[CONTRIBUTION FROM THE UNIVERSITY OF OREGON]

A New Apparatus for Measuring Diffusion in Solutions*

BY ROBERT B. DEAN

When a solute diffuses into a solvent the concentration will vary with time and distance in a unique manner depending on the boundary conditions and the diffusion coefficient. If either the concentration, c, or the gradient of concentration, dc/dh, is known as an empirical function of the time, t, and distance, h, the diffusion coefficient D, can be calculated.[1,2] When c is known as a function of h and t for free diffusion, D can be calculated directly from Boltzmann's equation[1,3]

$$D = -\frac{1}{2}\, dy/dc \int_0^c y\, dc \qquad (1)$$

where $y = h/\sqrt{t}$ (see also ref.[4]).

Any method for measuring c as a function of t and h should preferably do so without disturbing the diffusing system. This logically suggests optical methods. When the solute absorbs light its diffusion can be followed by obvious colorimetric methods.[5–7] Colorless solutes can be followed by observing the refractive index of the diffusion column. Nakamura[8] was apparently the first to measure the concentration by the critical angle of reflection at one face of the diffusion cell. He used a cell which was 1 cm. thick and formed the initial boundary by flowing the solution under the pure solvent. His initial boundary cannot have been sharp and convection currents would be hard to eliminate in such a thick cell. Furth and his co-workers[6,9,10,11] pioneered in the use of thin chambers which minimize convection but they formed the initial boundary by withdrawing a sliding partition. Any sliding surface inevitably produces mixing and the results from Furth's school show fluctuations of more than 10% in the estimation of D. Zuber's optical arrangement[9] was furthermore limited by the precision of his goniometer. Instead of recording the entire refractive index–height curve he measured the angle of extinction at a number of selected heights. The short optical path of his apparatus also limits the possible precision of his method.

The apparatus described in this paper was designed to produce a direct record of the variation of concentration with height and at the same time eliminate convection and sliding boundaries.

The apparatus (see Fig. 1) consists of a thin chamber (approximately 4 cm. square) formed between one face of a 60° prism and a special fused glass cell.[12] The glass plate which forms the distal wall of the diffusion chamber terminates in a horizontal "knife-edge" at the top. This plate is backed up by a glass cell having a capacity one hundred times that of the diffusion chamber. The glass cell is attached to the prism face with stopcock grease and pressed on to a tight fit. The central portion of the chamber is parallel to the prism to within one wave length of sodium light in a vertical direction. It is inclined to the prism face about six wave lengths (3×10^{-4} cm.) per cm. in the central region. The cell is 0.03 cm. thick and parallel walled to 0.1% in the direction of diffusion. A mask on the exit face of the prism limits the effective object to the central portion of the diffusion cell. At the edges of the cell the departures from parallel walls are two to three times greater than in the center.

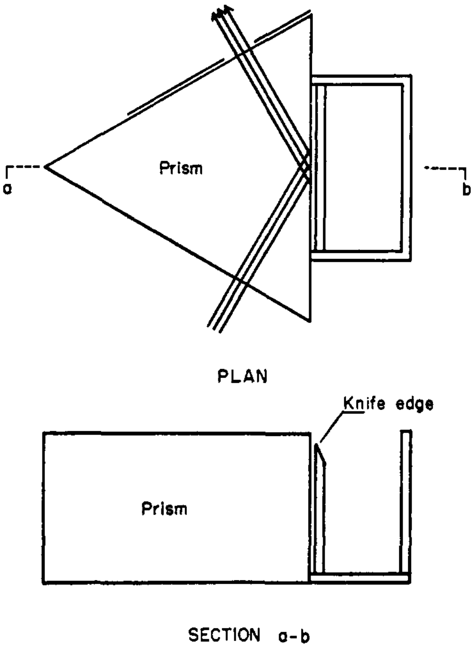

Fig. 1.—Diagram of diffusion cell and prism.

To start a diffusion run the chamber is filled with the 0.4 ml. of the more concentrated solution. The cell is then filled with 40 ml. of the more dilute solution, frequently water, at 25° and the time at which the top of the "knife-edge" floods is taken as zero time. As the solute in the chamber diffuses up to the "knife-edge" it falls over and sinks to the bottom of the large chamber. Approximately 20% of the contents of the chamber will have diffused into the outer cell when the concentration at the bottom falls to 99% of its original value. When this happens the boundary conditions no longer correspond to free diffusion in a semi-infinite prism and the run is ordinarily stopped. This quantity of solute will produce a

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(*) The material in this paper was presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at the 114th meeting in Portland, Sept. 14, 1948.

