LXXV. THE PENETRATION OF ELECTROLYTES INTO GELS. II: THE APPLICATION OF FOURIER'S LINEAR DIFFUSION LAW.

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(Received October 9th, 1920.)

I. INTRODUCTION.

THE ways of studying diffusion can be divided roughly into three classes, two of which, electrical measurements and quantitative analysis, may be described as the standard methods of determining diffusion rates; the third experimental procedure, marked off from the first two by its simplicity, has been named the indicator method. The characteristic of simplicity is appreciated on looking at the list of essential apparatus—a rack of test-tubes and a ruler. The tubes are filled half full with a gelatin solution containing some indicator, and after the formation of a solid jelly a solution of the substance under investigation is poured in and a colour change in the indicator demonstrates the forward march of the diffusing substance. When this is a neutral salt the change consists of the formation of a precipitate with the reagent placed in the jelly.

This method has been investigated recently by von Fürth and Bubanović [1918]. Their research on the quantitative aspects of the problem is a notable advance, but their method of calculation of the diffusion coefficient (defined below) merely gives ratios and not absolute values. This is a serious drawback, and Professor Stiles, who is revising the indicator method [1920], urged me to attempt the calculation if there was the slightest hope of success. The winning of new results is beyond the scope of this essay. It is limited to the effort to work out a theoretical formula free from arbitrary constants, and secondly the illustration of the method of using this formula by which new results can be won.

The mathematical expression arrived at is general, therefore it does not matter what substance is used in the experimental testing—accordingly it will be put to the trial with the familiar salt, sodium chloride. Anyone reading this account will see how essential is such a test, though unfortunately it expands the writing to an inordinate length. The theory, from the point of view of the laboratory worker, lacks the charming simplicity of the experimental technique.

This disadvantage is inevitable—in fact, it must be confessed that in the beginning, the prospect of working out the result looked small indeed. The given measurement was doubtless a function of the diffusion coefficient " κ ," but it was a function also of about a dozen other variables. The complexity of the theory might easily have discounted the advantages of the practice, but a review of these advantages had better follow the account of the method of calculation—a method mainly due to a lucky coincidence.

II. SUMMARY OF THE THEORETICAL PRINCIPLES OF DIFFUSION.

Leaving more general aspects, we may now proceed to the special problems of the calculation. The laboratory measurements are given in terms of centimetres of salt penetration. These distances depend on a variety of factors. Firstly, we have to consider the laws of diffusion, which are expressed in the form of differential equations, integrable for certain "boundary conditions," which are the second group of factors to be examined. Essentially they depend on the form of the mass of gelatin and the stirring of the salt solution. Thirdly, there are the phenomena peculiar to the experiment, for example, the temperature, the nature of the diffusing substance and the resistance of the medium.

The theory of the first two of these groups of phenomena belongs to the realm of mathematical physics, and was worked out by Fourier 100 years ago. The last group falls within the province of the experimenter.

The factors of interest to him all affect the diffusion coefficient, κ , so he has to reverse the original procedure, to find what value of κ must be assigned in the formulae to give the observed relation between concentration, time and place. This is easy in the two standard methods, but if an indicator is present, the problem becomes much more complicated, and there is nothing for it but to go back to first principles. The following portion of this section is devoted to the explanation of the terms in the formulae required, and the definition of the conditions under which they hold good. For the explanation of the formulae themselves, it is enough to give a general reference to Fourier's *Théorie Analytique de la Chaleur*, or the modern text-books of the mathematical theory of heat conduction, for example, Carslaw's *Fourier's Series and Integrals*. Even though we need only the simpler formulae it would take far too long and serve no useful purpose to go through the expansion of unity in a sine series—which is needed for formula (I) or Laplace's solution for the flow of heat in an infinite solid, required for formulae (II) and (III).

For our present work they are merely stated in the form most suitable for calculation with ordinary tables.

There is no possibility of avoiding these formulae. Von Fürth and Bubanović's penetration factor can be used for certain purposes, but the overwhelming reasons for calculating " κ " are stated below.

(1) There is no need to introduce an empirical law expressing the effect of concentration, so that the true effects of concentration are laid before us.

(2) We can test the absolute accuracy of the work by comparison with standard methods.

(3) Thirdly, κ must be known if we are to make any practical calculations on the diffusion of salt in the system.

(4) It is the fundamental constant which is of use to us in the study of the phenomena, in which we are interested—free from the complications due to the “boundary conditions.”

These reasons for making the attempt to calculate κ are quite decisive. The fundamental law, that the rate of diffusion is proportional to the concentration gradient, was published by Fick as a special case of Fourier's linear diffusion law.

$$\frac{\partial u}{\partial t} = \kappa \frac{\partial^2 u}{\partial x^2}$$

t = time in seconds,

x = distance in centimetres,

u = concentration of salt,

κ = diffusion coefficient.

The diffusion coefficient is the amount of salt in equivalents which would flow across an area of one square centimetre, if the concentration at one point was one equivalent per litre greater than that at another point, one centimetre distant in the line of flow.

This partial differential equation has, of course, many different solutions, depending on the initial and boundary conditions. We will consider first the example which resembles the type of salt penetration of most practical interest. In this example the surface is kept at constant salt concentration by immersion in a large bath of solution.

To define the conditions more accurately, let us call the direction of penetration the “ x ” axis, and at the surface of the gel let $x = 0$. Suppose the test-tube is 14 cm. long, and distances into it are reckoned positive. Let u = the salt concentration.

