# A Simple Method for the Determination of Diffusion Constants

**Leonard A. Walker**[1]

***University of California, Berkeley***

Measurement of the diffusion constant of a substance in solution depends upon the determination of the concentration of the solute as a function of time and distance from an initially sharp boundary between solution and solvent. Knowing the concentration of the solute, one may calculate the diffusion constant by means of the equations

$$C_x = \frac{C_o}{2}\left(1 - \frac{2}{\sqrt{\pi}}\int_o^y e^{-y^2}\,dy\right) \quad \text{and} \quad y^2 = \frac{x^2}{4Dt}.$$

These equations hold for free diffusion of the solute from one half of the tube, with initial concentration $C_o$, into the other half, with initial concentration $C_x = 0$, where $C_x$ is the concentration at any distance $x$ from the original boundary, and $y$ is a parameter related to the time $t$, the diffusion constant $D$, and the distance $x$, from the initial boundary by the second equation above. The method for the derivation of the above equations from Fick's first and second equations is given by Williams and Cady (*1*), and by Neurath (*2*). The boundary conditions are the concentrations as stated above, and the condition that no change in concentration shall occur at the ends of the tube during the measurements. The term $\frac{2}{\sqrt{\pi}}\int_o^y e^{-y^2}\,dy$ is the probability integral. Measuring $C_x$ and $C_o$, one knows the value of the integral, hence the upper limit of the integral (*3*). Then, using the second equation above, knowing $y$, $x$, and $t$, one can calculate $D$.

The present method depends upon the fact that if the substance the diffusion constant of which is to be determined can be prepared in radioactive form, the cpm that one observes in a thin cross-sectional slice of a column containing the substance is directly proportional to the concentration of the substance in the slice. Thus, if one can count activity in many such slices as a function of time and distance from an initial boundary between solution and solvent, one can calculate a diffusion constant for the diffusion of the substance into the solution. The method can also be applied to self-diffusion problems.

Fig. 1 shows the apparatus, which consists of a hollow brass tube, with walls about 6 mm thick to shield out $\beta$-radiation, and in internal cylindrical bore of about 14 mm diameter, just large enough to accommodate a lusteroid tube of about 13.5 mm outside diameter, and 87 mm long. Inside the brass tube, which is about 15 cm long, is a snugly-fitting brass disk which acts as a platform on which the lusteroid tube can ride up and down. The platform is moved up and down by means of a 1/32-in. pitch screw having 88 turns. When the disk is completely screwed in, the bottom of the lusteroid tube comes just opposite a slit in one side of the brass tube, 1/32 in. wide. The length of the screw is such that, with 8 ml of liquid in the lusteroid tube, any cross section of the liquid level can be brought in line with the slit. The length of the slit is increased by 44 mm by means of the adjustable brass blocks, as shown. These blocks increase the resolving power of the slit by reducing the geometrical error, for as the length of the slit is reduced, one observes through the slit not, as one should, a thin cross-sectional slice, but rather a solid angle subtended by the eye at the slit. An end-window Geiger tube is placed flat against the brass blocks opposite the slit, and all measurements during a given diffusion experiment are made in this fixed position. In order to form the boundary, exactly 4 ml of the radioactive material was introduced into the bottom half of the lusteroid tube. A tiny flat saucer made from 230-mesh stainless steel wire was carefully pushed into the tube by means of a cylindrical wooden peg just smaller than the inside diameter of the tube. The saucer was pushed flat onto the surface of the liquid, and small bubbles were removed by careful pressure with a fine glass stirring rod. The second layer was then slowly added, exactly 4 ml being used. The screen should allow free diffusion, yet prevent mechanical mixing.

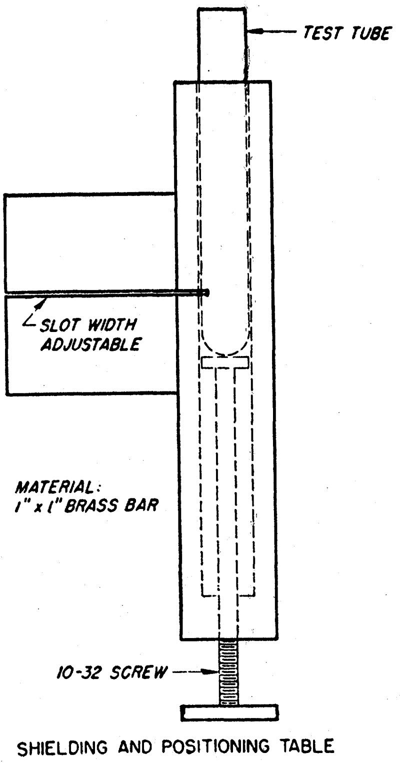

FIG. 1. Apparatus for diffusion experiments.

This method for determining diffusion constants is limited by several factors. Its principal disadvantages are the following: First, the slit must be of appreciable width in order to get enough counts through to the counter. In using a slit of finite width one is not measuring concentration in an infinitely thin slice.

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[1] Present address: University of Kansas Medical Center, Kansas City.

