CHAPTER 2

• EXPERIMENTAL •

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2.1 Measurement of Diffusion Coefficient in Gel Medium

The basic problem of measuring diffusion is to determine the transport of matter under conditions where it can be ensured that the transport is due to diffusion alone, free from transport by flow or convection. It is, therefore, essential to reduce to a minimum direct streaming, turbulence, and convection currents due to temperature variations. Though the most commonly employed techniques to achieve this are the diaphragm or the capillary tube methods, Arnikar[110] was amongst the early workers to study the possibility of employing a gel medium (of agar-agar) for these studies.

Gels have been looked upon historically as colloidal solutions consisting of two phases, one a solid disperse phase and the other a continuous liquid phase. If an agar-agar sol is cooled to below $40^{\circ}C$, the viscosity is found to have suffered an increase. In the course of gelation the particles in the sol unite to form a number of chains or fibrils which become interlocked and eventually a semi-solid form is acquired. Part of the dispersion medium may be involved in

solvation but the major portion is believed to be held by capillary forces between the fibrils and it is possible to immobilize as much as 98% water in these interstices whereby streaming and convection currents are practically eliminated.

In the present studies, we have chosen ^{54}Mn, ^{64}Cu and ^{65}Zn radioactive isotopes in the form of their different salts, to study the different aspects of diffusion in the agar gel medium using the zone-diffusion technique. These isotopes ^{54}Mn (half-life : 312 days), ^{64}Cu (half-life : 12.7 hours) and ^{65}Zn (half-life : 244 days) were obtained from the Bhabha Atomic Research Centre, Trombay, Bombay, in the form of $MnCl_2$, $CuSO_4$ and $ZnCl_2$ respectively.

As the isotope ^{54}Mn in the form of $MnCl_2$ was carrier--free, the experiments for the diffusion of $MnSO_4$ were carried out by simply adding appropriate quantity of $MnSO_4$ to it.

2.2 The Theory of Zone-Diffusion

The zone-diffusion technique was modified by Arnikar[111] and used in the study of electromigration in agar columns. This technique has since then been used by several workers[60,62,112,113] in the study of diffusion of different ions and electrolytes in agar gel medium.

The basic principle involved in the zone-diffusion

technique is shown in Fig. 2.1

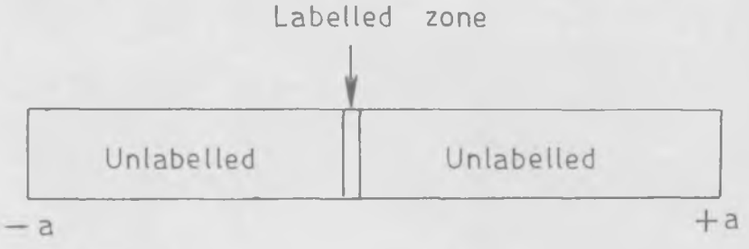

Fig. 2.1- Boundary conditions of zone - diffusion.

A uniform and infinitely thin layer of tracer is allowed to diffuse into semi-infinitely long diffusion column of length, a, of the medium corresponding to the boundary conditions for the activity $A_{(x,t)}$ at distance x from the origin and at time t :

$$A_{(o,o)} = A_o$$
$$A_{(x,o)} = 0 \text{ for } x \geq 0 \text{ at } t = 0$$
$$A_{(x,t)} = 0 \text{ for } x = \pm a$$

The solution of the Fick's II law for the given boundary conditions is the probability or error integral. The following derivation is based on the requirement, first noted by Boltzmann that although the concentration varies with both distance x and time t, these two variables must always occur in the ratio x^2/t for D to have the proper dimensions.

Consequently, if diffusion proceeds from an initially sharp boundary at $x = t = 0$ a new variable, y, may be defined by the relation $y = x/\sqrt{t}$. Then

$$\frac{\partial}{\partial t} = \frac{\partial y}{\partial t} \cdot \frac{d}{dy} = -\frac{1}{2} \cdot \frac{x}{t^{3/2}} \cdot \frac{d}{dy} \qquad ..(2.1)$$

and

$$\frac{\partial}{\partial x} = \frac{\partial y}{\partial x} \cdot \frac{\partial}{\partial y} = \frac{1}{\sqrt{t}} \cdot \frac{d}{dy} \qquad ..(2.2)$$

