[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

THE RATE OF ABSORPTION OF WATER BY RUBBER[1]

BY DONALD H. ANDREWS AND JOHN JOHNSTON

RECEIVED DECEMBER 12, 1923

It is well known that moisture exerts a profound effect upon the insulating quality of materials; consequently, if we are to investigate in any systematic way the insulating properties inherent in a material, we must study the effect of moisture upon these properties; and, as a preliminary to this, we must ascertain the maximum amount of water which may be absorbed by the material under various conditions, and the rate at which this water is absorbed, or released. If this rate is relatively small, as it is in rubber compounds, this fact must be taken into account in endeavoring to secure really comparable states of the material of which insulating properties are to be measured; for the effect of a given small proportion of water depends undoubtedly upon whether the water is, or is not, evenly distributed throughout the material. With this general end in view, measurements of the rate of absorption of water by a series of sheets of rubber were undertaken.

When a weighed sheet of rubber is immersed in water, and at intervals taken out, wiped off and reweighed, we find that its weight increases, rapidly at first and more and more slowly as it approaches a limiting value. For a given rubber compound this limiting concentration is independent of the thickness of the sheet which, however, exerts a very marked influence upon the time interval required for the attainment of a specified degree of saturation of the sheet. It seemed desirable to investigate this phenomenon as a means of learning more about the mechanism of the absorption of water in rubber and, in particular, to be enabled to predict, from the behavior of thin sheets, the time required for a given degree of saturation of a thick sheet immersed in water. The outcome is that the process of water absorption follows the usual law of diffusion, but this fact still leaves us uncertain as to whether the process is one of solution or one of absorption in an intricate network of small pores, or a combination of these. It does follow, however, that for a given rubber compound, the time required to reach a specified degree of saturation is proportional to the square of the thickness of the sheet and consequently that the behavior of the thicker sheets, in which substantial saturation may not be reached for more than a year, may be predicted from observation of thin sheets which become saturated in a few weeks.

The mode of experiment was, as already outlined, to weigh pieces of equal area cut from sheets of measured thickness, to immerse these in

---

[1] From a part of the dissertation presented by D. H. Andrews to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

water, and to take them out, wipe them off and reweigh them at suitable intervals. It is of course clear that this method will not lead to results of the highest accuracy, mainly because of the uncertainty involved in wiping off surplus moisture before reweighing; but it is accurate enough in view of (1) the difficulty of determining the thickness of such sheets with any high percentage accuracy; (2) the probability that the external layers of such sheets—which during manufacture had been in contact with the rolls—might differ somewhat in structure from the material towards the center. The experimental results, expressed as percentage of water absorbed (that is, as *average* concentration through the sheet) on sheets made up from a single rubber compound are presented in Table I. These results, it may be said, were all obtained before any theoretical interpretation was attempted and before, therefore, the most advantageous time intervals for sheets had been realized.

TABLE I

OBSERVED INCREASE IN WEIGHT OF RUBBER SHEETS (MADE FROM A SINGLE COMPOUND) AFTER VARIOUS INTERVALS OF IMMERSION IN WATER

Sheet	Sheet half-thickness Mm.	Original wt. G.	Average concentration of water (g. absorbed per 100 g. of rubber) attained after immersion of:						
			7 days	14 days	27 days	76 days	184 days	642 days	∞ days (calc).
1	0.315	21.15	0.93	1.10	1.18	1.18	1.23	....	....
2	0.316	21.04	.86	1.06	1.13	1.10	1.13	....	....
3	0.589	40.20	.67	0.82	0.98	1.21	1.23	....	....
4	0.605	40.20	.66	.80	.95	1.15	1.23	....	....
5	1.159	77.95	.44	.64	.76	0.98	1.12	1.28	....
6	1.150	78.86	.51	.67	.81	1.00	1.15	1.32	....
7	1.710	117.3	.38	.53	.64	0.84	1.02	....	1.37
8	1.722	115.8	.38	.50	.61	.80	0.97	1.17	1.31
9	2.38	167.3	.20	.28	.43	.63	.80	1.06	1.24
10	2.33	155.7	.18	.33	.44	.62	.79	1.08	1.22
11	2.89	191.9	.17	.29	.38	.55	.70	0.95	1.19
12	3.00	197.6	.17	.29	.38	.55	.70	.97	1.24
13	3.53	231.4	.20	.28	.36	.52	.67	....	1.25
14	3.57	236.5	.20	.28	.35	.51	.65	.86	1.22

