CHAPTER 3

REPRESENTATION AND ANALYSIS OF DIELECTRIC DATA

3.1 COMPLEX PERMITTIVITY

When an electric field $E$ is applied to a dielectric medium, it gets polarized. The measure of polarization $P$ is the dipole moment per unit volume. The equilibrium value of the macroscopic polarization consists of two parts (i) distortion polarization ($P_1$) and (ii) dipole orientation polarization ($P_2$). The distortion polarization reaches its equilibrium value almost instantaneously, in terms of the time interval we are interested in, but the remaining dipolar part ($P_2$) takes time to reach its equilibrium value. If we assume that $P_2$ increased at a rate proportional to its departure from equilibrium value then

$$\frac{dP_2}{dt} = \frac{P - P_1 - P_2}{\tau}$$

(3.1)

where $P$ is the equilibrium value of total polarization and $\tau$ is a constant called macroscopic relaxation time. If $P$ and $P_1$ be time independent for the time interval of our interest then equation (3.1)
can be written as

\[ \frac{d(P - P_1 - P_2)}{P - P_1 - P_2} = \frac{-dt}{\tau} \quad (3.2) \]

which on integration becomes

\[ \ln (P - P_1 - P_2) = -\frac{t}{\tau} + C \quad (3.3) \]

where C is a constant. Applying the boundary condition that field E has been suddenly applied i.e. at \( t = 0, \ P_2 = 0 \) gives \( C = \ln (P - P_1) \) which in turn results in

\[ P_2 = (P - P_1) \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right] \quad (3.4) \]

\( P_2 \) is related to the static permittivity \( \varepsilon_o \) and \( P_1 \) to the high frequency limiting permittivity \( \varepsilon_\infty \) by the following relations

\[ P = (\varepsilon_o - 1) \frac{E}{4\pi} \quad (3.5a) \]

\[ P_1 = (\varepsilon_\infty - 1) \frac{E}{4\pi} \quad (3.5b) \]

and then

\[ \frac{dP_2}{dt} = \frac{P - P_1 - P_2}{\tau} = \frac{(\varepsilon_o - \varepsilon_\infty)}{4\pi} E_0 e^{j\omega t} - \frac{P_2}{\tau} \quad (3.6) \]
where \( E = E_0 e^{j\omega t} \)

In steady state we can expect a solution of the form

\[
P_2 = A e^{j\omega t}
\]

(3.7)

Substituting this in the differential equation gives

\[
A = \frac{(\varepsilon_0 - \varepsilon_\infty) E_0}{4\pi(1 + j\omega \tau)}
\]

(3.8)

and

\[
P_2 = \frac{(\varepsilon_0 - \varepsilon_\infty) E}{4\pi (1 + j\omega \tau)}
\]

(3.9)

It is thus seen that \( 4\pi P_2/E \) is a complex quantity. This means that dipolar part of the polarization has a component right angle to the applied field and so there is loss of the energy in the medium. We may now write

\[
P_1 + P_2 = P' - jP'' = \frac{(\varepsilon_\infty - 1)E}{4\pi} + \frac{(\varepsilon_0 - \varepsilon_\infty)E}{4\pi(1 + j\omega \tau)}
\]

(3.10)

where \( P' \) and \( P'' \) both are real.

When the polarization is complex quantity,
permittivity also becomes complex and is denoted by \( \varepsilon^* \), where \( \varepsilon^* = \varepsilon' - j\varepsilon'' \). Here \( \varepsilon' \) is the real part of permittivity and \( \varepsilon'' \) is the imaginary part or loss factor. The loss factor is a measure of the conductance of the medium and its ability to dissipate energy. Hence

\[
\varepsilon^* = 1 + 4\pi \frac{(P' - jP'')}{E} \quad (3.11)
\]

or

\[
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \quad (3.12)
\]

and so,

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \quad (3.13a)
\]

and

\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2 \tau^2} \quad (3.13b)
\]

The physical significance of these eqns is that at frequencies for which \( \omega\tau \ll 1 \), that is, below the maximum in the absorption curve equilibrium will be set up in a short time compared with that for which the field is in one direction. In this case the maximum value of permittivity will be obtained and little energy will be absorbed. When the frequency approaches that for which \( \omega\tau = 1 \), the field will reverse in a time comparable with
\( \tau \), then polarization will not have time to reach the maximum. Thus the energy absorbed per cycle will be maximum. At frequencies for which \( \omega \tau \gg 1 \), there is no significant orientation of dipoles in each cycle and the measured permittivity does not contain a contribution from this particular polarization.

### 3.2 Representation of Data for Pure Liquids

One way of the representation of data is to plot the experimentally measurable quantities, the electrical permittivity \((\varepsilon')\) and dielectric loss \((\varepsilon'')\) against logarithms of frequency or wavelength. The curves obtained by plotting \(\varepsilon'\) and \(\varepsilon''\) vs. logarithms of frequency, are shown in Fig.(3.1) and are known as dispersion and absorption curves respectively. When the frequency of the applied field approaches zero, \(\varepsilon''\) approaches zero and \(\varepsilon'\) approaches the static permittivity \(\varepsilon_0\), and as the frequency approaches infinity, \(\varepsilon''\) again becomes zero, and \(\varepsilon'\) approaches \(\varepsilon_\infty\), the very high frequency (or optical permittivity). The dielectric dispersion covers a wide range of frequencies and dielectric loss reaches its maximum \((\varepsilon''_{max})\) at \((\varepsilon_0 - \varepsilon_\infty)/2\) at an angular frequency equal to the inverse of relaxation time \(\tau\) (\(\omega = 1/\tau\)). If the
DEBYE PLOT

\[ \varepsilon^* = \varepsilon_\infty + \left( \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega t} \right) \]

FIG. 3.2
data are represented by this method the relaxation time is determined by the inverse of the angular frequency at which the loss reaches its maximum value.

