

LXXXIII.—*Modification of Beckmann's Boiling Point Method of Determining Molecular Weights of Substances in Solution.*

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RECENT investigations in Physical Chemistry have greatly extended our means of determining the molecular weights of substances. Besides the ordinary method which depends on the determination of the relative density of a substance in the gaseous state—the so-called “vapour density” method—we have now, thanks to the labours of Raoult and others, various means of ascertaining molecular weights of substances in solution. Diminution of vapour tension, lowering of the freezing point or rise of the boiling point of a solvent, are the changes which accompany the dissolution of a solid in it, and each of these changes supplies us with a means of determining the molecular weight of the dissolved substance. These are mutually connected together by theoretical considerations, but for purposes of determining molecular weights, the method depending on the change in the boiling point far surpasses the others, both on account of the simplicity of the manipulation and of the greater accuracy in the results obtained. We are indebted to Beckmann (*Zeit. physikal. Chem.*, **3**, 603 [1889]; **4**, 532 [1889]; **5**, 76 [1890]; **6**, 437 [1890]; **8**, 223 [1891]) for this method; but, in spite of his indefatigable labours, there are some points in the practical carrying out of his method, which are capable of improvement and simplification. The object of the present paper is to describe a modification, which renders it available in every laboratory, and, at the same time, capable of yielding results which are even more concordant than those obtained by Beckmann himself.

It may, however, not be out of place to first briefly refer to the principle which underlies this method. From a study of the lowering of vapour pressure of various solvents produced by the substances dissolved in them, Raoult was ultimately led to formulate the law that “The relative lowering of vapour pressure is proportional to the ratio of the number of molecules of the dissolved substance to the total number of molecules in the solution.” Or expressed in a formula—

$$\frac{p - p'}{p} = c \times \frac{n}{N + n},$$

where p and p' are the vapour pressures of the solvent and of the solution, and N and n , the number of molecules of the solvent and of

the dissolved substance respectively. The constant c may be taken as equal to unity. If, then, G and g be the weights taken, and M and m the molecular weights, of the solvent and of the dissolved substance, all expressed in grams, we have—

$$\frac{p - p'}{p} = \frac{\frac{g}{m}}{\frac{G}{M} + \frac{g}{m}},$$

$$\text{or } m = M \cdot \frac{g}{G} \cdot \frac{p'}{p - p'}.$$

Hence, if M , G , and g are known, the molecular weight of the dissolved substance, m , is given by determining p and p' , the vapour pressures of the solvent and of the solution.

Now, the diminution of vapour pressure is proportional, on the one hand, to the lowering of the freezing point and, on the other, to the rise of the boiling point. The former relation, which was established by Raoult in a purely empirical way (*Compt. rend.*, **87** [1878]; **103** [1886]; **104** [1887]; **105** [1887]; **107** [1888]; (*Ann. Chim. Phys.* [6], **15** [1888]), had already been deduced by Guldberg (*Compt. rend.*, **70** [1870]) from the mechanical theory of heat. Moreover, Van't Hoff (*Zeit. physikal. Chem.*, 1887, **1**, 494) theoretically deduced the laws of the lowering of the freezing points of solutions from the relation which exists between vapour pressure and osmotic pressure.

The determination of the other relation, the rise of the boiling point, also affords us a means of ascertaining the molecular weight of the dissolved substance, inasmuch as it is possible to determine the temperatures at which the solvent and the solution exhibit equal vapour pressures, instead of ascertaining their vapour pressures at the same temperature. This method was first practically carried out by Beckmann (*loc. cit.*).

The calculation of the molecular weight is made by taking into consideration the proportionality which exists between the difference of pressure and the difference of temperature. Now, since the solutions subjected to examinations are all very dilute, the equation

$$\frac{p - p'}{p} = \frac{n}{N + n}$$

may assume the following form without causing any material difference in the results:—

$$\frac{p - p'}{p} = \frac{n}{N}.$$

The difference of temperature produced in the boiling point by the dissolution of the substance in the proportion of 1 gram-molecule to

1 gram-molecule of the solvent, and which corresponds to the above pressure-difference, is called the *molecular elevation of boiling point*.

