contained 22·8 per cent. of acetic acid, corresponding to a molecular weight of 153 for acetic acid; by dividing this number by 60, the molecular weight of $C_2H_4O_2$, it appears that approximately three simple molecules have coalesced to form a complex molecule. The molecular weight of alcohol, determined by the depression in freezing-point of a solution of 14·2 per cent. of alcohol in acetic acid, gave 58 as the molecular weight of alcohol; and this implies a commencement of association.

Substances which have no, or only a slight, tendency to associate simple to complex molecules, however, such as naphthalene (molecular weight, 128), show no such large deviations, even in a concentrated solution. Thus BECKMANN found the molecular weight of naphthalene to be 132, even when 20·5 per cent. of naphthalene was dissolved in benzene.

That such abnormal results are not unknown, even in the gaseous state, is proved by the density of sulphur vapour at temperatures not far removed from its boiling-point under normal pressure; BILTZ's results ('Zeitschr. Phys. Chem.,' vol. 2, p. 920) show that whether the formula be accepted as S_8, or whether the association be regarded as proceeding to an indefinite limit, the fact remains that association takes place with fall of temperature. (See also THORPE and HAMBLY's results with hydrogen fluoride ' Chem. Soc. Trans.,' vol. 55, p. 163.)

As to the reason of such condensation, it is, perhaps, premature to speak. A recent paper on Valency, by FLAVITZKY ('J. Prakt. Chem.,' N.F., vol. 46, p. 57), however, appears to suggest a clue. It may be that the oxygen in such molecules as acetic acid and the alcohols has not exerted its maximum valency, on account of the comparatively high temperature, and the distance between the molecules when alcohol is in the gaseous state; and that valency increases either with fall of temperature, or with closer approach between the molecules.

A further proof that association is furthered by the liquid condition has been furnished by CUNDALL ('Chem. Soc. Trans.,' 1891, p. 1076). The association of nitric peroxide molecules (NO_2) is greatly promoted by the liquid condition, for while a 1·44 per cent. solution in chloroform contains only 0·274 per cent. of NO_2, the gas at similar temperature and pressure corresponding to such dilution contains 0·96 per cent. NO_2.

5. *Complete Equation expressing the relation between Molecular Surface-energy and Temperature.*

All the previous work has been on the assumption that the rectilinear equation of $\gamma v^{\frac{2}{3}} = \kappa (\tau - d)$ holds for the substances examined. But it was mentioned on p. 651 that near the critical point this simple relation no longer holds. There can be little doubt that as the liquid reaches a higher and higher temperature its surface is exposed to a more vigorous bombardment from the gaseous molecules. The molecular volume, and therefore the molecular surface, is rapidly increasing near the critical point; and the surface-tension, as well as the surface-energy, decreases less rapidly as the critical point is approached than at lower temperatures. The force required to extend a surface is less decreased by unit rise of temperature at high than at low temperatures. Here we have no analogy to guide us, for gases have never been investigated where p approximates to zero, the volume of one gramme being kept constant, or in other words, we know nothing of the behaviour of gases near the absolute zero of temperature.

It is, moreover, possible that the distribution of molecules on the surface of a liquid at high temperatures is different from that in its interior; and as we have no clear idea of the condition of matters at the surface of a liquid, we can form no theory which would conduct us to a reasonable, and not empirical form of equation.

It was necessary, therefore, to seek for some expression which would represent this deviation as a function either of molecular surface or of temperature, and Mr. ROSE-INNES has kindly assisted us in this. The expression

$$\gamma \, (\mathrm{M}v)^{\frac{2}{3}} = \kappa\tau - \kappa d \, (1 - 10^{-\lambda\tau})$$

reproduces the results with considerable accuracy. At high temperatures, *i.e.*, where τ is small, the correction becomes of importance; and at temperatures lower than the critical temperature by 25° or 30°, the correction becomes insignificant. The results near the critical temperature are reproduced for ethyl oxide, methyl formate, ethyl acetate, and benzene in the following table :—

Ethyl oxide. $\kappa = 2\cdot1716.$ $d = 8\cdot5.$ $\lambda = 0\cdot03.$				Methyl formate. $\kappa = 2\cdot0419.$ $d = 5\cdot9.$ $\lambda = 0\cdot044.$			
$\tau.$	$\dfrac{\kappa d}{10^{\lambda\tau}}.$	$\gamma (Mv)^{\frac{2}{3}}.$		$\tau.$	$\dfrac{\kappa d}{10^{\lambda\tau}}.$	$\gamma (Mv)^{\frac{2}{3}}.$	
		Cal.	Found.			Cal.	Found.
0	18·45	0	0	0	12·1	0	0
4·5	13·6	4·9	5·5	4	8·1	4·2	4·0
9·5	·9·6	11·8	12·3	14	2·9	19·4	19·2
14·5	6·8	19·8	19·9	24	1·1	38·1	37·7
24·5	3·4	38·2	39·0	34	0·4	57·8	57·3
34·5	1·7	58·2	58·6	44	0·1	77·9	76·9
44·5	0·9	79·1	78·7				
54·5	0·4	100·3	100·4				
64·5	0·2	121·8	122·0				
74·5	0·1	143·4	143·6				
84·5	0·05	165·1	165·3				

Ethyl acetate. $\kappa = 2\cdot2256.$ $d = 6\cdot7.$ $\lambda == 0\cdot0312.$				Benzene. $\kappa = 2\cdot1043.$ $d = 6\cdot5.$ $\lambda = 0\cdot029.$			
$\kappa.$	$\dfrac{\kappa d}{10^{\lambda\tau}}.$	$\gamma (Mv)^{\frac{2}{3}}.$		$\tau.$	$\dfrac{\kappa d}{10^{\lambda\tau}}.$	$\gamma (Mv)^{\frac{2}{3}}.$	
		Cal.	Found.			Cal.	Found.
0	14·9	0	0	0	13·7	0	0
6	9·7	8·1	7·2	8·5	7·7	11·9	9·0
11	6·8	16·4	15·9	13·5	5·5	20·3	19·9
21	3·3	35·1	35·7	18·5	4·0	29·3	28·8
31	1·6	55·7	56·8	28·5	2·0	48·3	48·6
41	0·8	77·1	78·4	38·5	1·0	68·3	68·7
51	0·4	99·0	98·9	48·5	0·5	88·9	89·0
61	0·2	121·0	120·4	58·5	0·3	109·7	110·1
71	0·1	143·2	143·0	68·5	0·1	130·6	131·0
				78·5	0·1	151·6	151·9

6. *Historical résumé.*

The first experiments on the influence of temperature on surface-tension were made by FRANKENHEIM ('Jour. Prakt. Chem.,' vol. 23, p. 401). LAPLACE and POISSON, it is true, considered the question, but only in the sense that the diminution of density of the liquid would alter the length suspended. FRANKENHEIM, however, found that the capillary ascent diminishes much more rapidly with rise of temperature than the

density diminishes; and he discovered that the decrease in length of column supported, is approximately proportional to the rise of temperature. For water, he found that if the surface-tension, or coefficient of capillarity at 0° C., be placed equal to 1, the variation with temperature between 0° and 100° C. may be expressed with fair accuracy by the equation $\gamma = 1 - 0{\cdot}00191\,t$.

