



# A NOVEL VOLUME DILATOMETER FOR THERMAL EXPANSION STUDIES IN LIQUID MIXTURES

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## ABSTRACT

*A glass dilatometer of the volumetric type, with a novel provision for slight variations of the capacity of the dilatometer to cover a wide range of temperature, has been constructed for the study of thermal expansion of liquid mixtures. The performance of the dilatometer is studied by measuring the thermal expansions of pure liquids methanol and heptane. Thermal expansion measurements have also been performed in the critical region of the methanol + heptane system, showing logarithmic divergences close to the critical solution temperature.*

Key words: Thermal expansion; Liquid mixtures; Dilatometer; Critical phenomena.

## 1. INTRODUCTION

Among the various methods of measuring the thermal expansion of liquids, the dilatometer technique is perhaps the best known and convenient method. A volume dilatometer measures the volume of a given weight of liquid, whereas a gravimetric or weight type dilatometer measures the weight of a given volume of the liquid. Different types of volume dilatometers [1-7] and weight dilatometers [8-11] have been described in the literature. Weight type dilatometers [8-11] can be made quite accurate, but are not suitable for two phase and similar systems, especially in cases where the depletion of one of the phases alters the properties considerably. Hence volume dilatometry is more convenient for studies dealing with critical mixtures whose compositions have to remain unaltered.

The volume dilatometer described here is an improvement over the one used earlier [12] in this laboratory for the study of thermal expansion of binary liquid mixtures. The volume changes are followed from the positions of the meniscus in a glass capillary tube attached to a reservoir whose volume can be altered slightly using a teflon-glass seal of the type used in high vacuum systems. The dilatometer has also the advantage in

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convenience of assembly which allows the same dilatometer to be used with different samples. A single run serves to cover wide ranges of temperatures with adequate resolution over any given range.

## 2. DESCRIPTION

A schematic diagram of the dilatometer is given in Fig. 1. It has a cylindrical glass (pyrex) reservoir bulb at the bottom and a capillary stem,

