

June 14, 1894.

The LORD KELVIN, D.C.L., LL.D., President, in the Chair.

Mr. William Bateson, Mr. George Albert Boulenger, Professor Hugh Longbourne Callendar, Professor William Watson Cheyne, Mr. Robert Edmund Froude, Mr. Augustus Edward Hough Love, Mr. Francis Cranmer Penrose, Dr. Dukinfield Henry Scott, the Rev. Frederick John Smith, Mr. Joseph Wilson Swan, and Mr. Victor Herbert Veley were admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

- I. "The Molecular Surface-energy of the Esters, showing its Variation with Chemical Constitution." By Professor W. RAMSAY, Ph.D., F.R.S., and Miss EMILY ASTON, B.Sc. Received April 26, 1894.

The investigation of the thermal relations of a series of esters by Professor Young* has made it possible to determine their molecular surface-energies between ordinary temperature and their critical points; for the two important constants required for the calculation of these properties, the densities of the liquids and of their vapours in the saturated state (their orthobaric volumes) have been carefully determined by him. Professor Young has had the kindness to place his specimens at our disposal; their purity is sufficiently guaranteed by the proofs afforded in his paper. Before using them they were tested for acidity, to ensure that no hydrolysis had occurred during accidental exposure; but in no case was the reaction acid.

The chief question to which an answer was sought was: Do these bodies confirm the general law of which experimental proof was furnished by one of the authors in conjunction with Dr. Shields, which may be thus stated—

At approximately equal intervals of temperature below their critical temperatures all normal liquids possess equal molecular surface-energy?

The analogy of this law with that of Boyle is very striking; the latter may be expressed in almost identical terms—

* 'Trans. Chem. Soc.,' vol. 63, p. 1191.

At equal intervals of temperature above absolute zero all normal gases possess equal molecular volume-energy.

By "molecular volume-energy" is understood the product of pressure into molecular volume, that is, into the volume occupied by the molecular weight of the gas taken in grams; while molecular surface-energy signifies the product of surface-tension and molecular-surface, that is, the surface on which equal numbers of molecules are supposed to be uniformly distributed, equal to the two-thirds power of the molecular volume of the liquid.

The apparatus employed for low temperatures was that figured in the 'Transactions of the Chemical Society,' vol. 63, p. 1094. A double set of observations was made, each set with a different capillary tube. One of the tubes was accidentally broken during the experiments, and was replaced by one of approximately the same radius. The radii, as described in a previous paper, were measured by means of a microscope with micrometer eye-piece; tube A had a radius of 0.01843 mm.; tube B of 0.01708 mm.; and tube C of 0.01046 mm. These measurements were confirmed by determining the ascent of pure benzene in the tubes at known temperatures, and this is, on the whole, the easiest and most accurate method of determining their diameters.

For higher temperatures, the apparatus, described in the 'Philosophical Transactions,' 1893, A, p. 662, was employed. In order to apply a correction for the capillary rise in the barometer-tube in which the capillary tube D was confined, a determination was made with each ester at some temperature (usually the boiling point of alcohol under atmospheric pressure) at which capillary rise had been determined in a wide tube with tube A, B, or C, where correction was unnecessary, the ascent being taken, as customary, in inverse proportion to the radii of the tubes. As the variation of capillary rise with temperature is approximately a linear one, a sufficiently accurate correction may be obtained by assuming a rectilinear relation. Thus, for example, if at 78° the rise in the wide tube was 30 mm., and in the narrow tube 27 mm., it was necessary to add 3 mm. to the rise in the narrow tube at that temperature. At the critical temperature the correction is, of course, zero, since at that temperature there is no capillary ascent in any tube. It was held that this difference decreased in the barometer tube proportionately with rise of temperature, so that, for example, if the critical temperature were 278°, at the temperature 178° the correction applied amounted to 1.5 mm.

We regarded it as unnecessary to increase labour by taking observations at each 10° rise of temperature, since a few points on the curve serve to show whether the rectilinear relation holds. The plan of experiment was as follows:—The pressure tube containing the capillary tube was heated in the vapour of chlorobenzene, boiling under atmospheric pressure about 132°, the exact temperature

naturally depending on the barometric pressure of the day. As none of the esters boiled much above 100° at atmospheric pressure, it was possible by lowering pressure to cause them to boil at 132° , especially as in filling the tube a trace of air was purposely left in the liquid. It is not necessary that this air should be visible as a bubble, but it is sufficient if the liquid is not thoroughly boiled *in vacuo*. It may appear strange that such a course was followed, but repeated experience has shown that if a liquid is wholly deprived of dissolved gas by boiling it *in vacuo*, it is impossible to cause it to boil, even at atmospheric pressure, although heated to 100° above its normal boiling point.

