

On the Diffusion of Liquids.

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§1. The first thorough experimental study of the free diffusion of liquids was made by Graham⁽¹⁾ in 1850—1861, and soon after Fick⁽²⁾ developed a theory of the free diffusion of an aqueous solution of salt under the supposition that it obeys a law analogous to the conduction of heat. When the concentration u depends simply on time t and a coordinate x , then Fick assumed that the quantity of salt dS which passes through a cross section having an area equal to q and perpendicular to the axis of x during the time dt is proportional to $q \cdot dt$ and the gradient of the concentration $\frac{\partial u}{\partial x}$; or

$$dS = kq \cdot dt \cdot \frac{\partial u}{\partial x} \quad (1)$$

where k is a constant depending on the nature of the solution and is called the constant of diffusion. It is easy to deduce from (1) the following differential equation satisfied by u ,

$$\frac{\partial u}{\partial t} = k \frac{\partial^2 u}{\partial x^2} \quad (2)$$

Several experiments were conducted to test Fick's equation and

(1) Graham, *Phil. Mag.* [4] 3. 1862.

(2) Fick, *Pogg. Ann.* 94. 1855.

to determine the numerical value of k for various substances. The methods employed may be divided into two classes. In the first class, the quantity of salt which passed through a given section during a finite time was determined. To the second class belong those methods in which the concentrations at different depths were determined; the latter methods are preferable to the former, for they give us clear information respecting the state of the diffusing liquid at any given instant. A variety of methods were used by different experimenters. Graham, Beez,⁽¹⁾ Beilstein,⁽²⁾ Schuhmeister⁽³⁾ and others determined the quantity of salt passed through, or the concentration at any point, from the density of the liquid; Graham, and Wroblewski⁽⁴⁾ by evaporating the water out of the solution and weighing the salt left behind. Long⁽⁵⁾ and Scheffer⁽⁶⁾ used titrimetrical methods. Wild and Simmler⁽⁷⁾ who soon after the publication of Fick's paper, integrated his equation, said that the concentration at any point could be determined by a saccharimeter in the case of sugar. Hoppe-Seyler⁽⁸⁾ and Vait⁽⁹⁾ used this method. Wroblewski⁽¹⁰⁾ and Wiedeburg⁽¹¹⁾ used the photometrical method in colored solutions. Johannisjauz,⁽¹²⁾ at the suggestion of Kundt, used a liquid prism filled with the diffusing liquid and determined the index of refraction at different heights. Weber⁽¹³⁾ employed an electrical method for determining the difference

(1) Beez, Schlömilch-Zeits. IV.

(2) Beilstein, Ann. d. chemie u. Pharm. 99.

(3) Schuhmeister, Sitzungsber. d. k. Akad. d. Wissensch. zu Wien 79.

(4) Wroblewski, Wied. Ann. 7.

(5) Long, Wied. Ann. 9.

(6) Scheffer, Zeits. für phys. Chemie, 2.

(7) Wild and Simmler, Pogg. Ann. 100, 1857.

(8) Hoppe-Seyler, Medicinisch-chemische Untersuchungen, 1866.

(9) Vait, Pogg. Ann. 130, 1867.

(10) Wroblewski, loc. cit.

(11) Wiedeburg, Wied. Ann. 41, 1890.

(12) Johannisjauz, Wied. Ann. 2, 1877.

(13) Weber, Wied. Ann. 7, 1879.

of concentrations at two given points. It will be seen that, of these methods the optical and the electrical are better suited for our purpose, because if we use these methods, the liquid is not disturbed and we can day after day study how the diffusion is progressing, and get a clear insight into the phenomena. Optical methods, however, have one defect in common, as was first pointed out by Stefan.⁽¹⁾ His objection was that as the liquid is diffusing, the medium is un-homogeneous and consequently a ray of light meant to be sent along a given layer horizontally is curved out of that layer and tends toward that side which is optically rare, so that the concentration deduced from that experiment does not correspond to that of the layer in question. Wiener,⁽²⁾ however, availed himself of this very fact, and devised an arrangement which could be used in the determination of k and also of the conductivity of heat in liquids.