Hence, Fick's II law takes the following form

$$\frac{y}{2} \cdot \frac{dc}{dy} = -D \cdot \frac{d^2 c}{dy^2} \qquad ..(2.3)$$

Substituting $p = \frac{dc}{dy}$ and integrating equation (2.3) we get $-y^2/4 = D \cdot \ln IP$ where I is constant of integration. Rewriting the equation in terms of x and t, one obtains,

$$\frac{\partial c}{\partial x} = \frac{1}{I\sqrt{t}} \cdot e^{-x^2/4Dt} \qquad ..(2.4)$$

The integration constant I may be evaluated from the condition that the total area of the gradient curve $\int_{-\infty}^{+\infty} (\partial c/\partial x)\, dx$ must equal at all times the initial concentration C_o. Since each end of the column is at a physical infinity and since the

function (2.4) is symmetrical about the concentration axis, we can write as

$$C_o = \frac{1}{I\sqrt{t}} \int_{-\infty}^{+\infty} e^{-x^2/4Dt} \cdot dx = \frac{2}{I\sqrt{t}} \int_{-\infty}^{+\infty} e^{-x^2/4Dt} \; dx \qquad ..(2.5)$$

This integral has the value $\sqrt{\pi Dt}$ and $I = 2 \; D.\sqrt{\pi}/C_o$

Then equation (2.4) becomes

$$\frac{\partial c}{\partial x} = \frac{C_o}{2\sqrt{\pi Dt}} \cdot e^{-x^2/4Dt} \qquad ..(2.6)$$

and

$$C = \frac{C_o}{2\sqrt{\pi Dt}} \int_{x}^{\infty} e^{-x^2/4Dt} \; dx$$

$$\therefore C = \frac{C_o}{2\sqrt{\pi Dt}} \; e^{-x^2/4Dt} \qquad ..(2.7)$$

Replacing the concentration in terms of activity A, equation (2.7) can be written as

$$A_{(x,t)} = \frac{A_o}{\sqrt{4\pi Dt}} \; e^{-x^2/4Dt} \qquad ..(2.8)$$

where A_o is the constant representing the total activity in the

initial zone at t = 0 and $A_{(x,t)}$ is the radioactivity at distance x from the origin at time t.

2.3 Experimental Details of the Zone-Diffusion Technique

The experimental details are given below under two heads (i) The preparation of the diffusion column and (ii) Analysis of the diffusion column.

2.3.1 Preparation of the diffusion column

A required amount of agar (Bacto-Agar, Difco Laboratories, Detroit Michigan, USA) was weighed and dissolved in water in case of electrolyte-diffusion and in solution containing appropriate salt in case of tracer-diffusion. Then this solution is heated slowly and gently to above 80°C on a hot-plate. Sudden and excessive heating was avoided as it leads to charring of the gel. The solution on cooling sets into a semi-rigid solid state containing the aqueous phase electrolyte solution immobilized in the interstitial space of the agar-agar network. This gel which appears homogeneous and really translucent, was used for the preparation of the column.

A clean dry pyrex tube with plane edges and uniform diameter of 1.2 cm and length 30 cm was taken. With one end closed, this tube was filled with the viscous gel solution to half the length with desired concentration containing

unlabelled electrolyte in the case of tracer-diffusion and without electrolyte in the case of electrolyte-diffusion. This was cooled to a solid. Then after removing the cork, one end of the gel is brought out and from it a small piece was cut off with a clean, sharp blade along the edge of the tube so that plane boundary is obtained. The gel column was then allowed to slip back a little and 1 cm^3 of gel containing the labelled electrolyte was added above it and immediately cooled to a solid gel. Leaving a 0.5 cm band of this gel in the column, the remaining part was chopped off to a plane surface as before. The whole gel column was then moved to one side of the tube so that 0.5 cm band remained at the middle of the tube. The remaining part of the tube was then filled with the same gel which was used for the first column before the labelled zone and then immediately cooled. Once the column was ready, both ends of the tube were tightly corked and suspended horizontally in an automatically temperature regulated thermostat maintained to within $\pm$ 0.1°C at the desired temperature.

