CHAPTER II

LITERATURE REVIEW

2.1 Introduction to Molecular Mass Transport

Molecular diffusion or molecular transport is the transport or movement of individual molecules through a truly stagnant fluid by means of random, individual movements of the molecules. If the fluid is in la--minar flow, molecular diffusion can occur in all directions in the fluid. The molecules can be imagined as traveling in a blind manner only in straight lines and changing direction by bouncing off other molecules after collisions. Since the molecules travel in a random path, molecular diffusion is often called a random-walk process.[5]

Figure 2.1 shows the molecular diffusion process schematically for A molecules diffusing through B molecules. The dotted lines show the random path that an A molecule might take in diffusing from point (1) to (2). If at the start there are more A molecules near point (1) than at point (2), then it is obvious that more A molecules will diffuse from (1) to (2) than from (2) to (1). This means we have a concentration that is higher at (1). The net diffusion will be from the region of high to that of low concentration.

As another example of molecular diffusion, suppose a drop of blue ink dye is placed in a beaker containing water that is truly stagnant and not mixed by convection or stirring. A high concentration difference of

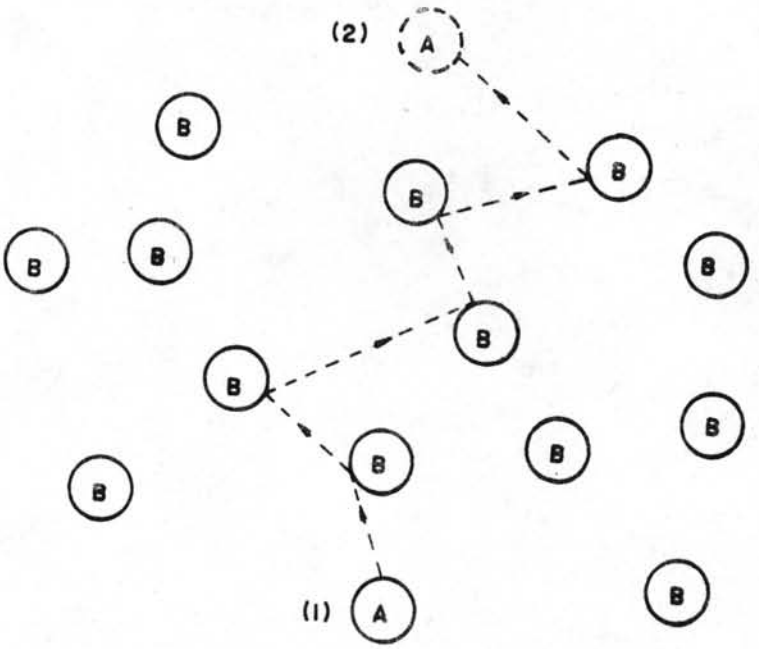

Figure 2.1 Diagram of molecular diffusion or random-walk diffusion process.

blue dye will exist between the drop of dye added and the adjacent water. The dye molecules will diffuse slowly by molecular diffusion to all parts of the water. Eventually the fluid will be almost completely mixed, but this process will take many days. If the contents are rapidly stirred with a stirring rod that is, turbulent or bulk motion of the fluid is introduced then the solution will be completely mixed in a few seconds. Hence, one can see that mass transport by turbulent motion as well as molecular diffusion is very rapid compared to molecular diffusion alone.

It should be evident that the rate of molecular diffusion in liquids will be many times slower than gases. Referring again to Fig. 2.1,

if B is a liquid, the molecules will be very close together compared to B as a gas. Hence, the molecule of A will collide with molecules of liquid B more often and diffuse more slowly. Also, mean free paths of gaseous molecules are much greater than liquid molecules. In general, the diffusivity in a gas will be of the order of magnitude of 10^5 times larger than in a liquid.

2.2 Molecular Transport Equations for Liquids

When the concentration of the solute is uniform at every point in the absence of bulk motion of the liquid, no further spontaneous change occurs and that as long as it is not yet uniform, the system spontaneously moves toward uniformity, the solute moving from a place of high concentration to a place of low. The rate at which a solute moves at any point in any direction must threrefore depend on the concentration gradient at that point and in that direction.

If, in a binary solution of A and B, the molar mass velocity in a given direction, or flux, of solute A is defined as J_A, moles of A per unit time per unit area (area measured normal to the direction of motion), then the diffusivity of A, D_A is defined as the ratio of the flux to the concentration gradient $\partial c_A/\partial z$

$$J_A = - D_A \frac{\partial c_A}{\partial z} \tag{2.1}$$

which is Fick's first law. The diffusivity is not ordinarily a constant for a given system but depends upon concentration and temperature.

The true "driving force" of the diffusion is probably not concentration, as Eq.(2.1) would imply, but rather chemical potential or activity,

which is emphasized that in a multiphase system the spontaneous movement stops not when concentrations but rather when activities are equal throughout. But concentrations are ordinarily used in defining diffusivity.