(1) L. G. Longsworth, *Ann. N. Y. Acad. Sci.*, **46**, 211 (1945).

(2) C. O. Beckman and J. L. Rosenberg, *ibid.*, **46**, 329 (1945).

(3) L. Boltzmann, *Wied. Ann.*, **53**, 959 (1894).

(4) W. G. Eversole, J. D. Peterson and H. M. Kindsvater, *J. Phys. Chem.*, **45**, 1398 (1941).

(5) W. G. Eversole and E. W. Doughty, *ibid.*, **39**, 289 (1935), and **41**, 663 (1937).

(6) R. Furth, *Physik. Z.*, **26**, 719 (1925).

(7) R. Furth, *J. Sci. Instruments*, **22**, 61 (1945).

(8) S. Nakamura, *J. College Sci., Tokyo Imperial Univ.*, **19**, 8 (1903).

(9) R. Zuber, *Z. Physik*, **79**, 280 (1932).

(10) E. Ullman, *ibid.*, **41**, 301 (1927).

(11) R. Furth, *et al.*, *Kolloid Z.*, **41**, 300 (1927).

(12) Made by Central Scientific Co.

maximum change of 0.02% in the concentration of the outer chamber if mixing is perfect. It is likely that mixing will not be perfect in the outer chamber and the concentration change will be correspondingly less. Convection cannot occur in the actual diffusion chamber because the walls are close together (0.3 mm.). Furthermore the density of the solution in the lower part of the cell is about 4% greater than at the top for 1 N potassium chloride. A temperature difference of 1° produces a density difference of only 0.02% so the possibility of thermal convection in the diffusion column can be ruled out for aqueous salt systems.

The lens system (see Fig. 2) consists of a plano cylindrical plus 2 diopter eyeglass lens (f = 50 cm.) and a plano spherical plus 2 diopter lens. The plane sides of the lenses face out and they are approximately 1 cm. apart. The focal line of the cylindrical lens is in the center of diffusion chamber and its axis is horizontal. The focal point of the spherical lens is on the photographic plate. There is a 0.6 cm. vertical slit mask on the exposed prism face and a 0.6 cm. horizontal slit mask between the lenses. The prism is illuminated through its third unpolished face by light from a mercury sun-lamp filtered through glass filters to isolate the green line at 5461 Å.

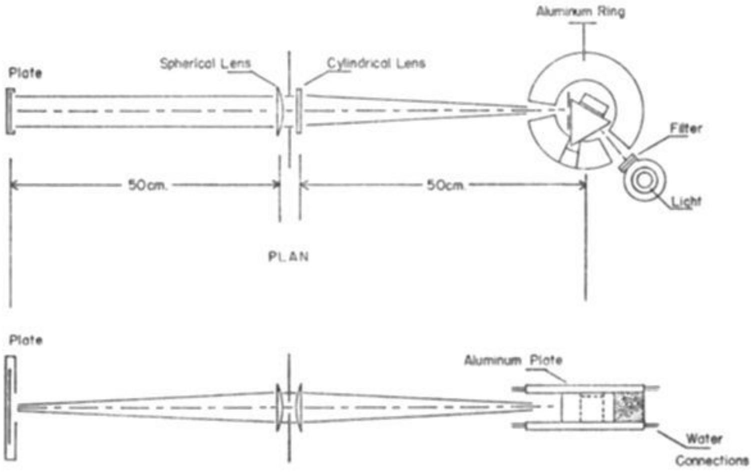

Fig. 2.—Plan and elevation (sectional) of optical bench.

Light entering the prism through the fine-ground face is scattered to produce even illumination over the entire diffusion chamber. Light striking the chamber at less than the critical angle is partially reflected and partially transmitted into the chamber where it is lost. Light striking at the critical angle or greater is totally reflected. In the horizontal plane the cylindrical lens is inoperative and the spherical lens focusses the parallel ray reflected at the critical angle, or any other angle, to a point on the plate corresponding to the angle of reflection. In the vertical plane light arising from any level in the diffusion cell is rendered parallel by the cylindrical lens and focussed to a corresponding level by the spherical lens.

