CHAPTER II
CHAPTER - 3

3.1 Introduction

The coupling of the concept of chaotic motion with the strong interaction in-between the constituent particles has made the study of liquid state a challenging problem. The formulation of rigorous mathematical description of molecular motion in liquids is in some ways alarmingly difficult, than the Kinetic theories of gases or of solids. It springs from the fact that the former has the simplifying features of low density (and hence weak interaction in between the constituent particles) and in the case of solids there is a regular lattice structure while the molecules of a liquid are in a dense short-range ordered state. Also the factors like the finite size of the molecules or the holes in crystals can be treated as perturbations, but the free molecules and holes both have to be taken into account, as both are of same importance in the theories of liquid state. There are numerous theories of liquid state, which are employed to give the theory of diffusion in liquids. A brief review of some of these theories will be given in this chapter.

These liquid state theories can provide valuable information about some properties of liquid state but these are not successful in elucidating all the properties of liquids.
The simulation and computational techniques have improvised the methods of carrying out the study of liquid state (for the last two decades) but those cannot afford us, the knowledge of the innate nature of liquids or the actual nature of molecular motion in liquids.

Depending on the nature of approach to the different theories it is better to classify them into three groups:

(1) **Hydrodynamic theories**: The hydrodynamic theory of diffusion considers the liquid as a continuum, in which the diffusional flow of the components is determined by a balance between the driving force and the frictional resistance.

(2) **Kinetic theories and the statistical theories**: The kinetic theories elucidate the molecular mechanism of diffusion and thus give a deeper explanation of the elementary process of diffusion. The molecular theories also give us a picture of the structure of liquids and describe diffusion by time dependent correlation functions.

(3) **Theories of Irreversible Thermodynamics**: A completely new approach has been initiated by a group of scientists who describe the diffusion from the standpoint of irreversible Thermodynamics.

It should be borne in mind that this classification is made just for the convenience of our discussion and the theories are not in strongly insulated compartments.
3.2 Hydrodynamic Theories

To have a full understanding of the factors affecting the diffusion coefficient in liquids, an adequate theory of liquid state is required, and in the absence of such a theory the understanding can be no more than partial. One of the oldest way of approaching the problem, was paved by the works of Liouville, Euler and other scientists. But the independent work of Einstein on Brownian motion ushered a new era in liquid state physics.

Einstein's theory intended to describe the diffusive motion of a big molecule embedded in a sea of small molecules. He calculated the coefficient of diffusion in two ways:

(1) From the irregular motion of the big suspended particles,
(2) From the difference in osmotic pressure between the different parts (due to differences in concentration) of the suspended particles which cause the diffusion phenomena. Then he equated these two expressions for the diffusion coefficient $D$.

Approaching in the first way Einstein has shown that, the diffusion coefficient is the product of mean square value of fluctuation distance with mean time of stay at a particular site. Both the direction and the jump length are presumed to be constant.
In course of calculating the diffusion coefficient in other way, the force acting on a single particle is first obtained. Again as the particle is suspended in a viscous medium that expression is equated with the force acting on a particle (provided it is assumed to be spherical) of radius $r$, moving in a continuous medium (which is the fundamental hypothesis of hydrodynamic theory) of viscosity $\eta$.

\[ D = \frac{kT}{6\pi\eta r} \quad \text{(3.1)} \]

This is Stokes – Einstein equation giving the diffusion coefficient of the Brownian particles. Using this equation, the 'Stokes law radius $r$' can be calculated for a solute molecule from its measured diffusion coefficients, especially if the uncertainty about the value of viscosity can be minimised. In spite of the limitations of the Stokes-Einstein's equation, the equation (3.1) has been employed by various workers to calculate the Stokes radii of different types of liquid molecules (other than Brownian). Surprisingly a close agreement in-between the experimental and calculated values of the radii is obtained.

So we may write that although this equation holds rigorously only if $r$ is far greater than the size of the solvent molecules, it is found that it holds quite well even for small diffusing molecules. The enormous success of this simple relationship is most striking. Bedeaux and Mazur
have shown that in the limit \( r \) tending to infinity the diffusion constant of a molecule does indeed approach the 'Stokes - Einstein' value.

Various modifications to eqn. (3.1) can be introduced within the limits of simple hydrodynamics, to account for the shape of the diffusing object and the 'stickiness' of its surface. The Stokes-Einstein law has been supplemented by Broersma\(^78\) taking into account the changes in viscosity with distance measured from the solute species.

According to Sutherland\(^79\) a small molecule diffusing through a solvent of comparable molecular diameter, the expression for the diffusion coefficient becomes:

\[
D = \frac{kT}{4\pi\eta R} \quad (3.2)
\]

So there is just a change in value of the constant. This view was also taken by other scientists but they have only improvised values of the constant. (e.g. Lamm\(^80\)).

