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A Rapid Method for Measuring Diffusion Coefficients for Solutions¹

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A rapid and inexpensive method has been devised for measuring diffusion coefficients of substances in solution. The procedure consists essentially of soaking a porous disc in the solution of interest and then suspending the disc in a bath of pure solvent. The rate of diffusion of solute from the disc is then ascertained by measuring the apparent weight of the suspended disc at various times. The rate of change of the apparent weight can be directly related to the loss of solute and hence to the diffusion coefficient of the material. The method has been thoroughly tested for aqueous solutions of inorganic salts whose diffusion coefficients are known. The process is sufficiently rapid to permit easy determination of the diffusion coefficients of slowly diffusing substances like high polymers.

Introduction

In the course of our research on high polymer materials, we were confronted with the problem of determining diffusion coefficients of such substances in solution. It was found, however, that the conventional methods available for measuring diffusion coefficients proved impractical for high polymer substances because of their low mobilities and slow rates of diffusion. Accordingly, we sought to devise a quick and inexpensive method for measuring diffusion coefficients. Such a procedure has been developed and we now discuss the techniques as well as preliminary results.

The principal difficulty encountered in the usual methods for measuring diffusion coefficients is the slow rate at which significant changes in concentration can be observed. By "usual methods" we have reference to procedures involving the use of diffusion cells in which concentration changes are measured by some conventional analytical technique. (The Tiselius cell method with its accompanying optical system eliminates this difficulty.) The method which we finally devised resulted from a careful consideration of diffusion rates in relation to apparatus dimensions, particularly the areas and volumes involved in the diffusion process. In place of an ordinary diffusion cell we found it highly practical to use an unglazed porous porcelain disc. This disc is initially soaked in a solution of the material to be investigated and is then suspended in a large bath of solvent. Diffusion then takes place from the disc to the solvent and by the simple expedient of measuring the apparent weight of the suspended disc, one can follow the rate at which solute escapes into the bath. From the solution of the differential equation for diffusion, subject to appropriate boundary conditions, it

then becomes possible to relate the apparent weight of the disc as a function of time to the diffusion coefficient of the material under consideration.

Although the work was initiated with high polymeric materials in mind, the first experiments were carried out on low molecular weight electrolytes to provide a test for the method. As will be seen below the procedure has proved to be very effective for the determination of relative diffusion constants. The results of applying the method to high polymer materials will be published later.

Outline of the Method.—A disc of unglazed porcelain, 1 to 5 mm. thick and approximately 7 cm. in radius is filled with a solution of definite concentration, C_1 , by allowing it to soak in such a solution for a sufficiently long time. The frit is then suspended in a large thermostated bath of pure solvent or solution at some different concentration, C_0 . The frit is suspended in the bath by a fine platinum wire which is attached to one arm of an analytical balance, so that it can be weighed from time to time during the period of diffusion (see Fig. 1). Except during the actual times of weighing, the solution in the bath is vigorously stirred, and the concentration of the outside solution is assumed to be C_0 throughout the experiment. As we shall show below, all that is required for a determination of the relative diffusion coefficient is a knowledge of the apparent weight of the frit as a function of time, t , including the value after infinite time. For KCl, even with a 5 mm. frit, half the salt will diffuse out of the frit in about 30 minutes. Moreover, almost as many measurements as are desired can be made in a single experiment regardless of the nature of the diffusing substance.

Basis of the Method.—For the sake of simplicity we shall assume that the diffusion coefficient, D , is constant. For a circular disc with parallel plane faces, the differential equation for diffusion is

$$\partial c / \partial t = D[\partial^2 c / \partial r^2 + (1/r)\partial c / \partial r + \partial^2 c / \partial x^2]$$

where c stands for concentration, t for time, r the radial distance and x the distance along the normal to the parallel plane faces. We shall assume that for each frit there exists a constant effective radius, R , and an effective thickness $2L$, such that the integral of $C(x, r, t)$ over the total volume so defined is equal to the quantity of salt actually within the frit at a given time. Since the volume of solution within the frit is smaller than the external volume of the frit, we can anticipate that the effective dimensions R and $2L$ will be different from the geometrical dimensions of the frit.

