

Citation:

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Consequently the metal will exhibit a potential that is more positive than the equilibrium potential.

OBSERVATION.

Analogous considerations as those on page 135, given there of a metal in a solution of its ions and electrons, hold for every equilibrium between coexisting phases which contain charged particles of different solubility. In this case a potential difference will always occur, given by the equation $\Delta = -\frac{\mu_1 - \mu_2}{vF}$, where μ_1 and μ_2 indicate the molecular thermodynamic potentials of the charged particles in the two phases. As these in general will not be the same, there must exist a potential difference.

This applies then also e.g. for a salt in equilibrium with its saturate solution, for a solid salt in equilibrium with its melt etc.

Amsterdam, May 25, 1916. Anorg. Chem. Lab. of the Univ.

Physics. — “*On Diffusion in Solutions.*” I. By Dr. J. D. R. SCHEFFER and Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of May 27, 1916).

1. *Introduction.* EINSTEIN has derived expressions which indicate how the mean square of the deviation of a Brownian particle and the diffusion constant depend on the nature of the substances and the temperature¹). The relation between the Brownian movement, indicated by :

$$\overline{\Delta^2} = \frac{RT}{N} \frac{1}{3\pi a \zeta} t, \dots \dots \dots (1)$$

and the diffusion constant is expressed by :

$$D = \frac{\overline{\Delta^2}}{2t}, \dots \dots \dots (2)$$

so that for the latter

$$D = \frac{RT}{N} \frac{1}{6\pi a \zeta}, \dots \dots \dots (3)$$

is found, an expression, which can also be found by a direct way by making use of the osmotic pressure, which as apparent force causes the diffusion, and the law of STOKES, which gives the resist-

¹) EINSTEIN. Ann. d. Phys (4) 19. 289. 371 (1906). Zeitschr. f. Elektrochem. 14. 235 (1908)

ance which a solid sphere encounters when moving in a medium in which the free path is small with respect to the radius of the sphere. EINSTEIN has namely demonstrated that for the cause of the diffusion we may substitute a force acting on the diffusing particles, which is equal to the osmotic pressure¹⁾. Like 1 the expression 3 holds, therefore, only for particles which are great with regard to the free path.

When we now examine what experimental confirmations for the expressions 1 and 3 are to be found in the literature, it appears that for particles with a diameter of the order 10^{-4} and 10^{-5} cm. chiefly equation 1 has been tested. Generally the procedure of testing is carried out in this way that the mean square of deviation is calculated from the observed deviations and then N is determined from equation 1. PERRIN's experiments, carried out with particles the radius of which varied between 2.10^{-5} and 5.10^{-4} cm., yielded values for N oscillating between 5.5 and $8.0 \cdot 10^{23}$. PERRIN's most accurate determinations carried out with particles of equal size, yielded $N = 6.9 \cdot 10^{23}$.²⁾ Of late values have been found for N which are lower³⁾ and have got closer to MILLIKAN's $6.06 \cdot 10^{23}$ ⁴⁾, which value is pretty generally considered as the most reliable one.

With regard to the diffusion it is noteworthy that the diffusion constant of these particles is very difficult to determine on account of the slight velocity at the ordinary temperature. Only by a very particular mode of procedure PERRIN has succeeded in finding a value for the diffusion constant. In his determinations the property was made use of that gamboge particles, moving in glycerine, adhere to a glass wall when colliding with it. So the quantity of particles adhering to the wall continually increases, when the suspension is brought into a vessel, and the diffusion constant can be calculated from the number that is found on the wall at different times. In this way BRILLOUIN found the value $N = 6.9 \cdot 10^{23}$ in PERRIN's laboratory⁵⁾. Accordingly the expressions 1 and 3 give satisfactory results for particles of the order 10^{-4} and 10^{-5} cm.

Likewise experiments have been made with colloidal solutions as a test of the equations 1 and 3. The Brownian movement has been

¹⁾ EINSTEIN. Ann. d. Phys. (4) 17. 549. (1905).

²⁾ PERRIN. Compt. rend. 146 seq. A summary of these experiments is found in DE HAAS—LORENTZ. Die Brownsche Bewegung und einige verwandte Erscheinungen. Die Wissenschaft. Band 52. (1913).

³⁾ NORDLUND. Zeitschr. f. physik. Chemie 87. 40. (1914).

⁴⁾ MILLIKAN. Phys. Zeitschr. 14. 796 (1913).