Though Einstein and Sutherland in their theories have chosen the osmotic pressure gradient as the driving force but nowadays the scientists are choosing the chemical potential (which has in general the same sign as the difference in concentrations) to be responsible for this flow of diffusion. This suggestion was first made by Gibbs\(^81\), though the modern developments of the concept are based on the independent work of Hartley\(^82\) and of Onsager and Fuoss\(^83\).
The hydrodynamic theory considers the liquid to be continuous and the diffusion flow of the components is determined by a balance of the driving force and the frictional resistance force. The most difficult problem of hydrodynamic theory of diffusion, is the calculation of the frictional resistance from the other data in solutions. A considerable number of workers have chased this problem of evaluation of the frictional resistance. While trying to develop the theory of transport properties a significant step was taken by Kirkwood and Bearman to evaluate the frictional resistances. The generalised Kirkwood diffusion equation is obtained by postulating that the thermodynamic driving force is culminated from the random forces.

Thus the hydrodynamic theory is revealing certain relationships which fits well to some liquids but as it is not based on the continuum picture of liquids, it is not providing the molecular mechanism of the phenomena.

3.3 Kinetic theories and statistical theories

To have a deeper understanding of the molecular mechanism of the transport phenomena the knowledge about the structure of liquid is essential, because the transport of mass, momentum or energy in a liquid are strongly influenced
by the local geometry, which can be obtained from the Kinetic and statistical theories of liquids. Ultimate objective of the statistical description of matter is of course, to relate the macroscopic observables to the details of intermolecular potential, operating between the particles in assembly.

3.3.1 Frenkel's Theory

Among the notable contributors in the development of kinetic theories of liquids we refer to the work of Frenkel first. Frenkel's theory emphasises that the liquids are more similar to solids than the compressed gases near melting point. He considered the diffusion in liquids as the thermally activated jump of an atom into a neighbouring 'hole' which are not the 'mere vacancy'. Frenkel visualised the necessity of the 'hole' concept. These holes may have varying dimensions (Furth have chosen them to be spherical).

An atom is not expected to surmount an energy barrier itself. So in order to explain its movement Frenkel identified the energy barrier with the energy of formation of 'hole' and obtained an activation energy for such a process. The activation energy was identified with the surface energy of formation of the critically sized spherical 'hole' in the case of liquid metals. The concept of activation was probably rightly chosen as evidenced from the Arrhenius' plot. Inspite of all these evidence, it is rather
difficult to say anything about the extent of validity of this activation energy concept. It is clear from the 'hole theory' that for the occurrence of diffusion a critically sized hole had to be postulated but all the workers in this field are astonishingly silent about the size of the hole for which diffusion would be possible. The hole conception of liquid state is obviously applicable in the region of, not too elevated, temperatures and pressures only.

3.3.2 Eyring's Theory

The most general of all the Kinetic theories of diffusion is Eyring's Theory of Reaction Rates. With the help of this theory a more satisfactory treatment of diffusion in solution can be given in a manner similar to that used for viscosity (as viscosity and diffusion are two closely related physical phenomena). Eyring assumed that diffusion occurs in series of activated jumps. In order to diffuse in solution one molecule is to slip past to another molecule, 

\[
D = D_0 e^{(E/E_kT)}
\]

(where \(D\) is the diffusion coefficient at temperature \(T\), \(D_0\) is the diffusion coefficient at absolute zero, and \(E\) is the activation energy of diffusional flow).

The variation of \(\log D\) vs. \(T\) is almost linear and the plot is called the Arrhenius plot.

*Note: The rate of diffusion decreases with increasing temperature and this dependence is approximately exponential in accordance with the Arrhenius relationship: \(D = D_0 e^{(E/E_kT)}\). The variation of \(\log D\) vs. \(T\) is almost linear and the plot is called the Arrhenius plot.*
as in the case of viscous flow. The distance through which a molecule of solute jumps in each step is the distance between the two successive equilibrium positions. The change in free energy with distance is given in (Fig. 3.1). In this treatment it is assumed that the standard free energy is same in equilibrium position (that the molecules attain in course of diffusion). Again for the occurrence of diffusion, the concentrations at the initial and final positions must be different. These two can be satisfied simultaneously only if the solutions are ideal. Hence the treatment given by Eyring and co-workers, is applicable to the ideal systems or to solutions which are so dilute that they behave virtually in an ideal manner.

