

CHAPTER II

A HIGH PRESSURE X-RAY CELL FOR LIQUID CRYSTALS

2.1 Introduction

Although a variety of high pressure experiments¹ have been conducted on liquid crystals, very few high pressure X-ray studies, which are important; in understanding the structural changes on a molecular level have been carried out. The need was therefore felt for the construction of a high pressure X-ray cell suitable for liquid crystal studies. After considering various possible cells for such a study, it was thought that an opposed diamond anvil cell would be the most convenient one for the purpose. The first diamond anvil cell, a device for producing high pressures by compressing materials between two opposed diamond anvils, was developed by Wier et al.² at the National Bureau of Standards, USA. Since that time, the cell has been modified extensively³ and refined in several research laboratories for various specific applications

like visual observations of the effect of pressure and temperature on solids undergoing polymorphic transformations,⁴⁻⁶ X-ray diffraction studies on both polycrystalline and single crystalline materials,⁶⁻¹⁵ infrared spectroscopy,¹⁶⁻¹⁹ Raman scattering, etc.²⁰⁻²¹ However, most of these experiments were conducted on solids, with OX without gaskets, and for pressures beyond a few tens of kilobars. On the other hand, the range of pressures over which liquid crystals can be studied is much less than even 10 kbar. This is because the phase transition temperatures usually increase with increasing pressure according to Clausius-Clapeyron equation¹ making it imperative to go to high temperatures if one has to study liquid crystals beyond a few kilobars. At such high temperatures, liquid crystals are known to decompose. Also, it is of great interest to study by X-ray techniques, the variation of the layer spacing of smectic liquid crystals by varying the pressure by small intervals. Considering these requirements, an opposed anvil high

pressure cell with special features which are of relevance to its applicability to the X-ray as well as optical studies on liquid crystals was developed for the first time. The details of its construction and operation will be described in this chapter.

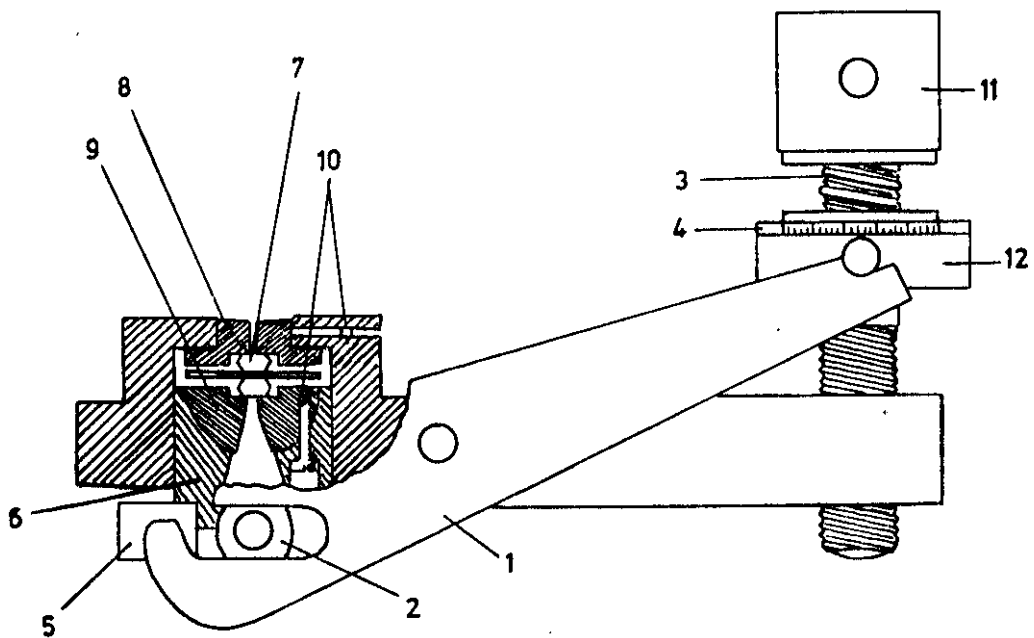
2.2 DESCRIPTION OF THE CELL

The schematic diagram of the cross section of the assembled cell is shown in figures 21 - 23. The scale drawings of the various parts of the cell are given in figures 2.4 - 2.16. A photograph of the assembled cell is given in figure 2.17.

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 5 high strength steel, viz., high carbon high chromium (HCHC) steel. This was heat treated to a hardness of about RWC 60-65 in order to be able to take the load when the diamonds are pressed together. A spring