The flux J of Eq.(2.1) is defined as the molar mass velocity with respect to the average molar velocity in the solution. Consider a volume of a binary solution containing substances A and B, of unit cross section, undergoing molecular diffusion. For simplicity, let the solution be ideal, so that the volume of the solution remains constant while diffusion occurs, and without net bulk movement. Then, if component A is diffusing from left to right at a volume rate or (since the cross section is unity) at a velocity v_A, the velocity of diffusion of B in the opposite direction v_B must be $v_B = -v_A$, since the solution volume remains constant, or

$$v_A + v_B = 0 \tag{2.2}$$

The volumes to the left and right of a stationary point then remain constant. The rate at which moles of A pass the stationary point is then $N_A = v_A c_A$ and for B, $N_B = v_B c_B$, where c_A, c_B are the respective molar concentrations. The net rate of passage of moles past the stationary point is then $N_A + N_B$. The molar average of the velocities is

$$v_M = \frac{c_A v_A + c_B v_B}{c} \tag{2.3}$$

where c = total concentration. Since the concentrations are not equal, it follows that v_M is not zero, and if one wished to observe no net molar flux, one would have to move at a velocity v_M. The number of moles of solution to the left and right of the moving observer would then remain

constant. The flux N_A with respect to the stationary point must therefore be larger than flux J_A by the amount of A in the volume rate v_M,

or
$$N_A = v_M c_A + J_A \tag{2.4}$$

or
$$N_A = (N_A + N_B)\frac{c_A}{c} - D_A \frac{\partial c_A}{\partial z} \tag{2.5}$$

Thus a stationary observer would see no net volume flow but would observe both a net molar and a net mass flow. In nonideal liquids there would be a net volume flow also. Fluxes referred to these flow have also been used to define diffusivity, and this leads to confusion. But if one is consistent in setting up the relationships, the end result with respect to a stationary position is the same, although different D's will be required.

Refer again to the solution above, where

$$c_A + c_B = c \tag{2.6}$$

writing the counterpart of Eq.(2.5) for component B and adding to Eq. (2.5) the result is

$$- D_A \frac{\partial c_A}{\partial z} = D_B \frac{\partial c_B}{\partial z} \tag{2.7}$$

From this it follows that $J_A = -J_B$, and substituting Eq.(2.5) in Eq.(2.7) it further follows that $D_A = D_B$ (at the prevailing concentration and temperature).

For a volume of the fluid of unit cross section and dz long, the rate at which A enters the face at $z = z$ is N_{Az} and the rate at which it leaves at $z + dz$ is $N_{Az} + (\partial N_A/\partial z)dz$. Consequently, the rate

of loss of A in the volume is the difference, or

$$\frac{\partial N_A}{\partial z} dz = - \frac{\partial (c_A dz)}{\partial t} \tag{2.8}$$

if $v_M = 0$ and D_A = constant, then Eq.(2.1) and Eq.(2.4) with Eq.(2.8) yield Fick's second law

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial z^2} \tag{2.9}$$

All the above have been considered only for unidirectional diffusion. All the expressions may be written for the three dimensions x, y, z. Thus, Eq.(2.9) becomes for constant D_A,

$$\frac{\partial c_A}{\partial t} = D_A \nabla^2 c_A \tag{2.10}$$

The dimensions of D are $(\text{length})^2/\text{time}$

2.3 Experimental Determinations of Diffusivity

The experimental determination of accurate diffusivities is extremely difficult. Many methods have been proposed for studying the phenomenon. It is not proposed to mention all the methods available but to concentrate on those which seem to offer the best answer to the practical problem of obtaining reliable diffusivity data rapidly, cheaply, and easily, which few wasted determinations.

The methods of measuring diffusivity fall into three distinct categories, based on the way diffusion occurs .

a) Free Diffusion

A sharp diffusion boundary is formed within a vertical diffusion cell. Mutual diffusion occurs, concentrations, on either side of the boundary, change with time and as long as the concentrations at the ends of the cell remains constant, the diffusion is said to be "free".

b) Restricted Diffusion

"Free diffusion" continues until the end concentrations change and then "restricted diffusion" occurs.

c) Steady State Diffusion

In methods of this type, the concentrations at either end of a column of solution are kept constant with time and, therefore, the concentration at all points within the column will remain constant.

The three versions of diffusion and their development will be discussed in some details.