As the concept of dissimilar molecules is introduced in this theory, a question about its validity in electrolytic solutions arises. It springs from the fact that when a large ion diffuses in a solvent (consisting of relatively small molecules) the work required to produce the necessary space would be large. So the rate determining step will not be the jump of the solute molecules from one equilibrium position to the other. There are now reasons to believe that diffusion occurs by the co-operative motion of many molecules rather than by the activation of a single one.
FIG. 3.1. THE FREE ENERGY BARRIER OF DIFFUSION IN IDEAL SOLUTIONS.
In a word, according to the present status of our knowledge, Eyring's theory reflects the elementary process of diffusion correctly as a whole, though the results cannot be considered satisfactory.

3.3.3 Panchenkov's Theory

Panchenkov\textsuperscript{94-96} gave a theory of the phenomena of diffusion and viscosity starting from a different angle. According to this theory two essential conditions for the displacement of a molecule from its equilibrium position to an adjacent one are -

1) The particle must gain sufficient kinetic energy to break the Van der Waals bonds with its neighbours. This requirement yields an energy term.
2) The adjacent molecules must be temporarily far enough apart to enable the diffusing molecule to pass between them. This yields an entropy term.

The two terms (as obtained from the requirement) together are equivalent to the free enthalpy of activation. The essential conclusions of this theory is similar to Eyring's Theory.
3.3.4 Onsager's Theory

In 1932 Onsager and Fuoss \(^{3}\) gave the statistical theory of liquid diffusion. As an electrolyte dissolves in water, dissociation of the solute takes place into positively charged particles (cations) and negatively charged particles (anions).

The electrolyte is supposed to contain ions of species 1, 2, 3 \(\ldots\) \(s\) with charges \(e_1, e_2, \ldots, e_s\) of concentrations \(n_1, n_2, n_3, \ldots n_s\) per c.c. The presence of any particular ion at a given point in the solution will effect the chance of finding any other ion at a nearby point. i.e. the space distribution of ions cannot be entirely random. Let us find a function which will give chance to find any two ions in two particular volume elements in the solution. Let there be two volume elements

\[ dV_1 = dx_1\, dy_1 \, dz_1 \]

and

\[ dV_2 = dx_2\, dy_2 \, dz_2 \]

in the solution, located by vectors \(\vec{r}_1\) and \(\vec{r}_2\) drawn from an arbitrary origin (fig. 3.2). The second is located with respect to the first by means of the vector \(\vec{r}_{21} = \vec{r}_2 - \vec{r}_1 = \vec{r}_{12}\) (where the order of the subscripts indicate the order of the terms in the subtraction). To simplify the description, generalised co-ordinates are introduced for the components
FIG: 3.2. DEFINITION OF VECTORS.
of $r_1$ and $r_2$ in the following way

$$q_1^1 = x_1, \quad q_1^2 = y_1, \quad q_1^3 = z_1$$

$$q_2^1 = x_2, \quad q_2^2 = y_2, \quad q_2^3 = z_2$$

$$q_k^1 = x_k, \quad q_k^2 = y_k, \quad q_k^3 = z_k$$

So $q_1^h$ or $q_2^h$ means $x_1$ or $y_1$ or $z_1$ and $x_2$ or $y_2$ or $z_2$ according to $h = 1,2,3$.

$\therefore q_{21}^h = q_2^h - q_1^h = -q_{12}^h$ gives the co-ordinates of $dv_2$ with respect to an origin at $dv_1$.

It has been postulated that the presence of an ion of a given species will affect the ionic concentration in its vicinity. Let $n_{ji}$ is the (time) average concentration of $i$-ions in the neighbourhood of a $j$-ion. Now $n_{ji}$ will depend on different variables, according to the situation to be investigated.

(1) It will depend on the distance $r$ between the $j$-ion and the point where the concentration of $i$-ions is sought,

(2) When forces act on the ions, in a particular direction in space, is specified, and $n_{ji}$ will then depend on the direction of $r$. 
(3) Finally if a variable velocity gradient is present in the liquid (viscosity), \( n_{ji} \) will depend on the location of the \( j \)-ion.

\[ n_{ji} = n_{ji}(r_1, r_2) \]  \hspace{1cm} (3.3)

and similarly \( n_{ij} = n_{ij}(r_2', r_{12}) \)

This gives the average concentration of \( j \) ions at a distance \( r_{12} \) in the direction of \( r_{12} \) from an \( i \)-ion located by \( r_2 \).