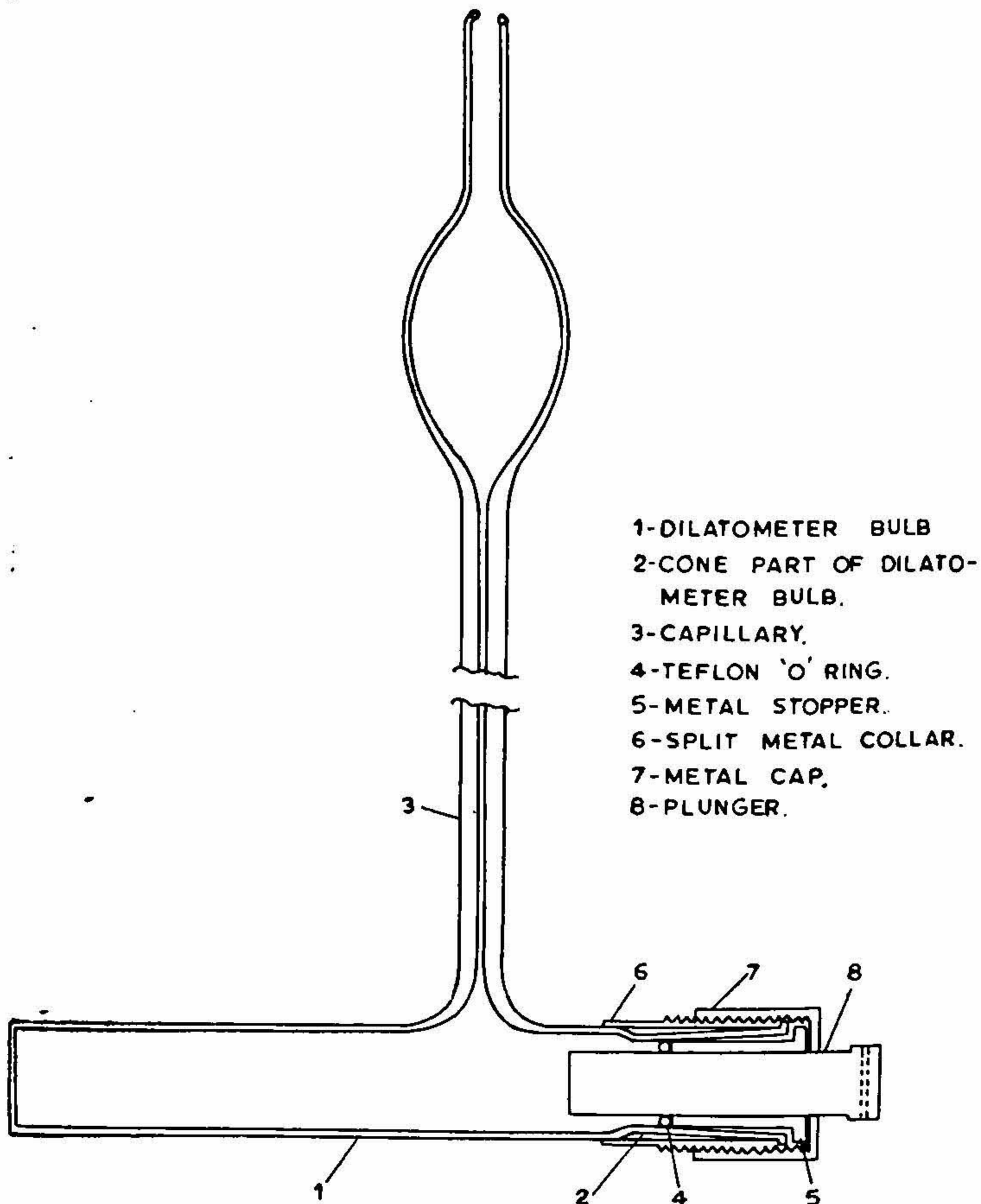


FIG. 1. Dilatometer.



having a uniform bore and of length about 20 cms. was sealed perpendicular to the bulb. The capillary diameter was 1.0 to 0.2 mm depending upon the experiments. The capillary opens into a large bulb with a tapering tube at the top. The cylindrical reservoir bulb is made from the female part of a B14 cone joint and the cone portion is provided with a mechanical seal. The components of the glass-teflon mechanical seal are shown in Fig. 2 and the seal is seen to be based on the principles used in the assembly of high vacuum equipment. All the components are made using conventional