⁵⁾ BRILLOUIN. Ann. chim et phys. (8) 27 412 (1913). Cf however WESTGREN. Zeitschr. f. physik. Chem. 89. 63. (1914).

closely studied especially with regard to gold sols by THE SVEDBERG ($N = 6.2 \cdot 10^{23}$), and also the diffusion determinations yielded values which on the whole present a same dependence on the radius as equation 3 leads us to expect¹⁾.

If we examine what the expressions 1 and 3 can yield for ordinary solutions, it appears that only 3 is liable to be tested, and that the following conclusions offer the best opportunity.

1. In the same solvent the product of diffusion constant and radius of the diffusing molecule is constant. The relative size of the dissolved substances can, therefore, be determined from the diffusion constant. It is clear that we can only speak of testing here, when it is possible to compute the radii by another way. According to expression 3 THE SVEDBERG found for the radius of some organic substances values which at least roughly²⁾ agree with our views of chemical structure. The volume of the dissolved substance in pure state and the atom constants which follow from the additivity of the b of the equation of state, can likewise furnish an estimation of the radius. Another method to find the radius of the diffusing particle has been given by EINSTEIN³⁾; it is founded on the change in viscosity which a solvent undergoes, when large solid spheres are suspended in it; we shall return to this later on.

2. for diffusion of a substance in different solvents at the same temperature the product of diffusion constant and internal friction is constant. Here we should call attention to an investigation by THOVERT; who for diffusion of phenol in ten different solvents found values for this product which only vary between 92 and 99, the ratio of the diffusion constants even rising to 300⁴⁾. For a number of substances diffusing in alcohol and water OEHOLM has found radii of about equal length; hence $D\zeta$ also for these substances differs little in alcohol and water⁵⁾. An extensive investigation by OEHOLM with other solvents, has, however, yielded values for the radius of the same diffusing particle which are to each other as 1:2 and even as 1:3⁶⁾; this may be attributed to difference in molecular size of the dissolved substance (association), to the non-

1) THE SVEDBERG and INOUE. Kolloid Zeitschr. 1 No. 7 (1910); 2 No. 9 (1911). Cf. also WESTGREN l. c.

2) THE SVEDBERG. Zeitschr. f. physik Chemie. 67. 105. (1909)

3) THE SVEDBERG and A. ANDREEN-SVEDBERG, Zeitschr. f. physik Chemie. 76, 145 (1911).

4) EINSTEIN. Ann. d. Phys. (4) 19, 289 (1906); (4) 34, 591 (1911).

5) THOVERT. Ann. chem. et phys. (9) 2, 369 (1914).

6) OEHOLM. Meddelanden Nobelinstitut. 2. No. 24 (1912).

7) OEHOLM. Meddelanden Nobelinstitut. 2. No. 26 (1913).

fulfilment of the condition that the radius is great with respect to the free path or to binding of the dissolved substance with the solvent.

It may finally be remarked that HERZOG calculates the molecular weight from the specific volume of the dissolved substance in solid state and the diffusion constant by the aid of equation 3, and that he finds it in agreement with the known value as far as the order of magnitude is concerned. He derives from this a method to determine molecular weights of large molecules, for which osmotic methods do not give results ¹⁾.

3. for the same substance in the same solvent the influence of the temperature can be examined. No data are to be found in the literature about this. The reason for this is that the determination of diffusion constants, which is attended with great experimental difficulties even under ordinary circumstances, becomes still more difficult with higher temperature. Of late we have been occupied with testing equation 3 at different temperatures; what follows gives the description of our experiments and the results yielded by this investigation.

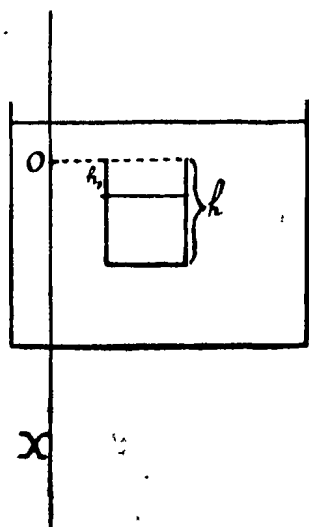


Fig. 1.