The Equation for Diffusion into a Slab

When the amount of water absorbed is plotted against the time interval, for the several sheets, the graph suggests that we are dealing with a process of diffusion. If this be so, the process is analogous to the conduction of heat, except that we are here measuring the analog of the total quantity of heat conducted, whereas it is in that case usual to determine the temperature gradient at various distances from the surface at highest temperature, the temperature being the exact analog of the concentration of water in our case. Before we can deduce the mathematical relation, applicable to our case, which should subsist between quantity of water absorbed, thickness of sheet, period of immersion and diffusivity of water in the rubber, we must make certain assumptions. These assumptions, which are *a priori* plausible and justified by the outcome, follow: (1) that the water enters only by diffusion; (2) that no physical or chemical change takes place as the water enters such as to change the rate of diffusion by changing the medium; (3) that the external surface is saturated instantaneously; (4) that the water enters through the surfaces of the slab (sheet), the area exposed on the edges being so small relatively that the water entering through the edges may be neglected.[2]

On this basis our case is one of diffusion in a single dimension, to which is applicable Fick's law,[3] namely, that

$$\frac{\partial \Theta}{\partial t} = k\left(\frac{\partial^2 \Theta}{\partial x^2}\right) \tag{1}$$

Θ representing concentration of water at the distance x and time t, and k the characteristic diffusivity constant. In order to proceed from this we must set up boundary conditions—that is, we must postulate the state of the surface of the slab initially, during the experiment, and finally.

When the rubber is plunged in the water, it may be imagined that a wall of water penetrates in from either face, the advancing walls meeting at a point midway between the faces if conditions are symmetrical. They will then penetrate each other; but by reason of symmetry the resultant concentration is the same as if there had been an impermeable membrane midway between the faces of the slab, from both sides of which the water is reflected. It is therefore logical to consider as the problem only what is happening on one side of the membrane, in one-half of the slab. The plane in which this imaginary central membrane lies, is chosen as the mathematical origin and distance is measured from it toward the face. If the thickness of the slab be called "$2a$" then $x = a$ is the locus of points on the face.

Initially the rubber is dry throughout, that is, when $t = 0$, $\Theta = 0$ for all values of x. We have already made the plausible assumption that on immersion, the rubber at the surface of the slab instantly becomes saturated, and hence remains saturated throughout the experiment; that is, for all values of t, when $x = a$, $\Theta = \Theta_1$ where Θ_1 is the saturation concentration. Finally, after a sufficient interval, the rubber is saturated with water throughout; that is, when $t = \infty$, $\Theta = \Theta_1$ for all values of x. For the boundary conditions specified the solution of Equation 1 is[2a]

$$\frac{\Theta_1 - \Theta}{\Theta_1} = \frac{4}{\pi} \sum_{m=1}^{m=\infty} \frac{\cos\frac{(2m-1)\pi\, x}{2a}}{(2m-1)\,(-1)^{m+1}}\, e^{-\frac{kt}{a^2}\,\frac{(2m-1)^2\pi^2}{4}} \tag{2}$$

---

[2] The case in which the edges are not negligible can also be handled. See Williamson and Adams: "Temperature Distribution in Solids during Heating or Cooling," [(a) *Phys. Rev.*, N. S., **14,** 110 (1919)] who give equations for (1) the brick, diffusion through three (all) faces; (2) the rectangular rod, two faces; (3) the slab, one face, (Equation 2, this paper).

[3] See Appendix A.