If the initial concentration (when $t = 0$) inside the finite cylinder $-L < x < +L$, $0 \leq r < R$, is C and if for all times the surface concentration is C_0 , the concentration $C(x, r, t)$ is given by²

$$C(x, r, t) = C_0 - (C_0 - C_1) \frac{8}{\pi} \sum_{m=1}^{\infty} \frac{J_0(r\beta_m/R)}{\beta_m J_1(\beta_m)} \exp(-Dt\beta_m/R^2) \quad (1)$$

$$+ \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \left[\frac{(2n+1)\pi x}{2L} \right] \exp(-Dt(2n+1)^2\pi^2/4L^2)$$

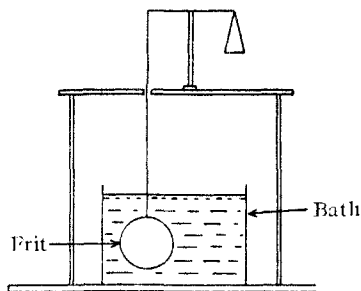


Fig. 1.—Diagram of apparatus.

(1) This work was supported in part by the Synthetic Rubber Division, Reconstruction Finance Corporation.

(2) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, New York, N. Y., 1947, p. 194.

where the β_m are the roots of $J_0(\beta) = 0$. $J_0(\beta)$ and $J_1(\beta)$ stand for the Bessel functions of the first kind of order zero and one. We note that

$$C(x, r, \infty) = C_0$$

and

$$C(x, r, 0) = C_1$$

since

$$\sum_{m=1}^{\infty} \frac{J_0(r\beta_m/R)}{\beta_m J_1(\beta_m)} = 1/2$$

and

$$\sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \frac{(2n+1)\pi x}{2L} = \pi/4$$

Now if the radius of the disc is large compared to the thickness, we can arrive at a simpler approximate solution by letting $a/L \rightarrow \infty$. Then

$$\lim_{a/L \rightarrow \infty} C(x, r, t) = C(x, t) = C_0 - (C_0 -$$

$$C_1)(4/\pi) \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos \frac{[(2n+1)\pi x]}{2L} \exp(-Dt(2n+1)^2\pi^2/4L^2) \quad (2)$$

This is, of course, the solution of the problem when the edges are sealed, or in other words for diffusion in one dimension only. Actually all of our frits are sufficiently thin so that diffusion through the edges is relatively small compared to diffusion through the large parallel faces. Hence, the factor in (1) that contains the summation over m never differs greatly from $1/2$, and we can regard its departure from constancy as a minor correction factor.

For comparison with experiment we shall ultimately need the integral of C with respect to x over the thickness. This is given by

$$(1/2L) \int_{-L}^{+L} (C(x, t) - C_0) dx = (C_1 - C_0)(8/\pi^2) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp(-Dt(2n+1)^2\pi^2/4L^2) \quad (3)$$

Except for very small times, the summation is dominated almost exclusively by the term $n = 0$. Actually for times large enough so that $Dt\pi^2/4L^2 > 0.2$, the integral of C with respect to x is given to a good approximation by

$$(1/2)L \int_{-L}^{+L} (C(x, t) - C_0) dx = (C_1 - C_0)(8/\pi^2) \exp(-Dt\pi^2/4L^2) \quad (4)$$

We shall now define an observable quantity W as

$$W = \{(\text{weight of frit at time } t) - (\text{weight of frit after infinite time})\}$$

Evidently

$$W = A \int_{-L}^{+L} [d(x, t) - d_0] dx \quad (5)$$

where A is the effective cross section of the frit, $d(x, t)$ the density of the solution within the frit, and d_0 is the density of the solution outside the frit. If the density can be expressed as a linear function of the concentration, such as

$$d(C) = d^0 + kC \quad (6)$$

where d^0 is solvent density, then

$$W = Ak \int_{-L}^{+L} [C(x, t) - C_0] dx \quad (7)$$

Upon substituting equation (4) into (7) we obtain

$$W = 2LAK[C_1 - C_0](8/\pi^2) \exp(-Dt\pi^2/4L^2) \quad (8)$$

In computing D from experimental results the log form of (8) is more useful, namely

$$\log W = Dt\pi^2/(2.303)4L^2 + \log 2LAK[C_1 - C_0](8/\pi^2) \quad (9)$$

Hence, plots of $\log W$ vs. t should yield straight lines of slope $-D\pi^2/(2.303)4L^2$, except for very short times. As can be seen from inspection of equation (3), the very short time

points should lie above the limiting straight line. Furthermore, for two experiments in which C_1 and C_0 are interchanged, identical values of W should be obtained.

