CHAPTER - II

THEORETICAL
In liquids the coefficient of ultrasonic absorption $\alpha$, measured per unit length of path, varies as the square of frequency $f$ of the ultrasonic beam. This has been shown theoretically by Stokes$^1$ and Kirchhoff$^2$, on the assumption that the absorption is caused due to viscosity and thermal conductivity of the medium. But in most of the cases the actually observed magnitude of $\alpha/f^2$ is many times larger than that due to these two causes (i.e. the classical causes). Such excess absorption is attributed to relaxation processes of structural or thermal origin.

Structural relaxation is found in a class of liquids like water and alcohols which are highly associative in character. Here the observed absorption is upto 3 times the calculated classical absorption and their ratio i.e. $\frac{\alpha_{\text{obs}}}{\alpha_{\text{class}}}$ remains remarkably constant over a wide range of temperature. To explain this it is assumed that these liquids have a relatively close bound structure which is disturbed by the passage of ultrasonic waves. It takes a comparatively long time to reestablish the equilibrium and this gives rise to absorption. The theoretical analysis based on this idea has been developed for the first time by Hall$^{10}$ (1948).
The second type of relaxation i.e. thermal relaxation, is observed in simple, unassociated polyatomic liquids like CS₂, C₆H₆ etc. Here the excess absorption is many times larger than that due to the classical causes and mostly this value increases with temperature. The effect is analogous to that observed in polyatomic gases. The excess absorption, here, is attributed to a time lag that occurs in the sharing of energy between the internal and external degrees of freedom of molecules. The time constant involved in the process is known as relaxation time. The theoretical treatment of the process has been developed by Herzfeld and Rice⁴(1928), Bourgin⁵,⁷(1929-36), Kneser⁶(1931-38) and others. An important consequence of the theory is that the absorption per wavelength i.e. \( \alpha \) (\( \alpha \) being the ultrasonic absorption coefficient and \( \lambda \), the wavelength), should increase to a maximum value at a frequency \( f_m \) related to the relaxation time \( \tau \) by the relation \( \tau = \frac{1}{2 \pi f_m \nu} \). The theory also predicts a change in velocity in the same range of frequencies.

On the basis of such relaxation theory developed by Kneser⁶(1938), Pinkerton¹⁹(1949) attempted to explain theoretically the observed variation of absorption¹⁶-¹⁸ in a mixture of two non-associated liquids. Almost at the same time Bauer²⁰(1949), too, considered the problem from a different approach and gave a theory which was more general than that of
Pinkerton. As the present piece of work is aimed at studying some binary mixtures of non-associated liquids, it becomes essential to consider these theories of binary mixtures and their subsequent modifications and developments by Sette (1950) and others (1971-74).

Pinkerton's theory:

Pinkerton explained the observed variation of $\frac{\alpha}{f^2}$ with concentration in a binary mixture of non-associated liquids taking into account Kneser's ideas regarding the relaxation processes occurring in these liquids. Kneser showed that if a single relaxation process gives rise to absorption in a medium, the expected variation of $\alpha$ with $f$ would be of the form

$$\frac{\alpha}{f^2} = \frac{A}{1 + \left(\frac{\varepsilon}{f_m}\right)^2} \ldots (2.1)$$

where $A$ is very nearly a constant and $f_m = 1/2\pi \tau$, is the relaxation frequency of the liquid. Eq. (2.1) shows that so long as $f \ll f_m$, $\alpha/f^2$ would be constant for a liquid. If $\varepsilon$ is the absorption per wave length in the liquid then
\[ \mu = \alpha \lambda = \left( \frac{\alpha}{f^2} \right) f^2 \lambda \]
\[ = \frac{\alpha v f}{\left\{ 1 + \left( \frac{f}{f_m} \right)^2 \right\}} \]
\[ = \frac{B (f/f_m)}{\left\{ 1 + \left( \frac{f}{f_m} \right)^2 \right\}} \] ...(2.2)

where \( B = \frac{\alpha v f_m}{2} \) - a new constant.

and \( v \) = the ultrasonic velocity in the medium.

From (2.2), at \( f = f_m \), \( \mu \) attains a maximum value \( \mu_{\text{max}} \) which is given by

\[ \mu_{\text{max}} = \frac{\alpha v f_m}{2} \] ...(2.3)

Since \( A \) and \( v \) can be known from experiment, an estimate of \( \mu_{\text{max}} \) gives a value of \( f_m \) for the liquid from eq. (2.3). It is possible to make a guess for \( \mu_{\text{max}} \) in a liquid from the value \( \mu_{\text{max}} \) obtained in gases if the absorption in the liquid is due to the slowness of exchanges of energy between the degrees of freedom.

\( \mu_{\text{max}} \) in gases is obtained from the relation

\[ \mu_{\text{max}} = \frac{1}{2} \pi \left( \sqrt{\gamma} - 1 \right) C_i/C_p \]

where \( \gamma = C_p/C_v \), \( C_p \) is the specific heat at constant pressure, \( C_v \) is the specific heat at constant volume and \( C_i \), the fraction of \( C_v \) relating to internal degrees of freedom. As pointed out by Herzfeld\(^4\), these specific
heats do not change by large factors in passing from gases to liquids, so that one may put

\[ (r'_{\text{max}})_{\text{gas}} \sim (r'_{\text{max}})_{\text{liquid}} \]

Using the specific heat data for several gases it has been found that \(2 \beta_{\text{max}}\) lies between 0.2 and 0.3 for several gases. In other cases it can be calculated from specific heats of the individual degrees of freedom obtained from spectroscopic data. Then one may approximately put that for all liquids,

\[ 2 \beta_{\text{max}} \sim 0.25 \quad \ldots(2.4) \]