The constant of diffusion k is not an absolute constant. It is a function of temperature and increases with it. It is also highly probable that it depends on the concentration. This was noticed by Graham, Wroblewski, Weber and Schuhmeister in ZnSO_4 and NaCl solutions, though their results do not agree with one another. It can be easily shown that when k is variable, the differential equation for u , is

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial u}{\partial x} \right) \quad (3)$$

where $k=f(u)$. Wiedeburg and Wiener took k as a linear function of u .

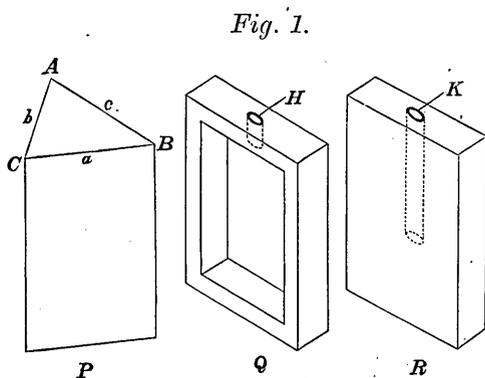
§2. My present communication relates to a new method of studying diffusion optically, which is quite free from Stefan's objection and is capable of giving an accurate value of k . I experimented upon ZnSO_4 and NaCl , and found that the diffusion in these cases agrees with

(1) Stefan, Sitzungsber. d. k. Akad. d. Wissensch. zu Wien, 78 and 79. 1878—1879.

(2) Wiener, Wied. Ann. 49, 109, 1893.

the assumption that k is independent of u . But as my present circumstances do not allow me to repeat the experiments and confirm the results hitherto obtained, I shall not at present, insist on the last statement. Let me describe my arrangement and the method of deducing k .

In the accompanying figure 1, P is a prism glass ; Q and R are made of any solid and of such size that when they are packed and pressed together slightly, the hollow space in Q, forms a closed rectangular water tight diffusion vessel bounded on one side by the prism



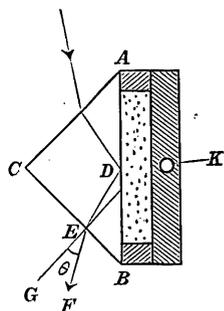
P and on the other by the plate

R. H is a hole for introducing the liquid, and is to be closed by a stopper. K is a hole bored in R, for admitting a thermometer. It does not communicate with the hollow space in Q, in order to keep the area of

the cross section of the diffusion vessel constant.

When a pencil of light is sent horizontally through the face b (fig 2) of the prism, it is reflected at the face c , where the glass is in contact with the liquid, and then emerges from the prism through the

Fig. 2.



face a . When the prism is optically denser than the liquid, total reflection will take place. Let EF be the emergent ray corresponding to the critical ray. If N and n be the indices of reflection of the glass and of the liquid respectively, and if the angle ABC of the prism be α and the angle FEG be θ , then

$$n = \sin a \sqrt{N^2 - \sin^2 \theta} + \cos a \cdot \sin \theta. \quad (4)$$

Now if the vessel be filled with the diffusing liquid, n and therefore θ will be different from layer to layer. By measuring θ , the concentration u at different heights can be deduced and k calculated.

It must be owned here that the above method involves one doubtful point. As the concentration is determined by the critical angle of total reflection, its value is that at and near the glass wall of the vessel. This may differ from the value at the interior of the liquid mass, owing to the molecular action of the wall, and the value of k deduced by this method may be influenced by the nature of the prism used. This is the point which requires further study. As I have not yet hit upon a suitable method of deciding this point, it is left as an open question (see however Wiener's paper). It may, I think, be investigated, by making the thickness of Q very small, say one-hundredth of a millimeter, and bringing the influence of the opposite wall R into the action.

