Chapter - II

Experimental Methods

Excess volumes, Isentropic compressibilities, Excess enthalpies and Solid-liquid Equilibria
EXPERIMENTAL METHODS

The purity of chemicals is of utmost importance in any experimental work on the thermodynamic properties. The chemicals used in the present work were purified by the standard methods described in the literature\textsuperscript{13}.

\textbf{N,N-dimethylacetamide (Sisco, India)} by shaking with barium oxide and distilled at reduced pressure from barium oxide. DMA was kept over night, over calcium hydride and was distilled at reduced pressure.

\textbf{N,N-dimethylformamide (Fluka)} was kept overnight over freshly ignited quick lime and distilled under reduced pressure. The middle fraction of the distillate was collected and kept over solid potassium hydroxide pellets for 24 hours. It was then distilled under reduced pressure.

\textbf{1,2-dichloroethane (Fluka)} was washed with dilute solution of potassium hydroxide and then with water. It was dried over phosphorous pentoxide and distilled twice and the middle fraction was collected.

\textbf{1,1,1-trichloroethane (Aldrich)} was washed with concentrated sulphuric acid, then with 10 percent sodium chloride solution. It was dried over calcium chloride and distilled twice and the middle fraction was collected. During the distillation about 0.5 grams of phenol was added as a stabilizer.

\textbf{1,1,2,2-tetrachloroethane (Fluka)} was stirred with concentrated sulphuric acid at 80\textdegree C for 10 minutes. The decoloured acid was removed and again 25 ml of the acid was added. The liquid was then washed with water, dried over potassium carbonate and distilled under vacuum. During the distillation about 0.5 grams of phenol was added as a stabilizer.
Trichloroethene (BDH) was steam-distilled from 10 percent calcium hydroxide slurry. The oil phase was cooled to -30°C to -50°C and ice was removed by filtration. The filtrate was fractionally distilled. The middle fraction was collected in a receiver covered with a black paper.

Tetrachloroethene (BDH) was dried over sodium sulphate and fractionally distilled.

Fluorobenzene (Aldrich) was dried with calcium chloride and fractionally distilled.

Chlorobenzene (E. Merck, India) was dried with calcium chloride and fractionally distilled.

Bromobenzene (BDH) was dried with calcium chloride and fractionally distilled under reduced pressure.

Nitrobenzene (BDH) was dried over anhydrous calcium chloride for two days and the dried sample was distilled in a fractionating column, under reduced pressure.

Aniline (BDH) was dried over caustic potash for about two days and distilled twice.

Ethylbenzene (Aldrich) was purified by shaking with 6 ml portions of concentrated sulphuric acid until the layer was colourless and then with sodium carbonate solution. The sample was then shaken with water and finally dried twice with magnesium sulphate. After two distillations over sodium, the middle fraction of the second distillate was taken.
Methylethylketone (BDH) was treated several times with saturated potassium carbonate solution. The two layers were then separated. The ketone layer was distilled to remove the water. It was then dried for one day over anhydrous potassium carbonate and fractionally distilled.

Methylisobutylketone (BDH) was dried over potassium carbonate for 3 days, then boiled for two hours and fractionally distilled.

Methylpropylketone (Fluka) was dried over with potassium carbonate for three days, boiled for two hours and fractionally distilled.

Diethylketone (Fluka) was dried over anhydrous sodium sulphate for two days and fractionally distilled.

Cyclopentanone (Fluka) and Cyclohexanone (BDH) were dried over anhydrous sodium sulphate for two days and then fractionally distilled.

Acetophenone (BDH) was kept over anhydrous calcium chloride for three days, filtered and then fractionally distilled.

Hydrocarbons commercially available with analytical grade n-alkanes were directly used without purification.

Mercury was first run into a fine stream through a long length of 5 percent nitric acid and the process was repeated second time and mercury finally
passed through a column of water. It was then dried by means of filter paper and then run through a hardened filter paper with a pin hole at the apex of the cone. The dried sample was finally distilled twice under reduced pressure using Gallenkamp mercury distillation apparatus.

**Water** deionised water (permunit process) was distilled twice. To each litre of the distillate 0.2 g of potassium permanganate and 0.5 g of sodium hydroxide was added. This alkaline solution was slowly distilled from an all-pyrex vessel and the middle fraction was collected. The purity of the sample was checked by measuring the conductivity.

The boiling points, corrected to one atmospheric pressure and densities determined at 303.15 K of the purified samples are presented in Table 2.1 along with the literature values\(^2\text{6}\). Dissolved gases in organic liquids are often a source of bubble formation which introduces an error in density and excess volume. In order to overcome this difficulty, all the liquids were degassed.
### TABLE-2.1

Boiling points and densities of pure components at 303.15 K.