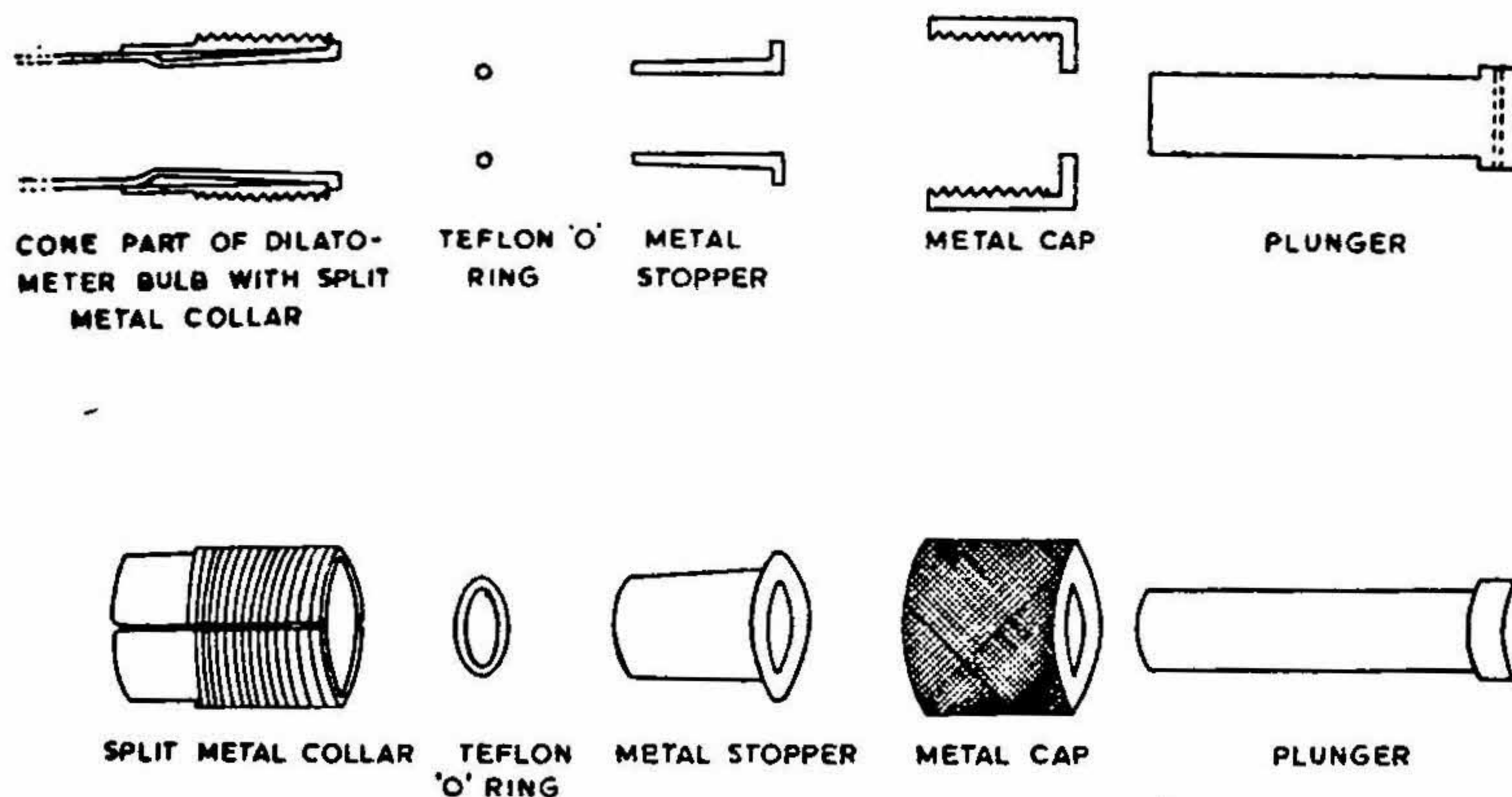


FIG. 2. Components of Mechanical Seal.

machining. This arrangement acts not only as a mechanical seal but also as a device to vary the capacity of the dilatometer and hence helps to cover a wide range of temperature; further, the seal facilitates the cleaning of the dilatometer after each run. No leaks developed with the dilatometer although some runs extended for 2 to 3 weeks. In order to obtain the exact cross-sectional area, the capillary was calibrated using a mercury thread and weighing the volume of mercury. The components of the mechanical seal are assembled in the order shown in Fig. 2; the split metal collar encircles the cone part of the dilatometer reservoir bulb and the metal cap turns over the split metal collar. The metal stopper keeps the teflon 'O' ring pressed in position.

The free end of the plunger is fixed into one end of a tubular screw which works through a fixed nut and is connected to a worm-gear device. The worm-gear can be operated from above the thermostat in order to move the plunger in or out of the dilatometer reservoir bulb. This makes



small changes in the capacity of the dilatometer. The meniscus can be moved easily from the top to the bottom of the capillary and *vice versa* facilitating the observations over a range of temperatures.

### 3. EXPERIMENT

A special thermostat, with temperature control and measurement to millidegree levels [12] was used in the thermal expansion studies. The thermostat capacity was about 15 litres, in view of the size of the dilatometer and clamping arrangements for the supports of the dilatometer.