FRANKENHEIM was the first to point out that at a certain high temperature, differing for each liquid, the capillary ascent would cease; and he suggested that the state observed by CAGNIARD DE LA TOUR, now known as the critical point, should be that temperature.

BRUNNER, in 1847 ('Pogg. Ann.,' vol. 70, p. 514), and WOLFF, in 1857 ('Ann. Chim. Phys.' (3), vol. 49, p. 230), also found proportionality between capillary ascent and temperature; they observed, however, that such proportionality did not always hold. The next researches on this subject in order of time were by R. SCHIFF ('Annalen,' vol. 223, p. 47), in 1884; but as he measured the capillary heights at only two temperatures, no conclusion can be drawn from his work relative to the question. Moreover, the capillary rise was measured with the surface of the liquid in contact with air, and not with its own vapour.

The problem was again experimentally attacked by EÖTVÖS (*loc. cit.*), in 1886. Starting with VAN DER WAAL's definition that corresponding states for different liquids are those at which

$$(1) \quad \frac{V_1}{V_2} = \frac{v_1}{v_2} = \frac{p_2 T_1}{p_1 T_2},$$

(where V_1 and V_2 are the molecular volumes of two saturated vapours; v_1 and v_2, those of their liquids in contact with saturated vapours; p_1 and p_2, corresponding pressures; and T_1 and T_2, corresponding temperatures on the absolute scale), he reasons as follows :—

For a surface on which n molecules lie, the pressure of the vapour on that surface is $np_1 v_1^{\frac{2}{3}}$, since $v^{\frac{1}{3}}$ is proportional to the mean linear distance between the molecules. On the other hand, the surface-tension across a line of m molecules is $m\gamma_1 v_1^{\frac{1}{3}}$. The first force may be measured in dynes per square centimetre, the latter, in dynes per linear centimetre. The corresponding expressions for another liquid are $np_2 v_2^{\frac{2}{3}}$ and $m\gamma_2 v_2^{\frac{1}{3}}$.

EÖTVÖS next assumes that bodies which are in corresponding states should possess similar mechanical properties, especially those which relate to the forces which act between their parts, and to their energies. On this assumption, he imagines proportionality between $\gamma v^{\frac{2}{3}}$, the surface-energy, and the product pv the volume-energy; and combining the relations given above, he obtains

$$(2) \quad \frac{\gamma_1}{p_1 v_1^{\frac{1}{3}}} = \frac{\gamma_2}{p_2 v_2^{\frac{1}{3}}}.$$

4 P 2

This equation seems to signify that the molecules are in a condition of equilibrium, inasmuch as it would imply that $\gamma_1 v_1^{\frac{1}{3}}$ and $\gamma_2 v_2^{\frac{1}{3}}$, the surface-tensions of the liquids, balance the pressures on the surfaces of the liquids ; but as a vertical pressure cannot be balanced by a horizontal stress, perhaps it is right to assume that only proportionality is meant.

Equation (2), by appropriate multiplication, becomes

$$(3) \quad \frac{\gamma_1 v_1^{\frac{2}{3}}}{p_1 v_1} = \frac{\gamma_2 v_2^{\frac{2}{3}}}{p_2 v_2} .$$

Now from (1)

$$\frac{p_1 v_1}{p_2 v_2} = \frac{T_1}{T_2} ,$$

hence

$$(4) \quad \frac{\gamma_1 v_1^{\frac{2}{3}}}{T_1} = \frac{\gamma_2 v_2^{\frac{2}{3}}}{T_2} .$$

When two substances are in corresponding conditions they remain so, according to VAN DER WAALS, when the temperatures change proportionally to T_1 and T_2, or, in other words, when the change of condition with temperature at any corresponding temperatures is proportional to the temperatures.   Hence EÖTVÖS argues that

$$T_1 \frac{d}{dT} \left(\frac{\gamma_1 v_1^{\frac{2}{3}}}{T_1} \right) = T_2 \frac{d}{dT} \left(\frac{\gamma_2 v_2^{\frac{2}{3}}}{T_2} \right).$$

This equation implies that the rate of change of temperature of the molecular surface-energy of any two liquids is the same.

We have deemed it necessary to enter at some length into the views of EÖTVÖS, because, although his conclusion is true for those liquids which we have investigated between wide ranges of temperature, his premises are scarcely justifiable.

This is best tested numerically ; and although YOUNG has done so in numerous papers, it will be convenient to show the magnitude of the error for a specific case.

It is easy to test equation (1) stated in the form $p_1 v_1 / T_1 = p_2 v_2 / T_2$, from data given by RAMSAY and YOUNG ('Phil. Trans.,' 1887, A, pp. 81 and 85) for ether, and by YOUNG ('Trans. Chem. Soc.,' 1889, pp. 501 and 504) for benzene.

	Benzene.	Ether.
Corresponding temperatures	339·95° Absolute	282·95° Absolute
Pressures at these temperatures . . .	495·5 millims.	291·1 millims.
Molecular volumes at these temperatures	93·95 cub. centims.	101·86 cub. centims.
$\frac{pv}{T}$	136·94	104·79

These numbers, according to EÖTVÖS, should be equal, $i.e.$, $136\cdot94 = 104\cdot79$.

The correspondence is better at higher temperatures.

	Benzene.	Ether.
Corresponding temperatures	521·5° Absolute	434·1° Absolute
,, pressures	21752 millims.	16088 millims.
,, volumes	137·81 cub. centims.	150·26 cub. centims.
$\frac{pv}{T}$	5748·2	5568·6

Here, again, Eötvös assumes that $5748·2 = 5568·6$, an assertion unwarranted by fact.

We next proceed to test equation (3), derived from equation (1), on the supposition of numerical correspondence between pv and $\gamma v^{\frac{2}{3}}$.

	Benzene.	Ether.	Benzene.	Ether.
Corresponding temperatures	339·95°	282·95°	521·5°	434·1°
$\gamma v^{\frac{2}{3}}$ in dynes	453·6	382·6	70·7	54·2
pv.	46552	29651	2997600	2417400
$\frac{\gamma v^{\frac{2}{3}}}{pv}$	0·009744	0·01290	0·0000236	0·0000224

Again the want of correspondence is less striking at high than at low temperatures.

