CHAPTER II

EXPERIMENTAL TECHNIQUES
2.1 REVIEW OF THE EXPERIMENTAL METHODS FOR THE

DETERMINATION OF ULTRASONIC VELOCITY IN LIQUIDS

The techniques that are employed for ultrasonic velocity measurements\(^1,\2\) may be broadly divided into two categories. The continuous wave techniques and pulse techniques. The former includes optical diffraction method, striation method, interferometer method and the Brillouin scattering method, and the latter comprises of the pulse echo method, the pulse superposition method, the pulse echo overlap method, the sing around and the pulse comparison method. Some of these methods are described in detail in Handbuch der Physik\(^3\).

ULTRASONIC VELOCITY MEASUREMENTS - CONTINUOUS WAVE TECHNIQUES:

Optical techniques\(^3-12\) are based on setting up of an acoustic phase grating in the liquid and measuring the grating constant either by employing the diffraction of light caused by the grating or by studying the secondary interference effects\(^1,10,13,14\).
Debye and others\textsuperscript{4,5} developed the optical diffraction method in which a parallel beam of ultrasonic waves acts as a diffraction grating in a transparent liquid. Though the grating moves with the speed of sound, the grating can be considered stationary for the propagation of light waves since the velocity of sound is very small compared with that of light. Knowing the wavelength of light, wavelength and hence velocity of sound in the liquid can be calculated.

By using phase detection of an optical beat technique\textsuperscript{15} the sound velocities have been measured. Photo electric detection of the first order spectrum in the double absorption of a laser beam by two successive ultrasonic waves makes it possible to generate a light beat at a difference frequency of the two ultrasonic waves. From a theoretical discussion of the phase of this light beat the measurements of sound velocity are evaluated. A change in sound velocity less than 0.05 m/sec can be detected when it is varying with time.

Ohtsuka\textsuperscript{16} developed a new optical method for measuring ultrasonic velocities. It is based on optical heterodyne detection techniques using a pair
of ultrasonic light modulators of slightly different frequency.

Two successive ultrasonic cells \(^{17}\) cause dual diffraction of a laser beam. A change in the time dependent sound velocities can be observed down to 0.05 m/sec in real time. Telschow and Stasiak have reported a modification of a continuous wave feed back technique involving the addition of a feed back loop which increases the precision of absolute velocity measurement, the accuracy being better than 80 ppm.

Bergmann \(^{18}\) developed striation method for the measurement of wavelengths. These wavelengths are employed to determine the velocity of ultrasonic waves. The sound waves from a crystal are reflected by a plane reflector and a system of standing waves are set up in the liquid column. The periodic changes in density gives rise to periodic refractions of light beam passing through the liquid. A series of equidistant bright and dark, parallel fringes are observed on the screen. The distance of separation of these fringes is directly proportional to the wavelength of sound waves. These methods are restricted to megacycle range. The estimated accuracy in velocity measurements by these methods is ± 0.1%.
The optical methods require large quantities of transparent liquid samples and are not convenient for temperature control.

Interferometric techniques are widely used and they are capable of yielding a very high accuracy in the measurement of velocity. The temperature of the interferometric liquid can be maintained steady with ease. Subba Rao and Ramachandra Rao developed a simple, rapid and accurate method for determining the temperature coefficient of ultrasonic velocity by modifying the fixed path interferometer method. Koo and Tripathi used a method in which stationary waves are produced and the effect of varying path length is investigated. The single crystal interferometer consists of a reversible transducer connected to an oscillator whose frequency can be adjusted until it coincides with the natural resonant frequency of the crystal transducer, which then vibrates. These waves from the transducer travel through the liquid to a plane reflector which is held accurately parallel to the crystal in the direction of the beam. When the distance between the transducer and the reflector is an integral multiple of half-wavelengths, standing waves are set up in the
medium. The reflected wave arriving back at the crys-
tal surface is then 180° out of phase with the motion of the crystal.

Recent advances in this technique permit higher accuracy i.e., a few parts per million in velocity measurements. The recent NRL measurements\textsuperscript{21,22} are accurate to ± 0.003%. The use of differential path lengths for the determination of wavelength and simple measurement of frequency as against a more tedious and difficult measurement of transit time in the pulse technique are some of the advantages of this technique. Several workers\textsuperscript{23–30} have found the interferometer to be more suitable for the determination of temperature coefficient of sound velocity. Del Crosso\textsuperscript{31} has discussed in detail several aspects of superiority of this technique.