In this type of measurement, the degassing of liquids is a very serious problem. Some workers have adopted an alternate heating and cooling procedure for degassing. Because of the presence of metal parts in the mechanical seal, this could not be carried out with the liquid in the dilatometer. Instead the liquid was taken in another container and heated to about 60°C; after cooling the liquid to the room temperature the container was slowly dipped in liquid nitrogen and allowed to freeze and then evacuated by connecting to a vacuum pump through a stopcock. After evacuation of the air, the stopcock was closed and the container taken out of the liquid nitrogen and kept at room temperature for a few hours to allow degassing. This procedure was repeated two or three times to ensure complete degassing of the liquids.

After the assembly of the mechanical seal, the empty dilatometer is first weighed and then filled with the liquid upto a certain level by means of a syringe and a long needle which could go up to the bottom of the dilatometer reservoir bulb. The second weighing gives the weight of the dilatometer *plus* liquid. The top end of the dilatometer is then flame sealed. For filling binary liquid mixtures, one can easily calculate the proportion by volumes of the liquids in order to get the desired composition by weight. The filling and sealing were done fairly quickly to see that there was negligible evaporation of the liquid between the filling and the sealing.

The dilatometer with supports and worm-gear assembly was mounted in a thermostat capable of controlling the temperature in the range of 35°C to 65°C with a short term stability of one mdeg. At any desired temperature, the liquid meniscus could be brought into the capillary by operating the worm-gear and adjusting the position of the plunger rod. The position of the meniscus in the capillary was read using a cathetometer correct to 0.001 cm. Thermistors were used for the measurement of temperature. Readings were taken at a series of equilibrium temperatures; sufficient time for thermal equilibrium (4–10 hours) was allowed before taking any reading.



The coefficient of apparent expansion of the liquid is calculated from the relation  $(\pi r^2 \Delta l)/(V \Delta T)$  where  $\pi r^2$  represents mean cross-sectional area of capillary,  $\Delta l$ , change in meniscus level corresponding to change in temperature  $\Delta T$  and  $V$  the volume of the liquid. The coefficient of real expansion of the liquid is obtained by taking into account the coefficient of cubical expansion of glass. Corrections may be necessary for various sources of error; the errors in dilatometric measurements have been discussed by Craig [13].

#### 4. DISCUSSION

The performance of the dilatometer was studied by measuring the expansions of pure liquids methanol and heptane for which standard values are available.

Figures 3 *a* and 3 *b* show the variation of the coefficients of thermal expansion with temperature for methanol and heptane respectively. These

