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To cite this article: Albert Griffiths M.Sc.(Vic.) A.R.C.S. (Lond.) (1899) L. A study of an apparatus for the determination of the rate of diffusion of solids dissolved in liquids , Philosophical Magazine Series 5, 47:289, 530-539, DOI: [10.1080/14786449908621294](https://doi.org/10.1080/14786449908621294)

To link to this article: <http://dx.doi.org/10.1080/14786449908621294>

Published online: 08 May 2009.

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L. *A Study of an Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids.* By ALBERT GRIFFITHS, *M.Sc.(Vic.), A.R.C.S.(Lond.)**.

SECTION I.

FOR some time the author has been engaged in some experiments with the object of determining the coefficient of diffusion of bodies dissolved in water. It may be some years before experimental results of any decided value are obtained; and perhaps he will be allowed to give an account of the calculations involved, and of the methods he has adopted in obtaining an idea of the probable order of magnitude of the errors to which the apparatus is liable.

solution respectively. A quantitative analysis is made of the liquid taken from the upper compartment.

SECTION II.—*Calculation of the Coefficient of Diffusion.*

Lord Kelvin has solved the problem of the flow of electricity along a cable possessing appreciable capacity. This

* Communicated by the Physical Society: read Feb. 24, 1899.

solution can readily be transferred to the problem under consideration.

It will be assumed that the upper extremities of the tubes are kept in contact with pure water, and the lower extremities in contact with a solution of constant strength.

Let γ = quantity of dissolved substance which enters the upper compartment in unit time, when the combined sectional area of the tubes equals unity.

k = coefficient of diffusion (C.G.S. system), assumed to be a constant.

L = length of tubes in centims.

T = quantity of substance per c. c. in the lower compartment.

t = time in seconds.

Then

$$\gamma = \frac{kT}{L} \left\{ 1 + 2 \sum_{i=1}^{i=\infty} (-1)^i e^{-\frac{i^2 \pi^2 k t}{L^2}} \right\},$$

where i is any integer.

[If $\frac{L^2}{\pi^2 k}$ log $\frac{4}{3}$ be taken as the unit of time, the topmost of the series of curves given on page 72, vol. ii., of Kelvin's 'Mathematical and Physical Papers,' shows graphically how γ rises to a maximum.]

Let q = total quantity of substance transmitted in t seconds. Integrating the preceding expression with respect to t , we obtain

$$q = \frac{kT}{L} \left\{ t + 2 \sum_{i=1}^{i=\infty} (-1)^i \frac{L^2}{i^2 \pi^2 k} - 2 \sum_{i=1}^{i=\infty} (-1)^i \frac{L^2}{i^2 \pi^2 k} e^{-\frac{i^2 \pi^2 k t}{L^2}} \right\} \quad (1)$$

When t is very large the third term within the brackets may be neglected, and

$$q = \frac{kTt}{L} + \frac{2LT}{\pi^2} \sum_{i=1}^{i=\infty} \frac{(-1)^i}{i^2} \quad . \quad . \quad . \quad (2)$$

or

$$q = \frac{kTt}{L} - \frac{2LT}{\pi^2} \frac{\pi^2}{12} = \frac{kTt}{L} - \frac{LT}{6} \quad . \quad . \quad . \quad (3)$$

The last equation shows that if t is large the quantity transmitted equals kTt/L minus a quantity which is independent of the coefficient of diffusion. Thus if in the adjoining figure abscissæ represent times, and ordinates the quantities

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diffused per second, the shaded area between the asymptote
and the curve is independent of the coefficient of diffusion.

Fig. 2.

The table below gives an idea of the rate at which the
steady state is attained when $L=4\cdot043$, and $k=3\times10^{-6}$.
The unit of quantity is the amount transmitted per week on
the attainment of the steady state.

No. of Weeks.	Total Quantity.	Quantity per Week.
1	0.104	0.104
2	0.703	0.599
3	1.567	0.864
4	2.519	0.952
5	3.505	0.986
6	4.500	0.995
7	5.498	
8	6.498	
9	7.498	
10	8.498	

[The above table gives the *integral* quantities transmitted.
The curve already mentioned shows the way in which the
rate of transmission varies. The unit abscissa $\frac{L^2}{\pi^2 k} \log_e \frac{4}{3} =$
2626 of a week.]

SECTION III.—*Error due to Differences of Temperature.*

The object of this section is to obtain the *order of mag-*
nitude of the errors produced by differences in temperature
between the various tubes.

