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XV. *Some Experiments on the Diffusion of Substances in Solution.* By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.*

THE following determinations of the comparative rates of diffusion of various non-electrolytes were intended to be preliminary to a more extended investigation, but, as I do not see my way at present to continue the work, I think it well to put on record those results which have so far been obtained.

Osmotic pressure is held to be due simply to the gaseous impact of the dissolved substance, and is therefore proportional to the number of molecules per unit volume, the temperature being constant. Now, by Graham's law, the rate of diffusion of a gas should be, *ceteris paribus*, inversely as the square root of its density, or of its molecular weight. Hence, at a given temperature and pressure the product of the molecular weight, m , by the square of the rate of diffusion, v , should be a constant. The relative values for v in the case of different bodies might be determined by simple diffusion-experiments if these could be conducted under perfect conditions: namely, the diffusing liquid remaining of a constant strength throughout, and the water into which diffusion is taking place remaining uncontaminated with the substance. The present results seem to show, either that the above supposition as to osmotic pressure is incorrect, or that the conditions obtainable in diffusion-experiments are very far from obtaining to ideal perfection; for the values deduced for mv^2 are by no means constant, even in those cases where the substances behave normally as to their osmotic pressure, *i.e.* where the solutions of equal molecular strength give the same osmotic pressure, this latter being measured by the depression exercised by them on the freezing-point of the water in which they are dissolved.

The method adopted was that termed by Graham jar-diffusion. The solutions under examination were placed in an open jar inside a large vessel of water, and the amount of substance which had diffused out of the former in a given time was ascertained by determining the strength of the remaining solution. The inner jars were beakers of a cylindrical form with ground flanges: they were ground also on the bottom, and rested on inverted ground-glass saucers placed in the centre of the large outer glass jars. Before being filled, each jar was placed in position and adjusted so

* Communicated by the Author.

that the mouth of the inner jar should be exactly level. The jars were marked so that they could be replaced in the proper position after being filled. When filled they were closed by glass plates with rods attached to them, and then lowered inside the larger jars which had previously been filled with water. The glass plates were then removed very slowly and carefully. At the end of the time allowed for diffusion the plates were replaced on the jars, the latter were removed from the water and the strength of their contents determined. Both the large and small jars were filled two days before the latter were placed inside the former, in order that the temperature of the cellar in which the determinations were made might be attained; and after the inner jars had been placed in position a further period of five hours was allowed before the glass plates were removed, so that any disturbance of temperature which had occurred in placing them in position might subside.

The capacity of the inner jars was 480 cubic centim., their internal diameter was 70 millim., and their internal height 125 millim. About three dozen of them were made, and of these the twelve which were found to be most uniform in size were used in the determinations. The extreme difference in the capacity of the largest and smallest of these twelve was 3.3 per cent., and the extreme difference of their superficies at the mouth was 3.8 per cent. The outer jars contained 12,000 cubic centim. of water, or twenty-five times the volume of the inner jars. The mouths of the jars were about midway between the surface and bottom of the water in the inner jars.

The strength of the solutions remaining in the jars at the end of the experiments was determined by means of their freezing-points. The solutions taken to start with were made up by weighing. The freezing-points of these, and also of weaker solutions obtained from them by dilution, were determined, and from these results the strength of any solution having a given freezing-point could be calculated. In order to minimize any errors due to possible irregularities of the freezing-points when plotted against composition, the solutions of known strengths, of which the freezing-points were determined, were selected so as to approach as nearly as possible to the strength of the solution left in the diffusion-jar.

The strength of the solutions taken was, as a rule, about 0.3 molecule to every 100 molecules of water, showing a depression of the freezing-point of water amounting to about 0°·3; about one third of the dissolved substance had diffused out by the end of the determination, the decrease in the

freezing-point measured being thus about $0^{\circ}\cdot 1$. The water into which the diffusion had taken place would at the end of the experiment contain only about 4 molecules of the substance to every 100,000 H_2O . These proportions had necessarily to be modified in several instances, and in such cases it was assumed that, in accordance with Graham's results (in support of which some of the present results may also be adduced), the rate of diffusion varied directly as the number of molecules present in a given volume of solution, or, more roughly, in a given weight of water.