Using eqs. (2.3) and (2.4) one gets

\[ \text{Avf}_m = 1/4 \]

or

\[ f_m = 1/(4 \text{Av}) \quad \ldots(2.5) \]

Here \( A \) is the constant value of \( \alpha/f^2 \) found experimentally for liquids at low frequencies. Thus one may calculate \( f_m \) from eq. (2.5).
Moreover, since

\[ \mu_{\text{max}} = \frac{A_v f_m}{2} \]

\[ A = 2 \mu_{\text{max}} / (v_f m) \]

and from eq. (2.1)

\[ \alpha / f^2 = \frac{2 \mu_{\text{max}}}{v_f m \left\{ 1 + (f/f_m)^2 \right\}} \]

or

\[ \lim_{f \to 0} \frac{\alpha}{f^2} = \frac{2 \mu_{\text{max}}}{v_f m} \quad \ldots (2.6) \]

The theory implies that the wide variation of \( \alpha / f^2 \) in liquids must be largely due to variation of \( f_m \), since \( \mu_{\text{max}} \) has been assumed to be nearly the same in all liquids and change in \( v \) with frequency is almost negligible. The relation (2.6) further shows that highly absorbing liquids must have small values of \( f_m \) which implies that they do not readily share their vibrational energy. This is what expected for liquids having small spherically symmetric molecules with no dipole moment.

In liquids, the frequency of molecular collision is of the order of \( 10^{12} \) per sec at room temperature, and an estimate of the relaxation frequency values for different liquids (from eq. 2.5) shows that
500 to 30000 collisions are required in them before external and internal energies come to equilibrium after an abrupt change in external conditions. It has been observed that in gases, for which life times of excited states are very long, \( f_m \) and, therefore, the absorption coefficient \( \alpha' \) are most sensitive to traces of impurities although \( \mu_{\text{max}} \) is not greatly affected. It is suggested that the impurity here acts as a catalyst in transfers of internal energy. Pinkerton\(^{19}\) has assumed that the same process may very well occur in mixtures of two liquids.

With certain assumptions, the relaxation mechanism is used to calculate approximately the variation of absorption with concentration in a binary mixture of two non-associated liquids. In such a mixture of liquids A and B, the equilibrium between energies associated with external and internal degrees of freedom is set up by collisions. Let there be four relaxation times, \( \tau_{AA}, \tau_{BB}, \tau_{AB} \) and \( \tau_{BA} \), involved in the processes. \( \tau_{AA} \) and \( \tau_{BB} \) are the relaxation times for collisions between similar molecules of type A and B respectively. Similarly \( \tau_{AB} \) is taken as the relaxation time for a collision of an excited A molecule with a de-excited B molecule and \( \tau_{BA} \) as
that for collision of an excited B molecule with a de-excited A molecule. Taking A as a highly absorbing liquid and B a low absorbing one, it is assumed that

\[ \tau_{AA} \gg \tau_{BB} \]

\[ \tau_{AB} \approx \tau_{BA} \approx \tau_{BB} \]

...(2.7)

The reason for this assumption is that if molecules of type B possess a stronger mutual interaction, then the interaction between A and B molecules may be of the same order as between molecules of B. Moreover, interactions of the type AB, BA and BB may be much greater than AA interactions.

It is further assumed that the molecules of A and B are of the same size i.e. their molecular diameters are of the same order.

Let the fractions of molecules of types A and B in the mixture be 'a' and 'b' respectively so that, \( a + b = 1 \). Then in a unit time a fraction 'a' of 'A' molecules will come into collision with these similar molecules so that this will correspond to a relaxation time \( \tau_{AA} \). The remaining fraction of
the interacting molecules of 'A' will come into collision with molecules of 'B' and it will correspond to a relaxation time \( \tau_{AB} \) or \( \tau_{BB} \) (\( \therefore \tau_{AB} \approx \tau_{BB} \)).

During a large interval of time \( \Delta t \), the number of molecules of 'A' having the occasion to undergo relaxation, will be proportional to

\[
\frac{\Delta t \cdot a}{\tau_{AA}} + \frac{\Delta t \cdot b}{\tau_{BB}} = \frac{\Delta t}{\tau_{A_{\text{eff}}}} \quad \ldots(2.8)
\]

where \( \tau_{A_{\text{eff}}} \) is the effective relaxation time for molecules of type 'A'. On simplification

\[
\tau_{A_{\text{eff}}} = \frac{\tau_{\text{AA}} \cdot \tau_{BB}}{a \cdot \tau_{BB} + b \cdot \tau_{\text{AA}}} = \frac{\tau_{\text{AA}}}{a + b \cdot (\tau_{\text{AA}} / \tau_{BB})} \quad \ldots(2.9)
\]

By assumption, since \( f_{\text{max}} \) is of the same order for all liquids, then from eq. (2.6) at low frequencies

\[
\frac{\alpha_A}{\alpha_B} = \frac{v_B f_m^B}{v_A f_m^A} = \frac{v_B}{v_A} \cdot \frac{\tau_{\text{AA}}}{\tau_{BB}} \quad \ldots(2.10)
\]
where $v_A$ and $v_B$ are ultrasonic velocities in $A$ and $B$ liquids respectively. Taking the example of Benzene-Toluene mixture it was assumed by Pinkerton\(^{(19)}\) that $v_A \approx v_B$ (which, of course, is not a valid assumption for other binary mixtures). Then from eq. (2.10)

\[
\frac{\alpha_A}{\alpha_B} = \frac{\tau_{AA}}{\tau_{BB}} = \frac{1}{y} \quad \text{(say)} \quad \ldots (2.11)
\]

or

\[
\tau_A^{\text{eff}} = \frac{\tau_{AA}}{a + b} \cdot \frac{\tau_{AA}}{\tau_{BB}} = \frac{\tau_{AA}}{a + b/y} \quad \ldots (2.12)
\]