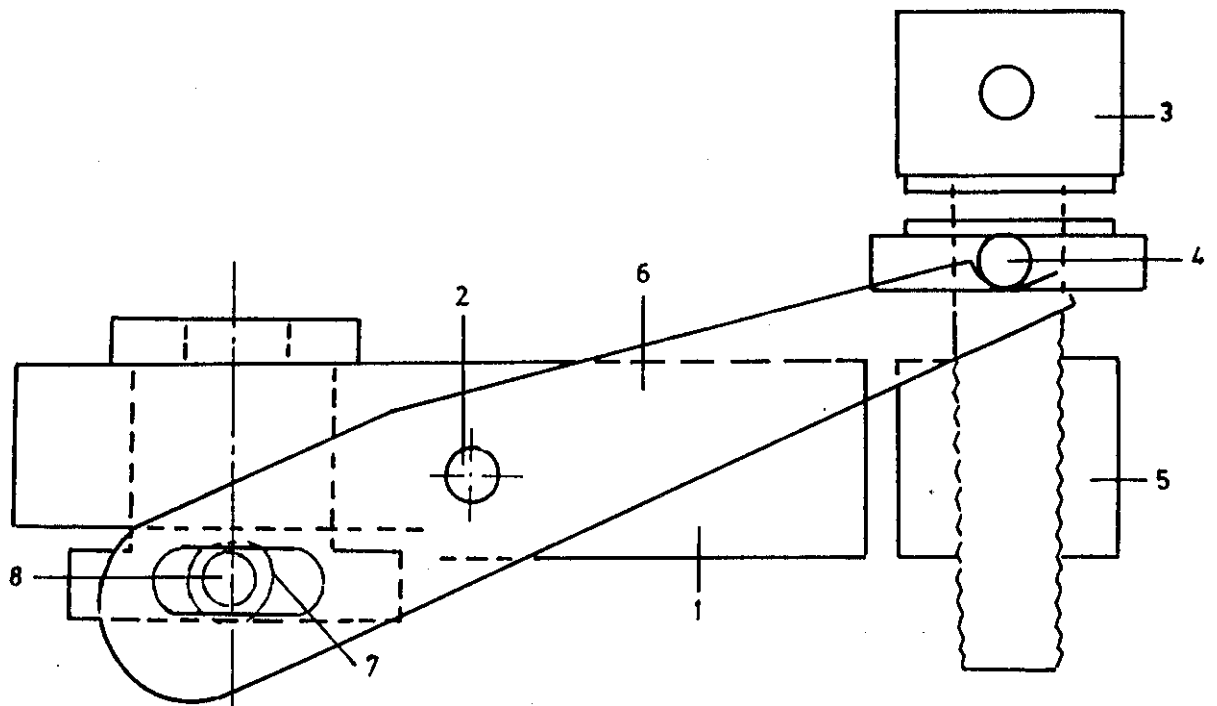
loaded lever arm assembly is employed to generate a uniform and continuously varying force by rotating the pressure bolt, to which a graduated screw head is attached (figure 21).

The cell body is made from a 1" thick stainless steel plate. Figs. 2.4 and 2.5 show the bottom and top view of the cell body. A side view of the cell body is shown in figure 2.6. As seen in figure 2.4, the cell body has a seating on the right hand side, for the translating piston plate. Three side holes drilled in the seating, 120° apart, have three 36 NF thread screws in them. These screws can position the translating piston plate in the seating. The side view of the cell body (figure 2.6) shows two $\frac{1}{4}$ " ream holes at A and B. The hole at A is for the body rod (figure 2.7) and that at B is for mounting the pivot nut (shown in figure 2.9). The body rod is affixed to the body using the body rod nuts [figure 2.7(b)]. The shoulder to shoulder length of the body rod is adjusted such that a minimum of 0.002 - 0.003" clearance is allowed when the lever



- 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

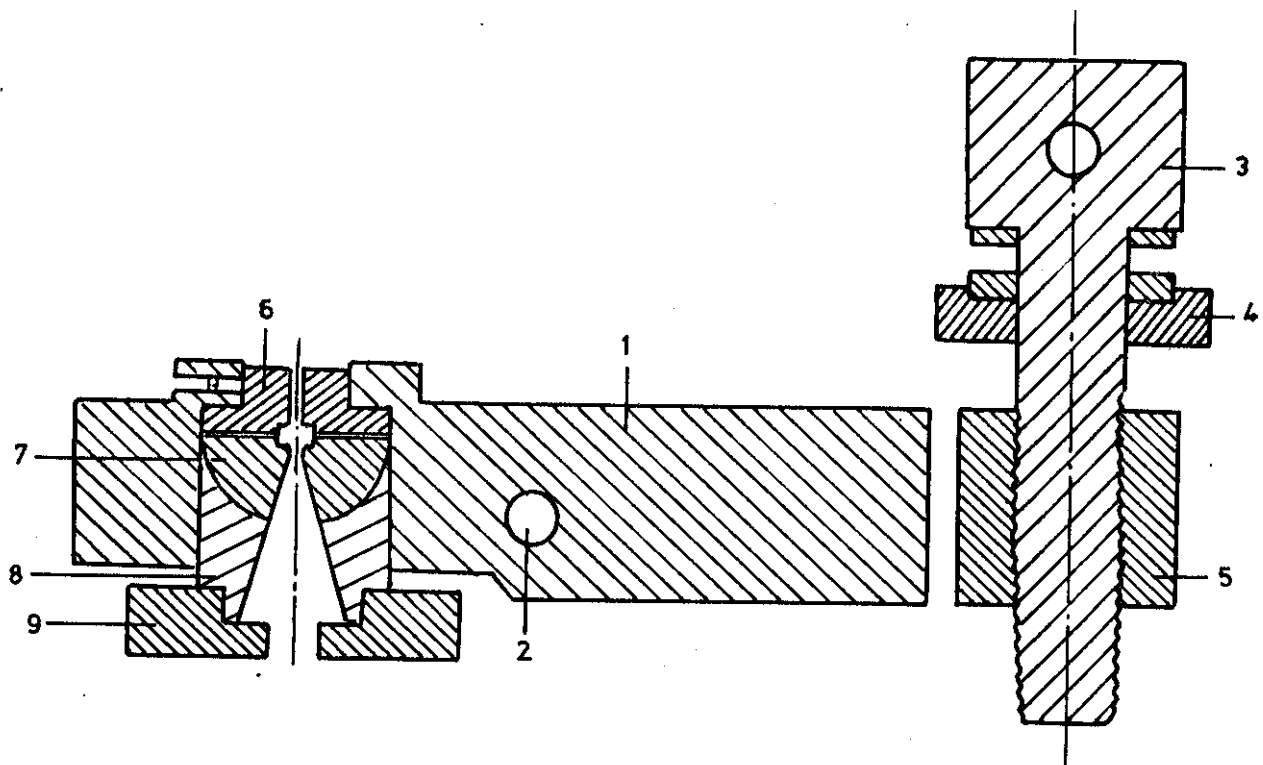
Figure 2.1: Schematic diagram of the high pressure cell