Lastly, it is possible to test equation (4), viz., $\gamma_1 v_1^{\frac{2}{3}}/T_1 = \gamma_2 v_2^{\frac{2}{3}}/T_2$. The same temperatures have been chosen, and the data are the same as those given above. The results are :—

	Benzene.	Ether.	Benzene.	Ether.
$\frac{\gamma v^{\frac{2}{3}}}{T}$	1·3343	1·3522	1·3557	1·2486

These results show that the basis of reasoning on which Eötvös founds his differential equation is a faulty one, and contrary to fact. The equation which he deduces from his differential equation, viz. :—

$$\gamma v^{\frac{2}{3}} = 0·227 \, (T - T'),^{*}$$

where T is the temperature at which $\gamma v^{\frac{2}{3}} = 0$ (*i.e.*, the critical temperature), and T' the temperature at which the observation is made, is identical with the first equation stated on p. 647, viz., $\gamma v^{\frac{2}{3}} = \kappa\tau$, and obviously does not hold.

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* The coefficient, 0·227, is expressed in milligrammes per square millimetre.

It should be remarked that we have confined our criticism to the rectilinear part of our work, and have not unfairly taxed the powers of Eötvös's equation in covering those parts of the observations where they approach the critical temperature and are represented by a curve. At best, Eötvös's reasoning leads only to a rough similarity, not to numerical identity.

Measurements of the surface-tension of ethyl oxide have recently been made by N. P. Kasterin, by a method which, from the figures and diagrams which he gives, evidently does not lead to trustworthy results. ('Jour. Russ. Phys. Chem. Soc.,' 24, Phys. Sect., p. 196.) De Vries, also, in an inaugural dissertation (Amsterdam, 1893), has obtained results with ether, which, although confirmatory of ours, are not sufficiently numerous to admit of any general conclusion.

7. *Experimental Details.*

It was necessary during the experiments on this subject to maintain the liquids investigated at constant temperatures, differing from each other by known amounts, and, when the temperatures were high, under considerable pressures. In order to

Fig. 2.
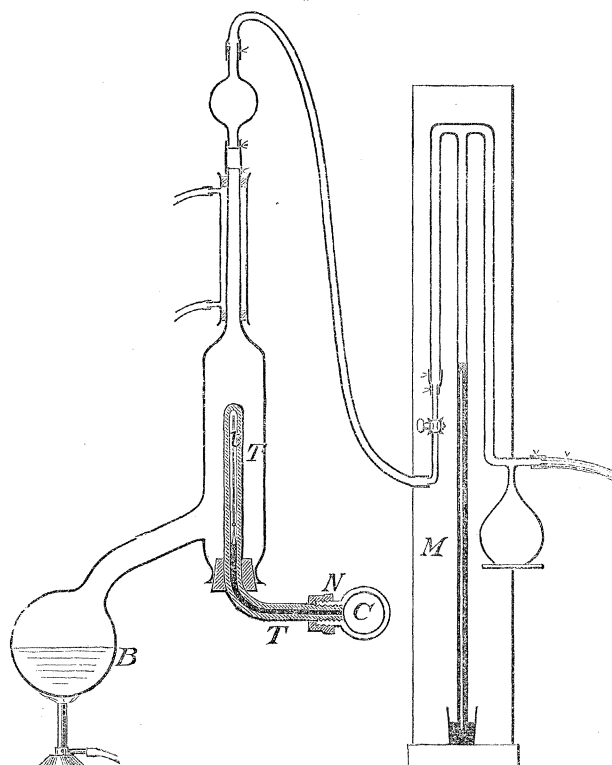
satisfy these conditions, the apparatus consisted essentially of three parts, a tube for observing the phenomena, a heating apparatus, and a pressure apparatus.

The liquid under experiment was enclosed air-free in a piece of thick walled barometer-tubing, *T*, secured in a neck *N* by means of an india-rubber joint com-

pressed by a screw; it entered an iron cylinder C, carrying a screw plunger, not shown in the figure. The cylinder was filled with mercury, and by screwing the plunger in and out the pressure could be varied within wide limits, and the liquid in the tube could be exposed to any desired pressure, greater than that of the atmosphere. The temperature of the liquid could be controlled by means of the vapour-jacket, by the arrangement shown in the figure. The liquids in the bulb B boiled under known pressures, regulated by the gauge M, and the temperature could be varied at will. (For further details see 'Trans. Chem. Soc.,' vol. 47, p. 640, and 'Phil. Trans.,' 1887, A, p. 69.) As in the experiments of RAMSAY and YOUNG, the liquids employed to secure constant temperatures were :—(1) Alcohol (40° to 70°), (2) chlorobenzene (70° to 130°), (3) bromobenzene (120° to 150°), (4) aniline (150° to 180°), (5) quinoline (180° to 230°), (6) bromonaphthalene (220° to 280°), and (7) dibenzylketone (280° to 330°).

The method of filling the tube free from air, was as follows :—The tube was disconnected, the cap N slipped along T towards the bend, and the projecting end of

Fig. 3.
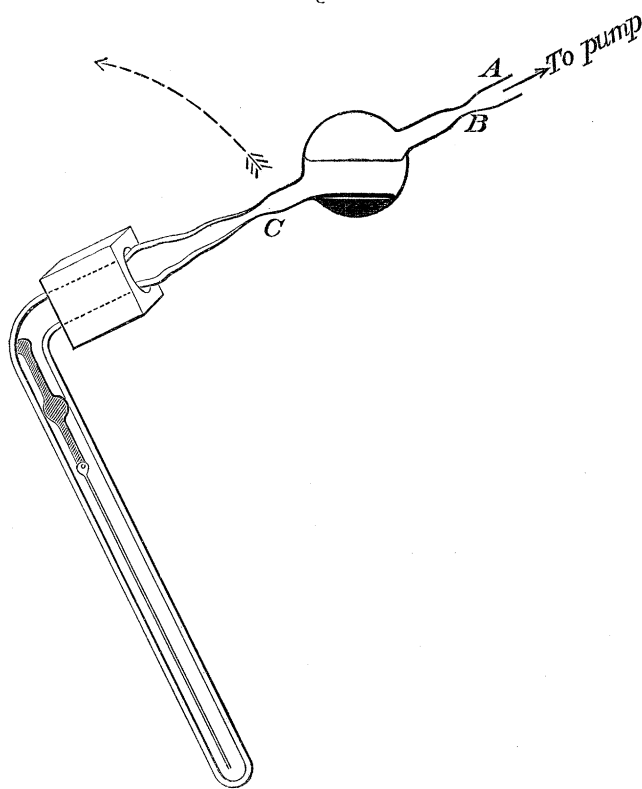
the glass tube was sealed to a bulb, a constriction being left between the tube and the bulb, and also on the tube on which the bulb was blown, as shown in the figure. The liquid was then introduced into the bulb, some mercury was added, and the tube A was then connected with an air-pump, the liquid being heated, if necessary. After

it had boiled vigorously for some minutes, and all air had been expelled from tube and bulb, the tube was drawn off at the constriction B. The liquid in the barometer-tube was then repeatedly boiled so as to remove all traces of air from the walls of the tube; the liquid forms pistons, which are pushed out by its vapour, and effectually expel all traces of air or dissolved gas. On cooling the barometer-tube, liquid enters; when a sufficient quantity has entered, the tube is tilted in the direction shown by the arrow, to cause mercury to enter; and when all is cold, the constriction C is cut, and after the cap has been slipped into position, the tube is inserted into the apparatus. It is easy to do this without admitting a trace of air, and the capillary ascent takes place, therefore, in presence only of the vapour of the substance.

