LXVI.—*The Molecular Weight of Iodine in its Solutions.*

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It is a matter of everyday observation that iodine has the property of dissolving with different colours in different liquids; in some it shows the reddish-brown hues of its solid and liquid states; in others it acquires the violet colour so characteristic of its vapour. The inference seems very natural that this diversity of colour must depend on a different form of aggregation of the iodine-atoms within the solvent. Since the molecules of solids and liquids appear to be more complex than those of gases, we might suppose that the red solutions contain more complex molecules of iodine than do the violet ones. This is, in fact, the usual assumption; but apart from certain qualitative indications, there has been no proof of its truth; quantitative evidence has not yet been forthcoming in support of the hypothesis. That I have been fortunate in obtaining such, I owe to those new

means of investigating the state of dissolved matter with which the happy generalisations of Raoult, and the skilful mathematical deductions of van't Hoff, have furnished us. I refer to the phenomena of "osmotic pressure," which can be measured by the depression of freezing point and vapour-tension which liquids experience when mingled with a foreign substance. By the advice of Professor Ostwald, I undertook to attack the problem of the molecular weight of iodine in its solutions by the vapour-tension method, and I now give the results of the experiments carried out under his direction at the Chemico-Physical Laboratory of Leipsic University.

Two liquids at once presented themselves as the appropriate solvents, ether and carbon bisulphide; they both have a considerable vapour-tension, and they may be considered as typical of the two kinds of solvents for iodine. For, whereas many iodine solutions show impure tints, that in ether is of a deep reddish-brown, and that in carbon bisulphide of a pure violet. It was not so easy to find a proper apparatus, as Raoult's was quite inapplicable. He operates in the Torricellian vacuum, and has merely to note the comparative heights of the mercury when the solution and the pure solvent are introduced above it. In the case of iodine, all contact with mercury must obviously be avoided. After various attempts, the following apparatus was devised, which is an adaptation of Regnault's manometer to the

present purpose. It consists of two bottles of nearly equal capacity, provided with carefully ground, hollow glass stoppers. To these stoppers, glass tubes are adapted, 60 cm. long, and of about 6 mm. bore, which are bent twice at right angles, so that there is an ascending limb and a horizontal piece of 10 cm. length each, and a descending limb, 40 cm. long, for each half of the apparatus. The lower ends of these two tubes are connected with each other by means of a T-tube, to which they are joined by short pieces of very stout rubber tubing; the third end of the T-tube serves as a communication with the exterior when needed, and carries a rubber tube with pinch-cock. The communication between the two halves of the apparatus can also be interrupted by means of a pinch-cock on one of the rubber joints. Into one of the bottles, the iodine solution is placed, whilst the pure solvent is put into the other. These liquids are contained in glass tubes, drawn out at both ends into capillaries that make an obtuse angle with the wider part. The tubes are first weighed, then filled, closed before the blowpipe, and again weighed. They contain about 3 c.c. of liquid, pass readily through the narrow necks of the bottles, and can be broken by moderately shaking the bottles. Before this is done, however, the bottles are closed with their stoppers—smeared with deliquesced phosphoric acid to insure a perfect joint—and are placed in a water-bath of constant temperature. The T-tube is now connected with a two-necked Woulff's bottle, filled with coloured distilled water, and communicating by its second neck with an air-pump. Air is exhausted, until the pressure within the apparatus is diminished to an extent equivalent to the amount of tension to be expected from the vapours of the liquids, and the pinch-cock is then closed, so as to interrupt communication with the Woulff's bottle. The air-pump being disconnected, atmospheric pressure is restored in the Woulff's bottle, and on carefully opening the pinch-cock the water is allowed to ascend half way up the long tubes; the pinch-cock is then closed, and the Woulff's bottle removed. The apparatus is thus converted into a very delicate differential manometer, affording direct readings of the difference of pressure in the two bottles in terms of water centimetres; for convenience, the two tubes are brought closely together (see Figure) and a scale is placed behind them.

The apparatus is quite independent of changes in the atmospheric pressure; the change in capacity, caused on either side by an alteration in the level of the water in the tubes, is, moreover, so slight in proportion to the volume of air in the bottles, that it can safely be neglected; the effect of capillarity in the two tubes is equal and opposite, so that this too may be left out of account. There remains only the effect of the air left in the apparatus by the air-pump. It

is obvious that equilibrium being once established, and the temperature in all parts remaining the same, the pressure of the air in the one half will always counterbalance that in the other. In fact, partial exhaustion was only resorted to as a means of preventing too great an outward pressure during the course of the experiment, since it was difficult to prevent leakage where there was any outward pressure upon the stoppers. Partial exhaustion, besides obviating this difficulty, proved directly advantageous by promoting a more rapid diffusion of the vapours, and thereby shortening the duration of the observations.