The foregoing equation gives the concentration of water (Θ), at the plane x and time t, in terms of the half-thickness (a) of the particular sheet, its diffusivity constant (k) towards water, and its saturation concentration (Θ_1). What we have measured, however, is not Θ, the concentration at a plane, but the aggregate amount of water through the sheet. To obtain an equation involving this aggregate amount of water taken up by the sheet, we must integrate Equation 2 with respect to x from 0 to a. The resultant[4] equation (3) gives the fractional saturation of the slab as a whole in terms of t, a and k, Q being the total percentage quantity of water in the slab at time t, and Q_1 the corresponding quantity at saturation:

$$\frac{Q}{Q_1} = 1 - \frac{8}{\pi^2}\left\{ e^{-\frac{\pi^2}{4}\cdot\frac{kt}{a^2}} + \frac{1}{9}e^{-\frac{9\pi^2}{4}\cdot\frac{kt}{a^2}} + \frac{1}{25}e^{-\frac{25\pi^2}{4}\cdot\frac{kt}{a^2}} + \dots\dots \right\} \tag{3}$$

This is in the form of a series; but so long as the quotient kt/a^2 is greater than 0.1 (corresponding to values of Q/Q_1 greater than 0.36), all terms except the first may, for the present purpose, be neglected.[5] With this limitation Equation 3 reduces to

$$\frac{Q}{Q_1} = 1 - \frac{8}{\pi^2}e^{-\frac{\pi^2}{4}\cdot\frac{kt}{a^2}} \tag{4a}$$

Transposing, taking logarithms of both sides, and again transposing, we have

$$\frac{kt}{a^2} = -\frac{4}{\pi^2}\,ln\left[\frac{\pi^2}{8}\left(1-\frac{Q}{Q_1}\right)\right] = -0.0851 - 0.933\ \log\left(1-\frac{Q}{Q_1}\right) \tag{4b^6}$$

---

[4] For method of integration see Appendix B.

[5] For instance when $\frac{kt}{a^2} = 0.1$, $\frac{\pi^2}{4}\cdot\frac{kt}{a^2} = 0.2467$ and

$$\begin{aligned}\frac{Q}{Q_1} &= 1 - \frac{8}{\pi^2}\left\{\frac{1}{e^{0.2467}} + \frac{1}{9\,e^{9\times 9.2467}} + \frac{1}{25\,e^{25\times 0.2467}} + \dots\dots\right\}\\ &= 1 - \frac{8}{\pi^2}\left\{0.781 + 0.012 + 0.0000824 + \dots\dots\right\}\\ &= 0.357.\end{aligned}$$

[6] Since this paper was submitted for publication the work of Kirchhof [*Kolloidchem. Beih.*, **6**, 1 (1914)] has come to our attention. He observed the rate of swelling of rubber in various liquids, noting the effect of temperature, of the nature of the liquid, and of the degree of vulcanization of the rubber; and expressed his results by the equation for the velocity of a reaction of the first order, as follows.

$$K = \frac{1}{t}\log\frac{Q_1}{Q_1 - Q}$$

where K is the reaction velocity constant and t, Q_1, and Q are as defined by us. This may be considered as a limiting form of Equation 4b, as may be seen by writing the latter

$$\frac{K}{a} = \frac{1}{t}\left[-0.0851 + 0.933\ \log\frac{Q_1}{Q_1 - Q}\right]$$

The relatively small term 0.0851 which throws the curve away from the origin, enters only as a consequence of dropping all terms after the first in Equation 3, a step necessary for solution in the logarithmic form.

From this equation it is clear that the graph of kt/a^2 against the corresponding values of log $(1 - Q/Q_1)$ is a straight line, so long as kt/a^2 is greater than 0.1. This result may be shown directly by using Equation 3 to compute, for given values of kt/a^2, the corresponding values of Q/Q_1 given in Table II, and hence of —log $(1 - Q/Q_1)$; the graph, shown as a broken line in Fig. 1, is practically linear except near the origin.