Equation (9) holds for a frit with sealed edges. In most of the experiments we have done so far, we have left the edges unsealed, which complicates matters somewhat. Obviously equation (1) is not nearly so easy to work with as (2); hence, whenever it is convenient, it is worthwhile to completely eliminate the edge correction by simply sealing the edges. In our preliminary work we intentionally avoided this to make certain that possible errors due to a poor choice of sealing material would not obscure the results. An examination of equation (1) shows, however, that for thin frits, $\log W$ should still be linear in Dt . For the thickest frit we used, a correction of only 3% was necessary because of sideways diffusion. In any event, if measurements are made on two different solutions using the same frit, the ratio of slopes should be equal to the ratio of diffusion coefficients.

Experimental

Description of Frits.—Porcelain plates rather than sintered glass frits were used in practically all our work simply because they are easy to grind and are readily available. Eight carefully ground frits of various thicknesses were prepared. Rough grinding to approximately the desired thickness was done on a cast iron lap, while final grinding was done by rubbing the plates with pieces of other plates using FFF grade carborundum. Thickness was determined with a deep throat micrometer caliper calibrated to 0.01 mm. The error in measurement was probably about 0.02 or 0.03 mm, because of the unfavorable nature of the porcelain surface. The data relating to the dimensions of the frits are given in Table I.

TABLE I
DIMENSIONS OF THE FRITS
(All lengths in millimeters)

Frit number	Average thickness, 2λ	Average deviation, Δ	Area within $2\lambda \pm \Delta$, %	Area outside $2\lambda \pm 2\Delta$, %	Maximum difference in thickness
1	4.25	0.02	65	7	0.11
8	3.38	.01	87	5	.07
2	2.85	.01	72	4	.07
3	2.84	.01	78	6	.08
4	2.06	.01	73	12	.07
5	1.10	.01	93	0	.03
6	1.07	.01	96	0	.03

In addition to the numbered frits described above, other frits, not so carefully ground, were used in some of our preliminary work. The thicknesses of these frits, quoted below, are accurate within about 10%. As will be seen below, carefully ground frits are not necessary for many purposes.

The 4 mm. frit was found to hold about 35 ml. of liquid. Since the radius of the frits was about 7 cm, it appears that about half the geometrical volume of the frits is available for liquid.

The volume of the outside solution was 16 liters. In the most unfavorable case, C_0 at the end of the experiment becomes about $C_1/500$. Hence the effect on the gradient caused by the increase in C_0 is negligible except for very large times. The effect on buoyancy due to changing bath concentration is probably more important. Thus for the 4 mm. frit with 0.4 M KCl, assuming that the volumes of solution and porcelain in the frit are equal, the buoyancy correction for W amounts to about 2 mg. at $t = 0$ and $t = \infty$. When half the salt has diffused from the frit into the outside solution the correction is zero. At $t = 0$, $W = 600$ mg. so the error in W is about one part in 300 at most. Actually the points in the neighborhood of the half-time are the ones used in determining the slope, so we have not bothered to make this correction.

Procedure.—The frits were filled first by allowing them to soak in water until they came to constant weight. Although filling with water was nearly complete in a day, about a week of soaking was required before there was no detectable change in weight. Once filled, the frits were always kept in water or some solution. They were filled with electrolyte solution by soaking them in successive baths

of that solution. The time required for filling with electrolyte is the same as the time required for the salt to leave the frit in an experiment where $C_0 = 0$. Even for the thickest frit a soaking period of one day was found to be long enough.

Weighings during the course of an experiment were made with a Christian Becker number 16 "chainomatic" balance which was mounted directly above the thermostated bath. Several schemes for weighing were tried, but for most of the work, the balance indicator was kept on zero by continuously cranking the chain and recording the readings at various intervals.

All measurements were made within 0.1° of 25° .

Results and Discussion

Preliminary Tests.—Until the present method was actually tested, we were not certain that it would be feasible. We were particularly concerned with the possibility that significant bulk flow of the solution might occur because of the different densities of the solutions outside and inside the frit; this might not only take place while the frit was suspended in the bath, but also while the frit was being transferred from one bath to the other. There was also the danger that currents in the outside solution, necessary to insure a uniform concentration immediately outside the frit, would disturb the solution inside. Finally, we could not be sure in advance that the proposed method of forming a sharp initial concentration boundary would succeed. In view of the experimental results, however, it appears that these fears were ungrounded and that the solution inside the frit behaves as if it were mechanically undisturbed by the outside treatment given the frits.