An ultrasonic interferometer\textsuperscript{32} having a fixed path length is used for measuring the propagation velocity of longitudinal ultrasonic vibrations in materials. The velocity is determined from the difference between the frequencies of certain acoustic resonances in a layer of the material which is kept in between the plane parallel surfaces of radiating and receiving
electroacoustic transducers. A method and apparatus is described which permit the error due to the frequency dependence of the phase shift during the reflection of the ultrasonic vibrations from the transducers to be compensated. The apparatus described is designed for measurement of ultrasonic velocity in small amounts of liquid, especially a biological fluid.

An ultrasonic interferometer with two fixed paths operating in the frequency range of 4-6 MHz is described by Kammoun et al\textsuperscript{33}. A simple phase-measuring technique permits a fast determination of ultrasonic velocity with an accuracy of 1 mm/sec. The isentropic variation of propagation velocity as a function of hydrostatic pressure is directly measured by this method. Leha et al\textsuperscript{34} developed an ultrasonic pulse interferometer for measuring ultrasonic velocities in electrolytes. Wada\textsuperscript{35} mentioned the recent developments in measuring techniques of ultrasonic velocity and absorption. Del Grosso\textsuperscript{36} developed an interferometer for measuring sound speed in sea water. A modified method of measuring sound velocities in liquids using ultrasonic interferometer was mentioned by Raghupati Rao and Krishna Rao\textsuperscript{37}. Ilgunas and Paulauskas\textsuperscript{38} used a modified version of
interferometer for the measurement of the absorption of ultrasonic waves in liquids. Sukatskas and Yoronis calculated the conditions for a maximum reflection coefficient in a simplified approach when a two transducer interferometer is used and experiments show that the theoretical expression provides a particularly useful lower bound values.

Thiry et al measured ultrasonic velocity in liquids and small biological tissue specimens using phase measurements. The phase measurements are obtained by varying the acoustic path of a stabilized continuous sinusoidal wave between two transducers which are kept fixed in a reference liquid and variations in acoustic path are obtained by moving, perpendicular to it, a precisely wedge shaped plexiglass sample container. This method is to be implemented as a part of an integral velocity and attenuation of ultrasonic continuous wave measurement system.

Leonard and Suguin designed an acoustical interferometer for velocity and attenuation measurements in liquids over a wide frequency range and from room temperature down to low cryogenic temperatures. The fre-
frequencies of the design permit direct and simultaneous measurements of the acoustic wavelength and attenuation.

An acoustic interferometer system is designed for measurement of the speed of sound at atmospheric pressures in approximately one litre quantities (at 20–40°C) within an accuracy of 0.03% by McCartney and Drouin. The phase measurement electronics are based on integrated circuit phase locked loops. Theory and performance of a differential optical interferometer for measuring both surface acoustic waves and bulk waves are described. Wright and Campbell developed an ultrasonic interferometer for the study of liquids in the frequency range of 0.1 to 1.5 GHz. The accuracy in the measurement of velocity is ± 1% and absorption is ± 3%. Leisseur and Priecer developed an improved interferometer for ultrasonic attenuation or velocity measurements, with good sensitivity for the detection of small ultrasonic velocities. For ultrasonic velocity measurements a double crystal interferometer was also used by Hunter and Durdy and Dobbs and Finegold. This method has the advantage of easy measurement at high pressures and over a wide temperature range. This technique was also used by Rudnick and Shapiro. A phase compari-
Son interferometer was used for measurement of ultrasonic velocity in aqueous solutions with an accuracy of ± 0.001%.

Mention may also be made of the interferometric methods used in the determination of ultrasonic velocities in solids and gases. Kritz developed an ultrasonic interferometer for the measurement of velocities in solids. Measurement of acoustic vibrations of objects with the help of an interferometer is described by Demidenko and Shevayvskic. A digital trigger delay unit was designed and developed by Blacker for the measurement of velocity and attenuation in gases.