TABLE II

CORRESPONDING VALUES OF Q/Q_1 AND kt/a^2 FOR THE SLAB CALCULATED BY MEANS OF EQUATION 3

kt/a^2	0.01	0.03	0.05	0.1	0.2	0.3	0.4	0.6	0.8	1.2	2.0
Q/Q_1 (calc.)	.119	.196	.252	.357	.504	.613	.698	.815	.887	.958	.994

AND INVERSELY BY INTERPOLATION

Q/Q_1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
kt/a^2	.009	.031	.069	.125	.197	.289	.403	.569	.850	∞

From Equation 4b, moreover, it follows that the graph of t/a^2 against —log $(1 - Q/Q_1)$ should be a straight line provided that k is constant for a series of sheets. Equation 3 implies that all of the experimental data should, when plotted in this way, lie upon a single curve, independently of the thickness of the several sheets; in other words that, to a specified degree of saturation Q/Q_1, there corresponds a single value of t/a^2, or that the time interval required for the attainment of this specified degree of saturation of the sheet as a whole should be proportional to the square of the (half-) thickness of the sheet.

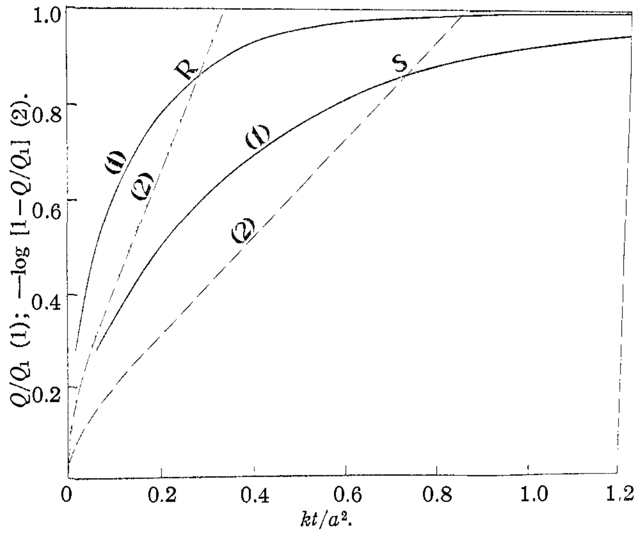

Fig. 1.—The relation between kt/a^2 and (1) Q/Q_1, (2) —log $(1-Q/Q_1)$, as computed for the slab (S) by Equation 3 and for the cylindrical rod (R) by Equation 6.

In the theoretical relation just derived, Q, the observed percentage increase of weight by absorption of water, appears as numerator of a fraction, the denominator being the corresponding quantity (Q_1) when the sheet has become saturated throughout. The data in Table I justify us in assuming that a period of 27 days sufficed for saturation of Sheets 1 and 2, 184 days for Sheets 3 and 4, and 642 days for Sheets 5 and 6; in other words, that the several values of Q_1 for these six thinner sheets are 1.18, 1.13, 1.23, 1.23, 1.28, 1.32, respectively. When for each of those sheets we divide the several values of Q by the proper Q_1, we obtain a series of values of the quotient Q/Q_1 which, when plotted against the corresponding values of t/a^2, should lie on a single curve. This curve is shown in Fig. 2, the data appearing as dots; and it is evident that this expectation is realized, within the limits of the experimental error.

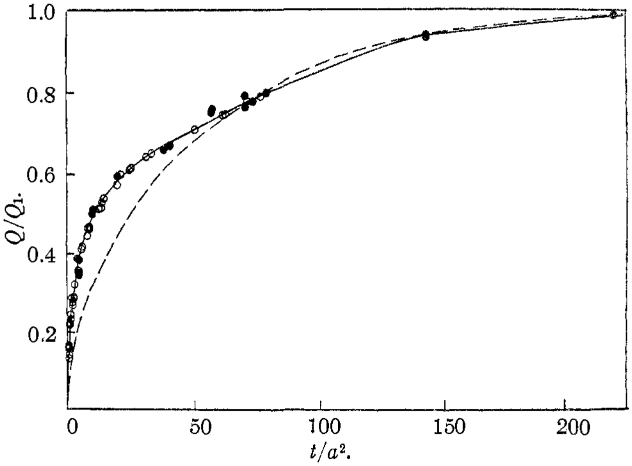

Fig. 2.—The relation between t/a^2 and Q/Q_1 as observed: points for the thinner sheets represented by dots; for the thicker sheets, which had not become saturated after 642 days, by circles. The broken line is the theoretical curve corresponding to k = 0.0074 (mm.^{2})/day.