This constant is obtained experimentally by determining the rise of boiling point of a solvent, following the dissolution of a known weight of a substance of known molecular weight in a known quantity of the solvent. Thus, for example, Beckmann (*Zeit. physikal. Chem.*, 1889, **3**, 603), found that 4.740 grams of ethyl benzoate dissolved in 100 grams of ether raised the boiling point of the latter by 0.665° . The weight of ethyl benzoate dissolved in 1 gram-molecule of ether (74 grams) is, therefore, $\frac{4.740 \times 74}{100} = 3.5076$ grams.

The rise of boiling point corresponding to the dissolution of 1 gram-molecule of ethyl benzoate (150 grams) in 1 gram-molecule of ether would then be—

$$\frac{0.665 \times 150}{3.5076} = 28.4.$$

Experiments with other substances give nearly the same value for the molecular elevation of the boiling point of ether. The molecular weight of any dissolved substance is then obtained from the equation

$$m = B \times g/\Delta,$$

where, in the case of ether, $B = 28.4$, g = weight of the substance dissolved in 74 grams of ether, and Δ = the observed rise of boiling point.

In practice, it is more convenient to refer the constant B to 100 grams, instead of to the molecular weight, of the solvent; the calculation is thus very much simplified. The formula then becomes—

$$m = B' \times g'/\Delta,$$

where, in case of ether, $B' = 28.4 \times 74/100 = 21.0$, and g' = weight of the substance dissolved in 100 grams of the solvent. As the mean of several determinations, Beckmann (*loc. cit.*) obtained the number 20.9 for the value of B' .

The constant B or B' may, moreover, be accurately calculated in the following manner from the latent heat of vaporisation and the boiling point of the solvent, as has been pointed out by Arrhenius (*Zeit. physikal. Chem.*, 1889, **4**, 550).

Suppose we have a solvent of molecular weight M , and of boiling point T (in absolute temperature) at pressure p . By dissolution of n gram-molecules in 100 grams of the solvent, the boiling point rises to $T + dT$. The relation between this rise, dT , and the dissolved mass, n , may be calculated thus:—

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The solution boils under pressure p at the temperature $T + dT$. The vapour pressure of the solvent at T is equal to p ; it is equal to $p + dp$ at the temperature $T + dT$. Between dT and dp the following relation exists, according to the second law of thermodynamics, as already shown by Van't Hoff (*Zeit. physikal. Chem.*, 1887, **1**, 494):—

$$\frac{dp}{p} = dT \cdot \frac{\omega}{2T^2},$$

where ω = latent heat of vaporisation of a gram-molecule of the solvent at temperature T .

Now, according to Raoult's law, the relation between the diminution of vapour pressure and the number of molecules of the solvent and of the dissolved substance is expressed by—

$$\frac{p - p'}{p} = \frac{n}{N + n},$$

$$\text{or } \frac{(p + dp) - p}{p + dp} = \frac{n}{N + n},$$

$$\text{or } \frac{dp}{p + dp} = \frac{n}{N + n}.$$

But, as the solution is very dilute, dp is very small compared to p , and n very small compared to N . The last equation may, therefore, be written as

$$dp/p = n/N,$$

or, as 100 grams of the solvent is employed and M = its molecular weight, we have—

$$dp/p = n \cdot M/100.$$

Equating this value of dp/p with that already obtained, we have—

$$\frac{n \cdot M}{100} = \frac{\omega \cdot dT}{2T^2}.$$

In this equation, ω being the latent heat of vaporisation of a gram-molecule of the solvent (M grams) in gram-calories, it follows that ω/M = latent heat of vaporisation of 1 gram of the solvent. Calling this W , we have—

$$\frac{n \cdot M}{100} = \frac{M \cdot W \cdot dT}{2T^2},$$

$$\text{or } dT = n \times 0.02T^2/W.$$

If s = weight of the substance dissolved in 100 grams of the solvent, and m = molecular weight of the dissolved substance, then