For simplicity, two tubes only will be considered whose lengths and sectional areas are the same. The expansion of the material of the tubes will be neglected. To make the problem amenable to mathematical treatment, it will be assumed that the density of water equals $(1-\alpha\theta)$, where θ is the temperature, and α is approximately equal to an ideal coefficient of expansion. It will also be assumed that

$$d = (1 - \alpha\theta + t),$$

where d = the density of the solution,
 t = the concentration.

Let θ_1 = the temperature of one tube.
 v_1 = the velocity of the liquid up the tube.
 θ_2 = the temperature of the second tube.
 v_2 = the velocity of the liquid up the tube.
 L = the length of each tube, assumed constant.
 k = the coefficient of diffusion, assumed constant.
 T = the concentration of the solution at the bottom of each tube.

From considerations similar to those adopted in "Diffusive Convection"*, Sect. II. and III., it can be shown that, neglecting viscosity,

$$\begin{aligned} g(1 - \alpha\theta_1)L + \frac{gTL}{1 - e^{-\frac{v_1 L}{k}}} - \frac{kgT}{v_1} \\ = g(1 - \alpha\theta_2)L + \frac{gTL}{1 - e^{-\frac{v_2 L}{k}}} - \frac{kgT}{v_2}. \end{aligned}$$

Dividing throughout by g , and expanding,

$$\begin{aligned} (1 - \alpha\theta_1)L + TL \left(\frac{k}{v_1 L} + \frac{1}{2} + \frac{v_1 L}{12k} + \&c. \right) - \frac{kT}{v_1} \\ = (1 - \alpha\theta_2)L + TL \left(\frac{k}{v_2 L} + \frac{1}{2} + \frac{1}{12} \frac{v_2 L}{k} + \&c. \right) - \frac{kT}{v_2}; \end{aligned}$$

and

$$(v_2 - v_1) = \frac{12k\alpha(\theta_2 - \theta_1)}{TL}, \text{ approx.}$$

* Phil. Mag. Nov. 1898, pp. 453-465.

Now

$$\frac{v_1}{v_2} = - \left(\frac{1 - \alpha\theta_2}{1 - \alpha\theta_1} \right);$$

hence

$$v_2 \left\{ 1 + \frac{1 - \alpha\theta_2}{1 - \alpha\theta_1} \right\} = \frac{12k\alpha(\theta_2 - \theta_1)}{TL},$$

and

$$\frac{v_2 L}{k} = \frac{12\alpha(1 - \alpha\theta_1)(\theta_2 - \theta_1)}{T(2 - \alpha\theta_1 + \theta_2)};$$

similarly

$$\frac{v_1 L}{k} = \frac{12\alpha(1 - \alpha\theta_2)(\theta_1 - \theta_2)}{T(2 - \alpha\theta_1 + \theta_2)}.$$

The correcting factor equals

$$\begin{aligned} & \frac{\left\{ 1 + \frac{1}{2} \frac{v_1 L}{k} + \frac{1}{12} \frac{v_1^2 L^2}{k^2} \right\} + \left\{ 1 + \frac{1}{2} \frac{v_2 L}{k} + \frac{1}{12} \frac{v_2^2 L^2}{k^2} \right\}}{2} \\ &= 1 + \frac{1}{4} \left(\frac{v_1 L}{k} + \frac{v_2 L}{k} \right) + \frac{1}{24} \left(\frac{v_1^2 L^2}{k^2} + \frac{v_2^2 L^2}{k^2} \right) \\ &= 1 + \frac{3\alpha^2(\theta_2 - \theta_1)^2}{2T} + \frac{3\alpha^2(\theta_2 - \theta_1)^2}{T^2}, \text{ approx.} \end{aligned}$$

As an example, if $(\theta_2 - \theta_1) = 0^\circ.1$ C., $T = 0.1$, and $\alpha = 0.00015$, the correcting factor equals 1.00000007.

When T is a small fraction of unity, as in general will be the case, the correcting factor equals

$$1 + \frac{3\alpha^2(\theta_2 - \theta_1)^2}{T^2}, \text{ approx.}$$

It may be noted that, approximately,

$$v_2 = -v_1 = \frac{12k\alpha(\theta_2 - \theta_1)}{TL}.$$

As an example, let $k = 3 \times 10^{-6}$, $\alpha = 0.00015$, $(\theta_2 - \theta_1) = 0.1$, $T = 0.1$, $L = 4$ cm.

Then

$$\begin{aligned} v_2 &= 1.35 \times 10^{-9} \text{ cm. per second,} \\ &= 0.04 \text{ cm. per year.} \end{aligned}$$

SECTION IV.—Errors due to Changes of Temperature of Apparatus as a whole.

Apart from the effects of any differences of temperature which may exist between the tubes themselves, there will in general be a flow set up along them one way or the other when the apparatus as a whole is heated.