- 1 CELL BODY
- 2 BODY ROD
- 3 PRESSURE BOLT
- 4 PRESSURE BOLT PLATE
- 5 PIVOT NUT
- 6 LEFT LEVER ARM
- 7 LEVER ARM WASHER
- 8 PISTON PRESSURE PLATE

ASSEMBLED VIEW OF PRESSURE CELL

Figure 2.2



- 1 CELL BODY
- 2 BODY ROD
- 3 PRESSURE BOLT
- 4 PRESSURE BOLT PLATE
- 5 PIVOT NUT
- 6 PISTON PLATE
- 7 PISTON HEMISPHERE
- 8 PISTON
- 9 PISTON PRESSURE PLATE

FIGURE 23

SYMMETRY CROSS-SECTION OF ASSEMBLED CELL

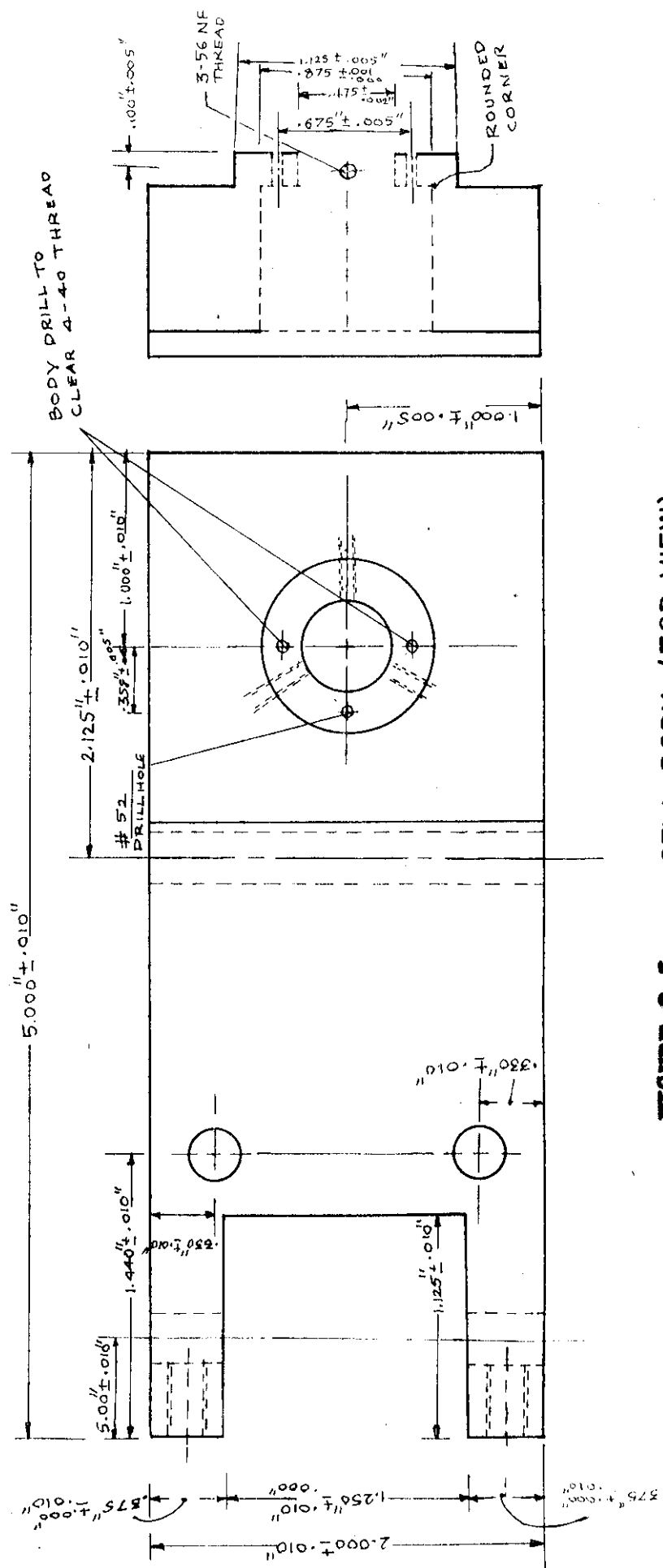


FIGURE 2.5: CELL BODY. (TOP VIEW)



FIGURE 2.6: CELL BODY (SIDE VIEW)