Brillouin predicted that if a monochromatic beam of light passes through a liquid through which a sound beam is propagated, scattering of light beam may occur. A light wave passing through a liquid medium generates an oscillating dipole at each point, which radiates electromagnetic energy in every direction. If the liquid is perfectly homogeneous, the vector sum of energy scattered in any direction except along the direction of the light wave is zero. The thermal motion of the molecules leads to inhomogeneities and to a period-
dic modulation of the scattering power of the liquid. The scattered light consists of a doublet split symmetrically about the incident frequency. The separation of the scattered light from the incident light equals the frequency of the sound wave responsible for the scattering. Bragg equation

$$n\lambda = 2\lambda_2 \sin \theta$$

($\lambda_1$ and $\lambda_2$ are wavelengths of light and sound respectively and $\theta$ is the angle between the incident light and the plane of grating), is used for obtaining the wavelength of sound. Piercy and Hanes$^{53}$, provided a conceptually simple model for the scattering process which yields the same results. Brillouin scattering has been used in recent times$^{54}$, to measure velocities at hypersonic frequencies ($10^9$-$10^{10}$ Hz). A detailed discussion of the methods for velocity measurement at hypersonic frequencies was presented in the review article entitled "Study of simple liquids by ultrasonic methods" by Sette$^{55}$.

A new method$^{56}$ for the accurate measurement of Brillouin line shift is presented. In this method the relative measurements of $35$ GHz hypersonic velocity with a $10^{-4}$ relative uncertainty is reported.
High-resolution Bragg technique has been used for simultaneous measurements of ultrasonic velocity and absorption in liquids over the frequency range 100-1000 MHz. The technique is applied to the study of vibrational relaxation in the UHF range. The measurement accuracy is better than ± 0.05%.

**VELOCITY MEASUREMENT - PULSE TECHNIQUES**

In the pulse technique, a piezo-electric crystal transducer radiates a short train of periodically repeated pulses returned from a plane parallel reflector which can be moved to and fro normal to the transducer. Direct measurement of transit time of a given pulse enables the evaluation of sound velocity in the medium. Two transducers can also be used instead of a single transducer. The first transducer changes the r.f. electrical pulse into an ultrasonic pulse, while the second transducer receives the ultrasonic pulse and converts it back into an electric pulse. On the other hand, the use of single crystal transducer complicates the electrical circuit because, it is necessary to block the receiver input during the time-interval of the transmitted pulses. But the single transducer method has an
advantage of reducing the dimensions of the measuring cell. The ultrasonic pulse after passing through the medium under investigation and after being converted into electric pulse, is amplified by an amplifier and displayed on the oscilloscope. The oscilloscope time base is triggered by the pulse generator. A change in the path length of ultrasonic pulse causes a change in its time delay, and this time delay is used for determining the velocity of sound. Parthasarathy and Pancholy\textsuperscript{61,62} have used pulse technique to measure ultrasonic velocity in liquids at 21 MHz in the temperature range of 10–50°C.

Cedrone and Curran\textsuperscript{63} have used electric pulse method to measure the velocity of sound in liquids and solids. The accuracy of velocity is better than 1 part in a thousand. Techniques capable of yielding an accuracy of $\pm 0.003\%$ have been developed recently\textsuperscript{24–27}. The range of frequencies employed in these methods is usually 5 MHz to 300 MHz. In exciting the pulse technique to higher frequencies in liquids, difficulties arise from short sound wavelengths and high absorption. This technique cannot be conveniently used for liquids below 5 MHz, because of diffraction problems. A simple and accurate method is described\textsuperscript{64} for determining
the transit time in ultrasonic velocity measurements in liquids using the pulse technique. A time delay measuring circuit is described for a pulse as it is passing through a medium under investigation. The circuit permits the velocity of the sound and its absorption to be measured simultaneously.

Pulse echo overlap (PEO) method is a highly accurate method for measuring ultrasonic velocities. The principle involved in this technique is to make the two signals of interest overlap on the oscilloscope by driving the X-axis with a frequency whose period is the interval between the signals. One signal appears on one sweep of the oscilloscope and the other signal on the other sweep. The X-axis sweep frequency is supplied by the continuous wave (CW) oscillator. Overlap is achieved by adjusting the CW frequency such that its period is equal to the time between the signals. The reciprocal of the CW frequency gives the travel time. The absolute accuracy is due to the fact that the method is capable of measuring accurately from any cycle of one echo to the corresponding cycle of the next echo. Thus, an accuracy of a few parts per million can be achieved.
The pulse superposition method\textsuperscript{68b,68c} is another type of pulse technique. It is also an accurate method but not so versatile as the PEO method, since it cannot accommodate buffer rods or broad band pulses and also multiple echoes are observed with a single transducer. Phase comparison technique\textsuperscript{69} is also one among the various pulse methods. In this method, two delay lines are maintained at a precisely fixed distance apart in the liquid by a fused quartz spacer of known thickness. A pulse of sound waves from the transducer is reflected at both the liquid interfaces. This method is used in the frequency range of 10-200 MHz\textsuperscript{70-72}.

