

CHAPTER II

DESCRIPTION OF THE EXPERIMENTAL SET UP

21 Introduction

The design of the experimental set up for high pressure investigation of liquid crystals presents certain problems which are not normally encountered in the study of the solid state, such as containment of the liquid crystalline material, low heats of transition, high chemical reactivity with most containing materials, etc. In addition to this, liquid crystals are also known to react with all pressure transmitting media, liquid or solid, which results in a drastic reduction in the transition temperatures, even if there is a minute contamination. If gas is used as the pressure transmitting medium, then it gets dissolved in the liquid crystalline sample and no meaningful measurements can be made. Fabrication of a high pressure cell for liquid crystals must therefore be done taking into account all these problems.¹ Three types of cells have been used in the present study, viz., an optical cell with sapphire windows, diamond anvil cell and DTA cell. The description of these cells forms the subject matter of this chapter.

2.2 Optical High Pressure Cell

Optical transmission technique was the earliest method to be used for the study of liquid crystalline transitions at high pressure.^{2,3} More recently, this technique has been extensively used with considerable success by Keyes et al,^{4,5,6} by Pollmann et al^{7,8} and by Gladis et al.^{9,10} This technique is extremely useful for the study of different types of liquid crystalline transitions including the smectic C - smectic A transition which cannot be detected by other techniques like DTA, volumetric, etc. In this section, we shall give, in detail, the constructional as well as the design aspects of the optical high pressure cell and describe its working.

2.2.1. Description of the optical cell

The schematic diagram of the basic parts (hardware) of the high pressure optical cell is shown in figure 2.1. It consists of a cylinder machined out of a low alloy hardenable Indian steel called EN24 which has the composition of 0.4% carbon, 0.2% silicon, 0.55% nickel. This steel which is roughly equivalent to the widely used AISI 4130 type, can be hardened to great strength by means of martensitic transformation. The alloying elements, in addition to increasing the hardenability of the alloy also

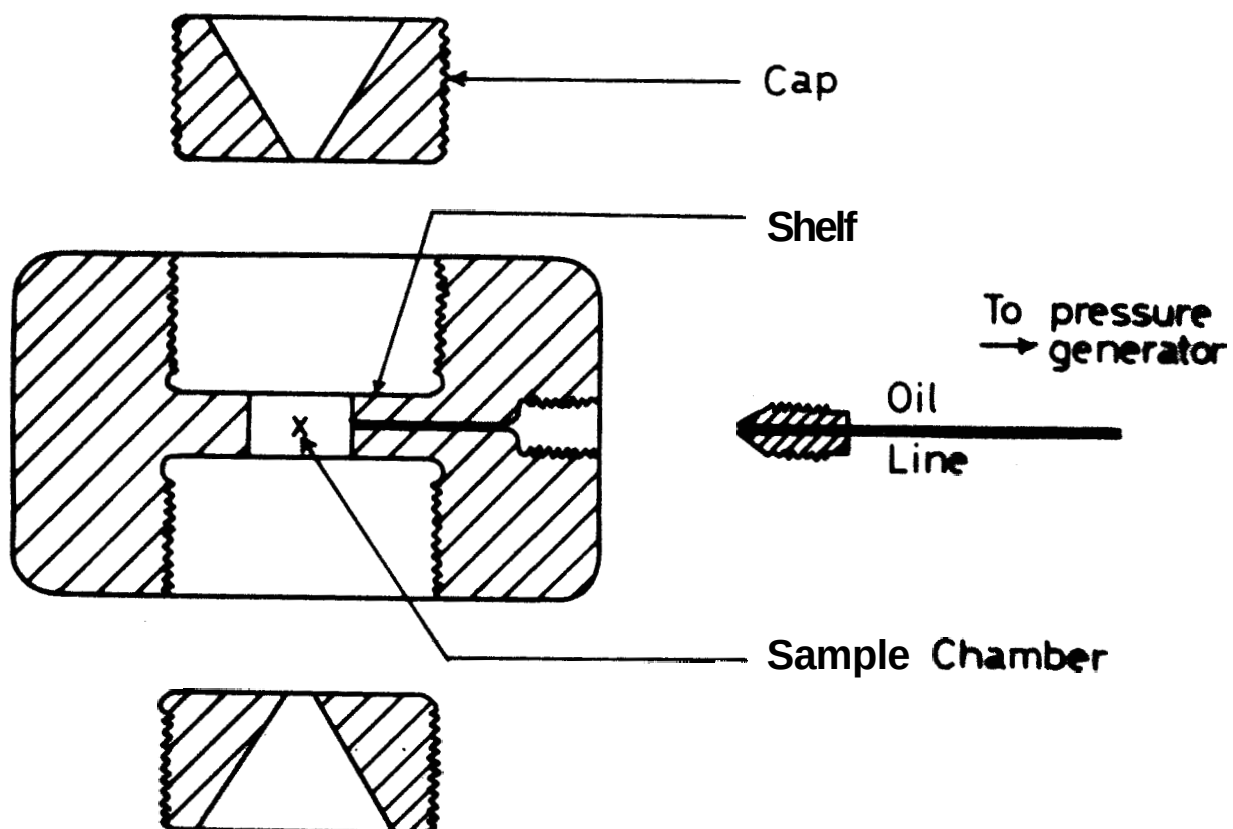


**Figure 2.1: Schematic diagram of the basic parts
(hardware) of high pressure optical cell**

contribute with some solid solution strengthening. The various parts of the cell are machined and heat treated to a strength of about 40 RC. The two plugs, which serve to keep the sample assembly in position, are also made out of the same material and heat treated to the same hardness as the cell body. The hole in the cell body for pressure connection consists of two stages, a smaller hole (about 1.2 mm dia) which extends from the interior of the body to about $\frac{2}{3}$ of the thickness (this hole ends in a 60° cone taper with a 2 mm opening) and which in turn joins a larger hole bored (10 mm in dia and 1 cm in depth) from the outside. The opening of the top and bottom of the cell have a dia of about 3.0 cm and are threaded (14 Thd BSW). Figures 2.2 and 2.3 are the schematic diagrams of the cell body and the plug. Both the plugs and the body are fully naged, the plugs have, on the outside, threads which exactly match those that cut in the pressure cell. It is important to have a wide viewing angle without reducing the strength of the plug. For this purpose, a 70° taper is provided in both the plugs. The plugs have a small protrusion on the inside which are made optically flat by handlapping. Two slots are made on the plugs to facilitate the tightening of the plug into the cell body.

CELL - BODY

EN-24

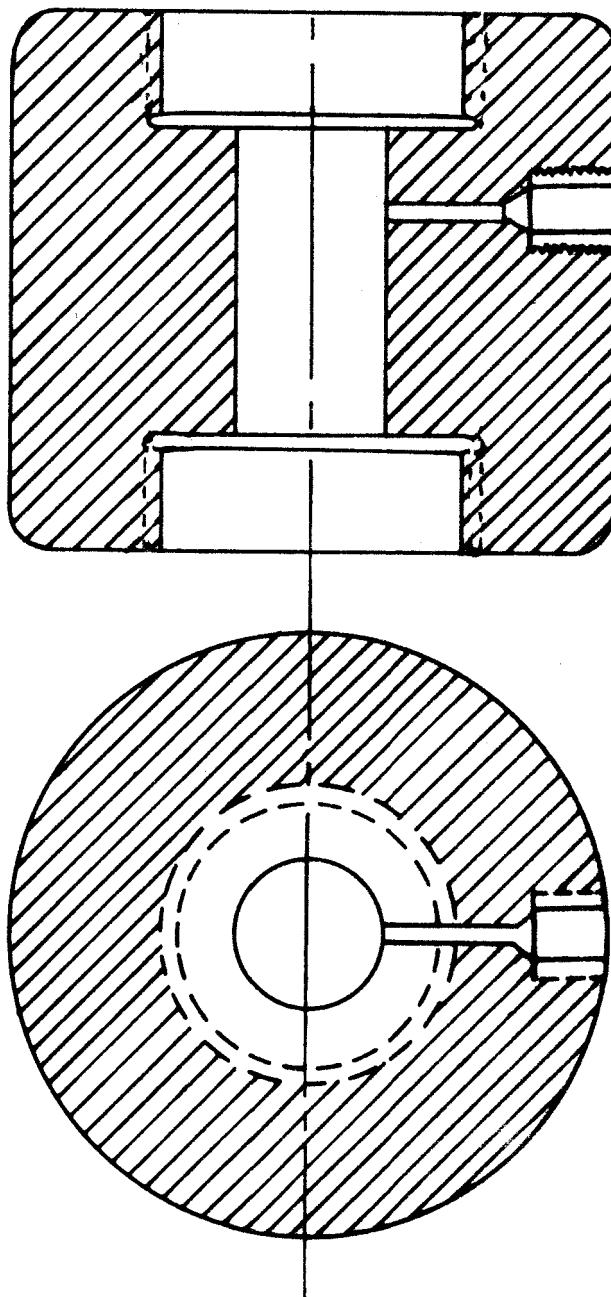


FIGURE 2.2

STEEL CAP

EN 24

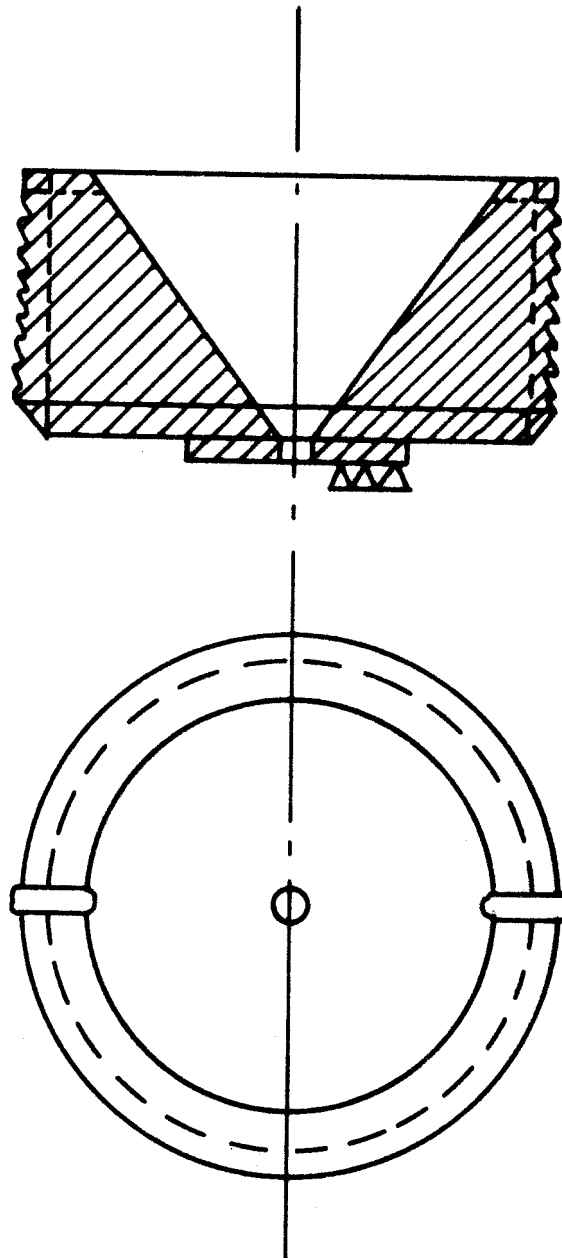


FIGURE 2.3

The complete assembly of the cell is shown schematically in figure 2.4. The detailed drawings of each part of the cell are given in figures 2.5 to 2.10. We have shown, for the sake of better visualisation both the cross sectional and the top view of each component. The liquid crystalline sample is in the small central chamber of the high pressure cell and the two steel plugs seal the chamber at both ends. It is connected to the oil pump by means of steel pressure tubings and a hole is drilled from the chamber to the outside of the cell. We shall describe below the construction as well as working of the various parts of the optical cell.