The $\varepsilon''$ falls to half its maximum value when
$$\omega_t = \frac{(1 + \omega^2 \tau^2)}{4} = 0.27 \text{ or } 3.73.$$ The $\varepsilon''$ is thus considerable over frequencies varying in value by a factor of more than 10. The phase lag between the polarization and the applied field leads to an absorption of energy in the dielectric. Any change in the polarization of the dielectric leads to a displacement current of density

$$i = \frac{dP}{dt} \quad (3.14a)$$

and Joule heating

$$H = E_i = E \frac{dP}{dt} \quad (3.14b)$$

per unit volume. The net rate of Joule heating can be found by averaging the above expression over a complete cycle of the electric field. This yields

$$H_{av} = \frac{E_0^2}{8\pi} \varepsilon'' \omega \quad (3.14c)$$

$\varepsilon''$ is called the dielectric loss, because it controls the rate at which the electrical energy
is converted into heat in the medium. The quantity \((\varepsilon''/\varepsilon') = \tan \delta\) is similarly called loss tangent.

In a static field the specific polarization can be represented as \(P_0\) when the field is removed at any instant \(t = 0\), the polarization produced by it will decay exponentially with time, then value \(P(t)\) at a subsequent time \(t\) is given by

\[
P(t) = P_0 \exp(-K \varepsilon) = P_0 \exp \left(-\frac{t}{\tau}\right) \quad (3.14d)
\]

Here \(K\) is the rate coefficient and \(\tau\) its reciprocal, the characteristic relaxation for the polarization.

Electric polarization shows exponential decay with time in a dielectric when the externally applied field is removed. The relaxation time is defined as the time in which the polarization in a dielectric is reduced to \(1/e\) times its original value.

However, when observations at few selected frequencies are available above method is not very convenient. By combining equations (3.13a) and (3.13b) we get

\[
\left[ \varepsilon' - \frac{(\varepsilon_0 + \varepsilon_\infty)}{2} \right]^2 + \varepsilon''^2 = \left[ \frac{(\varepsilon_0 - \varepsilon_\infty)}{2} \right]^2 \quad (3.14e)
\]
which is an equation of circle with centre at 
\[ \left( \frac{\varepsilon_0 + \varepsilon_{\infty}}{2}, 0 \right) \] and radius \( \frac{\varepsilon_0 - \varepsilon_{\infty}}{2} \), when \( \varepsilon'' \) is plotted against \( \varepsilon' \) in a complex plane, as shown in Fig.(3·2). The results of permittivity and loss measurements are very often displayed by above method by plotting \( \varepsilon' \) and \( \varepsilon'' \) in a complex plane and getting the semicircle as explained above. The curve in Fig.(3·2) is known as Debye semicircle[1].

It has been found from measurements on a large number of compounds that \( \varepsilon'' \) vs. \( \varepsilon' \) curve deviates considerably from the above predicted semicircular behaviour of Debye theory. Materials having long chain molecules or having a number of rotatable polar groups, show a broader dispersion curve and lower maximum loss than obtained from Debye behaviour and in such case \( \varepsilon'' \) vs. \( \varepsilon' \) curve may be an arc of the circle which falls inside Debye semicircle. The curve is known as Cole-Cole arc and is shown in Fig(3·3) for a typical system. Cole and Cole[2] have suggested an empirical relation of the following form

\[
\varepsilon'' = \varepsilon_0 + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + (j \omega \tau)^{1-\alpha}}
\]  

(3·15)

where \( \alpha \) represents the symmetric distribution
**COLE-COLE PLOT**

\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j\omega \tau)^{1-\alpha}} \]

\[ v/u = (\omega \tau)^{1-\alpha} \]

**FIG. 3.3**

**DAVIDSON-COLE PLOT**

\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1+j\omega \tau)^\beta} \]

**FIG. 3.4**
parameter of the relaxation times and lies between 0 and 1, i.e. $0 < \alpha < 1$. Rationalising above equation with the use of the relation

$$j^{(1 - \alpha)} = \exp [j\pi(1 - \alpha)/2]$$

one obtains

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1 + (\omega \tau)^{1-\alpha} \sin(\alpha\pi/2)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{1-\alpha} \sin(\alpha\pi/2)} \quad (3.16a)$$

and

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{(\omega \tau)^{1-\alpha} \cos(\alpha\pi/2)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{1-\alpha} \sin(\alpha\pi/2)} \quad (3.16b)$$

Above equations can also be written as

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{2} \left[ 1 - \frac{\sinh \Theta}{\cosh \Theta + \sin(\alpha\pi/2)} \right] \quad (3.17a)$$

and

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{2} \left[ \frac{\cos(\alpha\pi/2)}{\cosh \Theta + \sin(\alpha\pi/2)} \right] \quad (3.17b)$$

Where $\Theta = (i - \alpha) \ln \omega \tau \quad (3.18)$
Solving these equations for sinh $\Theta$ and cosh $\Theta$ we have

$$\sinh \Theta = \frac{\varepsilon_0 + \varepsilon_\infty - 2\varepsilon'}{2\varepsilon''} \cos (\alpha \pi/2) \quad (3.19)$$

$$\cosh \Theta = \frac{\varepsilon_0 - \varepsilon_\infty}{2\varepsilon''} \cos (\alpha \pi/2) - \sin (\alpha \pi/2) \quad (3.20)$$

and by eliminating $\Theta$ in equations (3.19) and (3.20), after some rearrangements one gets,

$$\left[ \frac{1}{4} (\varepsilon_0 - \varepsilon_\infty) - \varepsilon' \right]^2 + \left[ \varepsilon'' + \frac{1}{4} (\varepsilon_0 - \varepsilon_\infty) \tan (\alpha \pi/2) \right]^2$$

$$= \frac{1}{4} \left( \varepsilon_0 - \varepsilon_\infty \right)^2 \sec^2 (\alpha \pi/2) \quad (3.21)$$

which is again an equation of circle with the centre at $\left[ \frac{1}{4} (\varepsilon_0 + \varepsilon_\infty), -\frac{1}{4} (\varepsilon_0 - \varepsilon_\infty) \tan (\alpha \pi/2) \right]$ and radius $\frac{1}{4} (\varepsilon_0 - \varepsilon_\infty) \sec (\alpha \pi/2)$. The geometrical significance of the various parameters are shown in Fig. (3.3). In the limit when $\alpha \to 0$ the Cole-Cole plot reduces to the Debye semicircle.

