

XVI.—*The Molecular Formulæ of some Liquids, as determined by their Molecular Surface Energy.*

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IN continuation of researches published in these Transactions (1893, 63, 1089), we proceed to bring under the notice of the Society experiments on phenol,* bromine, nitric and sulphuric acids, and phosphorus. It has been our object to select liquids which, from their behaviour or from their analogy with others already investigated, promised to show a higher molecular weight than that expressed by their ordinary formulæ. It would have been interesting to have included sulphur in our list, but unfortunately the viscosity of liquid sulphur at temperatures but little higher than its melting point precludes observation by the method of registering ascent in a capillary tube.

It may be well here to recapitulate briefly that the variation of surface energy with temperature is, for non-dissociating liquids, a rectilinear function of the temperature, and that the value of the differential coefficients is, on the average, 2.121. Hence, for a normal or monomolecular liquid, the numerical value of $\frac{dE}{dt}$, or, as usually determined, $\frac{E_t - E_{t'}}{t' - t} = 2.121$, approximately. E represents molecular surface energy, or $\gamma(Mv)^{\frac{1}{3}}$, where γ is surface tension; M, gaseous molecular weight; v , specific volume; and $(Mv)^{\frac{1}{3}}$, molecular surface.

If the value of M has been wrongly chosen, a coefficient differing from, and less than, 2.121 is obtained. In calculating the true value of M, it has been assumed that the principal cause of variation from

* The experiments on phenol were made in conjunction with Dr. J. Shields.

this general mean is association, and that the association (x) varies only slowly with temperature. Let M_0 be the gaseous molecular weight, and xM_0 the actual molecular weight of the liquid under experiment,* then,

$$\frac{dt}{d} \left\{ \gamma x^3 (M_0 v)^3 \right\} = 2 \cdot 121, \text{ or}$$

$$x^3 \frac{d}{dt} \gamma (M_0 v)^3 + \gamma (M_0 v)^3 \cdot \frac{dx^3}{dt} = 2 \cdot 121,$$

and

$$x^3 K_0 + \gamma (M_0 v)^3 \cdot \frac{dx^3}{dt} = 2 \cdot 121.$$

It is assumed that $x^3 = K/K_0$, and $\gamma (M_0 v)^3 \cdot \frac{dx^3}{dt}$ is neglected as too small to affect the result considerably. In words, it is assumed that the alteration of association with temperature is negligible. It may be seen, by reference to the memoir on molecular surface energy (*Phil. Trans.*, **184**, A, 655), that acetic acid, and methyl and ethyl alcohols do not exhibit a very rapid variation of association with temperature, and we therefore regard our assumption as justified for the limits of temperature within which we determine the coefficients of variation of molecular surface energy.

In accordance with what has been said, it is easy to calculate the molecular weight of a liquid by the equation

$$M = \left\{ \frac{K(t' - t)}{\gamma v^3 - \gamma' v'^3} \right\},$$

where the symbols have the meanings previously attached to them.

We now proceed to give the results of experiments.

* 1. *Phenol*.—The sample employed was colourless, and had a constant boiling point. We have taken as correct the densities as determined by Kopp (*Annalen*, **95**, 312). It was easy to keep the substance liquid in the lower narrow tube, which held the lower part or stem of the capillary tube (see illustration, *loc. cit.*, p. 1094), by occasionally warming it with a Bunsen burner.

Phenol ($r = 0.01843$ cm.).

t .	h .	ρ .	γ .	$\gamma(Mv)^3$.	K .	x .	M .
	cm.						
46° 0	3.88	1.0407	36.81	736.9	1.682	1.42	133.5
78° 0	3.64	1.0121	33.32	683.1			
131° 7	3.19	0.9670	27.90	589.9	1.736	1.35	126.9
184° 0	2.70	0.9164	22.39	490.6	1.899	1.18	110.9

* Where the expression "actual molecular weight" or "mean molecular weight"

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The molecular weight of gaseous phenol is 94; and it is seen that between 131.7° and 184° , the value is rapidly approaching that number. In this it agrees with the alcohols; and as it has been previously noticed that the higher the molecular weight of acids and alcohols, the less the tendency towards association, it was to be expected that a substance of such high molecular weight as phenol would show small tendency to form molecules of great complexity. Experiment has shown the correctness of this expectation.

2. *Bromine*.—The difficulty in determining accurately the capillary rise of bromine is that its opacity prevents accurate reading of the level of the lower meniscus. An approximate result, however, can be found by reading the upper edge of the meniscus; and if, as seems probable, the height of this meniscus is not greatly altered by rise of temperature from 10° to 80° , the results may be accepted as approximating to truth.

Bromine ($r = 0.01046$ cm.).

t .	h .	ρ .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	K.	x .	M.
	mm.		dynes	ergs			
10.6	2.490	3.152	40.27	552.08	1.811	1.267	202.77
46.0	2.230	3.031	34.68	487.98			
78.1	1.972	2.917	29.51	426.09	1.928	1.154	184.59

The densities at these temperatures were calculated from Thorpe's determinations (Trans., 1880, **37**, 173).