2.2.2. Sample chamber

In order to develop high pressure in the sample chamber, it is essential to have a tight seal along both boundaries of the caps: one for the central hole and the other along the circular boundary of the chamber against the cap. The reason for the second seal is because the threads of the cap alone are not sufficient to hold the cap tightly against the main body of the cell. The high pressure normally raises the cap only slightly, but this is sufficient to make a thin clearance between the cap and the cell body, leading to a leak of the oil to the

HIGH PRESSURE OPTICAL CELL

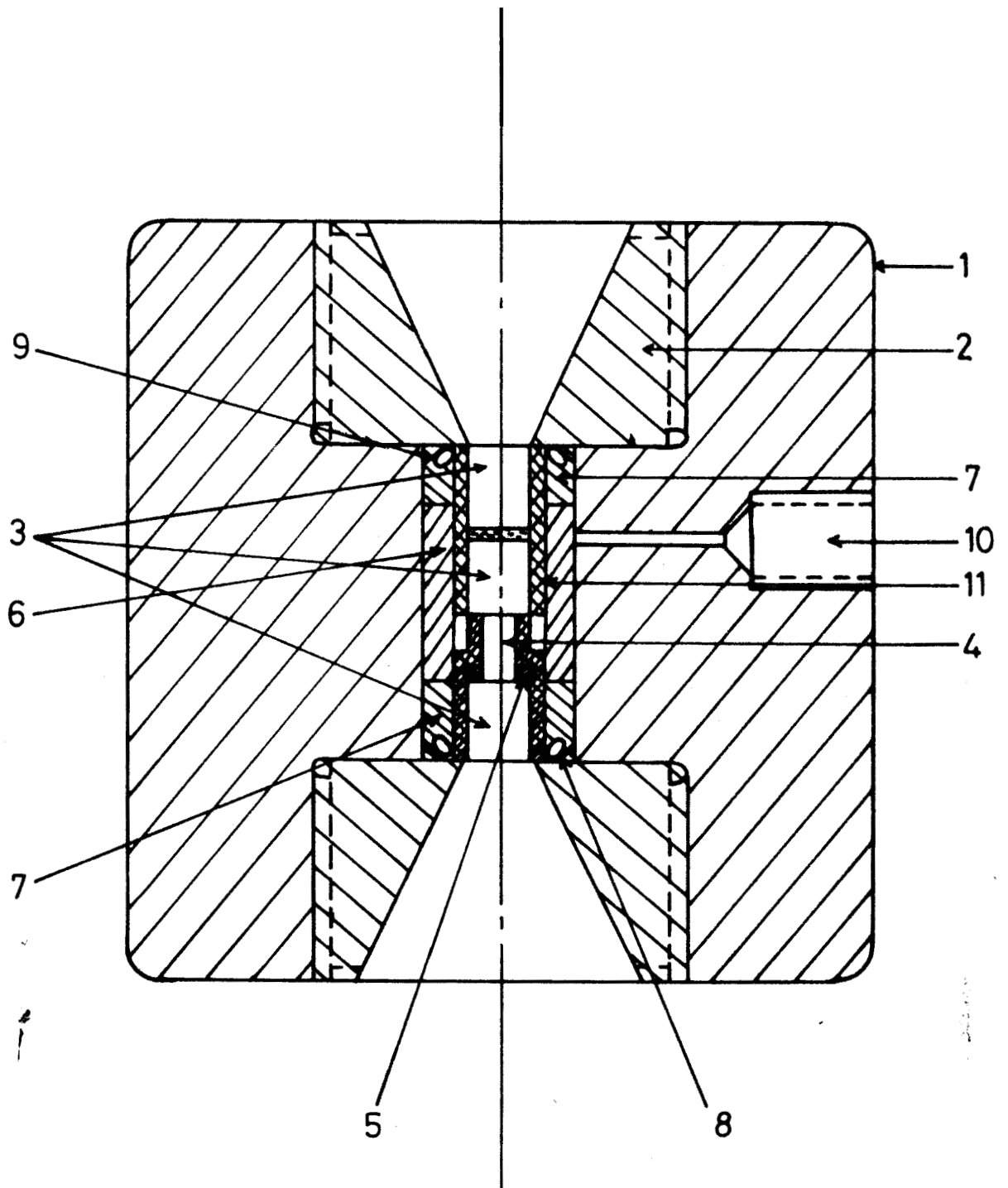


Figure 2.4: Schematic diagram of high pressure optical cell

1. Cell body 2. Steel plug, 3. Sapphire cylinders,
4. glass rod, 5. Washer and spring, 6. Centre spacer,
7. outer spacer, 8. 'O' ring, 9. Antiextrusion ring,
10. High pressure connection, and 11. Fluorin tube.

OUTER SPACER

EN 24

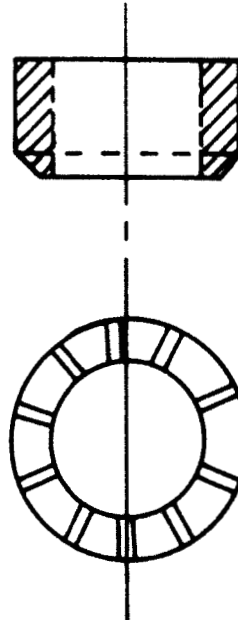


FIGURE 2.5

CENTRE SPACER

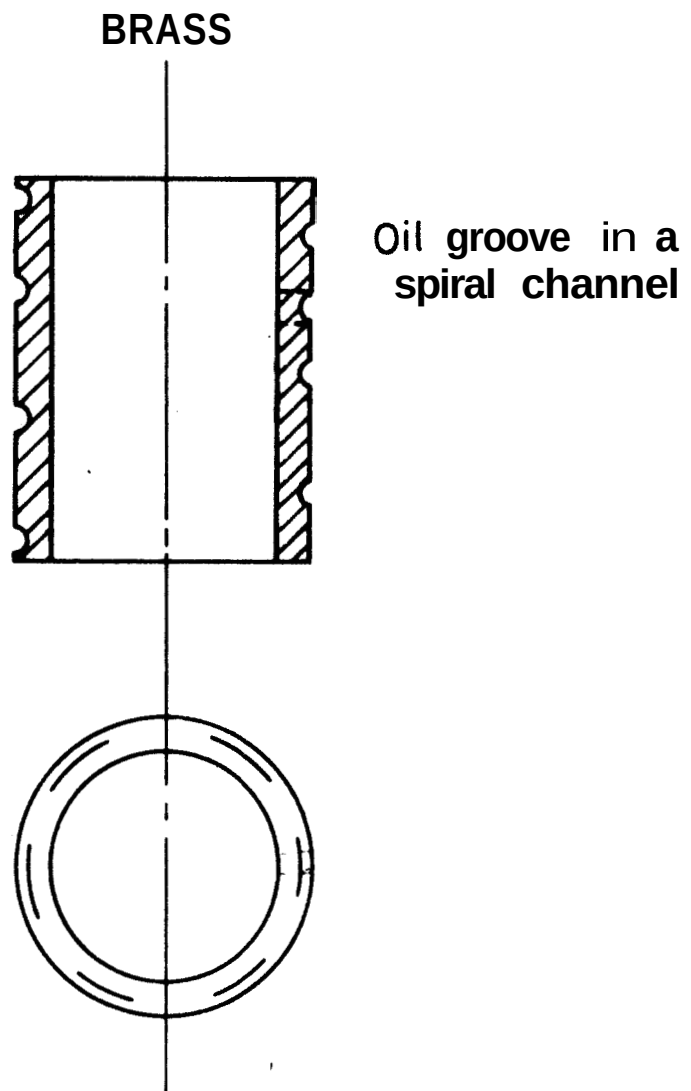


FIGURE 2.6

LOW PRESSURE SEALER

material - Brass

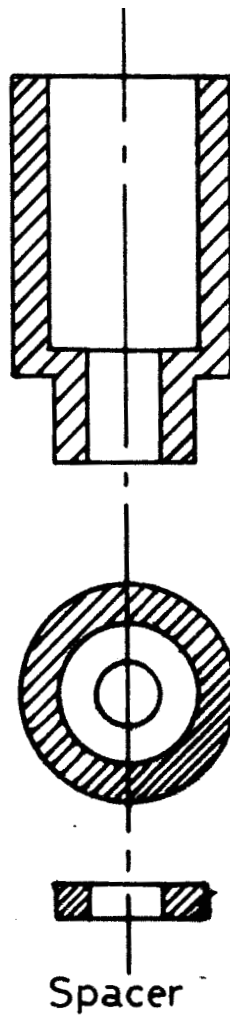


FIGURE 2.7

SAPPHIRE WINDOW

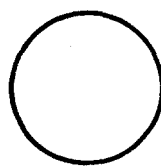


FIGURE 2.8

GLASS SPACER

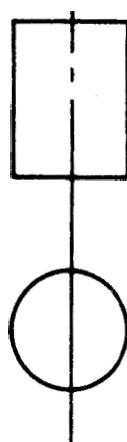


FIGURE 2.9

outside. This leak is avoided by placing a neoprene 'O' ring around the junction. As the oil pressure increases, the 'O' ring is pushed to the corner and the seal is made at the point where the 'O' ring touches the cell body. Once the seal is achieved, oil cannot leak out. The only problem is that at sufficiently high pressure, the 'O' ring itself extrudes through the small gap between the cap and the seating of the cell body. This eventual breaking of the seal naturally results in the leak. This problem has been solved by the use of an 'anti extrusion ring'.