This arrangement can be used as a demonstration experiment in diffusion, for the curve traced out by the critical ray EF can be projected on a screen and shown to a large audience. For this purpose, a cylindrical lens is placed in front of the face b in such a way that sun light sent toward it, is focussed at D (fig. 2) and forms there a bright vertical line. In order to avoid the heating of the liquid and the consequent convection current, an absorption trough for heat rays must be used. A long focus lens placed before the face a , will then project a curve on a screen at a proper distance. This curve consists usually of two vertical lines at its two ends connected by a curved portion having an inflexion point. This curved portion corresponds to the region where the diffusion is proceeding and the change in its form shows the progress of diffusion. Fig. 3 is from a photograph obtained by projecting the diffusion curve directly on a sensitive plate.

For the subjective experiment and for the determination of k , a different arrangement is necessary. The diffusion ves-

Fig. 3.



sel is to be furnished with adjustable tripods and placed on a spectrometer. A sodium flame is put before the face b , and directly in front of the face a , a cathetometer is placed. The telescope of the latter is provided with an auto-

collimating ocular, which is used for fixing the direction of the normal EG. When the vessel is filled with a *homogeneous* liquid, on looking through the telescope, one can at once see a sharply defined vertical boundary between the total and the partial reflections. But when the vessel is filled with the *diffusing* liquid, it is otherwise. With the full aperture of the telescope, one can not distinctly see the boundary which is curved in this case, for the evident reason that it is crossed by the vertical rays. It is necessary to cut down the rays entering the telescope to a narrow pencil in a horizontal plane. I covered the objective with a cap having a horizontal slit about 1 mm. broad, and only then was I able to see the diffusion curve distinctly. With the telescope thus furnished with a slit, it is a very simple matter to move the telescope vertically and measure the angles θ at different heights.

In passing, it will be noticed that this method may also be used for the study of diffusion through an opaque body like sand, or through a substance like agar-agar, as investigated by Voigtländer⁽¹⁾.

(1) Voigtländer, Zeits. für phys. Chemie, 3. 1889.

The experiment was conducted in the following way. The vessel was just half filled with distilled water, and then placed on the spectrometer and the verticality of the reflecting faces carefully adjusted. A glass tube drawn to a capillary in one end was introduced into the vessel so that its lower end reached the bottom of the vessel. The solution to be examined was poured very slowly, drop by drop, into the tube until the vessel was full of liquid. In this way, the solution was quietly made to occupy the lower half of the diffusion vessel. The hole H was then closed, care being taken to leave no air bubbles within the vessel. The whole was left untouched about two or three hours and then the measurement was made and repeated daily for about a week without disturbing the vessel during that time. The spectrometer and the cathetometer stood on a massive stone pier in a small room, the temperature of which never varied by more than 2° C.

§. 3. The relation between the concentration u of a salt solution and its index of refraction n is almost linear. According to Schütt,⁽¹⁾ the relation for NaCl solution is exactly linear. His result is given in Table I., in which u is the number of grammes of NaCl in 100 grammes of water, and n is the index of refraction for Na-light at $18,^{\circ}07$ C.

TABLE I. NaCl SOLUTION.

u	n
24.99	1.37789
19.99	1.36862
14.99	1.35959
9.99	1.35068
5.00	1.34191
3.00	1.33841
1.00	1.33491
0.30	1.33369
0.00	1.33316

(1) Schütt, Zeits. für phys. Chemie, 5. 1890.

In such cases, if we follow Fick's theory, n satisfies the differential equation (2), and there is no need of reducing n to u in calculating k . I examined the relation for ZnSO_4 by Abbe's refractometer by Zeiss and found that it was not exactly linear. The result is given in Table II. In such cases, one must reduce n to u for finding the value of k .

