SYNOPSIS.

In the Introductory Chapter we have described basic considerations underlying the phenomenon of diffusion in liquids. Motivation for the measurement of diffusion springs from various sources like its close connection with the sizes and shapes of the molecules and its relationship with other transport phenomena like viscosity. Starting with a brief historical background we have discussed the formulation of the two well-known laws of diffusion due to Fick, followed it by a consideration of the classification of diffusion measurements according to the nature of the diffusion process occurring in the cell such as (a) steady state diffusion (b) free diffusion (c) restricted diffusion. Then, for the sake of completeness as well as for comparison with the techniques used in self-diffusion measurements, we have discussed briefly various methods used for the measurement of mutual diffusion coefficients. We have reviewed (a) Clack's method, (b) diaphragm cell method and also (c) the optical methods in general. Then we have given a short introduction to self-diffusion phenomena. We have concluded the chapter stating the aims of the present thesis, which are (1) to review the previous methods for the measurement of diffusion coefficient; (2) to give a summary of
of the different theories of the liquid state; (3) to present the mathematical formulation of the method, developed during the present investigation, for the determination of the self-diffusion coefficient in liquids; (4) to describe the experimental arrangement and the results obtained with aqueous Thallous sulphate solution; (5) to measure the self-diffusion in mercury at different temperature and to compare this with the data of other workers, to correlate the data with the theories of the liquid state.

(In Chapter II we have discussed the standard methods employed for the measurement of self-diffusion in liquids.) The methods have been divided into (a) Sheared boundary method (b) Capillary tube technique (c) Diaphragm cell method and (d) Spinecho technique. We have discussed the work of Wang and Kennedy (1952) who measured the tracer diffusion coefficients of sodium and iodide ions in sodium iodide solutions, using wide capillary tubes. The work of Nachtrieb and Petit (1956) also has been mentioned. The development of the capillary tube technique by Anderson and Saddington (1949) has been discussed and the work of Hoffman (1952) has been discussed. It was followed by a discussion of the best experimental condi-
tions for the capillary tube experiments. Anderson's work (1947) on diaphragm cell method has been discussed thereafter. Then a detailed description of McBain-Dawson cell in connection with the work of Nielsen and Adamson (1952) has been given in some detail. We have also summarized the work of Brady and Salley (1948) who reported self-diffusion coefficients and transference of the small ions in colloidal electrolytes. Then the theory of the spin-echo technique by Hahn (1950) has been described. The work of Das and Saha (1954) in this field has been mentioned. Then we have given a short description of the work of Carr and Purcell (1954), who examined nuclear resonance techniques involving free precession and described a convenient variation of Hahn's spin-echo technique. Then we have described the experiments of Douglass and McCall (1958) who used the Carr-Purcell spin-echo technique and measured the self-diffusion coefficients of the normal paraffins. In the concluding sections we have tabulated the different methods with the name of typical investigators and the nature of work.

In Chapter III we have briefly described the various theories which have been proposed to explain the phenomena of
transport properties and indicated how the experimental findings could be correlated with their theoretical counterpart. It has been pointed out that X-ray investigations have revealed the similarity between the structure of liquids in microscopic regions and a solid crystal. Then we have given a summary of Eyring's theory. It treats viscosity and diffusion as two closely related phenomena and discusses the case where the solute molecules are much larger than the solvent molecule and where during diffusion the solute and solvent molecules slip past one another. Then we have briefly described Born's theory, which deals with the formulation of a rigorous mathematical description of the molecular motion in liquids. This is done by generalizing the conception of distribution function used in statistical mechanics. We have then discussed Frenkel's theory. It has been shown that this theory emphasizes the facts that the similarity between liquids and solids is much closer than that between liquids and compressed gases. The expression for the coefficient of diffusion in liquid on the basis of hole theory of liquids has been given. Then we have given a brief description of the theory of diffusion in liquids from the standpoint of fluctuation theory. It is stated there that
the diffusion results from the movements of atoms through small and variable distances as a result of local density fluctuations.

