

No. 16. — THE MEASUREMENT OF LARGE MOLECULAR MASSES.

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THE determination of the large molecular masses of such substances as the physiologist is occupied with, presents almost insuperable difficulties when attempted by the usual methods of the chemist. The vapour-density is unobtainable, and the molecular lowering of the freezing-point of a solvent produced by massive molecules is so small as to be merged in the experimental error of the freezing-point of the solvent in its purest obtainable state. The method to be proposed and discussed in this paper is founded on the measurement of the coefficient of diffusion of the substance through a solvent. The only difficulty about measuring the velocity of diffusion of a substance of large molecular mass is that the experiment for measuring it has to be prolonged for a time inversely proportional to the velocity in question. Graham, the pioneer in the investigation of diffusion, made measurements of the velocity of diffusion of albumen in water. If, then, we can establish a dynamical relation between the velocity of diffusion of a substance and the size of its molecule, it will be possible to measure the molecular mass of substances like albumen and its products of more or less complete disintegration.

It is true that a very simple relation has been discussed in connection with velocities of diffusion—namely, that the square of the velocity of diffusion of a substance through a given medium when multiplied by the molecular mass of the substance is a constant—that is, the kinetic energy of diffusion is constant for all molecules under like conditions. H. Euler (Wied. Ann., 1897, vol. lxiii.) proposed this law from an empirical study of known velocities of diffusion for non-electrolytes, Nernst having already supplied his beautifully simple theory for the diffusion of electrolytes. Obviously, the relation discussed by Euler is an attempt to treat diffusion through a liquid as a parallel phenomenon to the transpiration of gases through porous partitions, for which Graham had discovered his law that mv^2 is a constant. Indeed, in 1893 S. U. Pickering pointed out that by regarding osmotic pressure as the equivalent of gas-pressure one might be led to conclude that mD^2 would be constant for different substances of molecular mass m and velocity of diffusion D . He tested this relation by experiments on a number of substances (Phil. Mag., 1893, vol. xxxv.), and pronounced against its truth. But quite recently (Comptes Rendus, Paris, 1902, vol. cxxxv.) J. Thovert, who has developed a delicate and expeditious optical method of measuring velocities of diffusion and has applied it to a number of substances diffusing through water,

has found that for nineteen substances, ranging from methyl-alcohol, with a molecular mass 32, to raffinose, with one of 500, the product mD^2 shows a remarkable approach to constancy, ranging from 55×10^{-10} to 68×10^{-10} . But no dynamical proof that such a relation is to be expected has yet been furnished. The relation has been used by Nernst to calculate the molecular mass of albumen from Graham's data (see Arrhenius's "Text-book of Electro-chemistry"). But it is very desirable for such a purpose to have a dynamical rather than an empirical formula. Accordingly, I propose to apply to Nernst's theory of diffusion certain considerations advanced in "Ionization, Ionic Velocities, and Atomic Sizes" (Phil. Mag., Feb., 1902), in order to show what is the nature of the connection between velocity of diffusion and molecular size.

In Nernst's theory of the diffusion of an electrolyte the solution is assumed to be so dilute that the solute is entirely dissociated into ions along the whole path of the diffusion. The more rapid ion diffuses faster than the other, and so a separation of electric charges takes place, and causes an electro-motive force in the direction of diffusion. This electro-motive force increases until it causes the opposite ions to diffuse with equal velocities. Then there is a stationary state. The atomic charges of electricity are so powerful that this electro-motive force is produced by a difference of concentration in the two ions, which may be neglected so far as any other effects are concerned. Thus, if c is the concentration at a distance x along the diffusion-stream where the osmotic pressure is p , the ions of each sort in a cubic centimetre are subject to a driving force dp/dx on account of osmotic pressure. If E is the electro-motive force, then the cations in unit volume are subject to a driving force proportional to cE , while the anions experience an equal retarding force, denoted by bcE . If, then, U and V are the velocities which unit force can maintain in the two sorts of ion against the friction of the solvent, we have the following equations for the amount A of each ion crossing unit surface in unit time—

$$A = U \left(\frac{dp}{dx} + bcE \right) = V \left(\frac{dp}{dx} - bcE \right) \quad \dots \quad (1)$$

the two amounts being equal because the state is steady. Eliminating bcE , we get

$$A = \frac{2UV}{U+V} \frac{dp}{dx} \quad \dots \quad (2)$$

But according to the theory of osmotic pressure $p = cRT$, and so by definition of the coefficient of diffusion D of the solute we have

$$D = \frac{2UV}{U+V} RT \quad \dots \quad (3)$$

This formula has been remarkably well verified, both as to the relative and absolute coefficients of diffusion for electrolytes. The velocities U and V are derived direct from the ionic velocities of the two ions. But in my paper on "Ionization, &c.," it has been shown that the dielectric capacity of the atoms of the ions is fundamental in determining the electric forces acting on the ions. Yet dielectric capacity of the atoms is entirely ignored in Nernst's successful theory. It seems to me that from the electrical point of view Nernst is not justified in assuming uniform electro-motive force E , but that his assumption works out all right dynamically because the one kind of ion is thrusting the other back, while the other is thrusting the one forward by means of electric force. By writing the forces proportional to $+E$ and $-E$ Nernst introduces Newton's third law, which is all he really requires; and, as he eliminates the action and the reaction from his final result, the incompleteness in his electrical specification of the forces at play does not affect it. The point is of importance, because it is necessary to explain how dielectric capacity is of fundamental importance in ionic velocities and of none in diffusion velocities.

