NEW APPARATUS

A DIFFUSION CELL FOR THE PRODUCTION OF VERY SHARP BOUNDARIES

BY P. H. ELWORTHY*

From the School of Pharmacy, University of London, Brunswick Square, London, W.C.1

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A diffusion cell for the production of very sharp boundaries between aqueous liquids is described, and the Δt correction can be eliminated in most instances. The cell has been tested with substances whose diffusion coefficients are known. Some results for the diffusion of cetomacrogol 1,000 in water are reported.

GENERALLY in diffusion measurements, boundaries between solvent and solution, or between a concentrated and a dilute solution, are formed in sliding cells based on the Neurath type[1], or by flowing a layer of one solution on top of a layer of another[2]. Boundaries are sharpened by flowing out through a pipette tip, or through a slit in the cell placed at boundary level.

A sharp boundary is necessary to reduce the Δt correction to a minimum. The correction must be applied to the observed values of the diffusion coefficient (D′) obtained at different times, t, after the start of diffusion. Δt is defined as the time required for an infinitely sharp boundary to reach the state of the existing boundary when diffusion commences. Longsworth[3] gives:

$$D' = D\left(1 + \frac{\Delta t}{t}\right)$$

A plot of D′ against $1/t$ will have a slope of $D\Delta t$, and the intercept will be the true diffusion coefficient, D.

Even when Δt is small (20 seconds) a slight uncertainty is introduced in extrapolating to $1/t = 0$. A cell has been designed which virtually eliminated Δt, and which has no moving parts requiring grease to make them leakproof.

EXPERIMENTAL

Apparatus

The cell (Fig. 1) was made from a block of 1 inch thick brass. Two rectangular channels, A_1 and A_2, 0·5 cm. wide, were milled through the block. Brass plates were brazed over A_1, while A_2 was covered with the cell windows, made of optically flat ($\lambda/2$) glass. The windows were gasketted with a rubber resistant to organic solvents. The two channels were joined to one another at the bottom of the cell by a hole 0·5 cm. in diameter. At the top of each channel was a constriction 0·2 cm. diameter (B_1 and B_2). B_2 had a right angle bend before entering A_2.

* Present address: School of Pharmacy, Royal College of Science and Technology, Glasgow.

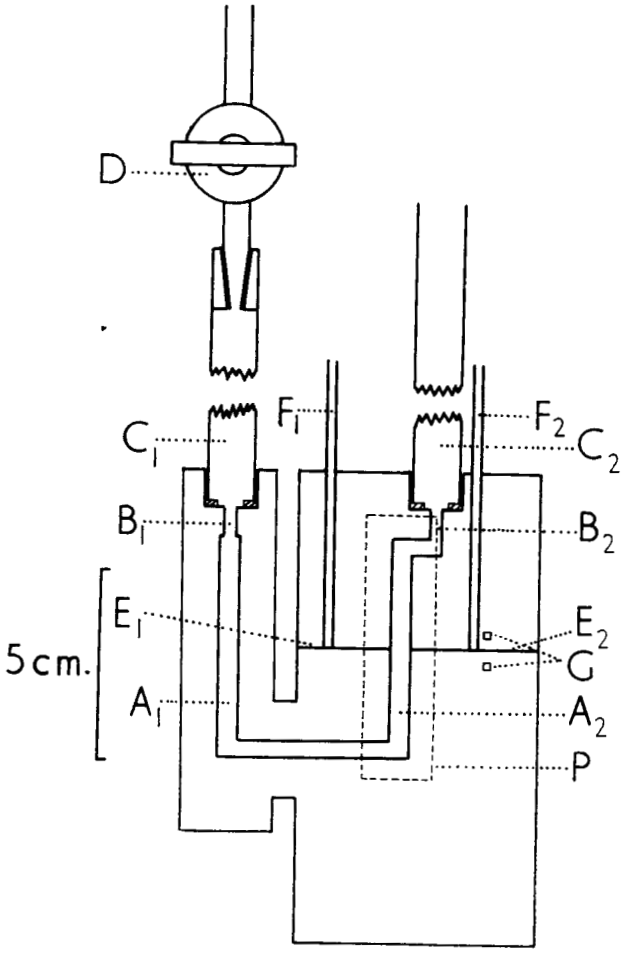

FIG. 1a. Vertical section of diffusion cell.