The apparatus having been made ready, communication between the two halves was temporarily interrupted, and the tubes containing the liquids broken by shaking the two bottles simultaneously. After 10—15 minutes communication was restored, and now the level of the water in the two manometer tubes, equal before, was seen to differ considerably, indicating a higher pressure in the bottle containing the pure solvent. Readings being made from time to time, this difference of level sometimes appeared virtually constant for hours, whilst in other cases it would exhibit considerable variations, which I ascribe to slight inequalities of temperature and to the unequal concentration of the solution in different parts of its bottle. After standing 24 hours, the aqueous vapour from the manometer tubes generally began to diffuse into the bottles, and rendered further observations useless by moistening the ether or carbon bisulphide.

The readings give the difference between the vapour-tension of the pure solvent and that of the solution; that is, the depression of tension which corresponds with the proportion of iodine to solvent in the solution. To calculate the concentration of the solution at the moment of observation, I required two data: the amount of iodine and of solvent introduced into the bottle (which I obtained from the weighings of the sealed tubes and from the known strength of the solution with which they were filled); and secondly, the amount of solvent which had assumed the gaseous state, and must therefore be deducted from the original quantity in solution. This was easily calculated by the regular gasometric formula, the volume of gas being 270 c.c., the temperature being known, and the pressure being that of the vapour of the pure solvent, less the depression formed by the direct observation. I found that I could employ the vapour-tensions of pure ether and carbon bisulphide from tables calculated from Regnault's measurements, as a few direct comparisons proved that they agreed with those given by my apparatus, within the limits of experimental error. The expression for the amount of solvent remaining in the solution at the moment of observation is therefore—

$$a - \frac{270.w.(f-e)}{760(1+at)},$$

where a = grams of solvent originally present; f = the tension at the temperature t of the pure solvent, expressed in millimetres of mercury; e = the depression of tension, also in terms of millimetres of mercury; w = weight in grams of 1 c.c. of the vapour under standard conditions. Now if b = the weight of iodine in the solution, and p = the ratio of solvent to iodine—

$$\text{I.} \quad p = \frac{b}{a - \frac{270.w.(f-e)}{760.(1+at)}}.$$

The concentration being thus ascertained, the calculation of the molecular weight of iodine was made according to the formula—

$$\text{II.} \quad M_1 = M_0 \frac{p(f-e)}{e},$$

M_1 and M_0 being the molecular weights of iodine and solvent respectively. This is a working formula derived by Raoult from an expression for the relation between the ratio of molecules of solvent and substance dissolved on the one hand, and the ratio between the tension of the pure solvent and the depressed tension on the other, where the dissolved substance itself has a comparatively insignificant tension. It is interesting to note that the latter expression was reached independently and simultaneously by Planck, both papers having appeared in vol. i, No. 7 of the *Zeitschrift für physikalische Chemie*.

In the following tabulated statement of my observations, the first two columns show the weights of the ingredients of the solution originally introduced; the third gives the temperature; the fourth, the depression of tension; the fifth, the true tension of the solution; the sixth, the concentration as calculated by formula I; finally, we have the molecular weight as calculated by formula II. Before giving the results obtained for iodine, I think it useful to give a summary of a few test experiments made on the molecular weight of naphthalene, which not only proved the trustworthiness of the method, but also showed that there is no specific difference between ether and carbon bisulphide which could invalidate the effect of the great difference of the molecular weights found for iodine.

Naphthalene in Carbon Bisulphide.

<i>a.</i>	<i>b.</i>	<i>t.</i>	<i>e.</i>	<i>f - e.</i>	<i>p.</i>	<i>M</i> ₁ .	Average.
5·4082	0·2586	27·5°	9·47	377·09	5·18	129	} 132
—	—	27·5	10·93	375·65	5·18	135	

Naphthalene in Ethyl Ether.

