The Measurement of Self-diffusion with a New Continuous Monitoring Method

I. Evaluation of the "Δl-Effect" in the Open-ended Capillary Method

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A new continuous monitoring capillary method is introduced. A mathematical treatment involving only the experimental values of the activity remaining in the capillary at various times gave evidence for the existence of a constant "Δl-effect" which could be calculated.

I. INTRODUCTION

Many authors have pointed out the fact that a possible source of error with the open-ended capillary method is due to convection disturbances at the top of the capillary.

Two effects can be distinguished, both of them tending to sweep out part of the active solution of the capillary, and leading therefore to effective diffusion paths shorter than the geometric length of the capillary. Such convection disturbances may occur:

— Firstly, when the boundary between the active and the inactive solutions is broken, *i.e.* when the capillary is immersed in the inactive bath. This effect, termed "immersion error", has been tested by Mills and Kennedy[1], Krauss and Spinks[2] and Mills and Adamson[3], who found activity losses in the capillary equal to 1.3 %, 0.5 % and 1.7 %, respectively.

— Secondly, when the outer inactive solution is stirred, in order to maintain the boundary condition $c = 0$ at the mouth of the capillary (c being the concentration of the labelled particles). If the stirring is too rapid or turbulent, part of the active solution may be swept more or less continually out of the capillary during the diffusion run. Wang, who termed this latter effect the "Δl-effect", has proposed a method for measuring it by using capillaries of different lengths[4]. But this method appears to be quite unsatisfactory, since it only gives an accuracy of the same magnitude as the "Δl-effect" itself, *i.e.* ± 2 %[1,3,4].

The only way to check whether a diffusion process out of an open-ended capillary is ideal should consist in a continuous registering of the activity inside the capillary during a whole diffusion run. In this case, the diffusion process should correspond to the solution of Fick's general diffusion equation for the actual boundary conditions:

$$\frac{I}{I_0} = \frac{8}{\pi^2} \sum_0^\infty \frac{1}{(2n+1)^2} \exp[-(2n+1)^2\pi^2Dt/4l^2] \tag{1}$$

where I = activity remaining in the capillary after a diffusion time t,
I_0 = initial activity in the capillary before diffusion
l = length of the capillary.

Mills and Godbole have recently made a first attempt in this direction by building an apparatus allowing them to make several measurements during a single diffusion run. [5] However ,the frequency of their observations (13 to 20 for a run) was not high enough for a complete and accurate survey of the whole diffusion run.

The following work was undertaken in order to observe, by continuous registering of the activity inside the capillary, how the diffusion really proceeds, when experimental techniques such as Wang's modification [6] of the initial Anderson and Saddington method [7] are used, i.e. with mechanical stirring of the outer inactive solution.

II. EXPERIMENTAL

1) Description of apparatus

The apparatus is shown in Fig. 1. The container for the inactive solution was a 3-liter glass beaker (A), with a lateral cylindrical connection (B) (diameter = 3.5 cm) terminated at right angles by another narrow cylindrical tube (C) (diameter = 0.8 cm) which contained the capillary. An opening (diameter = 0.8 cm) was made in tube (B), immediately above tube (C), to allow the lowering of the capillary into the cell. It could be closed with a rubber stopper (E). The solution was stirred mechanically by means of a propeller (F) placed vertically in the 3-liter beaker, and a plexiglas top (G) was laid over the beaker to prevent any evaporation. The capillaries used had internal and external diameters of 0.08 and 0.6 cm, respectively, and a length of (3.89 ± 0.01) cm.

A special G.M. tube for γ-ray counting (H), enclosed in a steel envelope, was tightly pressed to, and fixed along the wall of, the capillary. (For more details about the relative positions of capillary and G.M. tube, see further below.)

The whole diffusion cell and the G.M. tuber were immersed in a 30-liter water thermostat, kept at a temperature of (25.00 ± 0.01)°C.