In Fig. 2, $\log W$ has been plotted against t for experiments on potassium chloride using two frits of different thickness. While these frits were not accurately ground, the results obtained with them serve to illustrate certain points. A high value of the initial KCl concentration, namely, $2.2 M$ was chosen intentionally to exaggerate the possibility of bulk flow due to density differences. First of all, it will be noted that $\log W$ is a linear function of t , as required by equation (9), except for short times. As anticipated, the short time points fall above the limiting straight line. Moreover, as can be seen from curve 1 of Fig. 2, where the data for five identical experiments are plotted, the results are quite reproducible. For four of these experiments (excluding the points with tails downward) the mean deviation of W from the straight

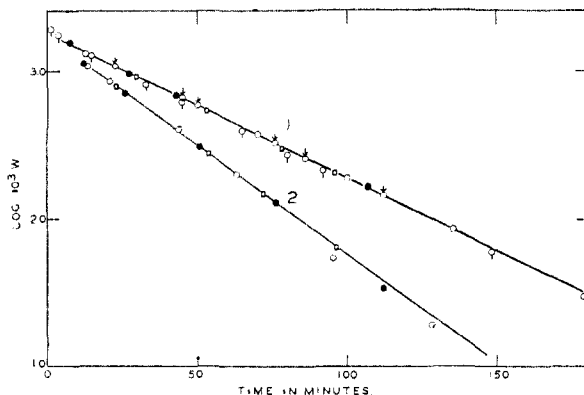


Fig. 2.—Diffusion of KCl in water: $C_1 = 2.2 M$, $C_0 = 0$; curve 1, 5 mm. frit (approximately); curve 2, 3.5 mm. frit.

line as drawn is 0.8% . The slopes were estimated from individual plots of the results, and the average deviation in the slopes is about 1% . Although the points for one experiment (tails downward) deviate appreciably from the straight line drawn through the others, they yield essentially the same slope. It is probable that the three-hour period allowed for filling the frit in this case was insufficient, since for the other four experiments the frit was allowed to stand in $2.2 M$ KCl solution overnight.

While the reproducibility of the results indicates that gravity flow is not a significant factor, even more conclusive proof of this is provided by the experiment indicated by arrows in Fig. 2. In the one case (arrows), the frit was suspended horizontally; in the other four (circles and squares), vertically. If the space in the frit is continuous, the effect of gravity flow in the vertical instance should have been many times greater than in the horizontal case. Experimentally there is no significant difference between the two cases; consequently we conclude that the solution in the frit is not disturbed by gravity flow.

It was noted in connection with equation (9) that on interchanging C_1 and C_0 identical results should be obtained. An experimental illustration of this point is given in Fig. 3. The open circles correspond to $C_1 = 0$, $C_0 = 0.52 M$ NaCl, the solid circles to $C_1 = 0.52 M$ NaCl, $C_0 = 0$. The two sets of points are in excellent agreement. Besides providing a good test of reproducibility, this finding lends support to our assumption that errors due to adsorption of electrolytes on the walls of the frit do not play an important part in the experiments. If the amount of salt adsorbed depended upon the concentration, then W in the two instances should not be identical.

These preliminary experiments confirm the form of equation (9) and indicate that errors caused by gravity flow, by mixing of the solutions as a result of stirring, and by failure to form sharp initial concentration boundaries are not serious.

Uniformity of Frits.—Although the frits used to obtain the results shown in Figs. 2 and 3 had an average deviation in thickness of about 10% , the $\log W$ vs. t plots are essentially linear. The thinnest frits used in the preliminary experiments

