Dispersion of soluble matter in solvent flowing slowly through a tube

By Sir Geoffrey Taylor, F.R.S.

When a soluble substance is introduced into a fluid flowing slowly through a small-bore tube it spreads out under the combined action of molecular diffusion and the variation of velocity over the cross-section. It is shown analytically that the distribution of concentration produced in this way is centred on a point which moves with the mean speed of flow and is symmetrical about it in spite of the asymmetry of the flow. The dispersion along the tube is governed by a virtual coefficient of diffusivity which can be calculated from observed distributions of concentration. Since the analysis relates the longitudinal diffusivity to the coefficient of molecular diffusion, observations of concentration along a tube provide a new method for measuring diffusion coefficients. The coefficient so obtained was found, with potassium permanganate, to agree with that measured in other ways.

The results may be useful to physiologists who may wish to know how a soluble salt is dispersed in blood streams.

1. Introduction

If a conducting solution (e.g. brine) is injected into a tube through which water is flowing, the region in which it is concentrated moves downstream. At a fixed point the conductivity will rise as the solution reaches it, and if the conductivity is measured there the conductivity-time curve can be used as a means of measuring the stream velocity. If the injected material would remain concentrated in a small volume the method would be simple, but the stream velocity varies over the cross-section of a pipe. A part of the injected material which was initially near the centre of the tube would be carried to the measuring point faster than parts which were near the walls. To use the method as a means of measuring the mean speed of flow therefore it is necessary to know which point on the conductivity-time curve corresponds to this mean speed. This method has been used to measure the flow in large water mains where it is turbulent (Allen & Taylor 1923) and in small blood vessels where it may be non-turbulent (Stewart 1894; White 1947).

A similar method was used by Griffiths (1911) in experiments designed to measure viscosity of water at very low speeds of flow. A drop of fluorescent solution was inserted as a marker or index in a stream of water flowing slowly through a capillary tube. Griffiths found experimentally that the colouring matter spreads out in a symmetrical manner from a point which moves with the mean velocity of the water in the tube. Since the present paper contains an analysis of the situation observed by Griffiths it is worth quoting his theoretical reasoning on the subject. He wrote (1911, p. 190):

'In this paper the full mathematical treatment is not attempted; but an elementary consideration, although not complete, will be of advantage in dealing with the experiments. It can easily be shown that if the intensity of colour were constant over a cross-section of the tube the colour would diffuse along the tube exactly as if the water travelled in a solid column. The intensity of the colour cannot be absolutely

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constant over a cross-section except in the theoretical case of a capillary tube of infinitely small bore but the experiments show that when the rate of flow is small the error involved in this assumption is not great. By stopping the supply of fluorescent solution and replacing it by water an approximately symmetrical column of colour of slowly increasing length can be obtained and when the slowly moving column is at a relatively long distance from the ends of the fine capillary it is obvious that the movement of the centre of the column must measure the mean speed of flow.'

The foregoing extract shows that Dr Griffiths had formed a good qualitative picture of the situation. The only parts of his statement that do not seem clear are those which follow the words 'It can easily be shown that...' and 'it is obvious that...'. The statement describes two experimental results which seem most remarkable though their discoverer does not comment on them in this sense. The first is that since water moves at twice the mean speed near the centre of the pipe and the patch of colour at the mean speed, the clear water in the middle must approach the colour patch, absorb colour as it passes into it and then lose colour as it passes out, finally leaving the patch as perfectly clear water. The second remarkable feature is that the colour patch spreads out symmetrically from a point which moves with the mean speed of the fluid in spite of the fact that the distribution of velocity over the section, which gives rise to this dispersion, is highly unsymmetrical.

All the authors cited calibrated their apparatus, using other methods for measuring the flow, and thus determined empirically the point on the conductivity-time curve which corresponded with the mean speed of flow. In the present communication the way in which salts are dispersed along a tube through which fluid flows in steady motion will be discussed. In a later paper dispersion by turbulent flow in a pipe will be treated. The dispersion in steady flow is due to the combined action of convection parallel to the axis and molecular diffusion in the radial direction. It is of interest to consider, first, dispersion by convection alone, and then to introduce the effect of molecular diffusion. The results may be useful to physiologists who may wish to know how a soluble salt is dispersed in a blood vessel, but they may also be useful to physicists who wish to measure molecular diffusion coefficients.

2. DISPERSION BY CONVECTION ALONE

In a circular pipe of radius a the velocity u at distance r from the central line is

$$u = u_0(1 - r^2/a^2),\tag{1}$$

where u_0 is the maximum velocity at the axis. If the solute at time $t = 0$ is distributed symmetrically so that the concentration C is

$$C = f(x, r),$$

after time t the concentration will be

$$C = f(x - ut, r).\tag{2}$$

In the experiments to be described later the mean value, C_m, of the concentration over a cross-section of a tube was measured; C_m is defined by

$$C_m = \frac{2}{a^2} \int_0^a Cr\,\mathrm{d}r.\tag{3}$$

Some calculated distributions of C_m along a tube are given below. They will be needed later for comparison with experiments.

Case A 1

Initially the space between two planes $x = 0$ and $x = X$ (X/a being small) is filled with solute of concentration C_0. From (2) it will be seen that the amount which lies between r and $r + \delta r$ is constant during the flow and equal to $2\pi r C_0 X \delta r$. The solute will be distorted in time into the paraboloid

$$x = u_0 t(1 - r^2/a^2). \tag{4}$$

The total amount of the solute between x and $x + \delta x$ is therefore $2\pi r C_0 X \dfrac{dr}{dx}\delta x$,

and from (4) $\dfrac{r\,dr}{dx} = -\dfrac{a^2}{2u_0 t}$, so that

$$C_m = \frac{1}{\pi a^2 \delta x} 2\pi C_0 X \,\delta x \,\frac{a^2}{2u_0 t} = \frac{C_0 X}{u_0 t}. \tag{5}$$

C_m therefore has the constant value $C_0 X/u_0 t$ in the interval $0 < x < u_0 t$ and is zero when $x < 0$ and when $x > u_0 t$.

Case A 2

Solute of constant concentration enters a tube which at time $t = 0$ contains only solvent.

