CHAPTER IV

EXPERIMENTAL
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This chapter covers the details regarding the purification and specifications of the various chemicals used and the experimental techniques employed to determine the excess functions.

A. CHEMICALS:

(1) Benzene :- A.R. quality thiophene free benzene was distilled first over phosphorus pentoxide and then over sodium metal. The fraction distilling at 78.5°C was collected.

(2) Carbon tetrachloride :- A.R. grade carbon tetrachloride was twice distilled over phosphorus pentoxide and the fraction distilling at 76.0°C was obtained.

(3) n-Octane :- Fluka, "purum" (99%) variety of n-octane was twice distilled over phosphorus pentoxide before use.

(4) n-Hexadecane :- n-hexadecane of A.S.T.M. grade was obtained from Humphrey Chemical Co. (America) and was used as such.

Purity of all these chemicals was checked by determining their densities, refractive indices, vapour pressures and boiling points. These values have been given in Table X. Agreement with the values given in literature is good.

(5) Mercury :- Mercury required for the vacuum line and for calibration of bulbs and pycnometer, was purified by trickling it repeatedly in a fine stream through a long column containing...
5% solution of nitric acid. The mercury removed from the bottom of the column was washed with distilled water a number of times. This was then dried and twice distilled under vacuum.

**Table X**

Properties of the pure components

<table>
<thead>
<tr>
<th>Substance</th>
<th>* Refractive index at 30°C</th>
<th>* Density at 30°C</th>
<th>* Vapour pressure at 25°C(mm)</th>
<th>* Boiling point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.4949</td>
<td>0.8684</td>
<td>95.06</td>
<td>78.5</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>1.4542</td>
<td>1.5746</td>
<td>113.26</td>
<td>76.0</td>
</tr>
<tr>
<td>n-octane</td>
<td>1.3924</td>
<td>0.6948</td>
<td>13.97</td>
<td>124.0</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>1.4316</td>
<td>0.7668</td>
<td>0.00</td>
<td>-</td>
</tr>
</tbody>
</table>

**B. TECHNIQUES**

(1) **Excess volume** :- In order to find excess volume of a mixture, its density determination and that of its pure components were carried out. The densities were measured pycnometrically. A modified form of Sprengel-Oswald type pycnometer has been used. It is a bicapillary pycnometer ensuring accuracy in the density determination more than ±5 x 10^-5. (Fig.1).

A bulb having capacity of about 9 ml. was blown out of a pyrex glass tube, which was fused at its two opposite ends into
two pieces of calibrated capillaries, bent at right angles and parallel w.r.t. each other. The capillaries were calibrated with freshly distilled mercury. To distinguish the two capillaries one of them was given bend at the top. Fine reference marks A, B were etched at suitable places on the capillaries and the volume of the bulb upto the marks was determined repeatedly with mercury and benzene.

The volume per cm. of the capillaries and the volume of the bulb upto the reference marks at 25°C are given below,

Volume of the straight side = 0.004434 ml/cm.
Volume of the bent side = 0.005157 ml/cm.
Volume of the bulb = 8.99176 ml.

Cleaning of the pycnometer:– The pycnometer was cleaned by filling it with chromic acid and keeping it as such over night. Then whole of the chromic acid was drained out and the pycnometer was washed a number of times with water and finally with distilled water. After draining out water it was dried in a vacuum desiccator by applying suction till it gave constant weight. It was not after every experiment that the pycnometer was cleaned like that, but rinsing twice or thrice with a low boiling solvent and then drying under vacuum served the purpose well.

Filling and weighing:– For every concentration studied fresh solution was prepared in weighing bottles fitted with standard joints. After making the buoyancy correction for each component the exact mole fraction was calculated. Dried and weighed
FIG. I. BICAPILLARY PYCNOMETER

- NICHCROME WIRE
- FIXED MARKS
pycnometer was then filled with the solution, wiped with a piece of lintless cloth and was then clamped in position in a water thermostat, which itself was kept in an air thermostat. The temperature of the water thermostat was controlled to ±0.005°C. The pycnometer was kept in the bath for about an hour to attain the temperature of the bath. Readings of the reference marks and those of the levels of the solution filling the pycnometer in each capillary were taken with a cathetometer with the accuracy of ±0.002 cm. The respective difference between the levels and the reference marks in each limb multiplied by the volume/cm. of each capillary gave the volume, to be added or subtracted from the calibrated volume of the pycnometer up to the fixed marks. The pycnometer was taken out of the bath, wiped clean, dried and then weighed. Thus knowing the volume and the weight of the solution, its density was calculated. Using this density, buoyancy correction was made to the weight of the solution and exact density was recalculated.

