3.1 Equilibrium Still

The equilibrium data were obtained using a vapour recirculating type equilibrium still which is a modified form of the one developed by Rao and coworkers [267]. The following modifications were incorporated:

1. The vapouriser was replaced by a U-tube followed by an inclined vapourising tube similar to the one used in the Jones still [137] so as to avoid back pressure and ensure total vapourisation.
double walled thermometer pockets were employed to eliminate the effect of localised surface heating of mercury from the neighbouring heater element turns which otherwise can cause significant errors in the temperature measurements.

iii an entrainment trap, to minimise entrainment was introduced in the vapour space at the top of the boiler tube.

iv joints were eliminated by making the apparatus as one single unit and stopcocks designed for use with high vacuum apparatus were used to reduce leakage to the minimum.

This equilibrium still has the advantage of eliminating concentration gradients in the boiler as well as the condensate receiver by thorough mixing with the aid of bubbling vapours. Detailed drawing of the still is given in Figure 2. A close-up photograph of the equilibrium still is shown in Figure 3. The details of the condensate receiver including the vapour bubbling nozzle could be clearly observed from Figure 4. The still consists of a boiling tube B, a condensate receiver C with bubbling arrangement for the vapours, and a vapouriser V. The sampling cocks K_1 and K_2 are for collecting the liquid and the vapour samples respectively. P_1 and P_2 are the double walled thermometer pockets and F is the opening provided with a stoppered B-10 standard joint for introducing liquid into the still. W is the double...
walled surface condenser fitted above the condensate receiver. Two 125 watt and one 250 watt 'Flexotherm' heating cords with woven glass wool sleeving were used to provide heating for the boiler tube, the vapour space above the boiler and the vapouriser respectively. A thin layer of glass wool was put all along the surface to be heated before heating coils were wound over them. The compensating heater over the vapour space was provided to avoid any condensation of the vapours in the boiler tube. The whole apparatus, except the condensate receiver, was heavily lagged with thick layers of asbestos cloth and glass wool. Each heater was separately controlled by a combination of a 'Sunvic' energy regulator and an auto transformer fitted on a control panel shown in Figure 1. The control panel provides a convenient and safe control for the heating devices. An A.C. voltage stabiliser, Model CVL/500, capable of controlling the voltage within 230 ± 1.0 percent was used to reduce voltage fluctuations and ensure uniform heating. The boiling tube and the condensate receiver were partly filled with 3.0 mm ceramic insulation beads to provide uniform heating and avoid bumping.

3.1.1 Measurement and Control

Temperatures were measured with the help of short range 'Anschütz' thermometers having an accuracy of 0.1°C. A magnifying lens was used to read the thermometer scale accurately. The atmospheric pressure was recorded from a barometer having an accuracy of ± 0.1 mm of Hg and equipped with a brass scale calibrated at 0°C. Temperature correction to the observed
readings was applied to account for the expansion of mercury and brass. Throughout the experiment, the pressure was kept constant at 760 ± 2.0 mm of Hg with the help of a small blower which was supplying into the system, the required amount of air continuously and venting off the rest through a combination of pinch cock and a needle valve used for rough and fine control of the pressure respectively. Pressure fluctuations in the system were minimised by providing in series two surge vessels having a total capacity of about 40 litres. The manometer was kept close to the still in order to minimise pressure drop. Air used for maintaining the pressure in the system was first dried by bubbling it through a vessel containing concentrated sulphuric acid and then passing through a series of U-tubes containing chemically pure anhydrous calcium chloride. The acid and the calcium chloride were replaced frequently to ensure complete dryness of air. Figure 1 is a photograph of the equilibrium still showing the details of the control equipment.

3.1.2 Operating Procedure

Each time the still was charged with 100 ml of liquid mixture whose composition was roughly adjusted for each run so as to cover the entire concentration range of the system. The blower was switched on and the pressure was adjusted to 760 mm of Hg with the help of the pinch cock and subsequently the needle valve. The condenser water was turned on and the heater load on the boiler was gradually increased by carefully controlling heater $H_1$. When no further rise in the temperature of the boiling
FIG. 2 EQUILIBRIUM STILL