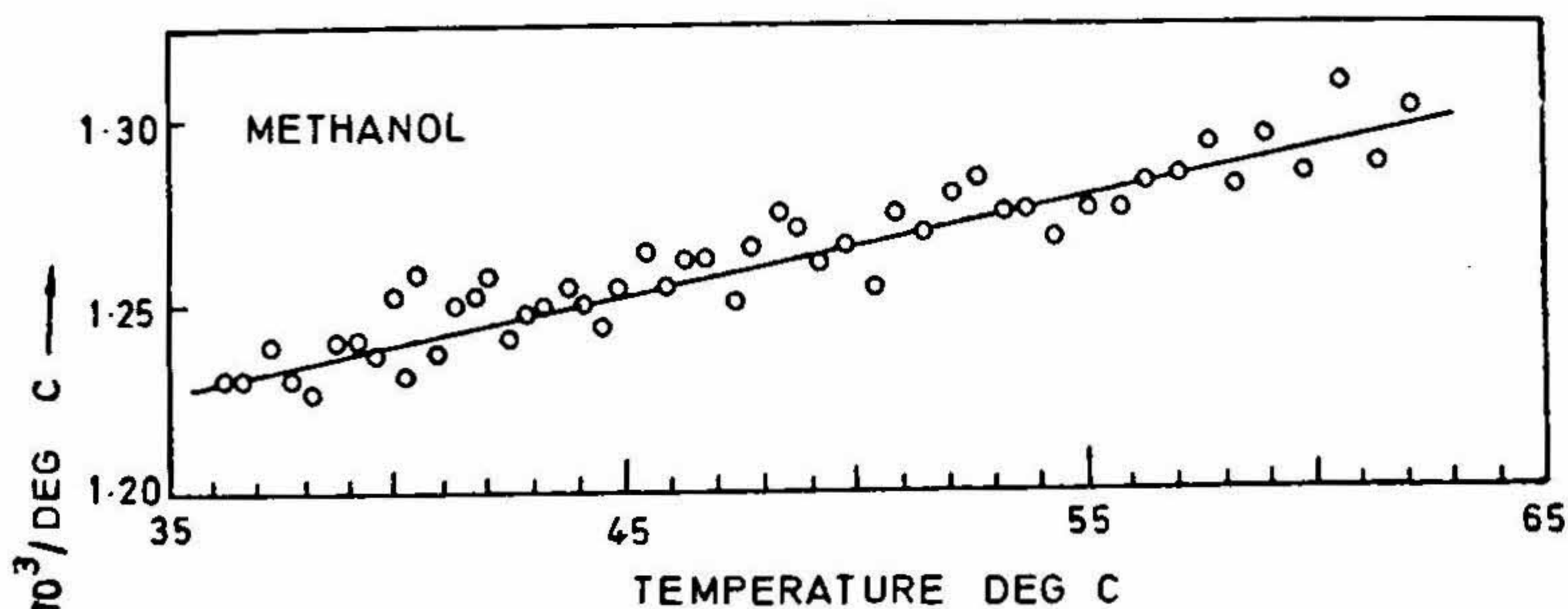


FIG. 3 *a*. Thermal Expansion of Methanol

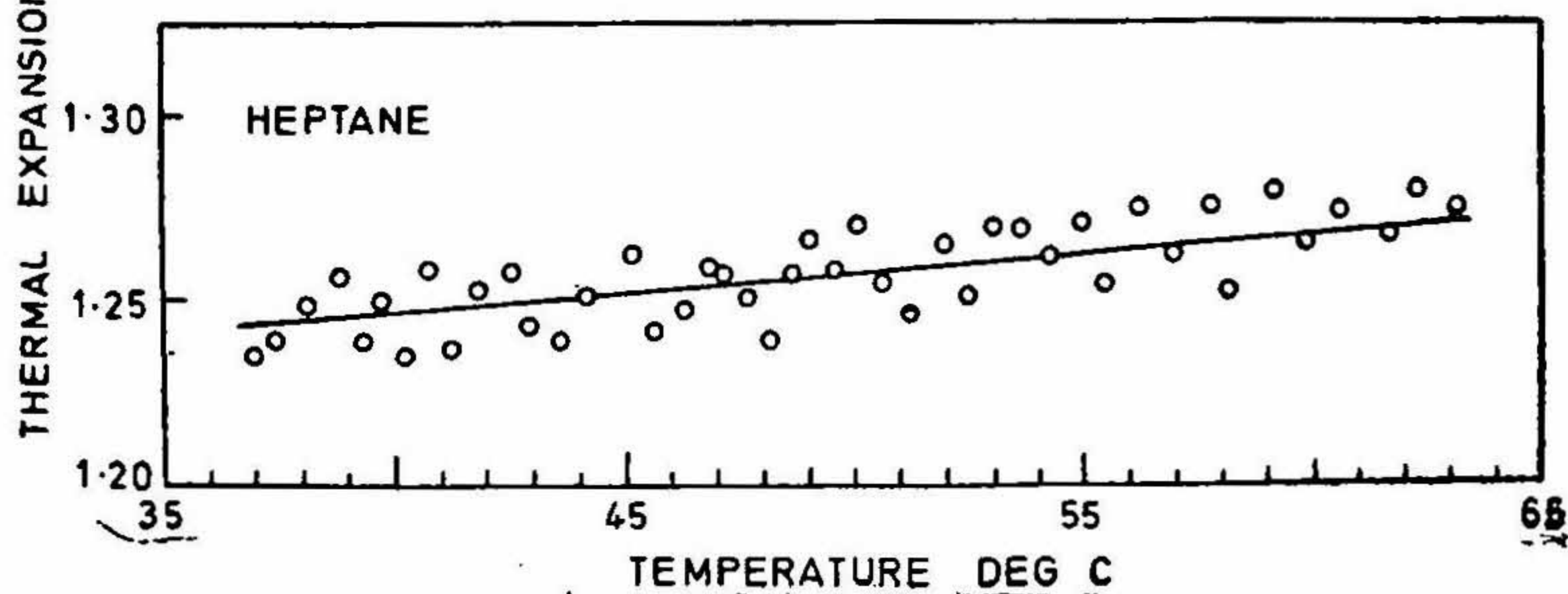


FIG. 3 *b*. Thermal Expansion of Heptane.

are almost straight lines showing a slight increase of thermal expansion with temperature. Using the tabulated density-temperature relations for methanol and heptane [14], one can easily calculate the thermal expansion at different temperatures. The thick lines in Figs. 3 *a* and 3 *b* correspond to thermal expansion values calculated from these relations; these seem to be in agreement with the experimental values. The scatter in the experimental values (Fig. 3) is expected in view of the fact that the long-time stability of the thermostat is about 2 to 3 m deg., and the capillary bore is not sufficiently fine for higher accuracy. Further the cross-sectional area of the capillary varied from 1.170 to 1.161 sq. mm, giving a scatter of the same order, of about 1%, as observed. The scatter can be reduced by attention to the mechanical assembly details and by using a capillary of finer and more uniform bore. Attention is being directed to these problems in a new apparatus under construction.

Thermal expansion measurements in the critical region on methanol + heptane system [15], using the volume dilatometer, show anomalies (Fig. 4) close to critical solution temperature. Specific heat measurements [16] on the same system show similar anomalies