Molecular weight in phenol solution: Calculated $(C_6H_8NO_5)_3 = 486$; found = 450.

The characters given by Skey for the karakin prepared by the animal-charcoal method differ in two important respects from those above described. The melting-point according to Skey is 100°, and the substance contains no nitrogen. At first sight it would therefore seem that the two substances are not identical. From Skey's paper, however, it would appear that the karakin was not recrystallized, and this would account for the difference in the melting-points. The failure, on the other hand, to detect nitrogen in organic substances has occurred so often in the history of chemical research, more particularly before the application of the metallic-sodium test had become general, that the authors do not attach much importance to this apparent discrepancy. They would add that they have prepared karakin by Skey's method and found it to contain nitrogen, and to have the same melting-point as the compound already described.

The expenses in connection with this investigation have been defrayed by a grant from the Royal Society of London.

ART. XLVII.—*Raoult's Method for Molecular Weight Determination.*

By Professor EASTERFIELD and JAMES BEE, M.A.

[*Read before the Wellington Philosophical Society, 5th November, 1901.*]

THE teaching of practical chemistry at the present day differs greatly from the teaching in vogue twenty-five years ago. At that time qualitative analysis only was, as a rule, taught to the elementary student, and experimental proof of chemical theory was either ignored or only practised in the lecture-room. Nowadays, however, the teaching of qualitative analysis is usually prefaced by a series of simple quantitative experiments, performed by the students themselves, and designed to illustrate modern chemical principles. Such an introduction greatly facilitates the understanding of the science.

So far as we are aware, no attempt has been made to teach the practice of molecular-weight determination by Raoult's method to the elementary student, it being generally supposed that expensive apparatus is necessary for such determinations. As a matter of fact, the experiment may be successfully carried out with the simplest of school apparatus, and with a very small expenditure of time and material.

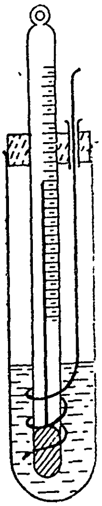
Raoult's law states that the depression in the freezing-point of a given solvent is directly proportional to the concentration of the solution and inversely to the molecular weight of the dissolved substance—*i.e.*,

$$D \propto \frac{w}{WM},$$

where D = depression in freezing-point, W = weight of the solvent, w = weight of the dissolved substance, and M = molecular weight of the dissolved substance. So that, if K represent the depression which the molecular weight of *any* substance (in grams) will cause in 100 grams of the solvent,

$$M = \frac{w \times 100}{W \times D} K.$$

This method of determining molecular weights is in every-day practice amongst research chemists, giving good results even for substances with very high molecular weights. With such substances the observed depression is so small that an exceedingly sensitive, and therefore expensive, thermometer is required. For class purposes, however, we must make the depression large enough to be easily registered on a common thermometer. This is easily done by choosing a solvent whose depression constant (K) is large, and dissolving in it some substance whose molecular weight is small.



Now, of all common substances water has the lowest molecular weight, whilst phenol has the highest depression constant (72); indeed, 1 per cent. of water depresses the melting-point of phenol about 4° C.

The apparatus needed is illustrated in the figure. As it consists only of a test tube, common centigrade thermometer, cork, and brass-wire stirrer, no explanation is necessary.

To perform the experiment about 10 grams of good carbolic acid is weighed into the test tube, thoroughly melted by immersing for a few moments in hot water, and the freezing-point determined by thoroughly stirring until the superfused liquid begins to crystallize and the temperature indicated by the thermometer becomes steady. This operation should, of course, be repeated. About 0·1 gram of water is now added to the carbolic acid in the tube, and the freezing-point again determined. The water is conveniently added from a dropping-pipette, the number of drops being carefully counted, and the number of drops which make up a cubic centimeter being determined in a separate experiment.

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.

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,

* Auwers, Zeit. Phys. Chem., 1893, &c.