$n = s/m$. Substituting this value of n in the above equation, and solving for m , we have—

$$m = \frac{0.02T^2}{W} \cdot \frac{s}{dT}.$$

In this equation, s and dT have the same meaning as g' and Δ respectively in one of the preceding operations (p. 991); and the constant, $0.02T^2/W$, for ether is found to be equal to

$$\frac{0.02 \times (273 + 34.97)^2}{90.1} = 21.0,$$

the value which we already obtained for B' in the same equation.

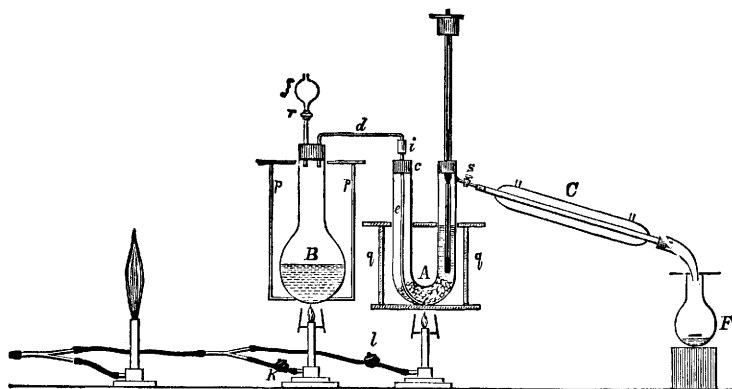
Now, turning to the practical side of the question, the great and the only difficulty which lies in the way is the exact determination of the boiling points, as has already been pointed out by Beckmann. Irregular boiling and bumping, attended with sudden alterations in the temperature of a boiling liquid, are phenomena which are too well known to be mentioned. Even when the liquid seems to be regularly boiling, there are still constant changes in the temperature of the liquid, as may be readily observed by the use of a delicate thermometer. Various means have been tried to overcome these difficulties. Bits of metallic wire or foil, of broken glass, &c., are almost useless. Raoult tried coating the thermometer bulb with a layer of palladium recently charged with hydrogen gas, but it did not lead to the desired result, as the evolution of hydrogen gas soon slackened, and in about 20 minutes stopped altogether.

Beckmann has succeeded in greatly overcoming the difficulties. He uses a piece of stout platinum wire which is fixed in the bottom of the boiling vessel by means of fusible glass. On account of the superior thermal conductivity of the metal, the boiling is said to take place exclusively from the piece of platinum, and bumping is avoided entirely. I regret to say that I have not yet had any experience in the use of Beckmann's apparatus. In fact, we ordered one from Germany, but on my first attempt to make trial of it, the boiling vessel was found to be cracked at the point of insertion of the platinum. This was merely an accident, but it is an accident which may not unfrequently occur. A small portion of the bottom of the boiling vessel is thickened by the fusible glass, and it is not surprising that the bottom should be cracked by the slightest carelessness in heating.

The means which I adopt in producing a constant temperature in the boiling liquid has already been described in my paper on "The Determination of the Temperature of Steam arising from Boiling Salt Solutions" (this vol., p. 495), and consists in passing a current

of the vapour of the solvent into the boiling liquid or solution, the amount of the vapour thus passed in from without being regulated by the height of the lamp. The degree of constancy of the temperature attained in this manner by the boiling liquid is really astonishing, a most delicate thermometer, capable of showing 1/1000th of a degree, remaining almost stationary.

