On the Molecular Weight of Caoutchouc and other Colloid Bodies

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found that they give a better result than when larger rings are used; but in some experiments with a small flow of water a ring 3½″ diameter gave as large a spark as one of 1½. In the dark, electricity is often seen to fly off from the rings, the water on them being made into pointed-shaped drops.

The machine in its present form is by no means powerful, as with a small Leyden jar attached to it the longest spark has hitherto been 1⅛″, the head of water being about 23 feet. The state of the atmosphere has very great influence on the working of this machine; for though in all states of the weather electricity will be generated, it requires a fairly dry atmosphere to give 1″ sparks.

It may be mentioned that the machine has only been tried in a small bath-room, which is a very unfavourable place for electrical experiments; and it perhaps is worth mentioning, that on one occasion sparks were only obtained when window and door were open and the machine was in a thorough draught.

To what extent the power of the machine may be increased it is difficult to predict; but the author thinks that the experiment with the atomiser points to high velocity in the water, combined with minute subdivision, as the direction in which any future attempts should be made.

Prof. S. P. Thompson enquired whether the length of the spark was limited by leakage along the glass rods or by the spray passing between the receivers, and in reply Mr. Fuller said he thought the former leakage the most important.

XXII. *On the Molecular Weight of Caoutchouc and other Colloid Bodies.* By J. H. Gladstone, *Ph.D., F.R.S.*, and Walter Hibbert, *F.I.C.**

During the last meeting of the British Association at Bath, we gave a preliminary account of some attempts to determine the molecular weights of caoutchouc and a few other substances by Raoult's method. We have since repeated most of the experiments and largely extended the inquiry, and it seems to us that the results have a certain physical as well as chemical interest.

It is evident that this method is the only one that offers

* Read May 25, 1889.

much hope of success in dealing with such substances as caoutchouc, but it is open to question how far the method itself is to be trusted for giving the correct molecular weight of compounds of this description. Our confidence in it, however, was strengthened by the following experiments, made on substances of the same ultimate composition ($nC_{10}H_{16}$), but of known molecular weight in the gaseous condition. We also made experiments on one or two closely allied bodies containing oxygen.

The compounds were dissolved in benzene which had a freezing-point of 5°·25 C., and the experiment was conducted in the usual manner. Each degree of the thermometer scale was divided into twentieths, and it was not difficult to estimate to the hundredth of a degree. Successive observations of a freezing-point nearly always agreed to less than 0°·02.

The following table gives :—in col. II. the recognized molecular formula, in col. III. the strength of solution, in col. IV. the amount of depression, and in col. V. the molecular weight calculated by Raoult's formula $M = \frac{T}{A}$, where T is the molecular depression constant (in this case = 49), and A is the depression given by 1 gram of the substance in 100 grams of solvent. These figures may be compared with col. VI., which gives the molecular weight deduced from the formula in col. II.

Substance.	Col. II.	Col. III.	Col. IV.	Col. V.	Col. VI.
		per cent.	°		
Oil of Turpentine......	$C_{10}H_{16}$	4·56	1·59	140·5	136
Oil of Lemon...........	,,	6·04	2·17	136·4	136
,, ...	,,	3·06	1·12	133·8	,,
Cedrene.................	$C_{15}H_{24}$	3·89	1·00	190·8	204
,, ...	,,	4·71	1·20	192·3	,,
Isoprene	C_5H_8	3·30	2·25	71·9	68
,, ...	,,	2·20	1·52	70·9	,,
Caoutchene	$C_{10}H_{16}$	5·38	2·01	131·1	136
Heveene................	$C_{20}H_{32}$	12·00	2·32	275	272
,, ...	,,	9·37	1·85	248	,,
,, ...	,,	7·68	1·53	246	,,
Camphor	$C_{10}H_{16}O$	4·69	1·59	144·5	152
Menthol................	$C_{10}H_{20}O$	3·21	0·93	169·1	156
,, ...	,,	4·93	1·31	184·4	,,
,, ...	,,	3·75	1·07	171·7	,,
Anethol	$C_{10}H_{12}O$	3·71	1·29	141·0	148

This table shows not merely that the method is applicable in the case of bodies of this description, but that the molecular weights of the liquids in solution have the same relative values as in the gaseous condition.