Let u_0 be the concentration of salt in the bath of solution. Then we have the following conditions:

$$u = 0, \text{ when } 0 < x < 14 \text{ at } t = 0,$$

$$u = u_0 \text{ at } x = 0,$$

$$du/dx = 0 \text{ at } x = 14.$$

This last condition is represented mathematically by adding another 14 cm. to the length, with the condition that

$$u = u_0 \text{ at } x = 28.$$

Both the differential equation and the boundary conditions are satisfied by the following series of sine and exponentials, where l is double the length of the test-tube:

$$u = u_0 \left\{ 1 - \frac{4}{\pi} \left(e^{-\frac{\kappa \pi^2 t}{l^2}} \cdot \sin \frac{\pi x}{l} + \frac{1}{3} e^{-\frac{9 \kappa \pi^2 t}{l^2}} \cdot \sin \frac{3 \pi x}{l} + \frac{1}{5} e^{-\frac{25 \kappa \pi^2 t}{l^2}} \cdot \sin \frac{5 \pi x}{l} + \dots \right) \right\} \dots (I)$$

This series converges too slowly to be very helpful in practical work, but with its aid we can define the limits within which a simpler formula will hold good. For this purpose the calculations need not be carried very far and in any case tubes do not agree in length to four places of decimals. Taking Öholm's figure $\kappa = 1.07$ per day, and assuming diffusion has been taking place for six days, we find that

$u = 0.0007N$ if the calculation includes the fourth term,

$u = 0.0003N$ if five terms are summed.

The amounts are so small that we shall probably not exceed the error in calculations with four figure tables if we assume that no salt has reached the end of the tube in the first two or three days of the experiment.

This conclusion greatly simplifies the problem, since the initial and boundary conditions may be re-stated with the assurance that the length of the tube does not enter into the problem, and for purposes of calculation may be taken as infinite.

$u = 0$, when $x > 0$ at $t = 0$,

$u = u_0$ at $x = 0$.

The solution for these conditions is

$$u = u_0 \left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^q e^{-q^2} dq \right\}, \dots\dots\dots (II)$$

where

$$q = \frac{x}{2\sqrt{\kappa t}}.$$

The formula could be stated more briefly if Kramp's table of the integral between q and infinity were more generally available, but the form given above is used because the probability integral tables are much more likely to be at hand. Given the table, it is the work of a few moments to determine " κ " when " u " is known.

The second type of experiment is carried out as follows. The salt solution is put in a tube half filled with gelatin and diffusion is allowed to take place without any circulation of the solution, so that we have a concentration gradient in the liquid itself.

If, as before, we consider only the first few days, and assume κ is constant, we have the following conditions:

$u = u_0$, $x < 0$,

$u = 0$, $x > 0$.

After reversing the sign of x the solution which satisfies these conditions is

$$u = u_0 \left\{ \frac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^q e^{-q^2} dq \right\}. \dots\dots\dots (III)$$

III. NEGATIVE SALT CONVENTION.

The formulae stated in the preceding section are well-established in the study of diffusion by the classical methods—they can be used to calculate " κ " directly. The indicator method, however, does not give us the direct

relation between u and u_0 at the point x and at the time t . At the demarcation surface, we could get the concentration of chloride ions from the solubility of silver chloride 0.00015 %, but this does not help us much. It is obvious that the more silver nitrate is streaming up, the more slowly will the precipitate advance, because there will be longer to wait for enough sodium chloride to stream down and precipitate all the silver ions in a given space.

Some method of handling the problem must be devised, and the most promising line of attack seemed to have as base the obvious fact that one silver ion removes one chloride ion from the sphere of action, when silver chloride is precipitated. The development of this idea is to assume that we can call the silver nitrate "negative sodium chloride."

That is to say, a gel with 0.01 g. molecules of the silver salt would be called a $-0.01N$ sodium chloride. Making the usual shift in the scale, this is described for the next calculation as 0, and at the zone of precipitation, where the sodium chloride really is 0, the concentration therefore becomes $+0.01N$ sodium chloride.

Calling the silver nitrate concentration v_0 and the sodium chloride concentration u_0 , we have at the edge of the precipitation the relation

$$u = \frac{v_0}{u_0 + v_0}.$$

This is a known fraction of u_0 , and therefore we can find $q = x/2\sqrt{\kappa t}$ from the tables of the probability integral. This formula is only a first approximation, as it neglects the rate of movement of the silver nitrate. Before entering on this secondary complication our policy is to find if the approximation gives us a result which is at all promising, because the next step must obviously depend on whether the percentage error is 10 or 10,000.

IV. EXPERIMENTS WITH ORIGINAL TECHNIQUE.

The first data which will be used to test the formula were obtained on July 29th, 1919, by the half test-tube method.

Table I.

Diffusion coefficient of sodium chloride in 1 % agar gel. July 29th, 1919.

NaCl solution poured into half test-tubes of gel.

Concentration of silver nitrate 0.005N.

κ_1 calculation of " κ " from 1st reading, 19 hours.

κ_2 calculation of " κ " mean of later readings.

$q = x/2\sqrt{\kappa t}$ taken from tables, using formula (III).

The values of κ are given in c.g.s. units $\times 10^5$.

Salt concentrations	2N	N	0.5N	0.2N	0.1N	0.05N
Corresponding " q "	1.98	1.82	1.65	1.39	1.18	0.94
Temp. 22° κ_1	1.54	1.55	1.54	1.79	2.0	1.84
22° κ_2	1.7	1.7	1.7	2.08	2.40	2.46
13.6° κ_1	1.19	1.18	1.21	1.48	1.65	1.75
13.6° κ_2	1.36	1.27	1.34	1.67	1.85	1.95
0° κ_1	0.82	0.86	0.87	0.99	1.16	1.42
0° κ_2	0.88	0.90	0.89	1.13	1.25	1.31

The error is generally nearer 10 % than 100 % in these figures, but it is quite clear that the indicator method is of no use unless it turns out more consistent results than these. Perhaps the most serious discrepancy is the difference between the κ calculated from the first reading and the mean κ . If this is a real physical fact, it would of course be very interesting, but there are other causes we must examine first.

(1) Is the "negative salt" formula too crude?

(2) Is there an error in the experiment?