The Cole-Cole arc is symmetrical about the line through the centre. Davidson and Cole[3] found that experimental points for a number of compounds do not have the above said symmetry. The $\varepsilon''$ vs. $\varepsilon'$ plot is a skewed arc of the form shown in Fig. (3.4). Davidson and Cole proposed an
empirical relation

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega \tau)^\beta} \quad (3.22)$$

where $\beta$ is a constant known as distribution parameter and determines the skewedness of the curve. Rationalising the equation (3.22) we have

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon - \varepsilon_\infty} = \frac{(1 - j\omega \tau)^\beta}{(1 + \omega^2 \tau^2)^\beta} \quad (3.23)$$

writing $\omega \tau = \tan \phi$, we have

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \exp(-j\beta \phi) \quad (3.24)$$

Separating the real and imaginary parts

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \cos \beta \phi \cos \beta \phi \quad (3.25)$$

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \cos \beta \phi \sin \beta \phi \quad (3.26)$$

The value of $\beta$ is determined by the angle at which the arc cuts the $\varepsilon'$ axis at high frequency end. Differentiating above equation with respect to $\phi$ we get
\[
\frac{d\varepsilon'''}{d\varepsilon'} = \frac{d\varepsilon''}{d\varphi} = -\cot(\beta + 1)\varphi \tag{3.27}
\]

In the high frequency limit \(\omega \tau \to \infty\)

\[
\varphi = \tan^{-1} (\omega \tau) = \pi/2 \tag{3.28}
\]

and

\[
\frac{d\varepsilon'''}{d\varepsilon'} = \tan(\beta \pi/2) \tag{3.29}
\]

The reason why experimental curves deviate from normal Debye behaviour is attributed to the distribution of the relaxation time. Thus Cole-Cole and Davidson-Cole behaviour can be thought of as arising from a continuous spread of relaxation times. In addition to Debye semicircle, Cole-Cole arc, and Davidson-Cole skewd arc other types of behaviour may also be encountered when \(\varepsilon''\) is plotted against \(\varepsilon'\) in a complex plane. One of such a behaviour is shown in Fig. (3.5) which may be thought of as a sum of a number of semi circular plots indicating the presence of multiple relaxation processes in the molecule.

A number of empirical and semiempirical relations have been proposed including various distribution functions, to explain the behaviour of the distribution of relaxation time. To account
for the distribution in relaxation time equation (3.12) should be modified as

\[ \varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_{\tau' = 0}^{\tau' = \infty} \frac{f(\tau')}{1 + j \omega \tau'} \, d\tau' \]  
(3.30)

where \( f(\tau') \) is a distribution function for the relaxation time and satisfies the normalization relation

\[ \int_{0}^{\infty} f(\tau') \, d\tau' = 1 \]  
(3.31)

Cole and Cole empirical equation (3.15) leads to a distribution function of the form

\[ f(\tau') \, d\tau' = \frac{1}{2\pi} \frac{\sin(\alpha \pi) \, d\tau'}{\cosh[(1 - \alpha) \ln(\tau'/\tau)] - \cos \alpha \pi} \]  
(3.32)

The distribution function for Davidson-Cole skewed arc is of the form

\[ f(\tau') = \frac{\sin \beta \pi}{\pi} \left( \frac{\tau'}{\tau - \tau'} \right)^\beta \text{ for } \tau' < \tau \]  
(3.33a)

\[ = 0 \quad \text{ for } \tau' > \tau \]  
(3.33b)

It is apparent from the above function that the distribution is asymmetric, having a low frequency cut off at \( \tau \). The parameter \( \beta \) determines the
sharpness of distribution.

Nee and Zwanzig[4] have proposed a theory of dielectric relaxation which is readily applicable to the experimental data and gives a theoretical basis of normally used distribution functions as described above. In the Nee and Zwanzig theory the model is of the form of a spherical Onsager cavity with a uniform dielectric background. The dipole undergoes rotational Brownian motion inside the cavity. When rotational Brownian motion is spherically isotropic, approximately Debye relaxation is found, when rotational Brownian motion is two dimensional, i.e. it is restricted to a constant angle with some fixed axis, approximately Davidson-Cole relaxation is found, and when rotational diffusion is three dimensional i.e. it is unhindered and spherically isotropic, approximately Cole-Cole plots are obtained by this theory.

Some other distribution functions for describing the spread of molecular relaxation times have also been proposed. Wagner[5] and Yager[6] have shown that a Gaussian probability function reproduces some experimental data satisfactorily when expressed in the form

\[ f(\tau') = \pi^{\frac{1}{2}} b e^{-b^2 \tau'^2} \]  

(3.34)
where \( b \) is a constant and determines the breadth of the distribution and \( S = \ln \frac{\tau}{\tau'} \) where \( \tau \) is the most probable relaxation time and \( f(S) \, dS \) is the probability of finding a relaxation time \( \tau' \) such that \( \ln \frac{\tau}{\tau'} \) lies between \( S \) and \( S + dS \).

For long chain polar molecules and polymers having probability of internal rotation and molecular vibration of some segments, Fuoss and Kirkwood[7] have derived a distribution function of the form

\[
f(\tau') = \frac{1}{2 \cos S + 2}
\]  

(3.35)

where again \( S = \ln \frac{\tau}{\tau'} \)  

(3.36)

This formula, however, is not in good agreement with experimental results.

Fuoss and Kirkwood[8] in another work have suggested that experimental data can be represented by the empirical relation

\[
\varepsilon'' = \varepsilon''_m \left[ \text{sech} \, \beta \ln \left( \frac{\omega}{\omega_m} \right) \right]
\]  

(3.37)

where \( 0 < \beta < 1 \). The corresponding distribution function is given as
\[ f(\tau') = \frac{\beta}{\pi} \frac{\cos(\beta \pi/2) \cosh(\beta S)}{\cos^2(\beta \pi/2) + \sinh^2(\beta S)} \quad (3.38) \]

where \( S = \log(\omega/\omega_m) \) and \( \omega_m \) is the frequency corresponding to the maximum value of \( \varepsilon'' \).