The measurement of the capillary rise was effected by means of a very fine capillary tube t, enclosed in the wider tube T. This tube, about 6 centims. in length, had a minute hole blown in a small bulb at its lower end, and at this point it was attached to a shorter and less fragile rod, which served as a support, and on which the glass was thickened in several places, so that it maintained a constant position in the tube T. Matters were so arranged that the small bulb with the hole in it was completely covered by the liquid. The liquid thus gained access to the capillary tube, and the heights to which it rose were measured by screwing in the plunger, so as to raise the meniscus in the capillary tube t to within a millimetre or two of its upper end. By so doing, all the readings were taken at a portion of the capillary tube of which the diameter had been measured, and corrections for its probably varying bore were thus rendered unnecessary. The diameter of the capillary tube was originally measured by cutting off a small cylinder of about half a millimetre in length from its upper end, and measuring its internal diameter by a microscope provided with a micrometer scale, the length of whose divisions was determined at the same focus by reading against a standard scale. The diameter of the tube used was 0·2587 millim.

In this way a series of heights was obtained for the liquids investigated; but these heights obviously do not represent the true capillary rise; for the liquid in the barometer-tube T always stood at a higher level than if the barometer-tube had been of wider bore.

Corrections.—To correct the read heights so as to make them represent the heights in the capillary tube standing in a tube so wide that capillary rise may be neglected, the tube T was opened at its upper end, after the measurement had been completed, and its lower end was sealed to a tube bent twice at right angles, and connected with a tube of about 3 centims. diameter, the axis of which lay parallel to the barometer tube. Readings of the height to which the liquid in the tube T (with the capillary tube still enclosed) ascended above the level of liquid in the wide-bore tube, where capillary rise is too small to be appreciable, were then made with the cathetometer at the ordinary temperature, 15° to 20° C., the temperature being accurately observed at each measurement. Knowing that the capillary rise is zero at the critical point of

the liquid, and knowing from our experiments that the relation between capillary ascent and temperature is a nearly linear one, the rise in the tube T could be calculated approximately enough for our purpose by constructing a diagram in which the rise at atmospheric temperature was made one end of a straight line connecting it with the critical temperature, where the rise is zero. At intermediate temperatures the rise in the tube T was read off from the diagram; it may be taken as practically accurate; for any divergence from truth is much less than the limits of error in reading the ascent in the narrow capillary tube. This rise was therefore added to the apparent rise in the capillary tube, and the sum was taken to represent the total rise.

No correction has been made for the increase in internal diameter of the capillary tube due to rise of temperature. The surface-tension is directly proportional to the diameter of the tube; but as the latter is increased by only 0·5 per cent. for a rise of temperature of nearly 400°, the correction was neglected.

Nor has any correction been introduced for the form of the meniscus. The total correction should have amounted to 0·05 millim. But readings were taken with the lower edge of the cross-line of the cathetometer on the lower surface of the meniscus, so that the minute error was thereby somewhat compensated.

In calculating the results of experiments so as to ascertain the surface-tension, it has been assumed that there is no angle of contact between the liquid and the glass. The reasons for this assumption are as follows:— *

A tube of capillary bore (0·65 millim.) contained ether free from air. It was connected with the pressure-apparatus, and its temperature was raised. Bubbles were made to appear in the tube, and it was found possible, at any given temperature, to keep them stationary; they did not ascend, or more correctly, the rate of ascent was exceedingly slow, so that a bubble might be kept for an hour, without rising a millimetre. A bubble in such a capillary tube is confined on its lower and upper surfaces by cups of liquid; the walls of the tube between these cups is wet, it is true, but by an exceedingly thin film of liquid; so thin that the transference of liquid from the upper to the lower part of the tube is very slow, and hence the almost stationary position of the bubble.

By decreasing the volume of the bubble on screwing in the plunger, the cups approached each other, the lower cup rising nearer to the dome confining the bubble of vapour on its upper side. The bubble began to ascend rapidly only when its vertical diameter had been made equal to its horizontal diameter; *i.e.*, when it was approximately spherical. Above 160° C. a bubble of ether refused to remain stationary in the tube, but at once ascended; and with ethyl alcohol, the ascent commenced above 220°. These temperatures are evidently conditioned by the stability of the

upper dome of liquid ; and with a narrower tube, the temperature above which the bubble could not be induced to remain stationary was much higher. In no case did it ascend until it had been made approximately spherical by compression.

Now, had there been an angle of contact, it would have been necessary to compress the bubble until its shape had become lenticular, *i.e.*, until its vertical diameter had become less than its horizontal diameter. This was never observed, and we conclude that there is, therefore, no angle of contact between a liquid which wets glass and the glass, if its surface is in presence only of its own vapour. But we have obtained evidence that the capillary rise in air differs to a small extent from that in the vapour of the liquid, and, under these circumstances, there may well be an angle of contact. For example, with ethyl oxide, the read height in air was 37·40 millims., while in contact with its own vapour the rise was 36·5 millims. ; with methyl formate, the numbers are 40·9 and 39·9 ; with carbon tetrachloride, 27·5 and 25·4 ; with benzene, 51·9 and 49·6.

Such discrepancies might be due to the angle of contact existing in presence of air, but not in presence of vapour; or it might be due to a film of moisture on the surface of the liquids. But it is noteworthy that those liquids which are most easily volatile at ordinary temperatures give measurements in air which most nearly corroborate the rectilinear relation. The surface-energies, moreover, calculated from the rise of a liquid in contact with its own vapour, lie on the curve prolonged to $-89°·8$; while those calculated from the capillary rise in air lie off the curves to a greater or less extent.

The reduction of the read heights in the capillary tube to dynes per linear centimetre was effected in the usual manner, by means of the equation

$$\gamma = \tfrac{1}{2}\, r.h.g.\, (\rho - \sigma),$$

where r is the radius of the tube, h the height to which the liquid is raised, g the gravitation constant, ρ the density of the liquid, and σ that of the vapour.

In the accompanying Tables the experimental results are stated. Column 1 shows the temperatures at which measurements were made ; column 2, the observed capillary rise in the narrow tube (h_1), which is corrected in column 3 (h_2), so as to eliminate the effect of the barometer tube in which the measurements were made ; column 4 (h_3) reproduces these numbers smoothed, so as to eliminate errors of experiment ; ρ and σ are the weights of 1 cub. centim. of the liquid and the gas respectively ; and γ is the surface tension, calculated by the equation already mentioned.