No. (1) may be dismissed for the time being, as it could not be held responsible for the difference of κ_1 from κ_2 . We are left with the second alternative. There are a great many possible sources of error—but some can be ruled out at once, as for instance the suggestion that the dense precipitate obstructs diffusion—such a phenomenon would produce an error in the opposite direction.

The most probable explanation of the discrepancy is that the salt solution was circulating in the test-tubes. The liquid at the gel surface continually loses salt, and, as the heavier solution is above it, mixing is bound to take place. This can be eliminated by a slight modification of the experimental technique.

The original method with the solution above the gel will be called type A. The modified method with tube inverted will be called type B. Type C unlike A and B requires formula (II), and it is theoretically more reliable because the diffusion gradient is in gel throughout, not one-half in gel, the other in water.

V. DATA OBTAINED WITH MODIFIED TECHNIQUE.

Some experiments by methods B and C are given in the tables below. They illustrate the theory and are not without value in showing what degree of consistency may be obtained in a first trial, but the numerical results are not very reliable, because the temperature was not controlled.

Table II.

Diffusion of sodium chloride into a 5 % gelatin gel, 0.0201N AgNO₃. "Depth" in cm. of ppt.
 "κ" in c.g.s. units $\times 10^5$. Temperature 12°.

Time		N NaCl		0.5N NaCl		0.1N NaCl	
hrs.	mins.	Depth	κ	Depth	κ	Depth	κ
1	0	0.55	0.99	0.5	1.11	0.3	1.06
22	36	2.5	0.92	2.2	0.97	1.3	1.14
25	44	2.8	1.01	2.4	—	1.5	1.15
28	53	3.0	1.02	2.5	0.98	1.9	1.18
35	50	3.7	1.25	3.2	1.26	2.0	0.99
48	16	3.8	0.99	3.3	1.02	2.6	1.08
73	15	4.6	0.96	—	—	—	—

The figures given in this table are a great improvement on those of Table I, with the exception of the readings taken at the 35th hour. The remaining determinations show that κ does not really change with time, and therefore

method A is discredited. The constant of diffusion, however, does vary with the concentration, being greater in the more diluted and therefore more highly ionised solution.

<i>N</i> NaCl	Mean κ	0.98×10^{-5}	Mean error 3 %.
0.5 <i>N</i> NaCl	Mean κ	1.02×10^{-5}	Mean error $4\frac{1}{2}$ %.
0.1 <i>N</i> NaCl	Mean κ	1.10×10^{-5}	Mean error $5\frac{1}{2}$ %.

The mean error on a single determination is large, but on the whole the results prove that the indicator method gives reasonable results at the first trial, a most important advantage where a diffusion coefficient must be measured as an incidental portion of a wider research.

The results in Table II were all obtained by method B, so our next step is to give observations, made with the surface of the gelatin kept at constant salt concentration by exposure to a large bath of stirred salt solution.

Table III.

Penetration of *N* NaCl into a gelatin gel, with 0.0201 gram-mol. of AgNO₃. Method "C." Depth in cm. of precipitate.

κ = diffusion coefficient in c.g.s. units $\times 10^5$.

Temperature 12°. Time, hours and minutes.

Time	1.0	2.49	4.9	6.0	7.30	11	22.36	25.44	28.53
Depth	0.6	0.9	1.2	1.5	1.62	1.95	2.85	3	3.3
κ	0.92	0.82	0.89	0.96	0.90	0.93	0.93	0.90	0.97
Time	48.16	53.30	73.15	96.20	120.6	197.30	219.0	263.30	
Depth	4.25	4.45	5.23	6	6.7	8.7	9.1	10	
κ	0.96	0.96	0.96	0.96	0.96	0.98	0.97	0.97	

The results in this table are in accordance with those in Table II, and because the method and formula are different, the "negative salt convention" is placed in a much stronger position than if it depended on one method alone; but the figures also prove that we must qualify the claim, made in the beginning, that all the apparatus needed is a rack of test-tubes and a ruler. The distances measured in the first few hours, when the temperature was constant, are so small that the experimental error with a wooden ruler is a large fraction of the whole, and if the experiment is protracted, the cupboard temperature cannot be relied upon. The night temperature would be below 12°. We must add a thermostat to our list of apparatus.

It is not absolutely essential because the heat reserve in a pan of water prevents much temperature variation, as is shown in Table IV, an experiment carried out to test the effect of varying the silver concentration, and also to get a direct comparison between the old method A and the method C, which was adopted for later experiments.

Table IV.

Penetration of 0.1*N* NaCl into 5 % gelatin, with 0.034 gram-mol. AgNO₃.

Time	0	17.3 hours	25.2 hours
Temp.	12.0°	12.3°	12.2°
Method A	$\kappa = 10^{-5} \times$	1.35	1.35
" C	$\kappa = 10^{-5} \times$	1.09	1.04
" A	depth in cm.	1.95	2.35
" C	depth in cm.	2.13	2.5

Method A makes " κ " come out much too large, an error we must put down to circulation inside the test-tube. The data for B and C are set forth below, and for comparison a calculation of κ for water is made from Öholm's data [1905] (using his value of the temperature coefficient, in the neighbourhood of 18°, a rise of 2.5 % per degree centigrade).

Table V.

Method B	$N \text{ NaCl } \kappa = 0.98 \times 10^{-5}$	$N/10 \text{ NaCl } \kappa = 1.10 \times 10^{-5}$
Method C	0.96	1.06
Öholm	1.06	1.11

The negative salt convention has been subjected to three tests:

- (i) Variation in the silver concentration.
- (ii) Variation in the sodium chloride concentration.

(iii) Alteration of the boundary conditions. If it was wildly in error, at least one of these tests should expose it, but if we allow for the nightly fall in temperature, the differences from Öholm's figures are about as large as the experimental error. The difference between the four experimental values of κ is in accordance with expectations.

A 5 % gelatin offers some resistance to diffusion, therefore "B" should give bigger values than "C," and the relatively faster movement of the ions causes the more highly dissociated 0.1N salt to diffuse more quickly than normal sodium chloride.