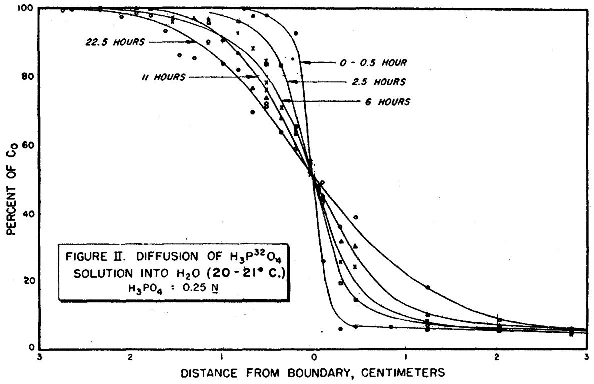

FIG. 2.

Second, even with the lengthened slit there is a slight solid angle in the solution subtended by the counter at the slit. Third, there is always a slight cloud of betas, caused by scattering from regions adjacent to the slice viewed by the slit. Fourth, measurements are limited to compounds tagged with isotopes that are pure β-emitters; γ rays will not be filtered out by the brass. It was hoped that scattering and absorption by the screen would not interfere and that values obtained on each side of the screen could be extrapolated together to form a smooth curve. Finally, since appreciable time intervals are involved in any series of counts along the tube, the resulting curve is not truly isochronal. This error becomes much less appreciable several hours after the beginning of the experiment.

All calculations were made from the curves for the bottom half of the tube since the boundary on that side does not contain the side of the screen.

One must make some distinction between the validity of values of $D$ obtained from the extreme ends of the curve, either very near or very far from the boundary, for the following reasons:

$$\text{Since } D = \frac{x^2}{4ty^2}, \qquad \text{then } \frac{dD}{D} = 2\,\frac{dx}{x},$$

and it is apparent that the fractional error in $D$ will always be twice that in $x$. The fractional error in $x$ will decrease as $x$ increases, provided the absolute error in $x$ is constant. Arbitrarily, only values of $x$ greater than 0.2 cm have been used in all the following calculations.

Also, calling the probability integral $\phi$, we have:

$$1 - 2\left(\frac{C_x}{C_o}\right) = \phi$$

Differentiating and dividing by $C_x$ we obtain:

$$\frac{dC_x}{C_x} = -\frac{d\phi}{1-\phi}$$

Since, as $C_x$ approaches zero, $\phi$ approaches 1.0, then the fractional error in $C_x$—namely, $\left(\frac{dC_x}{C_x}\right)$—approaches infinity. This means that one should not make measurements toward the tails of the curves. Arbitrarily, only values of $\left(\frac{C_x}{C_o}\right)$ greater than 0.05 have been used—that is, regions where the concentration is at least 5% of that in the deep regions (far from the boundary) on the active side of the tube.

All measurements were made in a constant temperature room at 20–21° C. Since the variation of the diffusion constant is given by $\frac{D_1}{D_2} = \frac{T_1}{T_2}$, where $T_1$ and $T_2$ are the absolute temperatures (*5*), it was felt that small changes in temperature would not cause appreciable error. The chief error would be caused by mechanical mixing, which was kept to a minimum by careful handling of the apparatus.

Fig. 2 shows 5 isochronal diffusion curves for 0.25 *N* phosphoric acid, for diffusion into water. Table 1 shows the values for $D$ for phosphoric acid from the 5 different isochronal curves, calculated for arbitrary points within the limits stated above. The average for all these values is $D = 0.86 \times 10^{-5}$ cm²/sec. The value from the *International Critical Tables* for the same solution at 22° C is $0.89 \times 10^{-5}$ cm²/sec (*4*). This agreement would indicate a reasonable accuracy in the method. The technique was developed to study the self-diffusion of an yttrium-hydroxy-citrate colloid that was too unstable to diffuse against water.

TABLE 1

DIFFUSION OF 0.25 N $H_3P^{32}O_4$ SOLUTION INTO WATER, 20–21° C

| Time elapsed after start of experiment, hr | Distance from boundary, cm | *D*, calculated, cm²/sec |
|---|---|---|
| 0.5 | 0.40 | $0.43 \times 10^{-5}$ |
| 2.5 | .40 | 0.54 |
| | .59 | 0.85 |
| | .79 | 1.52 |
| 6.0 | .40 | 0.72 |
| | .59 | 0.86 |
| | .79 | 1.05 |
| | 0.99 | 1.25 |
| | 1.19 | 1.42 |
| | 1.38 | 1.57 |
| | 1.58 | 1.70 |
| 11.0 | 0.40 | 0.80 |
| | 0.59 | .61 |
| | 0.79 | .68 |
| | 0.99 | .65 |
| | 1.19 | .62 |
| 22.5 | 0.40 | .54 |
| | 0.59 | .51 |
| | 0.79 | .57 |
| | 0.99 | .64 |
| | 1.19 | .72 |
| | 1.38 | .73 |
| | 1.58 | 0.74 |
| | Average | $0.86 \times 10^{-5}$ |

### References

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