2.3.1 Conductivity Method

This method was restricted diffusion type, developed by Harned and Nuttall[6]. The diffusion channel of their cell is rectangular in cross section (A in Fig.2.2) and its height α about 5 cm. is accurately measured. It is closed permanently at the top, and at the bottom fits against a sliding plate containing two small reservoirs B and C which have the same cross section as the channel A, so that by suitably sliding the plate either of them may be made to form a downward continuation of

the channel. In an inverted position, the channel A is filled with conductivity water and the plate is placed in the position with the reservoir B in line with A. On sliding the plate to the position shown, the excess water is carried off in B, leaving A completely filled. Reservoir C is filled with a salt solution of suitable concentration. The cell is then turned right way up and set up in an air tight thermostated box with the most stringent precautions against mechanical vibration. After allowing a day for attainment of thermal equilibrium, the sliding plate is moved by a remote control so that the solution in reservoir C is in line with A, and salt diffuses into A. When a suitable amount has entered, the plate is moved back to the position shown and the main run begins. The

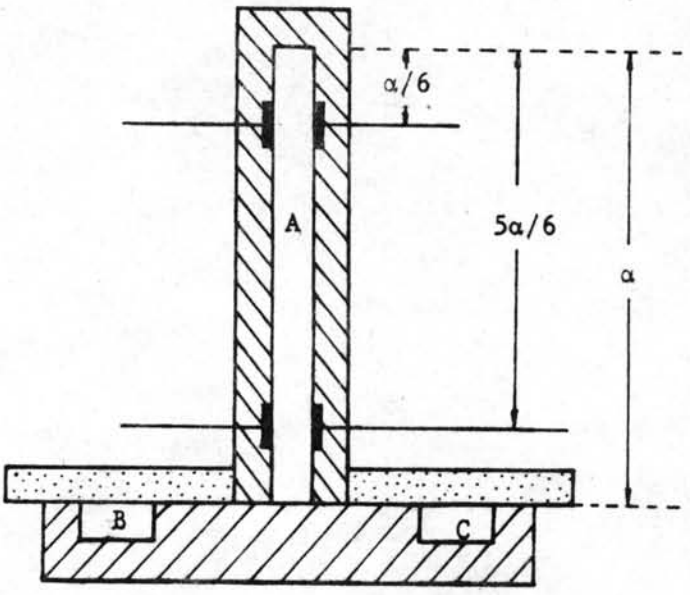

Figure 2.2 Harned's conductimetric diffusion cell

(Diagrammatic only)

concentration changes are followed by measuring the conductivity at two positions in the cell by means of pairs of very small electrodes set in opposite walls at heights $\alpha/6$ and $5\alpha/6$ above the sliding plate.

The boundary conditions are, since both ends of the cell are closed,

$$\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = 0 \quad \text{and} \quad x = \alpha$$

and the appropriate Fourier-series solution of Eq.(2.9) for the concentration c at a height x is

$$c = c_0 + \sum_{n=1}^{n=\infty} B_n \exp(-n^2 \pi^2 Dt/\alpha^2) \cos \frac{n\pi x}{\alpha} \qquad (2.11)$$

where c_0 and the B_n's are constants. Hence the difference in concentration between the planes $x = \alpha/6$ and $x = 5\alpha/6$ is

$$c_{\alpha/6} - c_{5\alpha/6} = \sum_{n=1}^{n=\infty} B_n \exp(-n^2\pi^2 Dt/\alpha^2) \left[\cos \frac{n\pi}{6} - \cos \frac{5n\pi}{6}\right] \qquad (2.12)$$

For even values of n, $\cos\frac{5n\pi}{6} = \cos\frac{n\pi}{6}$ and for odd n, $\cos\frac{5n\pi}{6} = -\cos\frac{n\pi}{6}$ so that all the terms for even n vanish since the factor in square brackets is zero; and for odd n the square bracket becomes $2\cos\frac{n\pi}{6}$ which equals $\sqrt{3}$ for $n = 1$, 0 for $n = 3$, $-\sqrt{3}$ for $n = 5$ and 7, etc. Eq.(2.12) therefore becomes,

$$c_{\alpha/6} - c_{5\alpha/6} = B_1' \exp(-\pi^2 Dt/\alpha^2) + B_5' \exp(-25\pi^2 Dt/\alpha^2) + \cdots\cdots \qquad (2.13)$$

where $B_1' = B_1\sqrt{3}$, etc. Since the leading term of this expression exceeds the second term by the factor $\exp(24\pi^2 Dt/\alpha^2)$ the series converges very rapidly even for small values of Dt/α^2, and after a few days only the first term need be considered at all. This rapid convergence is a result of the ingenious choice of the heights $\alpha/6$ and $5\alpha/6$ for the electrode pairs, which makes the term for $n = 3$ vanish at all times. The coefficient B_1' need not be determined, for by logarithmic differentiation one obtains,

$$\frac{d}{dt}\ln\left[c_{\alpha/6} - c_{5\alpha/6}\right] = -\frac{\pi^2 D}{\alpha^2} \qquad (2.14)$$

so that by plotting $\ln(c_{\alpha/6} - c_{5\alpha/6})$ against the time t a straight line of slope $-\pi^2 D/\alpha^2$ results.