The G.M. tube was connected to a counter, working on Preset Count. A special additive electronic device gave the apparatus the ability to choose, by itself, between two different preset number of counts to be registered, according to the radioactivity of the measured samples (UL and LL for high and low radioactivities, respectively). During a counting operation, the counter first worked on UL (i.e. it started as if it would count the higher preset number of impulses), but if the time for counting a certain number of impulses appeared to be too long, it turned over automatically to LL after 30 sec, (i. e. it would only count the lower preset number of impulses). Both for UL and for LL, the manipulator could select in advance one of two different preset number of counts, 10 000 and 5 000 counts for UL and 600 and 400 counts for LL, respectively.

The times corresponding to each measurement were printed on a paper roll by a registering device, connected to the counter (a number 1 or a number 2, printed before
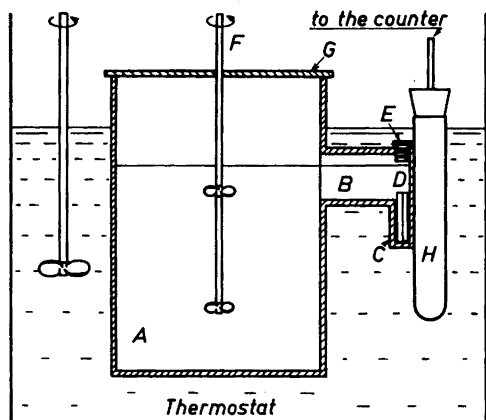
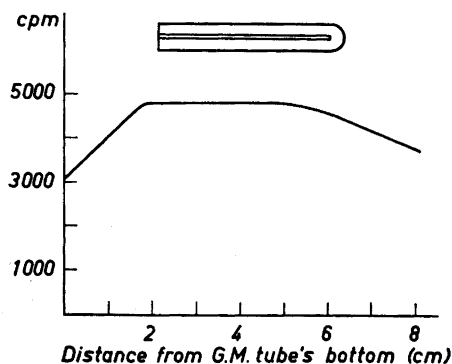*Fig. 1.* Apparatus for continuous monitoring open-ended capillary method.

Fig. 2. Efficiency curve of the G.M.tube. The representation of the capillary, at the same scale, shows the relative positions of the G.M.tube and the capillary.

the time data in different characters, indicated whether the counter had worked on UL or on LL). After each measurement, the counter stopped for one minute, and then restarted automatically.

2) Preparation of solutions

All experiments were performed with 0.001 M sodium iodide solutions.

The radioactive solutions were prepared by adding 5 to 15 μl of a carrier-free Iodine-131 solution (specific activity = 12 mC/ml) to 25 ml of the inactive sodium iodide solution. The corresponding activities were 9 000 to 15 000 cpm for the contents of a capillary. The isotope was provided by the Isotope Division AERE, Harwell, England.

3) Experimental procedure

The capillary was filled with the radioactive solution by means of a thin micropipette, operated with a medical syringe. A small drop of active solution was left on top in order to prevent evaporation during the time necessary to reach thermal equilibrium, and also to avoid as far as possible convection disturbances when the capillary was immersed in the inactive bath. Then the capillary was put in place in the holder (C), and the inactive solution, already at 25°C, was gently poured into the cell, along the walls of the beaker (A), until its level reached to 4/5th of the height of the capillary. After 10 min, the thermal equilibrium could be considered as established, and more inactive solution was slowly poured into the cell, until its total volume was about 1 600 ml. This last operation was done just before the counter started a new measurement. After 9 000 minutes, only about 15 % of the initial activity was left in the capillary, and the experiment was stopped.

4) Preliminary experiments

a. Relative positions of capillary and G.M.tube. The counting efficiency of the G.M. tubes we used has been measured by displacing a radioactive point source along the tube, and measuring its activity at all positions. It was found in this way that the counting

efficiency for each G.M. tube was constant along a region extending on both sides of its middle point. The length of this region was comparable to that of the capillary, but somewhat shorter. Fig. 2 represents the efficiency curve of one of our G. M. tubes as well as the position which was given to the capillary.