Fröhlich\[9\] has derived a distribution function for molecular relaxation times. The molecular process associated with the relaxation is thought of as due to passage of molecule over a potential barrier \( H \) hindering the rotation. It is then assumed that height of the energy barrier \( H \) is equally distributed among molecules over a range of values between \( H_0 \) and \( H_0 + v_0 \). When the interaction between the dipoles are neglected a range of relaxation times between \( \tau \) and \( \tau_1 \) can be defined such that

\[ \tau_1 = \tau \exp(\frac{v_0}{kT}) \quad (3.39) \]

The theory finally leads to the following equations

\[
\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = 1 - \frac{kT}{2v_0} \log \left[ \frac{1 + \omega^2 \tau^2 \exp(2v_0/kT)}{1 + \omega^2 \tau^2} \right] \quad (3.40a)
\]

and
\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{kT}{v_0} \left[ \tan^{-1}(\omega \tau \exp(v_0/kT)) - \tan^{-1}(\omega \tau) \right]
\]

(3.40b)

The factor \(v_0/kT\) determines the width of the range of relaxation time and this width is given by

\[
\frac{\tau_1 - \tau}{\tau} = \exp \left( \frac{v_0}{kT} \right) - 1
\]

(3.41)

and the form of the distribution function is given as

\[
f(\tau') = (\varepsilon_0 - \varepsilon_\infty) \frac{kT}{v_0} \frac{1}{\tau'} \text{ if } \tau \ll \tau' \ll \tau_1 = \tau e^{v_0/kT}
\]

(3.42a)

\[
= 0 \quad \text{ if } \tau' \ll \tau \text{ and } \tau' \gg \tau.
\]

(3.42b)

Debye formulae are obtained for \(v_0/kT = 0\).

Glarum[10] has proposed a defect diffusion model to account for the skewed arc behaviour of the substances. In the model it is assumed that skewed arc behaviour is not due to any distribution of the molecular parameters but arises from a co-operative relaxation process which means that molecules do not relax independently to one another but the motion of a particular molecule depends to some degree on its neighbours. In one dimensional system dipole relaxes when a defect travelling by the diffusion mechanism reaches the
The distribution function in terms of reciprocal relaxation time \( \alpha_0 = 1/\tau \) is given as

\[
F(\alpha) = \pi^{-1} \frac{(D/\ell_0^2)^{3/2}}{(\alpha - \alpha_0)^{3/2}} \cdot \frac{\alpha}{\alpha - \alpha_0 + D/\ell_0^2} \quad \text{for} \quad \alpha > \alpha_0
\]

\[
= 0 \quad \text{for} \quad \alpha < \alpha_0
\]

where \( D \) is the diffusion coefficient of the defect, \( \ell_0 \) is the average of the distance of the nearest defect from a given molecule at time \( t = 0 \). This function has been successful in explaining a good number of experimental data for skewed arcs.

Mc Duffie and Litovitz[11] have discussed the various models for distribution of relaxation times in order to explain their data for associated liquids. They have proposed that groups (regions of appreciable orders) exist in such liquids and dielectric relaxation is closely associated with structural breakup of such groups. Here breaking up is a necessary condition for dielectric relaxation. It is further proposed[12] that structural breakup is a co-operative process and it does not proceed exponentially, therefore, gives the nonresonant exponential decay of dielectric...
polarization.

Matsumoto and Higasi[13] presented a mechanism for distribution of relaxation times between two limits $\tau_1$ and $\tau_2$ with the following distribution function

$$f(\tau') = \frac{1}{(A \tau'^n)} \text{ where } 0 < n < \infty \text{ if } \tau_1 < \tau' < \tau_2$$  
$$= 0$$  

if $\tau' < \tau_1$ and $\tau' > \tau_2$  

(3.44a)  

(3.44b)

The lower limit $\tau_1$ is the relaxation time for the rotation of the end group in the molecule and $\tau_2$ corresponds to the overall rotation of the whole molecule in the extended form. Symmetrical arc is obtained for $n = 1$, right skewed arc is obtained for $n = \frac{1}{2}$, and if ratio of $\tau_1/\tau_2$ is very large the curve is very similar to Davidson-Cole skewed arc. Left skewed arc is obtained for $n = 3/2$.

If there are two very different relaxation times, two distinct dispersion regions are obtained and may be examined independent of each other[14]. Dielectric relaxation times of two mutually independent relaxation mechanisms may be considered to follow the following
equations[15,16]

\[
\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = C_1 \frac{1}{1 + (\omega \tau_1)^2} + C_2 \frac{1}{1 + (\omega \tau_2)^2} \quad (3.45a)
\]

\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_{\infty}} = C_1 \frac{\omega \tau_1}{1 + (\omega \tau_1)^2} + C_2 \frac{\omega \tau_2}{1 + (\omega \tau_2)^2} \quad (3.45b)
\]

where \(C_1\) and \(C_2\) are relative weights of each relaxation terms and \(C_1 + C_2 = 1\).

However, it may be noted that equations (3.45a) and (3.45b) are applicable for molecules with freely rotating groups and \(\tau_1\) or \(\tau_2\) should not be taken as the one corresponding to hindered group rotations. Fong[17] has shown that

\[
\tau_2 = \frac{\tau_1 \tau_0}{\tau_1 + \tau_0} \quad (3.46)
\]

where \(\tau_1\) is the group relaxation time, which may be very large due to high energy barrier, \(\tau_2\) may in no case exceed the value for overall molecular relaxation time.