VI. DERIVATION OF CORRECTED FORMULA.

The data given above are sufficient to establish the "negative salt" convention as a first approximation, and for diffusion experiments it is a fairly close approximation. To carry it further requires a considerable extension of the work, mathematical and practical.

The temperature control in particular must be very reliable but it is the former branch of the subject which must be considered here.

There are two difficulties in particular which were omitted in the preliminary treatment. The first of these is ionisation. As a general rule the undissociated molecule diffuses more slowly than the ions, so that other things being equal, the more dilute the solution, the larger is the value of κ . This variation in κ is quite big enough to be noticeable in the results calculated above. Each concentration of salt has a particular value of κ . In the gel the concentration varies from say N to 0. The κ we calculate will be that of some intermediate concentration, probably about $N/2$, but the indicator method does not give us information on this point, so it has perforce to be neglected.

The second and much the more important factor is the rate of diffusion of the silver nitrate. The original convention was that silver nitrate could be treated as negative sodium chloride. This assumption is arbitrary and it is to be feared it offends common sense.

In the following section, an attempt is made to treat the indicator method theoretically without this simplifying assumption. The change of κ with concentration will not be introduced into the calculations and the average value between the two limits will be used. This approximation is unavoidable.

The experimental facts to be considered have been stated before, but they must now be defined with greater precision. The silver nitrate is streaming down the tube. Let its concentration be v and its diffusion coefficient λ , then

$$\frac{\partial v}{\partial t} = \lambda \frac{\partial^2 v}{\partial x^2}. \quad \dots\dots\dots(1)$$

Similarly for the chloride

$$\frac{\partial u}{\partial t} = \kappa \frac{\partial^2 u}{\partial x^2}. \quad \dots\dots\dots(2)$$

At the position a , the demarcation line between the precipitate and clear gel, it is assumed that the concentrations v and u both equal 0. This is not strictly true. Really the product of their concentration is a constant, and it is possible that u for instance might be quite large. This possible complication need not be considered here, as at the boundary it is certain that the chloride concentration must be small. If this assumption is to be true, the amount of salt brought to the point " a " must be equalled by the amount of silver nitrate. Therefore at a

$$\lambda \frac{\partial v}{\partial x} + \kappa \frac{\partial u}{\partial x} = 0. \quad \dots\dots\dots(3)$$

In addition to these equations the following boundary conditions must be satisfied:

$$v = v_0 \text{ when } x > 0 \text{ at } t = 0,$$

$$u = u_0 \text{ at } x = 0,$$

$$u = v = 0 \text{ at } x = a.$$

Let

$$\phi_a = \frac{2}{\sqrt{\pi}} \int_0^a e^{-\beta^2} d\beta.$$

Then $\phi\left(\frac{x}{2\sqrt{\lambda t}}\right)$ and $\phi\left(\frac{x}{2\sqrt{\kappa t}}\right)$ are particular solutions of the differential equations (1) and (2). The combination of these two integrals in a general solution is not immediately obvious.

The only method is to make some trial assumptions, and find out what values must be assigned to the constants if the formula is to satisfy the conditions of the problem. The simplest possible guess we can make is that v and u are linear functions of $\phi\left(\frac{x}{2\sqrt{\lambda t}}\right)$ and $\phi\left(\frac{x}{2\sqrt{\kappa t}}\right)$. F. Neumann [Weber-Riemann] has shown that this method can be used successfully in solving a problem with similar equations, the formation of ice on a pool of still water.

Let

$$v = A + B\phi\left(\frac{x}{2\sqrt{\lambda t}}\right),$$

$$u = C + D\phi\left(\frac{x}{2\sqrt{\kappa t}}\right),$$

where A , B , C and D are constants determined by the experimental conditions.

The data below enable one to calculate them.

- (i) $at^{-\frac{1}{2}} = p$ = the penetration factor of von Fürth and Bubanović.
- (ii) $A + B\phi \frac{p}{2\sqrt{\lambda}} = 0$.
- (iii) $C + D\phi \frac{p}{2\sqrt{\kappa}} = 0$.
- $\phi_0 = 0, \phi_\infty = 1$.
- (iv) $A + B = v_0$.
- (v) $C = u_0$.
- (vi) $D = \frac{-u_0}{\phi \frac{p}{2\sqrt{\kappa}}}$.
- (vii) $B = \frac{v_0}{1 - \phi \frac{p}{2\sqrt{\lambda}}}$.

From formula (III), by differentiating the linear functions, we find

$$-\kappa \left\{ \frac{2D}{\sqrt{\pi}} e^{-\frac{x^2}{4\kappa t}} \right\} \frac{1}{2\sqrt{\kappa t}} = \lambda \left\{ \frac{2B}{\sqrt{\pi}} e^{-\frac{x^2}{4\lambda t}} \right\} \frac{1}{2\sqrt{\lambda t}}$$

at $x = a$,

$$-\kappa^{\frac{1}{2}} D e^{-\frac{p^2}{4\kappa}} = \lambda^{\frac{1}{2}} B e^{-\frac{p^2}{4\lambda}}.$$

Substituting for D and B , we arrive at our final formula:

$$\frac{\kappa^{\frac{1}{2}} u_0 e^{-\frac{p^2}{4\kappa}}}{\frac{2}{\sqrt{\pi}} \int_0^{\frac{p}{2\sqrt{\kappa}}} e^{-\beta^2} d\beta} = \frac{\lambda^{\frac{1}{2}} v_0 e^{-\frac{p^2}{4\lambda}}}{1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{p}{2\sqrt{\lambda}}} e^{-\beta^2} d\beta} \dots\dots\dots(\text{IV})$$

κ can be calculated from this equation if u_0, v_0, λ and p are known. When $\kappa = \lambda$ it simplifies to the old "negative salt" formula

$$\frac{v_0}{v_0 + u_0} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{\kappa t}}} e^{-\beta^2} d\beta.$$

VII. MODIFICATION OF FORMULA (IV).

In its present form, the new formula is not suitable for computations. The arithmetic with formula (IV) takes 50 times as long as that required for formula (II). If this work had to be gone through for each experiment, the beauty of the indicator method would be gone. Much less formidable would be the difficulties of bad electrodes, and of gravimetric analysis, when compared with the labour in the calculations. For example, the right-hand side of the equation is objectionable when the concentration of silver nitrate is small, because then " p " is large, consequently with five figure tables of the probability integral, the error in calculating the denominator may easily exceed 10 %. On the left-hand side, although this difficulty is avoided, we have a worse trouble, since κ , the unknown, can only be arrived at by the method of trial and error.