Here
$$\left.\begin{array}{ll} C = C_0, & x < 0 \\ C = 0, & x > 0 \end{array}\right\} \quad \text{at time } t = 0.$$

This case can be solved by imagining that the constant initial concentration for $x < 0$ consists of a number of thin sections of the type imagined in case A 1. In this way it is found that

$$\left.\begin{array}{l} C_m = C_0, \quad x < 0, \\[2mm] C_m = C_0\!\left(1 - \dfrac{x}{u_0 t}\right), \quad 0 < x < u_0 t, \\[2mm] C_m = 0, \quad x > u_0 t. \end{array}\right\} \tag{6}$$

Case A 3

Solute confined initially to a length X so that

$$\left.\begin{array}{ll} C = 0, & x < 0 \\ C = C_0, & 0 < x < X \\ C = 0, & x > X \end{array}\right\} \quad \text{at time } t = 0.$$

This case can be obtained by superposing two examples of case A 2, namely

$$\left.\begin{array}{ll} C = C_0, & x < X \\ C = 0, & x > X \end{array}\right\} \quad \text{and} \quad \left.\begin{array}{ll} C = -C_0, & x < 0, \\ C = 0, & x > 0. \end{array}\right\}$$

If $t < X/u_0$ the distribution is described by (7)

$$\left.\begin{array}{l} C_m = 0, \quad x < 0, \\[1mm] C_m = C_0 x/u_0 t, \quad < x < u_0 t, \\[1mm] C_m = C_0, \quad u_0 t < x < X, \\[1mm] C_m = C_0\!\left(1 - \dfrac{x - X}{u_0 t}\right), \quad X < x < X + u_0 t, \\[1mm] C_m = 0, \quad x > X + u_0 t. \end{array}\right\} \tag{7}$$

If $t > X/u_0$, it is given by (8)

$$\left.\begin{aligned}
C_m &= 0, \quad x < 0, \\
C_m &= C_0(x/u_0 t), \qquad 0 < x < X, \\
C_m &= C_0(X/u_0 t), \quad X < x < u_0 t, \\
C_m &= C_0\left(\frac{X + u_0 t - x}{u_0 t}\right), \quad u_0 t < x < u_0 t + X, \\
C &= 0, \quad x > X + u_0 t.
\end{aligned}\right\} \tag{8}$$

These three cases are illustrated in figure 1. It will be noticed that A 1 is a limiting case of A 3 when X is small.
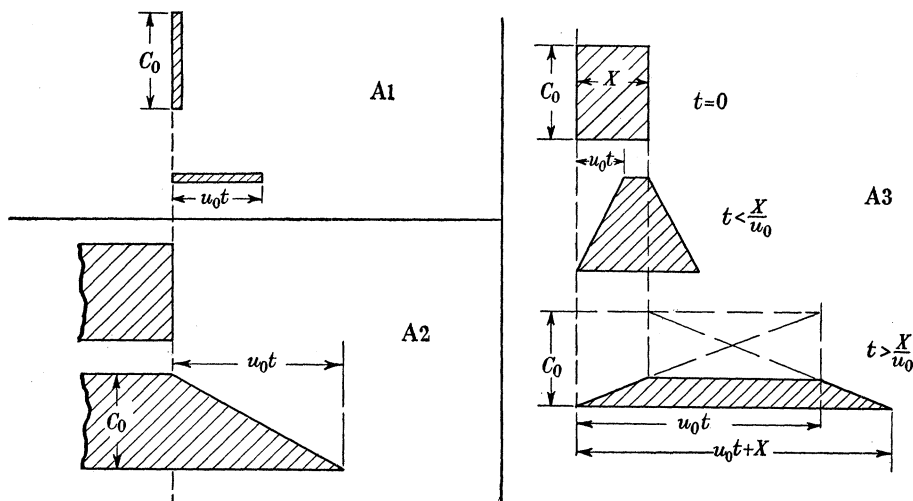

FIGURE 1. Distribution of mean concentration in three cases in absence of molecular diffusion.

3. EFFECT OF MOLECULAR DIFFUSION ON THE DISPERSION

It will be assumed that the concentration is symmetrical about the central line of the pipe so that C is a function of r, x and t only. The equation for diffusion is

$$D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x^2}\right) = \frac{\partial C}{\partial t} + u_0\left(1 - \frac{r^2}{a^2}\right)\frac{\partial C}{\partial x}. \tag{9}$$

Here D, the coefficient of molecular diffusion, will be assumed independent of C. This is not a strictly accurate assumption when the formulae are to be applied to soluble salts, but the error introduced by it is not large, and if this assumption is not made the analysis of problems of diffusion becomes difficult. In all the cases which will be considered $\partial^2 C/\partial x^2$ is much less than $\partial^2 C/\partial r^2 + r^{-1}\partial C/\partial r$.

Writing
$$z = r/a, \tag{10}$$

(9) becomes

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{z}\frac{\partial C}{\partial z} = \frac{a^2}{D}\frac{\partial C}{\partial t} + \frac{a^2 u_0}{D}(1 - z^2)\frac{\partial C}{\partial x}. \tag{11}$$

The boundary condition which expresses the fact that the wall of the tube is impermeable is

$$\frac{\partial C}{\partial z} = 0 \quad \text{at} \quad z = 1. \tag{12}$$

It would be difficult to find a complete solution of (11) giving the value of C for all values of r, x and t when the distribution of C at time $t = 0$ is known; on the other hand, approximate solutions can be found which are valid in the following limiting conditions:

(A) The changes in C due to convective transport along the tube take place in a time which is so short that the effect of molecular diffusion may be neglected. The solutions already given in §2 are of this type.

(B) The time necessary for appreciable effects to appear, owing to convective transport, is long compared with the 'time of decay' during which radial variations of concentration are reduced to a fraction of their initial value through the action of molecular diffusion.

To find the conditions under which B may be expected to be valid it is necessary to calculate how rapidly a concentration which varies with r degenerates into a uniform concentration. The solutions of (11) for which $\partial C/\partial x = 0$ and the variables z and t are separated are of the form

$$C = e^{-\alpha t} J_0(az\alpha^{\frac{1}{2}}D^{-\frac{1}{2}}), \tag{13}$$

where $J_0(az\alpha^{\frac{1}{2}}D^{-\frac{1}{2}})$ is the Bessel function of zero order. The boundary condition (12) ensures that

$$J_1(a\alpha^{\frac{1}{2}}D^{-\frac{1}{2}}) = 0. \tag{14}$$

The root of (14) corresponding with the lowest value of α is $a\alpha^{\frac{1}{2}}D^{-\frac{1}{2}} = 3\cdot8$, so that the time necessary for the radial variation of C represented by (13) to die down to $1/e$ of its initial value is

$$t_1 = \frac{a^2}{(3\cdot8)^2 D}. \tag{15}$$

If at any time the dispersing material is spread over a length of tube of order L, the time necessary for convection to make an appreciable change in C is of order L/u_0, so that in order that the limiting condition B may be applicable

$$\frac{L}{u_0} \gg \frac{a^2}{3\cdot8^2 D}. \tag{16}$$

4. Effect of using condition (B) in (11)

Since molecular diffusion in the longitudinal direction has been neglected (the justification for this will be given later) the whole of the longitudinal transfer of C is due to convection. We shall consider the convection across a plane which moves at constant speed $\frac{1}{2}u_0$, i.e. with the mean speed of flow. Writing

$$x_1 = x - \tfrac{1}{2}u_0 t, \tag{17}$$

(11) becomes
$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{z}\frac{\partial C}{\partial z} = \frac{a^2}{D}\frac{\partial C}{\partial t} + \frac{a^2 u_0}{D}(\tfrac{1}{2} - z^2)\frac{\partial C}{\partial x_1}. \tag{18}$$

Since the mean velocity across planes for which x_1 is constant is zero, the transfer of C across such planes depends only on the radial variation of C. If C were independent of x and condition (B) satisfied, it has been seen that any radial variation in C very rapidly disappears. The small radial variation in C can therefore be calculated from the equation

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{z}\frac{\partial C}{\partial z} = \frac{a^2 u_0}{D}(\tfrac{1}{2} - z^2)\frac{\partial C}{\partial x_1}, \tag{19}$$

and in that calculation $\partial C/\partial x_1$ may be taken as independent of z.