3.3 REPRESENTATION OF DATA FOR POLAR SOLUTES IN NON-POLAR SOLVENTS

Franklin et al[18] suggested that for a
dilute solution of polar solute in non-polar solvents, instead of plotting permittivity $\varepsilon'$ and dielectric loss $\varepsilon''$ in a complex plane, plots should be made between the slopes of the permittivity and dielectric loss with the concentration of the solutes. These slopes are defined by the following equations

\[
\begin{align*}
\varepsilon' &= \varepsilon'_1 + a' w_2 \\
\varepsilon'' &= \varepsilon''_1 + a'' w_2 \\
\varepsilon_0 &= \varepsilon_{10} + a_0 w_2 \\
\varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty w_2
\end{align*}
\]

(3.47)

where subscript 1 refers to the pure solvent, 0 refers to zero frequency measurements (static permittivity) and $\infty$ the high frequency limiting permittivity measurements (optical permittivity) $w_2$ is the concentration of the solute. The procedure has been justified by the fact that by plotting the permittivity and dielectric loss of solutions in a complex plane, semicircles are obtained with the sizes varying according to the concentrations of the solute, but has exactly the same shape as that obtained by $a'$ and $a''$ plot. Higasi[19] has justified the use of above equations and has shown that for representation of dielectric data
of dilute solutions $a'$ and $a''$ can be used for $\varepsilon'$ and $\varepsilon''$. Although the representation of data through the parameters $a'$ and $a''$ have been widely done[20-24] but it is also possible to analyse the data in terms of permittivity and loss even in the case of polar solutes in non polar solvents[25-30]. This has been possible mainly due to availability of a large number of high frequency points and increased accuracy of measurements.

3.4 DETERMINATION OF VARIOUS PARAMETERS FROM EXPERIMENTAL DATA

(a) DETERMINATION OF RELAXATION TIME AND DISTRIBUTION PARAMETER IN PURE LIQUIDS

From Debye arc plot

A simple method for determination of relaxation time for a system following Debye relation has been given by Cole[31]. From equation (3.12) writing $\omega \tau = x$ and multiplying this equation with $(1 + jx)$ the following relations are obtained

$$(\varepsilon' - j\varepsilon'')(1 + jx) = \varepsilon_\infty (1 + jx) + (\varepsilon_0 - \varepsilon_\infty)$$

or

$$(\varepsilon' + x\varepsilon'') + j (\varepsilon' x - \varepsilon'') = \varepsilon_0 + j\varepsilon_\infty x$$
Separating real and imaginary parts

\[ \epsilon' + \epsilon'' x = \epsilon_0 \quad \text{and} \quad \epsilon' x - \epsilon'' = \epsilon_\infty x. \]

i.e. \[ \epsilon' = \epsilon_0 - (\omega \epsilon'') \tau \] (3.48a)
and \[ \epsilon' = \epsilon_\infty + (\epsilon'' / \omega) / \tau \] (3.48b)

These equations are quite convenient for determination of \( \tau \), \( \epsilon_0 \) and \( \epsilon_\infty \), if system obeys Debye type behaviour.

**From Cole-Cole Arc Plot**

A system obeying the Cole-Cole type behaviour satisfies the equation (3.15) which is an equation of circle with centre at \[ \left( \frac{\epsilon_0 + \epsilon_\infty}{2}, -\frac{1}{2} \right) \left( \epsilon_0 - \epsilon_\infty \right) \tan \left( \alpha \pi / 2 \right) \] and the radius \[ \frac{1}{2} \left( \epsilon_0 - \epsilon_\infty \right) \sec \left( \alpha \pi / 2 \right). \] The relaxation time is calculated from the equation

\[ v/u = (\omega \tau)^{1-\alpha} \] (3.49)

where \( v \) is the distance on Cole-Cole plot between the experimental point and the point \( \epsilon_0 \) and \( u \) is the distance between same experimental point and the point \( \epsilon_\infty \), and \( \alpha \pi / 2 \) is the angle which the line joining the centre of the above circle (Cole-Cole plot) to the \( \epsilon_\infty \) point makes with the \( \epsilon' \) axis (see Fig. 3.3). Another method of
determining \( \alpha \) and \( \tau \) is obtained by taking logarithm of equation (3.49).

\[
\log(v/u) = (1 - \alpha) \log \omega + (1 - \alpha) \log \tau \\
= (1 - \alpha) \log \lambda_m - (1 - \alpha) \log \lambda
\]  

(3.50a)  

(3.50b)

where \( \omega \) is the angular frequency and is equal to \( 2\pi c/\lambda \) and \( \lambda_m \) is the critical wavelength related to the relaxation time by the equation \( \tau = \lambda_m/2\pi c \), where \( c \) is phase velocity of the e.m. wave. Values of \( \log(v/u) \) calculated from experimental points when plotted against \( \log \lambda \) give a straight line of slope \( (\alpha - 1) \) and intercept \( (1 - \alpha) \log \lambda_m \).

From the slope and the intercept, values of \( \tau \) and \( \alpha \) are determined.

From Davidson-Cole Arc

Equation (3.26) can be rewritten,

\[
\varepsilon' - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty) \cos^\beta \varphi \cos \beta \varphi ,
\]

and \( \varepsilon'' = (\varepsilon_0 - \varepsilon_\infty) \cos^\beta \varphi \sin \beta \varphi \)

where \( \tan \varphi = \omega \tau \)

and \( \tan \beta \varphi = \varepsilon''/(\varepsilon' - \varepsilon_\infty) \)
Therefore,

\[
\tau = \frac{1}{\omega} \tan \left[ \frac{1}{\beta} \tan^{-1} \frac{\varepsilon''}{(\varepsilon' - \varepsilon_\infty)} \right] \quad (3.51)
\]

An approximate value of \( \beta \) is obtained from the skewed arc as the high frequency side of the plot approaches asymptotically a line making an angle \((\beta \pi/2)\) with the real axis of \( \varepsilon' \). A better value of \( \beta \) is obtained by first plotting the theoretical Davidson Cole skewed arc curve for different values of \( \beta \) and then finding which of these curves find a better fit with the observed values, giving thereby the correct value of \( \beta \). Theoretical curve can be easily plotted with the help of equations \((3.26a, \text{ and } 3.26b)\) by taking one of the different values of \( \beta \) and varying the angle \( \varphi \) arbitrarily from \( 0^\circ \) to \( 90^\circ \). Once the value of \( \beta \) is known the relaxation time is easily calculated from equation \((3.51)\).

