CHAPTER - I

INTRODUCTION
A liquid is an intermediate state between a solid and a gas. Its molecules are so arranged that they are neither in a state of perfect order as in a solid, nor in perfect disorder as in a gas. Thus it has some peculiarities of its own like anomalous expansion of water, super fluidity of liquid helium, exceedingly high ultrasonic absorption in carbon disulphide and so on. As such it has attracted the attention of many researchers. Over the last several years there have been consistent attempts both experimentally and theoretically to study this state of matter to probe into the molecular processes occurring in different liquids. Experimental investigations have been made to study critically their several physico-chemical properties with modern techniques such as X-ray diffraction, nuclear magnetic resonance, atomic and electronic scatterings and ultrasonics etc. Theoretically it is also of great interest to analyse data from equations of state, irreversible thermodynamics, statistical physics and quantum mechanics etc. so as to reveal the basic principles involved in correlating different phases of the condensed state of matter. Even then the picture is not fully clear as yet and everyday new experimental results pile up in the field needing either new interpretations of the data or revision of established theories.
Ultrasonic methods have played an important role in such investigations. The ultrasonic waves being of high frequencies (above 20 kc/s), can be tuned into a fine beam of unidirectional and penetrating nature to interact with matter. The study of such interactions has led the development of a branch called ultrasonic spectroscopy which has taken a place of equal importance along with optical and X-ray spectroscopy. Usually the velocity and attenuation of these waves are measured during their propagation in the media. Experimental determination of such velocity together with the study of some other parameters, enables one to calculate with necessary precision many important properties of the media such as their compressibility and specific heats, whereas a knowledge of the attenuation of these waves provides valuable informations regarding their molecular association and atomic and molecular structures.

When an acoustic beam passes through a fluid, the density, pressure and temperature of an element of the fluid vary periodically with time. Assuming the medium to be nonviscous and thermally nonconducting, these variations in pressure and density take place reversibly and adiabatically and a beam of plane sound wave travels through it unattenuated. If any of these restrictions is removed
the pressure-density cycle becomes irreversible and, consequently in each cycle some of the sound energy is converted into the random thermal energy of the fluid. Such dissipation of energy gives rise to the phenomena of absorption and dispersion.

**Classical absorption:**

Stokes\(^1\) in 1845 first of all showed that the absorption of sound in fluid media is due to viscosity and obtained a formula for the coefficient of absorption \(\alpha\) as

\[
\alpha = \frac{2\eta \omega^2}{3 \rho v^3}
\]  

...(1.1)

where \(\eta\) and \(\rho\) stand for the coefficients of shear viscosity and density of the medium and \(\omega\) and \(v\) for the angular frequency and velocity of the wave in it respectively. Later on Kirchhoff\(^2\)(1868) observed that absorption in the medium also depends on its thermal conductivity additively and obtained an expression for \(\alpha\) as

\[
\alpha = \frac{k \omega^2}{2 \rho v^3 \left( \frac{1}{C_v} - \frac{1}{C_p} \right)}
\]  

...(1.2)

where \(k\) is the thermal conductivity of the medium and \(C_p\) and \(C_v\) are its two specific heats at constant
pressure and constant volume respectively. These two causes of absorption are known as classical ones and they suffice in general to explain the observed attenuation and dispersion in monoatomic fluids.

Relaxation phenomenon:

In polyatomic gases, however, the observed absorption was found to be many times larger than that resulting from the classical causes. This led to the development of a new theory of absorption known as relaxation theory. The theory was first of all considered separately by Herzfeld and Rice, Bourgin and Knese for gases and then developed by Bourgin, Datta, Ghosh, and others for liquids.

Relaxation in a medium corresponds to the delay in the adjustment of a given equilibrium condition once it is disturbed by some external agency and the appropriate time constant is known as relaxation time. It has been observed that the structure of polyatomic molecules and their arrangements (grouping or association) in a fluid play an important role in the absorption of ultrasound due to relaxation. Hence a knowledge of such absorption provides a method of analysing the molecular structure or association in them.
The relaxation processes in a fluid are mainly of two types: (i) thermal relaxation and (ii) structural relaxation.

