LXXV. *A dynamical theory of diffusion for non-electrolytes and the molecular mass of albumin*

William Sutherland

integral passes from 0 to $1/\beta$, as α passes through the value β *.

If the aperture of LL be reduced to a narrow annulus, the integral to be considered is

$$\int_0^\infty J_0(\alpha x)\, J_0(\beta x)\, x\, dx.$$

This assumes an infinite value when $\alpha = \beta$ †.

If the apertures be rectangular, the integrals take still simpler forms.

LXXV. *A Dynamical Theory of Diffusion for Non-Electro-lytes and the Molecular Mass of Albumin.* By WILLIAM SUTHERLAND ‡.

IN a paper communicated to the Australian Association for the Advancement of Science at Dunedin, 1904, on the Measurement of Large Molecular Masses, a purely dynamical theory of diffusion was outlined, with the aim of getting a formula for calculating from the data of diffusion those large molecular masses for which the ordinary methods fail. The formula obtained made the velocity of diffusion of a substance through a liquid vary inversely as the radius a of its molecule and inversely as the viscosity of the liquid. On applying it to the best data for coefficients of diffusion D it was found that the products aD, instead of being constant, diminished with increasing a in a manner which made extrapolation with the formula for substances like albumin seem precarious. After looking a little more closely into the dynamical conditions of the problem, it seems to me that the diminution of aD can be accounted for, and can be expressed by an empirical formula which enables us to extrapolate with confidence for a value of a for albumin, and so to assign for the molecular mass of albumin a value whose accuracy depends on that with which D is measured.

The theory is very similar to that of "Ionization, Ionic Velocities and Atomic Sizes" (Phil. Mag. Feb. 1902). Let a molecule of solute of radius a move with velocity V parallel to an x axis through the dilute solution of viscosity η. Then the resistance F to its motion is given by Stokes's formula

$$F = 6\pi V \eta a\, \frac{1 + 2\eta/\beta a}{1 + 3\eta/\beta a} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

* A theorem attributed to Weber. See Gray and Matthews' ' Bessel's Functions,' p. 228.
† See 'Theory of Sound,' § 203, equations (14), (16).
‡ Communicated by the Author.

where β is the coefficient of sliding friction if there is slip between the diffusing molecule and the solution. For N molecules of solute per c.c. of solution the total resistance will be N times this, and in the steady state of diffusion will equilibrate the driving force due to variation of the osmotic pressure of the solute, namely dp/dx, which by the osmotic laws is $RT dc/dx$, if c is the concentration of the solute at x and R is the gas constant.   Hence

$$RT \frac{dc}{dx} = 6\pi V \eta a N \frac{1+2\eta/\beta a}{1+3\eta/\beta a} ; \quad \cdots \quad (2)$$

and the required formula for the coefficient of diffusion with C for the number of molecules in a gramme-molecule is

$$D = \frac{RT}{6\pi\eta a C} \frac{1+3\eta/\beta a}{1+2\eta/\beta a} \cdot \quad \cdots \quad (3)$$

If $\beta = \infty$, that is, if there is no slipping of solution at surface of molecule, aD is the same for all molecules diffusing through a given solvent at a given temperature.   Now for a large molecule of solute moving amongst smaller ones of solvent, we can see that the slipping is probably small.   But in the other extreme case of a small molecule of solute moving amongst larger ones of solvent, an effect analogous to slipping will occur, since the small molecule will travel a good deal in the gaps which would be left if the molecules of solvent were forced almost into permanent contact.   We have thus two extreme cases of the formula.

When $\beta = 0$, $\qquad D = \dfrac{RT}{4\pi\eta a C}$

and when $\beta = \infty$, $\qquad D = \dfrac{RT}{6\pi\eta a C}$ $\qquad\qquad\cdots\quad (4)$

Thus with increasing values of a we should have aD diminishing from the upper limit $RT/4\pi\eta C$, when a is small, to the lower limit $RT/6\pi\eta C$, when a is large.   This is analogous to the actual behaviour of $B^{\frac{1}{3}}D$ obtained from experiment, B being the volume of the molecules in a gramme-molecule of solute.   The first of the following tables contains the coefficients of diffusion for various gases through water determined by Hüfner [*].   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 are taken mostly from " Further Studies on Molecular Force " (Phil. Mag. [6] xxxix.).   In the second last row are given the values of

* Wied. *Ann.* 1897, vol. xl., and *Zeit. f. Phys. Chem.* xxvii.

$10^6B^{\frac{1}{2}}D$ which we are studying. H. Euler's values for the diffusion coefficients of Cl_2 and Br_2 are added at the right hand of the table:—

	CO_2.	NH_3.	O_2.	N_2	N_2O.	Cl_2.	H_2.	Cl_2.	Br_2.
10^7D	166	132	167	178	156	127	474	154	101
B	30	21	19·3	22·7	29	38	8·6	38	52
$10^6B^{\frac{1}{2}}D$...	51	36	44	50	48	43	97	52	38
10^6 calcul.	44	50	51	48	44	40	73	40	37

In the next table the coefficients of diffusion are those found by Thovert for a number of non-electrolytes in water (*Comptes Rendus*, cxxxv.).

Alcohols.