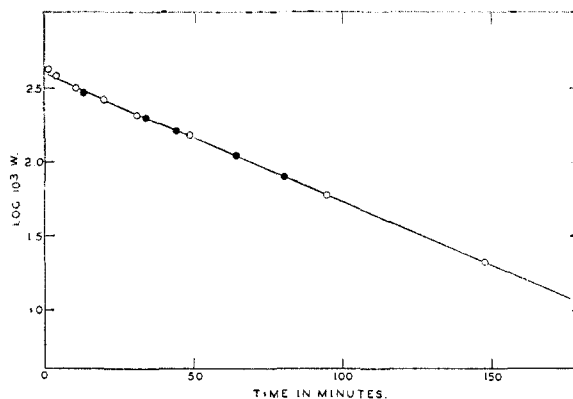


Fig. 3.—Illustrating interchange of inside and outside solutions. Experiments with 5 mm. frit: open circles, $C_1 = 0$, $C_0 = 0.52 M$ NaCl; solid circles, $C_1 = 0.52 M$ NaCl, $C_0 = 0$.

were about 1 mm. thick and had greater deviations in thickness, namely, about 25%. With these thin frits a detectable departure from linearity is found for the $\log W$ vs. t plots, although the effect is small. The curves are concave upward, as would be expected, since as time goes by the fraction of salt leaving the thicker parts of the frit becomes increasingly important.

Stirring.—In our early tests of the method, the stirring motor in the outside bath was operated between weighings. Since four or five minutes are required for the liquid in the bath to come to rest, such a procedure cannot be followed for experiments where the period of measurable diffusion is only ten or fifteen minutes. For experiments of this sort, the stirring motor was turned off and the liquid in the bath was allowed to come to rest before the frit was placed in the bath. A significant error might possibly be made in this way because of increase in concentration in the outside solution at the boundary of the frit. Fortunately it turns out that this effect is undetectably small.

Experimental verification of this resulted from two experiments on frit 1, with $C_1 = 0.50 M$ KCl, $C_0 = 0$. In one experiment, the stirring motor was not turned on for over 80 minutes. In the second case, the stirrer was turned on between 0 and 9, 26 and 29, and finally between 39 and 44 minutes. It was found that the points lie very nearly on a common line. It seems likely that any tendency for the concentration to become greater than C_0 at the frit boundary is largely overcome not only by gravity mixing of the outside solution but by stirring caused by slight oscillations of the frit during the process of weighing.

Examples of Weight vs. Time Data.—For illustrative purposes, the apparent weight of a frit is given as a function of time for one experiment (Table II). The measurements were made using frit number 1 with $C_1 = 0.40 M$ KCl, $C_0 = 0$. The edge of the frit in this case was sealed with paraffin. The points were found to fall very nearly on a straight line with the slope equal to $1.10 \times 10^{-2} \text{ min.}^{-1}$. As can be seen from Table II, W varies from about 0.5 g. at two minutes down to about 0.1 g. at 59 minutes. Assuming that the infinite weight is in error by 5 mg., a recalculated $\log W$ vs. t plot is still essentially linear, but with a slope equal to 1.07×10^{-2} , which is 3% smaller than the presumably correct value. However, since we believe that the actual uncertainty in infinite time weight is no greater than one milligram, it seems unlikely that the error in final weight can be responsible for more than a 1% error in the slope.

Results for Small Times.—For the foregoing examples, it is clear that the $\log W$ vs. t plot is linear over a considerable range in t . However, it is also of interest to see whether the positive deviations that occur at small times are in accord with eq. (3). If we include all the terms in the summation on the right-hand side of eq. (3) instead of the $n = 0$ term only, we find

$$W(t) = 2L Ak |C_1 - C_0| (8/\pi^2) \sum_{n=0}^{\infty} [1/(2n + 1)^2] \exp[-Dt(2n + 1)^2\pi^2/4L^2] \quad (10)$$

As $t \rightarrow 0$ $W(t) \rightarrow 2L Ak |C_1 - C_0| = W(0)$

Also as can be seen from eq. (9), extrapolation of the linear part of the $\log W$ vs. t curve to $t = 0$ yields

$$W_{\text{ext}} = W(0)(8/\pi^2)$$

TABLE II
EXAMPLE OF WEIGHT vs. TIME DATA. FRIT NUMBER 1 WITH EDGES SEALED

Time, minutes	Weight minus 44.000, g.	Obsd.	$C_1 = 0.40 M$ KCl, $C_0 = 0$; slope = 1.10×10^{-2}
			$W(t)/W(0)$ Calcd., Eq. (10)
2	0.817	0.837	0.838
4	.775	.767	.772
5	.758	.739	.745
6	.743	.714	.720
7	.730	.693	.698
8	.717	.671	.677
9	.706	.653	.657
11	.684	.616	.621
12	.675	.601	.604
14	.656	.570	.573
16	.639	.542	.543
18	.623	.515	.516
19	.615	.502	.502
Stirrer on 3 Minutes			
29	0.547		
31	.536		
33	.525		
36	.510		
Stirrer on 10 Minutes			
54	0.438		
56	.431		
59	.423		
1500	.313		