A solution of (19) which satisfies the condition $\partial C/\partial z = 0$ at $z = 1$ is

$$C = C_{x_1} + A(z^2 - \tfrac{1}{2}z^4), \tag{20}$$

where C_{x_1} is the value of C at $z = 0$ and A is a constant.

Substituting (20) in (19) it is found that

$$A = \frac{a^2 u_0}{8D}\frac{\partial C}{\partial x_1}. \tag{21}$$

The rate of transfer of C across the section at x_1 is

$$Q = -2\pi a^2 \int_0^1 u_0(\tfrac{1}{2} - z^2)\,Cz\,dz. \tag{22}$$

Inserting the value of C from (20) and (21), (22) becomes

$$Q = -\frac{\pi a^4 u_0^2}{192D}\frac{\partial C_{x_1}}{\partial x_1}. \tag{23}$$

Since condition (B) is assumed to hold the radial variations in C are small compared with those in the longitudinal direction, and if C_m is the mean concentration over a section $\partial C_{x_1}/\partial x_1$ is indistinguishable from $\partial C_m/\partial x_1$, so that (23) may be written

$$Q = -\frac{\pi a^4 u_0^2}{192D}\frac{\partial C_m}{\partial x_1}. \tag{24}$$

It will be seen therefore that C_m is dispersed *relative to a plane which moves with velocity* $\tfrac{1}{2}u_0$ exactly as though it were being diffused by a process which obeys the same law as molecular diffusion but with a diffusion coefficient k, where

$$k = \frac{a^2 u_0^2}{192D}. \tag{25}$$

The fact that no material is lost in the process is expressed by the continuity equation for C_m, namely

$$\frac{\partial Q}{\partial x_1} = -\pi a^2 \frac{\partial C_m}{\partial t}, \tag{26}$$

where the symbol $\partial/\partial t$ here represents differentiation with respect to time at a point where x_1 is constant. Substituting for Q from (24) the equation governing longitudinal dispersion is

$$k\frac{\partial^2 C_m}{\partial x_1^2} = \frac{\partial C_m}{\partial t}. \tag{27}$$

5. Special cases

Two well-known solutions of (27) describe dispersion in cases which can conveniently be subjected to experimental verification. These are:

(B 1) Material of mass M concentrated at a point $x = 0$ at time $t = 0$.

(B 2) Dissolved material of uniform concentration C_0 allowed to enter the pipe at uniform rate at $x = 0$ starting at time $t = 0$. Initially the pipe is filled with solvent, only ($C = 0$).

Cases B 1 and B 2 correspond to cases A 1 and A 2 in §2, except that the molecular diffusion in the latter case was assumed to have only a negligible effect.

The solutions of (27) are:

Case (B 1):
$$C = \tfrac{1}{2} M a^{-2} \pi^{-\frac{3}{2}} k^{-\frac{1}{2}} t^{-\frac{1}{2}} e^{-x_1^2/4kt}. \tag{28}$$

Case (B 2):
$$
\begin{aligned}
C/C_0 &= \tfrac{1}{2} + \tfrac{1}{2} \operatorname{erf} \left(\tfrac{1}{2} x_1 k^{-\frac{1}{2}} t^{-\frac{1}{2}} \right) \quad (x_1 < 0), \\
C/C_0 &= \tfrac{1}{2} - \tfrac{1}{2} \operatorname{erf} \left(\tfrac{1}{2} x_1 k^{-\frac{1}{2}} t^{-\frac{1}{2}} \right) \quad (x_1 > 0),
\end{aligned}
\tag{29}
$$

where
$$\operatorname{erf} z = 2\pi^{-\frac{1}{2}} \int_0^z e^{-z^2}\, \mathrm{d}z.$$

In case (B 1) the length L_1 which contains 90 % of the material is given by $\operatorname{erf} \left(\tfrac{1}{4} L_1 k^{-\frac{1}{2}} t^{-\frac{1}{2}} \right) = 0 \cdot 9$ and using tables this gives

$$L_1 = 4 \cdot 65 k^{\frac{1}{2}} t^{\frac{1}{2}}. \tag{30}$$

If $C_{\max.}$ is the maximum concentration at $x = \tfrac{1}{2} u_0 t$ the concentration at the ends of the length L is
$$0 \cdot 3126 C_{\max.}. \tag{31}$$

Similarly, in case (B 2), if L_2 is the length of the zone of transition in which C changes from $0 \cdot 9 C_0$ to $0 \cdot 1 C_0$ $\operatorname{erf} \left(\tfrac{1}{4} L_2 k^{-\frac{1}{2}} t^{-\frac{1}{2}} \right) = 0 \cdot 8$, and from tables

$$L_2 = 3 \cdot 62 k^{\frac{1}{2}} t^{\frac{1}{2}}. \tag{32}$$

It will be noticed that as t increases both L_1 and L_2 increase proportionally to $t^{\frac{1}{2}}$, whereas the distance traversed by the particles of fluid are proportional to t. Eventually as t increases L_1 and L_2 will become small compared with $\tfrac{1}{2} u_0 t$. In case (B 1) this means that in the central part of the pipe fluid which is free of the dissolved substance passes into the zone where the concentration is rising. The dissolved substance is then absorbed till C reaches its maximum value at $x = \tfrac{1}{2} u_0 t$. The fluid then passes through the region where C decreases with x and finally leaves this zone, having yielded up the whole of the dissolved substance which it had acquired. Analogous considerations apply to case B 2.

This theoretical conclusion seemed so remarkable that I decided to set up apparatus to find out whether the predictions of the analysis could be verified experimentally. Since making these experiments Professor G. Temple, F.R.S., has called my attention to those of Griffiths (1911), in which it was shown, incidentally, that the phenomenon predicted does occur. Griffiths however was not concerned with describing it, but with the fact that it could be used for measuring slow flow.