The determinations were made in two separate series, marked (1) and (2) respectively in Table I., which contains the results. In the first series the temperature varied from $12^{\circ}\cdot 1$ to $15^{\circ}\cdot 3$, the time allowed being *probably* 18 days, the record of the exact time having been unfortunately lost: in the second series the temperature was $16^{\circ}\cdot 0$ to $18^{\circ}\cdot 2$, and the time was 25 days. Various steps were taken to estimate the magnitude of the probable errors. In the first place, the error due to any disturbance occurring in removing and replacing the glass plate from the inner jar was found to be inappreciable. A blank experiment in which these operations were performed showed that the solution of cane-sugar which the inner jar contained gave exactly the same freezing-point before and after the operations, *i. e.* within the estimation-figure of the thermometric reading, which was $0\cdot 05$ millim. or $0^{\circ}\cdot 0005$. Secondly, in the first series duplicate determinations were made with each of the substances cane-sugar, acetic acid, and urea: the differences in the freezing-points of the solutions obtained in each pair were $\cdot 0011^{\circ}$, $\cdot 0062^{\circ}$, and $\cdot 0026^{\circ}$ respectively, mean $0\cdot 0033^{\circ}$, or about 3 per cent. of the actual decrease measured, a quantity fully accounted for by the difference in size of the jars. Three per cent. in the actual decrease, however, represents only 1·24 per cent. in the proportional decrease (or actual decrease $\div$ mean freezing-point), which is the quantity which is taken to represent the rate of diffusion v ; and an error of 1·24 per cent. here will represent an error of 2·4 per cent. on the values of the supposed constant mv^2 . Thirdly, glycerine solutions of the same strength were used in both series, and so also were cane-sugar solutions of nearly the same strength: the relative values for mv^2 in the two series were 1 : 2·586 in the case of glycerine, and 1 : 2·567 in the case of cane-sugar, the difference between the two ratios amounting to only 0·3 per cent.

The results of the diffusion-experiments are given in *Phil. Mag.* S. 5. Vol. 35. No. 213. Feb. 1893. K

Table I., the supplementary freezing-points necessary for the calculation of the strengths of the final solutions being given in Table II. (In the case of cane-sugar and acetic acid the determinations used for this purpose have already been published, *Berichte d. deutsch. chem. Gesell.* xxiv. p. 3329.)

The values in the table refer to the weight of anhydrous substance, the water of crystallization, whenever present, having been allowed for. This water, in the case of alloxan, was found to be $3\text{H}_2\text{O}$; whereas in the cases of gallic acid, tannin, and raffinose, 1, 2, and $5\text{H}_2\text{O}$ were taken as being respectively present. The proportional decrease of freezing-point or strength of the solution is the fraction which the actual decrease is of the mean freezing-point or strength. The molecular weight m' is deduced from the freezing-points in accordance with van't Hoff's formula

$$m' = \frac{\text{mean strength} \times 18.9}{\text{mean f.-p.}}$$

The values, it will be seen, agree fairly well in most cases with the theoretical molecular weights.

The sugars as well as the tannin and dextrin were obtained from Messrs. Trommsdorf. The dextrin, however, was doubtless very far from being pure (indeed pure dextrin has never yet been obtained), and very little weight can be attached to the results obtained with it. The sample of amylo-dextrin I owe to the courtesy of Mr. Horace Brown: unfortunately, however, the solution used deposited some of the substance during the experiments in the insoluble form, and hence the results with it are very doubtful; for not only is the mean strength of the solution uncertain, but the amount which had diffused out is also uncertain; for this had to be estimated in the diffusate, a large quantity of it being evaporated to a small bulk so as to obtain a depression of freezing-point sufficient for measurement; while, to correct for solids dissolved from the dish by the liquid during its evaporation, a similar volume of water was evaporated in the same manner. The calculated molecular weight of the amylo-dextrin was obtained from the freezing-point of the initial solution, and of that entered in Table II. The values which these gave were 2519.4 and 2452.8 respectively. The results with gallic acid are equally uncertain for a similar reason, the solution taken having been too strong, and having deposited crystals during the course of the experiment.

In the case of pyrogallol the liquid used to make the solu-

tion, and also that into which it diffused, was a very weak solution of sulphuric acid of which the freezing-point was $0^{\circ}0.441$. This prevented all but a trace of oxidation of the pyrogallol. The tannin used was probably not pure; but the difference in the calculated molecular weights deduced from the determinations in the two series is due to the solutions used being of different strengths, and to the fact that the molecular depression of the freezing-point diminishes rapidly as the strength of the solution increases. The depressions, I may mention, appear to show some marked irregularity; for when the four determinations (the two in Table I. at the initial strength, and the first two in Table II.) are plotted out, they do not all lie on any simple curve, either the determination at 12 parts to 100 giving much too small a value, or that at 16 parts too large a value. Another specimen of tannin was examined as to the freezing-points, and the results, which are the last four given in Table II., show the same peculiarity. This sample, however, gave throughout smaller values than that used in the diffusion-experiments, and the three stronger solutions of it deposited some tannin as well as ice in the freezing-point determination. The first sample did not do so.