In the early stages of the experiment the assumption of constant D may not be justified, but as the diffusion proceeds the concentration differences become smaller, and D is more nearly constant throughout the solution. The remarkably constant values of D given by Eq.(2.14) after the first day are evidence for the validity of the theoretical treatment. The constant value attained can therefore be treated as the differential diffusion coefficient at the average concentration of the solution, which is found by allowing the cell solution to mix under the action of thermal convection after completing the run, and measuring its concentration conductimetrically.

This method has been used to determine the diffusivity of a considerable number of electrolytes over the range 0.1 to 10 millimoles/litre. The method gives data which are simple to analyse arithmetically with an estimated accuracy of $\pm$ 0.1 %. However, due to the very slight

density difference involved, which is the only stabilizing effect against mixing due to vibration and convection, considerable precautions must be taken to eliminate such disturbances. The problem here is greatly magnified since each experiment occupies six days. The diffusivities obtained are extremely valuable to the theoretical chemist, but only in exceptional circumstances will the designer be interested in data at such low concentration. At higher concentrations the value of this method rapidly diminishes because conductivity as a means of determining concentrations becomes less sensitive. Other methods, more rapid and simple, are available.

2.3.2 Diphragm Cell Method

Few steady state liquid phase diffusion experiments are described in the literature. More common is the Gordon diaphragm cell as cited by Nienow[7]. He realized that it was only capable of giving integral diffusivity values and that it was necessary to have an accurately known and consistent solution for the standardization of the cell (KCl). Although the method had been used previously, no commonly agreed standard had been suggested, and it was difficult to obtain absolute values. This is because the method gives diffusivity values dependent on the size of pores employed in the diaphragm. Another problem encountered was the maintenance of uniform concentrations throughout the cell. These were to be maintained by placing the more concentrated solution above the dilute and allowing convective mixing, once diffusion had occured. This mixing was found to be inadequate and also gave rise to high diffusivity values due to streaming of the heavier solution through the pores. The new method

is to place the dilute solution above the concentrated solution and use magnetic stirrers of such a density that they just touch the diaphragm[8] Care must be taken to recalibrate the cell at interval because of wearing away of the sintered glass diaphragm, causing variation in the rates of diffusion[9]. The speed of stirring is found to have no effect on the rate of diffusion provided it is kept above a minimum of about 50 rpm. Also, it was found to carry out such measurement by placing the cell in the horizontal plane to prevent streaming[10]. The diaphragm was a glass disc, pore size 3-5 microns, 5.0 cm. in diameter and 0.5 cm. thick.

The method is simple to analyse since steady state conditions exist within the cell. This is usually ensured by allowing a period of preliminary diffusion while the steady state is reached within the pores of diaphragm. Then the upper, less concentrated, solution is changed for a fresh solution of exactly known composition. The diffusion is then allowed to continue for from one to six days and the final cell concentrations are determined. The cell will then give an integral coefficient for the mean, high, concentration to the mean, low, concentration solution. It is essential to have large quantities of liquid above and below the diaphragms so that the concentration changes are small. The calculation of the integral diffusivity was shown by Gordon[11] to be

$$D_{INT} = \frac{1}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \qquad (2.15)$$

where c_1, c_3 are the initial and final high concentrations, c_2, c_4 are the initial and final low concentrations, β is the cell constant and t is the time of the experiment.

This method is suitable for laboratory determinations since it has a number of advantages. Due to the narrow pores of the diaphragm and the relatively large density differences, the convection currents are easily damped out and truly molecular diffusion is obtained. This also means that the precautions required to eliminate bulk movement due to temperature changes, vibrations and other external effects. Analysis can be performed at leisure at the end of the run and the computations then required are simple. The major drawback to the method is the length of time required for any one determination and the fact that only integral values are determined directly from the cell. The difficulty in converting these into differential values varies with the system but it is most easily carried out for electrolytes where the diffusivity at finite dilution can be calculated from the Nernst equation and a simple graphical method employed[8].

2.3.3 Free Diffusion Method

Of the free diffusion methods employed the majority use the change in refractive index with time in the region of the interface as a means of following diffusion. The two interferometric methods will be discussed.