<table>
<thead>
<tr>
<th>Component</th>
<th>Boiling point °K</th>
<th>Density g/cm³</th>
<th>Component</th>
<th>Boiling point °K</th>
<th>Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
<td>Literature</td>
<td>Present work</td>
<td>Literature</td>
<td></td>
</tr>
<tr>
<td>N,N-dimethylacetamide</td>
<td>439.15</td>
<td>439.26</td>
<td>0.932 40</td>
<td>0.932 43</td>
<td></td>
</tr>
<tr>
<td>N,N-dimethylformamide</td>
<td>426.10</td>
<td>426.15</td>
<td>0.941 18</td>
<td>0.941 20</td>
<td></td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>356.70</td>
<td>366.63</td>
<td>1.238 43</td>
<td>1.238 47</td>
<td></td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>347.00</td>
<td>347.16</td>
<td>1.320 94</td>
<td>1.320 95</td>
<td></td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>419.25</td>
<td>419.35</td>
<td>1.578 57</td>
<td>1.578 60</td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>360.40</td>
<td>360.34</td>
<td>1.451 39</td>
<td>1.451 40</td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>394.45</td>
<td>394.35</td>
<td>1.606 41</td>
<td>1.606 40</td>
<td></td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>357.80</td>
<td>357.88</td>
<td>1.013 16</td>
<td>1.013 14</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>404.75</td>
<td>404.83</td>
<td>1.095 47</td>
<td>1.095 50</td>
<td></td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>429.15</td>
<td>429.05</td>
<td>1.481 47</td>
<td>1.481 50</td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>483.80</td>
<td>483.86</td>
<td>1.193 39</td>
<td>1.193 41</td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td>457.55</td>
<td>457.55</td>
<td>1.013 14</td>
<td>1.013 17</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>409.45</td>
<td>409.33</td>
<td>0.857 66</td>
<td>0.857 70</td>
<td></td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>262.68</td>
<td>262.79</td>
<td>0.794 49</td>
<td>0.794 52</td>
<td></td>
</tr>
<tr>
<td>Diethylketone</td>
<td>375.06</td>
<td>375.16</td>
<td>0.804 60</td>
<td>0.804 61</td>
<td></td>
</tr>
<tr>
<td>Methyl propyl ketone</td>
<td>373.48</td>
<td>373.55</td>
<td>0.796 61</td>
<td>0.796 56</td>
<td></td>
</tr>
<tr>
<td>Methyl isobutyl ketone</td>
<td>383.66</td>
<td>389.65</td>
<td>0.796 07'</td>
<td>0.796 10'</td>
<td></td>
</tr>
<tr>
<td>Cyclopentanone</td>
<td>403.76</td>
<td>403.80</td>
<td>0.928 98</td>
<td>0.929 02</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>428.70</td>
<td>428.80</td>
<td>0.937 60</td>
<td>0.937 61</td>
<td></td>
</tr>
<tr>
<td>Acetophenone</td>
<td>576.05</td>
<td>575.15</td>
<td>1.019 42</td>
<td>1.019 47</td>
<td></td>
</tr>
</tbody>
</table>

* at 298.15 K
Characteristics of the hydrocarbons are given in Table 3.20.
EXCESS VOLUME

Excess volumes of binary liquid mixtures can be determined in two ways: (i) Directly by observing the change in volume upon mixing the components in a dilatometer and (ii) Indirectly by measuring densities of pure liquids and liquid mixtures. The different methods for the determination of excess volumes were critically reviewed by Battino, Marsh, and Handa and Benson.

1. DIRECT METHOD

Direct methods are capable of giving more accurate and reliable results than the indirect methods. Two basic designs for direct measurement of $V^E$ are available; they are (a) batch or single composition dilatometers and (b) dilution dilatometers.

(a) Batch or single composition dilatometers

Batch dilatometers were designed by Keyes and Hildebrand (cf. Fig. 2.1) for direct measurement of $V^E$. Bellemans used an apparatus similar to that of K-H's apparatus which had a provision for degassing the liquids. It could be used for measurement of small values of $V^E$ with a precision of ±0.002 cm$^3$ mol$^{-1}$. Brown and Smith used a modified form of K-H's apparatus which is easier to fill and handle.

Kehlen and Sackmann used a similar apparatus to measure $V^E$ for mixtures of cyclohexane with several tetrachlorides. Diaz Pena and Hay...
Fig. 2.1: KEYES AND HILDEBRAND APPARATUS.
designed an apparatus and it had a precision of ± 0.001 cm³ mol⁻¹. Rastogi and Nath¹⁶ modified the dilatometer of Brown and Smith by attaching the capillary to the side of the bulb and ground glass stoppers to the two bulbs. This apparatus which permits the use of degassed solvents, is easy to fill and offers an accuracy of ± 0.001 cm³ mol⁻¹. Diaz Pena and McGlashan¹⁶ determined the volume change upon mixing using a double piezometer meant for the determination of isothermal compressibility. Staveley and Spice¹⁷ designed a dilatometer that had a total capacity of 110 cm³ and the volumes of the two components differed considerably. Therefore, this apparatus is useful for the measurement of VE of the mixtures wherein one of the components is in excess. Duncan et al.¹⁸ described a dilatometer which eliminates the use of ground glass stoppers. The volume change is measured by the change in height of meniscus in the capillary attached to the centre of the apparatus. Further, this apparatus permits the change of capillaries. The precision attainable is about ± 0.002 cm³ mol⁻¹. A modified form of K-H's apparatus was used by Wirth and Mills¹⁹ to measure volume changes on mixing for aqueous solutions of inorganic salts. Zamyatnin²⁰ has described a dilatometer capable of detecting volume changes of the order of 5 x 10⁻⁶ cm³ accompanying chemical reactions. Ahmed et al.²¹ and Brennan et al.²² have modified the dilatometer described by Powell and Swinton²³. The modified apparatus eliminates the error due to evaporation of volatile components during injection. Stookey et al.²⁴ have described a batch dilatometer technique for the determination of VE. In this method sixteen cells were used in a batch to cover the entire mole fraction range. These workers have also discussed in detail the errors associated with the determination of excess volume. It is
stated that the following factors contribute to the total error in $V^*$ measurement: (i) purity of the liquids, (ii) temperature fluctuations, (iii) uncertainty in cathetometer reading, (iv) component weighing, (v) capillary temperature correction and (vi) compressibility.