In order to make the results of the first series more easily comparable with those of the second, the values for mv^2 obtained in the former have been multiplied by $2.577 (=x)$, in accordance with the results obtained with glycerine and cane-sugar, as mentioned above. The values for mv^2 are, as will be seen, very far from being constant. They vary from 16.09 with pyrogallol (omitting the doubtful result with gallic acid) to 46.81 with the weakest solution of cane-sugar; a variation of some 200 per cent., which cannot be in any way explained by the purely experimental error, since this, as has been mentioned, does not exceed 2 to 3 per cent. When we take the molecular weight deduced from the osmotic pressure (freezing-point) itself, m' , instead of the theoretical molecular weight, the constancy is in most cases scarcely improved; and, indeed, in those three cases where these calculated molecular weights do not agree with the simple theoretical weight, the values for $m'v^2$ are made much less nearly constant, and attain the enormous proportions of from 72 to 260. This tends to show that there is a want of agreement between the values calculated for mv^2 from the depression of the freezing-point and the rate of diffusion.

TABLE I.—Results of the Determinations.

Substance.	Freezing-points of the Solutions.				Strength of Solutions.—Parts to 100 of Water by Weight.				Molecular Weight.		m^2 .	Mol. Dep.			
	Initial.	Final.	Mean.	Decrease.	Proportional decrease.	Initial.	Final.	Mean.	Decrease.	Proportional decrease.			Theoretical $=m$.	Calculated from f.p. $=m$.	
Acetic acid (1)	—3892	—2875	—3183	1017	3185	1142	811	977	331	3388	59.86	58.01	6.66=17.16	1.086	
Urea (1)	—3410	—2358	—2884	1052	3648	1068	738	903	330	3654	59.95	59.18	8.38 =21.40	1.066	
Glycerine (1)	—4434	—3360	—3900	1068	2739	2140	1421	1881	519	2759	91.79	91.16	6.99 =18.01	1.060	
" (2)	—4413	—2845	—3629	1568	4321	2140	1363	1752	777	4435	"	91.25	18.06	17.95	1.059
Phenol (1)	—3260	—2483	—2871	777	2708	1687	1254	1471	433	2944	93.78	96.84	8.13 x =20.95	1.019	
Pyrogallol (2)	—3394	—2851	—3123	1043	3850	2428	1681	2060	737	3573	125.70	135.52	16.09	1.229	
Alloxan (1)	—2314	—2174	—2244	9640	2587	2050	1550	1800	500	2773	141.74	136.41	10.94 x =28.19	1.085	
Tartaric acid (1).....	—4147	—3291	—3719	8856	2202	3079	2408	2744	671	2445	149.64	139.45	8.95 x =28.05	1.129	
Gallio acid (2)		—0886	—1014	9446	4398	1403	0900	1152	314	2726	169.59	191.99	12.60	1.035	
Dextrin (2)	—11775	—8245	—10010	3530	3527	48142	35409	41776	12773	3048	323.24*	770.82	30.03	71.61	0.451
Amorphodextrin (2) ..	—0874	—0620	—0747	9255	3299	11704	808	9892	3200	3235	323.24*	2486.1	32.84	260.11	0.136
Tannin (1)	—0781	—0668	—0724	9113	1561	5177	4167	4672	1010	2162	331.22*	1219.6	15.48 x =39.90	57.01=146.91	0.286
" (2)	—1463	—1185	—1324	9277	2092	15990	11914	13956	4084	2926	331.22*	1983.1	28.36	169.82	0.175
Cane-sugar (1)	—3631	—2981	—3306	9650	1966	6266	5149	5707	1115	1952	"	326.3	13.00 x =33.50	12.43 =32.04	1.068
" (2)	—13072	—9833	—11203	3729	3338	21588	15674	18631	5914	3174	341.2	314.32	34.38	31.67	1.142
" (2)	—8167	—5945	—7056	2222	3149	13798	10132	11965	3866	3064	"	320.49	32.03	30.09	1.120
" (2)	—3881	—2814	—3348	1067	3187	6638	4837	5767	1801	3139	"	323.87	33.63	31.92	1.109
" (2)	—1377	—1295	—1586	9582	3870	3242	2229	2785	1013	3704	"	325.92	46.81	44.71	1.102
Maltose (2)	—3388	—2502	—2945	9886	3019	6377	4789	5583	1588	2844	341.2*	358.29	27.60	28.98	1.002
Raffinose (2)	—3861	—2862	—3362	9996	2971	8826	6757	7792	2069	2655	502.8*	428.04	35.45	30.88	1.208

* Simplest empirical molecular weight.