The above mentioned methods can be applied to the solution studies for determination of relaxation time and distribution parameter by replacing \( \varepsilon' \)'s with \( a' \)'s in all the above formulae. It should be noted that relaxation times so obtained are macroscopic relaxation times.

In view of the limited knowledge available
about the structure of liquids attempts have also been made to calculate the relaxation time and other parameters empirically. Syamalamba and Premaswarup[32] have given two empirical equations to calculate the relaxation times in polar aliphatic and aromatic liquids by applying an empirical internal field correction factor to the Debye equation.

(b) DETERMINATION OF VARIOUS PARAMETERS IN SOLUTIONS OF POLAR SOLUTES IN NON-POLAR SOLVENTS.

The relaxation time and the dipole moment of dilute solutions of polar solute in non-polar solvents can be determined by Gopala Krishna[33] method. The method requires the measurement of permittivity and loss at varying concentrations at a single microwave frequency. The complex permittivity for dilute solutions of polar substance in non-polar solvent as a function of frequency can be written as

\[
\frac{\varepsilon^* - 1}{\varepsilon^* + 2} = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{4\pi N_o \mu^2}{9kT} \cdot \frac{1}{1 + j\omega \tau} \tag{3.52}
\]

with \( N_o \) as number of molecules per unit volume.

By separating the real and imaginary parts after
putting $\varepsilon^* = \varepsilon' - j\varepsilon''$ following equations are obtained

$$\frac{\varepsilon' + \varepsilon'^2 + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} = \frac{\varepsilon^{\infty} - 1}{\varepsilon^{\infty} + 2} + \frac{4\pi N_o \mu^2}{9kT} \frac{1}{1 + \omega \tau^2}$$

$$= X \text{ (say)} \quad (3.53a)$$

and

$$\frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} = \frac{4\pi N_o \mu^2}{9kT} \cdot \frac{\omega \tau}{1 + \omega \tau^2} = Y \text{ (say)} \quad (3.53b)$$

Writing $P = \frac{\varepsilon^{\infty} - 1}{\varepsilon^{\infty} + 2} \quad (3.54)$

equation (3.53) gives

$$X = P + \left[ \frac{1}{\omega \tau} \right] Y \quad (3.55)$$

In low concentration limit $P$ may be regarded as a constant. A plot of $X$ vs $Y$ will now be straight line of slope equal to $(1/\omega \tau)$ from which $\tau$ can be determined. Equation (3.53a) can also be written as

$$X = P + K \cdot w_2 \cdot d_{12} \quad (3.56)$$

where

$$K = \frac{4\pi N \mu^2}{9kTM} \frac{1}{1 + \omega \tau^2} \quad (3.57)$$
Since \( N_0 = \frac{Nd_{12}w_2}{M} \) where \( N \) is Avogadro number and \( M \) is the molecular weight of the solute. Also \( w_2 \) is the weight fraction of the solute and \( d_{12} \) the density of the solutions. At low concentrations, \( d_{12} \) may be taken as linear with \( w_2 \) and may be taken as \( d_{12} = d_o (1 + \alpha w_2) \), where \( d_o \) is the density of the solvent. From a graph between \( x \) and \( w_2 \), the slope \( (dx/dw_2) \) at \( w_2 \) equal to zero is found which is equal to \( Kd_o \) and from this dipole moment \( (\mu) \) is evaluated.

Higasi[19] gave a set of formulae for evaluation of distribution parameter and relaxation time from the solutions data. The slopes \( a', a'', a_o \) and \( a_\infty \) are first determined as usual and then \( \alpha \) and \( \tau \) are derived from the following equations.

\[
\alpha = 1 - (2/\pi) \tan^{-1} (A/B) \quad (3.58)
\]

and

\[
\tau = (1/\omega) \left[ \frac{A^2 + B^2}{C^2} \right] \frac{1}{2(1 - \alpha)} \quad (3.59)
\]

where

\[
A = a'' (a_o - a_\infty)
\]

\[
B = (a_o - a') (a' - a_\infty) - a''^2 \quad (3.60)
\]

\[
C = (a' - a_\infty)^2 + a''^2
\]
and \( \omega \) is the angular frequency of the measurement. Although the Higasi's equations are derived by assuming a Cole-Cole type symmetrical distribution and equations (3.58) and (3.49) can be shown to be identicals, yet it offers a method to determine distribution parameter from a single microwave frequency data without actually plotting the Cole-Cole arc.

Values of dipole moment calculated from microwave data using Gopala Krishna method is found to be less reliable than those obtained from data of static frequency measurements. We have used following equation due to Guggenheim [cf. Trans Faraday Soc.45, 714 (1949)] to calculate dipole moment of solute in non polar solvents. In this method density of solutions at each concentration is not required but only refractive index values are needed and they are more easily determinable than the density. The square of the dipole moment \( (\mu) \) is given by

\[
\mu^2 = \frac{9 \, kT}{4 \, \pi N} \cdot \frac{3}{(\epsilon_{10} + 2) \, (n_1^2 + 2)} \cdot \left( \frac{\Delta}{C} \right)_o \quad (3.61)
\]

with \( \Delta = (\epsilon_o - n^2) - (\epsilon_{10} - n_{10}^2) \), and

where \( \epsilon_o \) and \( n \) are the static permittivity and
refractive index of the solutions, ε_10 and n_1 are static permittivity and refractive index of pure solvents, C is the concentration of the polar solute in moles/cc, and \( \left( \frac{\Delta}{\varepsilon} \right)_0 \) is the slope of the straight line where  \( \Delta \) is plotted against concentration C at C = 0.