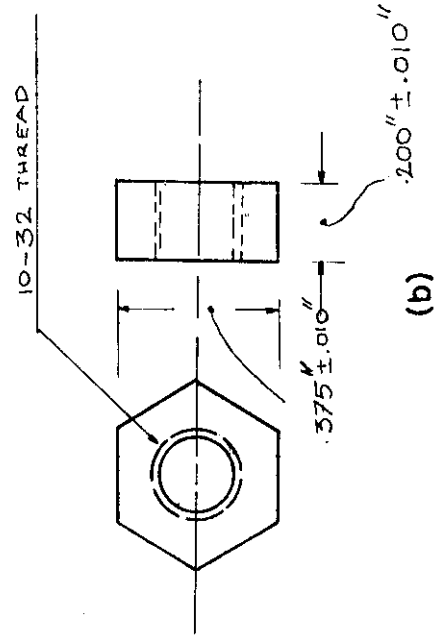
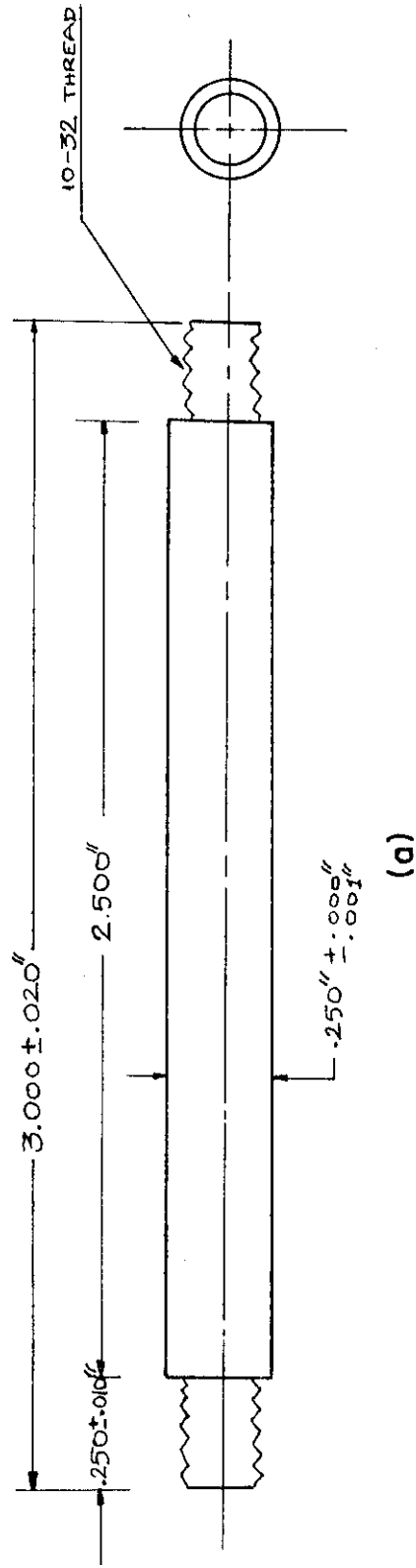


FIGURE 2.7: BODY ROD & BODY ROD NUT.

arms are assembled to the cell body and the body rod nuts are tightened to the shoulders of the body rod. Also, the diameter of the body rod is adjusted to fit snugly into the reamed hole in the cell body. The thrust generating pressure bolt (figure 2.8) is machined out of a $1\frac{1}{4}$ " diameter stainless steel rod. The head of this bolt has a 0.25" hole. A matching rod slides through this hole. The pressure bolt can be rotated by small angles by means of this rod. The screw of the pressure bolt, whose diameter is $\frac{1}{2}$ " with 20 threads per inch, moves in the pivot nut (figure 2.9). This pivot nut is affixed to the cell body by means of pins (figure 2.10) which fit snugly in the ream holes (at B, figure 2.6) of the body.

The two identical lever arms (figures 2.11 and 2.12) which are attached to the cell body, are capable of rotation about an axis passing through the body rod. Each arm (figures 2.11 and 2.12) has a curved step at one end (B) while the other end (A) has slots with bearing surfaces. The curvature of each step has a diameter of

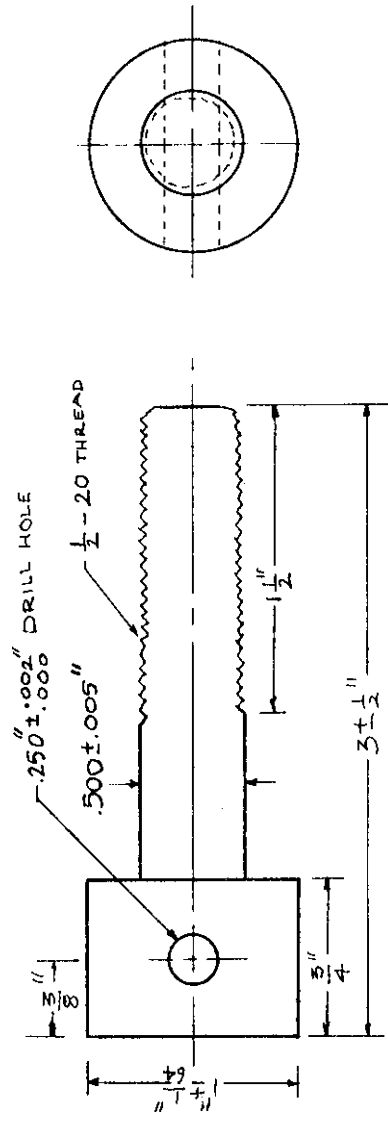


FIGURE 2.8. PRESSURE BOLT.