With a desire to observe the pair of volume elements \( dv_1 \) and \( dv_2 \) \((r_1, r_2 \) fixed temporarily) for a time \( t \), (which is large compared to the time involved in the Brownian movement of the ions), the attention is confined to any two particular species of ions (say \( i \), and \( j \)). Let \( t_j \) is the time during which a \( j \)-ion actually is in \( dv_1 \), out of the total time \( t \),

and thus, \( t_j/t = n_j dv_1 \)  \hspace{1cm} (3.4)

Similarly, for \( i \)-ion in \( dv_2 \) we get,

\[ t_i/t = n_i dv_2 \]  \hspace{1cm} (3.5)

Thus, if \( t_{ij} \) is the time during which the \( j \)-ion is in \( dv_1 \) and \( i \)-ion is in \( dv_2 \) simultaneously, within the total time \( t \), we have,

\[ t_{ji}/t_j = n_{ji} dv_2 \]

and \( t_{ji}/t_i = n_{ij} dv_1 \)
This is the probability of finding the i-ion in $dV_2$ and j-ion in $dV_1$ simultaneously at the same time. So this relation can be used to define the required distribution $f_{ji}$ or $f_{ij}$:

$$f_{ji}(r_1, r_{21}) = n_j n_{ji} = n_i n_{ij} = f_{ij}(r_2, r_{12})$$

In any steady state $f$ is independent of time and so

$$\text{div}_1(f_{ij} v_{ij}) + \text{div}_2(f_{ji} v_{ij}) = 0 \quad \cdots (3.7)$$

where $v_{ji}$ is the velocity of an i-ion in the vicinity of a j-ion, $v_{ji} = v_{ji}(r_1, r_{2i})$, and $v_{ij}$ is the velocity of j-ion in the vicinity of an i-ion $v_{ij} = v_{ij}(r_2, r_{12})$.

There are three effects contributing to the motion of the ions:

(1) forces on ions,
(2) thermal motion,
(3) flow of the solution itself.
If $f_i(=\frac{1}{W_i})$ is the friction coefficient of an i-ion then a force $k_i$ gives the ion a velocity $k_iw_i$ and the average diffusion velocity is $\left[(-kTw) \text{ grad ln}F\right]$. 

Assuming that, the concentration $n_{ji}$ of the i-ions in the vicinity of a j-ion can be determined from the energy $E_{ji}$, by Maxwell-Boltzman distribution, it can be written that,

$$n_{ji} = n_i \exp\left(-\frac{E_{ji}}{kT}\right) \quad \ldots \quad (3.8)$$

Then considering the perturbation of the ionic atmosphere, Onsager et. al. obtained the equation of continuity (specialised to suit our problem) which gave a system of $s^2$ differential equations connecting the $s^2$ distribution functions with a potentials and the known function. Then they eliminated the distribution functions by means of Poisson equation and solved the resulting system of differential equation for the potentials.

3.3.5 Kivelson's Theory

Kivelson et. al. elaborated a molecular theory of diffusion constants in liquids (independent of kinetic models of diffusion) in terms of suitably chosen collective dynamical variables (e.g. fluctuation in number density, spin magnetic moment etc.). This theory can explain the particle diffusion (the average motion of an individual particle, due to the random displacement) and the concentration diffusion.
The fluctuations or changes in concentration due to molecular motion) both keeping a sharp distinction between the two diffusion constants by means of a simple jump exchange model.

The new theory introduced by Kivelson developed in the language of time-dependent-correlation-functions and statistical-projection-operator. A correlation function (or its Fourier transform) can conveniently describe the transport data, particularly at near equilibrium. Correlation functions are averaged quantities and so they exhibit 'smoother' behaviour than the properties of individual molecules.

The particle diffusion constant $D^\alpha$ for the component $\alpha$ is defined by the relation

$$D^\alpha = \frac{1}{2r^2} \left< [z^{(a)}(t) - z^{(c)}(0)]^2 \right> \cdots (3.9)$$

where $z^{\alpha}(t)$ is the co-ordinate of the particle 1 of species $\alpha$ at time $t$. The time $t$ must be long compared to the time between the molecular collisions. Then, assuming the process to be an isotropic, stationary and stochastic, after rigorous mathematical steps $D^\alpha$ in the equation (3.9) took the form

$$D^\beta = k^T / (x^a \xi_{\alpha\beta} + x^\beta \xi_{\alpha\beta'})$$

where the extra superscript $\beta$ is added in $D^\alpha$ to indicate the particle diffusion of an $\alpha$ type particle in a solution of
\( \alpha \) and \( \beta \) molecules. \( \xi_{\alpha\alpha}, \xi_{\alpha\beta} \) are the friction constants, \( x_{\alpha} \) and \( x_{\beta} \) are the mole fractions of the species respectively. \( k_B \) is the Boltzmann constant and \( T \) is the temperature.