In the light of these considerations, the calculation of (IV) appeared to be a fruitless effort, but when the formula was placed before Mr Berry, Fellow of King's College, Cambridge, it was a source of much pleasure to a naturalist to see both of these difficulties immediately cleared away, the former by the use of a series formula, the latter by a rearrangement. Both sides of the equation could be so modified that the whole series of calculations could be carried out once and for all.

The modification necessary is given below.

$$\text{Let } \frac{p}{2\sqrt{\lambda}} = y,$$

$$\frac{p}{2\sqrt{\kappa}} = z,$$

$$\phi_a = \frac{2}{\sqrt{\pi}} \int_0^a e^{-\beta^2} d\beta,$$

then

$$\begin{aligned} \frac{\phi z}{\frac{p}{2z} u_0 e^{-z^2}} &= \frac{1 - \phi y}{\frac{p}{2y} v_0 e^{-y^2}}; \\ \therefore \frac{v_0}{u_0} &= \frac{y e^{y^2} \cdot (1 - \phi y)}{z e^{z^2} \phi z}. \end{aligned}$$

The problem of calculating κ is thus reduced to tabulation of these two functions of y and z , and when this has been done, the diffusion coefficient can be worked out with no trouble.

The logarithms of the functions are tabulated, to facilitate arithmetical work

$$f(y) = f \frac{p}{2\sqrt{\lambda}} = \log_{10} y + .4343y^2 + \log_{10} (1 - \phi y).$$

$$f(z) = f \frac{p}{2\sqrt{\kappa}} = \log_{10} z + .4343z^2 + \log_{10} (\phi z).$$

These functions are referred to elsewhere as the λ function and the κ function, because the physical significance of these symbols is an aid in distinguishing them—an association which is lost when y and z are used.

The computation of tables with the κ function is not a difficult matter, but with higher values of y , the probability integral tables are unsuitable for calculating the values of the λ function

$$\begin{aligned} &= \log [y e^{y^2} (1 - \phi y)], \\ \text{replacing } 1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy &\text{ by } \frac{2}{\sqrt{\pi}} \int_y^\infty e^{-y^2} dy \\ \text{we can use the series for } e^{y^2} \int_y^\infty e^{-y^2} dy & \\ &= \frac{1}{2y} - \frac{1}{2^2 y^3} + \frac{1.3}{2^3 y^5} - \frac{1.3.5}{2^4 y^7} + \dots \end{aligned}$$

VIII. EXPERIMENTAL VERIFICATION OF NEW FORMULA.

When calculations are made with these tables the gulf is a wide one between the experimental data and the diffusion coefficient, so the bridge requires testing before we can rely upon it. There are two methods of doing this—the first by trying the effect of different concentrations of silver nitrate, the second

by examining substances which diffuse at a rate differing from that of sodium chloride.

The problem will be treated initially by the negative salt method, on account of the lack of reliable data concerning the diffusion of silver nitrate in gelatin. The figures below, copied from Landolt and Börnstein, refer to water.

Table VI.

Conc. AgNO ₃	0.02	0.1	0.9	3.9	0.03	0.433
Temperature	12°	12°	12°	12°	7.2°	7.2°
κ (c.g.s.) $10^{-5} \times$	1.2	1.14	1.02	0.62	1.04	0.752

The measurement even for the most dilute solution differs by over 20 % from the coefficient calculated from Nernst's formula [Nernst, p. 273]. It may be remarked when a similar calculation is made for dilute NaCl, the difference is very much smaller—only 2 %.

Table VII.

Diffusion of *N* NaCl into 1 % agar with different concentrations of AgNO₃. *d*=depths in cm. κ =diffusion coefficient in c.g.s. units $\times 10^5$.

		Concentrations of AgNO ₃ (normalities)							
Time	Temp.	0.006	0.0154	0.06	0.114	0.006	0.0154	0.06	0.114
hrs. mins.	°C.	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>κ</i>	<i>κ</i>	<i>κ</i>	<i>κ</i>
16 6	36.4	4.1	3.61	2.78	2.4	1.92	1.91	1.92	1.88
25 3	36.4	5	4.7	3.45	3.02	1.88	2.06	1.90	1.91
39 48	36.4	—	6	4.39	3.8	—	2.13	1.94	1.90

Concentrations AgNO ₃								
Time	Temp.	0.006	0.0154	0.1143	0.006	0.0154	0.1143	
hrs. mins.	°C.	<i>d</i>	<i>d</i>	<i>d</i>	κ	κ	κ	
15 23	11.5	3	2.7	1.79	1.1	1.11	1.09	
24 50	11.7	3.77	3.42	2.24	1.09	1.12	1.07	
39 17	10.8	4.75	—	2.85	1.08	—	1.08	

Concentrations AgNO ₃								
Time	Temp.	0.5	0.1	0.02	0.5	0.1	0.02	
hrs. mins.	°C.	<i>d</i>	<i>d</i>	<i>d</i>	κ	κ	κ	
0 54	11.9	0.265	0.475	0.6	1.2	1.2	0.99	
2 50	—	0.45	0.765	0.99	1.06	0.99	0.88	
6 0	—	0.68	1.16	1.6	1.15	1.09	1.09	
8 56	—	0.8	1.35	1.95	1.06	0.99	1.09	

The examination of this table points to the conclusion that variations in the concentration of silver nitrate have less effect on " κ " than the errors of an individual observation, when the experiment is made with sodium chloride.