2. *Method of investigation.* The great difficulty which attends diffusion experiments at higher temperature is the keeping constant of the temperature; in the ways of research followed up to now a constant temperature is very difficult to attain on account of the large dimensions of the apparatus. We have tried to obtain satisfactory results by the application of a micromethod. GRAHAM'S first method which appeared to be suitable for this purpose is based on what follows. A diffusion vessel is filled with solution up to a certain height, then pure water is added till it is full, and it is placed in a vessel with pure water. If in fig. 1 the X -axis is laid vertically downward, the origin O at the level of the upper section, then the differential equation for the diffusion:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

yields on integration with the initial conditions:

¹⁾ HERZOG. Zeitschr. f. Elektrochem. 16. 1003 (1910).

$$c = c_0 \text{ between } x = h_1 \text{ and } x = h$$

$$c = 0 \text{ between } x = 0 \text{ and } x = h_1,$$

and the limiting conditions:

$$\frac{\partial c}{\partial x} = 0 \text{ for } x = h \text{ and}$$

$$c = 0 \text{ for } x = 0$$

the expression ¹⁾:

$$c = \frac{4c_0}{\pi} \sum_{p=0}^{\infty} \frac{1}{2p+1} \cos \frac{(2p+1)\pi h_1}{2h} \sin \frac{(2p+1)\pi x}{2h} e^{-\left(\frac{2p+1}{2h}\pi\right)^2 Dt} \quad (4)$$

The quantity which has flowed through the upper section in a definite time t , is indicated according to FICK'S law by:

$$Q = \int_0^t Dq \left(\frac{\partial c}{\partial x} \right)_{x=0} dt,$$

in which q represents the section of the vessel.

From 4 we find for this value:

$$Q = \frac{8c_0 q h}{\pi^2} \sum_{p=0}^{\infty} \frac{\cos \frac{(2p+1)\pi h_1}{2h}}{(2p+1)^2} \left(1 - e^{-\left(\frac{2p+1}{2h}\pi\right)^2 Dt} \right).$$

If we choose $h_1 = \frac{1}{3} h$, it is clear that in consequence of $\cos \frac{(2p+1)\pi h_1}{2h}$ becoming zero for $p=1$, the second term of the quickly converging series disappears; therefore the first term suffices for a great number of the determinations. This method of working had been applied by one of us before. ²⁾

In the determinations mentioned below we have taken $h_1 = 0$ for experimental reasons; the filling of the diffusion cylinders up to $\frac{2}{3}$ of their height for temperatures that differ from that of the surroundings is namely accompanied with great difficulties.

For our case $h_1 = 0$, and the cosine disappears from all the terms; the series, however, remains complete, so that generally two or three terms must be used for the calculation of the experiments. If Q_0 represents the quantity of substance originally present, the value of the relative rest for a time t becomes:

$$\frac{Q_0 - Q}{Q_0} = \frac{8}{\pi^2} \left(e^{-\frac{\pi^2}{4} \frac{Dt}{h^2}} + \frac{1}{9} e^{-\frac{9\pi^2}{4} \frac{Dt}{h^2}} + \frac{1}{25} e^{-\frac{25\pi^2}{4} \frac{Dt}{h^2}} + \dots \right) \quad (5)$$

¹⁾ SIMMLER and WILD, Pogg. Ann. **100**. 217. (1857).

²⁾ J. D. R. SCHEFFER. Ber. der Deutsch. Chem. Gesellsch. **15**. 788 (1882) and **16**. 1903 (1883).

From this equation table I has been calculated by means of which the value of the diffusion constant can be found if the time of diffusion and the height of the vessel are known.

TABLE I.

$\frac{Q_0-Q}{Q_0}$	$\frac{Dt}{h^2}$	$\frac{Q_0-Q}{Q_0}$	$\frac{Dt}{h^2}$
0.80	0.03141	0.54	0.16630
	322		718
0.79	0.03463	0.53	0.17364
	338		734
0.78	0.03801	0.52	0.18117
	354		753
0.77	0.04155	0.51	0.18886
	369		769
0.76	0.04524	0.50	0.19673
	385		787
0.75	0.04909	0.49	0.20478
	400		805
0.74	0.05309	0.48	0.21303
	417		825
0.73	0.05726	0.47	0.22145
	431		842
0.72	0.06157	0.46	0.23007
	448		862
0.71	0.06605	0.45	0.23891
	463		884
0.70	0.07068	0.44	0.24795
	480		904
0.69	0.07548	0.43	0.25721
	495		926
0.68	0.08043	0.42	0.26670
	511		949
0.67	0.08554	0.41	0.27643
	525		973
0.66	0.09079	0.40	0.28641
	542		998
0.65	0.09621	0.39	0.29664
	558		1023
0.64	0.10179	0.38	0.30714
	574		1050
0.63	0.10753	0.37	0.31793
	588		1079
0.62	0.11341	0.36	0.32901
	605		1108
0.61	0.11946	0.35	0.34041
	621		1140
0.60	0.12567	0.34	0.35216
	638		1175
0.59	0.13205	0.33	0.36424
	651		1208
0.58	0.13856	0.32	0.37671
	669		1247
0.57	0.14525	0.31	0.38957
	685		1286
0.56	0.15210	0.30	0.40285
	702		
0.55	0.15912		
	718		