If it be supposed that the capillary rise should have been a millimetre more in each case, the mean molecular weight is altered only to 201.79, and 183.15 instead of 160, that of Br_2 . Hence a constant small error in reading would have little influence on the results. Dr. E. P. Perman showed in 1890 (*Proc. Roy. Soc.*, **48**, 49), that even at pressures near saturation, and at 15° , the vapour density of bromine is normal; and Paternò and Nasini, in 1888, found that in aqueous and in acetic acid solutions the molecular weight corresponded with Br_2 . It would appear that even in the liquid state most of the molecules possess that formula; but some sign of association with fall of temperature appears to take place.

3. *Nitric acid*.—The sample of acid was prepared from nitric and sulphuric acid; it was then mixed with phosphoric anhydride, and

is used, it is not to be understood that the weight in question is that of a definite molecule, but is a mean result due to the fact that the liquid consists of molecules of different complexity. For example, a molecule of H_2O plus a molecule of H_3O_4 would have a mean molecular weight of 45.

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distilled over a water bath. A bulb was filled, and when diluted and titrated, it proved to contain 99·8 per cent. of acid. It had a very pale yellow colour, and fumed strongly on exposure to the air.

The tube was filled without warming the acid by exhausting a large globe provided with a stopcock, and attaching the neck of the latter with india-rubber tubing to the drawn-out end of the experimental tube containing somewhat more than the requisite amount of acid; on opening the stopcock, the acid evaporated under reduced pressure, and all air was expelled from the experimental tube. The tube was then sealed. The acid turned much darker on heating to 78°, and it appeared to contain some nitric peroxide, but, on cooling, it regained its original pale yellow colour.

Nitric acid ($r = 0\cdot01192$ cm.).

$t.$	$h.$	$\rho.$	$\gamma.$	$\gamma(Mr)^{\frac{1}{3}}$	K.	$x.$	$x \times M.$
11°6	4·613	1·5304	41·30	492·3	1·500	1·681	105·9
46·2	4·182	1·4696	35·95	440·4			
78·2	3·806	1·4133	31·46	395·6	1·400	1·864	117·4

The densities were determined in a pycnometer at 11·6° and at 46·2°. It was found impossible to prevent the acid from boiling at 78·2°, although its boiling point is given as 86°. The density at 78·2° was, therefore, estimated by extrapolation. The results show that nitric acid in the liquid state has a molecular weight greater than that expressed by the formula HNO_3 , and probably consists of a large proportion of molecules of $\text{H}_2\text{N}_2\text{O}_6$, mixed with simple molecules.

4. *Sulphuric acid*.—Acid of composition corresponding to the formula H_2SO_4 is unstable, and dissociates on warming into sulphuric anhydride and oil of vitriol, approximating to the composition $12\text{H}_2\text{SO}_4, \text{H}_2\text{O}$. It was this acid which was employed for the experiments, and analysis showed it to correspond exactly to the above formula. Its expansion was determined with the pycnometer at the temperatures at which its ascent in the capillary tube was measured. In calculating its molecular weight, the formula weight of the substance used has been assumed to be $(\text{H}_2\text{SO}_4, \frac{1}{12}\text{H}_2\text{O}) = 99\cdot5$; but, indeed, this is unnecessary, as the equation on p. 168 permits the determination of molecular weight, M , without any assumption. The acid wets the tube easily; it was sealed after warming in a Sprengel vacuum, so as to expel all dissolved gas. It was not viscous, but ascended easily,

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and gave concordant readings. The results are given in the annexed table.

Sulphuric acid ($r = 0.01843$ cm.).

$t.$	$h.$	$\rho.$	$\gamma.$	$\gamma(Mv)^{\frac{1}{3}}$	K from curve.	$x \times M.$
10.2	3.305	1.8493	55.26	787.6	0.209	32.3×99.5
46.4	3.290	1.8135	53.94	778.8		
78.5	3.283	1.7808	52.86	772.5		
182.5	3.275	1.7342	51.35	763.8		
184.6	3.244	1.6874	49.49	749.7	0.297	19.1×99.5
237.7	3.170	1.6341	46.84	724.9	0.599	6.7×99.5
281.0	3.045	1.5912	43.80	690.1	1.072	2.8×99.5

In mapping these results, it is obvious that the first four values of $\gamma(Mv)^{\frac{1}{3}}$ lie on a straight line; the mean value of R read from the line is 0.209, and the molecular weight appears to correspond to $(H_2SO_4)_{32}$. Of course the water present may account to some extent for this extraordinary result, but we are disposed to regard it as true; for what is termed the boiling point of sulphuric acid, lying near 360° , is in reality its temperature of dissociation under atmospheric pressure; its true boiling point must lie much higher. Moreover, the existence of complex sulphates such as $NaK_3(SO_4)_3$ implies a molecular weight corresponding to $(H_2SO_4)_3$. It is also worthy of remark that sulphuric acid possesses no appreciable vapour pressure at the ordinary temperature; for Johnson found (*Chem. News*, 68, 211) that no sign of a sulphate could be detected in caustic soda exposed in a vacuum desiccator, containing sulphuric acid, even after a month. The liquid alloy of sodium and potassium also failed to absorb any vapour from sulphuric acid after exposure for the same length of time. Now, under similar circumstances, a piece of gold leaf exposed to mercury vapour would have been heavily amalgamated. It would be worth while making similar experiments to detect the possible volatility of such metals as cadmium and zinc.