In the mixture the total absorption must be made up of the absorption of molecules of each separate liquid so that from eq. (2.6)

\[
\frac{\alpha(a)}{f^2} = \frac{2 \mu_{\text{max}}}{v} \left( \frac{1}{f^2_m} + \frac{1}{f^2_B} \right)
\]

\[
= \frac{2 \mu_{\text{max}}}{v} \left\{ 2 \pi \tau_A^{\text{eff}} \cdot a + 2 \pi \tau_{BB} \cdot b \right\}
\]

\[
= \frac{4 \pi \mu_{\text{max}}}{v} \left\{ \tau_A^{\text{eff}} \cdot a + \tau_{BB} \cdot b \right\} \quad \ldots (2.13)
\]

where $\alpha(a)$ corresponds to the absorption coefficient of the mixture with mole fraction 'a' of liquid $A$. 
Now putting the value of $\frac{\tau}{\text{eff}_{\text{eff}}}$ from eq. (2.12) in eq. (2.13) and simplifying

\[
\frac{\alpha(a)}{f^2} = \frac{4\pi \kappa_{\text{max}} \tau_{AA} y}{v} \left[ \frac{a}{ay + b} + b \right]
\]

...(2.14)

At $b = 0$, $\alpha(a) = \alpha_A$ and at $b = 1$, $\alpha(a) = \alpha_B$, so that from eq. (2.14)

\[
\frac{\alpha_A}{f^2} = \frac{4\pi \kappa_{\text{max}} \tau_{AA}}{v}
\]

...(2.15)

and therefore,

\[
\frac{\alpha(a)}{f^2} = \frac{\alpha_A}{f^2} \cdot y \left[ \frac{a}{ay + b} + b \right]
\]

...(2.16)

Expression (2.16) gives the proportional variation in absorption in the mixture in terms of the ratio $\frac{1}{y}$ of the absorption coefficients of the pure liquids and the molecular proportions 'a' and 'b'. Pinkerton showed that this theory i.e. formula (2.16) could explain the experimental results of absorption in Benzene-Toluene mixture. In Chapter IV we shall examine the applicability of the theory in the study of some binary mixtures of liquids.
2. Bauer's theory:

In the same year 1949, when Pinkerton's theory for binary mixtures of nonassociated liquids was published, Bauer\textsuperscript{20} gave a general theory for ultrasonic absorption in such liquids and extended it to the binary mixtures. He developed his theory from a thermodynamical analysis of the problem.

According to Bauer\textsuperscript{20} the absorption of ultrasonic waves in a nonassociated liquid arises because the passage of such waves disturbs the statistical equilibrium of the vibrational levels so that the effective vibrational specific heat depends on time. As such, a perturbation method is used and the velocity of sound is considered to be under conditions of perturbed equilibrium. To isolate the perturbation in the expression for velocity, the plane sound waves are represented by a complex exponential. As the perturbation depends on time, time-derivatives appear in the calculation. These are imaginary numbers and therefore, the absorption depends essentially on the imaginary part of the expression for the velocity of sound.
The complex velocity, $\Gamma$ of a plane harmonic wave is expressed by

$$\Gamma^2 = \left( \frac{\partial p}{\partial \rho} \right)_{\text{adiabatic}} \ldots (2.17)$$

where $p$ and $\rho$ are the pressure and the density of the fluid respectively. When the wave propagates in the $x$ direction, the wave motion is represented by

$$y = e^{i2\pi f(t - x/v)} \quad y = e^{i2\pi f(t - x/v) - \alpha x} \quad e \ldots (2.18)$$

so that

$$\alpha = - \pi v f \cdot J\left( \frac{1}{\rho^2} \right) \ldots (2.19)$$

where $i = \sqrt{-1}$, $\alpha$ is the ultrasonic absorption coefficient, $f$ is the frequency, $v$ is the measured velocity of sound which is equal to the real part of $\Gamma$ and $J(z)$ denotes the imaginary part of $z$ which is equal to $\Gamma^{-2}$. 
For an adiabatic change, the first law of thermodynamics is written in terms of internal energy $E$ and enthalpy $H$ as

$$\delta E + p \delta V = 0$$

$$\delta H - V \delta p = 0$$

where $V$ stands for the volume of the system and, $E$ and $H$ are written as

$$E = E' + \sum_j W_j a_j$$

$$H = H' + \sum_j W_j a_j$$

In eq. (2.21), $a_j$ is the fraction of molecules in the $j$th excited level of energy $W_j$ and primes refer to quantities excluding the contributions of the excited levels. All extensive quantities ($E$, $H$, $W_j$, $V$) are referred to one gram molecule as unit.

The change in temperature produced at any point in the liquid by the acoustic wave is taken as the
independent variable. Then from eqs. (2.17) and (2.20) one has

\[ \eta^2 = \frac{\rho}{\beta_T} \frac{(\partial H/\partial T)_s}{(\partial E/\partial T)_s} \quad \ldots \ (2.22) \]

Using standard thermodynamic relations this gives

\[ \eta^2 = \frac{\rho}{\beta_T} \frac{C_p/1T}{C_p \beta_T/1T} \quad \ldots \ (2.23) \]

where \( \rho \) is the coefficient of thermal expansion, \( \beta_T \) the isothermal compressibility, \( T \), the absolute temperature and \( C_p \) and \( C_v \), the principal specific heats.

