



ELSEVIER

On liquid diffusion

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A few years ago Graham published an extensive investigation on the diffusion of salts in water, in which he more especially compared the diffusibility of different salts. It appears to me a matter of regret, however, that in such an exceedingly valuable and extensive investigation, the development of a fundamental law, for the operation of diffusion in a single element of space, was neglected, and I have therefore endeavoured to supply this omission.

It was quite natural to suppose, that this law for the diffusion of a salt in its solvent must be identical with that, according to which the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory of heat, and it is the same which Ohm applied with such extraordinary success, to the diffusion of electricity in a conductor. According to this law, the transfer of salt and water occurring in a unit of time, between two elements of space filled with differently concentrated solutions of the same salt, must be, *caeteris paribus*, directly proportional to the difference of concentration, and inversely proportional to the distance of the elements from one another.

In mathematical language this may be thus expressed: — In a volume of salt solution, let the concentration in each horizontal elementary stratum be constant and $=y$, a function of the height x of this stratum above any other stratum which may be assumed as the primary horizontal plane; the limitation being made, that the function y must diminish as x increases, that is, each higher stratum must be less concentrated, and therefore lighter, than all the subjacent ones, because it is only under this condition, that the diffusion will not be interfered with by gravity; then from the

stratum between the horizontal planes at x and $x + dx$ (in which the concentration is y) there will pass, during an element of time dt , into the immediate superjacent stratum, bounded by the horizontal planes $x + dx$ and $x + 2dx$ (in which the concentration $y + dy/dx \cdot dx$ prevails), a quantity of salt $= -Q \cdot k \cdot dy/dx \cdot dt$, in which Q signifies the surface of the stratum, and k a constant dependent upon the nature of the substances. It is evident that a volume of water equal to that of the salt passes simultaneously out of the upper stratum into the lower.

Exactly according to the model of Fourier's mathematical development for a current of heat, we can obtain from this fundamental law for the diffusion-current, the differential equation

$$\frac{\delta y}{\delta t} = -k \left(\frac{\delta^2 y}{\delta x^2} + \frac{1}{Q} \frac{dQ}{dx} \cdot \frac{\delta y}{\delta x} \right), \quad (1)$$

when the section Q of the vessel in which the current takes place is a function of its height above the bottom. If the section be constant (*i.e.* the vessel cylindrical or prismatic), the differential equation becomes simplified to

$$\frac{\delta y}{\delta t} = -k \frac{\delta^2 y}{\delta x^2} \quad (2)$$

Several methods for the experimental confirmation of this differential equation, and consequently of the fundamental law above advanced, presented themselves. In the first place, by integration of equation (2) the expression $y = f(x, t)$ could be obtained, and the calculated value of y compared with its observed value. I have, however, entirely omitted this method, because

even in those cases in which the integral has a finite form, the numerical calculation of a sufficient number of values would have been extremely troublesome, whilst other unequivocal proofs were possible. For the same reason I also here omit to develop the particular integrals of equation (2) for special cases of diffusion-currents.

The experimental proofs just alluded to, consist in the investigation of cases in which the diffusion-current has become stationary, in which a so-called dynamic equilibrium has been produced, *i.e.* when the diffusion-current no longer alters the concentration in the spaces through which it passes, or in other words, in each moment expels from each space-unit as much salt as enters that unit in the same time. In this case the analytical condition is therefore $dy/dt=0$. Such cases can be always produced, if by any means the concentration in two strata be maintained constant. This is most easily attained by cementing the lower end of the vessel filled with solution, and in which the diffusion-current takes place, into a reservoir of salt, so that the section at the lower end is always maintained in a state of perfect saturation by immediate contact with solid salt; the whole being then sunk in a relatively infinitely large reservoir of pure water, the section at the upper end, which passes into pure water, always maintains a concentration = 0. Now, for a cylindrical vessel, the condition $dy/dt=0$ becomes by virtue of equation (2),

$$0 = \frac{d^2y}{dx^2} \quad (3)$$

The integral of this equation $y = ax + b$ contains the following proposition: – ‘‘If, in a cylindrical vessel, dynamic equilibrium shall be produced, the differences of concentration of any two pairs of strata must be proportional to the distances of the strata in the two pairs,’’ or in other words, the decrease of concentration must diminish from below upwards as the ordinates of a straight line. Experiment fully confirms this proposition.