(c) DETERMINATION OF TWO RELAXATION TIMES FROM EXPERIMENTAL DATA

In most of the discussions dielectric theories it is assumed that the molecules may be treated as rigid rotators, an assumption which is certainly not true for many molecules, which frequently contain groups capable of rotation about bonds within the molecule. Such molecules are said to show intramolecular as well as intermolecular rotation. Orientation polarization in a material made up of molecules of this kind can occur in two ways, by rotation of the group within the molecule and by the rotation of molecule as a whole. The latter process is expected to be dependent on the viscosity of the medium in a similar way to that for a rigid molecule, while the former, since it causes little or no disturbance of the surroundings will be fairly insensitive to the nature of
the medium. The relative lengths of the relaxation times associated with the two processes will vary from material to material, the relaxation time for the intramolecular process being dependent on the magnitude of the potential barriers the rotating dipole must overcome.

Bergmann, Roberti and Smyth[34] have proposed a method for determination of two relaxation times present for a system obeying Budo's equations (3.45a and b). A graphical method is used to select the values of $\tau_1$, $\tau_2$, $C_2$ and $\varepsilon_\infty$ in equation (3.45) which gives best fit to the experimental data. Fong and Smyth[35] gave another method called "double arc method" which can be used to analyse the data for two overlapping regions of dielectric dispersion. Perhaps the best way to obtain the values of $\tau_1$, $\tau_2$, $C_1$ and $\varepsilon_\infty$ is to fit the values of $\varepsilon'$ and $\varepsilon''$ on a computer[36,37]. However, we have used another graphical method, similar to that of Bhattacharya et al[38], for evaluation of two relaxation times $\tau_1$ and $\tau_2$. Writing $\omega \tau_1 = X_1$ and $\omega \tau_2 = X_2$ in equations (3.45a and b) we have

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1}{1 + X_1^2} + \frac{C_2}{1 + X_2^2} = a \quad \text{(say)} \quad (3.61a)$$
and

\[ \varepsilon' = \frac{C_1 \varepsilon_1}{1 + x_1^2} + \frac{C_2 \varepsilon_2}{1 + x_2^2} = (b) \text{ (say)} \quad (3.61b) \]

so \( a x_1 - b = C_2(x_1 - x_2)/(1 + x_2^2) \) \quad (3.62)

i.e. \( C_2 = \frac{(ax_1 - b)(1 + x_2^2)}{x_1 - x_2} \) \quad (3.63)

similarly

\[ C_1 = \frac{(b - ax_2)(1 + x_1^2)}{x_1 - x_2} \quad (3.64) \]

so \( C_1 + C_2 = 1 = \frac{(b - ax_2)(1 + x_1^2)}{x_1 - x_2} + \frac{(ax_1 - b)(1 + x_2^2)}{x_1 - x_2} \)

hence \( l = a - ax_1x_2 + b(x_1 + x_2) \) \quad (3.65)

or

\[ \frac{l - a}{b} = (x_1 + x_2) - \frac{a}{b} (x_1x_2) \quad (3.66) \]

or

\[ \frac{l - a}{b \omega} = (\tau_1 + \tau_2) - \frac{a \omega}{b} \tau_1 \tau_2 \quad (3.67) \]

so the values of \((l - a)/b \omega\) and \(a \omega/b\) obtained from the experimental values of \(\varepsilon', \varepsilon''\) etc., when
plotted as ordinate and abscissa respectively a straight line should be obtained with slope as \( \tau_1 \tau_2 \) and intercept as \( \tau_1 + \tau_2 \). From these slopes values of \( \tau_1 \) and \( \tau_2 \) can be determined. \( C_1 \) and \( C_2 \) can then be determined from equations (3.63) and (3.64).

In some cases, however, the estimate of two relaxation times can also be had from equations (3.48a) and (3.48b). It can be seen that for one relaxation process, \( \varepsilon' \) vs \( \varepsilon''/\lambda \) curve is a straight line with the slope equal to \( (2\pi c \tau) \). When the system contains two relaxation processes \( \varepsilon' \) vs \( \varepsilon''/\lambda \) curve is a resultant of two straight lines. If the two straight lines may be resolved, one can then determine the two relaxation times from the slopes of the straight lines.

A graphical method to evaluate \( \tau_1 \) and \( \tau_2 \) using Fröhlich distribution function have been proposed by Mansingh and Kumar[39], but the method is very sensitive to the accuracy of the measurements. Higasi[40] has also given a method to evaluate two limiting relaxation times for a system obeying Fröhlich type distribution function.

Higasi[40] has examined the situation for finite range by taking the following functional
\[ f(t) = \frac{1}{A\tau} \quad \tau_1 \leq \tau \leq \tau_2 \quad (3.69) \]

\[ = 0 \quad 0 < \tau < \tau_1, \quad \tau_2 < \tau < \infty \]

where \( A \) is a parameter associated with the distribution of relaxation time, Higasi et al[40] have shown that for \( A < 4 \), the semi ellipse of Fröhlich function is comparable with the Cole-Cole arc of the same system. For the Cole-Cole arc there is a relation[2]

\[ \tan \frac{\pi}{4} (1 - \alpha) = \frac{2 \varepsilon'_{\text{max}}}{\varepsilon_0 - \varepsilon_\infty} = \frac{a}{b} \quad (3.70a) \]

For the semi ellipse there is a relation[40c] between the ratio of the axis, \((a/b)\), and the parameter \( A \).

\[ \frac{a}{b} = \frac{2 \varepsilon''_{\text{max}}}{\varepsilon_0 - \varepsilon_\infty} = \frac{2}{A} \tan^{-1} \sinh \left( \frac{A}{2} \right) \quad (3.70b) \]

Comparision of eqns (3.70a) and (3.70b) gives

\[ \alpha = 1 - \frac{4}{\pi} \tan^{-1} \left[ \left( \frac{2}{A} \right) \tan^{-1} \sinh \left( \frac{A}{2} \right) \right] \quad 0 < \alpha < 1 \quad (2.70c) \]
It is found that

\[ \tau_0 = (\tau_1 \tau_2)^{\frac{1}{2}} = \frac{1}{\omega_{\text{max}}} = \tau_1 \exp \left( -\frac{A}{2} \right) = \tau_2 \exp \left( -\frac{A}{2} \right). \]  

(3.70d)

The limiting values of \( \tau \) can thus be expressed in terms of \( \tau_0 \) and \( A \), the latter being dependent upon \( \alpha \). The equations are

\[ \tau_1 = \tau_0 \exp \left( -\frac{A}{2} \right) \]  

(3.70e)

\[ \tau_2 = \tau_0 \exp \left( \frac{A}{2} \right) \]  

(3.70f)

\( \tau_1 \) and \( \tau_2 \) are very sensitive to the selection of the value of \( A \). For \( \alpha < 1 \) and \( A < 4 \), a good correlation is found

\[ A^2 = 37.6 \alpha \]

The transformation described by equations \((3.70e), 3.70(f)\) is permissible only in the range of \( 1 > \frac{\alpha}{D} > 0.6 \), i.e. \( \alpha < 0.30 \).