It is assumed that the entropy of the whole assembly i.e. \( S = S' + \sum_j a_j s_j \) is conserved where the prime and the suffix \( j \) have the same significance as before. Then from eqs. (2.17) and (2.23) one has

\[ \eta^2 = \frac{1}{\rho \beta_T} \frac{C_p}{C_v} = \frac{1}{\rho \beta_T} \left( \frac{C_p'}{C_v} + \sum_j w_j \left( \frac{\delta a_j}{\delta T} \right) \right) \quad \ldots \ (2.24) \]
Now from eqs. (2.19) and (2.24) one gets

\[ \alpha = - \pi v f \left[ \frac{\rho \beta_T \left( c_v + \sum_{j} \left( \frac{\delta a_j}{\delta T} \right) \right)}{c_p + \sum_{j} \left( \frac{\delta a_j}{\delta T} \right)} \right] \]

or

\[ \frac{\alpha}{f^2} = \frac{\pi v (1 - \gamma')}{f} \frac{\rho \beta_T}{c_p \gamma'} \cdot g \left[ \sum_{j} \left( \frac{\delta a_j}{\delta T} \right) \right] \]

...(2.25)

From eq. (2.24) it can be seen that when the vibrational degrees of freedom are absent

\[ \Gamma^2 = \frac{\gamma'}{\rho \beta_T} = v^2 \text{ (say)} \]

...(2.26)

Then from eq. (2.25)

\[ \alpha/f^2 = - \frac{\pi}{f} \left( \frac{v}{\gamma} \right) \left( \frac{\gamma'/1}{c_p} \right) \cdot g \left[ \sum_{j} \left( \frac{\delta a_j}{\delta T} \right) \right] \]

...(2.27)
The quantity $W_j$ ($\delta a_j / \delta T$) is called the vibrational specific heat or the relaxing specific heat. It is complex and depends on time. Because of high frequency sound waves this specific heat differs slightly from its equilibrium value. It can be calculated by setting up equations of detailed balance and considering it under conditions of slightly perturbed equilibrium.

First let us consider a single excited level $j$ in equilibrium with the ground state denoted by $0$. Then $a_j$ and $a_0$ ($= 1 - a_j$) are fractions of molecules that are excited and unexcited respectively. The equation of detailed balance is then written as

$$\frac{\delta a_j}{\delta t} = a_0 k_{0j} - a_j k_{j0} \tag{2.28}$$

where the $k_{ij}$ are rate constants. In equilibrium $\delta a_j / \delta t = 0$ and therefore

$$\frac{a_j}{a_0} = \frac{k_{0j}}{k_{j0}} = e^{-W_j/RT} \tag{2.29}$$

where $R$ is the universal gas constant.
Since the perturbation to the equilibrium is produced by plane harmonic sound waves of frequency
\[ f = \frac{\omega}{2\pi} \] where \( \omega \) is the angular frequency of the wave, one can write
\[ i\omega = \frac{\partial}{\partial t} \] and from eqs. (2.28) and (2.29) it is obtained that (when the perturbation is small)

\[ \delta \left( \frac{\partial a_j}{\partial t} \right) = k_j \delta \left( \frac{a_0 K_j / K_j_0 - a_j}{(a_0 K_j / K_j_0) - a_j} \right) \] ...(2.30)

Then taking temperature as the independent variable
\[ - \frac{W_j}{RT} \]
and neglecting \( e \) compared to unity, one gets

\[ \frac{\delta a_j}{\delta T} = \frac{W_j}{RT^2} e^{-\frac{W_j}{RT}} \left( 1 + i\omega / K_j \right)^{-1} \] ...(2.31)

Einstein's specific heat \( C_j \) is given by the expression

\[ C_j = R (\frac{W_j}{RT})^2 \left( \frac{e}{\frac{W_j}{RT}} \right)^2 \left[ \frac{\frac{W_j}{RT}}{-e - 1} \right] \]
and when $e^{W_j/RT} \ll 1$

$$C_j = R (W_j/RT)^2 \cdot e^{W_j/RT} \quad \ldots (2.32)$$

Then one gets after some simplification that

$$g \left[ \sum_{j=1}^{d} \left( \frac{f}{f_j} \right) C_j \left[ 1 + \left( \frac{f}{f_j} \right)^2 \right] \right] = - \left( \frac{f}{f_j} \right) C_j \left[ 1 + \left( \frac{f}{f_j} \right)^2 \right]^{-1} \quad \ldots (2.33)$$

where $f_j = K_j / 2 \pi$ and is called the dispersion frequency of the $j$th level and $C_j$ is the equilibrium value of the vibrational specific heat. In the case of polyatomic substances, there are always several vibrational levels, say 's' in number, the vibrational specific heat is given by the sum,

$$\sum_{j=1}^{d} \frac{C_j}{1 + \frac{if}{f_j}} = \frac{\sum_{j} C_j}{1 + \frac{if}{f_m}} \quad \ldots (2.34)$$
where the most important contribution to $f_j$ is $K_{j0}/2$
and $f_m$ is called the mean dispersion frequency defined
by eq. (2.34). In liquids like $\text{CS}_2$ and $\text{C}_6\text{H}_6$ all
vibrational levels do not relax at the same frequency,
so that $f_m$ has no detailed physical meaning, although
it gives the order of magnitude of the dispersive
frequency range in a liquid.