Since the greatest concentration changes occur in the upper end of the capillary, its top was placed in the constant efficiency zone. By taking into account the efficiency gradient of the G.M. tube and the activity gradient in the capillary, it could be demonstrated mathematically that the center of gravity of the total measured radioactivity in the capillary no longer moved after a diffusion time $t = 2\,000$ to $3\,000$ min. It may be noteworthy that Mills and Godbole came to the same conclusions for their own semicontinuous monitoring apparatus, with a 2 cm long capillary placed inside the hole (2 cm high) of a well-crystal of a scintillation counter [8].

b. *Background.* Before each diffusion run, the background was measured over a period of 15 min. It was of course impossible to check it during a run. We assumed that it kept approximately constant, and the measurement made at the beginning of each run (250 to 300 cpm) was used in the calculation.

c. *Control of convection in the cell.* A capillary was very accurately filled with the radioactive solution, and its contents (obtained by withdrawing them and rinsing five times with water) transferred using a micropipette into the inactive bath, right above the top of a sealed capillary in holder (C). Stirring was then started, and the radioactivity continually measured. It was found that with a stirring rate of 80 to 150 rpm, the radioactivity was evenly dispersed in the bath after 3 to 4 min. With a stirring rate of 320 rpm, uniform repartition was established in less than a minute. For our diffusion experiments, a stirring rate of 80 rpm was used.

d. *Influence of the radioactive species which have diffused out from the capillary.* The last experiment may be used for the determination of the constant ratio a between the number of counts per minute I'' corresponding to a certain amount of radioactivity evenly dispersed in the main body of the cell, and the number of counts I' corresponding to the same amount contained in the capillary. Five experiments yielded a mean value $a = 3.8\ \%$.

III. RESULTS AND DISCUSSION

1) The activities I_i' corresponding to the registered time data τ_i were calculated as follows:

$$I_i' = \frac{A}{\tau_i} - B \tag{2}$$

A being the number of registered counts (5 000 or 400)
B being the background.

As there was so much data, and as each individual value was known with a poor accuracy (the statistical counting accuracy), the individual values were not used for calculation, but mean values, I_i', of sets of 10 single values. It was assumed that in the case of Iodine-131, the half-life of the isotope was long enough for the radioactive decay between the measurements i and $(i + 10)$ to be neglected.

A mean diffusion time t_i, corresponding to each I_i' value was then calculated as follows:

$$t_i = \sum_{1}^{10(i-1)} (\tau_i + 1) + \frac{1}{2} \sum_{10_i-g}^{10_i} \tau_i \tag{3}$$

(it was assumed that the error arising from taking a linear mean time instead of a logarithmic one was negligible).

I_i' values were then corrected for radioactive decay over the period $t = 0, t = t_i$.

$$I_i'^0 = I_i'/e^{-\lambda t_i} \qquad (4)$$

λ being the decay constant of the isotope.

Then $I_i'^0/I_0$ was calculated, and corrected for the contribution of the activity, I'' which had diffused out, according to eqn. (5):

$$\frac{I_i^0}{I_0} = \frac{\dfrac{I_i'^0}{I_0} - \alpha}{1 - \alpha} \qquad (5)$$

Finally, D could be calculated from eqn. (1).

All these long calculations have been done with an electronic computer Alwac III E.

We reproduce in Fig. 3 two characteristic shapes of the curves $D = f(t)$.

It is seen that the experiments did not yield a constant value of D. It may consequently be deduced that the diffusion did not follow an ideal process.

The difference between curves (1) and (2) seems to be due to a difference in the size of the radioactive drop left on top of the capillary before immersion. Curves of type (2) were obtained when rather large drops were left (covering the whole top of the capillary tube), while curves of type (1) were obtained with smaller drops (4 to 6 % of the capillary volume).