To compare the results of experiment and calculation we have computed the ratio

$$W(t)/W(0) = (8/\pi^2)(e^{-\mu t} + (1/9)e^{-9\mu t} + (1/25)e^{-25\mu t} + \dots) \quad (11)$$

where

$$\mu = -2.303 (\text{slope}) = D\pi^2/(4L^2)$$

Values of $W(t)/W(0)$ have been computed using eq. (11) and are compared with the observed values of the ratio in Table II. The comparison is also made graphically in Fig. 4 where the continuous curve corresponds to the calculated values, while the circles represent two sets of experimental points. The dotted curve represents values of $W(t)/W(0)$ assuming the validity of eq. (9). Since W changes relatively rapidly over the interval 0 to 10 minutes,

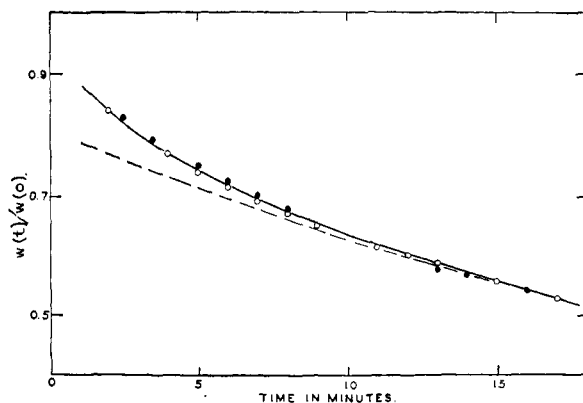


Fig. 4.— W as a function of t for small times: open circles, results of Table II; solid circles, duplicate experiment; continuous curve calculated by equation (10); dotted curve, exponential form from equation (9).

the values for small times are doubtless subject to greater error than those obtained after 20 to 30 minutes. Considering this, the fairly good agreement that exists between experiment and eq. (10) indicates that our fundamental assumptions are valid.

It is useful to be able to predict the time at which the short time deviations from linearity become negligible. For example we might want to compute the time, $t_{1.01}$, at which the observed value of W is 1.01 times the exponential value computed from eq. (9). By comparison of eqs. (9) and (10) it can be seen that this time is simply the solution of

$$1.01 = 1 + (1/9)e^{-8\mu t} + (1/25)e^{-24\mu t} + \dots \quad (12)$$

which gives

$$\mu t_{1.01} = 0.30$$

For the experiment under discussion, where $\mu = 2.53 \times 10^{-2} \text{ min.}^{-1}$, $t_{1.01}$ is about 12 minutes. In contrast, for a 1 mm. frit, again with $C_1 = 0.4 M$ KCl and $C_0 = 0$, $t_{1.01}$ is only about 1 minute.

Results for 0.1 M HCl and 0.1 M KCl.—In the discussion given above it has been shown that the form of the weight *vs.* time relation is in satisfactory agreement with eq. (10). With this established, the major point of interest is whether or not the observed slopes are actually proportional to D . While the results already given make it highly likely that this is true, we nevertheless felt that a direct test of this point should be made.

For this purpose we determined the slopes for 0.10 N HCl and 0.10 N KCl, using two different frits, so as to compare the ratio of these slopes for a given frit with the known ratio of the diffusion coefficients. Since the densities of these solutions, particularly for 0.10 M HCl, are rather low, the two thickest frits were used. The results are summarized in Table III. To give an indication of the accuracy possible, the approximate maximum values of W are included in the table.

TABLE III

EXPERIMENTS ON 0.10 M HCl AND 0.10 M KCl, $C_0 = 0$ IN ALL CASES

Frit	C_1	Approx. max. W , mg.	Slope $\times 10^2$	Average slope $\times 10^2$, min.^{-1}	Ratio of slopes HCl/KCl
1	0.10 M KCl	120	1.107, 1.118, 1.113	1.113	
1	.10 M HCl	60	1.78, 1.78, 1.73, 1.75, 1.64	1.74	1.56
3	.10 M KCl	50	1.95, 2.07	2.01	
3	.10 M HCl	25	3.08, 3.10	3.09	1.53

The observed ratios in the slopes are in good agreement with the ratios of the diffusion coefficients, namely, 1.585, found by James, Hollingshead and Gordon³ using the steady state technique. In general, taking into account the uncertainty in the slopes, it is seen that the ratios of the slopes are in satisfactory agreement with the ratio of the diffusion coefficients as determined by the steady state method.