An anti extrusion ring is a ring of steel with a triangular cross section. The schematic diagram of the anti extrusion ring is shown in figure 2.10. This blocks the extrusion of the 'O' ring, while the 'O' ring keeps the oil from leaking out. The seal at the central hole of the cap is made with highly polished sapphire windows and a small washer made of thin aluminium foil. The high pressure of the oil keeps the sapphire tight against the cap and the aluminium foil fills up any crevices on the surface of the cap. This provides a fairly efficient seal. The 'O' ring as well as the sapphire windows are held in position initially by the outer apaoer made of EN 24 (figure 2.5).

ANTI EXTRUSION RING

EN 24

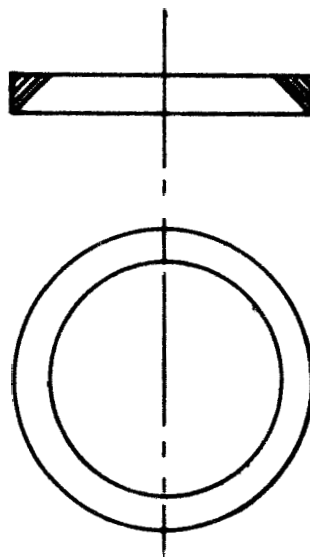


FIGURE 2.10

2.2.3. Encapsulation of the sample

As mentioned earlier in the chapter, liquid crystals react with the pressure transmitting oil. It is therefore imperative to completely encapsulate the sample so that the pressure transmitting fluid does not come into direct contact with the sample. This is achieved by using fluran tubing. Fluran is soft, flexible and is fluoro elastomeric in composition. It does not react with liquid crystal and can be used up to a maximum temperature of about 300°C. It is also soft and transmits pressure very well,

As seen in the schematic diagram (figure 2.4), the central hole of the upper cap is sealed by a sapphire window which also forms a part of the sample assembly. A thin section of the sample is sandwiched between this sapphire and a second sapphire which is essentially free as it is not used to seal the cap. These two sapphire rods sandwiching the sample fit snugly inside the fluran tube, and an effective seal is realised by tightly wrapping a thin steel wire round the tubing at the sapphire windows (figure 2.11). The inner spacer (low pressure sealer) washer and the spring center the bottom sapphire of the sample assembly and keep it under a light tension. The third sapphire which is completely isolated from the

SAMPLE ASSEMBLY

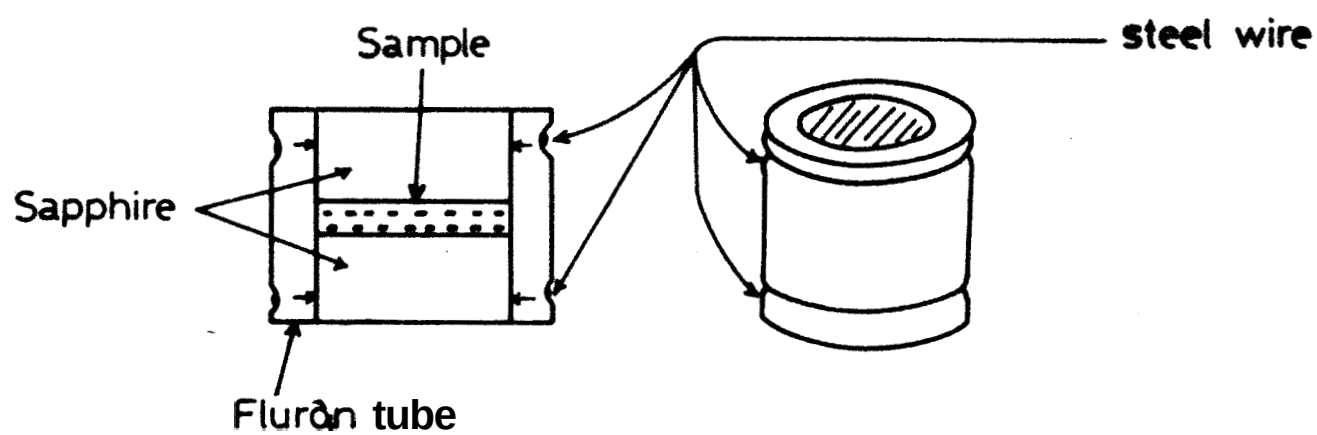


FIGURE 2.11

sample assembly seals the bottom end of the pressure cell. The space between this third sapphire and the bottom sapphire of the sample assembly is occupied by a glass rod which reduces the amount of oil between these two sapphires, thereby increasing the intensity of the transmitted light. The thickness of the sample can be fixed at any desired value by choosing washers of required thickness. Normally a sample thickness of 100 to 200 μ m was used in our experiment.

2.2.4. Description of the heater

As it is required to go to temperatures of about 250°C, it is necessary to design a heating system which heats the entire pressure cell to the required temperature. Figure 2.12 represents the schematic diagram of the heater and the cooling jacket. The heating system consists of an aluminium cylinder whose internal diameter is so machined that the pressure cell could be push fitted into it and hence the heater cylinder also acts as a binding ring. Eight through holes are made along the length of the cylinder and the heating elements are introduced in each of these holes. These heating elements are welded together in series so that we have a net effective heating capacity of about 1 kilowatt, which can heat the entire

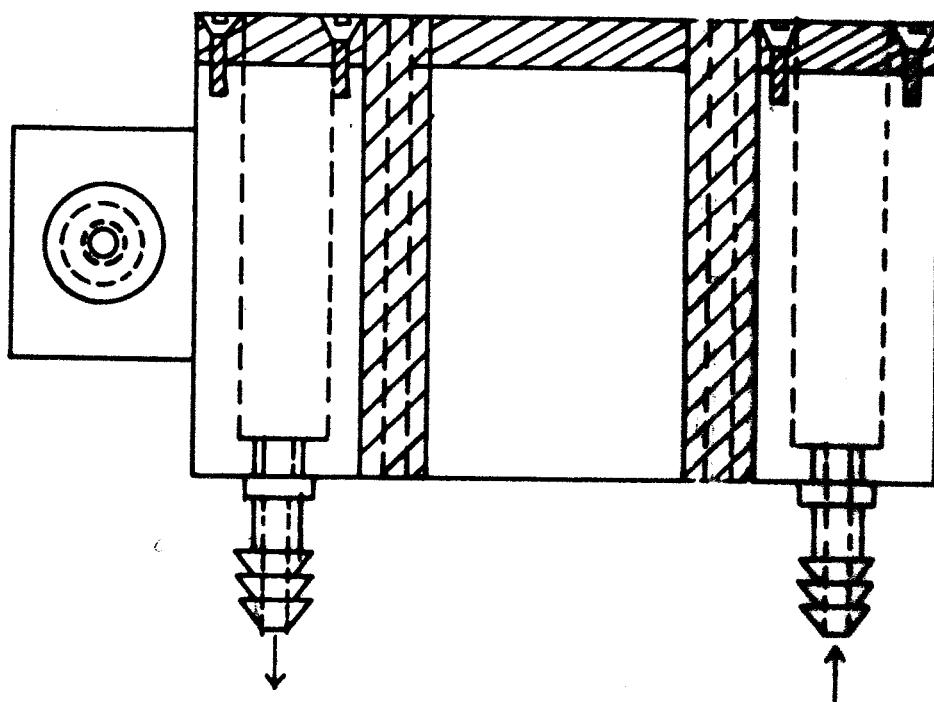
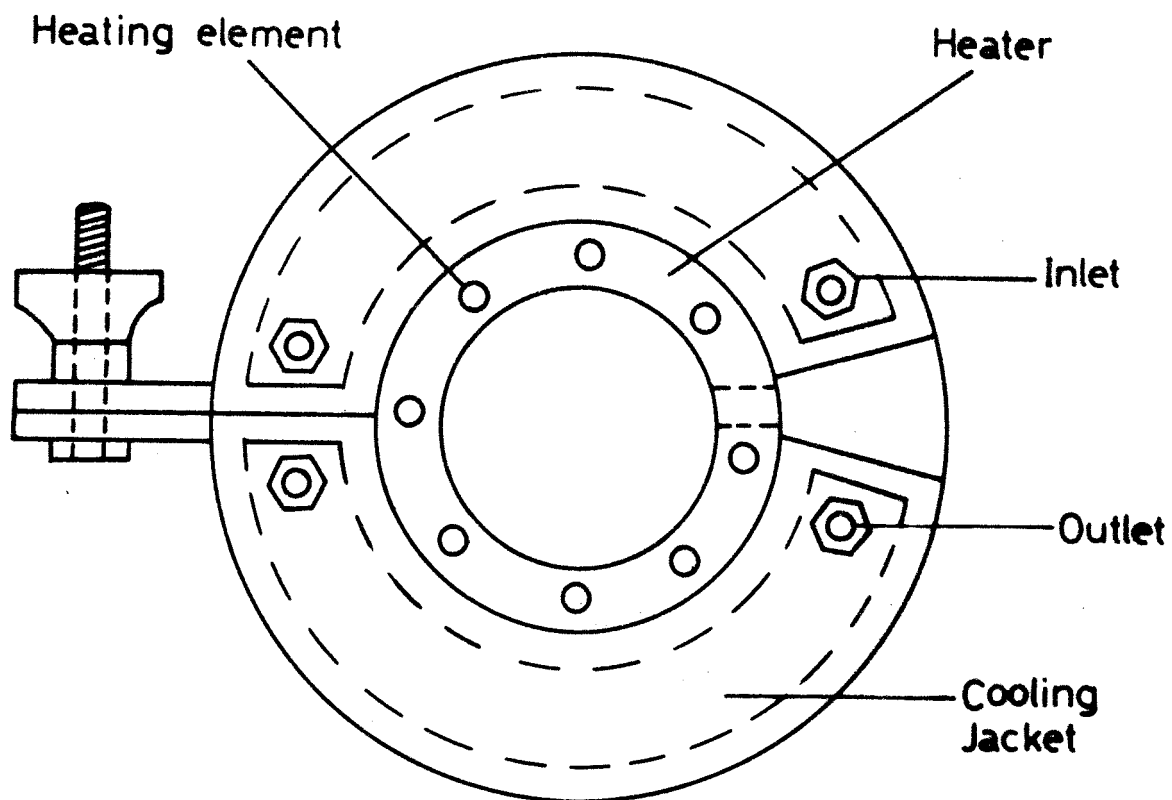


Figure 2.12: Schematic diagram of the heating assembly and the cooling jacket.

optical cell to the required temperature, A radial hole was made on this heater to **facilitate** the taking out of the pressure tubings from the pressure cell to the outside. **There is another small** radial hole for the introduction of the thermocouple (sheathed in a ceramic tube) which measures the **temperature sensed by the sample**. The thermocouple junction is so located that it just touches the cell body. **No holes are made on the cell body** for the insertion of the thermocouple **since** that would **considerably** weaken the cell body. **There** will be, of course, a gradient in the temperature of the **sample** and that **sensed by the thermocouple junction**. **This temperature gradient also depends** on the rate of heating of the sample. **Therefore careful calibration experiments using different rates of heating are performed** using which the true temperatures of the sample could be **computed**.