From eqs. (2.27) and (2.34), the absorption
coefficient is given by

$$\frac{\alpha}{f^2} = \left( \frac{v}{v'} \right) \left( \frac{v'}{c_p} \right) \cdot \frac{\sum C_j}{f_m} \cdot \frac{1}{1 + \left( \frac{f}{f_m} \right)^2} \quad \ldots (2.35)$$

This shows that when $f$ is very much larger than $f_j$,
the effective vibrational specific heat $\sum w_j (\delta a_j/\delta T)$
becomes negligibly small and the primed quantities which
do not include the contribution of the vibrational
levels, correspond to the case $f \gg f_m$. At $f = f_m$,
the absorption coefficient per wave length i.e. $\mu_{\text{max}}$
is given by

$$\mu_{\text{max}} = \frac{\pi}{2} \cdot \frac{\sqrt{v}}{v'} \cdot \frac{\sqrt{v'} - 1}{c_p} \cdot \sum C_j \quad \ldots (2.36)$$
and the mean dispersion frequency $f_m$ is calculated from the relation

$$f_m = \frac{2 f_{\text{max}}}{\nu} \cdot \frac{1}{\alpha/f^2} \quad \ldots (2.37)$$

for $f \ll f_m$

Formula (2.37) was given by Kneser (1938) and was used by Pinkerton to obtain approximate estimates of $f_m$.

Binary mixtures:

In the light of the theory derived as above, Bauer considered the problem of binary mixtures of two nonassociated liquids with very much different absorption coefficients. He then derived a formula for the $\alpha/f^2$ of the mixture as a function of the concentrations of the components.

Let A be the high absorbing liquid having a low dispersion frequency $f_A^m$ and B be the low absorbing liquid with a high dispersion frequency $f_B^m$. When both types of molecules are excited, the probability of deexcitation of A molecules is less than that for B molecules. For simplicity of calculation binary collisions are considered only and collisions between excited
molecules are neglected. Let $A$ and $A^*$ represent an unexcited and an excited $A$ molecule respectively and similarly $B$ and $B^*$. Since $f_m^A \ll f_m^B$, an $A^* A$ collision is much less efficient than a $B^* B$ collision. In a mixture of molecules of both species, $A$ and $B$, the probable collisions are $A^* A$, $A^* B$, $B^* A$ and $B^* B$. It is assumed that $A^* B$ and $B^* A$ collisions have a rather high deexcitation efficiency because it is in general impossible for a quantum of vibrational energy to be transferred from one type of molecule to the other without some loss of energy. It is further assumed that de-excitations produced by $B^* A$, $A^* B$ and $B^* B$ collisions are almost of the same order of magnitude and each is much greater than that produced by $A^* A$ collisions. Hence as the concentration of $B$ molecules increases in the mixture, the net efficiency of collisions tends rapidly to the value corresponding to the liquid $B$. Thus absorption falls rapidly.

Let us suppose that each molecular species has a single excited level of energy i.e. $W_A$ and $W_B$, for $A$ and $B$ respectively. Then considering 1 gram molecule of the mixture, let '$a$' be fraction of $A$ molecules and '$b$' that of $B$ molecules so that $a + b = 1$. Further in the fraction '$a$', let '$a_1$' be the excited and '$a_0$' be the unexcited molecules respectively. Similarly '$b_1$' and '$b_0$' are the excited and unexcited molecules in the fraction '$b$' so that
Let 'k', 'g', 'l' and 'h' be the transition probabilities for AA, AB, BA and BB collisions respectively. Then one may write two equations of detailed balance like

\[
\frac{\partial a_0}{\partial t} = (k_0 a_0 + g_0 b_0) a_0 - (k_{10} a_0 + g_{10} b_0) a_1 = \phi_{01} a_0 - \phi_{10} a_1
\]

and

\[
\frac{\partial b_1}{\partial t} = (l_0 a_0 + h_0 b_0) b_0 - (l_{10} a_0 + h_{10} b_0) b_1 = \psi_{01} b_0 - \psi_{10} b_1
\]

where

\[
k_0 a_0 + g_0 b_0 = \phi_{01}
\]

\[
k_{10} a_0 + g_{10} b_0 = \phi_{10}
\]

\[
l_0 a_0 + h_0 b_0 = \psi_{01}
\]

\[
l_{10} a_0 + h_{10} b_0 = \psi_{10}
\]
Taking temperature as the independent parameter as in eq. (2.31), one has

\[ \frac{\partial a_1}{\partial T} = \left( \frac{w_A}{RT^2} \right)_a \left[ 1 + \frac{i\omega}{\phi_{10}} \right]^{-1} e^{-\frac{w_A}{RT}} \]

and

\[ \frac{\partial b_1}{\partial T} = \left( \frac{w_B}{RT^2} \right)_{(1-a)} \left[ 1 + \frac{i\omega}{\psi_{10}} \right]^{-1} e^{-\frac{w_B}{RT}} \] \hspace{1cm} (2.41)

If \( C_A \) and \( C_B \) are the vibrational specific heats of \( A \) and \( B \) molecules respectively, then in analogy with eqs. (2.32), (2.33), (2.34), and (2.35) one gets after some simplifications,

\[ \frac{\alpha(a)}{\pi^2} = 2\pi \left[ \frac{\pi v}{v'}^2 (v' - 1) \frac{1}{C'_{p}} \right] \frac{a C_A}{\phi_{10}} + \frac{(1-a) C_B}{\psi_{10}} \] \hspace{1cm} (2.42)

At this stage the two assumptions are introduced.