TABLE II.—Supplementary Freezing-point Determinations.

Substance.	Parts to 100 of Water.	F.-p.	Substance.	Parts to 100 of Water.	F.-p.
Tartaric acid.....	2.152	—2966	Dextrin	27.484	— 8208
Alloxan	1.425	—2000	„	47.943	—1.1082
Glycerine	1.453	—3023	Tannin	2.557	— 0440
Maltose	4.670	—2463	„	12.310	— 1221
Pyrogallol	1.603	—2228	„	15.804	— 1110
Gallic acid.....	0.667	—0697	„	10.184	— 0844
„	0.133	—0180	„	4.983	— 0542
Raffinose	0.640	—2669	„	2.473	— 0342
Amylodextrin ...	7.940	—0609			

The “molecular” depression, which, on the theory of osmotic pressure, will be proportional to mv^2 , must, when we take the molecular weights calculated from it (m'), be an absolute constant, whereas the values for this same quantity ($m'v^2$), when deduced from the diffusion-experiments, and when these same molecular weights are used, are far from being constant; moreover, while the “theoretical” molecular weights give the values of mv^2 in the diffusion experiments with dextrin, amylodextrin, and tannin as being similar to those with the other substances investigated, they will, when used for calculating the molecular depression, give values from $\frac{1}{2}$ to $\frac{1}{8}$ th only of those obtained with the other substances investigated. These values are given in the last column of the table: molec. dep. = (mean dep. $\times m$) $\div$ (mean strength $\times 17.96$).

The fact that the results with dextrin, amylodextrin, and tannin are of doubtful accuracy must, it is true, weaken the strength of any conclusions based on them. But, on the other hand, the fact that they do not give exceptional values for mv^2 renders it probable that they are not very inaccurate; and, moreover, the exceptional values which they give for $m'v^2$ are not out of harmony with the results with the other substances; for the sugars, where the molecular weights are large, give values which are considerably larger than those given by the other substances examined. There seems indeed to be a general tendency for $m'v^2$ to increase with the molecular weight of the substance diffusing: thus, with the first seven substances entered in the table we have molecular

weights from 60 to 150, and the value of $m'v^2$ is generally about 20: with the last three substances in the table, where the molecular weights are high, 314 to 430 (taking the calculated values m'), $m'v^2$ is much larger, namely over 30; while dextrin, tannin, and amylodextrin show still larger, and, taken in their order, increasing molecular weights, and also larger and increasing values for $m'v^2$. Thus it would appear that with higher molecular weights the rate of diffusion is abnormally large.

The exceptionally large values for mv^2 in the case of the weakest solution of cane-sugar is remarkable, but in the absence of a duplicate determination it is well not to lay much stress upon it.

XVI. *Contact-Action and the Conservation of Energy.*

By Prof. J. G. MACGREGOR, M.A., Sc.D.*

SEVERAL years ago Prof. O. J. Lodge, in a series of papers published in this Magazine†, proposed new definitions of work done and energy, and claimed (1) that by their aid he had deduced from the third law of motion and the hypothesis of universal contact-action alone, a law (which he called *the law*) of the conservation of energy; (2) that the law thus deduced was an extension of, and fully as axiomatic as, the law ordinarily enunciated under the same name; (3) that action at a distance might be shown to be incompatible with Newton's third law, or the law of the conservation of energy, or both; and (4) that energy cannot be transferred without being transformed, or transformed without being transferred. These claims, though *prima facie* so extraordinary as necessarily to have drawn attention, have never, so far as I am aware, been seriously challenged, and it is, perhaps, somewhat late in the day to challenge them now; but the remarkable progress which has recently been made in the application of contact-action theories, seems to make it desirable that they should be subjected to examination.

(1) *The Deduction of the Conservation of Energy.*

In the first version of the argument by which this deduction is made‡, Prof. Lodge seems to me (a) to assume the ordinary law of the conservation of energy in addition to the third law

* Communicated by the Author.

† Phil. Mag. [5] vols. viii. (1879) p. 277, xi. (1881) pp. 36 & 529, xix. (1885) p. 482.

‡ Ibid. vol. viii. (1879) p. 278.