TABLE II. ZnSO_4 -SOLUTION.

u	n
71.10	1.3809
47.38	1.3696
31.92	1.3606
25.46	1.3559
21.02	1.3533
17.96	1.3509
13.95	1.3470
11.29	1.3453
9.50	1.3437
8.18	1.3427
6.40	1.3406
5.24	1.3399
4.44	1.3388
Temp. = 11.°5 C	

A solution of the equation (2) is

$$u = e^{-m^2 kt} (A \sin mx + B \cos mx).$$

m being a constant. In my arrangement, the diffusion vessel is rectangular and closed, its height being equal to H , and at its top and bottom $\frac{\partial u}{\partial x}$ is equal to zero. Takig the origin of coordinate at the bottom of the vessel, the boundary conditions are, therefore,

$$\begin{aligned} \text{at } x=0, & \quad \frac{\partial u}{\partial x} = 0 \\ \text{,, } x=H, & \quad \text{,,} \end{aligned}$$

which give us at once

$$A = 0$$

and $m = \frac{p\pi}{H}, \quad p = [0, 1, 2, 3, \dots],$

Thus u is given by

$$u = B_0 + B_1 e^{-\frac{\pi^2}{H^2} kt} \cos \frac{\pi x}{H} + B_2 e^{-\frac{4\pi^2}{H^2} kt} \cos \frac{2\pi x}{H} + \dots \quad (5)$$

Hence it follows that at $t = 0,$

$$u_0 = B_0 + B_1 \cos \frac{\pi x}{H} + B_2 \cos \frac{2\pi x}{H} + \dots \quad (6)$$

and at any time $t,$ u may be put as

$$u = b_0 + b_1 \cos \frac{\pi x}{H} + b_2 \cos \frac{2\pi x}{H} + \dots \quad (6')$$

where $b_0 = B_0,$

$$b_1 = B_1 e^{-\frac{\pi^2}{H^2} kt},$$

$$b_2 = B_2 e^{-\frac{4\pi^2}{H^2} kt},$$

.....

Thus we get

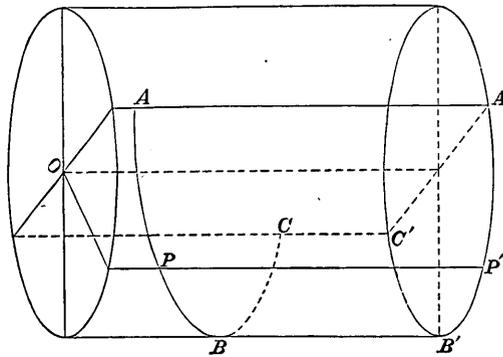
$$k = \frac{H^2}{\pi^2 t} \log_e \left(\frac{B_1}{b_1} \right) = \frac{H^2}{4\pi^2 t} \log_e \left(\frac{B_2}{b_2} \right) = \dots \quad (7)$$

Though k may be determined by any of these relations, the first relation is best suited for the purpose. In fact, when the vessel is filled with the salt solution nearly to the height $\frac{H}{2}$ initially the coefficients b_2, b_3, \dots become within two or three days so very small that they are of no practical use in the calculation.

The expansions (6) and (6') are Fourier's series. Their coefficients may be calculated by the ordinary method of multiplying $\cos \frac{\pi x}{H}, \cos \frac{2\pi x}{H},$ &c into u and integrating them, or by using harmonic analysers; but in the present case, it is more convenient to proceed as follows.

Let us suppose that we take a right circular cylinder of radius r with its axis horizontal. Draw a curve with u as the abscissa and x as the ordinate. The scale of the abscissa may be any whatsoever, but that of the ordinate must be so taken that when the curve is wrapped round the cylinder, it covers just half its surface. Let $OA'A$

Fig. 4.



be the initial meridian and $OB'B$ perpendicular to it. Project the curve $APBC$ orthogonally on the plane $OB'B$, then we shall get a curve $A''P''B''C''$. Denote the area bounded by $A''P''B''C''A''$ by s_1 . If the angle between the plane $OP'P$

and the initial meridian be θ , then evidently

$$s_1 = \int_0^{\pi} u \cdot r \cdot \cos \theta \cdot d\theta$$

But since $x : H = \theta : \pi$

$$\theta = \frac{\pi x}{H},$$

we have, therefore,

$$\begin{aligned} s_1 &= \frac{r\pi}{H} \int_0^H u \cdot \cos \frac{\pi x}{H} dx \\ &= \frac{r\pi}{H} \cdot \frac{b_1 H}{2} = \frac{\pi r}{2} b_1, \end{aligned}$$