Sing around method is also used to measure velocity of sound in liquids and solids. A sing around velocimeter\textsuperscript{73} is outwardly similar to the ultrasonic delay line employed in digital computers for information storage. The earliest description found is in a patent filed in 1937 by Shephard\textsuperscript{73}. Similar systems are described in later patents by Larsew\textsuperscript{74}. The name 'Sing-around' technique appears to have been coined by Hanson\textsuperscript{75}. Barett and Souni\textsuperscript{76} and several others have constructed apparatus similar to that described here. A pulse of sound waves from a transmitter pass through
the liquid and after amplification and reshaping, the signal is fed back to the transmitting crystal to again generate the next pulse of sound waves. If the repetition frequency of the complete cycle is determined then the velocity of the sound in the liquid can be estimated. The Sing-around technique developed by Greenspan and Tschiegg\textsuperscript{24} was a fixed-path type, and it automatically measures and/or records the speed of sound in non-dispersive liquids. Kock\textsuperscript{77} and several others\textsuperscript{78} have constructed apparatus based on the Sing-around principle.

A description of modifications to the Sing-around technique for velocity measurement has been given by Mayers et al\textsuperscript{79}. In the Sing-around method, a gate is incorporated which effectively lengthens the ultrasonic path by allowing re-triggering on multiply reflected pulses. This allows the use of short solid specimens having low attenuation. In this method an accuracy of 1 in 10\textsuperscript{4} parts can be achieved in measuring the transit time for 10 MHz waves through a low absorbing specimen before correction is made for the effect of transducer specimen bonds, etc. An improved Sing-around technique has been developed by Forgacs\textsuperscript{80}. A
further improved and highly sensitive Sing-around system was developed by the same author. Garnesey et al. developed the Sing-around technique for determining the velocities with an accuracy of ± 0.003%. An improved version of the Sing-around technique for the measurement of velocities in solids has been developed by Brammer.

Satyabala et al. developed a Sing-around technique to measure the ultrasonic velocities in liquids. The accuracy in measurement of velocities is ± 0.5 m/sec. The main feature of this velocity meter is simplicity in its circuitry and operation compared with other developments. Sanjev Chadda et al. developed an ultrasonic velocity meter capable of directly displaying velocity digitally with an accuracy of better than ± 0.3%.

A high speed ultrasonic Sing-around system has been developed by Whitehead and Palmer for the measurement of the velocity of sound in a solid sample to an accuracy of a few parts in 10⁴ in a period of 10 μs. Carstensen developed a differential ultrasonic velocimeter. Conway and Verrall made various improvements to Carstensen apparatus and measured ultrasonic velo-
cities to determine compressibilities.

Mitaku and Sankanishi\textsuperscript{88} have developed a differential ultrasonic velocimeter for the direct measurement of the difference in the ultrasonic velocity between a dilute suspension and the medium. The difference in the ultrasonic velocity in a sample and the medium is directly measured to cancel not only the change in the medium but also the electronic drift with an accuracy of about 5 ppm and a long-term stability of about 5 ppm/day.

Recently Woodward and Salman\textsuperscript{89} developed a programmable ultrasonic velocimeter which is capable of measuring the sound velocities both in liquids and solids with an accuracy of 0.1 m/sec. They designed this instrument for velocity measurements in sea water and it can be programmed to read the velocity to any desired range.

**PRESENT WORK**

For measurement of velocity, in addition to the accurate determination of path length, we need the measurement of frequency of a continuous wave in the
case of the interferometric technique which can be done easily as against the more tedious determination of transit time in the pulse technique. Interferometer has been found to be more suitable for the determination of temperature and pressure coefficient of sound velocity\(^{25-30,52,53,90}\). Aspects which demonstrate the superiority of the ultrasonic interferometer have been discussed in detail by Del Grosso\(^{31}\).

In the present investigation, a single crystal variable path interferometer has been designed and constructed and is used to determine the ultrasonic velocities in liquids. The interferometer consists of an electrically driven X-cut quartz transducer coupled to the liquid column whose length can be varied by moving the reflector parallel to the transducer. Whenever, the distance between the reflector and the quartz transducer corresponds to an integral number of half wavelengths of the travelling sound wave, the liquid column vibrates in resonance. This acoustic resonance gives rise to an increase in the motional impedance of the quartz which in turn gives rise to an electrical reaction on the generator driving the quartz crystal resulting in a sharp increase in the anode current of
the generator or in other words, a sharp dip in the voltage across the transducer. The current or the voltage exhibits a series of maxima or minima separated by half-wavelengths as the reflector distance is varied. The wavelength of the ultrasonic wave is determined by counting the maxima or minima as the reflector is moved towards the transducer through a distance of 20 mm. The velocity is computed using the relation \( U = f \lambda \), where \( f \) is the frequency of excitation of the transducer and \( \lambda \) the wavelength of the sound wave.