close to  $T_c$ . The thermal expansion data in the critical region indicate a nearly symmetric logarithmic singularity. For example, if the coefficient of thermal expansion is written as  $\beta_{PX} = C^\pm + D^\pm \ln |1 - T/T_c|$  with + sign for  $T > T_c$  and - sign for  $T < T_c = 325.02^\circ K$ , one has the following values;

$X^*$	$C^+$	$C^-$	$D^+$	$D^-$
60.64	$-0.280 \times 10^{-3}$	$-0.085 \times 10^{-3}$	$-2.67 \times 10^{-4}$	$-2.80 \times 10^{-4}$
61.36**	-0.165	+0.190	-3.13	-3.19
61.91	-0.210	+0.005	-2.17	-2.78
62.46	+0.455	+0.455	-1.85	-1.85

\* Composition in mole% of methanol.

\*\* Critical composition.

The fact that  $D^+ \approx D^-$  indicates that the logarithmic anomaly is symmetric about  $T_c$ . The temperature resolution and accuracy are such that one cannot rule out the possibility of a fit to the power law singularity  $\beta_{PX} = \bar{C}^\pm + \bar{D}^\pm |T - T_c|^{-\alpha^\pm}$  with  $\alpha^\pm = \frac{1}{8}$ . The analysis of the data for critical composition 61.36 mole% of methanol gives  $\bar{C} = -0.25 \times 10^{-3}$ ,



$\bar{D} = 2.28 \times 10^{-3}$  for  $T < T_c$ . These aspects of the critical phenomena will be discussed elsewhere [17].

Having indicated the type of useful results obtainable with ease using this dilatometer, it is finally pertinent to discuss the shortcomings. The first one is the problem of degassing the liquids, which cannot be done

