

The numbers obtained by the members of a large class of elementary students varied from 17 to 21 for the molecular weight of water. Still better results were obtained for the molecular weight of methyl alcohol. It is instructive to allow the students to perform a series of experiments at different concentrations. In the case of water in phenol the observed molecular weight increases very rapidly with the concentration (molecular association). Scarcely any such effect is noticed with methyl alcohol in phenol.

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ART. XLVIII.—*The Vapour Densities of the Fatty Acids.*

By Professor EASTERFIELD and P. W. ROBERTSON.

[*Read before the Wellington Philosophical Society, 11th February, 1902.*]

It is well known that a large number of substances have vapour densities at their boiling-points which are a little above those calculated from their molecular weights. This may in many cases be explained by the fact that the gaseous laws which are used in the calculations are not rigorously true at the point of liquefaction. In other cases, however, the abnormality is undoubtedly due to the fact that association of the molecules takes place at temperatures in the neighbourhood of the boiling-point.

The first substance to attract the attention of chemists was acetic acid. That the abnormality in this case is really due to the formation of molecular complexes is shown, first, by the fact that the normal vapour density is not reached till 110° above the boiling-point. Secondly, the value for the expression  $MW/T'$  (where  $M$  is the molecular weight,  $W$  the latent heat of vaporization) is 15, while for liquids of normal molecular weight a constant value of about 21 is obtained. This low value can only be explained on the assumption that the molecules are associated in the gaseous state.

Similarly, it was found that normal butyric and isovaleric acids were associated, although to a less extent. In general it may be said that this is true of all the lower fatty acids and their derivatives, which do not decompose on heating. This is quite analogous to their behaviour in solution. In benzene and naphthalene most hydroxyl compounds, and especially acids, associate.\* This is also true for the solvents bromoform, nitrobenzene, and parabromtoluene. Even in phenol,

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\* Auwers, *Zeit. Phys. Chém.*, 1893, &c.

which owes its wide application in cryoscopy to its slight tendency to cause bodies to associate, the experiments of the authors have shown that, while the alcohols and other aliphatic compounds remain fairly normal, the fatty acids associate strongly with rising concentration. This, however, will be discussed in a future communication.

1. Acetic acid has already been examined in detail. The following are a few of the numbers :—\*

Temperature. (Boiling- point, 119° C.).	Density. (Normal Molecular Weight, 2.08).
125° ... ..	3.20
130° ... ..	3.12
140° ... ..	2.90
160° ... ..	2.48
190° ... ..	2.30
219° ... ..	2.17
230° ... ..	2.09
250° ... ..	2.08

On plotting these results as a curve it is found that the rate of dissociation of these molecular complexes is a direct function of the temperature for 50° above the boiling-point. Then the rate is gradually decreased till 230° C., when the vapour density becomes constant.

2. We can find no record of any determinations made with propionic acid, the next member of the fatty acids. Accordingly we performed several experiments by the ordinary method of Dumas.

(a.) At 146° C. and at 760 mm. the vapour density was found to be 51. The normal value is 37; consequently at 5° above the boiling-point the vapour is associated 38 per cent.

(b.) At 192° C. and at 755 mm. the vapour density was found to be 45, indicating 22 per cent. association.

3. Normal butyric has already had its vapour density determined at different temperatures.† A normal value is reached at a temperature of about 100° above the boiling-point of the compound. By continuing the curve for butyric acid it is found that the vapour density 5° above its boiling-point would be 3.8—i.e., at that temperature it is associated 25 per cent. Thus for the three acids at 5° above their boiling-points—

	Vapour associated.
Acetic acid ... ..	54 per cent.
Propionic acid ... ..	38 "
Butyric acid ... ..	25 "

\* Cahours, "Comptes Rendus," xx., 51.

† Cahours, *loc. cit.*

Thus it is noticed that the amount of association decreases with rising molecular weight, which fact is of universal occurrence for homologous bodies in the liquid state (Ramsay and Shields; Traube) as well as for substances in solution (Biltz).

In this case, however, it happens that the amount of association is inversely as the square of the molecular weight:—

	Per Cent. Amount of Association.	Numbers Proportional to Inverse of Square of Molecular Weight.
Acetic acid ...	54	52
Propionic acid ...	38	36
Butyric acid ...	25	26

Further experiments are in progress with the object of ascertaining whether the same law holds for the higher members of the series.

ART. XLIX.—*The Latent Heats of Fusion of the Elements and Compounds.*

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Communicated by Professor Easterfield.

[*Read before the Wellington Philosophical Society, 11th February, 1902.*]

ABSTRACT.

CROMPTON states that  $\frac{Aw}{Tv} = K$ , where  $A$  is atomic weight,  $w$  latent heat of fusion,  $T$  melting point on absolute scale, and  $v$  the valency of the element. Now, the valency of an element is known to vary, and as the results were not very concordant the author, from theoretical grounds, replaced this by the relation  $\frac{Aw}{T\sqrt[3]{A}} = K$  where  $d$  is density and  $\sqrt[3]{\frac{A}{d}}$  represents

the space between the atoms. Just as the atomic heat of the elements is only constant for elements with atomic weights over about 40, so is this relation only true under the same conditions. In the case of the fourteen elements with atomic weights over 40 the value varies between 1 and 1.3, with the exception of the three, gallium, lead, and bismuth. But applying this rule to the compounds, and changing the atomic weight into molecular weight, still more concordant results are obtained. Out of thirteen inorganic compounds, with the exception of two the results vary from 1.9 to 2.3, being mostly near the mean 2.1. There is also good agreement among the organic bodies examined, the mean being about 2.4. The author intends to calculate more results, and to present fuller tables to the Society.

Various attempts have been made to arrive at a definite