In setting the diffusion column, three things were taken care off :

(i) No enclosure of air bubbles in the gel,

(ii) Good contact between the central zone and the column on the either side of it,

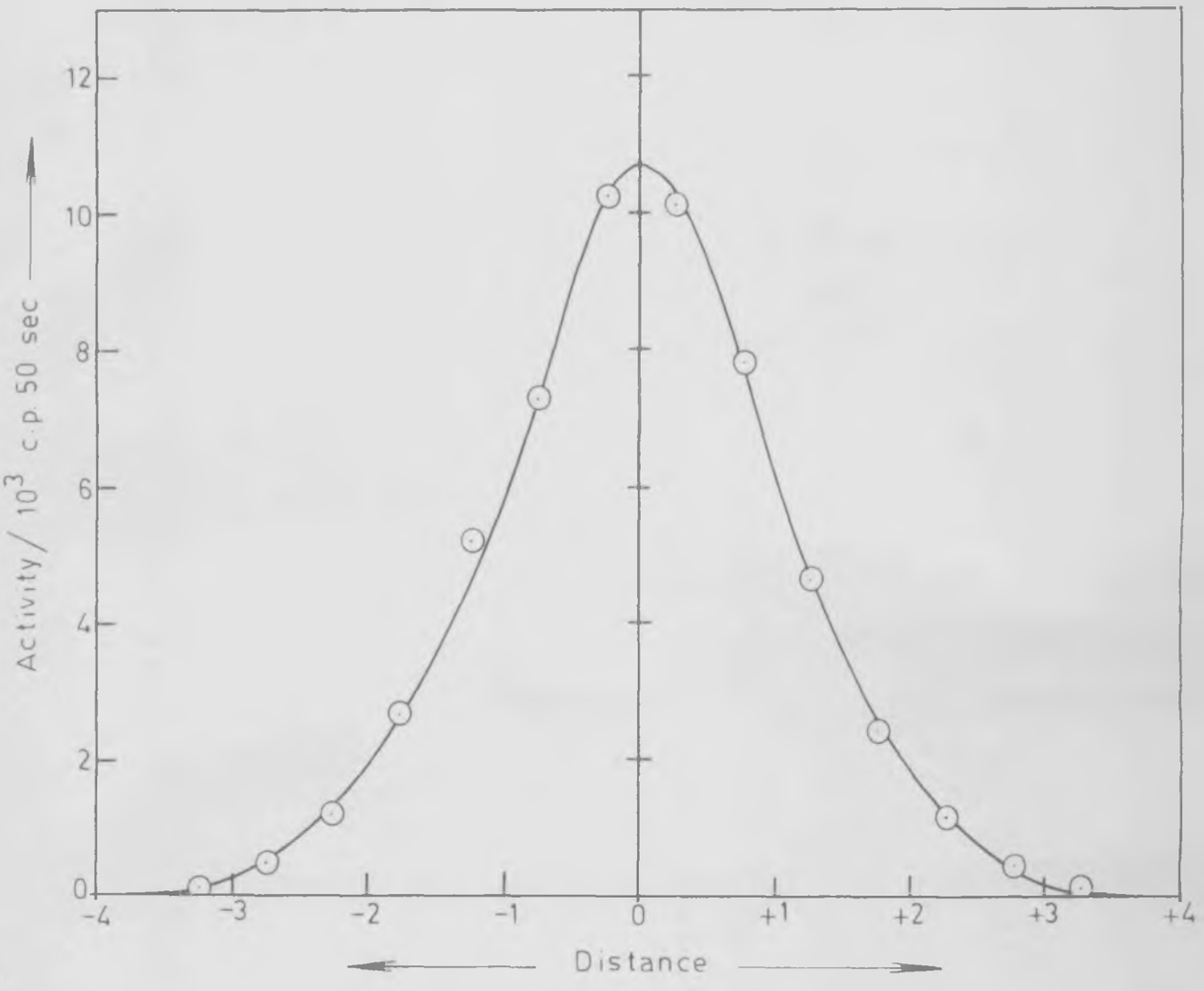

Fig. 2.2- Gaussion distribution curve for the electrolyte- diffusion of $MnSO_4$ (1×10^{-5} M) at 25°C in 1% agar gel.