ETHYL Oxide.

$t.$	$h_1.$	$h_2.$	$h_3.$	$\rho.$	$\sigma.$	$\gamma.$
°	millims.	millims.	millims.			dynes.
20	..	37·4*	36·48	0·7143	0·00187	16·49
40	..	..	32·40	0·6894	0·00373	14·05
50	28·10	30·40	30·38	0·6764	0·00508	12·94
60	26·20	28·30	28·38	0·6658	0·00677	11·80
70	24·40	26·40	26·34	0·6532	0·00892	10·72
80	22·50	24·30	24·30	0·6402	0·01155	9·67
90	21·00	22·65	22·35	0·6250	0·01477	8·63
100	19·00	20·50	20·33	0·6105	0·01867	7·63
110	17·00	18·30	18·30	0·5942	0·02349	6·63
120	15·00	16·20	16·20	0·5764	0·02934	5·65
130	13·10	14·10	14·10	0·5580	0·03638	4·69
140	11·30	12·15	12·03	0·5385	0·04488	3·77
150	9·30	10 00	9·90	0·5179	0·05551	2·88
160	7·35	7·85	7·70	0·4947	0·06911	2·08
170	5·30	5·70	5·60	0·4658	0·08731	1·33
180	3·30	3·50	3·40	0·4268	0·11350	0·64
185	2·15	2·30	2·30	0·4018	0·13200	0·38
188	1·50	1·60	1·60	..	..	..
190	..	..	1·20	0·3663	0·16200	0·16
191	0·70	0·75	0·92	..	..	..
193	0·30	0·31	0·50	0·3300	0·20120	0·04
194·5	..	..	..	0·2636	0·26360	..

METHYL Formate.

$t.$	$h_1.$	$h_2.$	$h_3.$	$\rho.$	$\sigma.$	$\gamma.$
°	millims.	millims.	millims.			dynes.
20	..	40·90	39·83	0·9745	0·0016	24·62
30	..	..	38·00	0·9598	0·0022	23·09
40	..	..	36·08	0·9447	0·0031	21·56
50	30·50	34·15	34·15	0·9294	0·0043	20·05
60	29·00	32·40	32·28	0·9133	0·0060	18·58
70	27·30	30·50	30·40	0·8968	0·0080	17·55
80	25·30	28·30	28·40	0·8803	0·0105	15·70
90	23·90	26·65	26·50	0·8635	0·0135	14·29
100	22·20	24·70	24·55	0·8452	0 0171	12·90
110	20·20	22·50	22·56	0·8264	0·0216	11·52
120	18·40	20·50	20·56	0·8070	0·0268	10·18
130	16·70	18·55	18·55	0·7860	0·0334	8·86
140	14·80	16·45	16·45	0·7368	0·0412	7·54
150	13·00	14·40	14·40	0·7403	0·0506	6·30
160	·11·05	12·25	12·25	0·7136	0·0623	5·06
170	9·10	10·10	10·10	0·6844	0·0763	3·90
180	7·20	7·95	7·85	0·6521	0·0943	2·81
190	5·20	5·70	5·64	0·6148	0·1178	1·78
200	3·20	3·50	3·30	0·5658	0·1524	0·87
210	0·95	1·05	0·97	0·4857	0·2188	0·06
214	..	..	..	..	..	..

* Read in a wide tube, requiring no correction.

ETHYL Acetate.

$t.$	$h_1.$	$h_2.$	$h_3.$	$\rho.$	$\sigma.$	$\gamma.$
°	millims.	millims.	millims.			dynes.
20	..	41·20	41·32	0·9005	0·0003	23·60
80	..	..	31·32	0·8245	0·0035	16·32
90	26·90	29·65	29·57	0·8112	0·0047	15·14
100	25·10	27·60	27·85	0·7972	0·0062	13·98
110	23·60	26·00	26·10	0·7831	0·0080	12·84
120	22·00	24·20	24·35	0·7683	0·0103	11·75
130	20·70	22·75	22·62	0·7533	0·0131	10·66
140	19·00	20·90	20·87	0·7378	0·0165	9·57
150	17·50	19·20	19·13	0·7211	0·0206	8·52
160	15·90	17·40	17·40	0·7033	0·0258	7·48
170	14·15	15·50	15·60	0·6848	0·0316	6·47
180	12·65	13·85	13·85	0·6653	0·0388	5·51
190	11·00	12·00	12·00	0·6441	0·0475	4·54
200	9·35	10·20	10·18	0·6210	0·0580	3·64
210	7·90	8·60	8·40	0·5944	0·0712	2·80
220	6·00	6·50	6·50	0·5648	0·0890	1·96
230	4·20	4·55	4·50	0·5281	0·1130	1·18
240	2·20	2·40	2·35	0·4778	0·1500	0·49
245	1·20	1·30	1·30	0·4401	0·1800	0·21
251	..	..	..	..	..	..

CARBON Tetrachloride.

$t.$	$h_1.$	$h_2.$	$h_3.$	$\rho.$	$\sigma.$	$\gamma.$
°	millims.	millims.	millims.			dynes.
20	..	27·50	25·40	1·5940	0·0008	25·68
80	18·20	19·95	20·05	1·4765	0·0061	18·71
90	17·70	19·35	19·16	1·4554	0·0079	17·60
100	16·90	18·45	18·24	1·4343	0·0103	16·48
110	15·90	17·40	17·35	1·4125	0·0131	15·41
120	15·10	16·50	16·42	1·3903	0·0163	14·32
130	14·30	15·60	15·52	1·3680	0·0203	13·27
140	13·20	14·45	14·59	1·3450	0·0248	12·22
150	12·35	13·50	13·68	1·3216	0·0302	11·21
160	11·65	12·70	12·76	1·2982	0·0365	10·22
170	10·80	11·75	11·85	1·2734	0·0439	9·24
180	9·95	10·85	10·90	1·2470	0·0525	8·26
190	9·20	10·00	10·00	1·2192	0·0625	7·28
200	1·40	9·10	8·97	1·1888	0·0742	6·34
210	7·45	8·10	7·97	1·1566	0·0879	5·40
220	6·60	7·15	6·92	1·1227	0·1039	4·47
230	5·60	6·05	5·90	1·0857	0·1174	3·56
240	4·20	4·55	4·80	1·0444	0·1464	2·74
250	3·25	3·55	3·92	0·9979	0·1754	1·93
260	2·25	2·45	2·60	0·9409	0·2146	1·20
270	1·20	1·30	1·55	0·8665	0·2710	0·59
283	..	..	..	0·5578	0·5578	..