Similarly if the scale of the abscissa be so taken that the curve covers the surface of the cylinder from $\theta=0$ to $\theta=p\pi$ and the area obtained by projecting it on the meridian at $\theta=\frac{\pi}{2}$ be denoted by s_p , then

$$s_p = \frac{p\pi r}{2} b_p \quad (8)$$

Hence if S_p be the corresponding area for the curve at $t=0$, we have

$$\frac{S_p}{s_p} = \frac{B_p}{b_p}$$

and therefore

$$k = \frac{H^2}{p^2\pi^2 t} \cdot \log_{10} \left(\frac{S_p}{s_p} \right),$$

so that if it is only required to find k , it is sufficient to determine S_p and s_p in any arbitrary unit.

I used only S_1 and s_1 in my reductions for the reason already given. The values of $\log_{10} \left(\frac{S_1}{s_1} \right)$ were tabulated against t , and the ratio $\log_{10} \left(\frac{S_1}{s_1} \right) / t$ was determined by the method of the least squares, and finally k was calculated by the equation

$$k = 2.3026 \frac{H^2}{\pi^2 t} \log_{10} \left(\frac{S_1}{s_1} \right). \quad (10)$$

§ 4. In my experiment, the diffusion vessel is made of brass (though evidently glass is preferable). Its height is 48 mm., its thickness 10 mm. and its breadth 56 mm. The spectrometer circle reads to 10'' by verniers, and the readings of two distinct settings for the diffusion curve seldom differed by more than 20''. The angles of the prism used are

$$A = 45^\circ \quad 2' \quad 25''$$

$$B = 44^\circ \quad 55' \quad 35''$$

$$C = 90^\circ \quad 1' \quad 30''$$

The index of refraction N was measured by filling the vessel with liquids of known indices, or when vacant, and the mean of several experiments gave

$$N = 1.53175.$$

In the tables III_a—III_c, which relate to a set of experiments on NaCl solution, n_{obs} is the value of the index of refraction at a point x deduced from θ by the equation (4), and n_{cal} is that value of n calculated by putting B_0 and B_1 or b_0 and b_1 obtained by harmonically analysing n_{obs} in the equation (6) or (6'). Δ is $n_{\text{obs}} - n_{\text{cal}}$, and shows how soon b_2, b_3, \dots become insignificantly small. In these experiments, the angle α of the prism = $45^\circ 2' 25''$.

Table III_a.

Time = 31. Jan. 14^h 58^m; temperature = $10^\circ, 7$ C

Spect. reading for the normal = $329^\circ 53' 10''$.

x	Spect. reading	θ	n_{obs}	n_{cal}	Δ
48	354° 11' 10"	34° 18' 0"	1.3348	1.3316	+0,0032
44	12 10	19 0	349	311	+ 38
39	12 10	19 0	349	334	+ 15
34	11 50	18 40	349	372	- 23
29	14 10	21 0	352	421	- 69
26	24 50	31 40	366	453	- 87
24	355 2 40	25 9 30	417	475	- 58
22	356 5 40	26 12 30	500	497	+ 3
20	357 0 20	27 7 10	569	524	+ 45
18	32 10	29 0	596	540	+ 56
16	40 50	47 40	619	560	+ 59
14	43 0	49 50	621	578	+ 43
9	44 40	51 30	623	616	+ 7
4	44 40	51 30	623	639	- 16
0	44 40	51 30	623	644	- 21

$$B_0 = 1.34749,$$

$$B_1 = +0.01693,$$

$$B_2 = +0.00207,$$

$$B_3 = -0.00453.$$

Table III_bTime=1. Feb. 10^h 50^m; temperature=9°.8 C

Spect. reading for the normal=329° 50' 30."