The thicker sheets had not become fully saturated even after 642 days, so that in these cases it was necessary to evaluate Q_1 indirectly. When values of Q/Q_1 based upon the average value of Q_1 (1.23), for the thinner sheets, were plotted as before, the points for an individual sheet tended to lie either all above or all below the curve for the thinner sheets, indicating that the proper Q_1 was in some cases lower, in other cases higher, than the average. Accordingly, we assumed for each of the thicker sheets that the largest value of Q/Q_1 would fall on the curve if the proper Q_1 were used. In other words, we read off the curve, at the value of t/a^2 corresponding to the largest observed Q, the value of Q/Q_1, and used this to evaluate Q;

the values so derived lie, with a single exception, as may be seen from the last column of Table I, within the same range as the directly observed saturation concentrations of the thinner sheets. The several quotients Q/Q_1, on this basis, were again plotted against the corresponding values of t/a^2; these points, designated by circles in Fig. 2, lie upon the same curve which fits the points for the thinner sheets, within the experimental error.

In Fig. 2 we have also drawn the graph for Equation 3 for $k = 0.00742$, from which it appears that the experimental curve does not coincide throughout with any graph of Equation 2, the difference being that the initial rate of absorption is relatively too great. This implies that some of the postulates underlying Equation 3 are not strictly true; it is to be attributed, we believe, to failure of the assumption that the sheets are homogeneous in structure throughout their thickness, for it is not unlikely that the structure of the surface of sheets made by calendering should differ somewhat (as, for example, in porosity) from that of the interior. However this may be, the fact remains that the points observed for a series of sheets do lie on a single curve; and it is, for present purposes, of less importance that the observed curve should fail to coincide with the theoretical one, for, by the use of the curve, the behavior of thicker sheets can be predicted from observations on thinner sheets of the same material, since for any thickness the degree of saturation Q/Q_1 at time t can thus be derived directly.

The rate of drying of sheets already saturated with water would presumably bear a somewhat inverse relation to the rate of wetting; if the rate of the two processes is substantially identical, it would be preferable to make the experimental observations on saturated sheets drying rather than on absorption by dry sheets during immersion. It is clear, however, that the drying of partially saturated sheets—or the absorption by incompletely dried sheets (which may have been the case with our thicker sheets) is a more complex process, for it would depend not only on the total quantity of water present but also upon its distribution through the thickness of the sheet.

The Equation for Diffusion into a Cylindrical Rod

In connection with the general problem of insulation it is important to know the rate of diffusion into a cylindrical rod such as an insulated wire or cable. This case is less easy to determine by direct experiment because the water is likely to enter also by the ends between wire and insulation and also to cause corrosion of the wire; but the problem is readily solved if the relation between Q/Q_1 and kt/a^2 for slabs of the material is known, provided that we may consider the structure of the material to be alike in the two cases. This assumption is doubtless substantially true, at least as a first approximation; it could be justified by comparing diffusivity in calendered and in extruded sheets, the insulation of wires being usually fashioned by an extrusion process.

For a cylindrical rod into which water is diffusing through the cylindrical surface but not through the ends, the equation analogous to Equation 2 for the slab, connecting point concentration (Θ) with the distance (x), time (t), diameter (a) and diffusivity (k) is

$$\frac{\Theta_1 - \Theta}{\Theta_1} = 2 \sum_{m=1}^{m=\infty} \frac{J_0\left(R_m \frac{x}{a}\right)}{R_m \, J_1(R_m)} e^{-R_m^2 \cdot \frac{kt}{a^2}} \tag{5}$$

in which[7] J_0 and J_1 denote the functions generally known as cylindrical harmonics or Bessel functions of the zero$^{\text{th}}$ and first order, and R_m denotes the roots of these functions. When expanded, J_0 and J_1 are in general expressed in the form of infinite series, but computations involving them may be performed by means of tables in a manner analogous to logarithmic computation.