2.2.5. Description of the cooling jacket

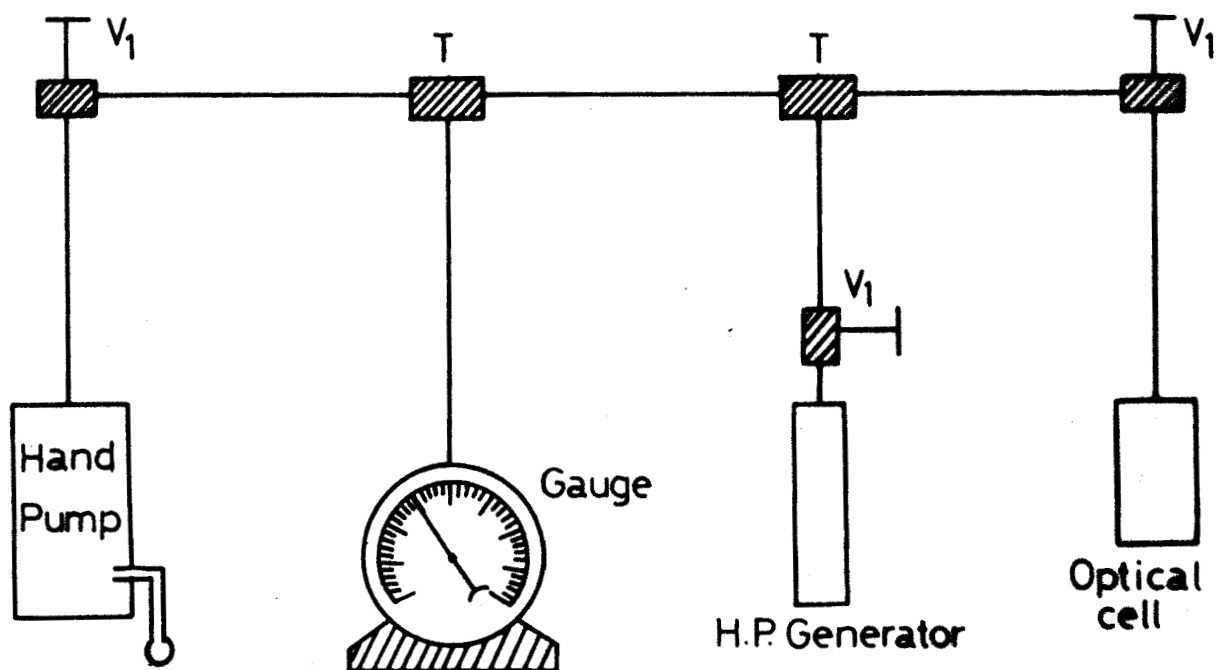
It **is** also **necessary** to **cool** the sample at a controlled rate while doing a number of **experiments**. **This is particularly necessary** when **recording a transition involving supercooled phases like the reentrant nematic phases** of a number of **compounds studied by us**. It was not **possible to control the temperature of the cell in the**

cooling mode by merely varying the current through the heating element. This is mainly due to the large thermal capacity of the cell. A cooling jacket into which the cell can be press fitted is made of aluminium. By suitably scooping out material from the jacket and by closing the top of the jacket with the aluminium lid provided with two sets of nozzles, water can be passed into the jacket without any leak. These nozzles are so located that water passes through practically the entire circumference of the jacket, thus making the cooling system very efficient.

2.2.6. High Pressure Plumbing System

The schematic diagram of the high pressure plumbing system used in the present study is shown in figure 2.13. A hand pump (PPI, USA) is used to generate the pressure in the cell. Fine variations of pressure are achieved by using a pressure generator with rather a small displacement capacity. This generator is essentially made of 316 stainless steel and 17-4 PH stainless steel, with teflon packing. The line pressure, which is nothing but the pressure experienced by the sample, is measured by Bourdon type gauge connected in line. Three two-way valves V_1 and two 'T' joints, all of which are capable of withstanding a line pressure of more than 10 kbar, are used

Schematic diagram of HIGH PRESSURE PLUMBING SYSTEM



V₁ → 2 way valve

T → Tee Joint

Figure 2.13: Schematic diagram of the high pressure plumbing system

in the plumbing system. Pressures are measured to an accuracy of ± 10 bare.

2.2.7. Determination of the phase transition temperatures

Figure 2.14 gives the schematic representation of the experimental set up used to determine the phase transition temperatures. Light from a He-Ne laser (Spectre Physics 2 mW) was made to fall on the sample in the optical cell and the intensity of the transmitted light was monitored continuously by a photocell (Motorola, USA, MRD 300). The output of the photocell measured as a voltage across a fixed resistance of $1\text{ K}\Omega$ was fed to the I-axis of a high sensitivity strip chart recorder (Riken Denshi F43P). The temperature of the sample was measured by a thermocouple (calibration experiment being performed as described below) used in conjunction with a digital multimeter ($4\frac{1}{2}$ digit). Keeping the pressure constant at any fixed value, the temperature of the sample was varied at the rate of approximately 1 to $2^\circ\text{C}/\text{minute}$. This rate is the same as that used in the temperature calibration experiment. At the phase transition there would be an abrupt change in the intensity of the transmitted light. The transition temperature at any pressure could be determined to an accuracy of $\pm 0.025^\circ\text{C}$.

Experimental set up

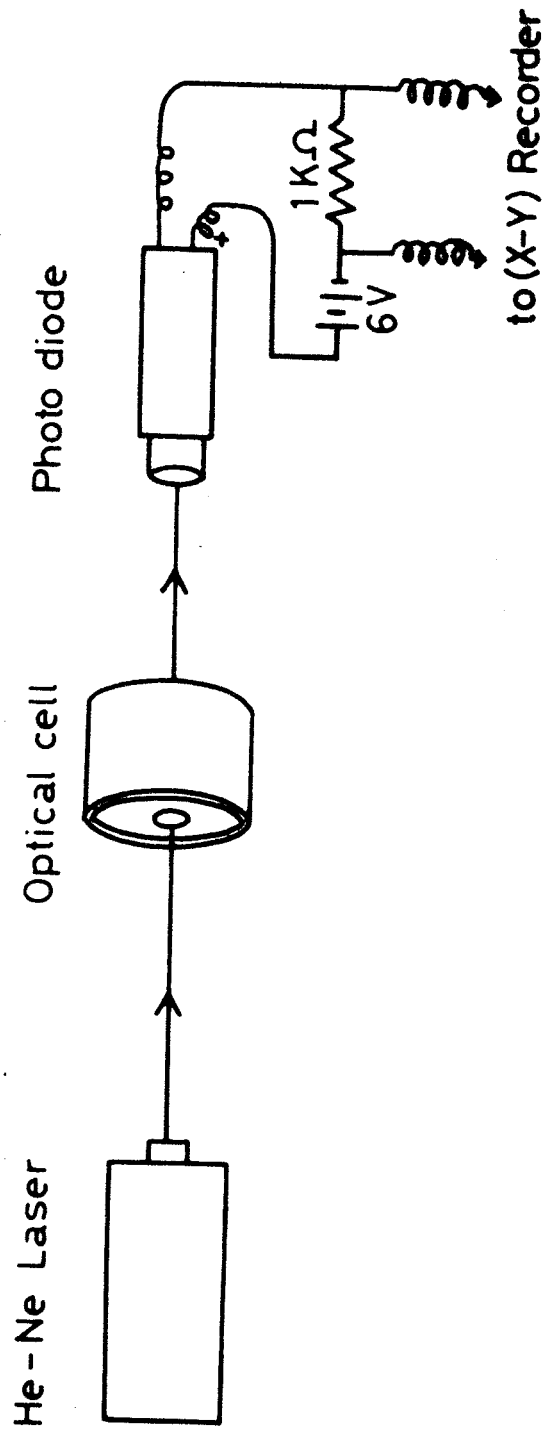


Figure 2.14: Schematic diagram of the experimental set up used for the determination of the transition temperature

2.2.8. Temperature calibration of the cell

For the temperature calibration of the cell during heating mode, several standard organic compounds of high purity were used. The compounds as well as their melting point are listed in table 2.1. The plot of the melting point of these compounds as measured in our experimental set up versus the melting point as given in the standard table is shown in figure 2.15. It is seen that the plot is linear with a constant slope of 0.993 which is therefore used in computing the true sample temperature for all our experiment in the range of about 50°C to 200°C.