6. Experimental technique

In order to satisfy the condition (B) of §3 it was necessary to use a tube of small bore. Two methods seemed suitable for determining C. If the dissolved substance is a good electrical conductor and the solvent (water) a bad one the conductivity can be determined as a function of time at the exit end of the pipe. This method had been used by several workers for determining the velocity of the blood stream in the arteries or veins of a living animal. It has also been used by engineers for determining the velocity in the large pipes which convey water to hydro-electric stations. It could not be used to determine C_m as a function of x at a fixed time. For this reason a colorometric method was devised which made it possible to do this without disturbing the fluid. The dissolved substance was potassium permanganate which is very strongly coloured. The pipe was a glass tube of approximately 0·05 cm internal diameter and 152 cm long. The initial concentration of the solution was 1 % by weight
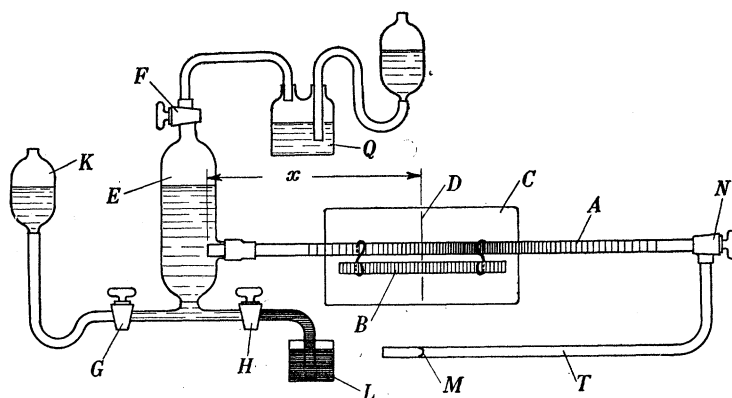

FIGURE 2. Apparatus set up with experimental tube horizontal.

of potassium permanganate and 99 % of slightly acidulated water. This is so dark that it looks almost black when seen in a bottle, but in a pipe of 0·05 cm bore it is a transparent dark purple. A number of solutions of known concentrations were made by mixing the 1 % solution with various proportions of distilled water. A glass comparison tube of the same external and internal bore as the flow tube was prepared and filled successively with fluid of varying known concentrations. The comparison tube was placed in a light frame which could slide along the pipe and the position where the colours of the comparison tube and pipe were identical was found. Thus x was determined as a function of C. This method had the advantage that comparisons were made only between colours whose spectrum and intensity were both identical at the determined position. No question arose as to how the intensity of colour varies with concentration.

The apparatus is shown diagrammatically in figure 2. A is the pipe, B is the comparison tube. C is a ground-glass plate illuminated as uniformly as possible by means of a mirror which reflects either daylight or light from an electric bulb. D is a line ruled on C. To make a measurement B is filled with solution of known concentration and moved till the colour intensity is about the same as that in the pipe

near its mid-point. The ground-glass plate C is then moved till the line D appears to cross the two tubes A and B at the point where their colours are identical. The distance x of the line D from the entry end of the pipe is then measured with a scale.

The flow through the pipe is controlled by a needle valve N or with a small bore capillary used as a leak at the exit end. The entry end projects into a glass chamber E out of which lead three tubes with glass taps F, G, H. F is connected with a vessel Q by means of which pressure or suction can be applied. G is connected by a flexible tube to a funnel K filled with distilled water. H leads to a small tube which dips into a vessel, L, containing 1 % solution of $KMnO_4$.

The flow tube and chamber E are first washed with distilled water. Then leaving the pipe full and the valve N closed, the water is drained out through H and the chamber refilled with 1 % solution of $KMnO_4$. A pressure is then applied to the liquid in E. The valve N is then opened slightly and a stop-watch started. When the front of the coloured column is approaching the exit end of the pipe the needle valve is closed. It was found, as had been expected, that the molecular diffusion in the longitudinal direction was so small that no appreciable change in colour at a fixed spot occurs in several hours after the closing of N. The values of x corresponding with all the prepared comparison samples were then determined in the manner already described.

This procedure was used for comparison with case (B 2), §5. For case (B 1) the needle valve was opened for a short time to allow a little of the $KMnO_4$ solution to enter. It was then closed and the chamber E washed out and filled with water. The experiment was then performed in the same way as in case (B 2).

To measure the mean speed of the fluid and also to know at what moment the valve should be closed the water which flowed through the needle valve entered a second pipe T in which the motion of the meniscus M in front of the water column could be observed and measured.

A 1 % solution of $KMnO_4$ was prepared and parts of it were diluted so as to form solutions with the following proportions by weight of $KMnO_4$, $10^{-4} \times 1, 2, 3, 4, 6, 8,$ 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100. The last is simply the 1 % solution.

7. EXPERIMENTAL RESULTS

The first experiments were designed to verify the conclusions of §2 when the effect of molecular diffusion is negligible. For this purpose it was necessary to carry them out so that the flow started and finished in a time small compared with $a^2/3 \cdot 8^2 D$. Since, for $KMnO_4$ in water, D is of order $0 \cdot 7 \times 10^{-5}$, $a^2/3 \cdot 8^2 D$ is $6 \cdot 2$ s for a tube $0 \cdot 5$ mm bore and 25 s for a tube 1 mm bore. For the first experiments a tube of approximately 1 mm bore was chosen.

Case A 2

To verify experimentally the distribution of C_m predicted in equation (6) and illustrated in A 2, figure 1, the reservoir E (figure 2) was filled with the 1 % solution and the experimental tube with water. The valve N was opened for about $1\frac{1}{2}$ s and then closed. In this time the colour had travelled 65 cm along the tube. The comparison tube was filled successively with the standard solutions and the corre-

sponding distances x were measured. The results are given in table 1. These are plotted as A 2 in figure 3. It will be seen that the experimental points lie very well on the line which was predicted in equation (6).
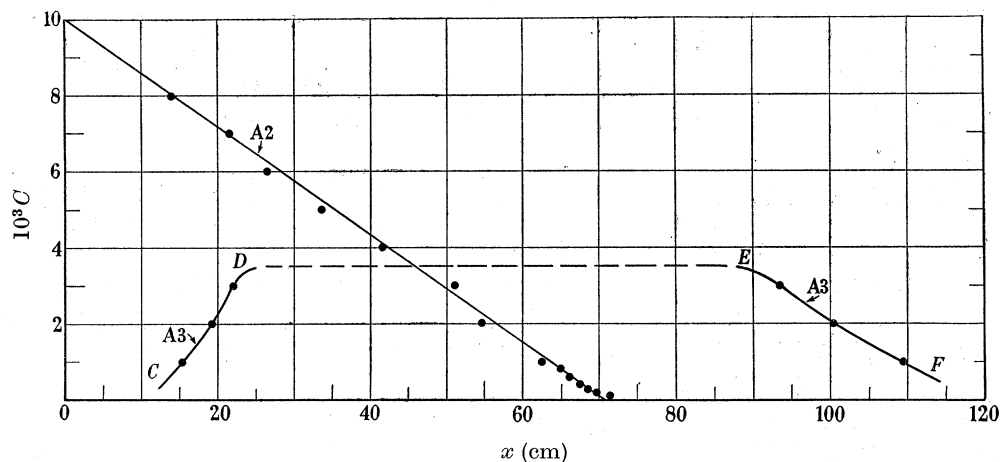

FIGURE 3. Measurements of concentration when dispersion occurred in $1\frac{1}{2}$ s.