**Thermal relaxation:**

The thermal relaxation is of primary importance in polyatomic gases and normal liquids. Such normal liquids are distinguished by the fact that in them the attractive interactions between the molecules play a minor role. In such media the total energy is distributed partly among their translational or external degrees of freedom and partly among their rotational and vibrational degrees (the internal degrees of freedom). At any particular temperature the energy distribution among them is such that the three states remain in equilibrium. When an acoustic beam propagates through the medium, the energy of an element of fluid is suddenly increased and a redistribution of energy takes place, thus disturbing the initial equilibrium condition. This requires an exchange of energy between the external and internal degrees of freedom of the molecules. The establishment of thermal equilibrium between the external and the internal modes is in general much slower and the energy received by the latter is not fully restored to the external modes during one complete cycle of the wave. Thus some energy gets separated from the propagating beam so as to be dissipated as heat. This gives rise to
the extra absorption in the medium in addition to that due to classical causes. This process is known as thermal relaxation because of its origin due to temperature fluctuations caused by the acoustic beam.

Thermal relaxation observed in polyatomic gases and normal liquids like Carbondisulphide, Benzene etc. may be called "vibrational relaxation". Here the translational energy imparted by the sound beam to the medium is converted into vibrational energy and the energy transfer takes place through binary collision process. In this type of collision, the energy transfer comes from a very few collisions with exceptionally very high energy just as in gases. In these collisions the molecule in question comes particularly close to and interacts almost exclusively with a single molecule of the surroundings but not with a group or complex.

There is another type of thermal relaxation in which the energy of the acoustic beam is transferred into two or more internal energy states of a molecule. It is known as "Isomeric relaxation". Here a change in temperature due to the propagation of the wave causes a change in population in the energy states of the molecule. Kaprovich has demonstrated the existence of such a relaxation process when the ultrasonic wave disturbs the equilibrium between two isomeric states of the molecules.
in a liquid. This type of absorption is exhibited by the esters and aldehydes, methyl and ethyl acetates and formates. Studies of relaxation processes such as these can give an estimate of the energy difference between the isomeric states and also of the energy barrier impeding the transition between the two states. The ultrasonic absorption is very sensitive in such cases and can detect even 1% of these isomeric forms.

**Structural relaxation:**

The second type of relaxation process i.e. structural relaxation is observed in associated and polar liquids. Here the molecules of the medium have a tendency to form groups or clusters due to the existence of relatively large intermolecular forces among them. The groups or clusters remain in equilibrium under normal conditions. The passage of sound beam perturbs this equilibrium condition resulting in changes of pressure and translational energy of the molecules. This brings about a new molecular rearrangement which takes a finite time and consequently there is a phase lag of volume against pressure in the medium. This produces the excess absorption.

In weakly associated liquids like Acetic acid structural relaxation arises due to the perturbation of equilibrium between the monomer and dimer molecules.
which normally exist in the liquid. But in highly associated and polar liquids like water the molecules exhibit two types of packing as assumed by Hall. In one type of packing they exist in a state characterized by higher volume and lower energy and here one molecule of water has four nearest neighbours which are arranged tetrahedrally. This is known as the ice-like structure. In the second type of packing the molecules exist in a state characterized by lower volume and higher energy and here a molecule of water is surrounded by twelve nearest neighbours. This is identified as the close-packed structure. The periodic changes in pressure produced by the sound waves causes the transition of some of the molecules from one state to another and this gives rise to the relaxation process. Excess ultrasonic absorption in water, has been well accounted for by this theory proposed by Hall. Later it has been used with some modification to explain the observed ultrasonic absorption in heavy water and alcohols. Structural relaxation is also exhibited by highly viscous but associated liquids like glycerol where strong absorption occurs. Here, however, several relaxation processes are assumed to exist simultaneously.

The validity of the above relaxation theories have been put to experimental test in cases of different liquids and gases and also in different mixtures of liquids and mixtures of gases.
Ultrasonic measurements in gases:

In the case of polyatomic gases main importance of ultrasonic measurements lies in the fact that they enable one to determine quantitatively the relaxation times ($\tau$) or the rates at which equilibrium is established between internal and external degrees of freedom. In many cases, therefore, such values have been obtained with sufficient accuracy. But for certain gases like oxygen and halogens $\tau$ values obtained by different investigators differed appreciably and such difference was found to be due to the presence of impurity in them. This led Knotzel and Knotzel$^{14}$ and Parker$^{15}$ et al. to measure $\tau$ in mixtures of oxygen with hydrogen, deuterium and helium as impurities in different concentrations. From a series of such values, the value for the pure gas was obtained by extrapolating the observed results to zero concentration of impurity.