(b) Dilution dilatometers

Dilution dilatometers for measuring excess volumes offer an advantage in which the composition range can be covered in two runs and partial molar excess volumes are readily obtained. Since the publication of design by the Geffeken et al. dilution dilatometers have undergone a number of modifications. Dilatometers employed in the initial stages had large mixing cells. The capacity varied from 250 to 600 cm$^3$. This was done in order to obtain good precision in detecting the volume changes. Recent developments have been aimed at making dilatometers with smaller mixing cells, fewer stopcocks or none at all and simple to operate without sacrificing precision.

Stakes et al. have described a dilution dilatometer with which they obtained a standard deviation of 0.0008 cm$^3$ mol$^{-1}$ for the test system, cyclohexane + benzene. Martin and Murray have slightly modified the design to facilitate the clearing, filling and calibration procedures and a simple version has been reported by Reeder et al. The later dilatometer has the disadvantage that there is always premixing of the two components. Hence, the commencement of dilution can not be defined clearly. However, with careful manipulation, error from this source can be reduced. The design
due to Dickison et al.\textsuperscript{32} offers advantages in the method of filling, the ease of operation and the elimination of premixing. They have reported a standard deviation of 0.002 cm\textsuperscript{3} mol\textsuperscript{-1} for the test system. Another dilution dilatometer similar to that of Pflug and Benson\textsuperscript{33} has been reported by Diaz Pena and Delgad\textsuperscript{34}. In almost all of these dilatometers, the mixing cells have a capacity of about 50 cm\textsuperscript{3}, part of which is occupied by mercury. Bottomley and Scott\textsuperscript{35} constructed a dilution dilatometer without greased stopcocks in which no stopcock is turned or adjusted during dilution runs. They have used this dilatometer for measuring excess volumes of the order of 0.005 cm\textsuperscript{3} mol\textsuperscript{-1}. Although the dilatometer is easy to operate it suffers from the drawbacks: (i) it is difficult to calibrate and (ii) filling, which is done under vacuum, is quite tedious. Further it is limited to measuring small volume changes only. Kumaran and McGlashan\textsuperscript{36} have published an improved version of grease free tilting dilution dilatometer which is easier to operate and can be filled under atmospheric pressure. It is easy to calibrate and can be used for measuring $V^2$ of any magnitude.

A drawback in almost all of the dilution dilatometers described so far is that they do not measure volume changes at a constant pressure. Consequently, a few designs for dilution dilatometers, which can be operated at constant pressure have been reported. Among such dilatometers the one due to Tanaka et al.\textsuperscript{37} which is a simple version of the one described by Chareyron and Clechet\textsuperscript{38}. The dilatometer, though difficult to operate, is capable of high precision. The reported standard deviation for the test system is 0.00043 cm\textsuperscript{3} mol\textsuperscript{-1}. A rather unconventional design for a dilution
The dilatometer used for measuring excess volumes in the present study, was similar to that of Brown and Smith\textsuperscript{12}, with an addition of detachable capillary arrangement. The dilatometer consisted of a U-tube of pyrex glass (cf. Fig. 2.2) with mercury at the bottom to separate the two components. One arm of the U-tube was terminated with B-10 standard joint (socket) and the other arm with B-14 joint (socket). One of the sockets was closed with B-10 stopper (or B-14 stopper) and the other was fitted with standard B-14 cone (or B-10 cone) fused on to a suitable capillary tube (i.d. 1.0 mm or 2.0 mm), having a teflon cap with a small orifice to insure that the pressure inside the capillary was equal to the atmospheric pressure. The cone and stopper are interchangeable. This permits the use of the apparatus for the measurement of $V^B$ over a range of composition. Four dilatometers of this type, which differed in the capacities of the compartments A and B, were used to cover the entire range of composition. Composition of each mixture was determined directly by weighing. This offers an accuracy in fourth decimal place. The dilatometer, along with the contents was kept in a water thermostat controlled at 303.15 ± 0.01 K. The dilatometer was allowed to stand in the thermostat till it attained the temperature of the thermostat. This was indicated by the constancy of the liquid meniscus in the capillary as seen through a travelling microscope which could read upto 0.01 mm. The position of the constant liquid level, relative to reference mark on the capillary tube, was then read. The dilatometer was removed from the
therrnostat and then were mixed thoroughly by tilting the apparatus repeatedly. The dilatometer was immersed in powdered ice in order to drain the liquid in the capillary into the compartment carrying the capillary. This facilitated the complete mixing of the components. This apparatus was kept in the thermostat. The position of the liquid level, relative to the reference mark, was again noted after the dilatometer attained the thermal equilibrium. The molar excess volume, \( V^* \) was calculated using the relation,

\[
V^* = \pi r^2 \Delta h \left( n_1 + n_2 \right)^2
\]  

(2.1)

Where \( r \) is the radius of the capillary, \( \Delta h \) is the change in liquid level on mixing and \( (n_1 + n_2) \) is the total number of moles of the mixture. The excess volumes are reproducible to \( \pm 0.003 \text{ cm}^3 \text{ mol}^{-1} \).

The performance of the dilatometer was checked by measuring excess volumes of the test system, cyclohexane + benzene at 298.15 K and comparing the results with those reported in the literature (cf. Table 2.2).

**TABLE-2.2**

Values of excess volume for equimolar mixture of cyclohexane benzene at 298.15 K.

<table>
<thead>
<tr>
<th>( V^* ) ( \text{cm}^3 \text{ mol}^{-1} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.640 ± 0.003</td>
<td>Present work</td>
</tr>
<tr>
<td>0.639 ± 0.007</td>
<td>Watson <em>et al.</em>(^{27})</td>
</tr>
<tr>
<td>0.639 ± 0.005</td>
<td>Powell and Swinton(^{23})</td>
</tr>
<tr>
<td>0.651 ± 0.004</td>
<td>Stookey <em>et al.</em>(^{24})</td>
</tr>
<tr>
<td>0.638 ± 0.003</td>
<td>Rao(^{40})</td>
</tr>
</tbody>
</table>
INDIRECT METHOD

The methods of density measurements may be classified into the following categories on the basis of apparatus used: (a) pycnometers (b) dilatometers and (c) other diverse methods.