We can now proceed to determine the connection between diffusion velocities and molecular radius exactly as in "Ionization, &c.," for ionic velocities and ionic radius. Let a molecule of solute of radius a move with velocity V through the solution of viscosity η , then the resistance experienced by the molecule is given by Stoke's formula—

$$F = 6\pi V \eta a \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

If there are N molecules of solute in a cubic centimetre their total resistance will be N times this, and in the steady state of diffusion will be equal to the driving force of osmotic pressure $dp/dx = RT \, dc/dx$, thus

$$RT \frac{dc}{dx} = 6\pi V \eta a N \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

By definition of coefficient of diffusion we have

$$D = \frac{RT}{6\pi \eta a} \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

Thus we find that, for solutions dilute enough to give osmotic pressure, according to the laws of gaseous pressure we have the coefficient of diffusion of a substance through a given medium inversely proportional to the molecular radius, and also inversely proportional to the viscosity of the medium.

In regard to this connection between coefficient of diffusion and viscosity there is a difficulty to be removed similar to one which appears in connection with ionic velocities. It is this: that substances diffuse almost as quickly through jellies pre-

pared with water as through water itself. Now, the molar viscosity of jellies is enormously greater than that of water. The inference, therefore, is that in a jelly the water is enclosed in meshes which interfere but little with the motion of single molecules. To the molecule the jelly is practically nothing but water, which is unconfined so far as its effect on the molecule is concerned. The first test of the formula (6) is, then, to see how the coefficients of diffusion of a given substance through different liquids are related to the viscosities of the liquids. According to (6) $D\eta$ should be constant. H. Euler has given the following data for the diffusion of Br and I through water and benzene at 12° and through CS₂ at 16° C. The viscosities of these liquids are given from Thorpe and Rodger (Phil. Trans., 1894):—

BROMINE.					
			H ₂ O	C ₆ H ₆	CS ₂
η
			.01234	.00732	.00378
D
			.8	1.75	3.11
$D\eta$
			.0099	.0128	.0118
IODINE.					
D
				1.41	2.55
$D\eta$
				.0103	.0096

These data show that on the whole the coefficient of diffusion varies inversely as the viscosity. For a small range of temperature Thovort (Ann. de Ch. et de Ph. [7], 26, 1902) finds that for 1° rise of temperature the coefficient of diffusion of salts in water increases by .0265 of the value at 0°. Now, for the viscosity of water Thorpe and Rodger give the formula

$$\eta = \frac{5.9849}{(43.252 + t)^{1.3423}}$$

whence by (6) the coefficient of diffusion would change by .0227 of its value at 0° C. for a rise of 1° near 15° C. Thus the connection between diffusion and viscosity given by (6) is verified within the limits of experimental error in these measurements. We proceed, therefore, to our main business—namely, the relation between coefficient of diffusion and molecular radius.

The following table contains the coefficients of diffusion for various gases through water determined by Hüfner (Wied. Ann., 1897, vol. lx.; and Zeit. F. Ph. Ch., 27). I have reduced these all to a temperature of 16° C., and expressed them with the second as unit of time instead of the day. The values of B, the volume of the gramme-molecule of the gases, are taken mostly from "Further Studies on Molecular Force" (Phil. Mag. [6], 39). In the last row are given the values of $10^6 DB^3$, which by (6) ought to be constant. H. Euler's values for the diffusion coefficients of Cl₂ and Br₂ are added.

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	CO ₂	NH ₃	O ₂	N ₂	N ₂ O	Cl ₂	H ₂	Cl ₂	Br ₂
10 ⁷ D ..	166	132	167	178	156	127	474	154	101
B ..	30	21	19.3	22.7	29	38	8.6	38	52
10 ⁶ DB ³ ..	51	36	44	50	48	43	97	52	38

Hydrogen is conspicuous as an exception to the constancy of DB³. If CO₂ in water is taken to exist chiefly as H₂CO₃, and NH₃ as NH₄OH, the values of B would be increased to 44 and 35, and those of 10⁶DB³ to 59 and 43. As regards H₂, it should be remembered that the ion H has a much larger velocity than should go with its size.

For ordinary electrolytes in water we will take the diffusion data of Thovert (Comptes Rendus, 135) :—

ALCOHOLS.

	Methyl.	Ethyl.	Allyl.	Propyl.	Butyl.	Amyl.
10 ⁷ D ..	137	111	99	98	88	88
B ..	26	42.5	52	59	75.5	92
10 ⁶ DB ³ ..	41	39	37	38	37	40

OTHER SUBSTANCES.

	Urea.	Urethane.	Glycerol.	Phenol.	Hydroquin.	Resorcin.
10 ⁷ D ..	98	87	79	80	73	75
B ..	51	75	72	80	85	85
10 ⁶ DB ³ ..	36	37	33	34	32	33

	Pyrogall.	Glucose.	Mannite.	Antipyrin.	Maltose.	Raffinose.
10 ⁷ D ..	66	57	55	57	41	35.5
B ..	90	134	141	166	254	374
10 ⁶ DB ³ ..	30	29	29	31	26	26

It will be noticed that the values of the product 10⁶DB³ diminish progressively with increasing size of molecule. The coefficient of diffusion appears to vary inversely as a rather higher power of B than the cube root. In fact, for some reason yet to be investigated the diffusion data as a whole could be better represented if the diffusion coefficient were taken to vary inversely as the square root of the molecular volume, rather than as the theoretical cube root. Since for these compounds as a whole the square root of the molecular volume varies approximately as the square root of the molecular mass, we see how the square of the diffusion velocity multiplied by the molecular mass may come to be nearly constant within the above range of molecular masses, without there being any genuine dynamical foundation in the idea that the kinetic energy of diffusion of all substances ought to be the same. If by means of further inquiry the theoretical relation between D and B can be brought into closer harmony with the experimental, the measurement of large molecular masses will be made possible with the aid of diffusion experiments.