1. Guoy Interference Phenomena[12]

Guoy fringes are formed by the passing of the converging horizontal beam of light through a diffusion cell in the region of the boundary. There is a symmetrical concentration gradient about this boundary which also corresponds to a symmetrical refractive index gradient. Thus, the beam of light is refracted different amounts at different heights and also,

the light leaving the cell is continuously changing in phase due to the different optical path lengths traversed. Therefore, the light from different heights of the cell crosses interferes, giving rise to a series of horizontal fringes focused at the point of convergence of the beam. The actual number of fringes within the pattern is constant since it is proportional to the refractive index difference between the top and bottom of the cell but the actual position of the maxima and minima (the light and dark zones) varies with time. Initially, since the refractive index gradient is extremely large, at the interface, the deviation is large and, at the focus plane, the horizontal fringes are widely separated at the lower end and extend their maximum distance vertically. However, as the diffusion proceeds the spacing of the fringes rapidly reduces and it becomes increasingly difficult to determine the exact number present. This is never easy since all the light from the ends of the cell, where no refractive index gradient exists, is always being focused at the center of the image plane as an undisplaced image. The light intensity therefore varies enormously from one end of the cell to the other and it is impossible to take a single photograph which will show all the fringes. Longsworth[13] in fact recognized this and tried to reduce the central intensity by a system of masks and filters but great care had to be taken to avoid introducing further interference effect[14]. The other possibility is to estimate the number of fringes formed and, on the basis of this and distance measurements taken on the photograph, to calculate the diffusivity fromanumber of different fringes. This is extremely tedious.

Thomas and Furzer[15] have used the more refined treatment of Gosting and Morris[16] in order to employ the Guoy method. They overcame

the two problems by means of computer. First, they used it to derive a very complete and accurate table of value of the complex function[15]. Secondly by assuming the number of fringes formed and taking fringe displacement measurements from photographs, the computer calculated the diffusivity for each fringe. Different numbers of fringes were chosen until the calculated diffusivities were consistent.

2. Rayleigh Interference Phenomena[7]

Two parallel, vertical, light beams, from the same source are formed and made to pass through two separate liquid cells and later recombine to give vertical interference bands. One of these is the reference cell, containing one of the diffusing components while, in the second cell, a sharp interface has been formed and diffusion is occurring Depending on the difference in refractive index between the two cells, the interference bands will be displaced to a greater or lesser extent and therefore any photograph of the bands gave a graph of difference in refractive index against height at any instant. Since, however, the refractive index difference is proportional to the concentration difference and diffusion is occurring in this vertical plane, it is also a direct graph of concentration change against distance from their interface. From each photograph a value of the diffusivity can be calculated at the time of measurement. The main advantage of Rayleigh fringes over the Guoy fringes is that they give a photograph which is much easier to analyse. This is because the spacing between one fringe and the next remains approximately constant throughout the whole photograph and also, by using monochromatic light, the intensity remains sufficiently constant for them all to be recorded on the same photograph. Finally, the thickness of each

fringe is small and therefore distances on the photograph, the biggest source of error in all this work, are more accurately measured.

The method of analysis is very simple for the concentration range chosen, the diffusivity can be assumed constant and the refractive index, a linear function of concentration difference. The calculation of diffusivity was shown by Eq.(2.16)[17]

$$D = \frac{j_m^2 \; b^2\lambda^2}{tC_t^2 \; 4\pi} \qquad (2.16)$$

where λ = wavelength, j_m = refractive index, C_t = constant, b = optical distance = $\Sigma \frac{1}{n}$, where 1 = distance through each meadium (air, glass, solution), n = its refractive index, t = time.

The big advantage of free diffusion method is that accurate values of diffusivity can be obtained (for electrolytes). The overall photographic treatment and mathematical analysis can be performed in three hours for simple cases. The value is differential one, provided the concentration range chosen is sufficiently small. This method is extremely accurate and its only disadvantage is its unsuitability at very low concentrations of solution (ie. very small refractive index differences).

2.3.4 Capillary Method

In the Anderson[18] capillary tube method for the study of self-diffusion, a uniform capillary tube of known length is filled with an isotopically 'tagged' solution, and immersed in a much larger vessel containing an isotopically normal solution of the same concentration, which may be gently stirred. At the mouth of the capillary, the concentration, c, of the tagged form is thus held at zero throughout the ex-

periment . After a measured time the total amount of tagged material in the capillary is measured and compared with the initial amount. The Eq. (2.9) may be solved assuming constant diffusivity. The boundary condition for a tube closed at x = 0 and open at x = a are

$$\text{At } t = 0,\ c = c_o \quad \text{for } 0 < x < a,\ c = 0 \quad \text{for } x > a$$

$$\text{At } t > 0,\ c = 0 \quad \text{at } x = a \text{ and } \frac{\partial c}{\partial x} = 0 \text{ at } x = 0$$

so that we obtained

$$\frac{c}{c_o} = \sum_{n=0}^{n=\infty} (-1)^n \frac{4}{\pi(2n+1)} \exp\left[-\pi^2(2n+1)^2 Dt/(4a^2)\right] \cos\frac{\pi(2n+1)x}{2a} \qquad (2.17)$$

the average concentration in the tube at time t is

$$c_{av} = \frac{1}{a}\int_o^a c\,dx \qquad (2.18)$$

whence

$$\frac{c_{av}}{c_o} = \sum_{n=0}^{n=\infty} \frac{8}{\pi^2(2n+1)^2} \exp\left[-\pi^2(2n+1)^2 Dt/4a^2\right] \qquad (2.19)$$