BENZENE.

t.	h_1.	h_2.	h_3.	ρ.	σ.	γ.
°	millims.	millims.	millims.			dynes.
80	..	..	39·45	0·8127	0·0027	20·28
85	35·30	38·70	38·60	..	..	..
90	34·60	37·90	37·72	0·8042	0·0036	19·16
100	33·00	36·15	36·03	0·7928	0·0047	18·02
110	31·40	34·40	34·28	0·7810	0·0060	16·86
120	29·70	32·50	32·50	0·7692	0·0076	15·71
130	28·00	30·65	30·72	0·7568	0·0095	14·57
140	26·60	29·10	28·95	0·7440	0·0118	13·45
150	25·05	27·35	27·18	0·7310	0·0144	12·36
160	23·00	25·15	25·38	0·7185	0·0173	11·29
170	21·60	23·60	23·60	0·7043	0·0209	10·20
180	19·85	21·65	21·80	0·6906	0·0249	9·15
190	18·20	19·85	19·97	0·6758	0·0298	8·16
200	16·70	18·20	18·13	0·6610	0·0355	7·17
210	14·90	16·20	16·25	0·6432	0·0421	6·20
220	13·20	14·35	14·37	0·6256	0·0503	5·25
230	11·60	12·60	12·45	0·6066	0·0599	4·32
240	9·45	10·25	10·45	0·5852	0·0715	3·41
250	7·80	8·45	8·50	0·5610	0·0857	2·56
260	6·00	6·50	6·42	0·5327	0·1040	1·75
270	4·05	4·35	4·22	0·4985	0·1289	0·99
275	3·10	3·30	3·18	0·4708	0·1450	0·66
280	2·30	2·45	2·05	0·4514	0·2209	0·29
288·5	0·00	0·00	0·00	0·3043	0·3043	0·00

CHLOROBENZENE.

t.	h_1.	h_2.	h_3.	ρ.	σ.	γ.
°	millims.	millims.	millims.			dynes.
150	26·8	29·30	29·17	0·9599	0·0054	17·67
160	25·5	27·85	27·90	0·9482	0·0068	16·62
170	24·5	26·75	26·63	0·9355	0·0083	15·67
180	23·3	25·45	25·33	0·9224	0·0102	14·66
190	22·0	24·00	24·05	0·9091	0·0124	13·69
200	21·0	22·90	22·77	0·8955	0·0150	12·72
210	19·5	21·25	21·48	0·8802	0·0180	11·75
220	18·4	20·05	20·15	0·8673	0·0215	10·81
230	17·4	18·90	18·84	0·8518	0·0255	9·88
240	16·0	17·40	17·50	0·8355	0·0301	8·94
250	14·8	16·10	16·16	0·8196	0·0355	8·04
260	13·3	14·50	14·80	0·8017	0·0418	7·14
270	12·2	13·25	13·46	0·7835	0·0494	6·27
280	11·1	12·05	12·05	0·7639	0·0580	5·40
290	9·9	10·70	10·76	0·7440	0·0667	4·54
300	8·8	9·50	9·43	0·7220	0·0778	3·79
310	7·4	8·00	7·95	0·6988	0·0909	3·05
320	6·0	6·45	6·47	0·6703	0·1075	2·35
333	4·7	5·00	4·80	0·6274	0·1360	1·47

Acetic Acid.

$t.$	$h_1.$	$h_2.$	$h_3.$	$\rho.$	$\sigma.$	$\gamma.$
°	millims.	millims.	millims.			dynes.
20	..	38·80	38·80	0·9532	0·0001	23·46
130	25·60	27·90	27·75	0·9233	0·0043	16·18
140	24·50	26·70	26·64	0·9091	0·0055	15·32
150	23·40	25·45	25·52	0·8961	0·0067	14·46
160	22·50	24·45	24·40	0·8818	0·0089	13·58
170	21·30	23·10	23·23	0·8689	0·0111	12·71
180	20·25	21·95	22·03	0·8555	0·0137	11·77
190	19·20	20·80	20·80	0·8413	0·0168	10·93
200	18·00	19·45	19·55	0·8264	0·0205	10·05
210	16·95	18·30	18·25	0·8117	0·0249	9·11
220	15·80	17·00	16·95	0·7943	0·0300	8·22
230	14·50	15·60	15·52	0·7758	0·0361	7·28
240	13·05	14·05	14·03	0·7576	0·0433	6·36
250	11·60	12·45	12·43	0·7359	0·0518	5·40
260	10·00	10·75	10·84	0·7138	0·0621	4·48
270	8·50	9·10	9·20	0·6897	0·0742	3·59
280	7·00	7·50	7·50	0·6597	0·0912	2·71
290	..	..	5·76	0·6337	0·1076	1·92
300	..	..	3·95	0·5956	0·1332	1·16
310	..	..	2·13	0·5423	0·1720	0·49
320	..	..	0·25	0·4615	0·2956	0·32
321·5	..	..	..	0·3523	0·3523	..

Methyl Alcohol.

$t.$	$h_1.$	$h_2.$	$h_3.$	$\rho.$	$\sigma.$	$\gamma.$
°	millims.	millims.	millims.			dynes.
20	..	45·90	..	0·7905	0·0002	23·02
70	34·20	37·20	37·35	0·7460	0·0015	17·64
80	33·20	36·05	35·88	0·7355	0·0021	16·70
90	31·75	34·40	34·30	0·7250	0·0029	15·72
100	30·50	33·00	32·93	0·7140	0·0040	14·80
110	29·15	31·45	31·40	0·7020	0·0054	13·85
120	27·55	29·70	29·72	0·6900	0·0071	12·88
130	26·15	28·10	27·95	0·6770	0·0094	11·84
140	24·50	26·30	26·10	0·6640	0·0122	10·79
150	22·70	24·30	24·30	0·6495	0·0156	9·77
160	21·00	22·40	22·20	0·6340	0·0199	8·65
170	19·00	20·25	20·10	0·6160	0·0253	7·53
180	16·90	17·95	17·85	0·5980	0·0319	6·41
190	14·30	15·20	15·36	0·5770	0·0401	5·23
200	12·00	12·70	12·70	0·5530	0·0508	4·05
210	9·30	9·85	10·03	0·5255	0·0652	2·93
220	6·80	7·15	7·05	0·4900	0·0864	1·80
230	3·45	3·65	3·75	0·4410	0·1187	0·77
234	..	..	2·40	0·4145	0·1381	0·42
235	1·85	1·95	2·05	..	..	..
236	..	..	1·72	0·3955	0·1505	0·27
240	..	..	..	0·2712	0·2712	..