This expression for the particle-diffusion-constant resembles very closely to the expressions used by Laity\(^{98}\).

\[
D_{ij} / k T = \frac{1}{(x_i' r_{ii} + x_j r_{ij})}
\]

where \( x_i' \) is the total mole fraction of the chemical species \( i \) in the solution, \( x_j \) is the mole fraction of chemical species in the solution. \( r_{ii} \) and \( r_{ij} \) are the frictional coefficients. \( R(=Nk_B) \) is the universal gas constant.

The friction coefficients defined in this theory resemble the expression introduced by Kirkwood\(^{99}\).

The concentration-diffusion-constant's expression, as derived by Kivelson, Ahn, and Jensen\(^{100}\) are given by

\[
D_{\alpha\beta} = \frac{k_B T}{\xi_{\alpha\beta}} \left[ 1 + x_\alpha \left( \frac{\partial}{\partial x_\alpha} \frac{\partial}{\partial x_\alpha} \right)_{T, P, N_\beta} \right]
\]

\[
D_{\beta\alpha} = \frac{k_B T}{\xi_{\beta\alpha}} \left[ 1 + x_\alpha \left( \frac{\partial}{\partial x_\alpha} \frac{\partial}{\partial x_\alpha} \right)_{T, P, N_\beta} \right]
\]

Now since \( \xi_{\alpha\beta}'' = \xi_{\beta\alpha}'' \), \( D_{\alpha\beta} = D_{\beta\alpha} \)

So it is similar to the Onsager's reciprocal relations\(^{100}\).
Essentially, the statistical theories of diffusion in electrolytes takes into account the consequences of the electric interaction between ionic charges. The electric attraction and repulsion of ions are to a certain extent, ordering effects (acting against the disordering effect of the thermal motion) alter the statistical distribution of ions in solution. This effect has been described by Debye-Hückel theory and its advanced form was outlined by Bjerrum, Onsager, Falkenhagen and others (section 3.4) giving the best approximation to reality so far.

3.4 Theories of Irreversible Thermodynamics

The calculations of transport coefficients was initiated by Maxwell, but certain general questions on the properties of the transport coefficients remained unanswered until 1931. These questions were answered most successfully by Onsager. Onsager's idea was based on the microscopic reversibility of equations of motion and the correlations among the fluctuations. He showed that the transport coefficients are symmetric tensors. This explained a whole range of the experimentally observed situation. Though his relations were borne out in practice but the underlying theory was debated for more than a decade until Onsager's reciprocal relations solved the problem. In 1957 Kubo succeeded in casting the theory of 'linear transport phenomena'
in a general form by expressing the transport coefficients in terms of correlations among the fluctuations. Other general aspects regarding the irreversibility of the phenomena have been studied by Prigogine, De Groot, Mazur, Meixner and others\textsuperscript{101}, and the field remains as a subject of intense activity.

3.4.1 Aqueous Electrolytic Solution

It is interesting to apply the principle of irreversible thermodynamics as developed by Onsager to the problem of electrolytic solutions. The physical picture of the aqueous solutions of any (strong) electrolyte can be best visualised from the original Debye–Hückel theory\textsuperscript{102} and its advanced form. In a highly ionised electrolyte, the ions are greatly influenced by coulombic interactions and hence, when diffusion in a particular electrolyte is considered one have to remember that it is moving through an electrostatic force field. Even at quite low concentrations the properties of the electrolytes are complicated by various effects (mainly - relaxation effect and electrophoretic effect, in connection with the transport phenomena)\textsuperscript{102} which are now recognised as consequences of the coulomb forces between the ions. The quantitative theoretical prediction of these effects has greatly advanced the understanding of
the electrolytes. Almost all the effects can be attributed to the fact that, in the vicinity of each ion, ions of opposite charge are in excess. Thus each ion in the solution is surrounded by an ion atmosphere of opposite charge. In general, the solvent of an electrolytic solution is pictured as a continuum of dielectric constant $\varepsilon$, in which the distribution of the ions is determined by the thermal energy of the electrostatic interaction of the ions. This distribution varies due to fluctuation and only its average value remains same where a particular ion undergoes a diffusive motion in solution. Each ion of the diffusing electrolyte experiences the forces due to -

(1) the gradient of chemical potential for that species of ion,

(2) the electrical field produced by the motion of the oppositely charged ions.