Of course exact agreement between the two methods is not to be expected. In the one method the concentration gradient in the frit is essentially uniform in space and changes slowly with time;

in the present method, the gradient is non-uniform in space and changes relatively rapidly with time. The effects due to variation of diffusion coefficient with concentration should then be different in the two instances.

To compute the effective frit thickness, $2L$, we shall use⁴ $1.830 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$ as D for the case where $C_1 = 0.10 M$ KCl and $C_0 = 0$, and $1.113 \times 10^{-2} \text{ min.}^{-1}$ as the slope. This leads to $2L = 6.54 \text{ mm.}$ for frit number 1, which is about 1.5 times the geometrical thickness, which is only 4.17 mm.

Results with 5 M HCl.—All the results discussed above are for moderately concentrated solutions. For the sake of completeness one series of measurements was made with a high initial concentration of electrolyte, specifically with $C_1 = 5.2 M$ HCl. As before, the log W *vs.* t plot becomes linear, but the linear portion of the curve starts at much higher times than predicted by eq. (12).

Now eq. (9) was derived on the assumption that D is constant, and experimentally all of our results with the exception of those for 5.2 M HCl are consistent with that equation. However, it is well known that D does vary with concentration, although usually only slightly. From the observed results for moderately concentrated solutions, it might be assumed that the expression applicable to a system with variable D will have the same form as eq. (9) providing D is taken as an appropriate average. In view of the results, however, it appears likely that the effect in question is negligible for dilute solutions. When C_1 is made large enough, as with 5 M HCl, the concentration effect gives rise to a W *vs.* t relation that is no longer simply exponential. With increasing t , the maximum concentration in the frit decreases until finally the range of D values within the frit becomes relatively narrow, whereupon the log W *vs.* t plot approaches linearity.

Temperature Control.—To gain some idea of the dependence of the results on temperature, an experiment was performed in which the temperature of the outside bath was intentionally decreased from 25 to 22° during the period of measurement. The results are shown in Fig. 5, where in addition to log W , the temperature of the bath is plotted as a function of time. In computing W the increase in density of the outside solution with decrease in temperature was taken into account. Frit number 1 with edges open was used with 0.44 M KCl. At 25° the slope was found to be $1.10 \times 10^{-2} \text{ min.}^{-1}$ (see Table III). Surprisingly, the points quite closely approximate a straight line of the same slope. A significant difference in the two cases might have been anticipated as a result of change in the diffusion coefficient, as well as by thermal diffusion brought about by thermal gradients within the frit and by contraction of the liquid originally within the frit. While the results with varying temperature are somewhat more erratic than those for constant temperature, it is apparent that highly precise temperature control is not necessary and that the tolerance of 0.1° allowed in the present work is certainly sufficient. This is fortunate, since during

(3) W. A. James, E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **7**, 89 (1939).

(4) A. R. Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).

periods of no stirring some fluctuation in temperature will occur.

Applications of the Method.—The results presented here demonstrate that with inside and outside solutions differing in density by 2% or more (the density of 0.5 *M* KCl is 1.02 times that of water at 25°), the diffusion coefficient of the solute can be measured within an accuracy of a few per cent. Obviously wherever the greatest possible precision is desired, as in the determination of the "differential" diffusion coefficients of simple electrolytes, the present method cannot compete with some of the conventional techniques. The principal advantage of our method lies in its combination of speed and simplicity. While it may be no more accurate than other methods of comparable rapidity, such as optical methods which employ an initial discontinuity in concentration, it is certainly simpler, for it requires no special and expensive equipment.

The use of frits in diffusion work has been criticized because of the possibility that adsorption and other effects influence the results. However, the recent work of Stokes on the steady state method⁵ indicates that adsorption in the case of simple electrolytes is not an important factor except at low concentrations (for KCl below 0.05 *M*). Experiments in this Laboratory on bovine plasma albumin using the present method are in agreement with the accepted value for the diffusion coefficient. Thus it seems likely that the method in question will be applicable to most substances.