The influence of the size of the drop may be roughly explained in the following way. When a large drop is left on top of the capillary, there may be no "immersion error". On the contrary, part of the active solution of the drop may remain for a while in the neighbourhood of the capillary, and the apparent D is then too low. After a certain time, a "Δl-effect" gradually takes place, and D increases slowly. When a smaller drop is left on top, there may be an "immersion error". The values for D found at the beginning of the run are consequently too high, but tend to decrease as the diffusion current again
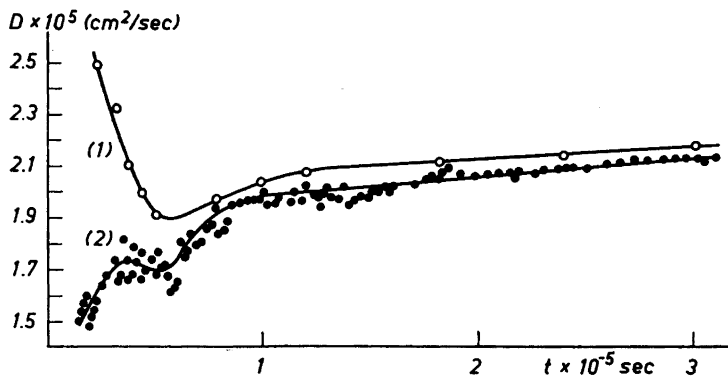

Fig. 3. Plot of D vs. t. O: experimental points for curve (1). ●: experimental points for curve (2).

fills the top of the capillary with radioactive solution. After a certain time, a "Δl-effect" is established, and D tends to increase again.

2) Plots similar to those of Mills and Godbole [5], *i.e.* plots of log (I^0/I_0) *vs. t.* gave approximately straight lines, as may be seen from Fig. 4. The slopes of these lines were calculated from the general equation:

$$ s = \frac{\sum\limits_{i=1}^{i=n} \log (I_i^0/I) - \sum\limits_{i=n+1}^{i=2n} \log (I_i^0/I_0)}{\sum\limits_{1=i}^{i=n} t_i - \sum\limits_{i=n+1}^{i=2n} t_i} \tag{6} $$

An example is given in Table 1, related to the curve in Fig. 4:

Table 1.

Number of points	Time interval	$D \times 10^{-5}$ (cm²/sec)
90	$2.18 \times 10^5 - 5.46 \times 10^5$	2.30
30	$2.18 \times 10^5 - 2.95 \times 10^5$	2.21
30	$2.95 \times 10^5 - 4.10 \times 10^5$	2.26
30	$4.01 \times 10^5 - 5.46 \times 10^5$	2.39

Two conclusions may be drawn from these results:

a) Obviously, the self-diffusion coefficients calculated are too high. For the very dilute solutions investigated here, they ought to be equal to the
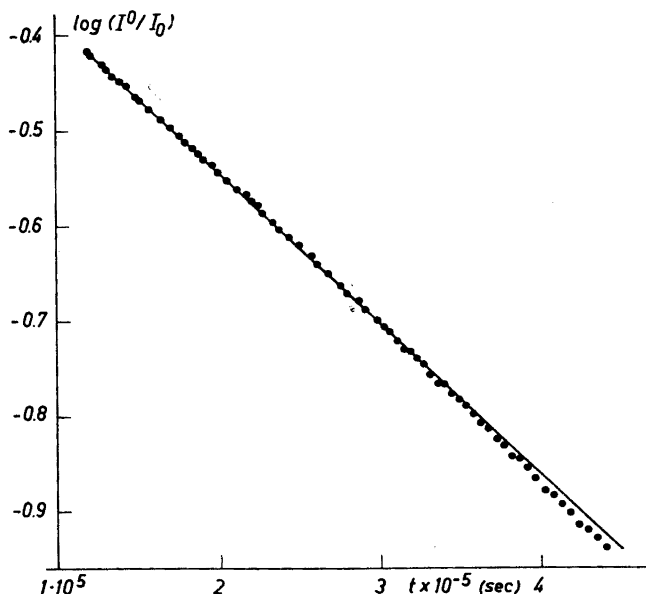