(a) Pycnometer

Density measurements using pycnometers still remain the simple and least expensive procedures in terms of readily available equipment but may be the most expensive in terms of time. Gay-Lussac described a pycnometer similar to a specific gravity bottle to determine densities which are accurate to fourth decimal place. The design of pycnometer has been modified by several workers. Parker and arker and Ward and Brooks designed a bicapillary pycnometer for measuring densities of a single sample at various temperatures. Pycnometer measurements are subjected to a number of corrections, the more important one being the corrections for buoyancy and amount of liquid or liquid mixtures in the vapour phase. Brown and Lane have exhaustively discussed the effects of various factors such as isotope composition, dissolved gases, impurities, pressure and temperature on density measurements.

(b) Dilatometers

Neubeck described a dilatometer for the determination of density in terms of the weight of the mercury expelled or added to the dilatometer when the temperature is raised. Improved versions of weight dilatometers were
Hildebrand and Carter\textsuperscript{51} described a double-armed dilatometer, which is used for the direct measurement of excess volumes and their temperature dependence between 298.15 K and 303.15 K.

(c) **Diverse methods**

(i) **Balancing column method**

It is based on the principle that the hydrostatic pressure of a given weight of liquid is proportional to its density and this method is useful when small quantities of liquids are available. It is capable of offering an accuracy of 2 in $10^4$ parts.

(ii) **Buoyancy method**

This method\textsuperscript{62,63} is based on Archimedes principle and can be used for temperature variation studies. However it is less widely used as it is difficult to maintain temperature and avoid surface tension effects. Under optimum conditions the method is capable of yielding an accuracy of 2 in $10^6$ parts.

(iii) **Mechanical oscillator densimeter method**

A densimeter which works on the basis of principle of mechanical oscillation was used by several workers\textsuperscript{54-58}. The major sources of error in this method are temperature fluctuations and variations in mole fraction during operation. These factors can easily be controlled in the manner suggested by Goates \textit{et al.}\textsuperscript{55} and Radvjkovic \textit{et al.}\textsuperscript{60}. Adams \textit{et al.}\textsuperscript{61} have described an automated apparatus for measuring the densities of the pure liquids and liquid mixtures of varying composition.
(iv) Magnetic float densimeter method

These densimeters operate on the principle of balancing the opposing effects of gravity, buoyancy and magnetic field on a float containing a permanent magnet or a soft iron core. This is done by passing current through a solenoid placed below the cell containing the liquid. Density is related to the current at which the float first lifts off from the bottom of the cell. Normally such densimeter can cover only a relatively small density range and requires relatively large volumes of the sample for good precision. The densities of liquids and liquid mixtures can be determined with an accuracy of 1 part in $10^6$. Recently Weeks and Benson and Barman and Rahim have used magnetic float densimeters for the determination of excess volumes. A few other designs have also been reported by Senter, Almeida and Crouch and Hodgins and Beams.

ISENTRONIC COMPRESSIBILITY

Isentropic compressibilities of liquids and liquid mixtures are determined directly by piezometric method or indirectly from precise sound speed and density.

(a) Direct piezometric method

The direct measurements are usually made by compressing the liquid in a glass tube or in a metal tube to a pressure of about one bar above atmospheric pressure. The change in isentropic volume when the excess pressure is suddenly released, can easily be observed if the vessel has a capillary neck. A small correction must be made to the measured value of $k_s$. This correction is ascribed to compressibility of glass or metal vessel.
Piezometric measurements involving organic liquids were first made by Tyrer. Two types of piezometers were used and one of it was made up of copper. It offered an accuracy of one percent. It was observed that the copper piezometer was convenient to handle and the correction to be made for the compressibility of copper was found to be negligible. Staveley et al. measured \( k_v \) values of a number of liquids and of binary liquid mixtures up to 343.15 K. Similar measurements were made by Harrison and Moelwyn-Hughes, and Shinoda and Hildebrand using all glass piezometers.

Díaz Pena and McGlashan designed a single piezometer to measure the isothermal compressibility of mercury, CCl\(_4\) and water at pressure up to 30 atm and temperature up to 333.15 K. Later Díaz Pena and McGlashan used a double piezometer to measure the compressibilities of mixtures of CCl\(_4\) + cyclohexane in the temperature range 283.15 K. Holder and Whalley measured the compressibilities of pure liquids and liquid mixtures of carbon tetrachloride and cyclohexane in benzene in the temperature range 298.15 K to 348.15 K and a pressure range, 5 to 100 bars, using all-glass piezometer. All the above measurements were accurate to one percent.

Ewing et al. measured isothermal compressibility, thermal expansivity and thermal pressure coefficient of benzene + cyclohexane at 298.15 K with the aid of dilution piezometer. The apparatus is capable of a precision of ± 2 TPa\(^{-1}\).

(b) **Indirect measurement of isentropic compressibility**

Isentropic compressibility \( k_s \) of liquids and liquid mixtures can be calculated using sound velocity \( u \) and density \( \rho \) using the expression:

\[
k_s = u^2 \rho^{-1}
\]  

(2.2)
SOUND VELOCITY (\(u\))

The techniques were used to measure the sound velocity can be broadly divided into two categories:

(a) Continuous wave technique and
(b) Pulse technique.

Continuous wave techniques include optical methods\textsuperscript{74-78} based on the study of acoustic grating and interferometric methods\textsuperscript{79-81}. Variable path interferometers have been widely used and recent advances permit accuracies of a few parts per million in sound velocity measurements. Hunter and Dardy\textsuperscript{82} measured sound velocity at 500 MHz with a double crystal serving as detector.