If the upper and lower compartments were of equal volume and the coefficients of expansion and the compressibilities of water and solution were the same, there would be no movement along the tubes; the liquid would simply be compressed slightly. The actual motion could only be calculated from a knowledge of the various coefficients of expansion and the compressibilities. The author has not the data for an accurate calculation, but to give an idea of the order of magnitude of the error, the case will be considered in which the taps of the upper compartment are open.

Let V = volume of lower compartment.

α = coefficient of cubical expansion of liquid.

θ = rise in temperature per second.

It will be assumed that the temperature increases at a constant rate, and that the steady state has been attained.

Let v = velocity *up* the tubes per second.

L = length of each tube.

$$\text{Then } v = \frac{V\alpha\theta}{A}.$$

The quantity of dissolved substance transmitted per second (see Diffusive Convection, Sec. IV.) equals, when VL/k is small,

$$\frac{kAT}{L} \left(1 + \frac{1}{2} \frac{vL}{k} \right) \text{approx.,}$$

$$\text{i. e. } \frac{kAT}{L} \left(1 + \frac{1}{2} \frac{VL\alpha\theta}{Ak} \right).$$

As an example, let the rise of temperature be 2°C. per week; let $\alpha = 0.00015$, $L = 4 \text{ cm.}$, $V = 40 \text{ c.c.}$, $A = 0.4$, and $k = 3 \times 10^{-6}$. Then $VL\alpha\theta/2Ak$ equals 0.033 ; and the error due to the flow produced by the expansion is more than 3 per cent.

It may be mentioned that if a bubble of air is present in the lower compartment, it increases the flow, and the corresponding error, considerably.

Even if the upper taps are not left continuously open, there is an error corresponding to the above; for opening

the top taps will allow a sudden rush to take place up the tubes.

It is obvious that a diminution of temperature produces an error in the opposite direction ; and the error produced by a fluctuating temperature will probably not be considerable in the long run.

SECTION V.—*Errors due to Changes in Volume produced by the Weakening of the Solution through Diffusion.*

In general, when a solution loses some of the dissolved substance by diffusion it diminishes in volume. The diminution depends on the nature of the dissolved substance and varies with the concentration. The diminution for any given loss can be calculated from a table of densities. For example, an aqueous solution of copper sulphate at a temperature of $23^{\circ}\cdot3$ containing 80 grams to the litre has a density of 1.080, whereas a solution containing 160 grams to the litre has a density of 1.154. It can be readily shown that the addition of 1 gram of anhydrous copper sulphate, between the given limits, on the average increases the volume by 0.075 c.c. approx.

As in Section IV. it will be assumed that the upper compartment is open to the atmosphere.

Since the diminution of volume of the lower compartment equals the quantity of copper sulphate transmitted multiplied by 0.075, with the aid of Sec. I. "Diffusive Convection," it can readily be seen that

$$v = \frac{-0.075 \times T \times v}{1 - e^{-\frac{vL}{k}}}.$$

Hence, neglecting the second and higher powers of $\frac{vL}{k}$,

$$\frac{vL}{k} = 0.075 \times T.$$

Let $T = 0.12$, then $\frac{vL}{k} = 0.009$.

The fractional diminution in the quantity transmitted equals $vL/2k$, i.e. 0.0045. Thus the motion along the tubes causes a diminution in the quantity transmitted by about one half per cent.

With salts whose solutions experience greater changes in volume, the error may be very appreciable.

Thus, between the limits of density 1.081 and 1.159, the addition of 1 gram of sodium chloride causes an average

increase in volume of 0.35 c.c. ; and with $T=0.12$, the error would be 2.1 per cent.

It may be noted that when a small quantity of copper sulphate is added to water, the resultant volume is about the same as the original volume of the water. Hence if the lower compartment were left open to the atmosphere instead of the upper one, there would be no error from the cause under consideration.

As before errors are produced when the taps are opened intermittently.

SECTION VI.—*Errors due to Circulations produced when the Liquids of the Upper and Lower Compartments are renewed.*

When the water in the upper compartment is renewed the pressure at the inlet is greater than the pressures at the outlet, and in consequence the pressures at the upper extremities of the tubes are not constant. Hence flows take place up certain tubes and down others.