Relaxation in liquids:

The study of relaxation mechanism in liquids is, however, not exactly similar with that in gases, where binary collisions are of prime importance. Also in liquids due to closeness of molecules one has to deal with the interactions of a molecule with its various nearest and next nearest neighbours besides taking into account binary collisions. Further the collision rate
among liquid molecules is much greater than that among gaseous molecules, raising the relaxation frequency in most instances. Also the usual liquid has a considerable number of vibrational states that may be excited and this complicates the entire relaxation process.

Liquids in which the main cause of absorption is thermal vibrational relaxation are known as Kneser liquids. Here the molecules are supposed to have negligible attractive interaction among them. It is only the temperature difference associated with the sound wave that causes lack of equilibrium between the internal and external degrees of freedom and energy exchange is brought about through binary collision process. If the efficiency of collision is more, the process of energy exchange is more rapid and consequently the absorption is less. In this regard it has been observed that binary collision between molecules of the same kind are less efficient than those between molecules of different materials and this fact, in particular, has been verified through the study of binary mixtures of liquids.

**Binary mixtures of liquids:**

In a high absorbing nonassociated liquid the efficiency of collision in establishing equilibrium among the external and internal degrees of freedom is much less. When a weakly absorbing liquid is added to it
the collisions between different kinds of molecules become efficient enough in establishing equilibrium more quickly among the external and internal degrees so that the deexcitation of the vibrational modes of the highly absorbing liquid becomes faster. Consequently absorption falls. To investigate into the process a number of liquid mixtures have been taken up by different workers and the absorption of ultrasonic waves in them was studied. Such studies in liquid mixtures as functions of concentration and temperature provide a means of explaining a number of problems associated with relaxation phenomena and molecular structures of liquids.

(a) Mixtures of two nonassociated liquids:

It has been reported by Claeys, Errera and Sack, Grobe and Bazulin etc. that the addition of a small amount of impurity to a high absorbing liquid causes the absorption coefficient, \( \alpha \), of ultrasonic waves in the latter to fall sharply. At lower limits of concentration of the high absorbing component the change in \( \alpha \) becomes less and less significant. The explanation to the above experimental findings was given by Pinkerton and Bauer on the basis of thermal relaxation of vibrational modes of the molecules. They assumed that when two liquids are mixed the deexitation due to collision between two dissimilar molecules is more than that due to
collision between molecules of the same type.
Experimentally observed absorption in a number of liquid mixtures could be explained with some success on the basis of the theory so established. The mixtures studied were Benzene-Toluene\textsuperscript{17,19,20}, Ether-Chlorobenzene\textsuperscript{18}, Ether-Carbontetrachloride\textsuperscript{18}, Chlorobenzene-Carbontetrachloride\textsuperscript{18}, Carbontetrachloride-Toluene\textsuperscript{21}, Carbontetrachloride-Acetone\textsuperscript{21}, Benzene-Nitrobenzene\textsuperscript{22} and Chloroform-Nitrobenzene\textsuperscript{22} etc. to mention a few. It is to be noted that in such mixtures the absorption coefficient of one component was much greater than that of the other and the liquids were supposed to be noninteracting between themselves.

In a separate study of binary mixtures of such non-interacting liquids, however, the experimental results were somewhat different when the components of the mixtures in their pure state had absorption coefficients of the same order. In such cases the absorption coefficient versus concentration curve passes through either a sharp or a flat minimum as the two liquids are added in different proportions. Further the minimum in absorption obtained is less than either of the $\alpha$ values for the pure components. To explain this peculiarity D. Sette\textsuperscript{23} applied Bauer's ideas of intermediate probability with certain modifications. According to Bauer\textsuperscript{20} if $A$ is the high absorbing liquid and $B$, the
low absorbing one then in a mixture of the two, binary collisions like $A^*B$, $B^*A$ and $B^*B$ are almost equally efficient in producing de-excitation among the molecules and each of them is much more efficient than $A^*A$ collisions. Sette\textsuperscript{23} modified it by saying that, the transitions relating to $A^*B$ and $B^*A$ collisions are much more effective than those relating to $A^*A$ and $B^*B$ collisions. The asterisks here refer to excited molecules. Sette's own experimental results\textsuperscript{23} in Benzene - Carbontetrachloride mixture in this connection were very much in agreement with his own theoretical predictions. Since then the theory has been put to test in many other binary mixtures of nonassociated liquids with moderate success.