A graph of the right hand side of Eq.(2.19) against Dt/a^2 can be prepared, interpolation on it at the experimentally determined value c_{av}/c_o gives Dt/a^2 and hence D. It will be noted that provided the tube is uniform, its cross section is not required, but only its length a. In computing the function of Eq.(2.19) for the graph, very few terms need in practice be taken as the series converges very rapidly for reasonably large times. The ratio of the first term (n = 0) to the second (n = 1) is $9\exp(2\pi^2 Dt/a^2)$. This ratio is greater than 1000 as soon as Dt/a^2 exceeds 0.24, and higher

terms fall off even more rapidly. In a tube 5 cm. in length, and with a diffusion coefficient of 10^{-5} $cm.^2 sec^{-1}$, the first term of Eq.(2.19) is therefore amply sufficient after a week, though for the shorter times which are more practically convenient a few more terms must be taken. To illustrate the rate of change, it may be remarked that when $Dt/a^2 = 0.24$, the average concentration in the tube has fallen to 45 per cent of its initial value.

This method had been extensively used for determining self- and tracer-diffusion coefficients of electrolytes, but agreement between different workers has often been poor, discrepancies of 10 per cent or more having been reported. In a critical study of the method, Mills[19] has concluded that serious errors can arise from the mode of stirring of the large container in-to which the diffusion proceeds. Turbulent flow near the capillary mouth appears to lead a 'scooping-out' of solution from the tube. On the other hand, if the solution is not stirred at all, a 'cloud' of the diffusing species may tend to accumulate at the mouth of the tube so that the boundary condition $c = 0$ for $x > a$ is not fulfilled. Mills has shown that correct results (ie. results in agreement with similar measurements using diaphragm cells) can be obtained by arranging for slow controlled streamline flow past the capillary mouth, Another difficulty concerns the complete removal of all the active material from the tube at the end of the run, for radio-active counting; he overcomes this by not removing it. Instead , he surrounds the tube by a scintillation-counter crystal, making it possible to measure the decrease in activity continuously throughout the run. These improvements lead to a precision of a few tenths of one per cent in the measurement of tracer-diffusion

coefficients.

2.3.5 Improved Capillary Method

The diffusion of ions in electrolyte from a capillary into an external electrolyte is governed by Eq.(2.20) in which diffusivity is assumed to be constant and the following dimensionless parameters are introduced

$$\Phi = \frac{c}{c_o} \quad ; \quad \tau = \frac{Dt}{L^2}$$

where c = concentration of diffusant, c_o = initial concentration of diffusant inside the capillary, L = length of the capillary, D = diffusivity, and t = time.

$$\frac{\partial \Phi}{\partial \tau} = \nabla^2 \Phi \tag{2.20}$$

For the region within the capillary, a uniform concentration at any cross section prevails so that a one-dimensional version of Eq.(2.20) may be used where the distance x, measured from the closed end of the capillary, is normalized to $\eta = x/L$, given as

$$\frac{\partial \Phi}{\partial \tau} = \frac{\partial^2 \Phi}{\partial \eta^2} \tag{2.21}$$

In order to treat the transport of species from the capillary purely in terms of diffusion, it has been customary to provide a fixed boundary condition at the mouth of the capillary, $\eta = 1$. Stirring of the bulk fluid outside the capillary has been used by many researchers in an attempt to produce the condition $\Phi = 0$ at $\eta = 1$. Stirring of the bulk solution, however,

introduces errors which tend to give values of the diffusivity which are too high. Such errors are due primarily to hydrodynamic effects, because the drag of the liquid past the interface produces a pressure gradient which physically forces liquid from the outside into the capillary, displacing some of the high concentration material out of the capillary. There is, in effect, a net convective removal of diffusing substance for a short distance, $\Delta\ell$, from the capillary neck, given an overestimate of the amount of material actually leaving the capillary by diffusion. Nanis et al.[20] studied this so called " $\Delta\ell$ effect " using rotating capillaries and were able to correlate the effect as a function of Reynolds number based on the capillary diameter. Davis[21] has extended this work to higher Reynolds numbers in a liquid metal system.