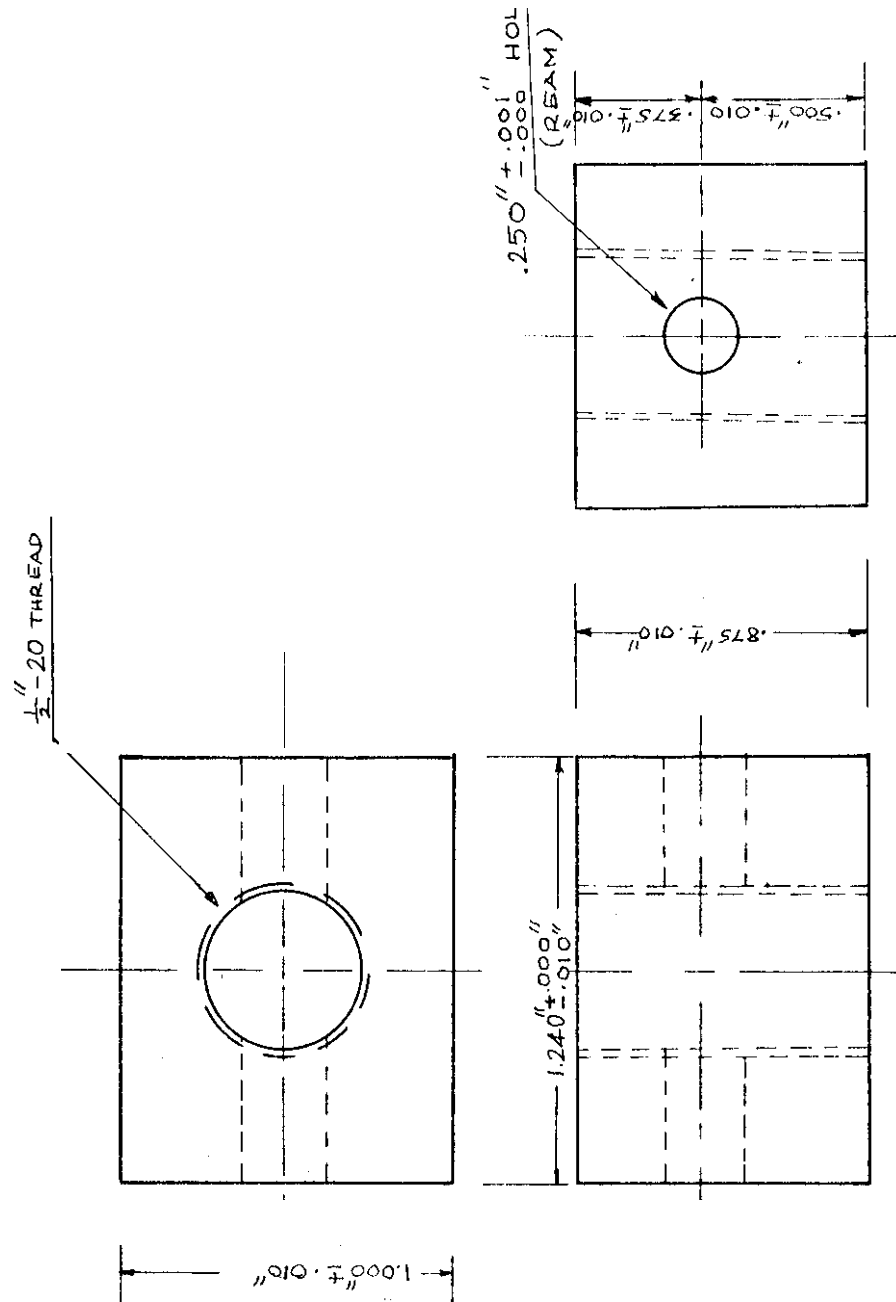
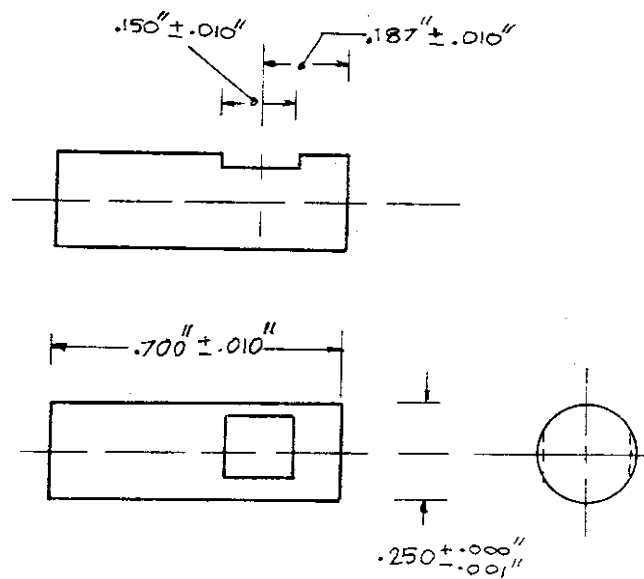


FIGURE 2.9: PIVOT NUT.



a. PIVOT NUT PIN.