(b) Mixtures of a nonassociated liquid with an associated one:

In a mixture of a highly absorbing nonassociated liquid like benzene with an associated liquid such as an alcohol\textsuperscript{22,24}, the absorption coefficient falls off very rapidly from that of the high absorbing component when the low absorbing liquid is added in a very small amount. The fall of absorption coefficient $\alpha$ with concentration of the second component is almost similar with that obtained in the case of two nonassociated liquid mixtures. However in some of the published papers\textsuperscript{25-28}
dealing with ultrasonic absorption in organic solvent-alcohol mixtures it has been shown that the absorption coefficient passes through a sharp maximum for certain combination of the component liquids. The phenomenon was attempted to be explained qualitatively by Mez and Maier\textsuperscript{29}. They assumed the occurrence of a new structural relaxation. According to them while propagating, the sound wave perturbs the equilibrium among the associated complexes in the mixture, causing an extra absorption over that due to thermal effects in the unassociated component. The effect has been also noticed\textsuperscript{25} in dilute solutions of phenol, alcohols and acetic acid in carbon tetrachloride, cyclohexane and chlorobenzene respectively. Later, in such mixtures, Lang and Zana\textsuperscript{30} have studied the influence of alcohol chain length and of the nature of organic solvents on the amplitude and position of the absorption peak as observed against concentration. Thus according to them the introduction of alcohol in a nonassociated solvent results in a variation of solvent absorption coefficient due to two effects, (i) the perturbation of trimerization equilibrium of the alcohol molecules and (ii) faster de-excitation of a molecule of the solvent liquid (non-associated) due to collisions with molecules of the impurity i.e. the associated one. The maximum in absorption is observed when the first effect is predominant over the second and it takes place for
certain specific composition of the mixture. In solvents like benzene, the decrease in $\alpha$ due to the second effect becomes much larger than its increase due to the first one and therefore the peak does not appear at all. However, the picture regarding such mixtures is not fully clear as yet and there is enough scope for further research.

(c) Mixtures of two associated liquids:

A mixture of liquids formed either by two associated components or by an associated and a polar component exhibit a maximum in absorption at an intermediate concentration. Sometimes the absorption peak is quite large as has been observed in mixtures (i) of water with alcohols, glycol, ethers or acetone, (ii) of ether with alcohol, (iii) of nitrobenzene with alcohols and (iv) of ethylmethyl ketone with dioxane. In the case of water-methyl alcohol mixture the maximum in absorption is not very much pronounced at room temperature but it appears prominently when the temperature is lowered. It has further been shown by Storey that the maximum absorption in such mixtures is frequency dependent and it decreases quickly as the temperature is increased. As an explanation of the loss processes in such systems it was assumed that there was association of the two types of molecules in solution and that the equilibrium condition was upset by temperature.
changes produced by sound waves resulting in excess absorption. In the system of water-ethyl alcohol, Storey\textsuperscript{27} estimated the relaxation frequency of the process to be 105 MHz at 25°C, such frequencies, however, being far above the then experimental frequencies. Further analysis by Sette\textsuperscript{31} has revealed that Storey's calculations involved some error as he assumed a linear dependence of the classical absorption for the mixture as a function of concentration of the components. Ultrasonic studies in mixtures of water and alcohols have also been carried out by Blandamer\textsuperscript{32-34} and his co-workers. In their study of water with monohydric alcohols they have reported in favour of two widely separated relaxation frequencies to account for the frequency dependence of ultrasonic absorption. Their experimental results in substituted alcohol-water mixtures have been analysed using two relaxation frequencies too and the analysis throws more light on the polar part of the molecules involved. Interesting results in this regard have also been obtained in the experimental study of ultrasonic absorption in binary mixtures of water and heavy water by Kor, Singh and Deorani\textsuperscript{35}. Assuming ideal mixing they have explained the excess absorption in this mixture by using Hall's two state model\textsuperscript{10} of structural relaxation. Very recently Bhadra and Basu\textsuperscript{36} have attempted to explain their experimental results in water-alcohol mixtures taking into
account the polar and dielectric characters of the liquids. Since their analysis is of purely qualitative nature, they have suggested for a quantitative investigation of the problem.