The mechanical assembly of the interferometer is designed to give an accuracy of 0.005% in the measurement of path length over a differential distance of 2.5 cms.

A tri-tet crystal controlled r.f. oscillator is used to excite the quartz transducer at 1.0 MHz. The frequency of the oscillator is measured with an accuracy of 1 in \( 10^6 \) parts using a digital frequency meter. The voltage variations across the quartz crystal transducer are observed using a FET Volt meter (Aplab-5001). The details of the electronic circuitry are given in the next section of this chapter.
The interferometer is immersed in a thermostatic water bath whose temperature could be maintained steady at any desired value with an accuracy of \( \pm 0.01 \) K (M/S, Concord Instruments (P), Ltd., - 2500 - India).

The actual cell, in which the test liquid is taken, is of a cylindrical shape with 6 cm inner diameter and a height of 9 cm. The thickness of the cell wall is 0.5 cm. The temperature gradients inside the cell are eliminated by stirring the contents of the cell. The block diagram of the interferometer assembly is shown in Fig. (2.1.1). The set up of the technique is presented in Fig. (2.1.2).

The ultrasonic velocities evaluated from the measurements of wavelengths near the source have to be corrected for diffraction error. The procedure adopted in the present work for the evaluation of diffraction errors is presented in section 2.5 of this chapter.

A number of precautions have been taken to avoid and eliminate sources of errors due to (a) lack of parallelism of the source and reflector, (b) irregularities in the vibration of the source, (c) diffra-
ction effects and (d) wave guide effect.

The interferometer has been selected for the measurement of velocity mainly for the following reasons.

1. The use of differential path length instead of total path length for the determination of wavelength.

2. A simple measurement of frequency as against a more tedious and difficult measurement of transit time in the case of pulse technique.

3. The temperature of the test liquid can be maintained easily and accurately as the cell itself is immersed into the water bath of the thermostat.

4. Low cost of fabrication and ease of operation of the instrument.

Besides eliminating errors due to diffraction, some more precautions taken in this investigation has been explained in detail in the section (2.4).
Fig. 2.1.1. Block Diagram of the Experimental Set up of the Interferometer
2.2 MECHANICAL ASSEMBLY OF THE ULTRASONIC INTERFEROMETER

The mechanical assembly of the interferometer is shown in Fig. (2.2.1) and Fig (2.2.2). The experimental cell of the interferometer 'A' is made up of chromium coated brass tube of 3.5 cm inner diameter. The bottom portion of the tube is partially closed leaving an opening of 1.95 cm in diameter. A gold coated quartz crystal (X-cut) 'O' is held tight to the opening with a teflon O-ring 'b'. This is achieved by holding the teflon ring 'D' in position and tightening three screws with optimum pressure using three nuts 'N'. The inner surface of the crystal touching the bottom of the cell acts as the ground terminal. A phosphor bronze strip 'H' fixed to the teflon ring by pressing it against the other face of the crystal forms the second lead for electrical connections. The experimental cell is rigidly mounted on chromium plated brass cup 'U' with a neoprene O-ring seal to prevent the outer surface of the crystal coming into contact with water when the interferometer is immersed in the thermostatic water bath.

A chromium coated metal reflector 'R' spring loaded
in the recess of head 'C' was actuated by the micro-
meter screw 'S' (type Mitutoyo No.110-102). The
pitch of the screw used to move the reflector 'R'
of diameter 2.4 cms is 0.5 mm and the head scale consi-
sts of 50 divisions. It consists of a vernier scale
and thus gives the reading to an accuracy of 0.0001 cm.
The bottom of the screw is coupled to the reflector rod
through a steel ball '3' which eliminates the errors
due to non-axiality between them besides keeping the
reflector free to move axially without rotating along
with the screw. A pin 'P' screwed into a slot connec-
ted to the head 'C', guides the reflector to move with-
out any rotation. The reflector is spring loaded to
eliminate back-lash in the screw. The head 'C' is
rigidly mounted on the cell 'A' by three screws with
a neoprene O-ring seal to prevent leakage of thermostat
water into the cell. The stirrer 'I' helps to elimi-
nate the temperature gradients in the experimental
liquid. The spring reflector and stirrer are chromium
plated. 'T' is a thermistor used to measure the tempe-
rature of the experimental liquid.