The apparatus in which the diffusion takes place, is represented in fig. 2; it consists of a glass beaker *A* of 2½ liters of wide shape, placed on a tripod with double copper gauze. In the beaker on the wooden frame *B*, which surrounds the whole apparatus, are suspended the toluol regulator *C* and six test tubes *D*, one of which (*D*₁) is filled halfway, its height with the solution, the others (*D*₂₋₆) with pure water. For the heating a BUNSEN burner is used. At the beginning of a diffusion experiment seven glass cylinder holders *E*,

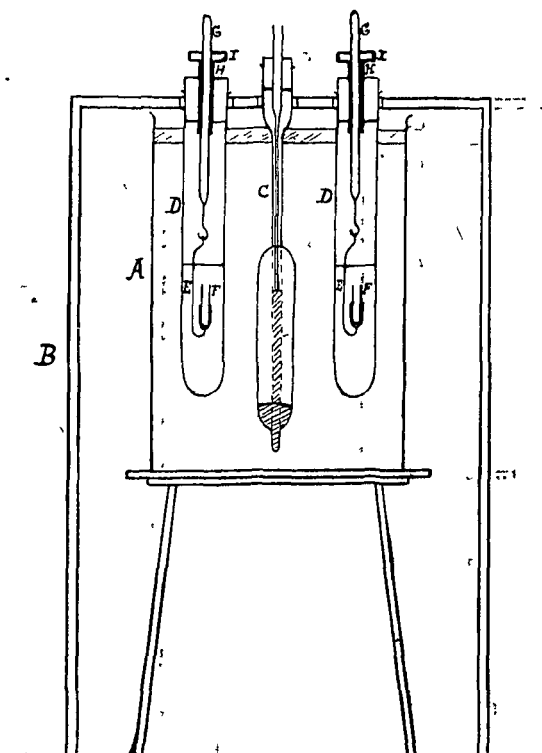


Fig. 2.

each provided with a diffusion cylinder *F* (*F*₁₋₇) are placed in the test tube with the solution (*D*₁), after the cylinders *F* of a diameter of 1½ mm. and a length of about 2 cm. have been filled with the solution by means of a pipette. When the whole apparatus has been brought to constant temperature, two or three of the cylinders (*F*₁₋₃) from the test tube *D*₁ are successively immersed in another (*D*₂) with pure water; this takes place by means of the tube *G*, which easily moves in the glass tube *H*; in rest it is supported by the movable cork disk *I*. These three cylinders (*F*₁₋₃) are taken out of the water immediately after the immersion. In the same way the cylinders (*F*₄₋₇), which have been left in *D*₁ are immersed

with holders in the test tubes D_{3-6} . The cylinders are taken out of the water after a definite time.

Then the contents are conveyed to a glass cup (K_{1-7}) by means of a pipette and by repeated rinsing of the cylinder with distilled water. The cups are made of small thin-walled glass spheres (diameter $\pm 1\frac{1}{2}$ cm.) which were cracked off along a small circle, the rim being fused a little to prevent the glass from further cracking (see

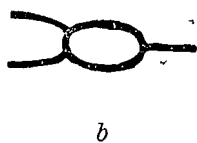
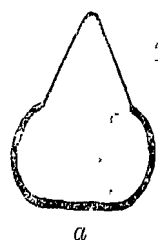


Fig. 3.

fig. 3a). Then the bottom side was heated, till a flat bottom was formed, and a platinum wire was fused with both ends to the upper edge. A light glass tray (fig. 3b) may be laid on the cup, which rests on the rim of

the cup with three glass rods, and serves to bear the weights. The cups K_{1-3} therefore contain the original solution, the other four K_{4-7} the diffusion rests. The ratio of the capacities of the diffusion cylinders was determined by weighing with mercury (for this purpose they were weighed empty, and after they had been filled with mercury and the superfluous mercury had been pressed off with a small glass plate they were weighed again). The filled cups were evaporated to dryness at 100° in an apparatus according to VICTOR MEYER¹⁾, and conveyed to a desiccator with strong sulphuric acid. The quantity of dissolved substance in the original solution of each cylinder H_{4-7} could then be calculated from the increase in weight