Description of Apparatus.—Instead of the three-necked flask with a piece of platinum wire fixed into the bottom, and with a complex condensing arrangement, used by Beckmann, I employ for the boiling vessel an ordinary U-tube A, about 2 cm. in internal diameter, and 21 cm. in height. Near the top of one of the limbs of this U-tube a hole is blown out by means of the blowpipe, which serves for joining on, with a piece of india-rubber tubing, a small side tube, having a glass stop-cock *s*. The side-tube is, in its turn, connected with an ordinary Liebig's condenser C. The boiler for generating the



vapour of the solvent is an ordinary round-bottomed flask B, provided with a cork, through which pass the stem of a tap-funnel, *f*, and a delivery tube, *d*. The latter is connected, by means of a piece of thick india-rubber tubing, *i*, with a tube, *e*, drawn out and slightly bent at its lower end, so that this end of the tube may just reach the bottom of the boiling vessel when the cork, through which it passes above, is fixed into the mouth of the U-tube, nearest to the boiler. This tube *e* thus establishes communication between the boiler and the boiling vessel. A tin-plate vessel, *pp*, with a hole in the bottom, and resting upon a tripod, serves to enclose the boiler, and to protect it from draughts. The boiling vessel is, on the other hand, enclosed by a box made of thick asbestos cardboard, *qq*, with a movable bottom. When the solvent is of low boiling point, such as carbon bisulphide or ether, a piece of plain asbestos cardboard serves as the

bottom of the box, and the boiling vessel is heated by indirect flame, as shown in the figure. In the case, however, of less volatile solvents, such as water, or even alcohol, a piece of asbestos cardboard, having a hole in the centre, is used instead, and the boiling is effected by the direct application of a flame.

The height of the flame both under the boiler and the boiling vessel has to be carefully regulated for each particular solvent according to its volatility; and, in order to avoid the effect of any alteration in the gas pressure, owing to constant openings and shittings of gas taps in other parts of the laboratory, the following arrangement is adopted and is found to answer admirably. The gas tube is connected with three Bunsen burners and, fully opening the gas tap, the burner nearest the tap is lighted. This acts as a gas regulator. The supply of gas to the other two burners is adjusted by means of screw-clips *k* and *l*; and, since the amount of gas supplied to the regulator burner is incomparatively greater than that supplied to the two others, no effect of alterations of gas pressure in the mains can be perceived in the latter. This circumstance is of considerable importance, because I am thereby enabled to use the bulb of the thermometer always naked, there being no necessity to envelop it with asbestos fibres, as when working with Beckmann's apparatus.

The thermometer which I use includes only a range of 6°C. , and is graduated into $1/100\text{ths}$ of a degree. Each of these divisions (about 0.4 mm.) can be readily estimated to $1/10\text{th}$ by means of a reading telescope, which I always use, so that the thermometer can indicate $1/1000$ of a degree. There is an arrangement in the instrument by which the quantity of mercury in the bulb may be increased or diminished, so that it can be used either for low or high temperatures. This instrument has already been described by Beckmann.

The whole arrangement is exceedingly simple, and can be set up by any one with materials commonly found in all laboratories. This, I venture to say, is a great advantage. The only costly part of the apparatus is the thermometer, but for good and accurate work in most physico-chemical inquiries, a delicate thermometer is indispensable and, after all, its cost is not disproportionate to the important services it can render.

Mode of Working.—For working with the apparatus described above, I begin by inserting the tube *e* into one limb of the boiling vessel, fixing it by means of the cork *c*. Small glass beads are then introduced into the boiling vessel through the other limb, till they quite fill the bent portion of the latter. (Beckmann recommends the use of small garnets or glass beads for preventing local differences of temperature, and I find them also very effective for thoroughly

mixing the vapour passed in with the boiling liquid and thus establishing a perfect uniformity of temperature.) The experimental liquid is now poured in, so that it occupies a space of three or four centimetres above the level of the glass beads in the open limb, and the latter is then closed by the cork carrying the thermometer. The lid of the asbestos box is next slipped down the two limbs of the tube, which pass through two holes previously made in it in proper positions, and the boiling vessel, after having been properly enclosed in the asbestos box and supported on the ring of a retort-stand, is connected, on the one side, with the boiler and, on the other, with the side-tube and condenser, as shown in the figure.