Densities of solutions between mole fraction 0 - 1 were determined by the method described above.

(2) Measurement of the Total Vapour Pressure: Static method has been used to measure the total vapour pressure of the binary mixtures at different temperatures and compositions. The detailed description of the apparatus, and its working is given below under separate heads.
Description of the apparatus: -

A high vacuum line consisting of a three stage mercury diffusion pump, worked by an efficient rotary oil pump, and a McLeod gauge was set up. The line can be divided into four major parts, which have been shown in Fig. 2.

1. Distillation assemblies
2. Measuring bulbs
3. Manometer
4. Mixing bulb.

A distillation assembly consists of 2 bulbs separated through a mercury cut off $M_1$ and then connected to the main vacuum line through another mercury cut off $M_2$. Similarly, the second distillation assembly is connected to the main vacuum line through mercury cut off $M_4$. Mercury cut off $M_5$ connects the two distillation assemblies and the measuring bulbs $a_1$, $a_2$, and $a_3$. A trap $T$ has also been provided between the bulbs and the mercury cut off $M_5$ so as to check the accidental flow of mercury from the mercury cut off to the measuring bulbs. The measuring bulbs are further connected to the mixing vessel through the mercury cut off $M_6$. The mixing bulb contains the magnetic stirrer operated by means of a solenoid. One limb of the manometer is connected to the mixing bulb through another cut off $M_7$ while cut off $M_8$ connects the two limbs of the manometer. The second limb of the manometer is connected to the common limb of a three way stop cock $T_1$. The other limb of the
FIG. 2. APPARATUS FOR THE MEASUREMENT OF VAPOUR PRESSURE.
stop cock is left open to air while the third is connected to the main vacuum line through another stop cock $T_2$. The mixing bulb is surrounded by a large beaker placed in a water thermostat. The water thermostat is well insulated by placing it into a wooden box and filling the void spaces with insulex and saw dust. The top was also well covered with insulex sheet. The leading tube L.T. of the mixing vessel was wrapped with cotton and an enclosure was built surrounding it by insulex sheets. A bulb of suitable wattage was kept on in this enclosure so that the temperature inside was always higher than that of the water thermostat and no condensation of the liquid in the leading tube was possible.

As shown in the Fig. 2, a b c d is an air thermostat, into which are enclosed the cut offs $M_6, M_7, M_8$ and the manometer.

(ii) Calibration of the bulbs :- Three bulbs of approximately 1, 2 and 5 ml. capacities were blown from a wide bore graduated capillary (stem of a micro-burette which could read upto 0.01 ml.). Then these were calibrated with pure double distilled mercury. The volume upto a fixed graduation mark was determined in each case.

Volume of the bulb $a_1$ upto the fixed mark = 1.289 ml.
Volume of the bulb $a_2$ upto the fixed mark = 1.783 ml.
Volume of the bulb $a_3$ upto the fixed mark = 4.811 ml.
(iii) **Temperature control** :- The temperature of the water thermostat, was controlled to ± 0.01°C with the help of a large toluene filled thermoregulator, an immersion heater and an electronic relay. An efficient stirrer run by an electric motor was used to keep the water circulating and ensure same temperature throughout the bath. The temperature of the air thermostat was similarly controlled by a thermoregulator and an electronic relay. The circulation of the air was rendered by a pair of mini fans, while the heating was done by a number of electric bulbs arranged in the thermostat. The temperature was controlled to 60 ± 0.2°C.

The absolute value of the temperature was found by determining the transition temperature (32.38°C) of Glauber salt on a Beckmann thermometer. With the help of this thermometer, a number of Beckmann thermometers were calibrated to read temperatures from 25 to 55°C. The absolute value of the temperature was further checked by finding the vapour pressure of pure benzene at 25°C and calculating back the temperature by Antoine equation,

\[ t°C = \frac{1211.033}{(6.90565 - \log (\text{Pmm. Hg}) - 220.790)} \]

A difference of 0.02°C was found.