Since the crystallisation temperature of these compounds depends on the rate of cooling, quantity of sample taken, etc. (i.e., the degree of supercooling is a function of the experimental conditions), the same compounds cannot be used for the temperature calibration of the cell during the cooling mode. For this purpose, some liquid crystal transitions which are highly reproducible were used in the cooling mode. The materials used in the calibration of the cell in the cooling mode are listed in Table 2.2 along with the transition temperatures as measured with the polarising microscope fitted with a hot stage Mettler FP52. The plot of this temperature

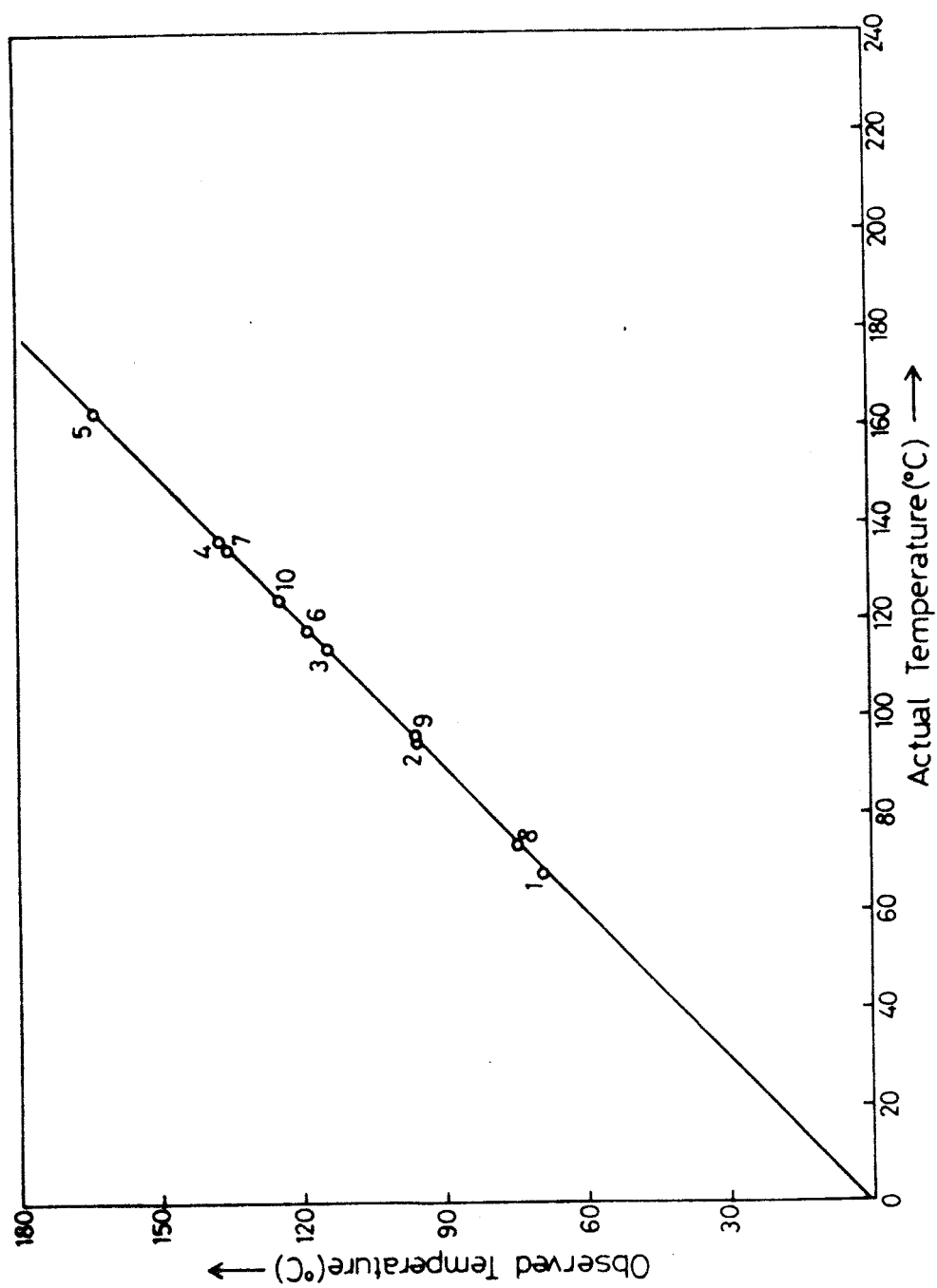


Figure 2.15: Temperature calibration curve of the high pressure optical cell in the heating mode using the standard substances listed in the table 2.1

versus the transition temperatures as measured in our experimental set up is shown in figure 2.16. The plot is again a straight line in the entire temperature range investigated thereby facilitating the calculation of the true temperature of the sample in the cooling mode.

2.2.9. Pressure calibration of the cell

In order to check the working of the cell, we conducted the first experiment on para-azoxyanisole (PAA), perhaps the most widely studied liquid crystal under high pressure. In all, there have been twelve determinations of $dT/dP^{2,3,11-20}$ and these data are tabulated in table 2.3. Of these 12 measurements, 8 agree quite well while the remaining 4 appear to be rather low (in at least two instances, namely, Deloche et al¹² and Tikhomirova et al¹⁵ the values might have been affected by the contamination of the sample as the authors themselves have indicated). Rejecting these four, the average value of dT/dP for solid-nematic and nematic-isotropic transitions are $31.3^{\circ}\text{C/kbar}$ and $47.7^{\circ}\text{C/kbar}$ which are probably accurate within a few %. The data obtained using the cell described above is given in table 2.4. Figure 2.17 gives the P-T diagram of PAA up to a pressure of 2 kbar. The value of dT/dP at 1 bar obtained by least

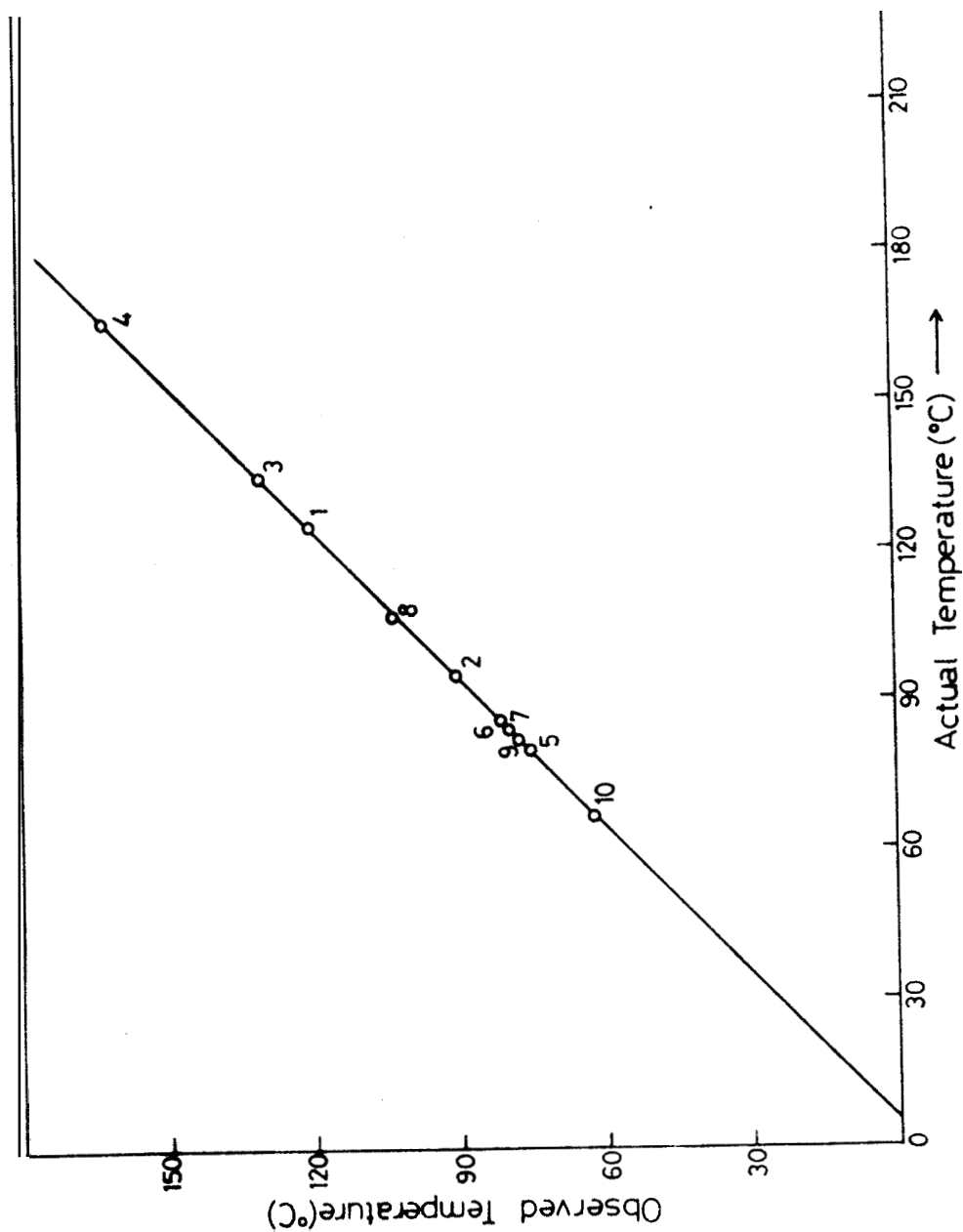


Figure 2.16: Temperature calibration curve of the high pressure optical cell in the cooling mode using the substances listed in Table 2.2.