x	Spect. reading	θ	$n_{\text{obs.}}$	$n_{\text{cal.}}$	Δ
48	354° 45' 10"	24° 23' 40"	1.3355	1.3351	+0,0004
44	47 20	25 50	358	355	+ 3
39	58 10	36 40	373	372	+ 1
34	355 13 50	52 20	394	400	- 6
29	41 0	25 19 30	430	435	- 5
24	356 11 50	50 20	474	474	0
19	46 20	26 24 50	514	514	0
14	357 20 50	59 20	558	550	+ 8
9	39 10	27 17 40	582	577	+ 5
4	52 30	31 0	598	594	+ 4
0	52 30	31 0	598	598	0

$$b_0=1.34747,$$

$$b_2=+0.00021$$

$$b_1=+0.01235,$$

$$b_3=-0.00037$$

Table III_cTime=2. Feb. 13^h 19^m; temperature=11°. 0C

Spect. reading for the normal=330° 20' 0."

x	Spect. reading.	θ	$n_{\text{obs.}}$	$n_{\text{cal.}}$	Δ
48	355° 13' 30"	24° 53' 30"	1.3395	1.3397	-0,0002
44	15 50	55 50	398	400	- 2
39	26 0	25 6 0	412	411	+ 1
34	39 0	19 0	429	430	- 1
29	58 20	38 20	455	454	+ 1
24	356 19 40	59 40	483	481	+ 2
19	41 10	26 21 10	510	508	+ 2
14	59 50	39 50	533	533	0

9	357 14 30	54 30	552	551	+	1
4	19 50	59 50	559	563	-	4
0	20 30	27 0 30	560	566	-	6

$$b_0=1.34814$$

$$b_1=0.00843$$

Table III_a.

Time= 3. Feb. 9^h 18^m; temperature=10.° 2 C.

Spect. reading for the normal=330° 20' 20''

x	Spect. reading	θ	$n_{\text{obs.}}$	$n_{\text{cal.}}$	Δ
48	355° 29' 50''	25° 9' 30''	1.3417	1.3419	-0,0002
44	31 40	11 20	419	421	- 2
39	39 0	18 40	429	429	0
34	50 50	30 30	445	443	+ 2
29	356 5 0	44 40	463	461	+ 2
24	19 30	59 10	482	481	+ 1
19	35 30	26 15 10	502	500	+ 2
14	48 10	27 50	518	518	0
9	58 40	38 20	531	531	0
4	357 3 30	43 10	538	540	- 2
0	3 50	43 30	540	542	- 2

$$b_0=1.34805$$

$$b_1=0.00614$$

Table III_e.

Time=4. Feb. 10^h 8^m; temperature=10°.OC.

Spect. reading for the normal=330° 18' 40.0''

x	Spect. reading	θ	$n_{\text{obs.}}$	$n_{\text{cal.}}$	Δ
48	355° 45' 20''	25° 26' 40''	1.3440	1.3438	+0,0002
44	46 40	28 0	441	440	+ 2
39	50 10	31 30	446	445	+ 1

34	58 0	39 20	456	455	+	1
29	356 8 10	49 30	469	467	+	2
24	18 30	59 50	481	481		0
19	29 20	26 10 40	497	495	+	2
14	38 50	20 10	509	508	+	1
9	46 10	27 30	518	518		0
4	50 10	31 30	523	524	-	1
0	50 10	31 30	523	525	-	2

$$b_0 = 1.34814$$

$$b_1 = 0.00407.$$

The curves a-e in plate I. are the $n-x$ curves with x as the ordinate and n as the abscissa; and those in plate II, are the curves obtained by projecting them supposed to be wrapped round a cylinder on the meridian plane perpendicular to the initial meridian, and are used in calculating B_1 and b_1 . Table IV and the line a in plate V show the relation between t and $\log_{10}\left(\frac{B_1}{b_1}\right)$. They show how nearly $\log_{10}\left(\frac{B_1}{b_1}\right)$ is proportional to t , as is required by Fick's law, and that fact may be looked upon as a proof that at least in NaCl, k is independent of the concentration.

Table IV.