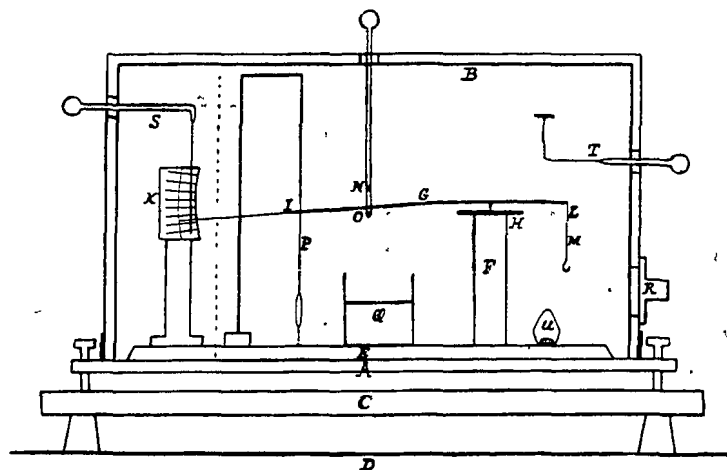


Fig 4.

¹⁾ V. MEYER. Ber. der Deutsch. Chem. Gesellsch. 18. 2999. (1885).

of the three first cups; its mean value furnished the initial quantity. The increases in weight of K_{4-7} yielded the diffusion rests.

The cups were weighed in the balance represented in fig. 4. The preparation of a micro balance suitable for our purpose has presented many difficulties; after a great many futile attempts we have succeeded in making an efficient apparatus, with which all the experiments described below have been carried out, and which has proved very satisfactory. The balance consists of a wooden bottom *A*, provided with three levelling screws and a detachable wooden case *B*, the front side of which consists of glass. The balance rests on a board *C*, which is placed with three rubber stops on the wall bracket *D*. On the bottom lies the glass plate *E*, on which the stand *F* has been cemented. The beam *G* consists of a thin glass rod provided with a piece of a razor, which is fastened to the beam with sealing wax, and rests free on the glass plate *H*. One extremity of *G* ends in a thin glass fibre *I*, which moves along a scalar division on the celluloid plate *K*. To the other extremity of the beam is fastened a very thin quartz thread *L*, provided with a glass hook *M*, which serves for the suspension of the cups. The beam is restricted in its movement by the horizontal glass rods *N* and *O*, so that only small oscillations are possible. Further the plumb *P*, hanging over a mark on the bottom, the drying vessel with concentrated sulphuric acid *Q*, and the plate *R*, which serves for the adjustment and removal of the cups, are indicated in the figure. During the weighing no displacement of the razor in the direction left-right takes place on careful manipulation, at least if the plate *H* has been placed quite horizontal by the aid of a level or a ball from a cycle bearing; the only movement that takes place is a small rotation round the vertical axis which removes the pointer somewhat from the scale *K*. The glass tube *S* serves to keep this distance always very small, which is required for the reading of the position of the pointer in the microscope, which stands horizontally before *K*. Tube *S* ends in a very thin glass thread, and can be rotated by a handle outside the case. If a movement of the beam in the direction left-right should have taken place, the original position can be restored by bringing the beam on *O* and the cork disk of *T*, which can again be rotated round a horizontal axis from the outside, and can be slid in and out. Accordingly the balance case need only be removed for the refreshing of the drying substance *Q*. The microscope has an ocular micrometer; the value of the scalar divisions *K* is expressed in that of the micrometer as unity. The weights used are likewise gauged by means of the ocular micrometer.

For this purpose the scalar value of the smallest weight was first directly determined and then that of the difference between two successive ones. Every weight, the largest weighs about 3 mgr., the smallest 0.2 mgr., corresponds therefore to a known number of scalar divisions. The weighing takes place according to the compensation method. A cup (fig. 3a) with the tray (fig. 3b) and a number of weights is hung on the balance, so that the pointer can freely move along the scale; its position is read in the microscope. If the cup is filled with substance, the pointer is again brought to about the same position by removal of weights from the tray. After correction for different position of the pointer before and after the weighing the removed weights show the quantity of substance in the cup, expressed in the scale of the ocular micrometer. Before and after every weighing the zero position of the balance is determined by the aid of a test tray U , which always remains in the balance. Every scalar division of the micrometer corresponds to 0.003 mgr. and allows an estimation down to fourths. To exclude temperature influences as much as possible during the weighing, the glass of the balance right of the scale is protected by a piece of white card-board.