We then made experiments on caoutchouc, whose empirical formula as usually given ($C_{10}H_{16}$) would indicate a molecular weight of 136, and we found that this was very far below that deduced from our results, as shown in the following table:—

Substance.	Weight in 100 grams of Solvent.	Depression.	Molecular Weight.
Caoutchouc (*a*) ...	3·1	Scarcely observable.	Extremely high.
„ (*b*) ...	8·8	„	„
„ (*c*) ...	14·6	0·11	6504

The caoutchouc used in solution (*a*) had been prepared from Penang rubber, by the process described in our previous paper (Chem. Soc. Journ., July 1888, p. 679). That in solution (*b*) was obtained from Para rubber, by dissolving it in ether, and precipitating the etherial solution with alcohol. Solution (*c*) was prepared from (*b*) by evaporation in a current of hydrogen. The greater depression observed can hardly be ascribed solely to the greater strength of the solution, since that would only give a proportionate effect. We are inclined to think it possible that there was a lowering of the molecular weight during a three days' gentle heating which was incidentally necessary. The observation, in fact, seems in harmony with other alterations in physical properties which we have sometimes noticed.

This very high molecular weight for caoutchouc strengthens a previous impression of ours that caoutchouc belongs to the class of substances known as colloids. The impression arose from the fact that caoutchouc is a substance showing not the least tendency to crystallize, which cannot be distilled without decomposition, which is subject to great alteration of properties by the action of heat, which is converted into an insoluble modification by small quantities of certain reagents, and which dissolves in its solvents in an extremely sluggish manner.

Graham, in his classic memoir on the subject* of Colloids, observed that "the equivalent of a colloid appears to be always high;" and he also suggested that the colloid molecule may be "constituted by the grouping together of a number of crystalloid molecules."

It seemed worth while therefore to examine bodies commonly regarded as colloidal by Raoult's method. The following table gives the results obtained with aqueous solutions of organic colloids, the molecular weights being reckoned for the ordinary value for T given by Raoult in the case of water :—

Substance.	Weight in 100 grams of Solvent.	Depression.	Molecular Weight. T=19.
Gum arabic	31·6	0°·3	2001
Ditto purified ...	14·0	0·165	1612
Caramel...........	8·76	0·105	1585
„	22·5	0·245	1745
Albumen	2·0	Scarcely observable.	Extremely high.

The molecular weight of these known colloids, as determined by Raoult's method, is very high and confirms the generalization of Graham.

Experiments have already been made upon the so-called carbohydrates by this process by Messrs. H. T. Brown and G. H. Morris †. They found that the sugars had a molecular weight agreeing with the received formula, but the noncrystallizable bodies like soluble starch &c. gave them results suggestive of specially high molecular weight.

We may also note that in some recent investigations by C. Lüdeking, he found that the addition of colloids to water makes no practical difference to the boiling-point, and in every case lowers the vapour-pressure very slightly ‡. These results all indicate the same general conclusion.

* Phil. Trans. 1861, pp. 183–224.

† Chem. Soc. Journ. 1888.

‡ *Ann. Phys. Chem.* [2] xxxv. pp. 552–557.

Our experiments were extended by making an examination of solutions of the colloidal hydrates of aluminium and iron. They were prepared by dialysing solutions of the basic chlorides, but, as is well known, a small proportion of the salt must be retained in order to prevent coagulation. The iron solutions contained almost exactly one molecule of chloride to fifteen molecules of the hydrate. The first aluminium solution contained one molecule of the chloride to five or six of the hydrate, the second one of chloride to nearly ten of the hydrate.

Substance.	Weight in 100 grams of Solvent.	Depression.	Molecular Weight. T=47.
Ferric Hydrate	1·16	About 0·01	5452
"	2·60	0·025	4888
Aluminic Hydrate...	0·523	0·060	409·6
"	1·37	0·06	1073·0

The figures here given for the molecular weights of the hydrates are calculated as if the whole depression were due to the hydrate in solution, but the chloride present must have exercised a considerable influence, especially in the first aluminium solution. If allowance be made for this, the molecular weights found would be higher than those given in the table, and would point to the soluble colloidal hydrates of iron and aluminium being many multiples of $Fe_2H_6O_6$, or $Al_2H_6O_6$, which would give a molecular weight of only 214 and 157 respectively. The molecular weights of ferric and aluminic chlorides, as determined by Raoult's method (T being 47), are about 114 and 106 respectively.

All our experiments, therefore, while affording additional illustrations of the value of Raoult's method, confirm the belief that the molecule of a colloidal substance is an aggregate of a very great number of atoms*.

* Since this paper was read we have found that办Paternò and Nasini have arrived at the same conclusion from experiments on albumen and gelatine (*Lincei*, April 7, 1889, p. 476).