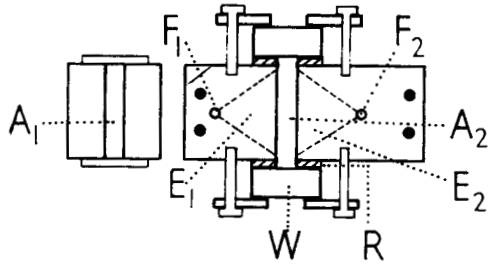

FIG. 1b. Horizontal section of diffusion cell at slit level.

Two reservoirs, C_1 and C_2, screwed into the top of the cell, their ends being seated on rubber gaskets. The top of C_1 was ground to receive a B10 glass joint. A good quality vacuum tap, D, was fused on above the joint.

E_1 and E_2 are two slits opening into the diffusion channel, and were spaced with thin polythene. Liquid could be withdrawn from the diffusion channel via the slits, and removed from the cell up the pipes F_1 and F_2. Two square holes, G, 1×1 mm. in size, were cut in the side of the cell.

The cell was mounted in a thermostat controlled to $25 \pm 0{\cdot}02°$, and fitted with optically flat ($\lambda/2$) windows. The thermostat was bolted to an optical bench.

The Gouy interference method was used to study diffusion: the green line (5461Å) was isolated by interference filters from a mercury vapour lamp, and illuminated a horizontal slit 15 μ wide. An image of the slit was focused through the diffusion cell on to a photographic plate by a lens. All components were mounted on an optical bench, which rested on a girder set on concrete pillars embedded in the floor of a basement laboratory.

Use of Cell

The cell was filled with solution from just below the level of the tap, D, to the middle of the constriction at the top of the diffusion channel A_2, and the tap was closed. After clamping the cell in position in the thermostat and allowing it to come to temperature, a series of photographs of the undeviated slit image and of the interference patterns produced by the square holes was taken. Solvent, or the more dilute solution in the case of a differential diffusion, was run into C_2 by pipette. Solvent and solution met in the constriction, which prevented them from mixing to any great extent, and allowed a crude boundary to be formed. Flow out through one of the slits, (either E_1 or E_2) was started, which lowered the boundary to the middle of the diffusion channel. Solvent was repeatedly added to C_2, and flow through the slit continued. This procedure washed all traces of solute out of the upper part of A_2, which was originally full of solution, and during this operation the boundary sank 2–3 mm. below the level of the slits.

More solvent was added until the level in C_2 was 3–4 mm. below the solution level in C_1. The tap D was opened, causing the boundary to move upwards to the level of the slits. Flow out from the cell was now reduced to about 0·2 ml./minute, and this rate was maintained for 20 minutes, to allow the newly added solvent to come to temperature.

The final stage of the technique was to sharpen the boundary. Liquid was drawn off the cell at an equal rate through both slits, the combined flow rate being raised to between 2 and 6 ml./minute (see later). To start the experiment the flow from the cell was stopped by closing clips placed across the polythene tubes which carried liquid away from the pipes F_1 and F_2. The time at which flow was stopped was taken as zero time, and could be measured with an accuracy of ± 1 second.

A mask of the type described by Gosting[4] was used with the cell. Photographs for evaluating fractional j_m were taken immediately after the experiment had started. The interference patterns produced by diffusion were photographed at timed intervals.

Materials

All materials used were Analar quality, except for the cetomacrogol, which was a commercial grade. All results fitted the theory for the diffusion of a single solute.

Results and Discussion

Table I gives the results of a differential diffusion experiment on barium chloride.

TABLE I

DIFFERENTIAL DIFFUSION OF BARIUM CHLORIDE IN WATER

Concentration difference between solutions* ($\triangle c$) = 0·03406M $l.^{-1}$. Mean concentration of two solutions ($\bar{c}$) = 0·04248M $l.^{-1}$. Flow rate = 4 ml./minute. $\triangle t$ = 1 second

$10^4 1/t$	11·17	6·390	6·390	4·751	2·822	2·447	1·983
10^5 D′ $cm.^2sec.^{-1}$	1·186	1·187	1·187	1·187	1·189	1·187	1·187
$10^4 1/t$	1·488	1·225	—	—	—	—	—
10^5 D′ $cm.^2sec.^{-1}$	1·184	1·186	—	—	—	—	—