Ethyl Alcohol.

t.	h_1.	h_2.	h_3.	ρ.	σ.	γ.
°	millims.	millims.	millims.			dynes.
20	..	44·00	43·80	0·7926	0·0001	22·03
40	..	..	41·14	0·7754	0·0003	20·20
60	..	..	38·44	0·7572	0·0008	18·43
80	33·60	36·40	35·56	0·7377	0·0017	16·61
90	31·40	34·05	34·05	0·7283	0·0025	15·63
100	30·00	32·50	32·50	0·7174	0·0035	14·67
110	28·50	30·80	31·00	0·7057	0·0049	13·69
120	27·20	29·30	29·30	0·6925	0·0066	12·68
130	25·50	27·45	27·56	0·6789	0·0088	11·63
140	24·00	25·80	25·70	0·6631	0·0115	10·59
150	22·20	23·80	23·76	0 6488	0·0149	9·52
160	20·40	21·80	21·75	0·6329	0·0192	8·45
170	18·35	19·60	19·65	0·6165	0·0245	7·34
180	16·10	17·20	17·45	0·5984	0·0311	6·23
190	14·10	15·00	15·08	0·5782	0·0397	5·13
200	11·75	12·50	12·40	0·5558	0·0508	3·99
210	9·30	9·90	10·00	0·5291	0·0655	2·91
220	6·80	7·20	7·20	0·4958	0·0854	1·87
230	4·00	4·20	4·20	0·4550	0 1135	0·91
234	..	..	3·06	0·4292	0·1296	0·59
235	2·30	2·45	2·80	..	..	..
236	..	..	2·42	0·4184	0·1401	0·43
240	1·60	1·65	1·10	0·3825	0·1715	0·15
243·1	..	..	..	0·2756	0·2756	..

Experiments at Low Temperatures.

To measure the capillary rise at $-89°\cdot8$, the temperature of nitrous oxide boiling under atmospheric pressure, an arrangement different from that described was resorted to. A tube, about 2 centims. wide and 20 centims. long, was sealed at one end; into it was inserted a capillary tube of known diameter, provided with three glass struts or knobs at each end, so as to make it stand vertically in the wider tube. After the capillary tube had been introduced, the wider tube was drawn off at its upper end, to form a narrow neck, through which it could be exhausted. The pure liquid was then introduced, and, after the tube had been rinsed with it several times, 3 or 4 cub. centims. were left in; the tube was then exhausted, and the liquid was made to boil under reduced pressure for some time, so that its vapour might expel all traces of air.

The capillary neck was then sealed. Observations were made of the capillary ascent at the ordinary temperature, the whole tube having been immersed in water for this purpose. It was then placed in a double-walled tube containing liquid nitrous oxide, with a few shreds of platinum at the bottom, so as to keep the liquid in constant ebullition. Such double-walled tubes, from the space between the walls of which the air has been exhausted as recommended by Dewar, make it possible to

keep a considerable quantity—say, 100 centims.—of nitrous oxide liquid for several hours; and if the liquid be filtered into the tube, to remove particles of ice, it is absolutely limpid and clear; and the radiation of heat through the walls is so slow that it is only occasionally necessary to wipe off the dew which deposits. Readings may be made with a cathetometer with perfect ease. It is, of course, necessary to have the nitrous oxide at a level considerably higher than that of the liquid in the capillary tube, so as to ensure that the *surface* of the liquid in the capillary tube shall be at the temperature — 89°·8, and some time must be given to allow the liquid to reach the low temperature. The rise is a slow one; but in half-an-hour the position of the liquid in the capillary tube is permanent.

The defect of this method is that readings must be taken at different parts of the capillary tube, for there is no means of adjusting the level of the liquid so that its surface is always at a definite point in the capillary. The differences which we have observed between the actual values of surface energy and the calculated values, which amount to about 2 per cent., are probably due to this cause, and to a slight error in determining the diameter of the tube; it was found by weighing the mercury which filled a known length, while the diameter of the other tube was found by the much surer method of direct reading.

DESCRIPTION OF PLATES 24 AND 25.

Plate 24 shows the height of ascent of liquid in the capillary tube, in millimetres, mapped against temperature as ordinates. Two points call for special notice. First, the continuous lines, indicating the rise, end abruptly at the respective critical points. In no case is there any change of curvature as the critical point is approached. Hence, although observations near the critical temperature are difficult to make, the correctness of readings from the curve is very probable, inasmuch as the curve could not follow any other course than that drawn. This enabled us to calculate the surface energy of chlorobenzene, a liquid which was not examined above 333°, and, moreover, it confirms the observations at lower temperatures of that and the other liquids. Second, it is to be remarked that the lines showing the difference of heights with temperature of acetic acid and of the two alcohols are much more curved than those representing the other substances.