First the boiler, half filled with the solvent, and then the boiling vessel are heated by carefully regulated lamps, the stop-cocks *r* and *s* both open; and, when the liquid in both vessels begins to boil properly, the stop-cock *r* is closed, and the two lamps very carefully regulated, so that the height of the column of the boiling liquid remains, as nearly as can be judged, level with the lid of the asbestos box for, at least, a quarter of an hour. This circumstance is used as the criterion that the boiler and the boiling vessel are each being heated by a properly adjusted lamp, so that evaporation and condensation balance each other in the boiling vessel. The thermometer rises rapidly at first, but more slowly afterwards, attains the maximum temperature in 10 or 12 minutes, and then remains perfectly constant. The top of the thermometer is now lightly tapped for some seconds, and the observation of the exact temperature made by the aid of a reading telescope. Finally, the volume of the distillate collected in the small flask *F* is noted and, after withdrawing the lamps, the stop-cock *r* is opened and the stop-cock *s* closed.

I make it a rule to repeat this observation of the exact boiling point of the solvent once or, in some cases, twice more in order to make sure of the temperature. For this purpose, the distillate is returned to the boiler and the whole of the above process repeated under exactly the same conditions as before, taking the final observation of the temperature when the distillate reaches the mark previously made on the receiver flask.

The next step is to introduce the substance into the solvent. This may be done in two ways. The first and simplest method, which should be used when the solvent is of low boiling point, consists in taking out the cork which carries the thermometer, adding the solid substance to the solvent, and then immediately replacing the cork in its original position. The other method, which is employed in the case of solvents of high boiling point, and where, therefore, if the first method were adopted, the highly heated thermometer would have to be suddenly exposed to the cold air, is as follows: After the

exact determination of the boiling point of the solvent has been made, the boiler is a little cooled without opening the stop-cock *r*, when a small quantity of the solvent runs up the tube *e* and flows down into the boiler. The stop-cock *r* is now opened and then, disconnecting the delivery tube *d* from the tube *e*, a small quantity of a concentrated solution of the substance, made beforehand, is introduced into the boiling vessel by means of a small funnel attached to the india-rubber tubing *i*. After removing the funnel, communication is re-established between the boiler and the boiling vessel.

The lamps, which have been put aside but not turned out, are next brought under the two vessels as before, and the boiling point of the solution determined in exactly the same manner and under exactly the same conditions as those in which the boiling point of the solvent was determined, collecting, of course, the same quantity of the distillate. When the exact temperature has been ascertained, the lamps are put out, the stop-cock *r* opened, the stop-cock *s* closed, and the whole apparatus allowed to cool.

After the solution has completely cooled, the percentage composition is determined, by transferring some of the solution to a weighed, stoppered bottle by means of a pipette, and, after ascertaining the weight of the solution taken, evaporating it at a gentle heat on a water-bath, and weighing the fixed residue. In the case of iodine, it is determined volumetrically by a standard solution of sodium thio-sulphate.

From the account of the process above given, it will be seen that it differs from that used by Beckmann essentially in that, whilst Beckmann takes a weighed quantity, both of the solvent and of the solid substance, and determines the boiling points in an apparatus provided with a reflux condenser, and, therefore, requires a complicated arrangement, the method here described requires no special apparatus, as it determines the boiling points in the ordinary manner, but obviates the usual difficulties of such determinations, and, at the same time, keeps the quantity of the boiling liquid constant, by passing in a current of the vapour of the solvent from without. Another difference, which, I venture to say, is also an improvement, is that the boiling point of the solution is ascertained just before its composition is determined, and the connection between these properties is, therefore, rendered more certain than in the case of Beckmann's method. The results of my determinations are contained in the following tables (pp. 998—1001).