Fig. 4. Plot of log(I^0/I_0) *vs. t.* (Same experiment as Fig. 3, Curve 1.)
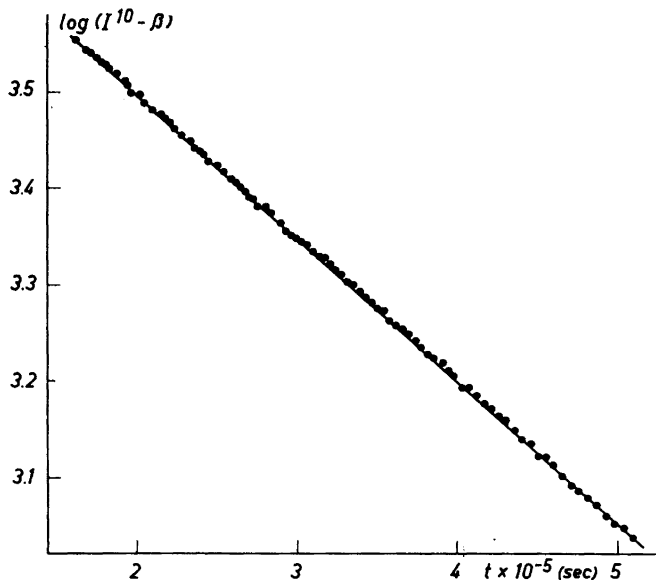
Fig. 5. Plot of $\log(I'^0-\beta)$ *vs. t.* (Same experiment as Fig. 4.)

Nernst limitimg value: $D^0 = 2.045 \times 10^{-5}$ cm²/sec. This discrepancy may be due to two factors: the poor accuracy of α and I_0, and probably the relatively high convection disturbances at the top of the capillary. This last factor is not to be regarded here as serious, since our purpose was in fact the investigation of these disturbances and their influence on the diffusion process.

b) As may be seen on Fig. 4, it is possible to draw a straight line through the experimental points of the plot $\log(I^0/I_0)$ *vs. t*, even if the diffusion process is far from being theoretical. Only calculations enable conclusions to be drawn about the diffusion process. So that it is regrettable that Mills and Godbole [5] did not report the data corresponding to their measurements during a single diffusion run. Although it is very probable that their own apparatus did not give rise to such important convection disturbances as ours, these authors have not yet given evidence that the convection disturbances were negligible.

3) We have already pointed out the fact that a source of error in the calculation of D was the poor accuracy of α and I_0.

It will be proved in the following part that if the convection disturbances at the top of the capillary have the same influence on the diffusion process as a constant "Δl-effect" *i.e.* if the experimental $I_i'^0$ values fit the case of an ideal process out of a capillary of effective length l_{eff}, shorter than its geometrical length, then it is possible to calculate the value of the product $\alpha\, I_0 = \beta$, by making use of only the experimental $I_i'^0$ values; this value, now exact, may then be used for the calculation of D/l^2_{eff}.

The abreviated diffusion equation

$$\frac{I_i'^0 - a\,I_0}{I_0\,(1-a)} = \frac{8}{\pi^2}\,\exp\,[-\pi^2 Dt_i/4l^2_{\text{eff}}] \tag{7}$$

(which is valid with in an accuracy of 0.2 % for $Dt/l^2 > 0.2$) may also be written

$$\ln(I_i'^0 - \beta) = \frac{\pi^2 Dt_i}{4\,l^2_{\text{eff}}} + C \tag{8}$$

C and β being constants.