(iv) **Preparation of the solution** :- Systems n-octane/benzene and n-octane/carbon tetrachloride are such in which both the components are volatile. The components to be studied were taken
in the flasks A₁ and A₃, and the two were thoroughly
degassed. The degassing was accomplished by surrounding the
(flask A₁) with freezing mixture and evacuating it. It was
however, found that only evacuation was not sufficient for
complete degassing. This was rendered by distilling the liquid
10-12 times from one limb of the distillation assembly (flask
A₁ or A₃) to the other limb (A₂ or A₄) and then back, under
vacuum and by surrounding the receiver limb with freezing
mixture and the other with hot water. Lastly the liquid was
stored in the flask A₁ and the mercury cut off M₁ closed.
The limb A₂ was opened to vacuum and when stick vacuum was
established, about 40 ml. of the liquid from the flask A₁ was
distilled into the bulb A₂, and cut off M₁ and M₂ were
closed. In the similar manner the second liquid was degassed
and requisite amount stored in the bulb A₄. Then the mixing
bulb, the measuring bulbs and the manometer were opened and
evacuated completely. Cut offs M₆, M₇ and M₈ were closed
and one of the components was distilled from the container
bulb into the measuring bulb of suitable capacity. When the
bulb was filled upto or above the fixed mark the container
bulb was cut off. Volume in the measuring bulb was read at
a fixed temperature by surrounding it with a constant temperature
bath. Then this measured amount of the component was transferred
into the mixing bulb by opening the cut off between them and
surrounding the mixing bulb with freezing mixture and the
measuring bulb with hot water. After the complete transference,
the cut off was closed and the measuring bulbs completely evacuated again by opening them to vacuum. Similarly the second component was distilled first into the measuring bulb and then into the mixing bulb. Knowing the volumes of the two components transferred and their densities at the temperature of transference, their respective masses and the composition of the mixture were calculated.

(v) Stirring :- The mixture in the mixing bulb was stirred by a magnetic plunger, which consisted of a pyrex glass tube sealed at its both the ends and enclosing an iron nail at its upper portion. It was gently lifted up intermittently by the magnetic field of a solenoid which surrounded the connecting tube at the appropriate position and was energised by a sunvic energy regulator through a step down transformer.

Measurement of the vapour pressure :- The temperatures of the water thermostat and the air thermostat were set at 25 and 60°C respectively. The stirring of the solution in the mixing bulb was started and it was exposed to one limb of the manometer. The equilibrium was attained and the manometer was read with the help of a cathetometer. The constancy of the reading was checked for about an hour and a set of 7-8 readings with an interval of about 10 minutes was taken. The maximum difference between the individual readings seldom exceeded ± 0.05 mm. A few sample experiments were carried for longer hours (12 hours). No change in the vapour pressure was noted.
The temperature of the thermostat was raised to next higher temperature to be studied and the vapour pressure was noted as above. Similar measurements were carried for 2 more temperatures (in all four). Then the water from the water thermostat was removed and a known amount of the desired component was transferred into the mixing vessel as explained earlier. This was left as such overnight and the readings were taken the following day. In all 10 - 12 concentrations of a mixture were studied.

The vapour pressures determined have been corrected for the density of mercury and have been given in mm. of mercury at 0°C. Necessary corrections in the compositions of the mixtures due to the space between the manometer and the mixing bulb were estimated and though very small were made. The vapour pressures of pure components were also determined, which provided a check on the purity as well.

The different steps in the preparation of the solution and the measurement of vapour pressure at that composition are given overleaf.
Mass of n-octane transferred = 7.0192 gm.
Moles of n-octane transferred = 0.06145
Mass of carbon tetrachloride transferred = 1.9411 gm.
Moles of carbon tetrachloride transferred = 0.01262
Mole fraction of n-octane = 0.3297
Vapour pressure at 35°C = 52.02 mm of Hg at 60°C

Mean = 52.04
Zero error = 0.22
Corrected = 52.26
Corrected vapour pressure = 51.69 mm of Hg at 0°C
Corrected mole fraction at 35°C = 0.8313
Moles of carbon tetrachloride transferred second time = 0.01328
Total moles of carbon tetrachloride = 0.02590
Second mole fraction of octane = 0.7035

In the similar manner 10 - 12 concentrations were prepared and their total vapour pressures determined.

In case of n-hexadecane, which is quite non-volatile (almost negligible vapour pressure at 55°C), a weighed amount was directly taken in the bulb and then sealed in position. n-hexadecane was degassed by alternate melting and freezing 10-12 times and evacuating when in frozen state.

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