(i) \( A^*B, B^*A \) and \( B^*B \) collisions are equally efficient in producing de-excitations so that

\[ g_{ij} = l_{ij} = h_{ij} = z k_{ij} \] \hspace{1cm} (2.43)

(ii) The quantity \( \left\{ 2\pi^2 \frac{\pi}{v'^2} (\gamma' - 1) \frac{1}{C'_{p}} \right\} \) varies linearly with concentration \( a \), because the total variation of this quantity is small and therefore written as \( M_B (1 - Fa) \)
Then from eq. (2.43) with some simplifications one obtains

\[
\frac{\alpha(a)}{M_B} = \frac{M_B}{q_{10}} (1-Fa) C_B \left[ \frac{(1-a) + \frac{az}{z-a(z-1)}}{C_B} \right]
\]

where

\[
F = 1 - \frac{\alpha_A}{\alpha_B} \cdot \frac{C_B}{C_A} \cdot \frac{1}{z}
\]

\[
z = \frac{f_m^B}{f_m^A}
\]

\[\alpha(a) = \text{absorption coefficient of the mixture having a concentration } a \text{ of liquid } A\]

and \[M_B = \text{a constant related to liquid } B.\]

In eq. (2.44) by putting \[a = 0,\] one obtains

\[
\frac{\alpha_B}{f^2} = \frac{M_B}{q_{10}} \cdot C_B, \quad \text{so that}
\]

\[
\frac{\alpha(a)}{\alpha_B} = (1-Fa) \left[ \frac{(1-a) + \frac{az}{z-a(z-1)}}{C_B} \right]
\]

Eq. (2.45) reduces to that of Pinkerton\textsuperscript{19} i.e. eq.(2.16) if \[F\] is put equal to zero. It was applied to explain well the experimental results of Grobe\textsuperscript{17} in Benzene-Toluene mixture. In the present work it has been tried in the case of some other mixtures of non-associated liquids to be discussed in Chapters IV and V.
(3) Modification of Bauer's theory by D. Sette.

In 1950, D. Sette\textsuperscript{23} observed that in a mixture of nonassociated liquids with almost the same absorption coefficient, the variation of $\alpha/f^2$ with concentration passes through a flat minimum from its value of the high absorbing component to that of the low absorbing one. The minimum so obtained was even less than the absorption value of the low absorbing component. It could not, however, be explained by Pinkerton\textsuperscript{19} or Bauer's\textsuperscript{20} expressions for $\alpha(a)/f^2$. So D. Sette\textsuperscript{23} proposed a modification to Bauer's theory which is as follows.

Sette's\textsuperscript{23} development of the theory is essentially in the same line as Bauer's\textsuperscript{20}. Taking the two liquids as A and B to form the mixture, the collisions to be considered, here are $A^*A$, $A^*B$, $B^*A$ and $B^*B$ and the transition probabilities relating to these collisions are '$k$', '$g$', '$l$' and '$h$' respectively. Then for a gram mole of the mixture one arrives at the same expression for $\frac{\alpha(a)}{f^2}$ as was obtained by Bauer\textsuperscript{20} i.e.

$$\frac{\alpha(a)}{f^2} = 2\pi \left[ \frac{\pi v}{v'2} \left( -1 \right) \frac{1}{C'_\beta} \right] \left[ \frac{aC_A}{\Phi_{10}} + \frac{(1-a)C_B}{\Psi_{10}} \right]$$

... (2.42)

where the meanings of the different symbols have already been explained.
D. Sette, here, has adopted two approximations. The first one is the same as used by Bauer\textsuperscript{20} i.e. the quantity \[ \frac{2 \pi \frac{v'}{v^2}}{C'_{p}} \left( \frac{\gamma' - 1}{\gamma' - 1} \right) \] varies linearly with concentration 'a' of component A, so that one may write it as \( M_B (1 - F_a) \).

The second approximation refers to the efficiency of different collisions in producing inelastic transitions. Here an \( A^*A \) collision is considered to have less efficiency than the \( B^*B \) collision since \( f_m^A \ll f_m^B \). If \( z = \frac{f_m^B}{f_m^A} \), then \( B^*B \) collisions are 'z' times more efficient than \( A^*A \) collisions in producing an inelastic transition. Mathematically

\[ z_{Kij} = h_{ij} \quad (i, j = 0, 1) \quad \ldots (2.46) \]

When an excited molecule (\( A^* \) or \( B^* \)) strikes against a molecule of different kind (\( B \) or \( A \) respectively) the collision has a higher de-excitation efficiency than when the collision occurs between two molecules of the same type. In fact it is generally impossible that a
quantum of vibrational energy will go from one molecule to the other without some loss of energy. It is therefore written that

\[ g_{ij} = tk_{ij} = \frac{t}{z} h_{ij} \]

and

\[ l_{ij} = uh_{ij} \]

where \( t \) and \( u \) are unknown parameters to be determined and they vary for different pairs of liquids. Then

\[ \phi_{10} = h_{10}a_0 + g_{10}b_0 \]

\[ = \frac{1}{z} h_{10}a_0 + \frac{t}{z} h_{10}b_0 \]

\[ = \frac{h_{10}}{z} \left( a_0 + t b_0 \right) \]

and

\[ \psi_{10} = l_{10}a_0 + h_{10}b_0 \]

\[ = uh_{10}a_0 + h_{10}b_0 \]

\[ = h_{10} \left( ua_0 + b_0 \right) \]
Using eq. (2.48) and simplifying, eq. (2.42) becomes

\[ \frac{\alpha(a)}{f^2} = \frac{2M_p}{h_{10}} \left[ \frac{a_2 C_A}{a+u(1-a)} \right] \]

Then identifying \( \frac{2M_p C_B}{h_{10}} \) as \( \frac{\alpha_B}{f^2} \) (i.e. when \( a = 0 \)) one has

\[ \frac{\alpha(a)}{\alpha_B} = (1-Fa) \left[ \frac{a_2 C_A}{a+u(1-a)} \cdot \frac{C_A}{C_B} + \frac{1-a}{1+a(u-1)} \right] \]

Eqs. (2.49) and (2.50) are reduced to corresponding expressions by Bauer by putting \( t = z \) and \( u = 1 \).