In other words, we have been lucky enough to find an indicator which fulfils the condition postulated, therefore silver nitrate does behave as negative sodium chloride.

We may infer that the diffusion coefficient of silver nitrate probably lies between 1.0 and 1.1×10^{-5} under these experimental conditions.

The study of bodies with diffusion rates differing from this figure will give more interesting results.

Table VIII. *Hydrogen Chloride.*

Diffusion of a 1.03*N* solution of HCl into 2 % agar with different concentrations of AgNO₃.
d = depth in cm. κ = coefficient in c.g.s. units $\times 10^5$. Temperature 11.9°.

Time hrs. mins.	Concentrations of AgNO ₃									
	0.5 <i>d</i>	0.1 <i>d</i>	0.02 <i>d</i>	0.004 <i>d</i>	0.0008 <i>d</i>	0.5 κ	0.1 κ	0.02 κ	0.004 κ	0.0008 κ
0 46	0.22	0.6	0.8	0.1	1.2	0.92	2.24	2.06	2.12	2.20
2 40	0.475	0.96	1.4	1.8	2.15	1.21	1.62	1.81	1.97	2.04
5 59	0.74	1.44	2.15	2.7	3.23	1.31	1.64	1.95	2.02	2.12
8 54	0.9	1.8	2.62	3.31	3.95	1.31	1.73	1.95	2.05	2.14
32 49	1.75	3.5	5.1	—	7.7	1.35	1.76	2.0	—	2.20

This table shows that the negative salt convention breaks down when applied to hydrochloric acid. The variation in κ is far greater than can be accounted for by the experimental error, even though the work was carried on for a brief period of time. The result that $\kappa = 1.35 \times 10^{-5}$ (with 0.5*N* AgNO₃) is obviously not a natural constant: it corresponds to an "artefact" in histology, produced by crude technique.

The first step to a more exact analysis of the problem is to work out λ , the diffusion coefficient of silver nitrate. This proved to be quite simple. Since the coefficient of sodium chloride is fairly close to that of silver nitrate, the "negative" method will give reasonable results if the sodium chloride is used as indicator in small concentrations. The results are given below.

Table IX.

Diffusion of 0.4*N* AgNO₃ into a 1 % agar gel, with 0.01*N* NaCl. *d* = depth in cm.
 κ = coefficient $\times 10^5$. Temperature 10°.

Time hrs. mins.	Experimental number							
	1 <i>d</i>	2 <i>d</i>	3 <i>d</i>	4 <i>d</i>	1 κ	2 κ	3 κ	4 κ
16 47	2.4	2.45	2.5	2.5	0.935	0.98	1.02	1.02
24 10	2.97	2.98	3.09	3.0	0.995	1.01	1.08	1.02
40 57	3.82	3.89	3.9	—	0.975	1.01	1.01	—

The diffusion of silver nitrate deserves a more extended study, but these figures seem to be consistent enough for us to use the figure 1.01×10^{-5} in further calculations—at any rate for a preliminary survey, which is all that can be attempted in this paper.

The figure is probably a fair enough approximation to illustrate distinctly the differences when calculations are made by the new and old formulae.

Table X. *Hydrogen Chloride.*

Diffusion of a 1.035*N* solution of HCl into agar gels with different concentrations of AgNO₃.
t = time (hours and minutes). *d* = depth in cm.

Temp. °C.	Concentrations of AgNO ₃									
	0.5 <i>N</i>		0.1 <i>N</i>		0.02 <i>N</i>		0.004 <i>N</i>		0.0008 <i>N</i>	
	<i>t</i>	<i>d</i>	<i>t</i>	<i>d</i>	<i>t</i>	<i>d</i>	<i>t</i>	<i>d</i>	<i>t</i>	<i>d</i>
10.0	16 20	1.29	16 15	2.4	16 7	3.46	16 0	4.3	15 54	5.1
10.3	23 50	1.55	23 45	2.93	24 41	4.2	23 39	5.3	23 37	6.19
9.7	40 29	2.05	40 21	3.83	40 14	5.49	40 7	6.9	40 3	8.05
10.0	48 41	2.265	48 44	4.21	47 48	6.00	48 47	7.6	—	—

The data in this table are probably more reliable than the figures in Table VIII: especially in cases where the depth of penetration was small—though this advantage is offset to some extent by temperature variations. The materials are now complete for carrying out calculations with the aid of our tables of the λ and κ functions.

Table XI.

Illustration of calculations made with the aid of tables of the κ and λ functions where κ is the diffusion coefficient of HCl and $\lambda = 1.01 \times 10^{-5}$ that of AgNO_3 .

Concentration of AgNO_3	0.5N	0.1N	0.02N	0.004N	0.0008N
" p^2 " = $\frac{x^2}{t}$ in seconds	2.86×10^{-5}	1.0×10^{-4}	2.05×10^{-4}	3.3×10^{-4}	4.51×10^{-4}
$\log_{10} v_0$	1.699	1.0	2.301	3.602	4.903
$\log_{10} u_0$	0.014	0.014	0.014	0.014	0.014
λ function	1.602	1.687	1.716	1.7265	1.733
κ function	1.917	0.701	1.429	2.1384	2.844
κ by new formula ...	1.38	1.65	1.84	1.96	1.98
κ by old formula ...	1.48	1.72	1.87	1.97 +	1.99
Error in old formula	7.2 %	4 %	1.6 %	0.7 %	0.5 %

The same method is applied to magnesium chloride below. The scale of the experiments is too small to eliminate chance errors, but in spite of this the essential difference between the two methods of calculation is well brought out.

Table XII.

Diffusion of N magnesium chloride into 2 % agar with various concentrations of AgNO_3 .
Temperature 11.9°. Time, 5 hours 55 minutes. $\lambda = 1.09 (\times 10^{-5})$.