If there exists a constant diffusion path l_{eff}, and if the apparent D does not vary with time, eqn. (8) will be satisfied by any experimental point $(I_i^{0\prime}, t_i)$. A set of 4 experimental points: (I'_1^0, t_1), (I'_2^0, t_2), (I'_3^0, t_3), (I'_4^0, t_4) will then satisfy the following equation:

$$\frac{\ln \dfrac{I'_1^0 - \beta}{I'_2^0 - \beta}}{\ln \dfrac{I'_3^0 - \beta}{I'_4^0 - \beta}} = \frac{t_2 - t_1}{t_4 - t_3} \tag{9}$$

β has been determined by a method of "trial and error" for 50 different sets of 4 points. The 50 values of β thus obtained differed from each other, as each $I_i'^0$ value is only known with the statistical counting error, but it has been verified that they followed a gaussian statistical distribution, and that they also were statistically distributed along the time axis. * An example is given in Table 2.

Table 2. $\bar\beta = (357 \pm 28)$ cpm. Relative dispersion $\sigma = 140$ cpm.

Interval	Frequency of β values
$\bar\beta - 2\sigma;\ \bar\beta$	24
$\bar\beta - \sigma;\ \bar\beta$	10
$\bar\beta;\ \sigma + \bar\beta$	10
$\bar\beta\ ;\ \bar\beta + 2\sigma$	24
$\bar\beta - 2\sigma;\ \bar\beta + 2\sigma$	48 = 96 % of total amount

The good statistical repartition of the β values proves that our initial hypothesis concerning an ideal diffusion process out of a fictive capillary of length l_{eff} was correct.

The plot of log $(I'^0 - \beta)$ vs. t. appears to be rigorously linear, as may be seen in Fig. 5. The slope of this line, K, has been calculated for 50 sets of 2 points, and the statistical distribution of the various K values analyzed, in order to detect possible deviations from a theoretical diffusion process. An example is given in Table 3:

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* This was only the case for experiments performed with relatively small drops left on top of the capillary before immersion. When larger drops were left, it was found that the positive deviations from the β mean value occurred at the beginning of the diffusion run, and the negative ones at the end.

Table 3. $\overline{K} = (1.481 \pm 0.003) \times 10^{-6}$ sec^{-1}. Relative dispersion $\sigma = 0.02 \times 10^{-6}$ sec^{-1}.

Interval		Frequency of K values
$\overline{K} - 2\sigma;$	$\overline{K}$	19
$\overline{K} - \sigma;$	$\overline{K}$	9
$\overline{K}\quad;$	$\overline{K} + \sigma$	8
$\overline{K}$	$\overline{K} + 2\sigma$	13
$\overline{K} - 2\sigma;$	$\overline{K} + 2\sigma$	49 = 98 % of total amount

The constant ratio D/l^2_{eff} may be now calculated from the value of $\overline{K}$.

If one assumes l_{eff} to be equal to l, the diffusion coefficient obtained is somewhat too high. If, on the other hand, one assumes l_{eff} to be different from l, and D equal to the Nernst limiting value, the magnitude of the "Δl-effect" can be determined. The following results were obtained:

if $l_{eff} = l = 3.89$ cm   then $D = 2.091 \times 10^{-5}$ cm^2/sec.

if $D = 2.045 \times 10^{-5}$ cm^2/sec   then $l_{eff} = 3.84_7 = 3.85$ cm.

Thus, the present method has enabled a precise determination of the magnitude of the "Δl-effect", which was evaluated to 0.4 mm, *i.e.* 1 % of the capillary's length.

Work is proceeding in this laboratory to investigate whether the "Δl-effect" is constant for various solutions, and to what extent it depends on the viscosity of the solutions. If it were found that reasonable changes in the viscosity have no influence on its magnitude, then a capillary could be calibrated with known solutions, *i.e.* dilute solutions for which $D = D^o_{Nernst}$, and used for the study of unknown solutions.

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