Due to the movements of ions there will sometimes be an excess of positive and sometimes be an excess of negative ions in the volume element $dv$. The time average calculations show that every ion is associated with an ionic atmosphere of the opposite sign. This is the essential postulate of the Debye–Hückel theory.
This celebrated theory has long been the basis for the interpretation of various properties of electrolytes in solutions. In the development of the D - H theory, some assumptions have been considered. Owing to those assumptions, this theory has met with limited success in the concentration ranges of practical importance. Benetto and Spitzer gave a modified theory. From a general solution of LPEE (Linearised Poisson Boltzman Equation) they derived an expression for the activity coefficient of a central polarised ion in an ionic sphere of non-spherical symmetry. A infinite dilution their expression reduces to the Debye - Hückel limiting law which has the form \( F(c) = F(\infty) - \alpha / \sqrt{c} \) where \( F(c) \) stands for any transport property and, \( F(\infty) \) are the constants. The term \( \alpha / \sqrt{c} \) represents the influence of concentration. The value of \( \alpha \) will in general depend on the limiting ionic mobilities or on the ionic forces. The function \( F(c) \) describes the irreversible processes and hence it is logical to attempt to describe these processes from the Non-Equilibrium thermodynamic considerations.

In doing so, it is to be borne in mind that in diffusion of electrolyte, the main effect of the electrostatic forces between the ions, is thermodynamic one; the gradient of the thermodynamic potential, which represents the
'driving force' upon the ions is less then it would be in an ideal solution for the same concentration gradient. For the sake of simplicity we consider the presence of two kinds of ions.

3.4.2 Dissipation Function

The diffusion in a simple electrolyte (i.e. consisting of two ions) can be best described by Fick's Law.

\[ J_i = -D \nabla C_i \quad \text{\ldots (i = 1, 2)} \quad \ldots (3.11) \]

Where \( C_i \) denotes the concentration per unit volume, \( J_i \) is the flow in corresponding unit and \( D \) is the diffusion coefficient. The above relation can be generalised as

\[ J_i = -\sum_k D_{ik} \nabla C_k \ldots (3.12) \]

for a system of \( i > 2 \), assuming that the relative velocities of the different components will be linear functions of the concentration gradient. The coefficient \( D_{ik} \) satisfies certain symmetry conditions which are derivable from the hypothesis of microscopic reversibility. Previously Onsager have shown that when those reciprocal relations hold good, the equations of transport processes can be expressed in terms of the thermodynamic functions and the so called dissipation function. Onsager defined the 'dissipation function' \( F \) for a system of \( N \) components at constant temperature, as

\[ F = \frac{1}{2} \sum_{i,k}^N R_{ik}(J_i, J_k) \quad \ldots \quad (3.13) \]
where the vector $J_i$ represents the local flux of component $i$ and $J_k$ represents the local flux of component $k$. Since the dissipation function represents half the rate at which free energy is dissipated (locally i.e. within the volume element $dv$) by the irreversible flows, Onsager imposed an additional restriction on $R_{ik}$:

$$\sum_{k=1}^{N} R_{ik} c_k = 0$$

where $c_k$ is the concentration of component $k$. (This restriction is imposed so that there will be no dissipation when all the velocities are equal). The coefficients $R_{ik}$ are related to the molecular 'coefficients of friction' $\beta_{k,i}$ as follows:

$$c_k R_{kk} = \rho_k$$

As the ions are recognised to be the kinetic units, Onsager described diffusion and electrolytic conduction together in one scheme. The dissipation function for combined conduction and diffusion of a simple electrolyte is given by

$$F = \frac{1}{2} \left[ R_{11} J_1^2 + 2 R_{12} (J_1 J_2) + R_{22} J_2^2 \right]$$

or

$$2F = \left( \frac{R_{11}}{c_1} \right) J_1^2 + \left( \frac{R_{22}}{c_2} \right) J_2^2 +$$

$$- \frac{e_1 e_2 \rho_1 \rho_2 k}{3 e K T} x \frac{(1 - q^{1/2})}{c_1 \sigma_1^2 + c_2 \sigma_2^2} \left| e_1 J_1 + e_2 J_2 \right|^2$$

$$+ \left\{ \frac{2}{3 n K e (1 + k a) k} \left| e_1 \rho_1 J_1 + e_2 \rho_2 J_2 \right|^2 \right\} -$$

$$\frac{q (\kappa a)}{3 n (e K T)^2} \left| e_1 \rho_1 J_1 + e_2 \rho_2 J_2 \right|^2$$

... (3.14)
where \( a \) is the least distance of the ions.

\[
\begin{align*}
\mu_1 &= \text{frictional coefficient of ion no. 1} \\
\mu_2 &= \text{frictional coefficient of ion no. 2} \\
e_1 &= \text{total electrical charge of ion no. 1} \\
e_2 &= \text{total electrical charge of ion no. 2} \\
J_1 &= \text{flow of ion no. 1} \\
J_2 &= \text{flow of ion no. 2} \\
\varepsilon &= \text{the permitivity} \\
k &= \text{the Boltzman constant} \\
T &= \text{the temperature in absolute scale} \\
\eta &= \text{the coefficient of viscosity} \\
\varphi(ka) &= e^{2ka}(1 + ka)^{-2} \int_{2ka}^{\infty} (e^{-t} - t) dt \quad \ldots \quad (3.17)
\end{align*}
\]