Sound velocity measurements were also carried out with other types of interferometers in which the resonance of a liquid filling cavity was studied. Dobbs and Finegold\textsuperscript{83} used a barium titanate cylinder, filled with the experimental liquid, plated in such a way that one half acted as a receiver. Sound velocity values for fourteen binary liquid mixtures using a single crystal interferometer at 400 KHz was measured by Fort and Moore\textsuperscript{84}. The interferometer was similar to that of Hubbard and Loomis\textsuperscript{85}, but it incorporated a barium titanate crystal instead of quartz, thereby avoiding the necessity of high voltage and consequent insulation difficulties. The uncertainty in the sound velocity measurements was 0.15 percent.

In pulse technique measurement of transit time for a given path length enables one to evaluate sound velocity in liquids\textsuperscript{86-87}. Techniques capable of giving an accuracy of 1 in 30,000 were developed by Greenspan and Tschieg\textsuperscript{88}, McSkimin\textsuperscript{89} and Barlow and Yazgan\textsuperscript{90}. Chase\textsuperscript{91} developed a double
crystal interferometer (pulsed) with which velocity changes can be
determined with an accuracy of 0.005 percent. Sing-around technique of the
type developed by Garnsey et al. is capable of giving an accuracy of 0.005
ms\(^{-1}\) in velocity measurements. The velocity measurements were made by
Kiyohara and co-workers with reference to pulses, using the pulse-echo-
overlap method in a multiple echo mode. In this method the velocity is
determined by measuring the time interval between a pair of echoes of an
ultrasonic wave travelling between a transducer and reflector.

The ultrasonic interferometer has some advantages over the pulse
techniques. The use of differential path length, instead of total path length
and their accurate measurement with an optical interferometer, has an
advantage over occurring to interferometers. In addition, the interferometer
requires a simple measurement of frequency as opposed to a more difficult
measurement of time interval in the pulse technique. Interferometer is
therefore, found to be more suitable for the determination of temperature and
pressure coefficients of sound velocity. The superiority of the ultrasonic
interferometer was discussed in detail by Del Grosso. The interferometric
method is, however, limited by the narrowness of the band of applicable
frequencies 10 to 100 MHz.

In the present investigation, a single crystal variable path
interferometer was used to measure the ultrasonic velocities. A sketch of
interferometer Cell is shown in Fig. 2.3. The interferometer cell of capacity
12 cm\(^3\) was made of a stainless steel tube of inner diameter 1.6 cm. A gold
plated quartz crystal tube of inner diameter 0.9 cm was cemented to the
bottom of the cell. The ultrasonic waves moves from this crystal till they are
reflected back by the movable reflector. A fused quartz rod was used as a
Fig. 2.3: INTERFEROMETER CELL
The reflecting surface was 1.4 cm in diameter. This was coupled to a micrometer screen assembly reading up to 0.01 cm using a teflon coupler via the steel rod. The micrometer assembly along with the reflector was fixed to the liquid cell with the help of a threaded up and teflon ring. A heavy pedestal gives the measuring cell the required stability. Provision was made for circulating water at any required temperature from a thermostatically controlled bath into jacket around the measuring space to maintain the experimental liquid at constant temperature during the experiment.

To excite the transducer (crystal) at a frequency 4 MHz, a crystal controlled r-f oscillator Fig. 2.4 was used. The H-T current to the output tube was fed through a bridge network including a micro-ammeter in such a way that the change in plate current can easily be observed on the micro-ammeter. Two controls to regulate sensitivity and to adjust initial current of the meter were also provided. The interferometer thus consist of an electrically driven quartz transducer coupled to the liquid column. The length of the liquid column can be varied by moving the quartz reflector, keeping its plane parallel to the quartz crystal. Whenever the distance between quartz transducer and the reflector corresponds to an integral multiple of half wave length, the liquid column vibrates in resonance. This lead to an increase in the motional impedance of the transducer which causes sharp dips in the r-f voltage across the transducer. The distance covered by reflector between any two consecutive dips corresponds to one half wave length, $\lambda/2$.

**Measurement of ultrasonic sound velocity**

The interferometer cell was filled with experimental liquid and was connected to the output terminals of the high frequency generator through a shielded cable. The cell temperature was maintained at 303.15 K by
LEGEND

Fig. 2.4: Oscillator circuit

\[ V_1 = \text{EF89} \]
\[ V_2 = \text{EF89} \]
\[ R_1 = 1 \text{ K ohm} \]
\[ R_2 = 4.6 \text{ K ohm} \]
\[ R_3 = 46 \text{ K ohm} \]
\[ R_4 = 33 \text{ K ohm} \]
\[ R_5 = 10 \text{ K ohm} \]
\[ R_6 = 100 \text{ K ohm} \]
\[ R_7 = 100 \text{ ohm} \]
\[ R_8 = 100 \text{ ohm} \]
\[ R_9 = 33 \text{ ohm} \]
\[ C_1 = 16 \text{ uF} \]
\[ C_2 = 0.047 \text{ uF} \]
\[ C_3 = 0.01 \text{ uF} \]
\[ C_4 = 0.01 \text{ uF} \]
\[ C_5 \text{ and } C_6 = \text{Variable} \]
\[ C_7 = 0.01 \text{ uF} \]
\[ L_1 \text{ and } L_2 = \text{Suitable} \]
\[ G = 1 \text{ K ohm (gain control)} \]
\[ S = 47 \text{ K ohm (sensor)} \]
\[ M = \text{Micro-ammeter} \]
circulating water from a thermostat which was controlled to within ± 0.01 K. When the liquid attained the temperature of the bath, the micrometer screw was slowly moved till the anode current meter showed a maximum and the reading of the micrometer was noted. This distance between the quartz transducer and the reflector plate was displaced by moving the screw downwards. To improve the accuracy of the measurement, several maxima were passed and their number n (in this case 20) was counted. The anode current was finally adjusted to the maximum and the reading of the micrometer was again recorded. The total distance moved by the reflector was given by \( d = n \lambda/2 \). The frequency of the quartz crystal \( f \) being accurately known (4 MHz) the sound velocity \( u \) was calculated using the relation, \( u = \lambda/f \). The value of \( u \) was obtained by moving the micrometer screw upwards. The values of the sound velocities were accurate to 0.15 percent. The performance of the interferometer was checked by comparing the sound velocities recorded in the present study with those reported in the literature (Table 2.3).