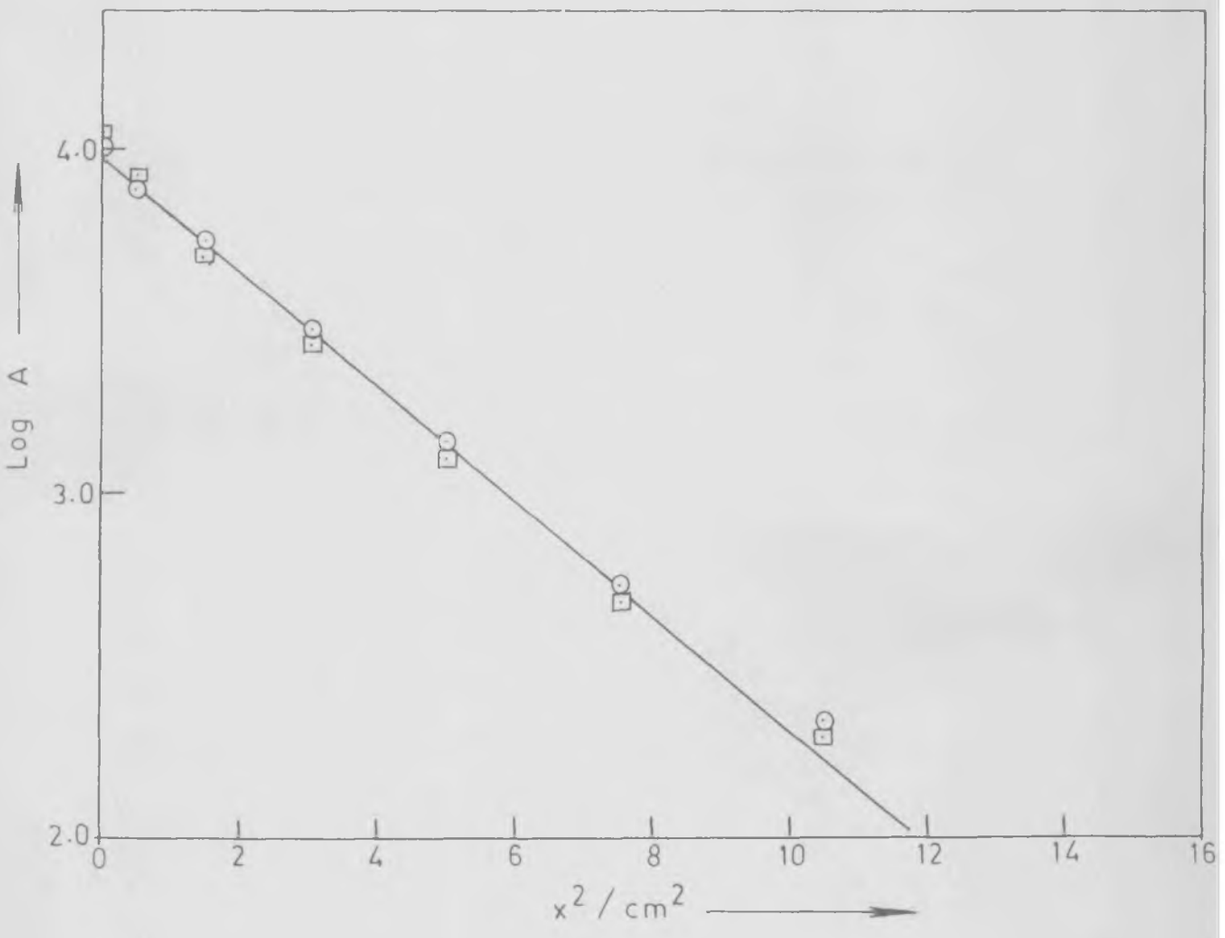

Fig. 2.3 - Electrolyte - diffusion of $MnSO_4$ (1×10^{-5} M) at 25°C in 1% agar gel.

(iii) No part of the gel sticks to the sides of the glass while being moved to and fro in the tube.

2.3.2 Analysis of the diffusion column

Diffusion is allowed to proceed for a definite time of the order of 24 hours, the gel column was then extruded carefully and the region of 5 cm on either side of the central zone was sliced into 0.5 cm long samples. These were transferred to aluminium planchettes and dehydrated under an infrared lamp. The radioactivity in each sample was measured using a well-type single channel gamma ray scintillation counter.

When the activity A is plotted versus distance, a Gaussian distribution curve is obtained which is shown in Fig. 2.2

The plot of log A versus x^2 gives a straight line as expected, with

$$\text{Slope} = -\frac{1}{2.303 \times 4 \times D \times t}$$

Knowing the time of diffusion t for a specific run, the diffusion coefficient is calculated. A typical plot of log A versus x^2 is shown in Fig. 2.3. Each value of D presented in the tables is an average of at least four independent measurements.