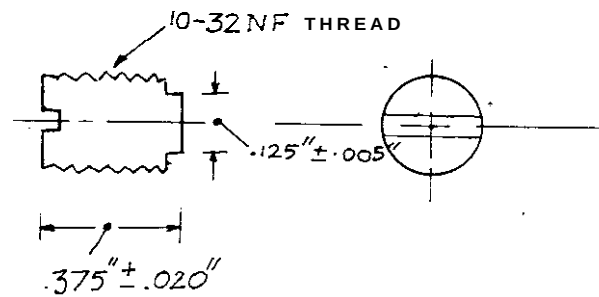


FIGURE 2.10: b. PIVOT NUT PIN SET SCREW



FIGURE 11: LEVER ARM

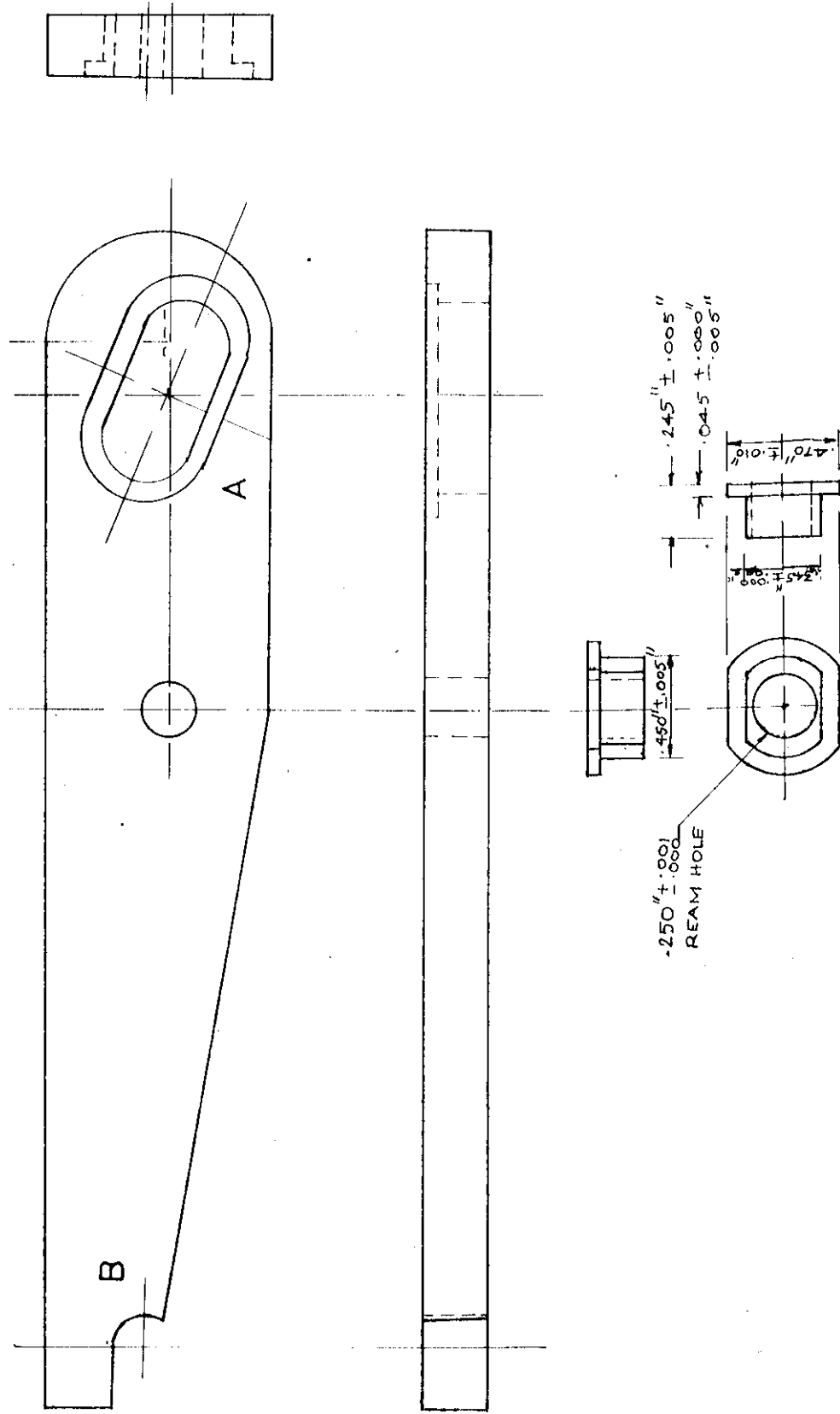


FIGURE 2.12: LEVER

$\frac{1}{4}$ " and this matches the diameter of the stud of the pressure bolt plate (figure 2.13a). The slots at the other end of the lever arm are made to match the lever arm washers. The washers accommodate the studs of the piston pressure plate (figure 2.14). The piston pressure plate has a circular pit which exactly fits the extended portion of the piston (figures 2.14, 2.15a). When the pressure bolt is rotated, the bolt plate presses the lever arm down and the piston pressure plate pushes the piston up, towards the cell body.