**TABLE 2.3**

**Sound velocities of some pure liquids at 303.15 K.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Sound Velocity ( u/\text{ms}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
</tr>
<tr>
<td>Benzene</td>
<td>1277.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1228.3</td>
</tr>
<tr>
<td>Carbontetrachloride</td>
<td>903.8</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>1173.2</td>
</tr>
<tr>
<td>1-butanol</td>
<td>1224.9</td>
</tr>
</tbody>
</table>
Measurement of density

In the present study a double stem pycnometer shown in Fig. 2.5 was used to measure the densities of pure liquids. The pycnometer was similar to that of Parker and Parker$^{45}$ in type with minor modifications. It consists of a bulb of capacity 12 cm$^3$. The stems were made up of capillary tube of uniform bore of about 1 mm. The stems were bent to sides making an abuse angle at the bend. The open ends of the stems were closed with teflon caps in order to prevent the loss of liquid due to evaporation. The caps had small orifices to ensure that the pressure inside the capillary was equal to the atmospheric pressure. A mark was made on each of the two stems at about the same level. The liquid level in each stem was read with reference to the mark. The following procedure was adopted in filling and weighing the pycnometer. The well cleaned and dried pycnometer was weighed accurately with reference to the dummy. The liquid was introduced into the weighed pycnometer with the help of a hypodermic syringe until the levels of the liquid in both the stems were very nearly corresponded with the marks on the stems. The pycnometer was kept immersed vertically in a thermostat maintained at ± 0.01 K for about half an hour. This permitted the unfilled part to be drained completely and allowed liquid-vapour equilibrium to be established. The amount of liquid at the initial filling was adjusted to allow for expansion (or contraction) due to the difference of temperature between bath and surroundings. The difference in heights of liquid between the mark and the lowest point in the meniscus in both the limbs were measured when the liquid levels were stationary. A travelling microscope, which could read to 0.01 mm, was used for this purpose. Since the meniscus in respect of water and other liquids used in this work was hemisphericals, one third of the radius of the capillary tube was added to the observed height. The pycnometer was then removed from the bath, wiped with a clean damp cloth.
Fig. 2.5: PYCNOMETER
and kept in the balance for 15 minutes before weighing. The dummy pycnometer was also put through the same treatment except for the liquid filling, to minimise the effects of moisture condensation on the surface of the pycnometer and errors arising from temperature difference and buoyancy.

The exact volume of the pycnometer included between the marks at 303.15 K was determined as described below. The volume of water \( (V_w) \) contained in the pycnometer was calculated using the formula \( M/\rho_w \), where \( M \) was the mass of water and \( \rho_w \) was the density of water at 303.15 K. The volume \( (dv) \) of the pycnometer from the marks to the water meniscus was calculated using the formula \( \pi r^2 h \), where \( r \) was the radius of the capillary and \( h \) was the corrected difference in heights between the mark and meniscus in both the stems. This volume \( (dv) \) was the difference between volume of water actually present in the pycnometer and volume of water that would fill the pycnometer up to the marks at 303.15 K. The exact volume \( (V) \) of the pycnometer included between marks was then obtained by adding (or subtracting) \( dv \) to (from) \( V_w \). The densities of pure liquids were calculated from exact masses and volumes using the relation \( \rho = M/V \). Where \( M \) and \( V \) denote mass and volume of the liquid respectively. The densities of the pure liquids were accurate to 2 parts in 10^5.

Densities in respect of mixtures were computed from the experimental excess volumes and compositions using the relation.

\[
\rho = \frac{x_1M_1 + x_2M_2}{V^o + V^E} \tag{2.3}
\]

Where the subscripted 'x' and 'M' represent the mole fraction and molecular weight of the corresponding component. \( V^o \) stands for ideal molar volume and \( V^E \) denotes excess molar volume.
The measured sound velocities and densities of pure liquids and liquid mixtures have been utilized to compute the isentropic compressibilities. The values of isentropic compressibilities are accurate to ± 1 TPa⁻¹.

EXCESS ENTHALPY

In principle, the molar excess enthalpy, $H^E$ may be derived from the temperature dependence of the excess Gibbs free energy.

$$H^E(T, P, x) = G^E(T, P, x) - T \frac{\partial G^E}{\partial T}$$

(2.4)

In practice, this is not a satisfactory method, as measurements of $G^E$ rarely extend over a temperature range of more than 15 percent of the temperature.