B  BOILER
C  CONDENSATE RECEIVER
E  ENTRAINMENT TRAP
F  FEED INLET
H₁, H₂, H₃  HEATING CORDS
K₁, K₂  SAMPLING COCKS
P₁, P₂  THERMOMETER POCKETS
T  CAPILLARY TUBE
V  VAPOURISER
W  CONDENSER
FIG. 4 Details of the Condensate Receiver
liquid was noticed the load on the compensatory heater $H_2$ was increased till the temperature of the vapours was slightly more than that of the boiling liquid. After the vapours started condensing in the condensate receiver, the load on heater $H_2$, over the vapouriser, $V$, was increased gradually and simultaneously the load on heater, $H_1$, was decreased. Such adjustments were carried out till there was no apparent wetting at the exit of the vapouriser tube, and bubbling remained steady and uniform. The loads on all the heaters were finally adjusted for smooth operation. Although steady state was achieved in about 30 minutes time, the operation of the still was continued for another three hours so as to ensure perfect equilibrium between the vapour and liquid phases. The barometer was read after every 30 minutes whereas the thermometer readings were taken at intervals of 15 minutes. The temperatures remained constant throughout the operation except that slight fluctuations of the order of $\pm 0.1^\circ C$ were noticed in the low concentration regions of the alcoholic components. The constancy of the thermometer reading was taken as a guide for the attainment of the equilibrium. At the end of three hours, small quantities of the stagnant liquid, collected in the legs of the sampling cocks, were drained off and each time about 7 ml of the liquid and vapour samples were collected in narrow necked chilled sampling bottles provided with B-14 standard joint stoppers. Such an arrangement was made to reduce the diffusion of components into the atmospheric air. The time lag between the collection of the vapour and liquid samples was kept to the minimum. After collecting the samples,
the blower and the heaters were switched off. The residual liquid was withdrawn and the fresh charge was put into the still for the next run.

3.2 Materials Employed

The correctness of the results is limited not only by the accuracy of the instruments but also to a considerable extent by the purity of the substances used. It is impossible to describe a universal experimental technique which could be successfully used for purifying all substances. Each case must be considered individually, taking into account both the nature of the material and the likely impurities. Distillation, sublimation, extraction, ion exchange etc, are the normal methods employed for purification. The values of physical constants like boiling point, melting point, density, refractive index, viscosity, dielectric constants, etc, and the results of chemical analysis give us an information regarding the purity. Some of the reliable sources for the values of the physical constants are Timmermans [327], Parisot [247], Driesbach [61] and International Critical Tables. Chromatographic analysis serves as a useful tool when in many cases traces of contaminants cannot be detected from a knowledge of the physical constants.

The sources along with the specifications of various materials employed in this work are given in Table C.2. The chemicals were first subjected to treatments aimed at the removal of moisture [348]. Then the dried liquids were finally purified
by the distillation method. Ethylbenzene, p-xylene and isopropylbenzene were dried by keeping them overnight over pure anhydrous magnesium sulphate. 2-propanol was dried by refluxing for four hours with pure quick lime whereas allyl alcohol, methyl cellosolve and cellosolve were dried by refluxing for about four hours with chemically pure anhydrous potassium carbonate. The clear liquid was then decanted off. Testing for the presence of peroxides in the case of 2-propanol, methyl cellosolve and cellosolve revealed no such contaminations. Further purification was done in a 30 mm well insulated glass column packed to a height of one meter with 4 mm helices made from 24 SWG nichrome wire. Figure 5 gives the details of the distillation unit without insulation. The materials after preliminary treatment were taken in a dry two litre flask. Heating mantles were used for supplying the necessary heat for distillation. The column was completely lagged with an asbestos rope with a further layer of asbestos cloth. Compensatory heating over the length of the column was provided by a 125 watt 250 volt 'Flexotherm' heater, 'Sunvic' control switches were used to provide steady heating. The column was run at total reflux for about half an hour and then the low boiling fractions were removed at a very slow rate. The reflux ratio was kept constant at 9:1 by a simple, flexible reflux head developed by Miller [201], the essential features of which could be noted from Figure 6. After the low boiling fractions were completely removed and the temperature remained constant for about half an hour, the heart cuts were collected. Care was taken to prevent the vapours from coming
in contact with the atmospheric moisture during distillation and handling processes. The materials were purified in small lots enough for each system and were stored in coloured bottles. Purity was checked by comparing the physical constants like the boiling point, refractive index and density values with the ones given in literature. Table C.3 gives the physical properties of the purified materials.

Special precautions were to be observed while handling allyl alcohol, which is a highly toxic compound. Implements like safety goggles, hand gloves and gas masks were used.

3.3 Analytical Techniques

Refractive index method was used for analysing the equilibrium samples. Refractive indices were measured by means of a Bausch and Lomb Abbe-3L refractometer, calibrated by means of a standard glass test piece having a nominal refractive index of 1.5126, using 1-bromonaphthalene as the contacting liquid. The prism temperatures were maintained to within ±0.1°C by using a 'Precision Scientific' constant temperature circulating bath controlled by a 'Precision' 'Merc to Merc' thermoregulator. Before measuring the refractive indices, the samples were maintained at the temperature of analysis for at least 20 minutes in an 'Ultra Thermostat' manufactured by Metrimpex, Hungary. The temperatures were controlled to within ±0.1°C by means of a mercury thermoregulator supplied by the same company. All the weighings were made on a 'Labor' (Metrimpex, Hungary) single pan analytical balance having a sensitivity of 0.1 mg. The accuracy of the
refractive index measurements were of the order of \( \pm 0.0002 \).

Calibration curves for the purpose of obtaining the compositions were drawn on enlarged scale to improve readability. Figure 5 is a photograph of the apparatus and equipment used for the purification of the chemicals and the analysis of the equilibrated phases.
FIG. 5 Analytical Equipment