The above assumption of zero concentration at the mouth of the capillary is equivalent to the fastest possible rate of removal of diffusing species from the capillary. As an opposite extreme where no stirring is allowed to influence the accumulation of diffusing species convection may assumed to be totally negligible both within the capillary content and in the external bulk liquid. The residual average concentration within a capillary will then not be subjected to the errors caused by hydrodynamic effects. The difficulty of obtaining an analytic solution for the case of three-dimensional diffusion with no stirring has prevented the application of this approach. In the absence of convective flow, the solution of Eq. (2.20) is required which links the regions internal and external to the capillary by accounting for the continuity of concentration and flux at $\eta = 1$. Gergely et al.[22] have analyzed the diffusion from a capillary without stirring in which the diffusion from the capillary mouth was

approximated as a centrally located point source in an impermeable plane bounding a hemispherical region, and obtained correction factors for the diffusivity based upon diffusion times and capillary radius. In this solution, the flux from the capillary mouth was assumed to be independent of concentration. Furthermore, only an approximate solution near the capillary mouth could be obtained. Nanis et al.[23] obtained a numerical solution for full three-dimensional diffusion from the capillary mouth, thus providing the concentration-time relation necessary for obtaining diffusivity values with a non-stirred capillary method. In experimental studies without stirring, however, it is essential to avoid errors from sources which provide unwanted stirring, such as natural convection arising from density or temperature gradients in the bulk solution.

The capillary method offers distinct experimental advantages, since the apparatus size may be reduced, limited only by the detectability of the analytical chemical technique used to assay the contents. In principle, by selecting suitable capillary diameter and length, as well as experimental time, the diffusivity may be determined to an accuracy controlled only by the analytical method available.

2.4 No External Stirring Capillary Diffusion Model

2.4.1 Mathematical Formulation

The diffusion of electrolyte from a capillary to an external bulk solution as shown in Fig.2.3 is governed by Eq.(2.22), in which diffusivity is assumed to be constant and the following dimensionless parameters are introduced

$$\Phi = \frac{c}{c_o} , \quad \eta = \frac{x}{L} , \quad \xi = \frac{y}{L} , \quad \beta = \frac{z}{L} , \quad \tau = \frac{Dt}{L^2}$$

where c = concentration of diffusant, c_o = initial concentration of diffusant inside the capillary, L = length of the capillary, D = diffusivity, and t = time

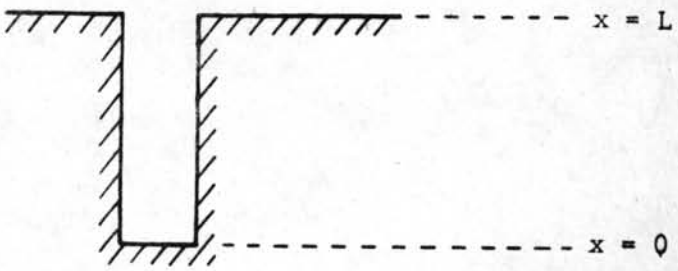

Figure 2.3 Diffusion of electrolyte from a capillary to an external bulk solution

In the region $0 \leqslant \eta \leqslant 1$, the diffusion is assumed to be one-dimensional, governed by

$$\left[\frac{\partial \Phi}{\partial \tau}\right]_1 = \left[\frac{\partial^2 \Phi}{\partial \eta^2}\right]_1 \qquad (2.22)$$

The subscript 1 indicates the region where one-dimensional diffusion prevails. The zero flux boundary condition at the closed end ($\eta = 0$) of the capillary is

$$\left[\frac{\partial \Phi}{\partial \eta}\right]_1 = 0 \; ; \; \eta = 0 \; , \; \tau \geqslant 0 \qquad (2.23)$$

The initial condition is

$$\Phi_1 = 1 \; ; \quad 0 \leqslant \eta \leqslant 1 \; , \qquad \tau = 0 \tag{2.24}$$

In the region $\eta > 1$, for the absence of convection, the diffusion is three-dimensional. The three-dimensional version of the diffusion equation is

$$\left[\frac{\partial \Phi}{\partial \tau}\right]_3 = \left[\frac{\partial^2 \Phi}{\partial \eta^2}\right]_3 + \left[\frac{\partial^2 \Phi}{\partial \xi^2}\right]_3 + \left[\frac{\partial^2 \Phi}{\partial \beta^2}\right]_3 \tag{2.25}$$

The subscript 3 refers to the three-dimensional region. The boundary condition is

$$\Phi_3 = 0 \; ; \quad \eta \to \infty \; , \quad \xi \to \infty \; , \quad \beta \to \infty \; , \quad \tau \geqslant 0 \tag{2.26}$$

The symmetry of diffusion perpendicular to the axis of capillary gives

$$\left[\frac{\partial \Phi}{\partial \xi}\right]_3 = 0 \; , \quad \left[\frac{\partial \Phi}{\partial \beta}\right]_3 = 0 \; ; \quad \xi = 0, \; \beta = 0, \; \eta > 1, \; \tau \geqslant 0 \tag{2.27}$$

The initial condition is

$$\Phi_3 = 0 \; ; \quad \eta > 1, \; 0 \leqslant \xi \leqslant \infty, \; 0 \leqslant \beta \leqslant \infty, \; \tau = 0 \tag{2.28}$$