For the determination of the decrease of concentration in the cylindrical vessel conducting the diffusion-current, I sunk into the stratum to be estimated a glass bulb suspended from the beam of a balance, and calculated the specific gravity from the weight which required to be placed in the other scale-pan to balance the glass bulb. This method creates little confidence at first sight, nevertheless preliminary experiments

showed it to be sufficiently accurate. The quotation of the numerical results of one experiment may suffice here.

Depth of Stratum below the Surface.

10 millims. 32.2 54.4 76.6 98.9 121.0 143.2 165.4
187.6 209.8 220.9.

Specific Gravity of Stratum.*

1.009 1.032 1.053 1.073 1.093 1.115 1.135 1.152 1.170
1.187 1.196.

That the degrees of concentration in the lower layers decrease a little more slowly than in the upper ones, is easily explained by the consideration, that the stationary condition had not been perfectly attained.

A second case of dynamic equilibrium was also observed, by replacing the cylindrical vessel in the above-described arrangement, by a funnel-shaped one with the apex downwards. As the section was now no longer constant, the condition for the dynamic equilibrium was deduced from the more general equation (1) in the form

$$0 = \frac{\delta^2y}{\delta x^2} + \frac{1}{Q} \cdot \frac{dQ}{dx} \cdot \frac{\delta y}{\delta x} \quad (4)$$

For a perfect cone with circular base (the funnel-shaped vessel), we have $Q = \pi \cdot \alpha^2 x^2$, if the origin be placed in the apex of the cone, and we call α the tangent of half the angle of aperture. By the substitution of this value, equation (4) becomes

$$0 = \frac{d^2y}{dx^2} + \frac{2}{x} \cdot \frac{dy}{dx},$$

the integral of which $y + c' = -c/x$. The two constants c and c' are to be so determined, that for a certain x (where the cone is cut off and rests upon the salt reservoir), y is equal to perfect saturation; and for a certain other value of x which corresponds to the base of the funnel, y becomes = 0. In an experiment made with this apparatus, the following numerical values were obtained: –

Depth of Stratum below the Surface.

27.7 millims. 55.5 72.1 88.8 105.4 122.1 138.7 155.4.

Observed excess of Specific Gravity above unity (proportional to the concentration).

0.000 millim. 0.008 0.019 0.030 0.040 0.055 0.075
0.105.

* The excess of which over unity is proportional to the concentration.

Temperature Centigrade during the operation	k , calculated from the quantity which passed through the <i>longest</i> tube	k , calculated from the quantity which passed through the <i>medium</i> tube	k , calculated from the quantity which passed through the <i>shortest</i> tube
Not determined	11.71	12.36	11.08
15.8°–14.8°	9.67	9.70	9.30
15.5°–16.0°	–	9.57	–
16.0°–16.5°	–	9.94	–
17.5–18.5°	10.79	–	–
18.0°–19.0°	10.71	11.08	10.50
20°	11.14	–	11.02
19.0°–22.0°	11.44	11.33	–
20.0°–21.0°	11.89	–	11.12

Calculated excess of Specific Gravity above unity.

0.006 millim. 0.015 0.023 0.031 0.043 0.057 0.078 0.107.

The determination of the constants for different salts could now be proceeded with, – a determination which measures their diffusibility, and is expressed by k in equation (1). It may be defined as the quantity of salt which, during a unit of time, passes through the sectional-unit, out of one stratum into the next adjacent one, when the rapidity of the diminution of concentration (dy/dx) is equal to unity. Let the sectional-unit be the section of our tubes, *i.e.* the surface of a circle of 1 millim. radius. The diminution of concentration (dy/dx) will then be equal to unity, if, through a column of liquid assumed permanently constant, and the height of which is equal to the linear-unit 1 millim., it has for its result a difference of concentration of both terminal surfaces of such a character, that the one possesses a concentration corresponding to absolute saturation, the other a concentration = 0. Let one day be a unit of time.