The small decrease of capillary rise with temperature and the corresponding small decrease of molecular surface energy with temperature are highly abnormal, and there appears no escape from the conclusion that the molecular weight of liquid sulphuric acid is exceedingly high.

Above 130°, however, the molecular weight shows rapid diminution. This may be due to one or to both of two causes, to the dissociation of such compound molecules, or to the partial dissociation of the compound into sulphuric anhydride and water. The method of experiment does not allow of a decision; but it is noticeable that faint fumes begin to be evolved from sulphuric acid at about 130°, which would imply the latter conclusion, whether the former conclusion is true or not. We incline to ascribe the fall of molecular weight to both causes acting in concert.

To calculate the molecular weight directly from the individual observations is in this case not satisfactory, for the differences in h and consequently in γ are so small that errors of experiment tell very distinctly. But taking the whole range from 10.2° to 132.5°, and calculating the molecular weight by the equation

$$M = \left\{ \frac{K(t' - t)}{\gamma v^{\frac{1}{3}} - \gamma' v'^{\frac{1}{3}}} \right\}^{\frac{2}{3}},$$

the number 3620 is obtained, which is not far removed from 99.5×32 . But the other method is better adapted to eliminate error in this instance where several observations have been made.

5. *Phosphorus*.—This substance gave a great deal of trouble, chiefly in discovering how to fill the tube. The phosphorus was first distilled in a current of carbon dioxide and received in a tube similar in form to the experimental tube, but having its narrow portion bent at an acute angle, and sealed to the experimental tube; a constricted portion between the two tubes was plugged tightly with glass wool, yet not so tightly as to prevent a stream of dry carbon dioxide from passing. After a sufficient quantity had distilled over, it was melted, and passed through the glass wool into the experimental tube as a limpid liquid with a very pale yellowish tinge. The phosphorus was then melted away from the constriction, which was sealed. The Sprengel pump having been filled with dry carbon dioxide, the upper portion of the experimental tube was constricted, and secured to the Sprengel pump, and a vacuum was made; the phosphorus was then melted, when a number of bubbles appeared, and were removed by pumping. It was at first thought advisable to boil the phosphorus in the vacuum, but this was found to produce some red phosphorus, and in later experiments the temperature was not raised so high as to cause ebullition. The tube was then sealed at the constriction, and jacketed with the usual vapours. The temperature of boiling carbon bisulphide is too little removed from the melting point of phosphorus to give good results; hence higher temperatures were chosen.

Liquid phosphorus does not satisfactorily wet glass, and to this also many of our difficulties are to be ascribed. It was only by sinking

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the capillary tube by means of the magnet and raising it quickly that trustworthy readings were obtained; after standing for a little, the cohesion between the phosphorus and the glass appeared to diminish.

We fear that it cannot be said that the angle of contact between phosphorus and glass is zero, as in the case of the other liquids investigated; but it would be sufficient for our purpose if the angle is not materially altered within the limits of temperature employed. However this may be, the experiment yields a probable result, for the molecular weight found corresponds to the formula P_4 , as shown by the following table.

Phosphorus ($r = 0.01708$ cm.).

$t.$	$h.$	$\rho.$	$\gamma.$	$\gamma(Mr)^{\frac{1}{3}}$	K.	$x.$	$x \times M.$
$78^{\circ}3$	3.00	1.714	43.09	748.2	2.205	0.94	117.0
132.1	2.55	1.664	35.56	629.6			

The molecular weight was here assumed to be 124, or 31×4 , and we think that the difference is caused by experimental error. At all events, it may be said that there is no sign of association.

In conclusion, it may be well to mention here that inasmuch as nitroethane was found to associate, an experiment was made with *chloropicrin*, $C(NO_2)Cl_3$, which gave normal results. The liquid is monomolecular.

Our results show that phenol, like the alcohols, forms complex molecules in the liquid state, which dissociate on rise of temperature; that bromine, too, is somewhat associated, and also gives simpler molecular groupings of Br_2 on rise of temperature; that nitric acid consists largely of molecular groups of the magnitude $(HNO_3)_2$; that sulphuric acid is a very complex substance at ordinary temperature, of probably not lower complexity than $(H_2SO_4)_{32}$, but that above 132° a rapid diminution of molecular weight is noticeable; and that phosphorus in the liquid state has a molecular weight equal to that of its gas, P_4 .

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