3. *Results.* For equation 3 to be applicable, the diameter of the dissolved substance must be large with respect to the free path

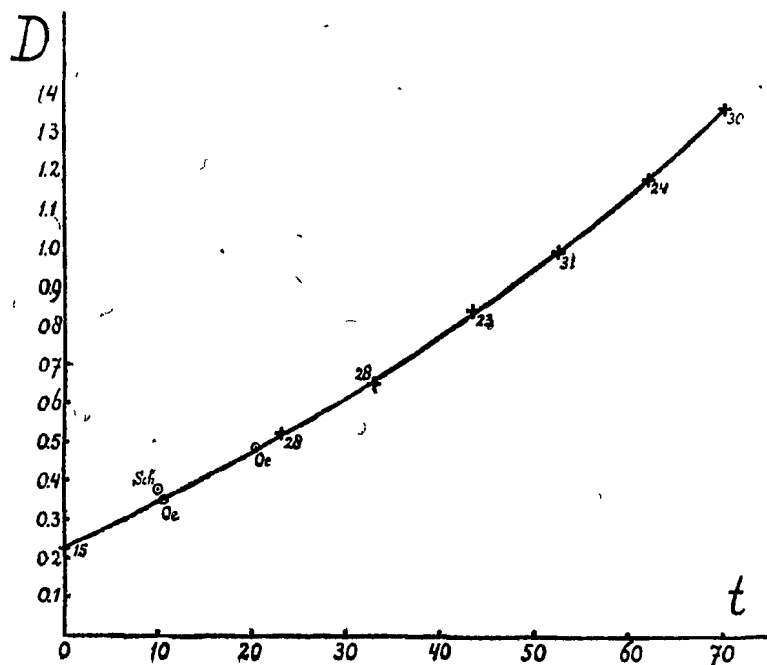


Fig. 5.

of the solvent. We have chosen mannite as dissolved substance for our experiments, because the molecular weight (182) is large compared with that of water, and because it can easily be determined by weight after drying at 100°. Mannite (Ph. Ned. IV) was recrystallized from alcohol and dried. (Spt. 166 $\frac{1}{2}$ °). To obtain sufficiently reliable values for the diffusion-constant, we have made a great number of determinations at different temperatures, and determined the mean values of the series of experiments; the results are recorded in table II, III, and IV, the mean values are given in a $D-t$ diagram (fig. 5) (see p. 157). ($D = [\text{cm}^2 \cdot 24 \text{ hours}^{-1}]$). At any point the number of observations is given which has contributed to that mean.

TABLE II.

Number of the cylinders	1	2	3	4	5	6	7	8
Capacity in mg. mercury (18°)	854.3	611.7	683.0	470.8	555.8	520.4	515.9	529.1
Height in cm. ¹⁾	—	—	—	1.748	2.050	1.895	1.935	—

4. *Conclusions concerning the radius of the mannite molecule.* Equation (3) is valid for infinitely diluted solutions, in which the dissolved particles move through the medium independently of each other. ζ represents the internal friction of the solvent, in our case water, and D the diffusion constant for infinite dilution.

OEHOLM derived 0.513 for D_{∞} from his experiments with the normalities 0.5, 0.25, and 0.125 at 20°, which value is about 6% higher than the value 0.485, which was found by him for a solution of 0.25 normal. This is comparable with our observations, in which the strength of the solutions varies between 30 and 70 grams per liter (± 0.2 and 0.4 norm.). The values found by OEHOLM for this concentration have been inserted in the graphical representation²⁾. If the same change of the diffusion constant with the concentration

¹⁾ The height was determined by means of a piece of a knitting needle which was slid into the diffusion cylinders till it reached the flat bottom. The total length and the part projecting outside the cylinder were measured by the aid of the ocular micrometer and of a millimeter division on glass.

²⁾ OEHOLM. Meddelanden Nobelinstitut. 2 No. 23 (1912): The value found by one of us before, viz.: $D_{100} = 0.38$ is, evidently slightly too high, which will probably be owing to variations of temperature, which were inevitable on account of the long duration of the experiments (21—27 days). (Ber. der Deutsch Chem. Gesellsch. 15. 797 (1882)).

TABLE III.

