

electrostatic to the electromagnetic measure of the capacity is v^2 . The result of the experiments, using Lord Rayleigh's value of the ohm, was that

$$“v” = 2.963 \times 10^{10} \text{ in C.G.S units.}$$

XI. “On the Molecular Weights of the Substituted Ammonias. No. I. Triethylamine.” By JAMES DEWAR, M.A., F.R.S., Jacksonian Professor, Cambridge, and ALEXANDER SCOTT, M.A., D.Sc. Received June 21, 1883.

The conduct of the experiments relating to a new determination of the atomic weight of manganese recently communicated to the Society* has led us to prosecute some further studies in this field of research. The following note deals with the preliminary results arrived at regarding the molecular weight of a member of a class of bodies which, strange to say, have not been previously selected for accurate determinations of this kind. The substituted ammonias are peculiarly fitted to reveal the effect of small differences from whole numbers in the conjoint values of the atomic weights of carbon and hydrogen. By selecting tertiary amines of high molecular weight it is possible to integrate these small positive or negative increments through the increase in the number of carbon and hydrogen atoms in the substituting radical. There is also a special advantage in employing the fully saturated ammonium derivatives for experiment. Theoretically it ought to be possible to ascertain by this method whether the atomic weight of hydrogen differs from unity, provided the atomic weight of carbon be accepted as sufficiently well defined, from other methods of investigation. The difficulty of getting perfectly pure substances for such work, together with the hygroscopic character of the ammonium compounds, introduces serious difficulties, and for the purpose of testing the accuracy of the proposed method, the preliminary experiments have been made with triethylamine.

The triethylamine employed was made by the action of chloride of ethyl on ammonia, and was transformed into the bromide of tetraethylammonium. This bromide of the fully substituted ammonium was decomposed by dry distillation into triethylamine and bromide of ethyl, and the base separated in the form of the chloride. The free base was separated from the chloride with caustic potash, and after careful drying with anhydrous oxide of potassium was subjected to fractional distillation. The portion boiling between 90° and 91° was converted into the hydrobromate and its equivalent relation to

* “On the Atomic Weight of Manganese,” “Proc. Roy. Soc.,” vol. 35, p. 44.

silver determined, after the method of Stas, with the following results :—

Weight of salt in vacuo.		Weight of silver in vacuo.		Molecular weight of $(C_2H_5)_3N.HBr.$
6·6248	3·9219	182·313
8·24088	4·8798	182·270

A portion of the same fraction of the base was now treated with nitrous acid in order to eliminate traces of primary and secondary amines, and the titration repeated with the following results :—

Weight of salt in vacuo.		Weight of silver in vacuo.		Molecular weight of $(C_2H_5)_3N.HBr.$
5·3165	3·1519	182·052
4·6237	2·74194	182·001

The effect of the nitrous acid treatment has been to lower the molecular weight, thus proving the presence of small quantities of bases derived from more complicated radicals than ethyl, probably propylamine.

After these preliminary determinations the whole of the sample of triethylamine was fractionated with great care, and the portion boiling between 90° and 91° C. selected for a repetition of the process. The middle portion of this second distillation boiling between $90^\circ\cdot2$ and $90^\circ\cdot4$ was again separated into three fractions by a new distillation and the molecular weights of the respective samples of the base determined. The following table gives the results of the different titrations :—

	Weight of salt in vacuo.	Weight of silver in vacuo.	Molecular weight of $(C_2H_5)_3N.HBr.$	Remarks.
I....	7·06272	4·18778	182·025	First samples, boiling point 90° — 91° .
II....	6·4418	3·8199	182·011	Second fraction of I, boiling point $90^\circ\cdot2$ — $90^\circ\cdot4$.
III....	15·46765	9·18495	181·756	First portion of II re-fractionated.
IV....	11·95685	7·0902	182·012	Middle and chief portion of II re-fractionated.
V....	13·9522	8·2664	182·166	Highest boiling point, portion of II re-fractionated.

The molecular weights of the different samples clearly prove that the base is not homogeneous, the presence of bases of higher

and lower molecular weights being revealed by the analysis. No doubt, the amount of this impurity is exceedingly small, but still sufficient to prevent a definite conclusion being reached as to the correct value for pure triethylamine. As Stas's method of titration is capable of giving concordant results within one ten-thousandth of the molecular weight, the large variation, amounting to one four hundred and fortieth of the mean molecular weight of the first and third sample of the last fractionation, shows that the material is by no means pure enough for the problem we desire to solve. At the same time, the middle and largest portion of the last distillation has probably a molecular weight very near that of the pure base, and may provisionally be accepted. If the molecular weight of the hydrobromate is 182.012, then the value for triethylammonium is 102.061; and if we subtract from this the value for ammonium found by a similar method of titration, viz., 18.074 (Stas), the resulting number 83.987 is the molecular weight of the hydrocarbon molecule C_6H_{12} . This value is probably as accurate a value of the molecular weight of a hydrocarbon as has been hitherto determined, and is sufficient to prove that if hydrogen has the atomic weight of unity, then carbon is twelve, and thus the addition of six atoms of carbon to twelve atoms of hydrogen results in a compound the molecular weight of which may be expressed as a whole number, viz., 84, within the limits of experimental error. This value may be due to the summation of positive and negative variations from the respective values of 1 and 12 for hydrogen and carbon required by Prout's law, and therefore in itself would not prove anything about the law of whole numbers in either atom, unless other methods enabled the atomic weight of carbon or hydrogen to be otherwise defined. Now the labours of Dumas and Stas have shown that if oxygen is taken as 16, then carbon is 12.005, so that the number 83.987 for C_6H_{12} would necessitate hydrogen being rather less than 1 instead of being more, as generally acknowledged when $O=16$ is taken as the standard. Whatever conclusions further investigation may induce chemists to adopt, there can be no doubt the present method is capable of very great refinement in the determination of the molecular weights of hydrocarbon radicals, and when exhaustively treated must lead to results of importance. We intend to continue this investigation, employing other bases than triethylamine, and trust to reach more definite conclusions by working on material of greater purity. We will leave for future discussion Schützenberger's investigation on the variability of the atomic weight of carbon, which is very far from being confirmed by the method of verification we have adopted.