The integrated form[8] of Equation 5, analogous to Equation 3, giving the fractional saturation Q/Q_1 in terms of kt/a^2 is

$$\frac{Q}{Q_1} = 1 - 4\left\{\frac{1}{5.783} e^{-\frac{kt}{a^2} \times 5.783} + \frac{1}{30.472} e^{-\frac{kt}{a^2} \times 30.472} + \frac{1}{74.895} e^{-\frac{kt}{a^2} \times 74.895} + \ldots\ldots\right\} \tag{6}$$

This, like Equation 3 for the slab, is in the form of a series; but when kt/a^2 is greater than 0.1 (corresponding to values of Q/Q_1 greater than 0.606) all terms except the first may for the present be neglected.[9]

With this limitation Equation 6 reduces to

$$\frac{Q}{Q_1} = 1 - \frac{4}{5.783} e^{-\frac{kt}{a^2} \times 5.783} \tag{7a}$$

Transposing, taking logarithms of both sides and again transposing, we have

$$\begin{aligned} \frac{kt}{a^2} &= -\frac{1}{5.783} \, ln \left[\frac{5.783}{4}\left(1 - \frac{Q}{Q_1}\right)\right] \\ &= -\,0.6375 - 0.3983 \log \left(1 - \frac{Q}{Q_1}\right) \end{aligned} \tag{7b}$$

From this equation it is clear that the graph of kt/a^2 against the corresponding values of log $(1 - Q/Q_1)$ is a straight line, so long as kt/a^2 is greater

---

[7] As given by Williamson and Adams, Ref. 2, who also give the equation for the cylinder, diffusion through both curved surface and ends, and for the sphere.

[8] For integration see Appendix B.

[9] For instance when $\frac{kt}{a^2} = 0.1$

$$\begin{aligned} \frac{Q}{Q_1} &= 1 - \left\{\frac{4}{5.783\, e^{0.5783}} + \frac{4}{30.472\, e^{3.0472}} + \frac{4}{74.895\, e^{7.4895}} + \ldots\right\} \\ &= 1 - 0.388 - 0.00588 - 0.00003045 \\ &= 0.606. \end{aligned}$$

than 0.1. This result may be shown directly by using Equation 6 to compute for given values of kt/a^2, the corresponding values of Q/Q_1 and hence of —log $(1 - Q/Q_1)$; the graph, shown as a broken line in Fig. 1, is practically linear except near the origin. From Equation 6 it follows, as in the case of the slab, that for all cylindrical rods with the same k, values of t/a^2 plotted against —log $(1 - Q/Q_1)$ or Q/Q_1 should lie on a single curve.

Table IV

Corresponding Values of kt/a^2 and Q/Q_1 for the Cylindrical Rod, Calculated by Means of Equation 6

kt/a^2	0.01	0.03	0.05	0.1	0.2	0.3	0.4	0.6	0.8	1.2	2.
Q/Q_1	.226	.360	.453	.606	.779	.878	.931	.978	.993	0.9993	0.9998

and Inversely by Interpolation

Q/Q_1		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
kt/a^2	for cyl. rod	.005	.008	.020	.040	.068	.099	.148	.215	.330	∞
	for slab	.009	.031	.069	.125	.197	.289	.403	.569	.850	∞

Comparison of the graph for the cylindrical rod of diameter $2a$ with that for the slab of thickness $2a$, shows that the degree of saturation of the former increases more rapidly, particularly in the early stages. If, for a given rubber, the graph of t/a^2 against Q/Q_1 has been determined on slabs, the time corresponding to a given degree of saturation of a cylindrical rod can be estimated by multiplying the appropriate value of t/a^2 for the slab by the ratio of the respective abscissas of the corresponding curves R and S of Fig. 1. However, the important application is to an insulated wire or cable, that is, to a cylindrical rod, not of rubber throughout, but with an impervious metal core. This case approximates to that of the slab when the diameter of the wire is large compared with the wall-thickness of the rubber, to the rod when the wire is relatively small. In most actual cases of insulated wire or cable, therefore, the rate of water absorption by slabs would furnish a good enough basis for prediction as to the behavior upon immersion in water.