The image thus consists of two fields differing in illumination. The location of the boundary between these fields depends upon the angle of total reflection in the prism which in turn depends upon the ratio of the refractive indices of the glass prism and the solution in the diffusion chamber. The critical angle for pure water against crown glass, n = 1.51, is 61° 59′. Light reflected at the critical angle reaches the exit face of the prism virtually perpendicular and undergoes only slight deviation at that face. For organic liquids a flint prism would be preferable. The variation in the critical angle is practically linear with the refractive index of the solutions in contact with the glass for the range of concentrations available. A 10% solution of most solutes produces a deviation of about 2 cm. on the photographic plate.

The aperture width of 0.6 cm. was chosen as the best compromise between diffraction and lack of focus. Since the object plane is necessarily inclined at 60° to the optical axis it is impossible to focus light from the cell exactly on a plane. The requirements of horizontal focussing are incompatible with those of vertical focussing and a sharp focus can only be obtained by narrow apertures which, however, introduce diffraction errors. For the dimensions chosen the optimum aperture is about 0.6 cm. which limits the theoretical resolution to 13″ of arc or approximately 0.003% salt solution. The observed resolution is not yet as good as this; it is possible to locate a boundary to within 0.02 mm. corresponding to 0.01% salt solution. Various Eastman Kodak Co. photographic plates have been used successfully including IVG and VG spectroscopic plates and Wratten Metallographic plates all used with Eastman D-19 developer to produce maximum contrast. Figure 3 shows a contact print of one of the plates.

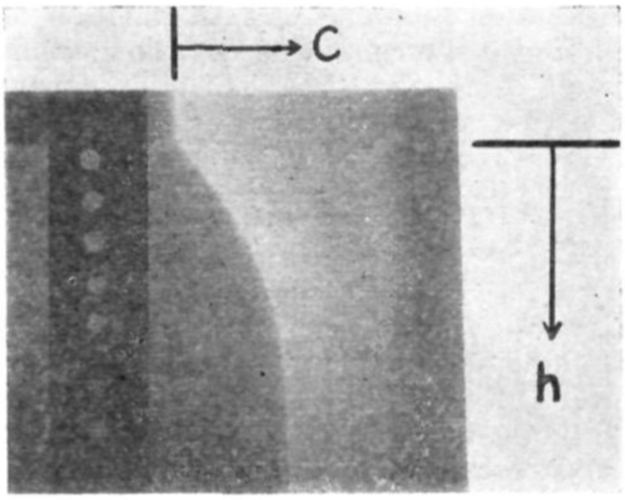

Fig. 3.—Print of a negative showing the variation of concentration with height in the diffusion cell.

The apparatus is mounted at one end of an optical bench which rests on a concrete pier. The prism and cell sit on a copper carrying plate which in turn sits on a hollow aluminum plate 8 in. in diameter. The prism and cell are surrounded by sections of a square cross section aluminum ring which is cut away to permit light to enter and leave the prism. Another hollow aluminum plate sits on top of the ring. Water is circulated by a centrifugal pump, from a tank containing heating and cooling coils, through the top plate of the prism, then through a glass tube containing a mercury thermoregulator and back through the lower plate to the tank. The heater is regulated by a thyratron controlled by the thermoregulator and operated from a 6-v. transformer. This thermostat maintains the temperature of the solution in the cell to within 0.02° or better. Care is taken not to let the mercury light shine on the cell except when a picture is being taken. Except for the mercury lamp the entire apparatus is housed in a plywood box with removable walls.

The image developed on the photographic plate should be measured with a coördinate comparator. Not all the parts for such a comparator have been received yet and the pictures obtained so far have been measured with a travelling microscope and eye-piece micrometer using a low magnification objective. This method is subject to errors caused by distortion of the image field and is furthermore very inconvenient. The results obtained are therefore of a preliminary nature and no attempt has been made to calculate D by Boltzman's equation, 1.

An estimate of D on the assumption that D is independent of c can be made conveniently by using probability paper. Since the concentration at the "knife-edge" is maintained essentially constant the boundary conditions in the initial stages correspond to diffusion into a semi-infinite prism. This is identical with one half of the case of diffusion from an initially sharp boundary into an infinite prism. The relation between c, h and t is given by the following equation for these conditions (1)

$$\frac{c}{c_0} = \frac{1}{\sqrt{4\pi D_0 t}} \int_{\infty}^{h} e^{-\frac{h^2}{4D_0 t}} \, dh \qquad (2)$$