In conclusion, a word may be said with regard to the molecular weights of iodine and of sulphur in solution. Paternò and Nasini (*Ber.*, 1888, **21**, 2153), by the depression of the freezing point, found that the molecular weight of iodine in very dilute benzene solutions

Solvent: *Water*.

Lat. Ht. Vap. = 536.4 (Regnault, 1847); b.p. = 100° C. $\frac{0.02T^2}{W} = 5.2$.

Substance.	B. p.		Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Rise.						
Mercuric chloride, $\text{HgCl}_2 = 271$	2.262	2.441	0.179	10.6755	0.8795	8.978	260.8	-3.8
	2.305	2.389	0.084	10.4385	0.4258	4.253	263.3	-2.8
Mannite, $\text{C}_6\text{H}_8(\text{OH})_6 = 182$	2.214	2.406	0.192	11.2302	0.6855	6.501	176.1	-3.2
	2.265	2.396	0.131	11.7120	0.5196	4.642	184.1	+1.2
	2.403	2.483	0.080	9.5396	0.2637	2.843	184.8	+1.5
	2.475	2.680	0.205	10.7289	1.2980	13.775	349.4	+2.2
Cane Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11} = 342$	2.317	2.447	0.130	11.7419	0.9175	8.476	339.0	-0.9
	2.649	2.713	0.064	10.6146	0.4392	4.316	350.7	+2.5
	2.653	2.688	0.035	10.7965	0.2579	2.447	363.5	+6.3

Solvent: *Ethyl Alcohol*.*

Lat. Ht. Vap. = 214.9 (Regnault, 1862); b.p. = 78°.3 C. $\frac{0.02T^2}{W} = 11.5$.

Substance.	B. p.			Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution.	Rise.						
Acetanilide, $C_6H_5NH.C_2H_3O = 135$. ..	3.720	4.191	0.471	8.0628	0.4338	7.6290	5.686	138.8	+2.8
„	3.554	3.705	0.151	8.3318	0.1410	8.1908	1.721	131.1	-2.9
„	3.793	3.906	0.113	8.2361	0.1090	8.1271	1.341	136.5	+1.1
„	3.581	3.667	0.086	8.0012	0.0817	7.9195	1.032	138.0	+2.2
Salicylic acid, $OH.C_6H_4.COOH = 138$.	3.984	4.515	0.531	8.0762	0.4772	7.5990	6.280	136.0	-1.5
„	3.775	4.092	0.317	7.0653	0.2523	6.8130	3.704	134.4	-2.6
„	4.240	4.367	0.127	8.3855	0.1279	8.2576	1.549	140.3	+1.7
Mercuric chloride, $HgCl_2 = 271$	4.050	4.521	0.471	6.8492	0.6717	6.1775	10.873	265.5	-2.0
„	3.731	4.111	0.380	8.2052	0.6612	7.5440	8.765	265.2	-2.1
„	3.702	3.848	0.146	8.4119	0.2774	8.1345	3.413	268.9	-0.8

* Rendered anhydrous by distillation, first from freshly ignited lime and then from a small quantity of sodium.

Solvent: *Ethyl Ether*,*
 Lat. Ht. Vap. = 90.1 (Regnault, 1862); b.p. = 34.9 C. $\frac{0.02T^2}{W} = 21.0$.