Summary

Measurements of the rate of absorption of water by a series of sheets of rubber have shown that the fractional saturation of the sheet as a whole is a function of t/a^2, when t is the period of immersion and a the half-thickness of the sheet; in other words that, when properly plotted, all of the data lie on a single curve. This fact, which is in substantial accord with the theory of diffusion, enables us to predict the behavior of thicker sheets, in which substantial saturation is attained only after an interval measured in years, from observation of thin sheets for a period of weeks. Such information is of importance in connection with the general question of insulation, since the water content of a material affects its insulating properties.

Appendix A

The physical significance of this differential equation may be shown as follows.

Assume that diffusion in through the surface is the same at all points on the face of the slab and that therefore every plane in the slab, parallel to the face, is a plane of uniform concentration of water. At any instant the rate of diffusion between two planes is proportional to the difference in concentration between them. The rate of diffusion past a given plane is proportional to $\partial\Theta/\partial x$, the space rate at which the concentration changes along a line perpendicular to the plane.

Consider a small cubical section within the rubber slab, so chosen that two opposite vertical faces are parallel to the surface of the slab. Water will diffuse in through the vertical face (No. 1) nearer the surface at a rate proportional to $\partial\Theta/\partial x$ at this face, and out through the opposite face (No. 2) at a rate correspondingly proportional to $\partial\Theta/\partial x$ at that face, the second rate being less than the first as this point is further from the surface of the slab. By the first hypothesis $\partial\Theta/\partial x$ perpendicular to the other four faces is zero and there is no diffusion of water across them. But water is coming into the cubical section through face No. 1 faster than it is going out through face No. 2 so the net result is an increase in the amount of water in the cubical section. The rate of accumulation of water, that is, increase in concentration, is thus proportional to the difference between $\left(\frac{\partial\Theta}{\partial x}\right)_{\text{No. 1}}$ and $\left(\frac{\partial\Theta}{\partial x}\right)_{\text{No. 2}}$; or in the notation of the calculus: $\frac{\partial\Theta}{\partial t} = k\left(\frac{\partial^2\Theta}{\partial x^2}\right)$, which is Fick's law.

Appendix B

Integration of Equation 3, (the slab).

$$\frac{\Theta_1 - \Theta}{\Theta_1} = \frac{4}{\pi} \sum_{m=1}^{m=\infty} \frac{\cos\frac{(2m-1)}{2a}\pi x}{(2m-1)(-1)^{m+1}}\, e^{-\frac{kt}{a^2}\cdot\frac{(2m-1)^2\pi^2}{4}} \tag{3}$$

$$Q = \int_0^a \Theta dx = \int_0^a \Theta_1 dx - \frac{4\Theta_1}{\pi}\int_0^a \sum_{m=1}^{m=\infty} \frac{\cos\frac{2m-1}{2a}\pi x}{(2m-1)\ (-1)^{m+1}}\, e^{-\frac{kt}{a^2}\cdot\frac{(2m-1)^2\pi^2}{4}} dx$$

$$Q = Q_1 - \frac{4\Theta_1}{\pi}\overset{a}{\underset{0}{\Big[}} \sum_{m=1}^{m=\infty} \frac{\frac{2a}{(2m-1)\pi}\sin\frac{(2m-1)}{2a}\pi x}{(2m-1)\ (-1)^{m+1}}\ e^{-\frac{kt}{a^2}\cdot\frac{(2m-1)^2\pi^2}{4}} \Big]$$

$$Q = Q_1 - \frac{4\Theta_1}{\pi}\left\{\frac{2a}{\pi}\ e^{-\frac{kt}{a^2}\cdot\frac{\pi^2}{4}} + \frac{2a}{9\pi}e^{-\frac{kt}{a^2}\cdot\frac{9\pi^2}{4}} + \frac{2a}{25\pi}e^{-\frac{kt}{a^2}\cdot\frac{25\pi^2}{4}} + \ldots.\right\}$$

$$\frac{Q}{Q_1} = 1 - \frac{8}{\pi^2}\left\{e^{-\frac{kt}{a^2}\cdot\frac{\pi^2}{4}} + \frac{1}{9}e^{-\frac{kt}{a^2}\cdot\frac{9\pi^2}{4}} + \frac{1}{25}e^{-\frac{kt}{a^2}\cdot\frac{25\pi^2}{4}} + \ldots.\right\} \tag{4}$$