In principle, the period of diffusion can be made conveniently short for any substance, no matter how small its diffusion coefficient, by decreasing the

(5) R. H. Stokes, *THIS JOURNAL*, **72**, 763 (1950).

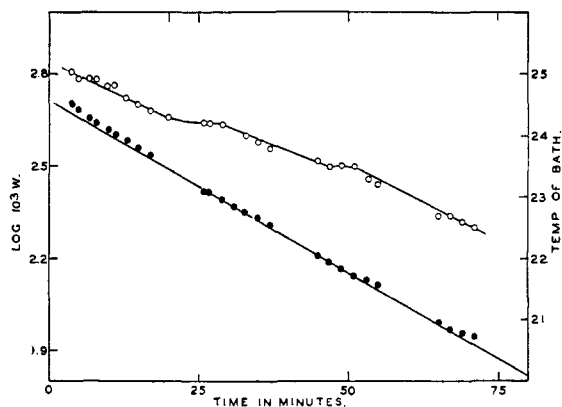


Fig. 5.—Experiment with variable temperature: frit number 1, edges open, $C_1 = 0.44 M$ KCl, $C_0 = 0$: solid circles, corrected for change in density of outside solution; slope of straight line $1.10 \times 10^{-2} \text{ min.}^{-1}$; open circles, temperature of outside solution, right hand scale.

frit thickness. With frits one millimeter thick, a period of diffusion of about one day is required for polyacrylic acid. For this substance, however, solutions two or three per cent. by weight must be used to attain a maximum W of 50 mg. Since the maximum W is approximately proportional to thickness, it is apparent that more concentrated solutions would be required if the thickness (and hence the period of diffusion) is to be decreased significantly. Analysis by weighing the frit will then not be equally useful in all cases. For example, it could not be used with success for many long chain electrolytes since the aqueous solution densities of these compounds are nearly the same as that of water.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Polarographic Behavior of the Nitroanilines in Absolute Ethyl Alcohol¹

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The reducibilities of the nitroanilines were compared with those for the nitrophenols and nitrobenzene in buffered absolute ethanol solutions. *o*-Nitroaniline (as the free base) was more easily reduced than *p*-nitroaniline, but both were more difficult to reduce than *m*-nitroaniline. The latter exhibited practically the same reducibility as *m*-nitrophenol and nitrobenzene. The influence of the amino and hydroxyl groups on the reducibility of the nitro group was discussed in relation to the acidity of the environment. Diffusion coefficients, separately measured, led to the calculation of 6 electrons involved in the reduction of *o*- and *p*-nitroaniline and 4 to 5 electrons for *m*-nitroaniline.

The polarographic behavior of *o*-, *m*- and *p*-nitrophenols,^{3a,4a} *N*-nitrophenyl-*N'*-phenylacetamidines,⁵ and nitroacetanilides⁶ indicate the greatest ease of reduction for the chelated ortho-

isomer, with para the most difficult and meta intermediate. The purpose of this investigation was to examine *o*-, *m*- and *p*-nitroanilines in buffered absolute ethyl alcohol solutions for a similar order of reducibility of the isomers and to determine the influence of structure on the half-wave potentials and the generality of the effect of chelation in facilitating reduction of the nitro group. Earlier work⁷ on these compounds failed to show this ease of reduction for the ortho compound even though infrared spectrum methods⁸ show *o*-nitro-

(1) Abstracted from a thesis by Mervin E. Runner, presented to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the Ph.D. degree, February, 1950.

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(3) (a) M. J. Astle and W. V. McConnell, *THIS JOURNAL*, **65**, 85 (1943); (b) M. J. Astle and W. P. Cropper, *ibid.*, **65**, 2395 (1943).

(4) (a) J. Pearson, *Trans. Faraday Soc.*, **44**, 692 (1948); (b) *ibid.*, **44**, 683 (1948).

(5) M. E. Runner, M. L. Kilpatrick and E. C. Wagner, *THIS JOURNAL*, **69**, 1406 (1947).

(6) M. E. Runner and E. C. Wagner, *ibid.*, **74**, 2529 (1952).

(7) M. Shikata and E. Taguchi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **29**, 1 (1934).

(8) W. Gordy and S. C. Stanford, *THIS JOURNAL*, **62**, 497 (1940).