The piston (see figures 2.3 and 2.15a) sits smoothly in a cylindrical hole provided in the cell body. The fit of the piston to the hole in the cell body is critical and it should be as close as possible. The piston has a through hole, along its axis, having a critical angle of $\sim 30^\circ$. The other side of the piston (opposite to the one in contact with the pressure plate) has a spherical surface with a radius of curvature 0.406 ± 0.001 ". This curvature of the piston exactly matches the curvature of the convex surface of the piston hemisphere (figure 2.15b).

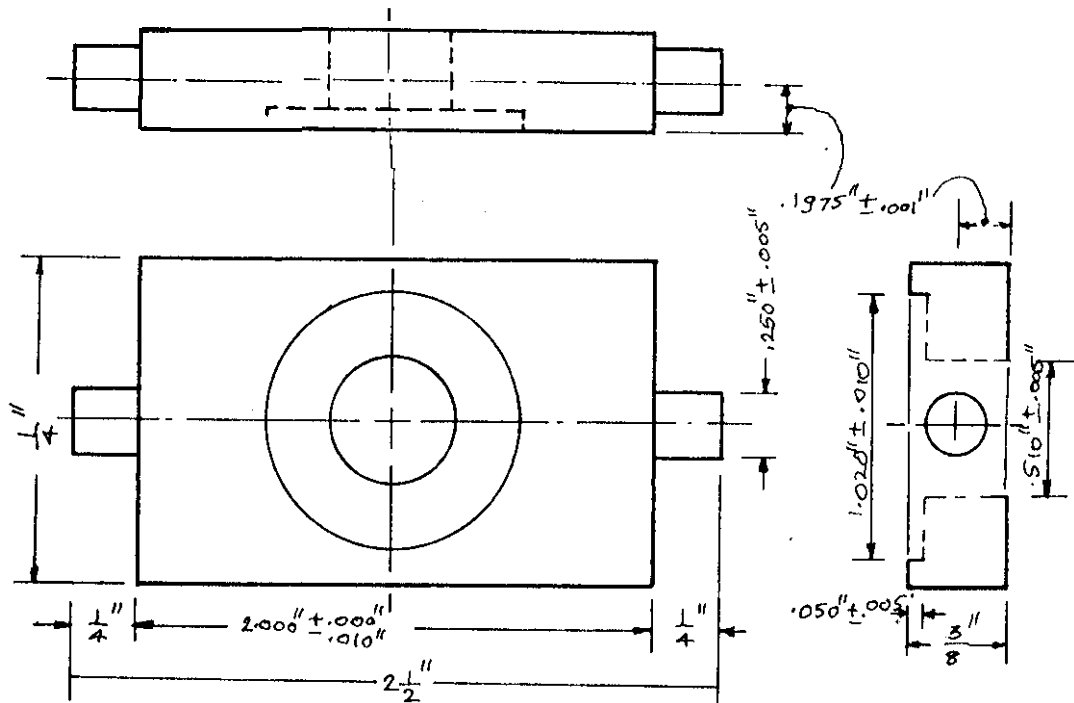


FIGURE 2.13: a. PRESSURE BOLT PLATE.