The broken lines represent the surface tension in dynes. Here it is to be noticed that acetic acid and the alcohols give lines of double curvature, while the other substances give continuous curves.
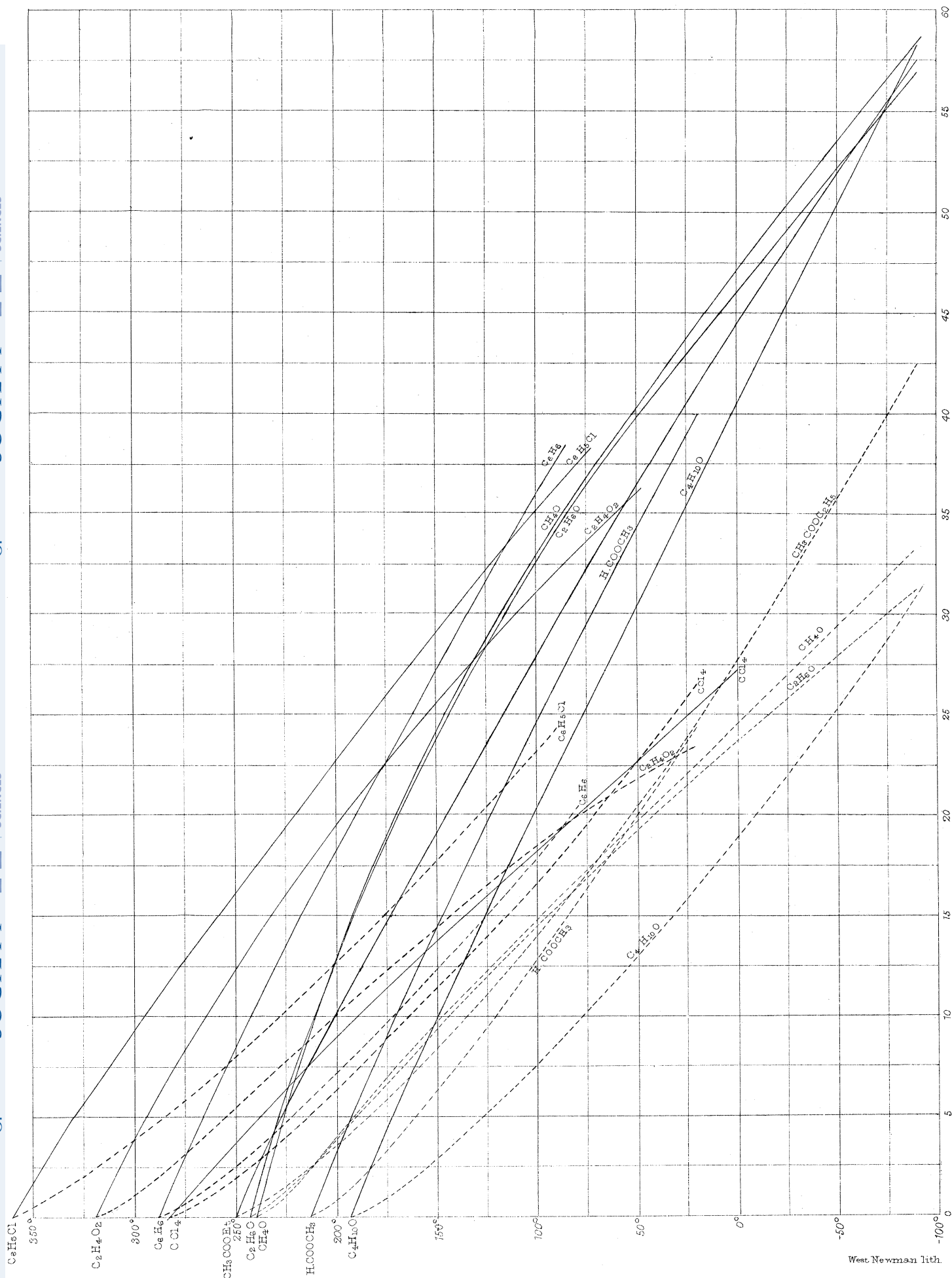
It is difficult to explain the behaviour of methyl formate below 20°. Readings taken on two separate days at — 89°·8 gave practically the same height, viz., 39·8 and 40·1 millims. rise, in the wider capillary; this corresponds to 54·5 and 54·9
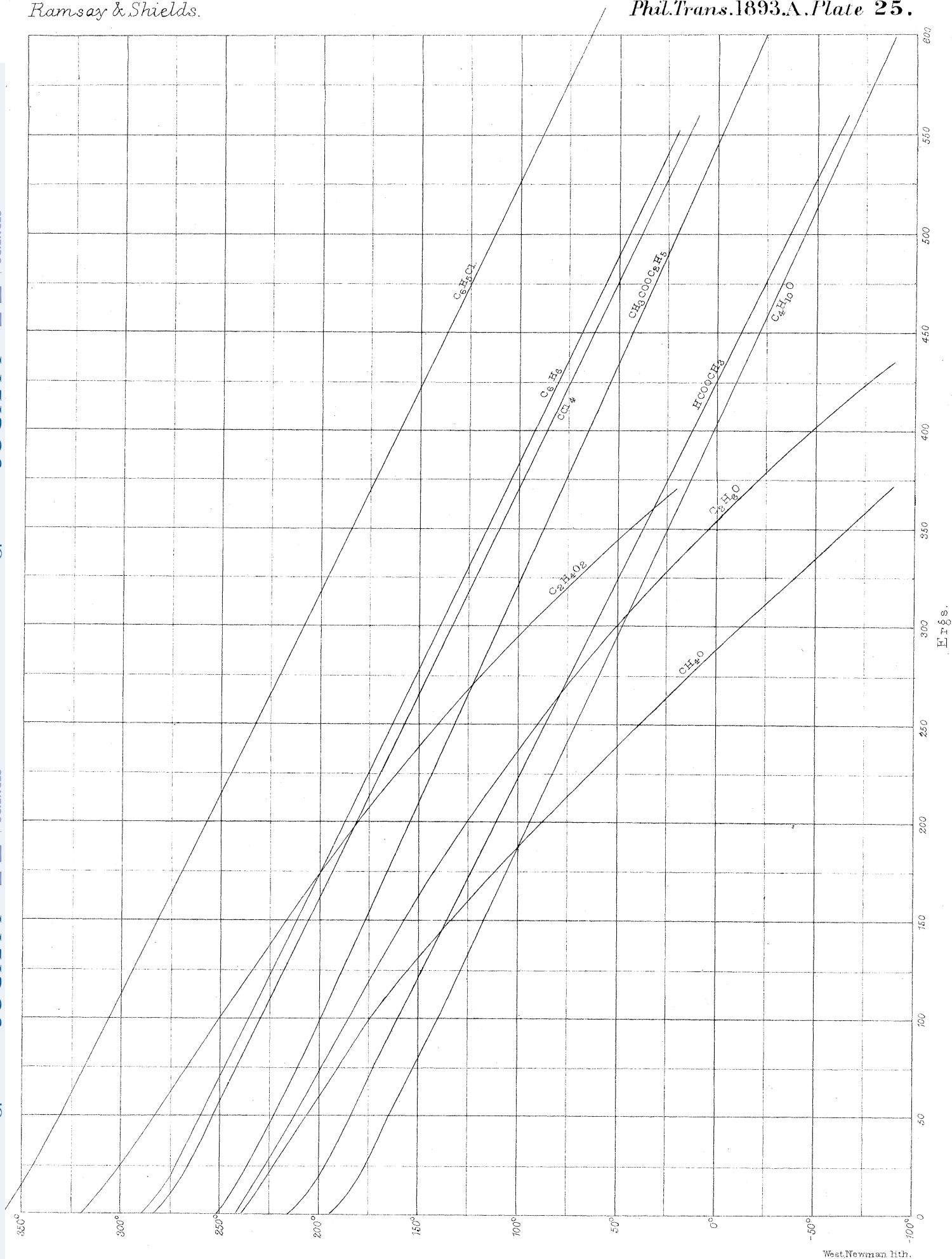
millims. rise in the narrow capillary with which the other observations were made. But such observations demand abrupt change of curvature between $+\,20°$ and $-\,90°$. As we have no intermediate observations to guide us, the lines are not drawn.

Plate 25 exhibits the variation of surface-energy with temperature. The close approach to parallelism of the straight lines is noteworthy; κ, in the equation $\gamma\,(\mathrm{M}v)^{\frac{2}{3}} = \kappa\,(\tau - d)$ has nearly the same numerical value for all substances, except, of course, for those which associate. The steeper slope of the curves of acetic acid and of the alcohols is well marked, and also the reflex curvature; for at temperatures near the critical temperatures, the deviation, $\kappa d\,(1 - 10^{-\lambda\tau})$ begins to tell; while at low temperatures the lines are curved owing to association of simple molecules to complex molecular groups.

West Newman lith.

Ramsay & Shields.

Phil.Trans.1893.A.Plate 25.

C_6H_5Cl
C_6H_8
CCl_4
$CH_3COOC_2H_5$
$HCOOCH_3$
$C_4H_{10}O$
$C_2H_4O_2$
C_3H_8O
CH_4O

Ergs.

350°
300°
250°
200°
150°
100°
50°
0°
-50°
-100°

0
50
100
150
200
250
300
350
400
450
500
550
600

West,Newman lith.