An X-cut quarts crystal with a fundamental frequen-
cy of 1.0 MHz used as transducer to measure the
velocities at 1.0 MHz.

The interferometer has the following features to achieve the nearest approximation to the ideal conditions required by theories\textsuperscript{91,92}. The present crystal mounting is a good approximation to a piston in an infinite baffle. The ratio of the cell diameter to the crystal diameter is \( \sim 2 \), which is close to the recommended ratio of two or greater than two\textsuperscript{91,92}. 
Fig. 2.2.1. ULTRASONIC INTERFEROMETER.
A tri-tet crystal controlled oscillator was constructed to produce steady electrical signals. The control crystal is of 1.0 MHz frequency. The operational features of the tri-tet oscillator (employing a pentode) are essentially the same as those of a conventional tuned plate crystal controlled oscillator except that the tank circuit is in series with cathode and the screen grid is effectively grounded to radio frequencies. The tank circuit in the plate of oscillator valve is tuned by the capacitor $C_5$. The tuning is observed on an oscilloscope, (SPL-SBO-31058). The output voltage of the oscillator is coupled to the transducer 'Q' via the tuned circuit. The variations of the voltage across the crystal due to changes in the motional impedance are detected using a difference amplifier and detector.

The difference amplifier provides a high gain in detecting the minima points accurately. One of the grids of the difference amplifier is fed with the r.f. voltage developed across the transducer while the other grid is maintained at a suitable d.c. potential which
can be varied with the help of the potential division network. This controls the sensitivity of the difference amplifier. When the current through both the sections of the valve is nearly the same, the voltage across the FET voltmeter terminals tends to zero value.

Variation of the radiator to reflector distance through the liquid medium causes changes in the motional impedance of the transducer leading to r.f. voltage variation across one of the grids. These variations after amplification are measured by the electronic FET voltmeter which has provision for measurement of both negative and positive voltages. The voltage minimum is first detected with a higher range of the meter which was then switched over to lower range and final adjustment is made to locate the position of minimum voltage. In order to prevent any possible heating of the experimental liquid, the voltage developed across the crystal is always kept at low value. The required high tensions for the oscillator and the amplifier are drawn from an electronically regulated power supply. The frequency of oscillator after tuning is exactly measured using a frequency counter. (Power Systems and Projects Limited, Counter/Timer 3077, India).
2.4 EXPERIMENTAL PROCEDURE:

The ultrasonic velocities for the binary systems studied are measured at three different temperatures viz., 303.15 K, 313.15 K and 323.15 K for nine systems.

Method of determination of ultrasonic velocity has been described in section 2.1 of this chapter. However, the actual method of finding the wavelength at 1 MHz is presented in this section.

The readings of the position of the first six successive minima (the minima are found to be sharp at higher resolution) are noted first and then counting the dips upto 21st, the readings of the 21st to 26th successive minima are taken. The difference of the readings of 21st and 1st, 22nd and 2nd, and upto 26th and 6th in succession give six sets of $20\lambda/2$ values. The six sets are found to be almost equal. This also confirms the proper measurement of velocity, stability of temperature of water in the bath and the absence of temperature gradient in the cell containing the experimental liquid. By taking the average of these values the wavelength is calculated and hence the velocity. The calculated error in velocity obtained by this pro-
procedure is ± 0.003% (which is approximately 0.05 metres at a velocity of 1600 m/sec).

The performance of interferometer is checked by comparing the sound speed values recorded in the pure liquids with those reported in the literature, and the values are presented in the Table (2.4.1).

Table : 2.4.1

Sound velocities of some pure liquids at 303.15 K.

<table>
<thead>
<tr>
<th>Component</th>
<th>Sound velocity U m/sec</th>
<th>Present work</th>
<th>Literature(^{24, 137})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbontetrachloride</td>
<td>905.08</td>
<td></td>
<td>904.00</td>
</tr>
<tr>
<td>m-xylene</td>
<td>1302.88</td>
<td></td>
<td>1302.00</td>
</tr>
<tr>
<td>heptane</td>
<td>1111.85</td>
<td></td>
<td>1112.00</td>
</tr>
<tr>
<td>1-butanol</td>
<td>1226.49</td>
<td></td>
<td>1225.00</td>
</tr>
<tr>
<td>triple distilled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>1509.14</td>
<td></td>
<td>1509.44</td>
</tr>
</tbody>
</table>

2.5 **Effect of Diffraction on Velocity Measurement**

Diffraction of the ultrasonic beam very often leads to appreciable errors in the velocity and absorption mea-
surements\textsuperscript{94,95}. These errors are predominant near the radiator and decreases for differential distances farther from it. The velocities measured near the source are higher than plane wave velocities. These errors are systematic in nature and amenable to theoretical and empirical studies.