In Chapter IV we have given the theory of the method developed for the present investigation. The starting point of the theory is Fick's second law for a unidirectional flow. It has been at first solved for the case of a solvent of length $l_2$ being superposed on a solute of length $l_1$. The solution has been expressed as a summation series. Then the experimental condition ($l_1 = l_2$) has been applied which simplified the expression a great deal. Then we have found out the expression for the count rate observed by the detector (placed vertically over the diffusion column) at any time $t$ as a function of the integrated weighted average of the count rate due to the different layers of the diffusion column. Then we have shown that under suitable conditions the final expression takes the simple form $N_0 - N_t = A \exp(-kt)$. Where $N_0$ = saturated count rate, $N_t$ = count rate at time $t$, $A$ = constant, $k = \frac{D}{4l^2}$ and $2l$ = total length of the diffusion column. We have then considered the higher order terms and have shown how the correction terms modify the final expression
for the determination of D. We have then discussed the possibility of using this technique in the case of mutual diffusion. Finally we have considered the effect of inequality of the solute and solvent heights. It has been shown that if they are unequal by less than 2% the correction factor can be neglected.

In Chapter V we have discussed the experimental technique and the measurements with Thallous sulphate solution to test the consistency of the method. In the opening section we have discussed the diffusion cell based on sliding cell technique. Then we have described the counting system which consisted of a thin window anthracene counter. Then we have discussed how the temperature was kept constant at 5.5°C by keeping melting benzene in equilibrium with its liquid phase under normal atmospheric pressure. It was followed by short description of the experimental procedures, namely the filling of the diffusion columns to equal heights and the precautions to be taken for. After the diffusion process starts the count rate observed by the counter increases and at suitable time intervals it is noted. The method for measuring saturation count rate has been described. Then
the plot of $N_t$ against $t$, $\log_e(N_0 - N_t)$ against $t$ were plotted to find out the values of $D$. The effect of the correction terms were also calculated. Measurements were made at the same concentration with several cell lengths to see the consistency of the method. Then measurements were made at several concentrations. For each concentration two sets of observation were taken one for mutual diffusion of $\text{Tl}^{204}$ in water and the other for self-diffusion. It is seen that the mutual diffusion coefficient is larger than the self-diffusion coefficient and with increasing concentration the diffusion coefficient decreases. At the end of the chapter we have given a very brief discussion on electrolytic solutions.

(In Chapter VI we have described the self-diffusion measurements carried out on liquid mercury.) In the first section we have given a summary of the work carried out by Hoffman, who used the capillary tube technique. It was followed by the description of the work of Nachtrieb and Petit who used sheared cell technique. Then we have narrated present investigation. The investigation was carried out with the above mentioned cells. A detailed description of the methods employed for controlling mechanical vibration and thermal fluctuations...
is then given. Then the experimental procedure used in the present investigation has been given. After that we have indicated how to calculate the diffusion coefficient from the experimental data. The data was compared with those of Hoffman and Nachtrieb and Petit. The measured diffusion coefficients are smaller than those of Hoffman and larger than those of Nachtrieb and Petit at the same temperature. It has been suggested that the disagreement between the various sets of results is due to the convective loss of radioactive mercury because of the 250 r.p.m. stirrer used by Hoffman, and due to the fact that the diffusion coefficients found by Nachtrieb and Petit are not strictly integral. Then the data has been analysed by Eyring's equation and Stokes-Einstein equation. The radius of mercury atoms were calculated with the Stokes-Einstein equation and was found to be \(0.82\pm0.01\) where as the atom radius is about 1.4Å. In spite of this the agreement is considered reasonable, because the "continuous medium" condition for the validity of Stokes-Einstein equation is certainly not satisfied by monatomic liquids which are more nearly like hard spheres.

The data were also analysed in the light of Swalin's treatment.
of liquid metals which predicted that the \( \log D vs. \frac{1}{T} \) curve should be linear, our experimental data agree to this. In the last sections we have pointed out the advantages of this simple method for the measurement of self-diffusion in liquids. It has been pointed out that it has the advantages of integral measurements and needs no zero time correction, it can be applied for all types of radioactive radiations and as far as accuracy is concerned it compares favourably with other techniques, which have been so far used in the measurement of self-diffusion in liquids.