In eq. (2.50) the value of \( F \) can be found by putting \( \alpha = \alpha_A \) for \( a = 1 \).
Then

\[ F = 1 - \frac{1}{z} \cdot \frac{C_B}{C_A} \cdot \frac{\alpha_A}{\alpha_B} \quad \text{with} \quad z = \frac{f_B^m}{f_A^m} \]

The two parameters 't' and 'u' are of much interest in illustrating the characteristics of molecular relaxation. Their introduction here, has been of some significance if relaxation phenomena are not complicated by other factors such as interaction between 'A' and 'B' molecules. The values of 't' and 'u' are calculated from experimental results of absorption coefficients in two mixtures very rich in liquids 'A' and 'B' respectively.

Using this theory D. Sette\textsuperscript{23} explained the experimentally obtained concentration dependence of absorption in Benzene-Carbontetrachloride binary mixture. The theory has been considered here in the present study in Chapter V.
(4) Recent theory of Hunter, Dossa, Haus and Sette:

Recently Hunter et al.\textsuperscript{85,86} (1971-74) have performed some relaxation experiments in binary mixtures of Kneser liquids and have given theoretical interpretations of the experimentally observed absorption as functions of concentration and frequency which were of the order of several hundred MHz range.

Essentially they took into consideration the assumptions of Pinkerton\textsuperscript{19}, Bauer\textsuperscript{20} and Sette\textsuperscript{23} as regards the efficiency of different types of binary collisions. Further the liquids used were assumed to be completely nonassociative and the parameters of the reaction rate equations were taken to be constant with concentration.

In the conventional theory of absorption of sound in binary liquid mixtures, one considers the total absorption to consist of two additive terms. The first one is assigned to the 'A' liquid and the second to the 'B' liquid. It is assumed that the partial contribution of a certain component to the total absorption is proportional to the amount of that liquid present. Thus, in the absence of any interaction between the two liquids in the mixture, the plot of absorption versus concentration would be a straight
line running between the absorptions of the two liquids in their pure states. But liquid 'A' in the mixture does not absorb in the same way as it does in the pure state, because absorption is connected with energy transitions, and transition probabilities of 'A' molecules in collision 'B' molecules are different from that for collisions with like 'A' molecules. This shows that the average reaction time of the molecules of the 'A' liquid is changed by mixing and so also is its relaxation frequency. The experimental relaxation frequency of the 'A' liquid is now no longer susceptible to direct experimentation because of the presence of other liquid. The only quantity that is now subject to relaxation measurements is a kind of average relaxation frequency of the liquid as a whole, together with the total absorption.

The discussion is based on the role of energy-interchange factors, which are four in number. They are \( f_A^*, f_A^{AB}, f_B^*, f_B^{BA} \). As regards their significance, the factor \( f_A^{*} \), for example, has to do with energy transition into or out of a vibrational state in the 'A' molecule, brought about by collision with one 'B' molecule. It can be looked upon as a transition probability and is usually greater.
and never less than the factor \( f^* \) which is the probability of an energy transition in an 'A' molecule in collision with a like molecule. A similar pair of energy interchange factors exists for the 'B' molecules and it is \( f^* \) and \( f^* \). Mathematically

\[
\frac{f^*_{AB}}{f^*_{AA}} \geq \frac{f^*_{BB}}{f^*_{BA}}
\]

...(2.51)

When a sound wave passes through a liquid mixture, the equilibrium between external and internal (vibrational) modes of energy is cyclically disturbed and the instantaneous energy distribution is a function of these four energy interchange factors since energy transition can take place only through collisions. The situation is complicated when the frequency of the sound wave is comparable with the reaction rates associated with these factors. But in the low frequency limit i.e. when the experimental
frequency is much less numerically than the reaction rates involved, the problem is rather simpler. Now it may be shown by relaxation theory that

\[
\left( \frac{\alpha}{f^2} \right)_{\text{LF}} \cdot f_{\text{relax}} = (A \text{ constant}) \ C_{\text{vib}} \quad \ldots (2.52)
\]

where

\[
\left( \frac{\alpha}{f^2} \right)_{\text{LF}} \quad - \text{low frequency absorption of the liquid,}
\]

\[f_{\text{relax}} \quad - \text{the relaxation frequency of the liquid}
\]

\[C_{\text{vib}} \quad - \text{the vibrational specific heat of the liquid.}
\]

and the constant contains static and frozen specific heats of the liquid and the sound velocity in it.

Eq. (2.52) shows that anything which raises the reaction rate of a substance will proportionately lower its absorption rate, if other factors remain the same.