The first two terms in the equation (3.15) represent the dissipation function without allowance for the effects of the coulomb forces.
The third term is due to the relaxation effect. The relaxation effect is appreciable only in the case when positive and negative ions move in the opposite directions under the effect of an external potential gradient. In the diffusion, the ions of opposite charge move in identical directions and the relaxation effect does not markedly influence the velocity of diffusion. So the third term vanishes if there is no electric current.

The last two terms represent the electrophoretic effects of first and second order, with approximate allowance for the finite dimensions of the ions. The electrophoretic effect in diffusion alters the mobilities of the ions. The interaction of the ionic charges slows down the ions of higher mobility, while it accelerates those of lower mobility in diffusion. Consequently the electrophoretic effect increases the mobility of ions of lower mobility and vice-versa. If the mobilities of different ions are identical, the electrophoretic effect vanishes.

So on specialising the equation for diffusion we get,

\[ 2F = \frac{\zeta_1}{C_1} j_1^2 + \frac{\zeta_2}{C_2} j_2^2 + \frac{2|e_1 q_1 J_1 + e_2 q_2 J_2|^2}{\eta KT\varepsilon (1 + k\alpha) K} \]

\[ - \frac{\varphi(k\alpha)}{3\eta(\varepsilon k\tau)^1} \left| e_1^2 q_1 J_1 + e_2^2 q_2 J_2 \right|^2 \cdots \cdots (3.18) \]

On considering the migration of the ions the question at once comes into our mind, is the 'velocity' with which the
ions are transported through the solutions. In absence of the externally applied field, both the positive and negative ions in solution move about, in random directions with random velocities. The resultant speed of both +ve and -ve ions must finally be equal, since it is an experimental fact that a macroscopic charge separation does not occur. So,

$$\frac{J_1}{C_1} = \frac{J_2}{C_2} = V$$

$$\therefore 2F = \sqrt{\pi} \left[ \rho_1 C_1 + \rho_2 C_2 + \frac{2(\rho_e \epsilon_d)^{\frac{1}{2}} (\rho_1 - \rho_2)^2}{3 \eta e_k T (1 + \kappa \alpha)} \right]$$

$$\frac{\phi(k \alpha)(\rho_e \epsilon_d)^{\frac{1}{2}}}{3 \eta (e_k T)^{\frac{1}{2}}} (\rho_1 - \rho_2)^2$$

Fick's law (1.1) may be written in the alternative form

$$\dot{J} = -\Omega \text{grad } \mu$$

where $\mu$ is the chemical potential and $\Omega$ is the function of conductance and the coefficient of diffusion.

$$D = \Omega \left( \frac{\partial \mu}{\partial c} \right) \rho, T$$

From $(\Omega_{ik} = \Omega_{ki})$ and (3.20)

$$- \text{grad } \mu_i = \sum_{k=1}^{m} R_{ik} J_k$$

or

$$\text{grad } \mu_i + \frac{\delta F}{\delta J_i} = 0$$

Thus knowing the dissipation function, $\mu$ and thence $D$ can be determined by the help of eq.3.21 and we get the following
simple limiting law for the coefficient of diffusion of an ion whose transference number is very small

\[ D_j = \omega_j \left[ kT - \left( \kappa e_j^2 / 3 \varepsilon \right) \left( 1 - \sqrt{d(\omega_j)} \right) \right] \]  \hspace{1cm} (3.22)

\[ \omega_j = \frac{RT\lambda_j^o}{12F^2} \]  \hspace{1cm} (3.23)

with

\[ d(\omega_j) = \frac{\lambda}{\bar{\lambda}} \sum_i \frac{t_i}{n_i e_i^2 \omega_i} \]  \hspace{1cm} (3.24)

\[ \bar{\lambda} = \sum_i n_i e_i^2 \omega_i \]  \hspace{1cm} (3.25)

\[ t_i = n_i e_i^2 \omega_i / \bar{\lambda} \]  \hspace{1cm} (3.26)

\[ k^o = \frac{4\pi}{\varepsilon kT} \bar{\lambda} \]  \hspace{1cm} (3.27)

\[ \bar{\lambda} = \sum_i n_i e_i^2 \]  \hspace{1cm} (3.28)