Higasi[40] has also given the curve between \( e^{A/2} \) vs. \( \alpha \) which is reproduced in Fig. (3.6). From this curve \( e^{A/2} \) can be determined from the known value of \( \alpha \) and thereby \( \tau_1 \) and \( \tau_2 \).
Sufficient experimental data are available [41-46] showing the existence of multiple relaxation processes. The locus of $\varepsilon^*$ in some cases may be interpreted as the overlapping of several relaxation processes which could arise from the reorientation of different polar groups in the molecules. Such a curve can be represented by superposition of a number of Debye type relaxation processes with the help of following equation

$$\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \sum_{i=1}^{n} \frac{C_i}{1 + \omega^2 \tau_i^2}$$ \hspace{1cm} (3.71a)$$

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_{\infty}} = \sum_{i=1}^{n} \frac{C_i \omega \tau_i}{1 + \omega^2 \tau_i^2}$$ \hspace{1cm} (3.71b)$$

Dannhauser[47] has given a method for analysis of multiple relaxation data assuming it to be the superposition of arbitrary number of dispersion curves with a restriction that lowest frequency dispersion must obey Debye equation and that its amplitude and relaxation time must be appreciably greater than that of the next dispersion. Dannhauser has been able to show that skewed arc dispersion may be resolved, with usual experimental errors, into closely overlapping Debye dispersions.
For dilute solutions of polar solute in non-polar solvents, Higasi[48] has discussed the use of equation of type (3.45a) and (3.45b) and has shown that it is possible to have approximate values of two relaxation times present in the system from the properly selected single microwave measurements.

Higasi[40] and Smyth et al[49] gave a more general form

\[ f(\tau) = \frac{1}{At^n} \quad 0 < n < \infty \quad (3.72) \]

The reduced dielectric permittivity and losses are given by

\[ \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \frac{f(\tau) \, d\tau}{1 + \omega^2 \tau^2} \quad (3.73) \]

\[ \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \frac{f(\tau) \, d\tau}{1 + \omega^2 \tau^2} \quad (3.74) \]

For \( n < 1 \), equation (3.72) gives right skewed arc

For \( n > 1 \), equation (3.72) gives left skewed arc.

As the ratio \( \tau_2 / \tau_1 \) increases, the distribution for a given \( n \) increases and the skew becomes greater. Thus both the \( n \) value and the ratio
determine the amount of skew. For $n=0$, a superposition of a large number of a Debye peaks of equal heights which are spaced at equal intervals of freqs or relaxation time are obtained. For $n=1$, we can consider two different ways. Firstly one assumes that the Debye absorption peaks are equally spaced as above but the weights are different. Secondly one may consider that they have equal weights but they are spaced at equal intervals in logarithmic scale of freqs. A distribution similar to right skewed arc may be represented by Cole-Davidson function[3].

(d) DETERMINATION OF THERMODYNAMIC PARAMETERS

Treating the dipole orientation as rate process Eyring[50] gave an equation of the frequency 'K' the dipole jumps over the free energy barrier $\Delta G$ as

$$K = \frac{kT}{h} \exp\left(-\frac{\Delta G}{RT}\right) \quad (3.75)$$

Since relaxation time ($\tau$) is reciprocal of the constant $K$, we have

$$\tau = \frac{h}{kT} \cdot \exp\left(\frac{\Delta G}{RT}\right) \quad (3.76)$$

Since

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = \Delta H - T \Delta S \quad (3.77)$$
\[ \tau = \frac{h}{kT} \exp \left( \frac{\Delta H_\varepsilon}{RT} - \frac{\Delta S_\varepsilon}{R} \right) \quad (3.78) \]

where \( \Delta G_\varepsilon \), \( \Delta H_\varepsilon \), and \( \Delta S_\varepsilon \) are most probable free energy, enthalpy and entropy of activation for dielectric relaxation process. Taking logarithm of equation (3.78) we have

\[ 2.303 \log (\tau T) = 2.303 \log \frac{h}{k} - \frac{\Delta S_\varepsilon}{R} + \frac{\Delta H_\varepsilon}{RT} \quad (3.79) \]

A plot of \( \log (\tau T) \) against \( 1/T \) is a straight line of the slope equal to \( \Delta H_\varepsilon /R \) from which \( \Delta H_\varepsilon \) can be calculated and is given as

\[ \Delta H_\varepsilon = 2.303 R \cdot \frac{d(\log \tau T)}{d(1/T)} \quad (3.80) \]

Taking logarithm of equation (3.76)

\[ \ln \tau = \ln \frac{h}{k} - \ln T + \frac{\Delta G_\varepsilon}{RT} \]

or \( \Delta G_\varepsilon = RT \ln \tau - RT \ln(h/kT) \)

or \( \Delta G_\varepsilon = 2.303 \ RT \log \left( \frac{kT \tau}{h} \right) \quad (3.81) \)

Knowing \( T \) and \( \tau \), \( \Delta G_\varepsilon \) is calculated from the above equation. Moreover, since \( \Delta H_\varepsilon \) and \( \Delta G_\varepsilon \) are related by equation (3.77), \( S_\varepsilon \) can also be obtained if \( \Delta H_\varepsilon \) and \( \Delta G_\varepsilon \) are known.
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