(d) Aqueous solutions of some non-associated liquids:

Investigations on aqueous solutions of some non-associated liquids also show an excess ultrasonic absorption over the classical ones. The excess absorption passes through a maximum over that due to the individual components. Barfield and Schneider have measured such absorption along with ultrasonic velocity, density and shear viscosity of di-ethylamine-water mixtures. They have found that the absorption which is strongly temperature dependent reaches a maximum at a composition of nearly 10 mole percent of amine. The maxima observed in density and shear viscosity were, however, less pronounced. The system also exhibited a volume change on mixing which was attributed to a compressional relaxation. Besides this the excess ultrasonic absorption may also be due to a simple two state model of the system that is based on the formation of hydrogen bond between like and unlike molecules. Other aqueous mixtures of amines, ketones and ethers have been studied too and the available data have been summarized by Andrae et al. Blandamer and his co-workers have discussed the frequency
dependence of such absorption and have interpreted the results with reference to the structure of amines. The data of ultrasonic velocity and absorption in aqueous solutions of 2-chloroethanol have been analysed on the basis of relaxational phenomena coupled with molecular association. According to Hammes and Konche ultrasonic absorption in a mixture of water with di-oxane is due to the formation of intermolecular hydrogen bonded complexes. Recently Kor et al. have extended such studies to heavy water-dioxane mixture. Here the excess absorption in the system has been attributed to the formation of intermolecular hydrogen bonded complex involving heavy water and dioxane molecules in 2:1 and 2:2 ratio. The equilibrium established on the formation of these complexes are perturbed by the pressure and temperature changes associated with the ultrasonic wave and hence the relaxational absorption occurs. Such complex formation has also been noticed in mixtures of water with glycerol, and of dioxane with glycerol. Ultrasonic measurements at 0.3 MHz and 0.5 MHz have revealed for the first time that the complexes so formed between molecules of water and glycerol are of the type AB and AB₂ where A and B refer to glycerol and water molecules respectively.

**Binary liquid mixtures in critical region of solution and temperature:**

In the mixtures of two liquids one being partially soluble in the other, the increase in absorption
has been found to be due to a thermal relaxation process. Here a high absorption has been observed \(^{50,51}\) in the critical region of solubility or in the region of both the vapour-liquid critical temperature and the critical solution temperature of binary liquid systems. In all cases the characteristic excess sound absorption became evident at a temperature approximately \(2^\circ\) on either side of the transition point and increased rapidly as the transition temperature was approached. The excess absorption in the critical region has been postulated to be due to a structural relaxation mechanism. Besides this, two alternative mechanisms namely viscosity absorption and attenuation due to scattering of sound beam have also been found to be the possible causes. However, this and other considerations being of qualitative nature, have not been fully satisfactory to explain all the experimental findings. Fixman \(^{52,53}\) has presented a theory for the excess heat capacity, absorption and dispersion of sound in the critical region of liquid-liquid and liquid-gas systems. According to him fluctuations in density or composition in the system due to the propagation of sound beam would cause associated fluctuations in the heat capacity and the resultant temperature variation would lead to energy dissipation. Fixman's theory \(^{52-53}\) has been used with considerable success to explain qualitatively the experimental data of composition dependence and frequency dependence of ultrasonic
absorption and dispersion in binary mixtures of nitrobenzene-n-hexane and aniline-cyclohexane. However, it has been pointed out that many of the additional assumptions introduced by Fixman for a quantitative evaluation of his model may lead to a break down of the theory either close to critical temperature $T_c$ or at high frequency. Later a more general theoretical treatment developed by Kawasaki has led to a closer quantitative agreement between theory and experiment. Very recently, some publications in this context, however, reveal that more rigorous theoretical considerations are necessary for a good quantitative explanation of experimental findings.