The recent literature indicates that most of the measurements have been made using adiabatic calorimeters. In an adiabatic experiment, the two liquids are mixed in a vessel which is thermally isolated from its surroundings. If $H^E$ is positive (endothermic), then there will be a lowering of the temperature. In practice, electrical energy is usually supplied to the calorimeter partially to nullify the temperature drop. If $H^E$ is negative (exothermic) then the temperature of the calorimeter rises on mixing. A second experiment is necessary to determine the amount of energy required to produce the same temperature rise. Alternatively, two identical calorimeters can be used. A known amount of electrical energy is added to the second calorimeter in such a way that the temperature difference between the two calorimeters is minimized. The two main requirements of mixing calorimeters are: (a) the absence of a vapour space and (b) some
means to allow for the volume change which occurs on mixing. McGlashan\textsuperscript{90} has reviewed the mixing calorimeters and concluded that most of them were deficient in terms of the aforesaid requirements. All the calorimeter reviewed were of the adiabatic type. Larking and McGlashan\textsuperscript{100} described a calorimeter which has been widely used and meets the above requirements.

Malcolm and co-workers\textsuperscript{102,103} described an isothermal apparatus based on the Bunsen calorimeter. The mixing vessel is surrounded completely by a vessel containing a liquid, part of which is frozen to give a mantle around the inner walls. Any energy released or absorbed during the mixing process causes melting or freezing of the mantle and volume change that accompanies the process is measured by the movement of the liquid or mercury in a capillary tube. Bunsen calorimeters can be used to measure energy changes in slow processes. A major disadvantage in this is that measurements can only be made at the melting temperature of the calorimeter fluid. Recently Davis and Pritchard\textsuperscript{104} have discussed in detail the stability and accuracy of Bunsen type calorimeters.

A further method for the determination of excess enthalpy makes use of an isothermal dilution calorimeter. For an endothermic system, one component is slowly injected into the second component with simultaneous addition of electrical energy sufficient to maintain the calorimeter isothermal. An apparatus suitable for endothermic systems was first described by Van Ness and Mrazek\textsuperscript{106}. Several other calorimeters based on the original design have been reported in the literature\textsuperscript{106-112}. An apparatus which is more suitable for measuring exothermic enthalpies has been described by Van Ness and Gibbs\textsuperscript{113}. Murakami and Benson\textsuperscript{106} have constructed a similar apparatus except that the cooling module is located in a second plug at the base of the
vessel Tanaka et al.\textsuperscript{111} described an apparatus which uses the same injection technique as the Van Ness type calorimeter with a vessel of fixed dimensions in which mercury is displaced as in the Stokes and Marsh type calorimeter. A number of other isothermal dilution calorimeters which contain a vapour\textsuperscript{114,115} have been described.

In a flow calorimeter the two liquids are injected into a mixing chamber at a study and known rate. For an endothermic system the power in the heater is adjusted so that the temperature of the mixed liquid is resorted to that of the unmixed liquid. A few measurements have been made with flow calorimeters. The most accurate results are obtained by McGlashan and Stockli\textsuperscript{116}. The major problem with flow calorimeters is that of producing a constant, but readily variable flow rate. Using a vapour pressure driven flow system, McGlashan and Stockli obtained a reproducibility of 0.25 percent in the flow rates. These workers concluded that \( H^\circ \) could be measured with an accuracy of one percent. Harsted and Thomsen\textsuperscript{117} determined a calibration constant for their LKB calorimeter by using various results determined by Marsh and co-workers. They estimated that their modified flow calorimeter was accurate to about 2 J mol\(^{-1}\). Goodwin and Newsham\textsuperscript{118} have described a flow calorimeter for alcohol + water systems.

Picker \textit{et al.}\textsuperscript{118} have described an interesting calorimeter. These workers managed to obtained the complete excess enthalpy curve in less than one hour by reducing the time taken to reach a steady state in a flow calorimeter to less than one minute and by continuously varying the flow rates of the two liquids. Becker \textit{et al.}\textsuperscript{120} have described a continuous method which required two runs to cover the whole composition range. First component is added at a constant rate to a container of fixed volumes,
initially containing the second component. The mole fraction of the mixture gradually changes in a known way depending on the flow rate and the volume. The calorimeter was designed to have a very rapid response time so that the mole fraction-excess enthalpy curve could be recorded in a continuous manner. The calorimeter is capable of giving results with a precision, less than one percent.

The major advantage of flow calorimeters is that these are readily adoptable for measurements over a wide range of temperature and pressure.

Description of the new Parr 1451 solution Calorimeter and experimental procedure

In the present investigation, the new Parr 1451 solution calorimeter Fig. 2.6 was used to measure excess enthalpies. This calorimeter consist of an assembled compact cabinet of a glass Dewar chamber with a rotating sample cell, a thermistor probe and a specially designed temperature measuring bridge. All operations are straightforward and easy to handle.

Rotating Cell

The two-piece cell which serves both a sample holder and agitator, consist of a glass cell which is closed with a detachable teflon dish. The dish fits snugly in the bottom of the cell without requiring a gasket or sealing ring to secure a tight seal. Liquid sample is weighed directly into the cell. The glass rod which is used to open the cell and to start mixing is inserted from the top of the calorimeter through the stirring shaft and into a socket in the
Fig. 2.6: Parr 1451 solution calorimeter
sample dish. When this rod is pushed downwards, the dish slides out of the cell and remains attached to the rod, held at a fixed distance above the bottom of the Dewar vessel. In this position the rod and dish rotate with the cell slinging the components into the solution and serving as an additional impeller in the stirring system. Heat leak from the cell to non wetted parts of the system is held to a minimum by a low conductivity, thin walled glass stem on the sample cell and a plastic coupling which fastens the cell to the stirring shaft. The cell is easy to load, easy to clean and interchangeable. The dish itself is made of teflon reinforced with glass fibre for excellent resistance to most chemical reagents and for good dimensional stability.

Stirrer drive

The stirrer mechanism consist of an externally mounted electric motor with a drive belt which turns the stirring shaft at a constant speed (approximately 450 rpm) with no slippage and very little bearing friction. The hollow shaft terminates at the underside of the calorimeter cover where it joins the plastic coupling on the end of the sample cell.