Attempts have been made by a number of workers\textsuperscript{90,94-101} to evaluate diffraction errors by considering free-field diffraction, piston source in an infinite baffle, large enough source and other geometric conditions.

Krasnushkin\textsuperscript{102} has discussed in detail the nature of errors due to diffraction effects under free-field conditions. The excess velocities derived from the theory are given by

\[
\frac{\Delta C}{C} = \frac{\lambda^2}{31.5 a^2} \quad (2.5.1)
\]

where \( \lambda \) is the wavelength and \( a \) is radius of the piston source.

Del Grosso\textsuperscript{90,96,97} by considering the fluid to be right circular cylinder of finite radius and the length terminated at one end by piston transducer set in an
infinite baffle and closed at the other end by a plane reflector and considering the iterative reflection modes of the fluid, has derived radiation impedance of the crystal using the King's expression for velocity potential. The real and imaginary parts of the radiation impedance were studied as a function of the source to reflector distance for certain standard reference parameters. The excess velocities evaluated from these studies indicate that, as the separation between the reflector and the radiator increases the error decreases.

The free-field diffraction predicted by the theoretical expression due to Bass and Williams as cited by McSkimin is given by

\[
\frac{\Delta C}{C} = \frac{\lambda}{4\pi^2 \alpha z^{3/2}} \quad (2.5.2)
\]

where 'z' is the distance between the radiator and reflector. Measurements carried out by McSkimin on solids confirm the above relation of Bass and Williams. Ilgunas et al. have studied diffraction effects in liquids, but they have not attempted to correlate their results with theory.
Subrahmanyan et al.\textsuperscript{106} have studied the diffraction effects in liquids in order to test the applicability of the relation given by Bass and Williams. They found that the diffraction errors are 3.2 times the value envisaged in the theory. Hence,

$$\frac{\Delta C}{C} = \frac{3.2 \lambda}{2 \pi^2 a z^{1/2}} \quad (2.5.3)$$

This relation has been used in the present work to evaluate the diffraction errors and the experimental velocities are corrected accordingly since the mechanical assembly of the interferometer is similar to the one used by these workers. The velocities measured in triple-distilled water after applying diffraction correction are in good agreement with Greenspan\textsuperscript{24} values.
2.6 MEASUREMENT OF DENSITY

2.6.1 Brief Review of Previous Work Done:

Determination of isentropic compressibilities and other thermodynamic parameters requires an independent measurement of density. As the density is one of the factors in determining the ultimate accuracy of these parameters, the density measurement should be made with a high precision.

The methods of density measurements may be classified into the following categories on the basis of apparatus used:

(a) Pyknometers
(b) Dilatometers and
(c) Other diverse methods.

(a) Pyknometers:

The measurement of density by using pyknometers is the most simplest and least expensive in terms of readily available equipment but may be the most expensive in terms of time. Bauer and Lewin have thoroughly reviewed the methodology of density measurement. A
filatometer to determine densities to the fourth decimal place was described by Gay-Lussac. An improved form of Gay-Lussac’s pyknometer bottle was constructed by Johnston and Adams, which was useful for both solids and liquids. This pyknometer gives density values which are accurate to 5 parts in $10^6$. Wood and Brusic designed single armed pyknometer which can be used for determination of densities up to fourth decimal place. Mathot and Desmyter designed a pyknometer which consists of a cylindrical bulb provided with two parallel graduated capillary tubes and capable of fifth decimal place accuracy. Sprengel and Ostwald employed a pyknometer which was essentially a U-tube in shape with side arms being made of small bore capillaries. It could be filled with less evaporation and, therefore, was suitable for solutions of volatile liquids. Bi-capillary pyknometers which can be used for measuring densities of a variety of organic liquids were described by Robertson, Parker and Parker, Smith, and Ward and Brooks. designed a bicapillary pyknometer for measuring densities of a single sample at various temperatures. Lipkin et al. also describes a convenient bi-capillary pyknometer which is self-filling in
type and which offers an accuracy of 1 to 2 parts in $10^4$ in the case of volatile liquids. These workers also reported that loss of vapour due to diffusion becomes negligible when the total length of the unfilled capillary is over 10 cm in length.