* If C_1 and C_2 were the concentrations of two solutions used in an experiment, then $\Delta c = C_1 - C_2$, and $\bar{c} = \frac{c_1 + c_2}{2}$

The diffusion coefficient appears to be constant over a tenfold change in t, while a decrease of D′ with time would have been expected if the boundary had not been sharp. To test if Δt was eliminated, within the limit of experimental error, the slope of the D′ against 1/t plot was calculated by the method of least squares. The slope was $7{\cdot}34 \times 10^{-6}$, and the intercept, $D = 1{\cdot}186 \times 10^{-5}$ $cm.^2sec.^{-1}$, giving $\Delta t = 1$ second. The literature value of D is $1{\cdot}186 \times 10^{-5}$ $cm.^2sec.^{-1}$.

In Table II the results for the diffusion of a number of other substances are given. In all experiments D′ was measured over a tenfold change in t.

TABLE II

DIFFUSION COEFFICIENTS OF VARIOUS SUBSTANCES

Substance	$\bar{c}$	Δc	Flow rate
Sucrose	0·75 per cent	1·5 per cent	0·8 ml./minute
Sucrose	0·75 ,,	1·5 ,,	1·8 ,,
Sucrose	0·75 ,,	1·5 ,,	3·4 ,,
Sodium chloride	0·08026M $l.^{-1}$	0·1045M $l.^{-1}$	6·0 ,,
Potassium chloride	0·1000M $l.^{-1}$	0·2000M $l.^{-1}$	3·8 ,,
Cetomacrogol	0·669 per cent	0·669 per cent	7·0 ,,

	10^5 D $cm.^2sec.^{-1}$	Δt	10^5 D $cm.^2sec.^{-1}$ (literature)
Sucrose ..	0·5158	38	0·5170[6]
Sucrose ..	0·5176	20	0·5170
Sucrose	0·5171	0	0·5170
Sodium chloride	1·489	1	1·490[5]
Potasium chloride ..	1·850	0	1·851[7]
Cetomacrogol	0·0520	1	—

Generally, too slow a flow from the cell results in a Δt value, as shown by the sucrose experiments. The flow rate necessary to reduce Δt until it falls within the limit of experimental error appears to vary from system to system. If sucrose solutions were drawn off the cell too quickly (above 6 ml./minute), considerable mixing appeared in the boundary region, and no worthwhile results could be obtained. A disadvantage of this type of cell is that flow off conditions are critical, and have to be investigated for each type of system studied, e.g., for electrolyte solutions any reasonably fast flow off suffices to eliminate Δt; sucrose requires careful handling, while detergents, like cetomacrogol, can be drawn off quickly. Similar conclusions have been reached using a cell with one slit (Thomas, private communication).

Some experiments were also made on cetomacrogol solutions (Table III).

There is little variation of diffusion coefficient with $\bar{c}$, indicating that only small electrical effects are present during diffusion, as would be expected with a non-ionised material. The diffusion coefficient appears to be slightly concentration dependent ($\bar{c}$), and extrapolation to zero concentration gives $D = 5{\cdot}10 \times 10^{-7}$ cm.^{2}sec.$^{-1}$. Δt's of less than two seconds were found in this series of experiments.

TABLE III

DIFFERENTIAL DIFFUSION COEFFICIENTS OF CETOMACROGOL IN WATER

$\bar{c}$ per cent	0·300	0·669	0·673	0·762	1·303
Δc per cent	0·400	0·669	0·601	1·016	0·897
10^7 D (cm.^{2}sec.$^{-1}$) ..	5·13	5·20	5·18	5·24	5·31

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REFERENCES

1. Neurath, *Science*, 1941, **93**, 431.
2. Saunders, *J. chem. Soc.*, 1953, 519.
3. Longsworth, *J. Amer. chem. Soc.*, 1947, **69**, 2510.
4. Gosting, Hanson, Kegeles, and Morris, *Rev. Sci. Instruments*, 1949, **20**, 209.
5. Vitagliano and Lyons, *J. Amer. Chem. Soc.*, 1956, **78**, 1549.
6. Gosting and Morris, *ibid.*, 1949, **71**, 1998.
7. Gosting, *ibid.*, 1950, **72**, 4418.