Three tubes of different lengths were now arranged exactly as the cylinder and funnel above described, and after the establishment of the stationary condition, the amount of salt was determined which diffused out of the terminal section of the tube in measured spaces of time, and which therefore also, in the same time, passed through any single section of the cylindrical tube. In this case the whole of the values required for the determination of k were known, and the rapidity of the diminution of concentration (dy/dx) was especially determinable, inasmuch as it produced permanently, throughout the entire length of the tube, the difference between perfect saturation below and 0 above.

It is easy to perceive, that if our law be correct, the amounts of salt, passed through the three tubes in the

same time, must be inversely proportional to the length of the tubes; and that if these amounts be divided by the time and multiplied by the length (expressed in millimetres), the same value, *viz.* the above-defined k , must be obtained for all three tubes. I here annex a short table of the best experiments with common salt, to which I have hitherto confined my attention (see table).

If we take into consideration the unavoidable sources of error, a nearer identity of numbers could scarcely be expected. The table shows, as might be already expected from Graham's experiments, that the value k increases with increase of temperature; probably, however, this dependence upon temperature is not a simple one. On the relations of k to other values expressing the essential properties of bodies, as, for instance, to atomic weight, nothing can be said until extensive series of experiments with different substances have been made.

It is now of importance to make the views thus obtained furnish an insight into the diffusion of salt solutions through porous partitions. Brücke* first made an attempt to give a mechanical explanation to these phenomena. He went upon the assumption that the substance of the partition attracted the particles of water more strongly than the particles of salt. This assumption gained important support from the experiments of Ludwig[†] and Cloetta^{††}, who found that the solution of salt, imbibed by an animal membrane, was richer in water, and poorer in salt, than the solution in which the membrane was immersed. Brücke's theory, which was only indeed obscurely intimated, can be more clearly

* Poggendorff's *Annalen*, vol. lviii. p. 77.

† Ibid. vol. lxxviii. p. 307.

†† Experiments on Diffusion through Membranes with two Salts. Zürich, 1851.

determined by the help of our fundamental law as follows.

Let us imagine a cylindrical pore of the radius ρ , in a membrane which is immersed in a saturated solution of a salt, and let us assume with Brücke, a stronger attraction between water and the molecules of the membrane, than between the latter and the salt molecules; then the density of the solution in each concentric cylindrical film of radius r , of the porous partition will evidently be constant, and $=f(\rho-r)$. Respecting the nature of this function, it can only be said that its value for $r=\rho$, which is equal to 0, and that from this point it must increase (probably very rapidly) with the decrease of r ; but if necessarily under all circumstances for $r=0$, it must be increased up to the density of the circumambient solution, is left undetermined, and appears to me, in fact, for very narrow pores very improbable. In a word, the density in the pore will increase from the wall towards the centre, and in the cylindrical film of the radius r there can certainly occur no higher concentration than $f(\rho-r)$ (but possibly a lower one). The radius ρ of the pores must be imagined so small, that a filtration of liquid, by virtue of their cohesion, together with the attraction of the membrane itself, is prevented, even under high pressure; and that also equalization of the differences of pressure when liquid is present on both sides of the porous membrane, if possible at all, is only so in a relatively long space of time; further, that currents of mixture, by virtue of the variations of specific gravity within the pore, cannot occur.

Let us now suppose that a membrane of this description separates a saturated solution of salt from pure water, and further, that the former is above, and the latter is under this horizontal membrane. In any cylindrical pore of the said membrane, whose radius may be again $=\rho$, let us suppose a concentric elementary stratum, bounded by two cylindrical films infinitely near to each other, the radii of which are respectively r and $r+dr$. At the upper extremity, the highest possible concentration, $f(\rho-r)$, of the layer will immediately be produced. On the other hand, the lower extremity, by immediate contact with a relatively infinite quantity of pure water, will be constantly maintained at a concentration $=0$; and when a stationary condition is brought about, the degrees of concentration, within the assumed elementary stratum, must increase from 0 to $f(\rho-r)$, in proportion to the height above the lower boundary