where \( e_i \) is the absolute electric charge and \( Z_i \) the charge in electronic units of ion \( i \), \( \lambda_i^o \) is the inverse-mean-radius of the ion atmosphere, \( n \) is the concentration in number of ions per c.c., \( \lambda_i^o \) is the limiting ionic conductance of ion \( i \), \( \varepsilon \) is the dielectric constant of solvent, \( k \) is the Boltzmann constant, \( R \) is the gas constant, \( F \) is the Faraday constant and \( T \) is the absolute temperature.
If we express \( \lambda_j^o \) (coulomb/sec) x (cm\(^2\)/volt)* F in coulombs (i.e. \( F = 96487 \) coulombs), \( R \) is Joules per °C per mole (i.e. \( R = 8.3 \times 10^7 \) cal/mole) and replace \( n \) by \( c \) which denotes concentration in moles/liter the expression in the r.h.s. of (3.22) becomes

\[
D_j = \frac{kT \lambda_j^o}{|Z_j| F} - \frac{\lambda_j^o |Z_j| F}{3N_e} \times 2.694 \times 10^{16} \\
\times \sqrt{\frac{4\pi}{ekT}} (1 - \sqrt{d(w_j)}) \times \sqrt{\sum_{i} c_i z_i^2}^2 \quad \cdots \quad (3.29)
\]

The equation (3.29) is showing the dependence of concentration on diffusion coefficient.

To study the concentration dependence of the diffusion coefficient (theoretically) the conductivity function is to be computed for each particular case. For this, the expression (3.23) is modified in terms of the known quantities as

\[
d(\omega_j) = \frac{1}{\sum_{i} c_i z_i^2} \sum_{i} \frac{c_i |Z_i| A_i^o}{|Z_i| + |Z_j|} \quad \cdots \quad (3.30)
\]

Now by substituting the values of the different constants from the standard literature \( d(\omega_j) \) and thence the limiting equation for various (specific) electrolytic solutions may be obtained. This would be discussed in a more detailed way in Chapter 5.
3.4.3 Phenomenological Coefficients

For a fluid made up of any kind of molecules and under any arbitrary conditions of temperature and pressure, it is not possible at the present time to use statistical mechanics to obtain the form of the flux vectors and to derive an expression for the transport properties, in terms of intermolecular forces. For general fluids a certain amount of information may be obtained from the thermodynamics of irreversible processes. Onsager's phenomenological equations are of immense significance in the study of thermodynamics of the irreversible processes.

To find out the coefficients $L_{11}$, $L_{12}$, $L_{22}$ for the case of diffusion in monovalent salt solutions one has to know the electrical conductance, transference number and diffusion coefficient for the solutions. The related equations are

$$L_{11} = \frac{-D}{\mu} + \frac{t_1^2}{F^2}$$  \hspace{1cm} (3.31a)

$$L_{12} = \frac{D}{\mu} + \frac{t_1 t_2}{F^2}$$  \hspace{1cm} (3.31b)

$$L_{22} = \frac{-D}{\mu} + \frac{t_2^2}{F^2}$$  \hspace{1cm} (3.31c)

where $D$ is the diffusion coefficient, $\mu$ is the chemical potential, $F$ is the Faraday constant, $t$ is the transference
number, \( p \) is the electrical conductance of the solution. So \( L_{11}, L_{22} \) and \( L_{12} \) can be determined at different concentrations of the solution if \( D, \mu, t_1, t_2, p, P \) are known. Miller \(^{105} \) first calculated \( L_{ij} \)'s from the experimental data for \( \text{HCl}, \text{LiCl}, \text{NaCl}, \text{KCl}, \text{CaCl}_2, \text{BaCl}_2 \) and \( \text{LaCl}_3 \) at 25° in the concentration range from 0 to 3N. He also described the interesting aspects of the relative values of \( L_{ij} \) and their concentration dependence. Dunsmore et al \(^{106} \) have measured the equivalent conductances of aqueous \( \text{CsCl} \) in the concentration range 0.1N-3.5N and calculated the phenomenological coefficients. Then they have discussed about the relative sizes of these coefficients in terms of solvation number and water structure while comparing with other alkali Chloride salts. Abnormalities observed in Caesium-Chloride interactions are tentatively ascribed to the ion association. Studies have been made in this angle on Rubidium Chloride \(^{107} \), Zinc Chloride \(^{108} \), Zinc Perchlorate \(^{109} \), and these data were used to calculate mobility \( (L_{ik}) \), resistance coefficients using irreversible thermodynamic theory. The isotopic diffusion coefficient for Rubidium ion in Rubidium Chloride \(^{110} \), Cadmium in Cadmium Iodide \(^{111} \) were also determined. The irreversible thermodynamic analysis shows that there is a positive fluctuation in isotope-isotope coupling contribution to 'D' values.