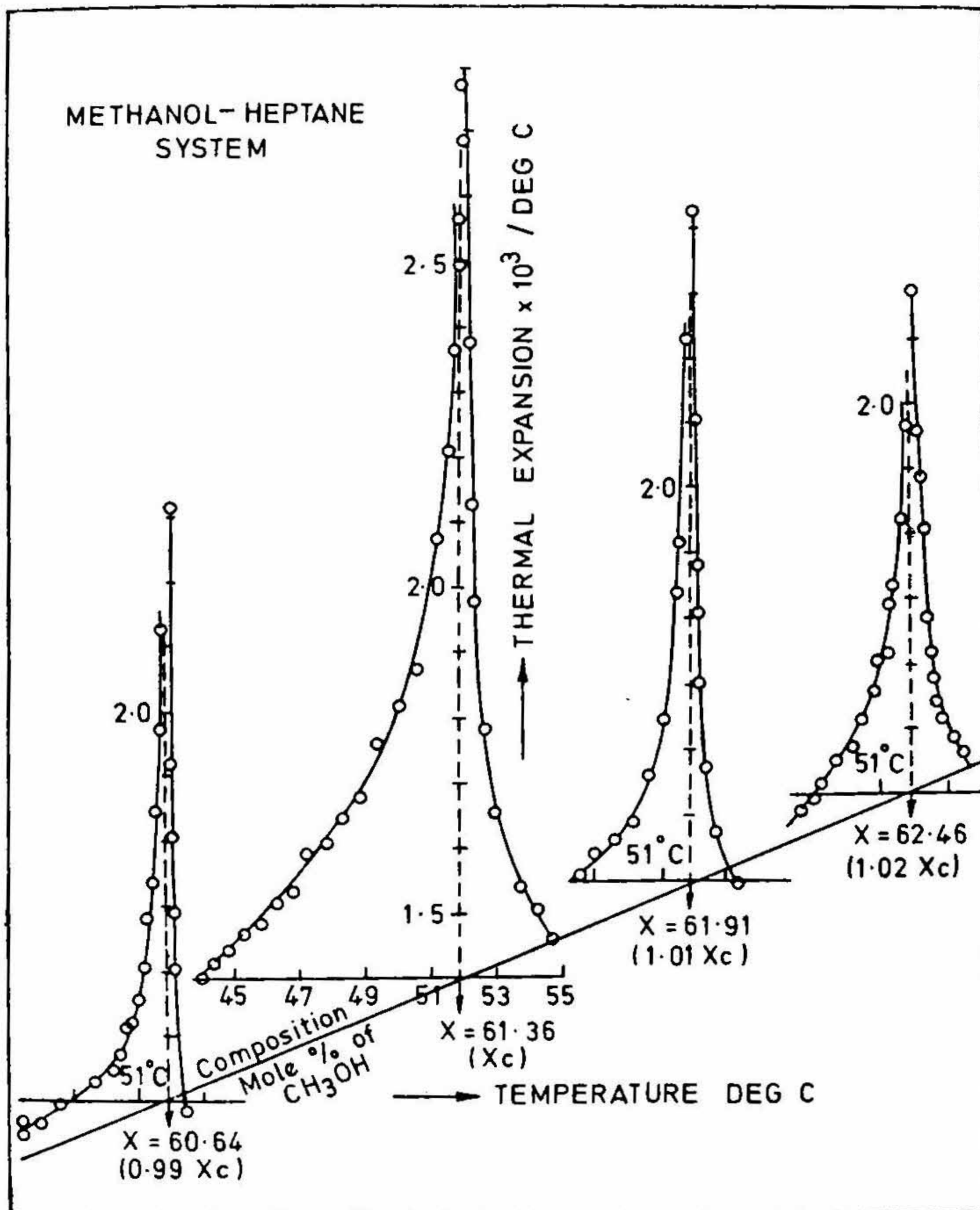


FIG. 4. Thermal Expansion of Methanol + Heptane System.

inside the apparatus. One has to use liquid samples which are already degassed and so far no difficulty has been encountered even at elevated temperatures. The second is the use of teflon seal which means that temperatures of operation must be less than about 200° C. The third concerns the possible plastic deformation of the teflon under the continued compression. Indeed one of the teflon 'O' rings was appreciably deformed after 8 months of use. This deformation would have changed the reservoir volume of about 30 ml by about 0.005 ml over this period. Therefore the errors caused by a change in reservoir volume, due to the plastic deformation of the teflon, being mistaken for an apparent thermal expansion during the course of an experiment are entirely negligible.

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