Concentration of AgNO_3	0.5	0.1	0.02	0.0008
Depth of penetration ...	0.5	1.0	1.4	2.05
κ by new formula ...	0.765	0.835	0.857	0.88
κ by old formula ...	0.628	0.82	0.845	0.875
Error in old formula ...	11 %	1.8 %	1.5 %	0.6 %

With the data given in this table we may bring to a close our compilation of experimental material, and proceed to discuss the results.

IX. REVIEW OF THE EXPERIMENTAL DATA.

Sodium chloride. The results with this salt are satisfactory when the negative salt convention is used, on account of the lucky coincidence that silver nitrate diffuses as quickly as sodium chloride.

The numerical values of κ at 12°—in the two sets of experiments of Table VII—are 1.04 and 1.09×10^{-5} . Öholm's figure at that temperature, obtained by interpolation, works out at 1.06×10^{-5} for a normal solution. No stress can be laid on the accuracy of the agreement—the number of experiments is far too small, but it supports Voigtländer's observations on the smallness of the effect of agar gels in retarding diffusion. A 5 % gelatin appears to have a much more noticeable effect.

Hydrogen chloride. The results obtained with this substance are interesting, but the interpretation is doubtful. Table XI shows that the negative salt convention is not reliable, especially when the concentration of silver nitrate is high. Put into words, the table shows that the slower rate of diffusion of silver nitrate helps the hydrogen chloride to advance, and the assumption that the silver nitrate streams up with equal rapidity to meet it cannot give a reliable result. The coefficient appears to be larger than is actually the case, because the weakness of the opposition is ignored.

The difficulty is overcome by the new formula, but it only serves to emphasise the second trouble—the coefficient is far too small when there is a high concentration of silver nitrate in the gel. It is necessary to exercise caution in working out the explanation of this difficulty because we have no right to assume that the silver chloride precipitate has no influence on the rate of diffusion—the precipitate from a strong solution of silver nitrate in the presence of acid may quite easily differ from that formed in a neutral medium. In the absence of direct evidence, this danger can only be mentioned as a possibility—it is not likely that it will prove to be the real explanation. The root of the difficulty is that hydrogen chloride cannot be considered as a simple body. If the compound $\text{HCl} \cdot \text{AgNO}_3$ was formed, the formula would give accurate results at all concentrations. In reality, the hydrogen ions are not eliminated—therefore the diffusion of fresh hydrogen chloride is retarded. In other words, the “effective concentration” of acid is reduced. Below are given the strengths of HCl which, but for this complication, would give the observed penetration.

Normality of AgNO_3	0.5	0.1	0.02	0.004	0.0008
Strength of HCl ...	0.63	0.71	0.82	0.98	1.035

As a matter of fact, this difficulty is rather academic, because the silver nitrate is put in as an indicator—in small concentration—therefore the complications which turn up when its concentration is high are of no practical importance. Nevertheless, it demands our consideration, when deciding what concentration of silver nitrate is the highest we can use. The strength is best kept above 0.0008*N* to ensure the distinctness of the demarcation surface.

Magnesium chloride. The experiments on this substance are on too small a scale to justify any confidence in the absolute numerical values—but as chance errors will affect both results equally, they serve to illustrate the case where the diffusing substance travels more slowly than the silver nitrate—in complete contrast to hydrochloric acid.*

In Table XII it will be observed that the negative convention makes the diffusion coefficient of magnesium chloride appear too small, because the “opposition” of the silver is thereby arbitrarily reduced, but the material is not sufficient for further developments of the theory.

CONCLUSION.

The number of definitions required foils any attempt to give a brief account of certain sections, but rather than repeat lengthy explanations, an illustration is given to show the simplicity of the calculation required in practice.

The indicator technique differs from the standard methods in securing rapidity of execution at the expense of theoretical simplicity. This sacrifice has been of sufficient importance to cause the neglect of the indicator method in the past. The diffusion of two salts resulting in the formation of a zone of precipitate is a problem too full of complications to admit of a rigorous treatment. This disadvantage need not concern us practically, for such a treatment would lead to long calculations consuming more time than that gained by the rapidity of the experimental work. Consequently it is necessary to make some approximations. These are described in sections III and VI, but the following terms are re-defined: " u " = conc. NaCl, " u_0 " = conc. NaCl in bath, " κ " = diff. coeff. of NaCl, " v_0 " = conc. AgNO_3 in jelly, " λ " = diff. coeff. of AgNO_3 , p = penetration " x " divided by square root of time " t ."

The first approximation, called the negative salt convention, leads to the formula

$$\frac{v_0}{u_0 + v_0} = u = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{\kappa t}}} e^{-\beta^2} d\beta. \quad \text{.....(II)}$$

The second approximation, which allows for the different velocity of silver nitrate, leads to the formula

$$\frac{\kappa^{\frac{1}{2}} u_0 e^{-\frac{p^2}{4\kappa}}}{\frac{2}{\sqrt{\pi}} \int_0^{\frac{p}{2\sqrt{\kappa}}} e^{-\beta^2} d\beta} = \frac{\lambda^{\frac{1}{2}} v_0 e^{-\frac{p^2}{4\lambda}}}{1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{p}{2\sqrt{\lambda}}} e^{-\beta^2} d\beta}. \quad \text{.....(IV)}$$

The calculation of κ with these formulae is a matter of two or three minutes' work at most, but this can be best shown by an illustration, that having once looked up the factor in the table, κ can be worked out in 45 seconds, using formula (II). Given a jelly with 0.005*N* silver nitrate, then κ in c.g.s. units is equal to the square of the penetration in cm. divided by the product of the time in hours and 10,000 times the factor—given below the corresponding strength of the salt solution.