Mixtures of strongly polar and associated liquids:

Some binary mixtures of strongly polar and associated liquids exhibit a definite minimum in ultrasonic absorption at certain specific composition of the components. Although the shapes of such curves are similar to those found in the case of two non-associated liquids with nearly equal absorption coefficients, the origin of the relaxation processes are somehow different. In such mixtures $\alpha_{\text{exp}}/\alpha_{\text{class}}$ does not vary much with temperature while the total absorption coefficient decreases fast when temperature increases. This suggests that the main dissipative process causing excess
absorption is probably due to a structural relaxation phenomenon found in the case of pure, associated liquids.

Mixtures of Carbon disulphide (CS₂):

This brief review on ultrasonic absorption in binary liquid mixtures shows that studies on the mixtures of liquid carbon disulphide (CS₂), the prominent kneser liquid, have been rather few. Though simple in structure, its high value of ultrasonic absorption (\( \alpha / f^2 = 6000 \times 10^{-17} \text{cm}^{-1} \text{sec}^2 \)) is simply surprising. Such high absorption in the liquid has been attributed to the relaxation of three vibrational modes and it is established that the total vibrational specific heat relaxes at one frequency.

It has been generally reported\(^{16-18}\) that the absorption coefficient of this liquid would fall rapidly with the addition of impurity but it seems no quantitative analysis of the results could be made. In early 60's, however, Slie and Litovitz\(^{64}\) studied the effect of alcohol as impurity on the ultrasonic vibrational relaxation of the liquid and concluded that the relaxation frequency increased with the addition of impurity. The increase was further found to be a linear function of impurity concentration. However, this represented the mixture of a nonassociated liquid with an associated one and there was no established theory for such mixtures to analyse the
concentration dependence of absorption. It may be
recalled here that theories developed by Pinkerton\textsuperscript{19},
Bauer\textsuperscript{20} and Sette\textsuperscript{23} have their limitations of being
applicable to binary mixtures of non-associated liquids
only. Samal and Das\textsuperscript{65} first of all attempted a systematic
study regarding binary mixtures of carbondisulphide so as
to have a comparison between the theoretical and
experimental results of absorption. In their first report
it was pointed out that impurities with lower absorption
coefficients were more effective in reducing the
absorption coefficient of CS\textsubscript{2} than those with higher
absorption coefficient. It was further pointed out that
the experimental results in Carbondisulphide-Xylene
mixture as a function of concentration were not in full
conformity with the theories proposed by Pinkerton\textsuperscript{19} and
Bauer\textsuperscript{20}. This motivated the author to apply the theories
to other binary mixtures of CS\textsubscript{2} and to verify their
suitability in explaining the experimental results of
absorption.

With this idea in mind six unassociated liquids
of ultrasonic absorption coefficients at different ranges
were selected to be added as impurities to CS\textsubscript{2} and their
concentration effects on its absorption coefficient were
studied. The liquids were Benzene, Carbontetrachloride,
Chlorobenzene Nitrobenzene, Methyl Iodide and Ethyl Iodide
with widely varying absorption coefficients. The
experimental results at very low limits of impurity
concentrations were compared with the calculated values of \( \alpha/f^2 \) using the theories of Pinkerton and Bauer. The deviations were as high as 23%. However, Sette's modified theory could not be applied to such mixtures as the experimental results were confined to very low concentrations of impurities only and this did not enable the author to evaluate the unknown parameters used in his equation. Here the ultrasonic absorptions in different mixtures were determined with an optical arrangement reported by Samal. Now it was proposed to repeat the ultrasonic studies in the same mixtures with wide variations of impurity concentrations. But to do so the use of the optical method, put forth the following inconveniences:

1. It required the use of large quantities of liquids in a long vessel movable on a spectrometer stand.
2. Some of the liquids used were highly volatile (for example \( \text{CS}_2 \), \( \text{C}_6\text{H}_6 \), \( \text{CH}_3\text{I} \), \( \text{C}_2\text{H}_5\text{I} \) etc.) and evaporation became unavoidable due to long duration of a set of observations taken to cover a wide range of impurity concentration.