Cases A 1 *and A* 3

To verify the distributions calculated in equations (5) and (7), the flow tube was filled with water and the reservoir with 1 % $KMnO_4$. The valve was opened for an instant and a few centimetres of the tube thus filled with the solution. The reservoir was then washed out several times with water. The valve N was then again opened and closed after about $1\frac{1}{2}$ s. The coloured column thus formed appeared to be of

TABLE 1

type of experiment	A 2 (figure 3) $t = 1\frac{1}{2}$ s $a = 0\cdot05$ cm	A 3 (figure 3) $t = 1\frac{1}{2}$ s $a = 0\cdot05$ cm
concentration, $10^4 C$ (g/ml.)	$C_0 = 0\cdot01$ x (cm)	x (cm)
1	71·2	15·5 and 109·2
2	69·7	19·3 and 100·3
3	68·5	22·0 and 93·4
4	67·5	—
6	66·0	—
8	64·7	—
10	62·5	—
15	—	—
20	54·5	—
30	51·0	—
40	41·7	—
50	33·5	—
60	26·5	—
70	21·5	—
80	14·0	—
90	—	—

uniform intensity over most of its length. The colorometric measurements given in table 1 were then made. They are shown as A 3 in figure 3. It will be seen that the concentration rises between $x = 10$ to $x = 22$ cm from $C = 0$ to $C = 0 \cdot 0003$. From $x = 22$ to $x = 93$ cm its colour was so nearly uniform that it was not possible to detect any variation in C. In this range C was between $0 \cdot 0003$ and $0 \cdot 0004$. This is represented in figure 3 by the broken line at $C = 0 \cdot 00035$. This experimental result is in good agreement with the prediction of equation (7) which is illustrated as A 3 in figure 1.

It will be noticed that the calculation for the case A 3 assumed that a section of length X is filled initially with solution of uniform concentration. The time which elapsed between the introduction of the permanganate and turning of the valve N was long enough to ensure that the concentration over every section was uniform when the flow started. It was not uniform along the tube as is assumed in the calculation, but this lack of uniformity would make no difference to the uniformity of the concentration of the long middle portion of the curve A 3 in figure 3. It would merely make the sloping ends CD, EF figure 3 curved instead of straight as they would be if the initial distribution of concentration were uniform (see A 3 figure 1).

8. Effect of molecular diffusion

Case B 2

In order that condition B of § 3 may be satisfied it is necessary that the time of the flow shall be long compared with $a^2/3 \cdot 8^2 D$. To attain this the 1 mm tube was replaced by one of diameter $0 \cdot 0504$ cm and the needle valve was opened so little that the flow was only a small fraction of a centimetre per second. In the first experiments of this type the conditions were those of case A 2, § 2, except for the reduction in flow. In one case the flow was so slow that it took over 3 h to carry the colour 30 cm. The results of four experiments which ran for 4, 12, 240 and 11 220 s are given in

Table 2. Experiments of type B 2

time of flow (sec) ...	about 4	12	240	11 220
$\frac{1}{2}u_0 t$ (cm) ...	33	80	63·2	31·9
concentration, $10^4 C$ (g/ml.)	x (cm)			
1	63·5	134	80·4	34·75
2	62·4	129	79·5	34·4
4	58·5	120·4	77·0	34·0
6	56·4	117	76·0	33·85
8	55·0	114·5	75·0	33·70
10	53·1	111	74·0	33·65
20	47·8	101	71·1	33·0
30	44·4	93	68·0	32·55
40	40·0	89	66·7	32·4
50	33·8	82	63·8	31·7
60	29·5	73	60·5	31·4
70	24·0	63	58·0	31·3
80	17·4	56	53·7	30·8
90	11·6	41·0	45·0	30·0
100	—	—	—	—

table 2. To compare the observed distribution of C with that calculated theoretically the values of C/C_0 for the case when $t = 11\,220\,\text{s}$ are plotted in figure 4. Taking $\frac{1}{2}u_0t = 31 \cdot 9\,\text{cm}$, the value of x_1 in (29) is $x - 31 \cdot 9$. The value of $(4kt)^{-\frac{1}{2}}$ which gives best agreement with observations is $(4kt)^{-\frac{1}{2}} = 0 \cdot 552$. The curve

$$\frac{C}{C_0} = \tfrac{1}{2} \pm \operatorname{erf}\{0 \cdot 552(x - 31 \cdot 9)\} \tag{33}$$

is shown in figure 4. It will be seen that the observed points fall very closely on the curve.
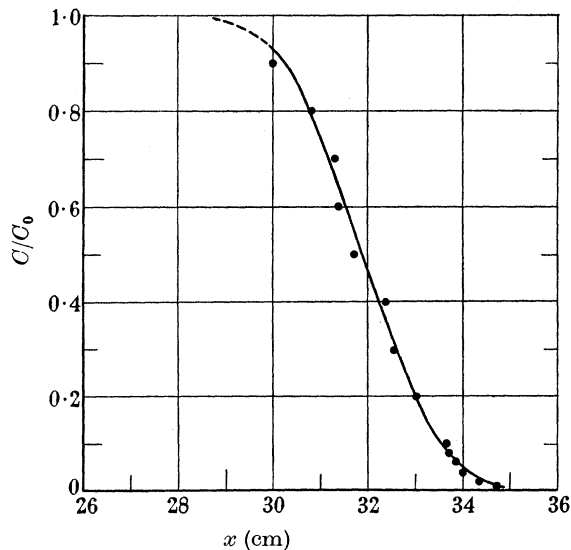