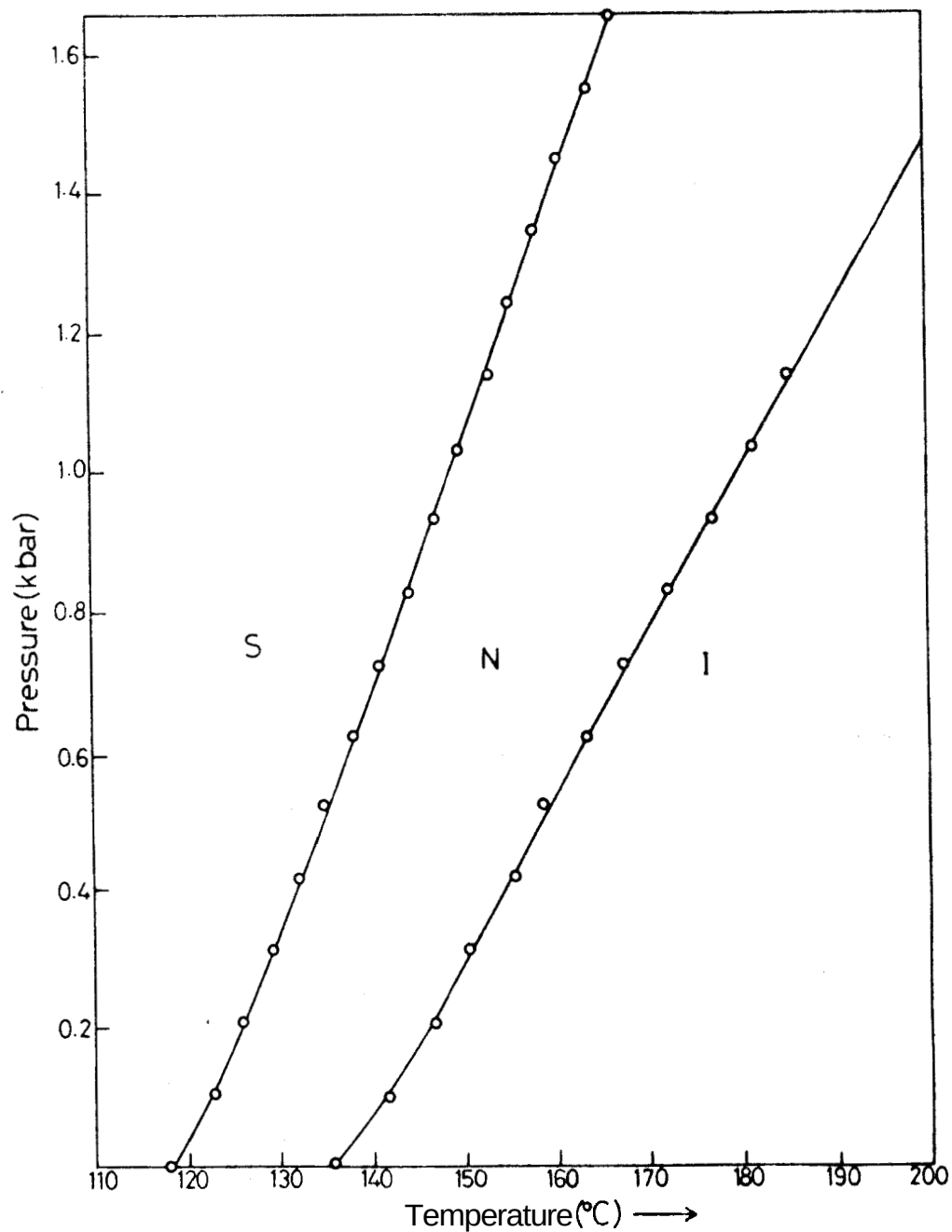


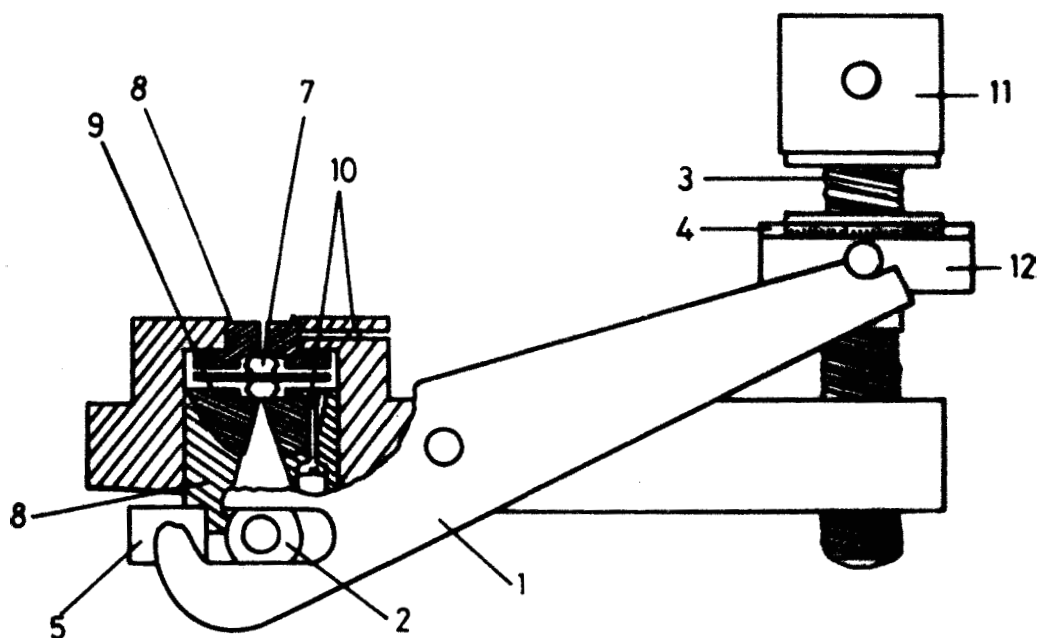
Figure 2.17: Pressure calibration of the high pressure optical cell - phase diagram of PAA.

square fit of the experimental data for solid-nematic and nematic-isotropic transitions to a straight line are $32.15^{\circ}\text{C/kbar}$ and $48.03^{\circ}\text{C/kbar}$ respectively, which are in very good agreement with the average value of the previous determinations. It must also be mentioned that the experiments were conducted by both increasing and decreasing the pressure and it was found that the transition temperature at any pressure was independent of the pressure cycling. This showed that the sample in the cell was subjected to hydrostatic pressure during the experiment.

2.3 Diamond Anvil Cell

The optical cell described in the previous section can be used to a pressure of about 4 kbar. But we had to go to pressures beyond 4 kbar in some experiment~(see chapter V). For these experiments, an opposed diamond anvil cell specially fabricated by Shashidhar and Rao²¹ for high pressure X-ray and optical studies of the liquid crystal has been used. We shall describe this cell in brief and then discuss its working.

The schematic diagram of the cell is given in figure 2.18. Essentially the cell is similar to that



- 1 LEVER ARM
- 2 LEVER ARM WASHER
- 3 SPRING
- 4 GRADUATED SCREW HEAD
- 5 PISTON PRESSURE PLATE
- 6 PISTON
- 7 DIAMOND ANVILS
- 8 TRANSLATING PISTON PLATE
- 9 PISTON HEMISPHERE
- 10 ADJUSTING SCREWS
- 11 PRESSURE BOLT
- 12 PRESSURE BOLT PLATE

Figure 2.18: Schematic diagram of opposed diamond anvil cell for high pressure Xray and optical studies.

designed at the National Bureau of Standards by Piermarini and Block²² for the study of solids at high pressure. All the components of the cell except the parts which seat the diamonds are made of stainless steel 310. The translating piston plate and the piston hemisphere, which seat the diamonds were made of a high strength steel, viz., high carbon and high chromium (HCHC) steel consisting of 2% carbon and 12% chromium. This was heat treated to a hardness of about 60-65 RC in order to be able to take the load when the diamonds are pressed together. A spring loaded lever arm assembly is employed to generate a uniform and continuously varying force by rotating the pressure bolt, to which a graduated screw head is attached. By rotating the pressure bolt through known angles (as read on the graduated screw head), the lever arms can be roved down. This will, in turn, move the piston in contact with the piston pressure plate up, thereby making the diamond anvils to press against each other,

2.3.1. The anvils, their alignment and their use in the gasketed configuration

Each anvil is a brilliant cut gem quality atone (approximately 1/3 carat) with the culet removed by grinding, the ground faces are then polished to form an

octagonal flat surface, One of the anvils is cemented to the translating plate while the other anvil is fixed to the piston hemisphere by epoxy. Using the Allenhead screws in the piston assembly, the anvil in the hemisphere is suitably tilted to obtain parallel anvil surfaces. The parallelism of the anvil surfaces was ascertained by observation of interference fringes through a low power microscope. The other anvil fixed to the translating plate can be positioned for axial alignment by the three screws in its seating. The two anvils are thus positioned to have a common axis. Once the alignment is done, two screws fixed to the seating of the plate in the cell body, fasten the plate to the body. The alignment then becomes permanent. It is retained so long as there is no indentation in the metal support holding the diamonds. The high carbon high chromium piston hemisphere and the translating plate could be used for several experiments without any visible sign of indentation.

The anvils were used in the gasketed configuration as shown in figure 2.19. Inconel and waspaloy which are often used as gaskets^{22,23} were found to be unsuitable for containing the fluid sample at the relatively low

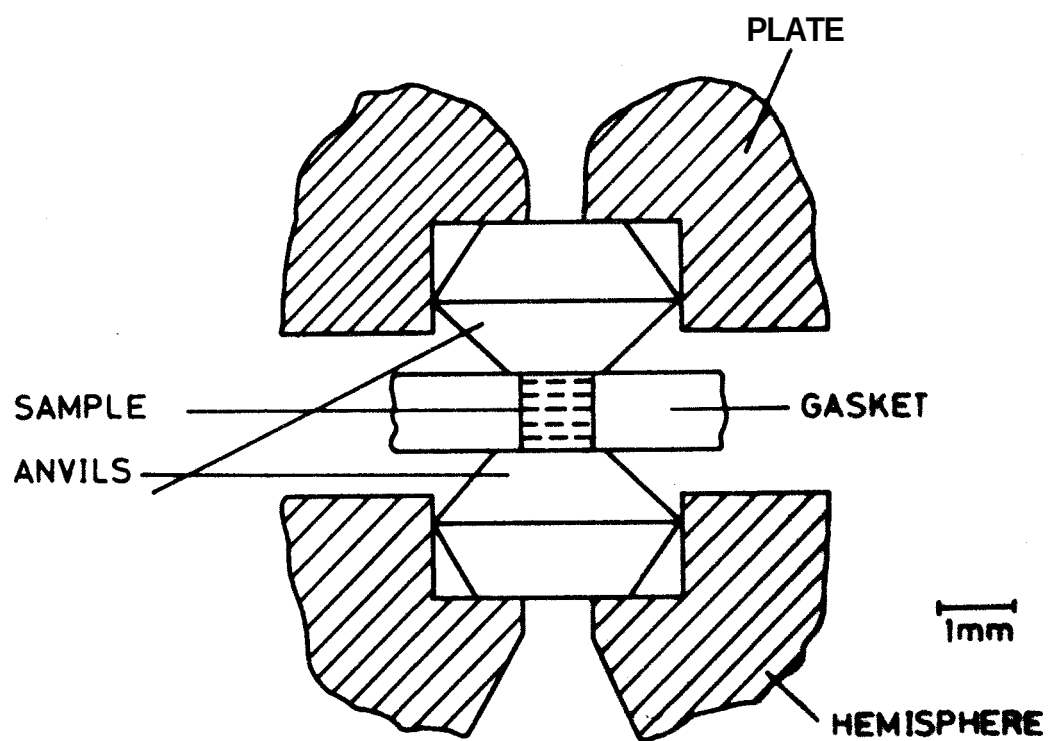


Figure 2.19: Sample encapsulated in aluminium gasket between diamond anvil cells

pressures of interest in our study. After **trying** out various materials like lead **and nickel**, it was finally found most **useful** to use **aluminium** as the gasket material. It was also found **necessary** to **make** the anvil **faces** of **slightly** different area so that when the **anvils** are **pressed** together, the flow of the **gasket material** around the **conical** surface of the smaller **area** anvil acts as a supporting belt to the gasket. In this **manner**, two important functions are **achieved**:

- 1 **The liquid crystal sample is maintained under**
hydrostatic conditions for long **periods** of **time**
without **any** pressure leaks, and
- 2 **the cell, which is normally used for pressures**
beyond a few tens of **kilobars** only, **is** found
applicable to **pressures** as low as a few hundred
bars.