Time.	Temp.	t (day)	B , and b ,	$\log_{10}\left(\frac{B_1}{b_1}\right)$
31. Jan. 14 ^h 58 ^m	10°.7C	0.000	+0,01693	0,0000
1 Feb. 10 50	9.8	0.828	1235	0,1370
2 „ 13 19	11.0	1.931	843	0,3029
3 „ 9 18	10.2	2.763	614	0,4405
4 „ 10 8	10.0	3.798	407	0,5882

$$k = 0.841 \left(\frac{\text{cm}^2}{\text{day}} \right) = 9.73 \times 10^{-6} \left(\frac{\text{cm}^2}{\text{sec}} \right)$$

Mean temp = 10°.3 C

§5 In the experiment for Zn SO_4 , the angle α of the prism = $44^\circ 55' 35''$. The results are given in Tables Va—Vf. As n is not a linear function of u , we have to reduce n to u in this case. In the following tables, the numbers in the column u are the number of grammes of Zn SO_4 in 100 grammes of water. I have dispensed with calculating B_0, B_1, \dots , and the areas S_1 and s_1 in an arbitrary unit were determined only, because the fact that the phenomena of diffusion is fairly well represented by the equation (5), was made clear by the experiments on NaCl , and because in the determination of k , a knowledge of S_1 and s_1 is sufficient.

Table Va.

Time = 13. Feb. 16^h 43^m; temperature = $12^\circ.0\text{C}$

Spect. reading for the normal = $358^\circ 54' 20''$

x	Spect. reading	θ	n	u
48 ^{mm}	23° 24' 10"	24° 29' 50"	1.3348	0.98
43	24 10	29 50	348	0.98
38	24 20	30 0	349	0.98
33	26 50	32 30	352	1.24
31	35 0	40 40	363	2.22
29	24 1 50	25 7 30	399	5.24
27	58 10	26 3 50	474	14.09
25	26 34 30	27 40 10	596	30.42
23	28 0 30	29 6 10	700	48.22
21	28 10	33 50	733	53.04
18	32 40	38 20	738	56.20
13	32 30	38 10	738	56.20
8	32 30	38 10	738	56.20
3	32 30	38 10	738	56.20
0	32 30	38 10	738	56.20

$S_1 = 1073.5$

Table V_b.Time=14. Feb. 13^h 29^m; temperature=11°. 2 C.

Spect. reading for the normal=358° 55' 40".

x	Spect. reading	θ	n	u
48 ^{mm}	23° 28' 10"	24° 32' 30"	1,3352	1.24
43	28 30	32 50	352	1.24
38	40 50	45 10	369	2.76
33	24 12 0	25 16 20	411	6.82
28	25 18 20	26 22 40	498	16.73
23	26 50 0	27 54 20	613	33.20
18	28 0 10	29 4 30	698	47.38
13	28 20	32 40	731	54.70
8	35 10	39 30	740	56.58
3	35 30	39 50	740	56.58
0	35 30	39 50	740	56.58

 $s_1=1006.0$ Table V_c.Time=15. Feb. 10^h 25^m; temperature=10°.3 C.

Spect. reading for the normal=358° 54' 50".

x	Spect. reading	θ	n	u
48 ^{mm}	23° 35' 10"	24° 40' 20"	1,3363	2.22
43	40 0	45 10	369	2.75
38	56 40	25 1 50	390	4.58
33	24 30 40	35 50	437	9.50
28	25 27 10	26 32 20	511	18.21
23	26 36 0	27 41 10	597	28.76
18	27 32 20	28 37 30	666	42.23
13	28 12 20	29 17 30	713	50.93
8	27 50	33 0	731	54.68

3	33 20	38 30	739	56.38
0	33 20	38 30	739	56.38

$s_1=920.0$

Table V_d.

Time=18. Feb. 9^h 26^m; temperature=11.°OC.
Spect. reading for the normal=358° 54' 50."

x	Spect. reading	θ	n	u
48	24° 15' 20"	25° 20' 30"	1.3416	7.29
43	19 10	24 20	422	7.74
38	35 30	40 40	443	10.17
33	25 3 10	26 8 20	479	14.88
28	39 50	45 0	526	20.12
23	26 21 40	27 26 50	579	28.22
18	27 2 20	28 7 30	629	35.88
13	36 10	41 20	670	42.92
8	28 0 50	29 6 0	700	47.46
3	12 30	17 40	714	51.15
0	12 30	17 40	714	51.15

$s_1=692.0$

Table V_e.