At the mouth of the capillary ($\eta = 1$), where one- and three-dimensional regions join, equality of fluxes gives

$$\left[\frac{\partial \Phi}{\partial \eta}\right]_1 = \left[\frac{\partial \Phi}{\partial \eta}\right]_3 + \left[\frac{\partial \Phi}{\partial \xi}\right]_3 + \left[\frac{\partial \Phi}{\partial \beta}\right]_3 \tag{2.29}$$

at $\eta = 1$, $\xi = 0$, $\beta = 0$ and $\tau \geqslant 0$

the boundary conditions given here implicitly contain the assumption that the capillary mouth is a point source for the three-dimensional region, rather than an actual disk. The error arising from this assumption will

be minimal unless the capillary diameter is a significant fraction (several per cent) of the length.

2.4.2 Finite Difference Formulation

A set of an explicit form of finite difference equations may be used to represent Eq.(2.22) - Eq.(2.29) for both one-dimensional and three-dimensional regions.

Let i = index for the step movement in x-direction (i = 1,2,...M), j = index for the step movement in y-direction, k = index for step movement in z-direction, n = time, $\Delta\tau$ = step increment in dimensionless time, $\Delta\eta$ = step increment in η-direction, $\Delta\beta$ = step increment in β-direction, $\Delta\xi$ = step increment in ξ-direction, M = $1/\Delta\eta$: number of grid points in the capillary, $\lambda_1 = \Delta\tau/(\Delta\eta)^2$, $\lambda_2 = \Delta\tau/(\Delta\beta)^2$, and $\lambda_3 = \Delta\tau/(\Delta\xi)^2$.

For the one-dimensional diffusion region $0 \leq \eta \leq 1$, Eq.(2.22) becomes

$$\Phi_{i,1,1,n+1} = \left[1 - 2\lambda_1\right]\Phi_{i,1,1,n} + \lambda_1\left[\Phi_{i-1,1,1,n} + \Phi_{i+1,1,1,n}\right] \quad (2.30)$$

where $1/\Delta\eta > i$.

At the closed end of the capillary (i = 1), the zero flux boundary condition, Eq.(2.23) leads to

$$\Phi_{0,1,1,n} = \Phi_{2,1,1,n} \quad (2.31)$$

The initial condition, Eq.(2.24) becomes

$$\Phi_{i,1,1,0} = 1 \quad (2.32)$$

For the three-dimensional diffusion region, $\eta > 1$, $0 \leq \xi \leq \infty$, $0 \leq \beta \leq \infty$,

Eq.(2.25) becomes

$$\Phi_{i,j,k,n+1} = (1 - 2\lambda_1 - 2\lambda_2 - 2\lambda_3)\Phi_{i,j,k,n} + \lambda_1(\Phi_{i-1,j,k,n} + \Phi_{i+1,j,k,n}) + \lambda_2(\Phi_{i,j-1,k,n} + \Phi_{i,j+1,k,n}) + \lambda_3(\Phi_{i,j,k-1,n} + \Phi_{i,j,k+1,n}) \quad (2.33)$$

For $i > 1/\Delta\eta$

Boundary condition, Eq.(2.26), Eq.(2.27) are

$$\Phi_{i,j,k,n} = 0 \text{ as } i \to \infty,\ j \to \infty,\ k \to \infty \quad (2.34)$$

$$\Phi_{i,0,k,n} = \Phi_{i,2,k,n} \quad (2.35)$$

$$\Phi_{i,j,0,n} \quad \Phi_{i,j,2,n} \quad (2.36)$$

For simplicity, the capillary is considered as a drilled hole in a block. In order to account for the impermeable plane at the mouth level, $\eta = 1$, $\xi > 0$, $\beta > 0$, the following statement allows for zero flux perpendicular to the plane by the use of imaginary points below the plane, e.g.

$$\Phi_{M+1,j,k,n} = \Phi_{M-1,j,k,n} \quad (2.37)$$

The initial condition given by Eq.(2.28) becomes

$$\Phi_{i,j,k,n} = 0 \text{ as } \tau = 0,\ i > 1/\Delta\eta,\ 0 \leqslant j \leqslant \infty,\ 0 \leqslant k \leqslant \infty \quad (2.38)$$

At the junction of the one- and three-dimensional regions just at the capillary mouth ($i = M$, $j = 1$, $k = 1$) Eq.(2.29) becomes

$$\Phi_{M,1,1,n+1} = \frac{\Phi_{M-1,1,1,n} + \Phi_{M+1,1,1,n} + \Phi_{M,2,1,n} + \Phi_{M,1,2,n}}{4} \quad (2.39)$$

Equation(2.39) is based on implicit finite difference approximation, together with the assumption of equal spacing in the three-dimensional region ($\Delta\eta = \Delta\xi = \Delta\beta$).