

A Study of an Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1897 Proc. Phys. Soc. London 16 443

(<http://iopscience.iop.org/1478-7814/16/1/345>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 137.149.200.5

This content was downloaded on 03/09/2015 at 14:51

Please note that [terms and conditions apply](#).

Noting that $a_1 + c = L_1 - b_1$, $a_2 + c = L_2 - b_2$, it can be shown algebraically that

$$W = vA \left\{ \frac{2kqT}{v} + \frac{gTL_2}{1 - e^{-\frac{vL_2}{k}}} - \frac{gTL_1}{1 - e^{-\frac{vL_1}{k}}} + g(b_1 - b_2)T \right\}.$$

This is exactly the same result as that obtained in an earlier section.

General Explanation of the Loss of Heat when Work is done by the Apparatus.

For simplicity let the thickness of the diaphragm be zero.

Transmission of dissolved substance along the tubes is accompanied by a fall of substance in the upper compartment, and a rise of weakened solution in the lower compartment, both of which actions produce heat. The rate of production of heat depends on the rate of flow of the liquid.

The *greater* the rate at which work is done by the apparatus, the less the rate of production of heat.

The rate of absorption of heat due to transmission of dissolved substance through the tubes is independent of the flow, and need not be considered in this general explanation.

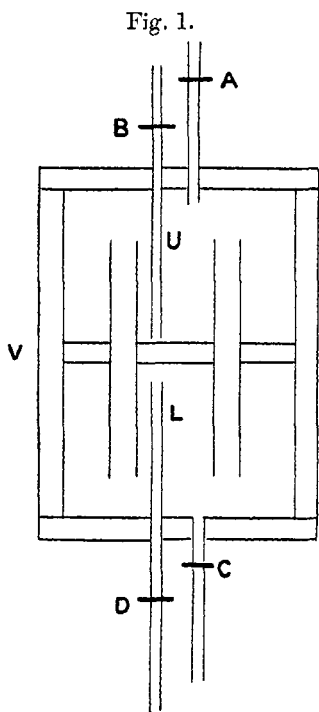
XLIII. *A Study of an Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids.* By
ALBERT GRIFFITHS, *M.Sc.(Vic.), A.R.C.S.(Lond.).**

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.

* Read March 10, 1899.

The apparatus consists of a vessel *V*, divided into two compartments, *U* and *L*, by a diaphragm through which pass a



number of equal vertical tubes of which two only are shown in the figure. Two tubes, *A*, *B*, provided with stop-cocks, pass into *U*. One, *A*, just enters *U*; the other passes down to the bottom. Similarly two tubes *C* and *D* pass into *L*; *C* just enters, and *D* reaches to the top. The vessel is first completely filled with water, and in the case of a substance which produces an aqueous solution with a specific gravity greater than unity, the tubes *A* and *B* are closed, and the solution is passed in through *C*, the water of *L* being allowed to escape through *D*. Diffusion along the vertical tubes now commences, and the compartments *U* and *L* are alternately and periodically refilled with pure water and solution respectively. A quanti-

tative 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 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

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

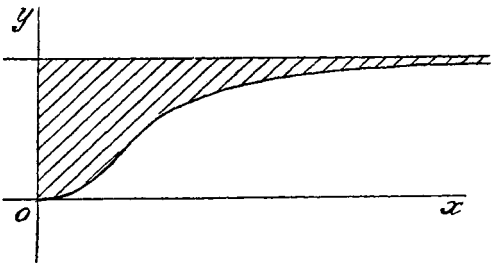
or

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

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

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 $\frac{L^2}{\pi^2 k} \log_e \frac{4}{3} = \cdot2626$ of a week.]

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

The object of this section is to obtain the *order of magnitude* 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,

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

Dividing throughout by g , and expanding,

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

* *Ante*, pp. 230-243; Phil. Mag. Nov. 1898, pp. 453-465.

and

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

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

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

As an example, if $(\theta_2 - \theta_1) = 0.1$ 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.

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,

$$\begin{aligned} &\frac{kAT}{L} \left(1 + \frac{1}{2} \frac{vL}{k} \right) \text{ approx.,} \\ \text{i. e. } &\frac{kAT}{L} \left(1 + \frac{1}{2} \frac{VL\alpha\theta}{Ak} \right). \end{aligned}$$

As an example, let the rise of temperature be 2°C. per week ; let $\alpha=0.00015$, $L=4$ cm., $V=40$ 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 $23^{\circ}.3$ 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

$$12 \times (.01)^2 / (.981)^2 (0.1)^2 \times 4^2, \text{ or } 7.8 \times 10^{-9}.$$

It is clear that the error from this cause is not 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 $\sum v_r = 0$, $\sum \delta_r = 0$, 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.

University College, Sheffield.

DISCUSSION.

THE PRESIDENT described an apparatus he had used for a thermostat. A double-walled cylinder of copper sheet, with a little water in the interspace, is exhausted at atmospheric temperature until the water boils; it is then sealed up. Water-vapour is a powerful equaliser of temperature, and a vapour-jacket of this kind is very efficient when it is required to maintain uniform temperature—not constant temperature.

Mr. WATSON described an arrangement used by Mr. E. H. Griffiths in which tap-water is employed as a negative source and a gas-flame as a positive source—with extremely good results—as a thermostat for constant and for uniform temperatures of about 15° C.

XLIV. *The Joule-Thomson Thermal Effect; its Connexion with the Characteristic Equation, and some of its Thermodynamical Consequences.* By E. F. J. LOVE, M.A., F.R.A.S., Assistant Lecturer and Demonstrator of Natural Philosophy in the University of Melbourne*.

(1) *Introductory.*

THE results obtained by Lord Kelvin and the late Dr. Joule in their famous investigation into the “Thermal Effects of Fluids in Motion” have hitherto been utilized almost exclusively for one special purpose, viz. for determining the relation between various gas-thermometer scales and the absolute scale of temperature. But this is not the only information that can be obtained from them; and the present paper has been written partly in order to deduce some of their further consequences.

This deduction, however, is not the writer’s sole object. He desires to indicate the relation which must exist between the formula assigned to the Joule-Thomson effect, considered as a function of the temperature, and the particular form adopted for the characteristic equation of a gas: in this way it is

* Read February 24, 1899.