Time=20. Feb. 14^h 21^m; temperature=10°.7 C.
Spect. reading for the normal=358° 55' 50."

x	Spect. reading	θ	n	u
48	24° 37' 50"	25° 42' 0"	1.3436	9.37
43	43 0	47 10	452	11.18
38	54 30	58 40	467	13.48
33	25 17 30	26 21 40	496	16.62
28	45 50	50 0	532	20.89

23	26	18	10	27	22	20	573	27.64
18		51	20		55	30	614	33.30
13	27	19	50	28	24	0	650	39.48
8		41	50		46	0	676	43.95
3		51	50		56	0	688	47.25
0		51	50		56	0	688	47.25

$$s_1 = 577.5$$

Table V_f.

Time = 21. Feb. 16^h 33^m; temperature = 10°.7 C.

Spect. reading for the normal = 358° 55' 50."

x	Spect. reading	θ	n	u
48	24° 48' 10"	25° 52' 20"	1.3459	12.23
43	50 20	54 30	462	12.70
38	25 3 50	26 8 0	479	14.88
33	22 40	26 50	503	17.34
28	49 10	53 20	537	21.70
23	26 15 50	27 20 0	571	27.11
18	46 30	50 40	608	32.26
13	27 12 20	28 16 30	640	37.77
8	33 30	37 40	666	42.20
3	42 40	46 50	677	44.14
0	42 40	46 50	677	44.14

$$s_1 = 509.5$$

Figures a-f in plate III. are $u-x$ curves, and those in plate IV are the curves used in determining S_1 and s_1 . Table VI. and the line b in plate V show the relation between t and $\log_{10}\left(\frac{S_1}{s_1}\right)$.

Table VI.

Time.			Temp.	t (day)	$\log_{10} \frac{S_1}{s_1}$	S_1 and s_1
13.	Feb. 16 ^b	43 ^m	12.0C	0.000	0.0000	1073.5
14	„ 13	29	11.2	0.865	282	1006.0
15	„ 10	25	10.3	1.720	670	920.0
18	„ 9	26	11.0	4.697	1907	692.0
20	„ 14	21	10.7	6.901	2693	577.5
21	„ 19	33	10.7	7.985	3237	509.5

$$k = 0.2145 \left(\frac{\text{cm}^2}{\text{day}} \right) = 2.483 \times 10^{-6} \left(\frac{\text{cm}^2}{\text{sec}} \right).$$

Mean temp. = 11° C.

§ 6 I conclude from the preceding experiments that so far as NaCl and ZnSO₄ are concerned, k is independent of the concentration, and Fick's law is satisfied fairly well by them. As to the numerical values of k , the results of several experimenters do not agree with one another. Table VII is formed by reducing the experiments of Graham, Scheffer and Schuhmeister under the supposition that k is a function of temperature only.

Table VII.

Substance	Temperature	$k \left(\frac{\text{cm}^2}{\text{day}} \right)$	Observer
NaCl	10.0 C	0.95	Graham
„	„	0.86	Schuhmeister
„	„	0.87	Scheffer
„	10.3	0.84	Nakamura
ZnSO ₄	10.0	0.20	Schuhmeister
„	9.5	0.18	Weber
„	11.0	0.21	Nakamura

§ 7. If k be taken as a linear function of u as was supposed by

Wiedeburg and Wiener, and be put equal to $a + \beta u$, then the differential equation (3) gives at once,

$$\frac{\partial u}{\partial t} = a \frac{\partial^2 u}{\partial x^2} + \frac{\beta}{2} \frac{\partial^2 (u^2)}{\partial x^2}.$$

As $u-x$ curves for various values of t are known, we can determine $\frac{\partial u}{\partial t}$ and $\frac{\partial^2 u}{\partial x^2}$ graphically for given values of x and t , and by plotting u^2 against x , we can also determine $\frac{\partial^2 (u^2)}{\partial x^2}$, and thus calculate a and β . But as this method is lacking in accuracy, I did not undertake the task.

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