Typically, the **gasket** was about 1 mm thick with a central hole of 1 mm diameter. Two **guide** holes are provided **near** the **edges** of the gasket. **These** holes match the guide pins in the **translating** piston plate. The guide holes and the pins facilitate the alignment of the gasket. **When** the gasket is positioned inside the cell with the **help** of the **guide** pins, the alignment should be such that the central

hole is at the centre of the anvil faces. This has to be ascertained before the sample is filled in the gasket hole. Otherwise, the material surrounding the hole may flow and close up the hole due to non-uniform compression. The sample was finely powdered and packed into the hole in the gasket avoiding air pockets. The moving piston was placed in position over the gasket and the piston pressure plate was pressed against the piston by rotating the pressure bolt. The part of the cell body surrounding the translating plate and the hemisphere were enclosed in an electrically heated furnace provided with a suitable aperture for the passage of laser beam.

2.3.2. Transition temperature measurement

The cell body is provided with a 2.3 mm hole from the side near the piston and the translating plate. Through this hole, a ceramic tube containing the thermocouple could be inserted. The ceramic sleeve of the thermocouple was so positioned that the junction just touches the periphery of the gasket. To measure the temperature of the sample in the gasket, a chromel-alumel thermocouple was used in conjunction with a $4\frac{1}{2}$ digit panel meter. A temperature calibration was necessary since there was always a difference between the

temperature experienced by the sample and that sensed by the junction touching the gasket. This was carried out by taking several standard organic compounds of high purity which are listed in Table 2.1, in the gasket hole and observing their melting point. Since the melting temperature of these compounds are known, a calibration graph can be drawn. Such a graph was obtained for a wide range of temperatures, viz., room temperature to about 180°C. This graph was used for all further determination of the temperature of the sample in the gasket.

At any fixed pressure, the transition temperature, were determined by the same way as that in the case of optical cell described in 2.2.7.

2.3.3. Measurement of pressure

The pressure experienced by the sample in a diamond cell is normally determined by the ruby fluorescence technique developed by Forman et al.²⁴ This was refined to a greater precision by Piermarini et al.²⁵ In this method, a small fragment of ruby, placed with the sample in the gasket, serves as a continuous pressure sensor. Fluorescent R line emitted by the ruby, excited by a high intensity light beam, can be analysed for wavelength displacement due to the effect of pressure. The pressure

experienced by the sample can be determined by the spectral shift of the pressure dependent ruby R line.

But the method described above could not be adopted in the present work. This is because, the pressure shift of the ruby fluorescence line is extremely small, approximately $0.36 \text{ \AA}$ per kbar.²² Thus, even with the best commercially available monochromator system, one cannot determine pressure variations to an accuracy better than ± 300 bare. This accuracy is not adequate since, as already stated, we are interested in fine variations of pressure. Hence an indirect but nevertheless accurate method was employed. In this, an 'in situ' optical determination of the transition temperature of the sample in the cell was made as described earlier. The P-T diagram of the sample, determined accurately by differential thermal analysis technique, was used to read the pressure experienced by the sample. The accuracy of the pressure values estimated from the P-T diagram is approximately ± 15 bare. The efficacy of the method is self evident later when we discuss the results pertaining to multicritical points like 'NAC' point.

2.4 Differential Thermal Analysis (DTA) Cell

As remarked earlier, in order to bring the diamond anvil data to an absolute scale, it is necessary to have a knowledge of the (P-T) phase boundary of at least one transition of the same compound. A convenient method of obtaining the phase boundary is therefore with the DTA cell. Another situation wherein the DTA cell becomes very useful is when it is required to ascertain whether a transition is first or a second order in character. A coaxial DTA cell designed by Reshamwala and Shashidhar²⁶ for liquid crystal has been used in the present work. A 200 ton hydraulic press which incorporates the piston cylinder device was used to generate the pressure in the DTA experiments. We shall give a very brief description of the press and the DTA cell used in these experiments.

2.4.1. Features of 200 Ton Hydraulic Press

A schematic diagram of the assembled 200 ton hydraulic press incorporating the piston cylinder device is shown in figure 2.20. This press which offers facilities to conduct DTA experiment up to a pressure of 20 kbar has the following important features,

- 1 Use of an end load pressure to keep the pressure plate always under compression to prevent its bursting during the experiment.

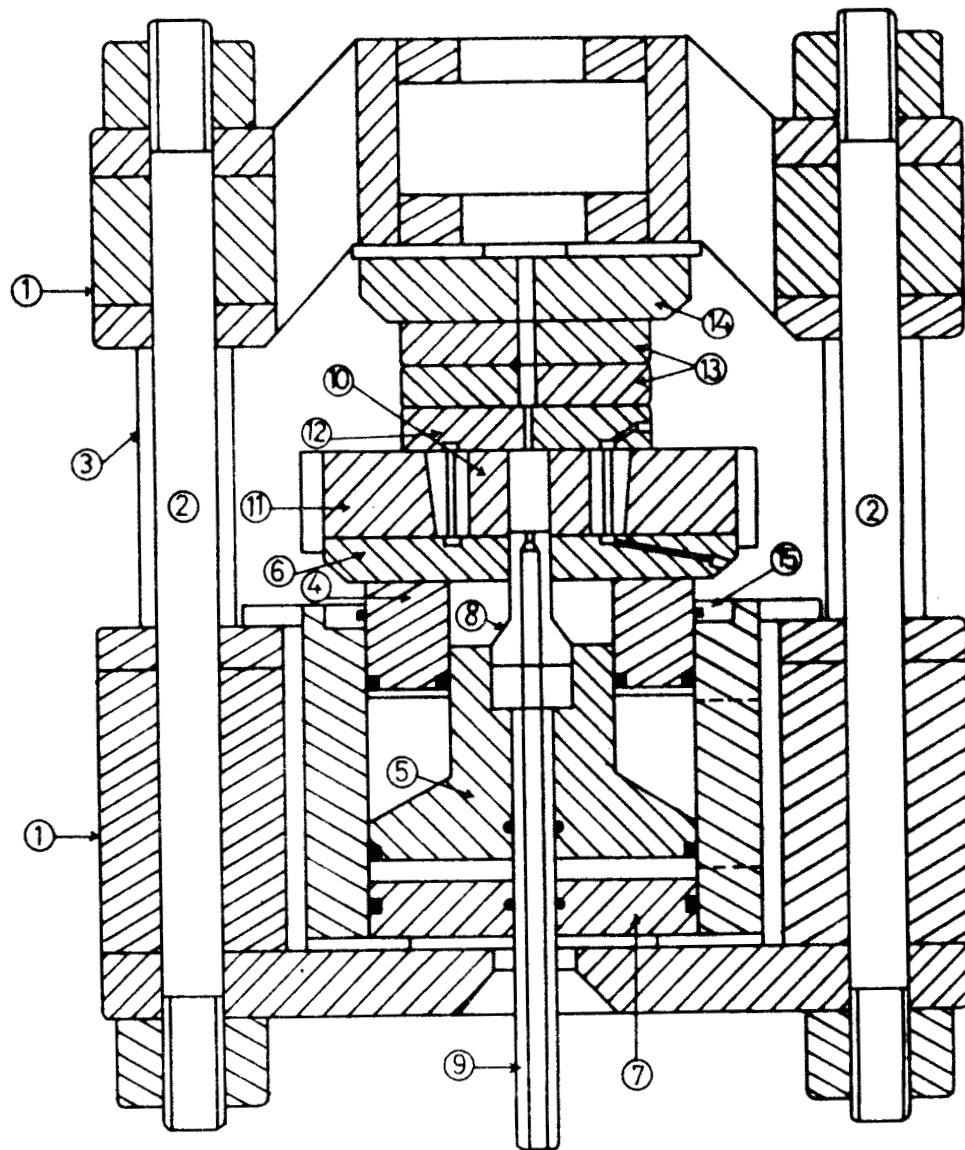


Figure 2.20: Schematic diagram of 200 Ton Hydraulic Press

- | | | | |
|---|--------------------------|----|---------------------------|
| 1 | Platens (top and bottom) | 9 | Piston connecting rod |
| 2 | Tie rods | 10 | Pressure die |
| 3 | Spacers (steel tubes) | 11 | Binding ring with cooling |
| 4 | End load ram | 12 | Insulating groove pad |
| 5 | Master ram | 13 | Support pad |
| 6 | End load plate | 14 | Top platen pad |
| 7 | Static steel plate | | |
| 8 | Piston | | |

- 2 Use of a cooling **assembly** to keep the **pressure** plate always at room temperature while the **sample cell assembly** is heated to higher temperatures.
- 3 Fine **controlling** of pressures to an **accuracy** of ± 5 bare even under static conditions using relief valves.

The linearity of the pressure measurements was checked by determining the variation of **resistance** of the **manganin gauge** with **pressure** using a Wayne Kerr Bridge (Model B642). The true **pressure** on the **sample** were determined by obtaining the **phase diagram** of freshly distilled CCl_4 and using it as a secondary standard. The **accuracy** of the absolute **pressure** measurements is reckoned to be of the **order** of $\pm 2\%$ over the entire range of our study.