Let there be n tubes ; and let p_1, p_2 , &c. be the respective *excesses* of the pressures at the tops of the tubes above the *average* pressure. Assuming the attainment of the steady state, and making the usual approximations, it can readily be shown that the correcting factor equals

$$1 + \frac{12}{g^2 T^2 L^2} \left(\frac{p_1^2 + \dots p_n^2}{n} \right).$$

Let p_r be the greatest of the p 's ; then the fractional error is less than $12 p_r^2 / g^2 T^2 L^2$. Neglecting inertia effects, the value of p_r must be less than the difference of pressure between the inlet and outlet, an estimate of which could be made practically. The author has not made any practical measurements, but has made a guess as to the order of magnitude of the difference of pressure by making a crude analogy between the upper compartment and a cylindrical tube. Thus, if 100 c.c. of water pass along a tube 3 cm. in diameter in an hour, the difference of pressure (assuming the formula for a capillary to hold) between two points on the axis 3 centim. apart, if we take the coefficient of viscosity equal to 0.01, is 0.004 dyne. Let $p_r=0.01, T=0.1, L=4$, then the fractional error equals

$$12 \times (0.01)^2 / (981)^2 (0.1)^2 \times 4^2, \text{ or } 7.8 \times 10^{-9}.$$

It is clear that the error from this cause is appreciable.

SECTION VII.—*Error due to Diffusive Convection.*

Inequalities in the lengths of the tubes and inaccuracies in placing them in the diaphragm will, in general, produce convection-currents. There is no intrinsic difficulty in calculating flows of small magnitude, if the tubes are of unequal length; but, to simplify the algebra, in the following the tubes will be taken of equal length and of equal sectional area.

Let n = number of tubes.

δ_1 = distance between the top of one tube and the average of the tops of all the tubes.

δ_r = corresponding distance for the r th tube.

v_1 = velocity up the first tube.

v_r = „ „ „ r th tube.

Making the usual assumptions, it can be shown that

$$\frac{(v_1 - v_r)L^2}{12k} = \delta_r - \delta_1.$$

Noting that $\Sigma v_r = 0$, $\Sigma \delta_r = 0$, it can readily be shown that

$$\frac{v_r L}{k} = \frac{-12\delta_r}{L},$$

and that the correcting factor equals

$$1 + \frac{12}{L^2} \frac{\delta_1^2 + \dots \delta_n^2}{n}.$$

With ordinary care in the construction of the apparatus, the correcting factor will deviate very little from unity.

SECTION VIII.—*Some Experimental Results.*

One apparatus has 15 tubes, of average length 4.043 centim., and a total sectional area 0.4102 square centim. It was placed in a cellar the temperature of which fluctuated through a range of about 3° C. per week. The lower compartment contained a solution of copper sulphate holding 0.0506 of copper to the c.c. At intervals of a week the upper compartment was renewed with pure water; similarly the lower compartment was renewed with fresh solution. The tubes were originally full of pure water. The average temperature was about 8° C. By the end of the first week 0.0026 gram of copper had been transmitted; by the end of the second a total of 0.0077; end of third, 0.0144; end of fourth, 0.0226; end of fifth, 0.0311; end of sixth, 0.0403; end of eighth, 0.0559; end of ninth, 0.0662.

Taking as a basis the quantity transmitted in nine weeks, the coefficient of diffusion equals 28.7×10^{-7} . This result, and others not recorded, indicate that the errors due to the various causes studied are, at any rate, not enormous.

To diminish the variations of temperature, in one experiment the whole apparatus was put inside a copper cylinder; but, unfortunately, some air-bubbles were accidentally allowed to form within the compartments, and the quantities of copper sulphate transmitted were irregular and of large value. At present the author is experimenting with the tubes full of a weak gelatine jelly, with the intention, ultimately, of stopping each tube with a short plug of jelly, and thus preventing circulations of all sorts. The plugs will probably be made insoluble with formaldehyde. Mr. Hibbert has helped me with the analyses, and the results are hopeful; but, as already indicated, progress is inevitably slow.

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LI. *The Application of an Interference-Method to the Investigation of Young's Modulus for Wires, and its Relation to Changes of Temperature and Magnetization; and a further Application of the same Method to the Study of the Change in Dimensions of Iron and Steel Wires by Magnetization.* By G. A. SHAKESPEAR, 1851 Science Scholar, Trinity College, Cambridge*.

MUCH work has been done with the object of elucidating the relation between temperature and elasticity, and more remains to be done.

The problem presents many difficulties, not a few of which arise from the fact that it is not easy to maintain at a constant temperature, more or less high, a sufficient length of the material under investigation. Again, very slight differences of temperature between the wire undergoing traction and the scale on which the alteration of length is measured may easily lead to erroneous results.

These difficulties may be lessened by having the length of wire small; but this involves the necessity of some means of measuring accurately very small changes of length; interference supplies such a means. In the present work it has not been found necessary to go to a higher order of accuracy than $\frac{1}{10}$ of the distance between successive interference-bands of sodium light, which represents a length of about $.000003$ cm.,

* Communicated by Prof. J. J. Thomson, F.R.S.