It is assumed that (i) the total absorption in a mixture is the sum of the contributions due to the individual components; and (ii) a given liquid in the mixture does not absorb in the same way as it
does in its pure state. Then, let \((\alpha/f^2)_A\) be the absorption of liquid 'A' when it is in the mixture and let \((\alpha/f^2)_{A,0}\) be its absorption in the pure state. Similarly let \((\alpha/f^2)_B\) and \((\alpha/f^2)_{B,0}\) be the respective values of absorption of liquid 'B'. Let \(f_A\) and \(f_B\) be the energy interchange factors of 'A' and 'B' liquids respectively when they are in the mixture. The factors \(f_A\) and \(f_B\) are defined by

\[
 f_A = x_A f_A^* + x_B f_B^*, \quad \ldots (2.53)
\]

and

\[
 f_B = x_B f_B^* + x_A f_A^*. \quad \ldots (2.54)
\]

where \(x_A\) and \(x_B\) are the mole fractions of the components 'A' and 'B' in the mixture respectively.

So that,

\[
 x_A + x_B = 1 \quad \ldots (2.54).
\]

Usually \(f_A > f_A^*\) and \(f_B > f_B^*\). But from eq. (2.53)

\[
 f_A = f_A^*\text{ when } x_B = 0 \quad \text{or when } f_A^* = f_A^*, \quad \text{and similarly,}
\]

\[
 f_B = f_B^*\text{ when } x_A = 0 \quad \text{or when } f_B^* = f_B^*. \quad \text{Now the}
\]
absorption in a liquid is controlled by its reaction rate. The absorption rate \((\alpha/f^2)_A\) therefore corresponds to the reaction rate \(f_A\) whereas \((\alpha/f^2)_{A,0}\) corresponds to the reaction rate \(f_{A*}\).

Since absorptions are inversely proportional to the reaction rates, one may write

\[
\frac{(\alpha/f^2)_A}{(\alpha/f^2)_{A,0}} = \frac{f_{A*}}{f_A}
\]

and

\[
\frac{(\alpha/f^2)_B}{(\alpha/f^2)_{B,0}} = \frac{f_{B*}}{f_B}
\]

Then considering the additive nature of the absorption, its proportionality with concentration of a particular component and the change of reaction rate brought about by mixing, the low frequency absorption in the mixture is given by

\[
\left(\frac{\alpha}{f^2}\right)_{\text{mix}} = x_A \left(\frac{\alpha}{f^2}\right)_{A,0} + x_B \left(\frac{\alpha}{f^2}\right)_{B,0} + \frac{f_{A*}}{f_A} + \frac{f_{B*}}{f_B}
\]

\(...(2.56)\)
After substituting the values of $f_A$ and $f_B$ from eq. (2.53) one obtains

$$
\begin{align*}
\left( \frac{\alpha}{f^2} \right)_{\text{mix}} &= \left( \frac{\alpha}{f^2} \right)_{A,0} \left( \frac{x_A^f A^* A}{x_A^f A^* A + x_B^f A^* B} \right) + \left( \frac{\alpha}{f^2} \right)_{B,0} \left( \frac{x_B^f B^* B}{x_B^f B^* B + x_A^f B^* A} \right) \\
\text{or} \quad \left( \frac{\alpha}{f^2} \right)_{\text{mix}} &= \left( \frac{\alpha}{f^2} \right)_{A,0} \left[ \frac{1}{1 + \frac{x_B}{x_A} F_A} \right] + \left( \frac{\alpha}{f^2} \right)_{B,0} \left[ \frac{1}{1 + \frac{x_A}{x_B} F_B} \right]
\end{align*}
$$

...(2.57)

where

$$
\frac{f_{A^* B}}{f_A^* A} = F_A \quad \text{and} \quad \frac{f_{B^* A}}{f_B^* B} = F_B
$$

...(2.58)

These two new factors $F_A$ and $F_B$ stand for the relative effectiveness of collisions between the like molecules and those between unlike molecules. In any experiment the concentration and the low frequency absorption of the pure liquids being known, the behaviour of the absorption of the mixture as a function of concentration becomes a function of these two parameters i.e. $F_A$ and $F_B$. 
The theory derived thus is not self sufficient, however. It has been observed by Hunter et al.86 that in a mixture of carbontetrachloride with dichloromethane, addition of minute amounts of CCl₄ produces a rapid fall of absorption. At about 10% of CCl₄ the fall ceases abruptly and the absorption begins to rise to the value for pure CCl₄. This behaviour defies fitting the experimental results with a theoretical curve by any choice of reaction parameters which are constant with concentration. As an explanation to this, it is pointed out that in such mixtures the cross parameters like fₐ₀ₐ and fₐ₀ₐ do not remain constant with concentration but change. Hence Hunter et al. have proposed an empirical law which governs the variation of the parameters Fₐ and Fₐ with concentration (x) of any one liquid. The relation is of the type

\[ F_A(x) = F_{A0} (1 - k_A x^n) \]  \hspace{1cm} (2.58)

where \( F_{A0} \) is the value of the parameter for zero concentration and \( k_A \) and \( n \) are adjustable constants. For a frequency independent case \( k_A \) would be zero. Otherwise, both \( k_A \) (or \( k_B \)) and \( n \) are to be chosen so as to find the concentration dependent parameters like
$F_A(x)$ or $F_B(x)$. It is practically impossible to arrive at unique values for them. However, a value of $1/3$ for $n$ with appropriate $k$ values seems to be acceptable somehow. The values $k_A$ and $k_B$ are finally decided upon, analysing the experimental curves in question.

It seems that such concentration dependence of the parameters $F_A$ and $F_B$, occurs in some special cases where the absorption versus concentration curves have some peculiar shapes. The parameters $F_{AO}$, $F_{BO}$, $k_A$ and $k_B$ etc. are therefore determined by trial and error method so as to fit the experimental curve obtained. This is how one arrives at an unhappy state of matter where one has to beg the experiment to explain the findings obtained out of it. This may be clearly evident from our work described in Chapters IV and V.