surface of the membrane. This arrangement would have the effect of producing a diffusion-current in the elementary stratum, which, according to our laws, would deliver a quantity of salt $2\pi \cdot k \cdot f(\rho-r)/h \, dr$ downwards, and an equal volume of water upwards, if we understand by k , as above, the diffusion-constant for the combination of salt and water in question, and by h the thickness of the membrane, consequently the length of the pore. No regard has been paid, however, to the retardation which the flowing molecules suffer from the attraction of the substance of the membrane along the sides of the pores; it is certain, however, that the total quantity of salt, passed through the entire pore, could not be greater than

$$2\pi \frac{k}{h} \int_0^{\rho} f(\rho-r) \, dr.$$

But the passage of the water to the other side requires a separate consideration. We have seen, namely, that at the upper extremity of the cylindrical stratum-unit, with the internal radius r , no higher concentration could take place than $f(\rho-r)$, which is certainly less than perfect saturation, and, in fact, becomes proportionally smaller the greater r is assumed to be. If, as we suppose, a relatively inexhaustible volume of saturated solution (obtained by the addition of crystals) be present on the upper side of the membrane, then, at the upper extremity of our elementary stratum, there must take place a sudden increase in the concentration, from $f(\rho-r)$ to perfect saturation. If we assume that this is the case for the first moment, there will now be, according to the general principles of diffusion, from the elementary stratum a relatively (in comparison with the amount which a continual transition of density requires) infinite quantity of water required, and an equally infinite amount of salt forced in. The latter will be inevitably hindered by the nature of the membrane, and the excess of salt forced against the pore must in some way glide off laterally; on the other hand, more water, than the arrangement of the densities in our elementary stratum requires, can easily, to a certain extent, be drawn through towards the denser solution, so that in the pore, the particles of water move upwards with a greater velocity than the particles of salt move downwards. The excess of water now spreads out on all sides, into the saturated solution (as the mouths of the pores must lie at a certain distance from each other), partly by

diffusion, partly by mixing streams proceeding from difference of specific gravity; until a stationary condition has been in such a way produced, that a conical space increasing upwards is supported upon the upper annular section of the elementary stratum, in which space the concentration $f(\rho - r)$ increases to perfect saturation, and which determines a diffusion-current of such a strength, that thereby exactly as much water is passed upwards, as in the same time can diffuse itself into the reservoir of saturated solution from the upper end of the space, without changing the concentration. Then the above-mentioned space would evidently be immediately lengthened upwards, (and thereby the intensity of the diffusion-current be diminished) so soon as more water passed through, and therefore the concentration at the upper end of the space continues to vary; and if, on the contrary, less water passed upwards, sudden transition of concentration must immediately occur in certain places, which sudden changes determine, as it were, a diffusion-current of infinite strength, and therefore again immediately draw the requisite quantity of water. Now, this quantity of water, which, *caeteris paribus*, during the unit of time, can diffuse itself into the saturated solution without sensibly altering the concentration at that point, depends upon the easy mobility of the particles of the solution. The space in which the compensation takes place must therefore also be, *caeteris paribus*, so much shorter, and consequently the stream of water towards the saturated solution stronger, the more easily mobile the particles of the solution are. I was unable to verify this theoretical conclusion by direct experiment. I expected that the excess of water passing through the membrane, above the quantity of salt passing in the contrary direction, must be found much smaller, when the mobility of the upper solution was impeded by the addition of chalk magma. No such diminution of this excess, however, could be remarked in the experiment.