Having determined the capillary rise at 132° , the pressure in the jacket was lowered, so as to cause the chlorobenzene to boil at 78° or 80° , care being taken not to allow the gas present in the upper part of the tube to condense wholly. The rise was again noted. The tube was then jacketed with quinoline vapour at about 185° , as well as at higher temperatures, and readings were again taken. Some six or seven points on the curve were thus determined, a sufficient number to characterise it.

It will conduce to clearness to give the essential data at this stage, reserving details of experiment to the Appendix, where they are tabulated. For completeness' sake, the results previously published in the 'Philosophical Transactions' for methyl formate and for ethyl acetate are here included.

As the molecular surface-energy of a liquid, provided it does not dissociate with rise of temperature, may be calculated by means of the equation

$$\gamma(Mv)^{\frac{2}{3}} = k(\tau - d)$$

(where k is a constant characteristic of each liquid but varying only slightly from 2.1, τ is the temperature measured from the critical point downwards, and d is a constant), the liquid is sufficiently characterised by giving the values of k , the critical temperature, and d . They are as follows:—

Table I.

Ester.	Critical temperature, C. $^{\circ}$	k .	d .
Methyl formate	214.0	2.042	5.9
Methyl acetate	233.7	2.109	4.5
Methyl propionate	257.4	2.182	5.3
Methyl butyrate	281.25	2.220	3.75
Methyl isobutyrate.....	267.55	2.248	5.25

Table I—*continued.*

Ester.	Critical temperature. C.°	k .	d .
Ethyl formate.....	235·4	2·020	4·5
Ethyl acetate.....	251·0	2·226	6·7
Ethyl propionate.....	272·9	2·240	4·9
Propyl formate	264·85	2·110	4·85
Propyl acetate.....	276·2	2·227	5·0

It is evident at the first glance that it is the acid radical which determines the value of k , for it increases progressively with the progressive increase of its molecular weight. Young has noticed a similar relation to hold with the ratios of absolute temperatures at corresponding pressures to absolute critical temperatures, but in other relations which he has investigated, there does not appear to be any analogous regularity.

As regards the values of d , they appear to fluctuate as the series is ascended in the order of complexity of acid radical, but too great dependence must not be placed on the values given. A very small change in k would make a considerable difference in the value to be assigned to d .

An attempt has been made to ascertain whether molecular volumes admit of more regular comparison at temperatures at which molecular surface-energies are equal. This appears, however, not to be the case. Thus, at the value 390 ergs, the group of four isomerides gives the following numbers:—

Ester.	Molecular volume.
Methyl butyrate	126·17
Methyl isobutyrate.....	125·93
Ethyl propionate.....	126·80
Propyl acetate	127·16

The agreement is no better than at their boiling points under normal pressure.

An attempt has also been made to find whether the boiling points at corresponding pressures bear a constant ratio to the temperatures of equal molecular surface-energy. Taking that ratio of pressure to critical pressure given in the fifth line of the table on p. 1245 of the paper in the 'Transactions,' and dividing the corresponding temperature for each liquid by the temperature of equal molecular surface-energy, the following ratios are obtained:—

		Ratio.
Methyl formate.....	295·6/280·1	= 1·055
Ethyl formate.....	311·4/310·9	= 1·002
Methyl acetate	313·75/317·5	= 0·9879
Propyl formate.....	332·5/348·2	= 0·9545
Ethyl acetate.....	327·7/342·1	= 0·9625
Methyl propionate	331·1/346·3	= 0·9559
Propyl acetate.....	346·75/369·2	= 0·9393
Ethyl propionate	344·6/367·0	= 0·9391
Methyl butyrate.....	348·3/375·0	= 0·9290
Methyl isobutyrate.....	338·75/362·0	= 0·9356

These numbers may be roughly arranged into four groups: methyl formate, the isomerides of the formula $C_3H_6O_2$, those of the formula $C_4H_8O_2$, and those of the formula $C_5H_{10}O_2$. They suffice to show that the molecular surface-energies are not comparable for non-isomeric bodies at corresponding pressures.

It must, therefore, be concluded that, although a certain rough analogy exists between the corresponding temperatures and pressures of the esters and their molecular surface-energy, yet the causes which determine deviation from the deductions from the equations of condition for fluids, are still more operative in causing deviations when surface forces are under consideration.

These experiments add eight more compounds to the list of six given in the 'Phil. Trans.,' 1893, A, p. 662, showing that within wide limits of temperature the molecular surface-energy of non-associating compounds is a linear function of the temperature; and as the law has been found to hold between more restricted limits of temperature for other thirty ('Trans. Chem. Soc.', vol. 63, p. 1191), it may be taken as placed on a firm basis.