Temperature	Time (in minutes)	Original quantity			Diffusion rest and constant				Constant (mean)
		1	2	3	4	5	6	7	
0	2366	665.1	479.3	—	226.8 0.214	296.5 0.202	259.8 0.224	248.3 0.264	0.226
0	2313	693.5	494.2	553.8	229.9 0.236	299.6 0.230	269.8 0.228	—	0.231
0	1892	880.8	626.7	707.8	316.5 0.221	407.5 0.209	361.0 0.230	362.5 0.227	0.222
0	2316	879.2	631.7	705.7	297.3 0.225	381.2 0.231	344.5 0.225	345.8 0.224	0.226
23	1668	838.7	594.3	670.2	225.0 0.543	303.0 0.559	267.0 0.551	271.0 0.544	0.549
23	1447	848.2	608.8	677.7	241.5 0.559	324.7 0.558	290.7 0.538	296.8 0.519	0.544
23.3	1234	849.8	604.2	677.5	266.7 0.515	348.7 0.520	308.0 0.535	309.5 0.535	0.526
23.3	1268.5	—	609.8	679.8	263.8 0.522	351.3 0.501	312.7 0.504	318.0 0.485	0.503
23.3	1746	868.0	625.3	696.5	238.5 0.502	319.2 0.519	277.5 0.530	280.3 0.529	0.520
23.3	1195	868.7	620.5	—	278.0 0.507	358.5 0.530	325.5 0.502	329.0 0.491	0.508
23.3	1921	874.8	627.3	—	222.2 0.526	314.5 0.497	268.0 0.524	272.8 0.517	0.516
32.3	417	824.5	—	659.7	328.7 0.636	414.3 0.593	374.0 0.637	378.5 0.585	0.613
32.4	733.5	834.0	596.2	666.3	289.2 0.646	372.8 0.633	336.2 0.632	331.5 0.673	0.646
33.1	761	—	552.3	617.2	262.2 0.668	334.7 0.695	310.3 0.617	310.3 0.621	0.650
33.1	820	834.2	593.0	673.5	282.2 0.630	359.2 0.665	320.5 0.677	324.5 0.656	0.657
33.1	975	839.7	600.0	677.8	261.5 0.675	346.3 0.659	308.5 0.661	312.2 0.647	0.661
33.1	994	856.2	603.7	685.8	269.5 0.632	351.8 0.639	306.3 0.687	313.7 0.650	0.652

Temperature	Time (in minutes)	Original quantity			Diffusion rest and constant				Constant (mean)
		1	2	3	4	5	6	7	
33.1	1032	857.0	614.5	691.7	261.0	346.5	308.7	312.2	0.666
					0.677	0.668	0.665	0.653	
43	707	785.2	565.8	—	260.5	332.5	295.8	297.5	0.824
					0.782	0.829	0.845	0.841	
43.3	667	—	532.3	596.5	238.5	—	287.0	287.8	0.852
					0.909	—	0.822	0.824	
43.3	821	1048.5	—	—	310.7	421.7	373.3	627.8)	0.856
					0.891	0.833	0.844	—	
43.5	678	980.2	701.5	—	320.5	416.5	—	378.0	0.833
					0.842	0.843	—	0.815	
43.5	973	985.0	—	—	287.2	369.3	335.7	603.3)	0.840
					0.801	0.894	0.825	—	
43.5	969	1008.0	714.0	—	284.7	390.8	335.8	612.5)	0.834
					0.846	0.798	0.858	—	
43.5	1101	—	953.2	823.0 ²⁾	350.8	481.0	420.3	429.7	0.849
					0.856	0.852	0.855	0.832	
52.2	1159	1066.8	765.0	—	254.0	358.5	306.2	306.5	0.982
					0.970	0.962	0.985	1.009	
52.2	648	1076.0	750.3	690.2 ²⁾	335.5	457.2	399.3	400.7	0.961
					1.014	0.893	0.967	0.970	
52.2	1146	1110.8	801.0	700.5 ²⁾	265.0	377.0	325.7	323.3	0.985
					0.990	0.968	0.972	1.011	
52.2	717	1132.8	809.8	—	343.0	455.5	396.5	399.5	0.996
					0.977	0.964	1.023	1.020	
52.3	535	1504.7	—	943.7 ²⁾	503.5	649.5	584.8	586.3	1.021
					1.016	1.031	1.017	1.020	
52.4	750	1438.3	1017.7	904.8 ²⁾	427.8	572.8	518.2	—	0.948
					0.980	0.958	0.907	—	
52.4	477	1498.3	1072.2	932.5 ²⁾	516.5	672.5	601.5	594.8	1.007
					1.021	0.964	0.995	1.048	
52.4	1314	—	1179.3	1012.2 ²⁾	348.5	514.5	435.0	451.3	0.984
					1.009	0.973	0.993	0.960	

1) Original substance.