A second conclusion from the hypothesis just developed can be thus expressed: the excess of the diffusing water, above the salt passing in the opposite direction, is smaller, the wider the pores of the separating partition. Or if, according to Folly's* method, we define, as the endosmotic equivalent, the quotient obtained by dividing the amount of water diffused by the quantity of salt contemporaneously passed, the endosmotic equivalent is smaller the larger the pores of the parti-

tion. This conclusion is confirmed by experiment. Two membranes, which differ only in the diameter of their pores, cannot, it is true, be obtained; nevertheless we are safely warranted in assuming, that a transparent film of collodion possesses pores so very much narrower, than an animal membrane formed of interlacing fibres, that all other differences between the two tissues influencing diffusion, disappear in this difference of the size of pores; in fact, an animal membrane was found to possess a very much smaller endosmotic equivalent than a collodion film; for whilst, by the use of pig's bladder, only from 4 to 6 times as much water as common salt passed through, there diffused through a collodion film, during the time that an imponderable trace of chloride of sodium passed, a considerable quantity of water, probably many thousand times greater than that of salt.

Let us now suppose, that, instead of pure water, a solution of a certain concentration c of the same salt which is present on the upper side of the membrane in concentrated solution, be placed on the under side of that membrane, then the following considerations present themselves. All the elementary strata, from the wall of the pore, to an imaginary cylindrical film of the radius r , that $f(\rho - r) = c$, can only be filled from the top to the bottom with solution of the there *highest* possible concentration, and cannot therefore give origin to a usual double diffusion-current. Water will, however, pass over from the lighter to the denser solution, because a force of suction comes into play on each side of the membrane, proportional to the difference of concentration, consequently a stronger force at the upper side corresponding to the saturated solution. On the other hand, all those strata lying nearer to the axis, behave exactly in the above manner, with the single difference, that in them the concentration, instead of increasing from 0, now increases from below upwards from c to the respective maxima, and consequently an absolutely weaker diffusion-current is produced. It therefore follows in this case, that in places where, in the first instance, salt passed to the one side and water to the other, only a single diffusion of water takes place, consequently the proportion between water and salt (the endosmotic equivalent) must be *greater* here than there. If, for instance, $c > (\rho - r)$ (which is possible in the case of very fine pores), *no salt whatever* could

* Poggendorff's *Annalen*, vol. lxxviii. p. 361.

pass through; the endosmotic equivalent would be $= \infty$, or the current one-sided.

This conclusion is also confirmed by experiment. Even the above-cited experiments of Ludwig and Cloetta intimate this to be the case. I have myself obtained still more decided results. A membrane which gave an equivalent between 5 and 6, when it separated a saturated solution from pure water, yielded an equivalent $= 11.05$, in another case even $= 17.05$, when the pure water was replaced by a solution of common salt of 22 per cent. Lastly, if we analyse the case in which, instead of a saturated solution, a dilute one be placed above, and again pure water below. Let us again express the concentration of the upper solution by c . Evidently in an axial cylinder whose radius r is so great, as exactly to make $f(\rho - r) = c$, the concentration from the lower to the upper end, will now regularly increase from 0 to c , and a usual diffusion-current take place, which will pass a volume of salt downwards, exactly equal to the volume of water propelled upwards. Only in those layers situated nearer to the wall, can the concentration at the upper end never rise to c , and there will therefore pass through these layers alone, according to the previous considerations, more water than salt. The radius r , of the above-mentioned axial cylinder, is evidently

as much greater as c is smaller, therefore the endosmotic equivalent must also decrease very rapidly with c ; and we might expect that, for moderately small values of c , the endosmotic equivalent would be found smaller than unity (because a volume of salt weighs more than an equal volume of water). Ludwig's experiments with common salt are perfectly in accordance with this conclusion; in some cases in his experiments, the equivalent sunk from 4 to 1 when the concentration of the upper solution was decreased from saturation to 2 per cent. My own experiments in the same direction with common salt gave a purely negative result, as the equivalent was not perceptibly decreased.

The comparison of the experiments adduced above with the hypothesis developed on the foundation of the diffusion law, shows, though not absolutely, that the truth of this hypothesis may be determined; and it is in fact highly probable that, with or without modification, such an hypothesis may serve as the foundation of a subsequent theory of these very dark phenomena.

A. Fick (1829–1901), On Liquid Diffusion, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, Vol. X (1855) 30–39. Abstracted by the author from the German original: Über Diffusion, Poggendorff's Annalen der Physik und Chemie, 94 (1855) 59–86.