This is identical in form with the equation for the probability integral

$$Z = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{\infty}^{h} e^{-\frac{h^2}{2\sigma^2}} \, dh \qquad (3)$$

where z varies from zero to 1. From equations 2 and 3 it is evident that

$$\sigma^2 = 2D_0 t \text{ or } D_0 = \frac{\sigma^2}{2t} \qquad (4)$$

Values of z as a function of h are readily available in tables and it is also possible to purchase probability graph paper[13] ruled from 0 to 100% in such a way that a plot of z *vs.* h is a straight line. The value of σ is equal to the difference in the h intercepts at 50% and either 15.87 or 84.13%. D_0 can of course be estimated from the 15.87 or the 84.13% intercept alone but it has been found safer to plot the values of c *vs.* h on probability paper and draw the best straight line through the points to obtain the h intercepts. To do this the c values are converted to C' values from 50 to 100 by the relation

$$C' = (50c/c_0) + 50 \qquad (5)$$

or the equivalent reaction for values from 0 to 50

$$C' = 50 - (50c/c) \qquad (6)$$

Figure 4 shows data from two photographs of one run with 1 N potassium chloride. The D values obtained, 1.8 and 1.9 × 10^{-5}, show satisfactory agreement with the integral value of 1.85 × 10^{-5}, calculated from the data given by Vinograd and McBain[14] corrected according to Gordon.[15] This agreement is partially fortuitous since D for potassium chloride varies by 10% over the range from 0 to 1 N. The probability integral method is essentially equivalent to the height and area method for analysing curves of dc/dh obtained by the scale method.[16]

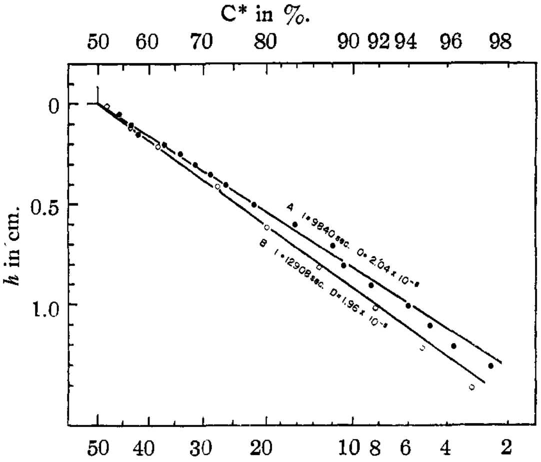

Fig. 4.—Diffusion of 1 N KCl at 25° plotted on probability paper.

Summary

1. An apparatus is described in which diffusion takes place in a narrow chamber along one face of a prism into an effectively infinite volume of solvent.

2. The initial boundary is formed by flooding the top of the thin chamber.

3. The concentration of diffusing material is determined from the angle of total reflection which is recorded photographically.

4. The apparatus is suitable for solutions containing of the order of 1% solute.

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[13] From Keuffel and Esser.

[14] J. R. Vinograd and J. W. McBain, THIS JOURNAL, **63**, 2008 (1941).

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

[16] E. M. Bevilacqua, *et al.*, *ibid.*, **46**, 309 (1945).

[CONTRIBUTION FROM THE STANFORD RESEARCH INSTITUTE, STANFORD UNIVERSITY]

Studies of Protein Foams Obtained by Bubbling[1]

BY WILLIAM C. THUMAN,[2] A. G. BROWN[2] AND J. W. MCBAIN

Introduction

The foaming of protein solutions is of theoretical interest, and also has wide applications in the baking industry and in fire fighting practice. It is known to be greatly dependent upon pH and the presence of salts, though but little systematic work has been published in this field.

Recently it was shown by Perri and Hazel[3] that a soybean protein solution exhibited a maximum foaming capacity in the neighborhood of the isoelectric point. Barmore[4] in studying the properties of egg white foams as a problem of the baking industry reported that organic acids and acid salts considerably increase foam stability. Peter and Bell[5] found the stability of foams from the protein of whey to be increased by addition of

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[1] (a) This investigation was conducted under Contract N-7onr 321 between The Stanford Research Institute and the Office of Naval Research, supervised by Professor J. W. McBain; (b) presented at the 115th meeting of the American Chemical Society, San Francisco March, 1948.

[2] Present address: Stanford Research Institute, Stanford, California.

[3] J. M. Perri and F. Hazel, *J. Phys. Colloid Chem.*, **51**, 661 (1947).

[4] M. A. Barmore, Colorado Agricultural College Technical Bulletin, 9, 1934.

[5] P. N. Peter and R. W. Bell, *Ind. Eng. Chem.*, **22**, 1124 (1930).