Hence fresh sets of observations were taken by an Interferometric method which could overcome the difficulties just pointed out. Further this method had another added advantage of using nontransparent mixtures. In fact with this method ultrasonic absorption and
velocity as functions of concentration have been measured by Saraf, Mishra and Samal in reconstituted powdered milk.

Before measuring ultrasonic absorption in liquid mixtures and other liquids the commercially available interferometer (manufactured by M/S Mittal Enterprises, New Delhi, India) was studied in detail. It needed some modifications in its mechanical and electrical designs discussed elaborately in the Chapter III of the thesis. Then coefficients of ultrasonic absorption of some standard liquids (both high and low absorbing) were measured with it and the results have been reported by Mishra, Saraf and Samal. Maximum error in such measurements was within ± 10% only. Velocity could be measured with this instrument with an accuracy of ± 0.1%.

The interferometer was first of all used to measure ultrasonic absorption in the mixture of CS₂ with benzene as a function of concentration. To compare the experimental results with theoretically calculated values using Bauer's and Sette's equations, it was necessary to investigate regarding the correct value of relaxation frequency (fₘ) of benzene. With extensive calculations it was shown by the author that fₘ = 1200 MHz for benzene, as proposed by Bauer and used by many workers yielded absurd results in the case of its mixture with CS₂. Therefore the values of fₘ = 533 MHz, 608 MHz and
4400 MHz, as reported from Brillouin scattering and other studies\textsuperscript{76-83} were tried. It has been concluded that a frequency value around 600 MHz is the most appropriate one to be used in the present work and also in the work of others\textsuperscript{23,72-75}.

Then other binary mixtures studied by Interferometric method were those of CS\textsubscript{2} with Carbontetrachloride, Chlorobenzene, and Nitrobenzene. In such studies\textsuperscript{84} it has been shown that in no case Bauer's equation\textsuperscript{20} alone accounts for the observed variation of \( \alpha/\varepsilon^2 \) with concentrations of the components. Moreover application of Sette's modified relation\textsuperscript{23} in these cases reveals that marked deviations are noticed in the mid-concentration range of the mixtures containing polar liquids like chlorobenzene and Nitrobenzene but not so when the two components are nonpolar. A qualitative explanation of the above deviations has been proposed\textsuperscript{84} taking into account the polar characteristics of the impurity liquids. To confirm the anomaly the study has been further extended to binary mixtures of CS\textsubscript{2} with toluene and of benzene with nitrobenzene. Lastly to get more insight regarding the intermolecular processes occurring in these liquid mixtures some thermoacoustic parameters like adiabatic compressibility (\( \beta_s \)), intermolecular free length (\( L_\varepsilon \)), molar sound velocity i.e. Rao's constant (\( R \)) and molar compressibility i.e.
Wada's constant (W) have been calculated as functions of concentration. The peculiarities observed have been discussed in the light of the polar and nonpolar characteristics of the liquids.

Scope of the work under report:

1. Absorption coefficient of ultrasonic waves in binary mixtures of CS$_2$ with liquids like C$_6$H$_6$, CCl$_4$, C$_6$H$_5$Cl, C$_6$H$_5$NO$_2$, CH$_3$I and C$_2$H$_5$I have been determined by the optical diffraction method suggested by Samal, at very low concentrations of the impurities. The experimental results have been compared with those calculated theoretically from relations developed by Pinkerton and Bauer.

2. A commercially available ultrasonic interferometer has been used to measure $\alpha/\nu^2$ in some standard nonassociated liquids with due modifications in its experimental set up and procedure. Such measurements have been extended to some binary mixtures of CS$_2$ and other liquids at different concentrations of the components.

3. A critical analysis has been made in ascertaining the relaxation frequency of liquid benzene from the study of ultrasonic absorption in its binary mixtures with CS$_2$ and some other liquids.
(4) The applicability of Bauer-Sette relation concerning ultrasonic absorption has been thoroughly examined in the different binary mixtures under report and the results have been interpreted on the basis of polar and nonpolar characteristics of the liquid molecules.

(5) Calculation and study of some thermoacoustic parameters like $\beta_s$, $L_f$, $\alpha$ and $W$ of the mixtures have been made from experimental results of ultrasonic velocity and density so as to get an insight regarding the molecular interactions which confirm the interpretations suggested.