2.4.2. Coaxial DTA Cell

It is well known that DTA is a sensitive probe to detect the liquid crystalline transitions at high pressure. The figure 2.21A gives the schematic **diagram** of the **coaxial DTA cell**²⁶ used in the present experiment. The **sample** is contained in a **capsule** made of PTFE of normal grade (hereafter referred to as Teflon). The advantages of using teflon are that it does not react with any of the liquid crystalline materials and that it can be **pressure** sealed easily. The capsule is provided with a **teflon oap**

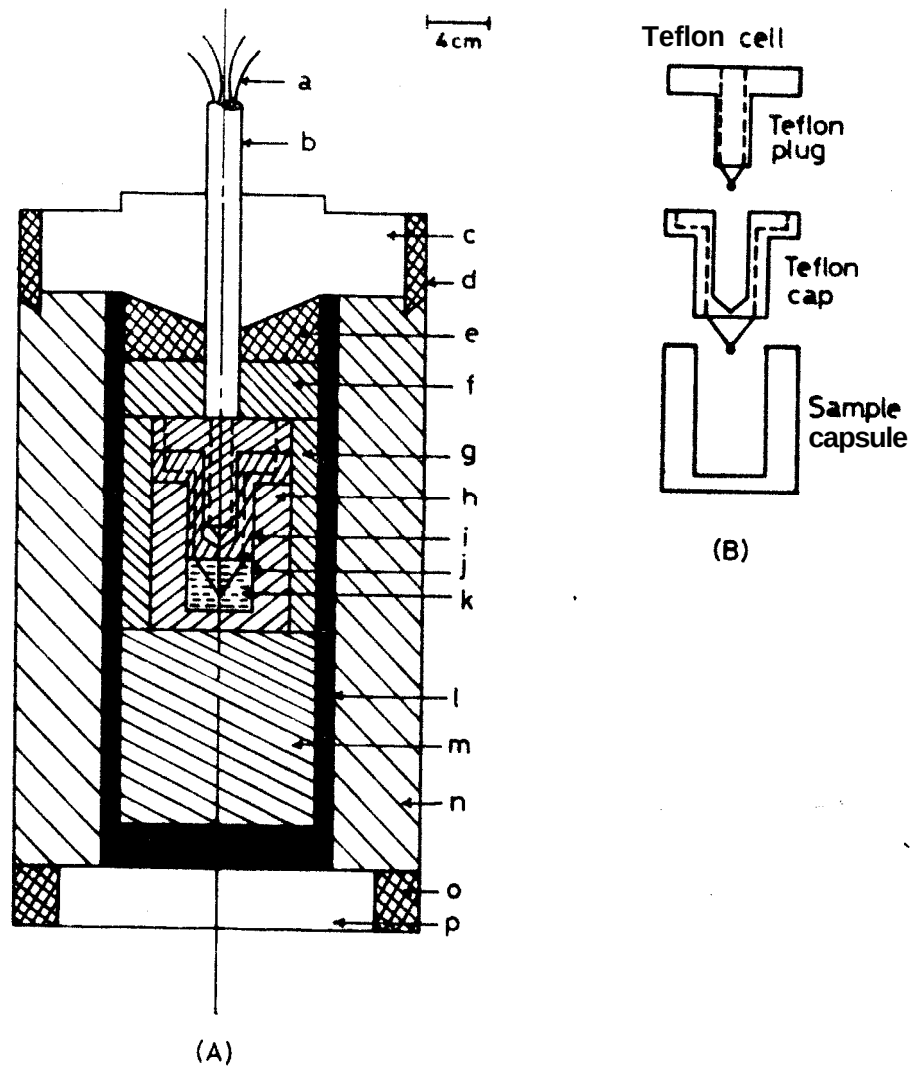


Figure 2.21: A) Schematic diagram of DTA Cell

B) Details of the sample capsule

- (a) Thermocouple leads, (b) four hole ceramic tube,
- (c) stainless steel cone, (d) pyrophyllite top ring,
- (e) pyrophyllite cone, (f) talc disc, (g) talc cylinder,
- (h) sample capsule, (i) teflon cap, (j) sample thermo-
- couple, (k) sample, (l) graphite sleeve, (m) talc pad,
- (n) talc body, (o) pyrophyllite ring, (p) stainless steel disc.

(figure 2.21B) which is press fitted into the capsule after filling it with the sample in an inert atmosphere in the isotropic phase. Chromel and alumel wires are pierced through the cap and a junction is made so that this junction sits amidst the sample when the cap is fitted into the sample capsule. The teflon cap has a central bore into which another teflon plug can be fitted. The reference junction, also made from chromel-alumel wires, is pierced through this plug and positioned so that it is separated from the sample by about 1 mm of teflon. By this we have achieved two important things: (1) the reference and the sample junctions, both being surrounded by teflon are heated almost to the same extent during the experiment, and (2) since the sample thermocouple junction is immersed in the substance, we can detect even faint first order transitions,

Considering that the use of a liquid transmitting media is impracticable,²⁶ the obvious pressure transmitting media is talc which is known to be hydrostatic to 85 - 90%. The sample capsule is suitably surrounded on all sides by talc as shown in figure 2.21A so that the pressure gradient are minimised. The entire unit slides into a cylindrical sleeve of graphite which acts as a heater.

The temperature profile in such a graphite heater used in conjunction with a piston cylinder device will in general have a non-uniform temperature zone near the ends and a constant temperature zone in the region of a geometrical centre of the heater.²⁷ By keeping a number of probes along the axis of the graphite cylinder, it was found that the constant temperature zone was about 8 mm long, the temperature variation within this zone being less than 0.25°C . The length of the zone diminishes for temperatures above 250°C . The heights of the top talc disc and the bottom talc pad are now so adjusted that the sample is well inside the constant temperature zone. In order to bring out the thermocouple wire from the high pressure area to the atmospheric pressure region the thermocouple leads are threaded through a four hole ceramic tube and connected to the appropriate wires coming out of the cap of the teflon cell by spot welding.²⁸

The heater assembly is then inserted inside a thick talc body. The outer diameter of this talc cylinder is machined so that it can just slide inside the 25 mm hole of the pressure plate. A pyrophyllite cone kept on the talc disc has a cone angle exactly matching the cone angle of the stainless steel piece kept on the top of it (see

parts c and e in figure 2.216). When pressure is applied, the **stainless steel** cone which is touching the top of the graphite heater comes into **contact** with the **groove** pad, whereas the bottom of the graphite heater is **connected** through a bottom **stainless steel** enclosed by a **pyrophyllite** ring to the pressure plate. The **groove** pad and the **pressure** plate being insulated from each other, **serve** as **convenient** ends through which current can be passed through the graphite heater. The heater is powered by a **high current, low voltage transformer** which has a **maximum** output capacity of 200 **amps** at 20 **volts**. The input voltage on the primary **side** of the transformer can be varied **continuously** with the help of a variable **speed** gear box which is coupled to an autotransformer. This permits to select any **desired** rate of heating.

The difference in temperature between the **sample** and reference **junctions** (ΔT) was fed to a **Keithley nanovolt** amplifier (Model 140) whose output was displayed on the Y **axis** of a **Riken Den,shi X-Y recorder** (Model F43). The sample temperature was simultaneously read on a digital **millivoltmeter**. An **amplification** of 1000 was used to record most of the liquid **crystalline transitions**. The sensitivity on the Y **axis** was **suitably** reduced to

record the solid-liquid crystal transition. In series with the differential ΔT , a zero suppression unit was used to suppress the thermocouple signal with a resolution of one microvolt. The variation of thermo e.m.f. with pressure is negligible in the pressure ranges of our interest.²⁸

2.4.3. Pressure Calibration and Measurement

As already described, the linearity of the pressure measurements was ensured by measuring the variation of resistance with pressure of manganin gauge^{28,29} immersed in silicone oil filling the sample capsule. It was observed that in the pressure range up to about 8 kbars, the variation was linear.

The line pressures were measured by a calibrated transducer (type PT21UA made by ISRO) reading to an accuracy of $\pm 0.2\%$. However, this is not the true pressure experienced by the sample. The true pressure is less than the line pressure, the correction being dependent upon the thickness and the grade of the teflon used and also on the inside geometry of the cell. The phase diagram of the freshly distilled CCl_4 was obtained and on comparison with that of Bridgman's³⁰ it was noted that our data

agreed with those of Bridgman's within 2 to 3% over the entire range of pressure investigated. Also, PAA, a widely studied liquid crystal (see section 2.2.9) was used as another secondary standard. The values obtained for this compound was again in agreement with the earlier data. Hence the accuracy of the absolute pressure measurement is reckoned to be about $\pm 2\%$ over the entire range of pressure studied.

TABLE 2.1

Temperature calibration of the optical cell
during heating

S.No.	Compound	Transition	Actual Temp. °C	Observed Temp. °C
1	Azobenzol.	melting	68.5	68.6
2	Benzil	"	95.0	95.43
3	Acetanilidine	"	114.0	115.02
4	Phenacetin	""	137.0	137.62
5	Benzanilid	"	163.0	164.49
6	PAA	solid- nematic	118.0	118.81
7	PAA	nematic- isotropic	135.0	135.92
8	HOAB	S - S _C	74.4	75.0
9	HOAB	S _C - N	95.4	95.52
10	HOAB	N - I	124.2	125.0

TABLE 2.2

**Temperature calibration of the optical cell
during cooling**

Sl. No.	Compound	Transition	Transition temp. °C	
			as measured ON a Mettler hot stage	measured from exptl. set up
1	HOAB	N - I	125.0	120.53
2	HOAB	C - N	95.5	91.65
3	PAA	N - I	135.0	130.57
4	PAP	N - I	166.50	163.22
5	8 OCB	N - I	80.5	75.33
6	7OPDOB	N - I	86.0	80.85
7	7OPDOB	A - N	84.5	79.10
8	CB00A	N - I	106.90	103.95
9	CB00A	A - M	82.5	77.84
10	8 OCB	A - N	67.0	62.78

TABLE 2.3 **dT/dP in $^{\circ}C/kbar$ for PAA**

Sl. No.	Investigators	Solid- nematic	Nematic- isotropic	Techniques used
	Hulett	32.0	48.6	Optical transmission ²
2	Puschin and Grebenschtschikow	25.6	39.5	volumetric ¹¹
3	Robberecht	32.0	48.0	Optical transmission ³
4	Deloche et al	24.5	27.0	NMR ¹²
5	McColl and Shih	—	46.3	NMR ¹³
6	Chandrasekhar et al	32.0	47.0	DTA ¹⁴
7	Tikhomirova et al	23.2	31.3	DTA ¹⁵
8	Klement and Cohen	31.0	48.0	DTA ¹⁶
9	Baskakov et al	—	31.4	volumetric ¹⁷
10	Spratte and Schneider	29.5	50.0	DTA ¹⁸
11	Stishov et al	—	45.9	Piesometric ¹⁹
12	Venkatesh et al	31.2	47.0	DTA ²⁰
13	Present work	32.15	48.03	Optical transmission

TABLE 2.4

Paraazoxyanisole (PAA)

Solid $\xrightarrow{118.0}$ Nematic $\xrightarrow{135.0}$ Isotropic

Sl. No.	Pressure in kbar	Transition temperature °C	
		Solid-nematic	Nematic-isotropic
1	atmospheric pr.	118.0	135.0
2	0.10	123.0	141.50
3	0.21	126.19	147.15
4	0.31	128.94	151.04
5	0.41	131.93	155.38
6	0.52	135.23	158.67
7	0.62	138.12	163.50
8	0.72	141.16	167.60
9	0.83	144.40	172.53
10	0.93	147.15	177.32
11	1.03	149.64	181.31
12	1.14	153.13	185.56
13	1.24	155.38	
14	1.35	157.87	
15	1.45	160.86	
16	1.55	164.11	
17	1.66	166.60	
18	1.76	169.54	
19	1.86	172.34	
20	1.97	174.83	
21	2.07	177.32	

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