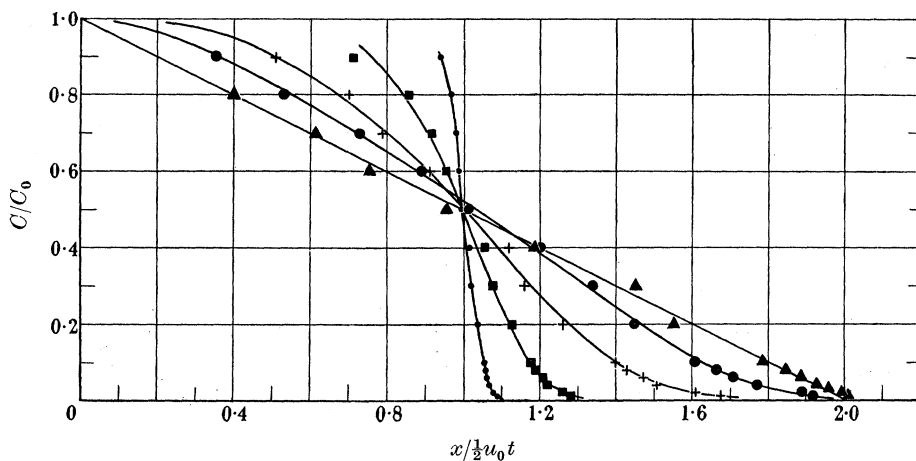FIGURE 4. Comparison between measured and theoretical distribution of concentration, $t = 11\,220$ s.

FIGURE 5. Distributions of concentration about point $x = \frac{1}{2}u_0t$.

symbol	•	■	+	●	▲
t (sec)	11 220	240	12	4	$1\frac{1}{2}$

To demonstrate the effect of molecular diffusion on the distribution of concentration in the transition zone between clear water and the solution the observed values of C/C_0 are plotted against $x/\frac{1}{2}u_0 t$ in figure 5. The strong tendency for molecular diffusion to prevent dispersion along the tube is shown very clearly. The limiting distribution as t tends to 0 is shown and the observed points for $t = 1\frac{1}{2}$ s have been transferred from figure 3.

Case B1. Dispersion of material initially concentrated in a small volume.

The initial experimental conditions were those described for case A3 and the experiments were performed in the same way except that the duration of the flow was long compared with $a^2/3\cdot8^2 D$. In the first experiment, 1 % solution was admitted and after filling the vessel E (figure 2) with water the flow was run for 5 min during which time the point of maximum concentration moved to $x = 52\cdot5$ cm. The measured positions of the standard concentrations are given in table 3 and shown

TABLE 3. EXPERIMENTS OF TYPE B1

	figure 6		figure 7		figure 8					
duration, t (sec)	300		660		1740		2160		330	
$\frac{1}{2}u_0 t$ (cm)	52·5		110		58		$94-58=36$		$122\cdot5-94=28\cdot5$	
middle of colour (cm)	52·5		110		58		94		122·5	
$10^4 C$ (g/ml.)	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
1	39·2	72·4	91·2	131·1	50·7	66·8	83·9	104·2	109·8	135·0
2	39·7	70·9	92·1	128·3	51·0	66·2	84·6	103·1	111·2	134·0
4	41·0	69·5	94·7	125·9	51·6	65·2	85·2	102·6	112·3	132·4
6	42·0	68·1	95·3	124·7	52·2	64·7	85·8	101·8	113·2	131·6
8	42·5	68·1	96·0	124·3	52·4	64·1	86·3	101·2	113·7	130·9
10	43·2	67·1	96·5	122·7	52·7	63·7	87·2	100·8	114·5	129·9
20	44·2	65·2	99·8	120·1	53·5	62·6	88·0	99·2	116·6	127·3
30	46·0	63·0	104·4	115·6	54·6	62·0	85·5	98·7	118·2	124·0
40	48·0	59·8	107 to 113		54·9	60·9	89·9	97·0	120 to 123	
50	47·0	57·0	—	—	55·1	59·6	—	94·3	—	—
60	50·5	54·5	—	—	56·2	59·2	—	—	—	—

in figure 6. It will be seen that the (C, x) curve is not symmetrical. It seemed probable that this was due to the asymmetry of the initial distribution. Since the 1 % solution of $KMnO_4$ was introduced rapidly the initial distribution of C_m must have been triangular starting with $C_m = 0\cdot01$ at $x = 0$ and decreasing linearly (as in case A2, figure 1). By measuring the area of the curve of figure 6 the total amount of $KMnO_4$ was found to be $\pi a^2(0\cdot01)(10\cdot5)$. The initial length of the column must therefore have been $2 \times 10\cdot5 = 21$ cm. The initial distribution deduced in this way is shown in figure 6. It will be seen that the molecular diffusion has had the effect of clearing the $KMnO_4$ out of the first 39 cm, but the dispersion has not been great enough to eliminate the asymmetrical shape of the initial distribution which covered nearly two-thirds of the length of the dispersed distribution.

Since one of the remarkable predictions of the analysis of §5 was that an initially concentrated mass would be dispersed symmetrically about the point $x = \frac{1}{2}u_0 t$ in spite of the great asymmetry of the distribution of velocity over cross-sections, the experiment was repeated, introducing a small volume of more concentrated solution

and increasing $\frac{1}{2}u_0 t$ to 110 cm. The results are given in table 3 and are plotted in figure 7. It will be seen that the distribution of concentration about $x = 110$ cm is very symmetrical.

To compare these experimental results with the theoretical prediction of equation (28), the error curve

$$C = 0.0041\, e^{-(x-110)^2/121} \tag{34}$$

is shown in figure (7). The constants in (34) have been chosen so that the error curve is as near to the experimental points as possible.
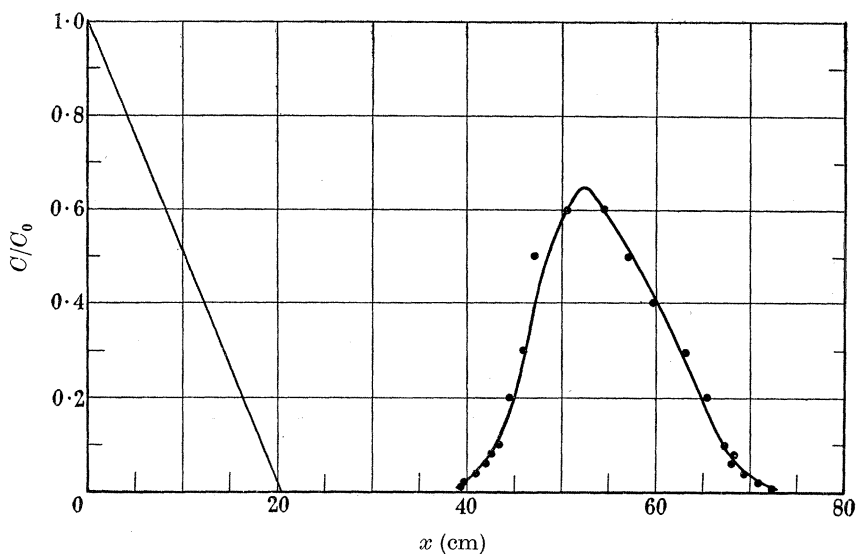