<i>a.</i>	<i>b.</i>	<i>t.</i>	<i>e.</i>	<i>f - e.</i>	<i>p.</i>	<i>M</i> ₁ .	Average.
2·8359	0·1462	27·5°	21·12	557·27	6·53	127	} 127·5
—	—	27·5	21·08	557·31	6·53	128	
—	—	27·5	21·14	557·25	6·53	127	
—	—	27·5	21·17	557·22	6·53	128	
—	—	—	—	—	—	—	

Average in CS₂..... *M*₁ = 132Average in C₄H₁₀O *M*₁ = 127·5Theory for C₁₀H₈ *M*₁ = 128.*Iodine in Carbon Bisulphide.*

<i>a.</i>	<i>b.</i>	<i>t.</i>	<i>e.</i>	<i>f - e.</i>	<i>p.</i>	<i>M</i> ₁ .	Average.
5·6528	0·4388	27·3°	9·72	373·92	8·37	239	} 264
—	—	27·3	8·59	375·05	8·37	278	
—	—	27·3	8·81	374·83	8·37	271	
—	—	27·3	9·08	374·56	8·37	268	
5·1862	0·4026	27·5	8·10	378·48	8·46	300·5	} 300·5
—	—	27·5	8·10	378·48	8·46	300·5	
5·4579	0·2594	27·5	4·60	381·98	5·15	324	} 320
—	—	27·5	4·51	382·07	5·15	332	
—	—	27·5	4·66	381·92	5·15	320	
—	—	27·5	4·76	381·82	5·15	314	
—	—	27·55	4·80	382·52	5·15	310	
4·9030	0·2330	27·5	4·67	381·91	5·20	326	} 326·5
—	—	27·5	4·60	381·98	5·20	327	

Total average..... *M*₁ = 303·25 ± 5·10Theory for I₂..... *M*₁ = 254Theory for I₃..... *M*₁ = 381.

Iodine in Ethyl Ether.

<i>a.</i>	<i>b.</i>	<i>t.</i>	<i>e</i>	<i>f - e.</i>	<i>p.</i>	<i>M</i> ₁ .	Average.
3·2578	0·2546	27·2°	8·20	563·69	9·59	488	} 504·7
—	—	27·2	7·50	564·39	9·59	534	
—	—	27·2	7·81	564·08	9·59	512	
—	—	27·35	8·09	567·05	9·60	497	
—	—	27·3	8·16	565·90	9·60	492·5	
3·2864	0·2058	27·3	7·46	566·60	7·68	443	} 577·2
—	—	27·3	4·84	569·22	7·68	653	
—	—	27·3	5·04	569·02	7·68	642	
—	—	27·3	5·66	568·40	7·68	571	
3·6809	0·2305	27·4	6·51	569·72	7·50	486·5	} 480·7
—	—	27·4	6·48	569·75	7·50	487	
—	—	27·45	6·77	570·54	7·51	468·5	
3·4343	0·3151	27·5	6·99	571·40	7·62	461	} 466·1
—	—	27·5	7·14	571·25	7·62	451	
—	—	27·5	6·43	571·96	7·62	501·5	
—	—	27·5	7·14	571·25	7·62	451	

Total average $M_1 = 507·2 \pm 10·5$

Theory for I_4 $M_1 = 508$.

It seems very probable, therefore, that iodine in its red solutions has a molecular weight corresponding to I_4 , whilst in the violet solution in carbon bisulphide there is a less complex aggregation, giving a value between I_2 and I_3 . I may as well remark that the values for p in the ether solutions correspond approximately with the ratio of one iodine molecule in 100 molecules of the solutions; in the carbon bisulphide solutions, this ratio varies between 1·100 and 1:200. Whilst greater dilution might appear more advisable from a theoretical point of view, it offers an apparently insurmountable difficulty in practice. A glance at the formulæ used in the calculation shows that the value of e enters three times in such a manner that any error attached to it would be tripled. As e decreases with the concentration, it is evident that a greater dilution than that employed by me will soon bring e to a point where the chance errors of observation become proportionately very great. Hence I agree with Raoult when he says that the method of determining molecular weights by the depression of the freezing point is preferable to the method by vapour-tensions. But for the problem which immediately interested me I lacked a liquid which would solidify, and also dissolve iodine with a pure violet colour, benzene, for instance, giving a very

impure bluish-brown. Nevertheless I endeavoured to obtain what corroborative evidence I could by experimenting on the freezing points of iodine in acetic acid and in benzene, but was forced to give up the attempt by the very slight solubility of iodine in these menstrua at low temperatures; the molecular weight of iodine as calculated from various series of observations seemed to increase continuously with the concentration, so that there was no point in the narrow limits between extreme dilution and saturation at which the molecular weight would appear constant, and could be accepted as trustworthy. A paper published since then by Paternò and Nasini (*Ber.*, **21**, 2155) on this subject contains a few figures for the molecular weight of iodine in acetic acid and benzene solutions, but I am unable to draw any other inference from them than from my own.