A certain number of substances, among which are to be found the alcohols and the acids, show deviation from this law. Reserving to another occasion the grounds for inferring that this deviation points to molecular complexity, it is advisable to inquire here whether it is legitimate to assume for compounds which follow the law that their molecular weight in the state of liquid is the same as that of their gases.

Strictly speaking, the conclusion does not follow. The similar form of the surface-energy equation to that expressing volume-energy is a mere analogy; there is no physical connexion as yet manifest between the two.* There is no positive evidence to show that the molecules of such liquids as follow the law do not associate in twos, or threes, on assuming the liquid state. But one thing is certain, if they do, all associate to an equal extent, and the degree of association is not altered by rise of temperature.

* This conclusion must be modified in view of the recent memoir by van der Waals (see p. 181).

These two assertions are probably not true; it is unlikely that mere liquefaction should produce in all cases equal association; and it is unlikely that a rise of temperature should not cause the dissociation of an associated body. Change from the gaseous to the liquid state may be regarded as essentially equivalent to increase of pressure, since each produces approach between the molecules, diminishing intermolecular distance, and bringing so-called chemical forces into play. Now it is well known that equal rise of pressure does not always produce equal increment of association; hence it is unlikely that association to an equal extent should be caused by the reduction of the volumes of compounds until they are approximately equal.

This kind of proof is not unknown to chemists; it is employed, tacitly perhaps, in the fundamental statement that the molecular formulæ of hydrogen, oxygen, nitrogen, &c., are H_2 , O_2 , and N_2 . On this basis rests the usually accepted molecular formulæ of all compounds, and they are accepted because they are the simplest expressions which admit of equations of chemical interchange being written. It is true that subsequently to the adoption of such a standard its justice was confirmed by Kundt and Warburg's determination of the ratio between the specific heats of mercury gas at constant pressure and at constant volume, thereby rendering it extremely probable that the molecular formula of mercury is Hg_2 , and consequently that of hydrogen H_2 ; and by the discovery by Victor Meyer that the molecular formula of iodine at high temperatures corresponds with I_2 . But such confirmations merely supported the generally received assumption (for assumption it was then) that the molecular formulæ of most gases are directly comparable with that of hydrogen as H_2 .

Even at this present date the doctrine of the uniform expansion of gases at high temperatures rests on a similar basis. It has been shown by Victor Meyer that at the highest temperature attainable in a gas-furnace—some 1700° —hydrogen, oxygen, and nitrogen maintain the same ratio of expansion towards each other. One of two conclusions follows:—either that the expansion of all three gases is uniform with increase of temperature, or that all three gases dissociate equally with equal rise of temperature. Needless to say that the first alternative is universally adopted.

We have thought it well to state in full the reasons for adopting the assumption that the molecular weights of such liquids as the esters are not changed on their assuming the liquid state. It is now evident that such a statement is an assumption, a hypothesis; but it is one for which there is a great deal of probability, probability of the same kind as that which led to the adoption of the usually received molecular formulæ for gases.

APPENDIX.
I. Experimental Results at Low Temperatures.

Substance.	Radius = 0·01843 cm.				Radius = 0·01046 cm.			
	<i>t.</i>	<i>h.</i>	γ .	$\gamma(\text{Mp})^{\frac{1}{3}}$.	<i>t.</i>	<i>h.</i>	γ .	$\gamma(\text{Mp})^{\frac{1}{3}}$.
Ethyl formate..... Crit. temp., 235·30°.....	10·0° 46·5 78·5	2·851 2·430 2·072	24·08 19·50 15·68	443·5 371·5 309·2	10·0° 46·5 78·5	5·051 4·327 3·650	24·22 19·71 15·68	446·0 375·5 309·1
Methyl acetate..... Crit. temp., 233·7°.....	10·0° 46·2 78·3	2·970 2·502 2·121	25·22 20·32 16·28	462·8 383·9 318·2	10·0° 46·2 78·3	5·200 4·442 3·752	25·06 20·49 16·35	459·9 387·2 319·5
Propyl formate..... Crit. temp., 264·85°.....	10·0° 46·2 78·2	3·017 2·612 2·300	25·02 20·67 17·52	523·6 446·3 387·0	10·0° 46·2 78·2	5·325 4·611 4·033	25·06 20·71 17·44	524·4 447·1 385·2
Methyl propionate..... Crit. temp., 257·4°.....	10·0° 46·2 78·2	3·248 2·816 2·430	25·23 20·85 17·11	524·3 447·3 378·8	10·0° 46·2 78·2	5·364 4·629 4·002	25·51 20·98 17·26	530·2 450·2 381·9
Propyl acetate..... Crit. temp., 276·2°.....	10·0° 46·2 78·2	3·291 2·896 2·518	24·80 20·86 17·35	580·2 503·0 431·0	10·0° 46·2 78·2	5·392 4·723 4·126	24·83 20·84 17·41	582·0 502·2 432·3
		Radius	= 0·01708 cm.					