FIGURE 6. Initially asymmetrical distribution of concentration which has not yet become symmetrical.
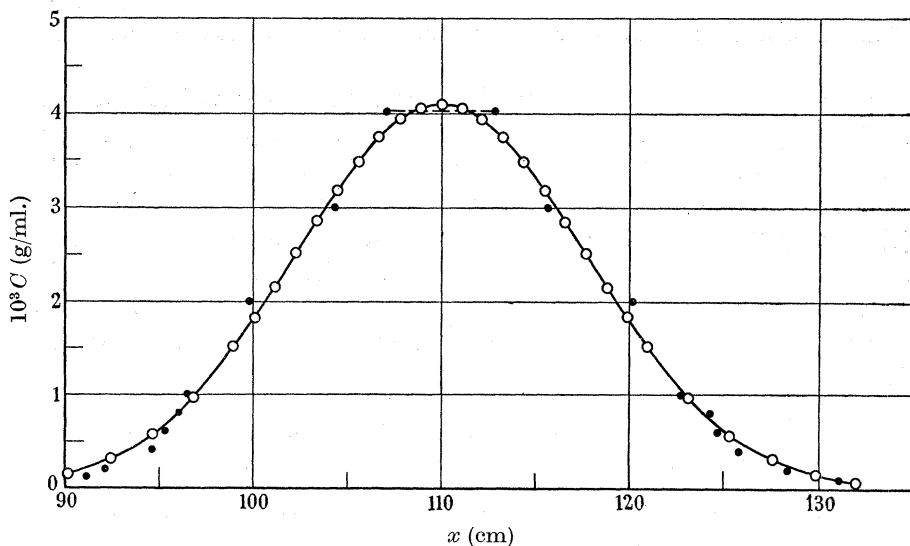

FIGURE 7. Initially asymmetrical distribution which has become symmetrical owing to dispersion. ○, $C = 0.0041 \exp\{-(110-x)^2/121\}$; •, experiment; time = 11 min.

Another set of measurements is shown in figure 8. The apparatus was set going first for 29 min when the needle-valve was shut and the measurements shown in curve I were obtained. The valve was then opened, unfortunately a little too far, the column of colour was seen to be moving rather rapidly along the tube so it was shut down till a slow movement was obtained. After 36 min it was again closed and the measurements shown in curve II were made. It was then opened again and closed down after a further period of $5\frac{1}{2}$ min. The measurements shown in curve III were then obtained.
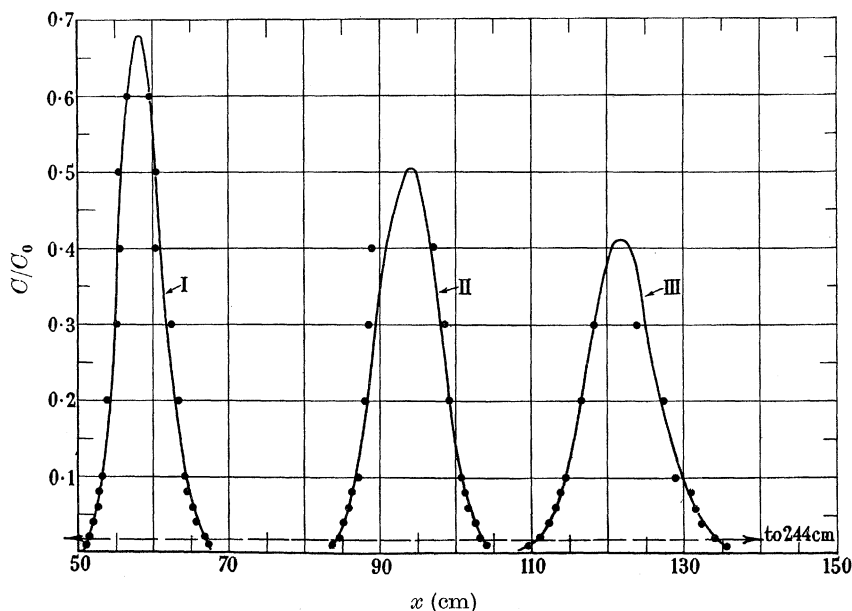

FIGURE 8. Distributions of concentration at three stages of dispersion. Broken line shows distribution in the absence of molecular diffusion for comparison with curve III.

The very great effect of molecular diffusion in preventing a dissolved substance from being dispersed can be appreciated by comparing the concentration shown in curve III, figure 8, with what it would have been if there had been no diffusion and the dissolved substance had been dispersed convectively and therefore uniformly (see (5)) through $2 \times 122 = 244$ cm of the tube. The total amount of dispersed material can be found by measuring the area of curve III. If this were distributed uniformly along 244 cm the concentration would have been only $0 \cdot 018 \, C_0$. This may be compared with the observed maximum concentration shown in curve III, namely, $0 \cdot 4 \, C_0$.

9. CALCULATION OF MOLECULAR DIFFUSION COEFFICIENT FROM MEASUREMENTS OF LONGITUDINAL DIFFUSIVITY

The work was undertaken to find out how a soluble substance is dispersed when injected into a stream of solvent flowing through a tube. The idea that it might form a basis for a simple method of measuring coefficients of molecular diffusion was not in my mind when the experiments were carried out. For that reason, the conditions

necessary for that purpose were not in all cases satisfied. For instance, in the experiments illustrated in figure 8, in the first two runs which carried the mean position of the colour to $x = 94$ cm, no precautions were taken to ensure the constancy of the flow. The last run which carried the colour to $x = 122\cdot5$ cm in $5\frac{1}{2}$ min was checked for constancy so that it can be used. The experiment illustrated in figure 7 can be used because the spread is large compared with the length of column which would contain the whole of the dispersing salt at its initial concentration. Of the experiments given in table 2 only the one taking 240 s can be used. The first two must be rejected because the duration of flow (4 and 12 s) was too short for the theory to be applicable. The last experiment taking 11 220 s can hardly be expected to give an accurate result because when the tube is horizontal the effect of gravity acting on the slight difference in density between the 1 % solution and pure water is to increase the rate of longitudinal dispersion. This effect will be discussed in a subsequent paper on the combined effect of gravity and diffusion in which it will be shown that errors are to be expected when the time of diffusion is of order 10^4 s but are small when t is of order 10^3 s under the conditions of the experiments here described.