Integration of Equation 5 (the cylindrical rod).

$$\frac{\Theta_1 - \Theta}{\Theta_1} = 2\sum_{m=1}^{m=\infty} \frac{J_0\left(R_m\frac{x}{a}\right)}{R_m J_1(R_m)}\, e^{-\frac{kt}{a^2}(R_m)^2} \tag{5}$$

$$\Theta = \Theta_1\left\{1 - 2\sum_{m=1}^{m=\infty} \frac{J_0\left(R_m\frac{x}{a}\right)}{R_m J_1(R_m)}\, e^{-\frac{kt}{a^2}(R_m)^2}\right\}$$

$$Q = \int_0^a 2\pi x\Theta dx = \int_0^a 2\pi x\Theta_1 dx - \int_0^a 2\pi x \cdot 2\Theta_1 \sum_{m=1}^{m=\infty} \frac{J_0\left(R_m \frac{x}{a}\right)}{R_m\, J_1\,(R_m)}\, e^{-\frac{kt}{a^2}\,(R_m)^2} dx$$

$$Q = 2\pi\Theta_1 \int_0^a x dx - 4\pi\Theta_1 \int_0^a x \sum_{m=1}^{m=\infty} \frac{J_0\left(R_m \frac{x}{a}\right)}{R_m\, J_1\,(R_m)}\, e^{-\frac{kt}{a^2}\,(R_m)^2} dx$$

$$Q = \pi a^2\Theta_1 - 4\pi\Theta_1 \Big[_0^a \sum_{m=1}^{m=\infty} \frac{\frac{a}{R_m} x J_1\left(R_m \frac{x}{a}\right)}{R_m\, J_1\,(R_m)}\, e^{-\frac{kt}{a^2}\,(R_m)^2} \Big]$$

$$Q = \pi a^2\Theta_1 - 4\pi\Theta_1 \sum_{m=1}^{m=\infty} \frac{\frac{1}{R_m} a^2\, J_1\,(R_m)}{R_m\, J_1\,(R_m)}\, e^{-\frac{kt}{a^2}\,(R_m)^2}$$

$$\frac{Q}{Q_1} = 1 - 4 \left\{ \frac{1}{(R_1)^2} e^{-\frac{kt}{a^2}(R_1)^2} + \frac{1}{(R_2)^2} e^{-\frac{kt}{a^2}(R_2)^2} + \dots \right\}$$

$$\frac{Q}{Q_1} = 1 - 4 \left\{ \frac{1}{5.78} e^{-\frac{kt}{a^2} \times 5.78} + \frac{1}{30.47} e^{-\frac{kt}{a^2} \times 30.472} + \frac{1}{74.895} e^{-\frac{kt}{a^2} \times 74.895} + \dots \right. \qquad (6)$$

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE BUREAU OF STANDARDS OF THE UNITED STATES DEPARTMENT OF COMMERCE]

A METHOD FOR STUDYING THE RAPID ABSORPTION OF GASES BY LIQUIDS[1]

BY P. G. LEDIG AND E. R. WEAVER

RECEIVED DECEMBER 15, 1923

This paper is a report of experimental work carried out at the Bureau of Standards with the purpose of developing a method for the accurate study of the absorption of gases in liquids. The data given relate to the absorption rates of sodium hydroxide solutions for carbon dioxide, not because of any special interest in this particular reaction, but because it is a convenient reaction for use in developing the method. This study was made as the first part of a general investigation of the rates of solution of gases in liquids. A later complete report will include other methods of attack used in the study of absorption, but the apparatus and the results to be described here are of such interest that they are reported separately.

The method used is very simple in principle. A bubble of carbon dioxide is absorbed in a closed system, open to the air only through a capillary tube. The resulting contraction of the bubble produces motion in the thread of solution in the capillary tube and a photographic method is used to obtain a time record of this motion.

---

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.