

SHORT COMMUNICATIONS

CALCULATION OF DIFFUSION COEFFICIENTS WITH THE CONTINUAL MONITORING CAPILLARY METHOD*

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A recent paper by Mills and Godbole (1958) described a precise method of determining single ion diffusion coefficients by the continual monitoring of radioactivity in open-ended capillaries. In that paper, the treatment of data to obtain diffusion coefficients, involved measurement of c_0 , the radioactivity content of the capillary before the commencement of diffusion. However, such determinations are accompanied by appreciable error which stems essentially from two sources. The first and more serious of these arises from the difficulty in filling the capillary very precisely to its upper boundary, then sealing it effectively, for immersion in the outer solution. Replicate determinations of c_0 values seldom have a precision better than ± 0.4 per cent. The continual exposure of the photomultiplier tube and scintillator to light during these operations is probably a contributory cause of this imprecision. The second source of error may arise from the necessity to apply an appreciable "gradient correction" to the $c_{av.}$ figures. As explained in the above paper, this correction is necessary so that the activity measured after diffusion, when a gradient exists, can be compared to that prior to diffusion, when it is uniformly distributed.

A method has now been developed in which ion-diffusion coefficients can be obtained solely from repeated measurements of $c_{av.}$. By this device, errors arising from the procedures detailed in the last paragraph can be eliminated.

Method of Calculation

The diffusion equation used in this treatment is the abbreviated form suitable for long diffusion times (Wahl and Bonner 1951):

$$\pi^2 Dt/4l^2 = \ln(8/\pi^2 \times c_0/c_{av.}). \quad \dots\dots\dots (1)$$

This equation can be expressed in the form

$$(\pi^2 D/4l^2)t_1 + \ln c_{av.i} = \ln 8c_0/\pi^2, \quad \dots\dots\dots (2)$$

where t_1 refers to a particular period of diffusion and $c_{av.i}$ the residual activity at the end of such a period.

A plot is now made of $\ln c_{av.}$ against t and the slope of the best straight line through these points gives the value of $\pi^2 D/4l^2$ whence D can be calculated. Alternatively, a least squaring procedure can be used to calculate the slope

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directly. It should be pointed out that in the previous procedure in which $\ln c_0/c_{av.}$ was plotted against time, the experimental points were least squared in relation to a fixed pivoting point. The position of this intercept is in effect a function of c_0 and thus any error in the measured value of the latter would be reflected in the slope of the line. In the present method the slope of the line is dependent only on the precision of the $c_{av.}$ measurements. It has been found experimentally that the best precision is obtained if the measurements are made after equally spaced intervals of a few hours.

Gradient Correction

In our previous paper (Mills and Godbole 1958) the "gradient correction" allowed comparison of $c_{av.}$, the activity gradient measurement with c_0 the initial, uniformly distributed activity. In the amended procedure described above, however, any corrections necessary are those among a series of activity gradients only. Calculations have been made of the relative efficiency of counting the gradients present after known periods of diffusion, and suitably normalizing them by use of the correction factor

$$\int_0^l c(x)\bar{r}(x)dx / \int_0^l c(x)dx \cdot \int_0^l \bar{r}(x)dx.$$

This expression represents the factor by which the measured activity at any time would have to be multiplied in order to compare it with a uniform distribution of the same total activity. In Table 1, these factors have been calculated for Na^+ ion diffusing in 1.44M aqueous sodium chloride solutions at 25 °C using capillary tubes 2 cm in length. For this system $D=1.202 \times 10^{-5} \text{ cm}^2/\text{sec}$ (Mills 1955). The scintillation crystal had a diameter of 3.8 cm and a height of 2 cm.

TABLE 1

Diffusion Period (hr)	Correction Factor for Uniformity	Correction Factor for Gradient
24	1.0096	1.0001
36	1.0094	1.0003
48	1.0097	1.0000
60	1.0097	1.0000
72	1.0093	1.0004

It will be observed in this instance that although a correction of 1 per cent. is necessary to compare the activity gradients with a uniform distribution, the intercomparison of the former alone requires corrections much less than 0.1 per cent. Corrections of this order are normally well below the statistical counting error and can therefore be safely neglected.

References

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