To use the experiments of type B 2 to measure the diffusion coefficient D it is necessary to choose the parameter $(4kt)^{-\frac{1}{2}}$ in equation (29) so that the theoretical curve passes as nearly as possible through the observed points. This has been done for the case where $t = 11\,220$ s (figure 4). Applying the same method to the case given in column 4 of table 2 where $t = 240$ s, the expression which gives the best fit is

$$\frac{C}{C_0} = \tfrac{1}{2} \pm \ \text{erf}\,\{0\cdot0828(x-63)\}, \tag{35}$$

so that $4kt = 960k = (0\cdot0828)^{-2}$ and $k = 0\cdot152$. The mean velocity is

$$\tfrac{1}{2}u_0 = 63 \ \text{cm}/240\,\text{s},$$

so that $u_0 = 0\cdot524$ cm/s. Using (25) and remembering that $a = 0\cdot0252$ cm,

$$D = \frac{(0\cdot524)^2\,(0\cdot0252)^2}{(192)\,(0\cdot152)} = 0\cdot60 \times 10^{-5} \ \text{c.g.s. unit}. \tag{36}$$

To use experiments of type B 1 the most accurate method would be to produce an error law distribution of concentration by running the apparatus for a time and then stopping it and making measurements. The flow would then be started again, run for a measured time and stopped again. If the curve fitted to the first set of observations is

$$C = A_1\,\text{e}^{-\beta_1(x-X_1)^2} \tag{37}$$

and the second is

$$C = A_2\,\text{e}^{-\beta_2(x-X_2)^2}, \tag{38}$$

the fact that the same amount of the dispersed substance is present on both occasions leads to the condition that (37) and (38) have the same area, so that

$$\frac{\beta_2}{\beta_1} = \left(\frac{A_1}{A_2}\right)^2. \tag{39}$$

If the flow had been running at the constant speed which it had between the two sets of measurements and the solution were initially very highly concentrated the

first distribution would have been attained at time t_1 and the second at time t_2 where $t_2 - t_1 = $ actual time of running and

$$\frac{1}{4kt_1} = \beta_1 \quad \text{and} \quad \frac{1}{4kt_2} = \beta_2.$$

Hence,

$$k(t_2 - t_1) = \frac{1}{4}\left(\frac{1}{\beta_2} - \frac{1}{\beta_1}\right). \tag{40}$$

The error curves (28) which fit the observations of table 3 which are shown in figure 8 have the following parameters:

$$\text{I:} \quad A_1 = 0\cdot65\,C_0, \quad \beta_1 = 5\cdot86 \times 10^{-2},$$

$$\text{II:} \quad A_2 = 0\cdot51\,C_0, \quad \beta_2 = 3\cdot72 \times 10^{-2},$$

$$\text{III:} \quad A_3 = 0\cdot41\,C_0, \quad \beta_3 = 2\cdot30 \times 10^{-2}.$$

These do not exactly satisfy conditions (39) owing to experimental errors.

Applying (40) to II and III and inserting $t_2 - t_1 = 330\,\text{s}$ (table 3)

$$k = \frac{1}{4 \times 330}\left(\frac{100}{2\cdot30} - \frac{100}{3\cdot72}\right) = 1\cdot25 \times 10^{-2}. \tag{41}$$

From table 3 $\frac{1}{2}u_0(t_2 - t_1) = 122\cdot5 - 94 = 28\cdot5\,\text{cm}$, so that $u_0 = \frac{57}{330} = 0\cdot173\,\text{cm/s}$. Hence, from (25),

$$D = \frac{(0\cdot173)^2(0\cdot0252)^2}{192(1\cdot25 \times 10^{-2})} = 0\cdot79 \times 10^{-5}\,\text{c.g.s. unit.} \tag{42}$$

As another example the observation used in figure 7 may be used. Here the concentration was not observed at any except the final position so that less accuracy may be expected. If the formulae (28) and (34) are used directly, assuming the start of the diffusion to be from a highly concentrated source, it is found from table 3 and figure 7 that

$$k = \frac{121}{4(660)} = 0\cdot0459, \quad u_0 = \frac{2110}{660} = 0\cdot333\,\text{cm/s},$$

so that

$$D = \frac{(0\cdot333)^2(0\cdot0252)^2}{192(0\cdot0459)} = 0\cdot80 \times 10^{-5}\,\text{c.g.s. unit.} \tag{43}$$

10. COMPARISON WITH PREVIOUS MEASUREMENTS

Measurements of the diffusion coefficient for $KMnO_4$ are quoted in Landolt & Börnstein's tables from Furth & Ullmann (1927). These figures are quoted in cm²/day. To reduce them to c.g.s. units they must be divided by 86 400, the number of seconds in 24 h. The measurements were made at 18° C which was approximately the temperature prevailing during the measurements described in the present paper. They covered a range $0 < C < 0\cdot01\,\text{g/ml}$. and in that range the diffusion coefficient ranged from $0\cdot435 \times 10^{-5}$ to $1\cdot5 \times 10^{-5}$. They are shown in figure 9 as circles and a smooth curve has been drawn to pass as nearly as possible through them.

In estimating the value of D which most nearly corresponds to the observed distribution of concentration, a constant D was assumed and the corresponding

theoretical distributions of C were compared with those observed. It is possible to deduce from the present measurements shown in figure 5 the variation of D with C, but certain inaccuracies make the results of doubtful value. I hope later to describe improvements in the apparatus which will make it possible to give more accurate values of D. Some values of D obtained in the experiments here described are shown in figure 9 and the range of values of C covered in the experiments are
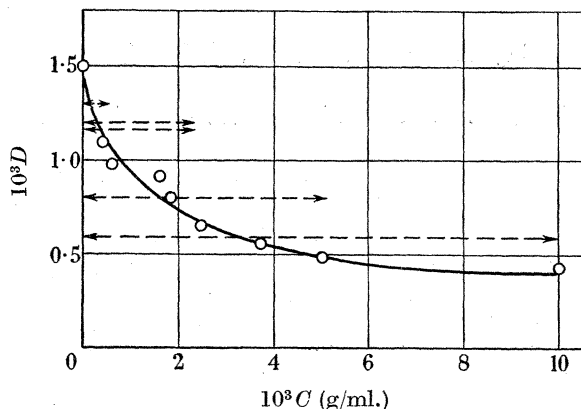

FIGURE 9. Diffusion coefficient for $KMnO_4$ at $18°$ C. Comparison between present measurements (broken lines) and those of Furth & Ullmann (represented by circles).

shown by means of broken lines. The experiment represented by the broken line at $D = 0.6 \times 10^{-5}$ is that of equation (36) and figure 5. The experiment represented by the line at $D = 0.8 \times 10^{-5}$ is that of equation (43) and figure 8. The lines at $D = 1.15$, 1.20 and 1.30×10^{-5} were obtained in experiments of type B 1 under conditions similar to those of figure 8, but with smaller amounts of potassium permanganate. It will be seen that they are not inconsistent with the measurements of Ullmann, which probably give approximate values of C over the range $0 < C < 0.01$ g/ml., even though the validity of the theory used by this author in interpreting his experimental results may be questioned.

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