Substance.	B. p.			Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution.	Rise.						
Salicylic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH} = 138$.	1.013	1.397	0.384	6.9880	0.1733	6.8147	2.543	139.1	+0.8
"	1.337	1.661	0.324	7.2700	0.1591	7.1109	2.237	145.0	+5.1
"	0.986	1.236	0.250	7.1384	0.1174	7.0210	1.672	140.4	+1.7
Naphthalene, $\text{C}_{10}\text{H}_8 = 128$	0.739	1.464	0.725	7.2743	0.3128	6.9615	4.493	130.1	+1.7
"	1.038	1.541	0.503	7.0014	0.2143	6.7871	3.159	131.9	+3.0
"	1.275	1.542	0.267	7.0232	0.1112	6.9120	1.609	126.6	-1.1
Iodine, $\text{I}_2 = 254$	1.295	1.615	0.320	7.1600	0.2678	6.8922	3.886	255.0	+0.4
"	1.098	1.302	0.204	7.2838	0.1796	7.1042	2.528	260.2	+2.4
"	1.174	1.255	0.081	6.9250	0.0692	6.8558	1.009	261.6	+3.0

Redistilled over sodium.

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Solvent: *Carbon Bisulphide*.*

Lat. Ht. Vap. = 84.8 (Regnault, 1862); b.p. = 46°.2 C. $\frac{0.02T^2}{W} = 24.0$.

Substance.	B. p.		Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Rise.						
Naphthalene, $C_{10}H_8 = 128$	3.480	0.380	7.6888	0.1433	7.5455	1.901	120.0	-6.2
„	3.385	0.333	12.4832	0.2192	12.2640	1.795	130.5	+1.9
Iodine, $I_2 = 254$	3.887	0.397	11.3537	0.4714	10.8823	4.332	261.9	+3.1
„	3.680	0.225	11.4810	0.2600	11.2210	2.317	247.1	-2.7
„	3.709	0.183	7.9370	0.1534	7.7836	1.971	258.5	+1.8
Sulphur, $S_8 = 256$	3.551	0.590	10.5998	0.6247	7.9751	6.263	254.8	-0.4
„	3.430	0.361	12.2753	0.4488	11.8265	3.795	252.3	-1.7
„	3.682	0.188	10.2030	0.1998	10.0032	1.997	254.9	-0.4

* Purified by shaking with mercury and then distilling from dry litharge.

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is represented by I_2 , whilst it possesses higher values in more concentrated solutions. They found also that iodine is more or less dissociated into the atomic state in its solution in glacial acetic acid. Loeb (*Zeit. physikal. Chem.*, 1888, **2**, 606), however, could not verify these conclusions by the same method, and, both on account of the small solubility of iodine in either benzene or glacial acetic acid, and of the great variations in the results according to concentration, he ultimately gave up these experiments. By determining the vapour pressures of solutions of iodine in ether and in carbon bisulphide, Loeb showed, on the other hand, that the molecular magnitude of iodine in brown ethereal solutions is represented by I_4 , whilst in carbon bisulphide it is less complex, and corresponds to the formula $I_{2.4}$. Lastly, Beckmann (*ibid.*, 1890, **5**, 76) found, by the aid of his boiling method, that no appreciable difference exists in the molecular magnitude of iodine, whether dissolved in ether or in carbon bisulphide, and that it corresponds to I_2 in both of the solutions. The numbers he obtained varied between 235 and 256 in ethereal solutions, and between 250 and 272 in carbon bisulphide solutions ($I_2 = 254$). More recently, Hertz (*ibid.*, 1890, **6**, 358), by the freezing method, obtained numbers varying between 255.5 and 276 for the molecular weight of iodine in its dark red solution in naphthalene, and pointed out that the red colour of the iodine solution is not due to the existence of complex molecules, as already shown by Beckmann. My own determinations also fully confirm the results obtained by the latter.

With regard to the molecular weight of sulphur in carbon bisulphide solution, Beckmann, by the boiling method, obtained numbers varying between 245 and 281, and, therefore, pointing to the existence of complex sulphur molecules represented by $S_8 = 256$. The formula S_8 had generally been regarded as the maximum molecular formula of sulphur, and the results obtained by Beckmann, therefore, needed confirmation. The experiments by Hertz, who obtained numbers varying between 262.3 and 279.4 (*loc. cit.*), and, still more conclusively, my own determinations, put Beckmann's views beyond any doubt.