I. Experimental Results at Low Temperatures—continued.

Substance.	Radius = 0.01708 cm.				Radius = 0.01046 cm.			
	t .	h .	γ .	$\gamma(Mv)^{\frac{2}{3}}$.	t .	h .	γ .	$\gamma(Mv)^{\frac{2}{3}}$.
Ethyl propionate	10.0°	3.253	24.57	574.0	10.0°	5.335	24.67	576.2
Crit. temp., 272.9°	46.2	2.856	20.58	496.1	46.2	4.672	20.62	496.9
	78.2	2.501	17.24	428.1	78.2	4.082	17.22	427.8
Methyl butyrate*	10.0°	3.115	25.63	595.0	10.0°	5.460	25.50	591.7
Crit. temp., 281.25°	46.2	2.786	21.50	514.5	46.2	4.795	21.39	511.8
	78.2	2.410	18.15	446.9	78.2	4.223	18.05	444.4
Methyl isobutyrate	10.0°	3.195	24.11	563.6	10.0°	5.213	24.08	563.0
Crit. temp., 267.55°	46.2	2.806	20.29	487.3	46.2	4.572	20.04	486.1
	78.2	2.426	16.70	415.0	78.2	3.964	16.64	415.1

* The tube used had the radius 0.01843 cm.

II. Experimental Results at Higher Temperatures.

Radius of Tube = 0.011197 cm.

Substance.	<i>t</i> .	<i>h</i> .	γ .	$\gamma(\text{Mv})^{\frac{1}{3}}$.	$\gamma(\text{Mv})^{\frac{1}{3}}$ Calc.	<i>k</i> and <i>d</i> .
Methyl formate	2.042 <i>d</i> = 5.9°
Ethyl formate	80.0° 131.6 185.0 210.0	3.381 2.344 1.224 0.685	15.50 9.51 3.86 1.75	306.2 201.0 91.5 44.7	304.9 198.8 92.7 42.2	2.020 <i>d</i> = 4.5°
Methyl acetate	78.2° 132.4 185.0 200.0 215.0	3.498 2.392 1.202 0.872 0.512	16.31 9.81 3.90 2.51 1.21	318.9 206.0 91.0 61.3 31.5	318.5 204.2 93.2 61.6 30.0	2.109 <i>d</i> = 4.5°
Propyl formate	85.0° 131.7 185.0 210.0 237.0	3.665 2.796 1.740 1.251 0.659	16.60 11.53 6.14 3.86 1.68	371.9 272.5 157.2 104.2 49.2	369.2 270.7 158.2 105.4 48.5	2.110 <i>d</i> = 4.85°
Ethyl acetate	2.226 <i>d</i> = 6.7°
Methyl propionate ..	78.0° 132.6 184.9 237.7	3.750 2.682 1.634 0.500	17.31 11.09 5.73 1.14	383.1 261.8 147.0 34.3	379.3 260.7 146.7 31.4	2.182 <i>d</i> = 5.3°
Read from curve .. {	240.0 250.0	0.440 0.188	0.96 0.31	29.3 10.1	26.4 4.4	
Propyl acetate	100.0° 132.6 185.0 210.0 238.2	3.474 2.877 1.893 1.412 0.854	15.10 11.78 6.76 4.57 2.30	382.8 310.2 191.5 135.5 73.5	381.3 308.7 192.0 136.3 73.5	2.227 <i>d</i> = 5.0°
Ethyl propionate...	100.0° 132.2 185.0 210.0 237.6	3.442 2.880 1.864 1.384 0.812	14.97 11.77 6.59 4.41 2.14	380.1 310.2 187.5 131.5 68.8	376.2 304.1 185.9 129.9 68.1	2.240 <i>d</i> = 4.9°
Methyl butyrate	100.0° 132.5 185.0 210.0 238.0	3.591 3.001 2.033 1.532 0.980	15.92 12.49 7.41 5.09 2.81	400.2 325.3 207.3 148.7 87.7	394.1 321.9 205.3 149.8 87.7	2.220 <i>d</i> = 3.75°
Methyl isobutyrate ..	100.0° 132.2 185.0 210.0 237.6	3.311 2.728 1.726 1.250 0.694	14.36 11.10 6.03 3.90 1.73	365.0 292.8 172.1 117.0 56.6	364.8 292.3 173.8 117.6 55.5	2.248 <i>d</i> = 5.25°