Concentration	5 <i>N</i>	<i>N</i>	0.5 <i>N</i>	0.2 <i>N</i>	0.1 <i>N</i>
Factor	7.8	5.68	4.78	3.65	2.83

The negative salt convention introduces a serious error if the velocity of the diffusing salt is very different from that of silver nitrate unless the concentration of the latter is very small. The method of working out κ , illustrated in Table XI though it takes a few minutes longer, still has the advantage of checking the first result even though the indicator has been diluted enough to conceal the error.

To work out a formula by neglecting secondary phenomena is one thing, but the proof that these can be overlooked is another. The judgment of the

experimental test is a delicate matter for the experimenter, but it is advisable to draw attention to one table, No. XI. The errors in the indicator method are obviously due to the complications caused by silver nitrate and these increase as the strength of the latter is increased; 100 times the normal amount of nitrate gives a difference of 35 %, four times gives 7 %, but when we get down to a 0.005*N* silver nitrate, further dilution is practically without effect.

This shows that we can deliberately increase the magnitude of the "errors of method" but to do this unusual concentrations of silver nitrate are required.

A balanced account of the indicator method would require a description of the advantages comparable in length with the discussion of the difficulties, but the space taken by these leaves little room for the other side of the question. But because there are other diffusion methods, it seems necessary to give some reasons for departing from them.

(1) The measurement of length is direct, it can be made with great accuracy, and the same tube can be measured again at different times. The presence of gelatin or agar-agar, so useful to avoid mechanical mixing, apart from its intrinsic interest, complicates the technique of the standard methods.

(2) The ease with which a large number of experiments can be performed makes the method particularly suitable for an introductory survey even if it gives only a two figure accuracy—and the rough preliminary experiments described above could be greatly improved upon. Specially interesting results could be verified by other methods—but much time would be saved in finding where accurate measurements were most needed.

(3) The fact that no special apparatus is needed enables a worker to determine several diffusion coefficients at a few hours notice, a useful point when these figures are required for another research—for example the comparison with simple diffusion of the rate of absorption of nutrient salts by living tissues.

For educational purposes there is a further advantage due to the simplicity of the apparatus, combined with the fact that the readings can be taken whenever it is convenient.

Data can be obtained to illustrate the methods of handling numerical results in a branch of science which generally demands long experiments before a table or graph can be constructed. The temptation to continue the list of applications must be suppressed, for after all, the special qualities of the method are matters of laboratory technique in which experience is superior to description, but I cannot conclude this account without acknowledging my indebtedness to Professor Stiles, but for whom the work would never have been attempted, and Mr Berry, Fellow of King's College, Cambridge, for his help in dealing with formula (IV).

APPENDIX.

Table of values of the " λ " function.

$$f \frac{p}{2\sqrt{\lambda}} = \log_{10} \frac{p}{2\sqrt{\lambda}} \cdot e^{\frac{p^2}{4\lambda}} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{p}{2\sqrt{\lambda}}} e^{-\beta^2} d\beta \right).$$

For values of $\frac{p}{2\sqrt{\lambda}}$

$\frac{p}{2\sqrt{\lambda}}$	$f \frac{p}{2\sqrt{\lambda}}$	$\frac{p}{2\sqrt{\lambda}}$	$f \frac{p}{2\sqrt{\lambda}}$	$\frac{p}{2\sqrt{\lambda}}$	$f \frac{p}{2\sqrt{\lambda}}$
0.4	1.429	1.8	1.699	3.4	1.734
0.5	1.488	1.9	1.703	3.6	1.736
0.6	1.532	2.0	1.709	3.8	1.737
0.7	1.566	2.1	1.712	4.0	1.739
0.8	1.593	2.2	1.715	4.5	1.741
0.9	1.614	2.3	1.718	5.0	1.743
1.0	1.631	2.4	1.720	5.5	1.744
1.1	1.646	2.5	1.722	6.0	1.745
1.2	1.657	2.6	1.723	6.5	1.746
1.3	1.668	2.7	1.725	7.0	1.747
1.4	1.676	2.8	1.726	8.0	1.748
1.5	1.683	2.9	1.727	9.0	1.749
1.6	1.689	3.0	1.729	10.0	1.750
1.7	1.695	3.2	1.732	∞	1.751

Table of values of the " κ " function.

$$f \frac{p}{2\sqrt{\kappa}} = \log_{10} \frac{p}{2\sqrt{\kappa}} \cdot e^{\frac{p^2}{4\kappa}} \left(\frac{2}{\sqrt{\pi}} \int_0^{\frac{p}{2\sqrt{\kappa}}} e^{-\beta^2} d\beta \right).$$

For values of $\frac{p}{2\sqrt{\kappa}}$

$\frac{p}{2\sqrt{\kappa}}$	$f \frac{p}{2\sqrt{\kappa}}$	$\frac{p}{2\sqrt{\kappa}}$	$f \frac{p}{2\sqrt{\kappa}}$	$\frac{p}{2\sqrt{\kappa}}$	$f \frac{p}{2\sqrt{\kappa}}$
0.4	1.3034	1.4	0.956	2.4	2.88
0.5	1.5240	1.5	1.138	2.5	3.112
0.6	1.7154	1.6	1.305	2.6	3.36
0.7	1.8890	1.7	1.48	2.7	3.60
0.8	0.0516	1.8	1.66	2.8	3.85
0.9	0.2074	1.9	1.845	2.9	4.115
1.0	0.3600	2.0	2.036	3.0	4.38
1.1	0.5115	2.1	2.238	3.5	5.864
1.2	0.6637	2.2	2.442	4.0	7.551
1.3	0.8182	2.3	2.659		

REFERENCES.

- von Fürth and Bubanović (1918). *Biochem. Zeitsch.* **90**, 265; **92**, 139.
 Nernst. *Theoretical Chemistry*, 273.
 Öholm (1905). *Zeitsch. physiol. Chem.* **50**, 309.
 Stiles (1920). *Biochem. J.* **14**, 58.
 Weber-Riemann. *Part. Diff. Gleich.* **2**, 117.