(b) Dilatometers:

Neubeck\textsuperscript{118} described a dilatometer for the determination of density in terms of weight of the mercury expelled or added to the dilatometer when the temperature is raised. Improved versions of weight dilatometers were reported by Burlew\textsuperscript{119} and, Wirth and Losourdo\textsuperscript{120} Hildebrand and Carter\textsuperscript{121} described a double armed dilatometer which is used for both direct measurement of excess volumes and their temperature dependence.

(c) Diverse methods:

Among the other methods the buoyancy method is one. This method\textsuperscript{122, 123} is based on Archimedes principle and can be used for temperature variation studies. Under optimum conditions, this method is capable of yielding an accuracy of 2 in $10^6$ parts.

Mechanical oscillator densimeter is another method. It works on the basis of the principle of mechanical
oscillator and was used by several workers\textsuperscript{124-129}. An improved version of the above method was suggested by Coates et al.\textsuperscript{129} and Radojkovic et al.\textsuperscript{130}. An automated apparatus for measuring the densities of the pure liquids and liquid mixtures of varying composition was described by Adams et al.\textsuperscript{131} and Picker et al.\textsuperscript{128}.

Sauer and Lewin\textsuperscript{107} have described another method known as "Temperature floatation or isopycnic temperature method". Mention may also be made of Magnetic float densimeters. An excellent account of various precautions to be taken for the design of such densimeters has been given by Hales\textsuperscript{132}. Weeks and Benson\textsuperscript{133} used this type of densimeters for the determination of excess volumes and claimed an accuracy of 20 ppm. In recent years there appeared a number of other designs\textsuperscript{134-136}. 
g.2.6.1 Pyrometer
2.6.2 PRESENT EXPERIMENTAL TECHNIQUE—PYKNOmeter METHOD

In the present work a double stemmed pyknometer (Fig. 2.6.1) was employed to determine the densities of pure liquids and liquid mixtures. The pyknometer was similar to that of Parker and Parker type with minor modifications. It consists of a bulb that holds about 10 c.c. of liquid. The stems were made up of a capillary tube of uniform bore of about 1 mm. The stems were bent to the sides making an obtuse angle at the bend. The marks were also made on the two stems at about the same level to conveniently read the difference between the liquid levels and marks in the two stems. The open ends of the stems were closed with teflon caps in order to prevent the loss of liquid by evaporation and to ensure that the pressure inside the capillary tubes was equal to the atmospheric pressure. The well cleaned and dried pyknometer was weighed accurately with reference to a dummy. The weighing is done with a chemical balance. The liquid was introduced with the help of a hypodermic syringe until the levels of liquid in both the stems very nearly corresponds to the marks on the stems. To measure the density at constant temperature, the pyknometer was kept vertically in a thermostatic bath main-
tained at a constant temperature for about half an hour. This permits the unfilled part of the stems to be drained completely and allow liquid vapour equilibrium to be established. The amount of liquid at the initial filling was adjusted to allow for expansion (or contraction) due to difference of temperature between the bath and the surroundings. The difference in heights of the liquid between the mark and the lowest point in the meniscus in both the limbs were measured using a travelling microscope which could read up to 0.01 mm. In obtaining the difference between the mark and meniscus correction was employed for the liquid contained in the meniscus above the lower point. Since the meniscus in the case of water can other solutions employed in this work was hemispherical, one-third of the radius of the capillary tube was added to the observed height. The pyknometer was then removed from the bath, wiped with a clean damp cloth and kept in the balance, and allowed to hang for a few minutes before weighing. If $V_1$ is the volume of the pyknometer between the marks, the density of the enclosed liquid can be determined using,

$$
\rho = \frac{M}{V_1 + dv}
$$
where 'M' is the buoyancy corrected mass of the liquid, and dV is the volume of the experimental liquid above or below the reference marks. The volume (dV) was calculated using the formula $\pi r^2 h$, where 'r' is the radius of the capillary tube and 'h' the corrected difference in height between the mark and meniscus in both the stems. An accuracy of 1 to 2 parts in $10^5$ in density measurements was realised when the experimental liquid was maintained at $\pm 0.01^\circ C$ by the thermostat.

2.7 **Purification of Compounds**:

The chemicals n-octanol (BDH), n-decanol (Fluka), n-dodecanol (BDH), formamide (BDH), 1,4-dioxan (BDH) and cyclohexanone (BDH) were purified by the standard methods described in the literature 137-140.
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