	Methyl.	Ethyl.	Allyl.	Propyl.	Butyl.	Amyl.
10^7D	137	111	99	98	88	88
B	26	42·5	52	59	75·5	92
$10^6B^{\frac{1}{2}}D$...	41	39	37	38	37	40
10^6 calcul.	46	39	37	36	33	32

Other Substances.

	Urea.	Urethane.	Glycerol.	Phenol.	Hydro-quinone.	Resorcin.
10^7D	98	87	79	80	73	75
B	51	75	72	80	85	85
$10^6B^{\frac{1}{2}}D$...	36	37	33	34	32	33
10^6 calcul.	37	33	34	33	32	32

	Pyrogallol.	Glucose.	Mannite.	Antipyrin.	Maltose.	Raffinose.
10^7D	66	57	55	57	41	35·5
B	90	134	141	166	254	374
$10^6B^{\frac{1}{2}}D$...	30	29	29	31	26	26
10^6 calcul.	32	29	29	28	26	25

In spite of irregularities it can be seen that the chief tendency is for the product $10^6B^{\frac{1}{2}}D$ to diminish with increasing value of B and to seemingly converge to a lower limit, as is required by the theory. But the case of H_2 makes it impossible to recognize convergence to the upper limit required by the theory. The other gases in an irregular way fall in with the idea of convergence to an upper limit.

Under the circumstances it seems to me best to express the connexion between D and $B^{\frac{1}{3}}$ by an empirical equation, namely :—

$$10^6 B^{\frac{1}{3}} D = b + k/B^{\frac{2}{3}} , \quad . \quad . \quad . \quad . \quad (5)$$

where b and k are constants for a given solvent at a given temperature. For water at $16°$ C. $b = 21$, and $k = 220$, and with these values the last row of numbers in the previous tables marked " calcul." have been obtained. This empirical formula gives a connexion between velocity of diffusion and molecular radius for substances ranging from hydrogen with a molecular mass 2 to raffinose with a molecular mass 500. It makes $10^6 B^{\frac{1}{3}} D = 21$ when $B^{\frac{1}{3}}$ is large. For molecules of large radius we have thus good reason to rely on the relation

$$10^6 B^{\frac{1}{3}} D = 21 . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

as approximately true. To illustrate its application we can use it to calculate the molecular mass of egg albumin from the value of $10^7 D$ calculated by Stefan from Graham's data, namely 7. This makes $B^{\frac{1}{3}} = 30$, and $B = 27,000$. This is the volume of a gramme-molecule of egg albumin.

Representative minimum molecular formulæ for albumin obtained from chemical considerations are given in Cohnheim's *Chemie der Eiweisskörper.* Hofmeister for serum albumin gives $C_{450} H_{720} N_{116} O_{140} S_6$ with a molecular weight (mass) 10166. For egg albumin he gives a minimum of 5378. For hæmoglobin Hüfner and Jaquet assign 16669 for the minimum molecular mass. From the lowering of the freezing-point in albumin solutions Sabanajew and Alexandrow found for egg albumin the molecular mass 14270, but the experimental error due to impurities allows little reliance to be placed on this estimate. Now to pass from the gramme-molecular volume 27000 to the molecular mass we may proceed thus. From the values of B published in previous papers of mine we can estimate the limiting volume of a gramme-atom of C as 8, of H as 4, of N as 8, of O as 6, and of S as 18. The average percentage composition of egg albumin is C 52·5, H 7·2, N 15·3, O 23·5, and S 1·5. Hence if x is the number of carbon atoms in the molecule of egg albumin we have the equation

$$x \left\{ 8 + \frac{12}{52 \cdot 5} \left(4 \cdot \frac{7 \cdot 2}{1} + 8 \cdot \frac{15 \cdot 3}{14} + 6 \cdot \frac{23 \cdot 5}{16} + 18 \cdot \frac{1 \cdot 5}{32} \right) \right\} = 27000$$

and $x = 1436$. Thus the Graham-Stefan coefficient of diffusion leads to $C_{1436} H_{2364} N_{359} O_{482} S_{15}$ as the formula for egg albumin, the molecular mass being 32814, which is a small multiple of

the above minima. But as the preparation of pure crystal-lized albumins was not known in Graham's day, it is necessary that his diffusion experiments should be repeated with various pure albumins and with their products of disintegration, such as peptones, if we are to arrive at accurate estimates of the size of albumin molecules and their parts.

Melbourne, March 1905.

LXXVI. *On the Stresses in the Earth's Crust before and after the Sinking of a Bore-hole. By* C. CHREE, *Sc.D., LL.D., F.R.S.**

CONTENTS.

§ 1. IN 'Nature,' October 20, 1904, p. 602, there appeared letters by Mr. G. Martin and the Hon. C. A. Parsons dealing with the size of the stresses in the Earth's crust and speculating as to what would happen if a hole were bored to a depth of twelve miles.

The letters indicate that some interest attaches to the problem, but its true character seems to stand in need of care-ful consideration. We know at present so little of the nature of the earth's material, even at such small depths as twelve miles, and have such scanty knowledge of the combined effects of high temperature and high pressure, that there are no data for making an *exact* calculation. Rocks as we know them at the earth's surface are not isotropic or even homogeneous solids, and they are not perfectly elastic for any considerable stresses †; but the crust of the earth seems to behave as a solid so far as can be inferred from earthquake-waves, and nothing that is positively known forbids the hypothesis that the material a few miles down is elastic for moderate changes

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