Reaction Vessel

Excellent thermal insulation is provided by a fully silvered glass Dewar which serves as a mixing chamber. 90 to 120 ml of solution should be placed in this vessel to properly cover the rotating sample cell. The cell itself will hold upto 20 ml of liquid sample or upto 2 grams of most crystalline solids. The Dewar is supported with in a stainless steel air-can from which it is easily removed for filling are clean.
Thermometer

Temperature measurements in this calorimeter were taken with a glass-sheathed thermistor probe combined with a special bridge in a system designed for linear response over the temperature range from 20 to 30°C. Within this range, each 100 microvolt change in output from the bridge represents a temperature change of exactly 0.001°C. Thus, when fed to a recording potentiometer and plotted on 10, 100 or 1000 millivolt chart, temperature can be read directly from the chart without applying a conversion factor. At the start of a run the recorder was adjusted to zero and a base reading from the bridge was recorded. Any subsequent deviation from the starting temperature was then recorded directly in celsius degrees.

In the measurement of excess enthalpies, the known mass of component 1 was taken into the Dewar vessel and the component 2 weighed in a scaled glass rotating cell. Both the components were kept in thermal contact with each other in the Dewar mixing chamber at 298.15 K. After attaining the thermal equilibrium, component 2 in the rotating cell was mixed with the component 1 in the Dewar vessel by pushing the glass rod. The temperature change accompanying the mixing process was sensed by the thermistor and recorded on the strip chart recorder. The excess enthalpy, $H^E$ was then calculated knowing the energy equivalent of the system by using the relation:

$$H^E = (W_1 C_{p1} + W_2 C_{p2} + E) \Delta t/n$$

Where, $W_1$ and $W_2$ are the mass of the corresponding components, $C_{p1}$ and $C_{p2}$ are heat capacities of respective components, $E$ is the energy equivalent of the calorimeter, $\Delta t$ is the temperature change and $n$ is the number of moles of mixtures.
The performance of the solution calorimeter has been checked for both endothermic and exothermic reactions with known systems (1) benzene + carbontetrachloride and (2) chlorobenzene + toluene respectively. The experimental data were very well in agreement with the reported data in literature\textsuperscript{121,122} as shown in Fig. 2.7. It was not possible to measure the excess enthalpies for some chloroethanes, substituted benzene and some alicyclic and aliphatic ketones, as the experimental facility was not available in our laboratory. The other components used in the present investigation instead of aforesaid chemicals are ethylbenzene and acetophenone.

**SOLID-LIQUID EQUILIBRIA**

A knowledge of solid-liquid equilibrium data is essential for the design of crystallization and in chemical process handling solids. The solid-liquid equilibrium phase diagram is useful in a number of chemical engineering process such as extraction and crystallization. The solid-liquid equilibrium study in binary mixtures provides information on the intermolecular forces between solvent and solute and, eventually, on the formation and nature of intermolecular compounds in the solid phase\textsuperscript{123-127}. Moreover, SLE data can be used to evaluate the contribution of the combinatorial entropy term to the excess Gibbs energy of the mixture\textsuperscript{128} for practical purposes, solubilities of solids in pure or mixed solvents are of interest in chemical process design, especially when process conditions must be specified to prevent precipitation of a solid. Polymorphism is a characteristic feature of a number of straight-chain homologous series. Through X-ray diffraction investigations, the observation of cooling curves and the values of dielectric constants, as well as
Mole fraction of benzene

Fig. 2.7: Heats of mixing for benzene with carbon-
tetrachloride (o) + chlorobenzene with toluene (△)
at 298.15 K
differential scanning calorimetry studies, at least two or three crystal forms for the normal alcohols have been discovered. The included two forms (β and γ) which are stable or metastable at lower temperature and a waxy phase (α), which is stable just below the melting point. Plesnar and Bylicki and Ksiazczak have observed stable crystal forms in corresponding temperature range: α, β and γ as well as a metastable α form or β form, respectively. There is a divergence amongst the various investigations as to the temperature of the phase transition, as well as to the type or the sequence of α, β and γ phases. These divergences arise mainly from differences in the method of observation or the rates of heating or cooling. However, the transition phenomenon has been known to be affected by the presence of extremely small amounts of impurities as well as by variations in the measurement technique and by variations in the variations in the thermal historians of the materials.

Experimental

Solid-liquid equilibrium temperatures were determined using a dynamic (synthetic) method described in full detail by Buchowski et al. Mixtures of solute and binary solvent, prepared by weighing were heated very slowly (heating rate did not exceed 2 K h⁻¹ near the equilibrium temperature) with stirring kept inside a pyrex glass cell, placed in a thermostat. The temperature at which the last crystals disappeared (decline of solution dullness) was taken as the temperature of the solution-crystal equilibrium. Measurements were carried out in a wide range of solute concentrations from 0.001 to 0.98 and over a temperature range from 276 to 334 K. The accuracy
of temperature measurements was $\pm 0.05$ K. Reproducibility of measurements was 0.01 K, which corresponded to a relative error in composition < 1%. The crystal disappearance temperatures, detected visually, were measured with Anschütz (TGL 11986, H. Schlegel, Ilmenau, Germany) thermometer totally immersed in the thermostating liquid. The same procedure was reversed and the crystallization point was noted. The average between temperature of crystal appearance and crystal disappearance was taken as the solubility temperature. However, if any error occur from impurities and the dynamic character of the method, such an error may be concluded from the comparison of the data obtained using the technique described by Domanska\textsuperscript{392}. The characteristics of the solutes were collected in Table 3.20. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The error in the mole fraction did not exceed $x_1 = 0.005$. 

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