2) Cylinder 8.

Temperature	Time (in minutes)	Original quantity			Diffusion rest and constant				Constant (mean)
		1	2	3	4	5	6	7	
59.6	843	892.8	—	699.6	234.0	309.0	282.1	276.2	1.146
					1.110	1.208	1.093	1.172	
61.9	981	—	799.2	680.0 ¹⁾	256.8	355.2	327.0	309.3	1.199
					1.192	1.248	1.102	1.252	
62.2	741	1079.5	—	669.2 ¹⁾	297.3	392.0	352.8	364.3	1.180
					1.171	1.254	1.180	1.114	
62.4	530	1038.5	748.0	647.2 ¹⁾	340.2	423.8	389.2	389.7	1.165
					1.085	1.263	1.150	1.161	
62.6	717	991.7	712.0	615.7 ¹⁾	280.2	371.2	335.5	329.2	1.170
					1.150	1.201	1.125	1.203	
63.2	568	—	852.8	736.7 ¹⁾	364.2	496.3	435.5	433.7	1.149
					1.204	1.079	1.141	1.173	
68.2	557.5	1106.6	783.9	—	334.2	434.7	385.3	—	1.295
					1.250	1.317	1.319	—	
69.9	688	798.3	568.3	—	222.2	286.6	263.4	254.4	1.300
					1.225	1.379	1.233	1.365	
70.2	521	843.1	614.8	703.9	258.3	354.8	300.0	315.0	1.323
					1.377	1.225	1.427	1.262	
70.2	549	—	678.2	761.5	—	384.8	335.5	330.7	1.308
					—	1.233	1.306	1.384	
70.3	684	1052.7	—	831.9	280.7	—	329.9	326.8	1.389
					1.335	—	1.385	1.446	
70.3	304	1183.7	844.1	—	427.3	552.9	487.5	—	1.321
					1.342	1.231	1.390	—	
70.7	461	1097.9	783.7	880.5	337.3	—	404.0	410.8	1.393
					1.468	—	1.381	1.329	
70.7	550.5	1196.5	861.3	—	347.7	463.8	411.3	411.0	1.422
					1.413	1.422	1.411	1.441	
71.2	574.5	711.2	—	583.5	207.8	272.6	240.9	—	1.419
					1.369	1.449	1.439	—	

continues to exist also at other temperatures, then on substitution of the values of D found by us in equation 3 values for α will be found, which may diverge a few percentages from the real ones.

¹⁾ Cylinder 8.

The real values can then be about 6% *smaller* than those calculated in table IV. The calculated values are of the expected order of magnitude, and change little with the temperature.

TABLE IV.

T	D	$5 \cdot 10^6$	$a \cdot 10^8$
0	0.22 ⁶	1797	4.2
23.2	0.52 ⁴	935	3.8
32.9	0.64 ⁹	755	3.9
43.4	0.84 ¹	618	3.8
52.3	0.98 ⁷	531	3.9
62.0	1.16 ⁸	459	3.9
70.2	1.35 ²	406	3.9

In the calculation of the radius use has been made of the determinations of the internal friction of BINGHAM and WHITE¹⁾ and of the N -value of MILLIKAN²⁾.

In a following paper we shall communicate the results of a series of experiments, which enable us to determine the value of the radius by another way.

The diffusion experiments will be continued with other substances.

Physiology. — “*The movements of the heart and the pulmonary respiration with spiders*”³⁾. By Dr. V. WILLEM (Ghent). (Communicated by Prof. VAN RIJNBERK).

(Communicated in the meeting of May 27, 1916).

We do not know anything about the respiratory movements with spiders. The only modern investigator who has tried to find them experimentally, was F. PLATEAU, he applied in vain to Arachnida the artificial methods that had succeeded with insects; not a single method of investigation made him find the slightest change of the shape of the body that could be attributed to inhalation or exha-

¹⁾ BINGHAM and WHITE. Zeitschr. f. physik. Chemie 80 684 (1912).

²⁾ l. c.

³⁾ According to investigations made in the Physiological Laboratory of the University of Amsterdam.