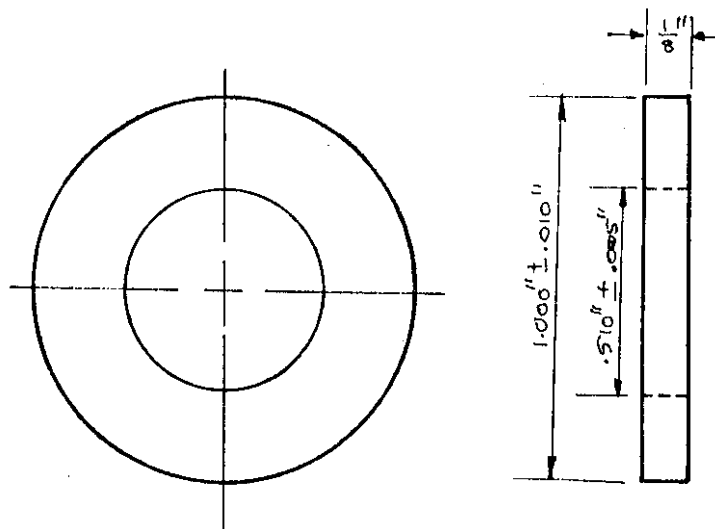


FIGURE 2.13: b. PRESSURE BOLT WASHER

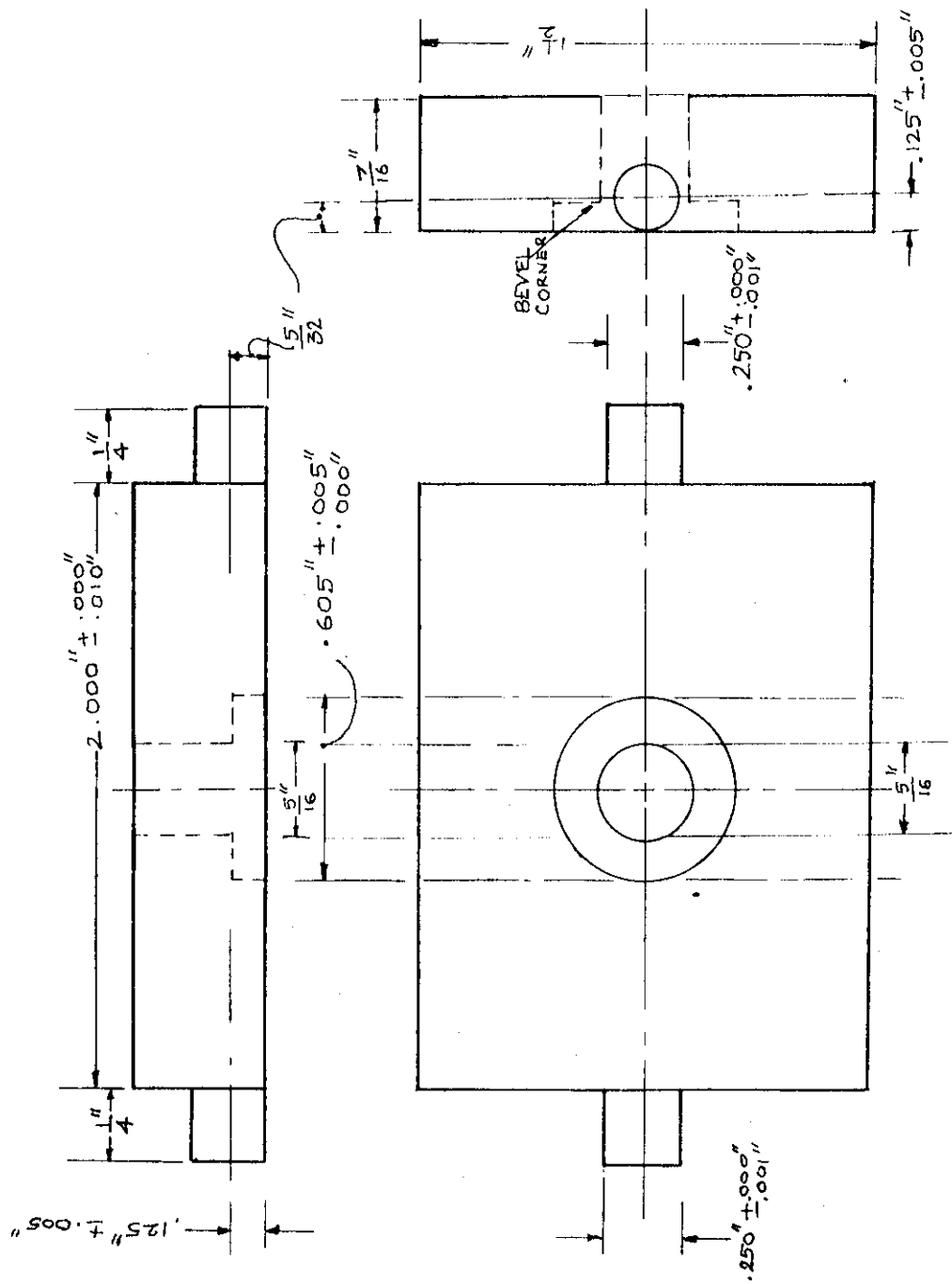


FIGURE 2.14: PISTON PRESSURE PLATE.

For a perfect fit. hand lapping of the two contact surfaces is necessary. Three 2-56 Allenhead pull screws are provided in the three holes of the piston. These screws work through the threads in the hemisphere and their ends reach the flat surface of the hemisphere when the hemisphere is assembled into the piston and the screws tightened uniformly. Using these screws, the hemisphere could be tilted by small angles (5° approx.). The hemisphere is therefore called the tilting hemisphere.

The tilting hemisphere seats one of the diamond anvils in a pit made at the centre. The other diamond anvil is fixed at the centre of the piston plate (figure 2.16a) which is opposite to the hemisphere. The piston plate has a through hole of about 1 mm diameter along its axis. Three 56 Allenhead grub screws (figure 2.16b) which are 120° apart provided in the seating (see figure 2.4). permit a translational adjustment of the plate in its seating. Hence it is called the translating piston plate or the translating diamond mount plate. Both the translatory movement of the fixed anvil and the tilting

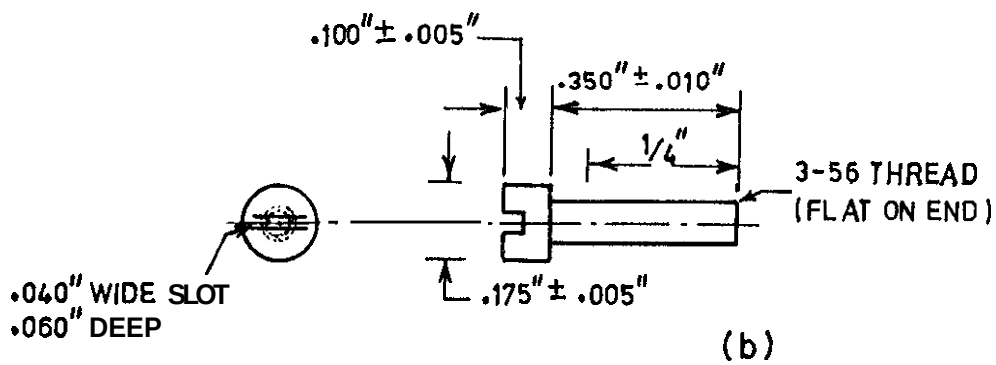
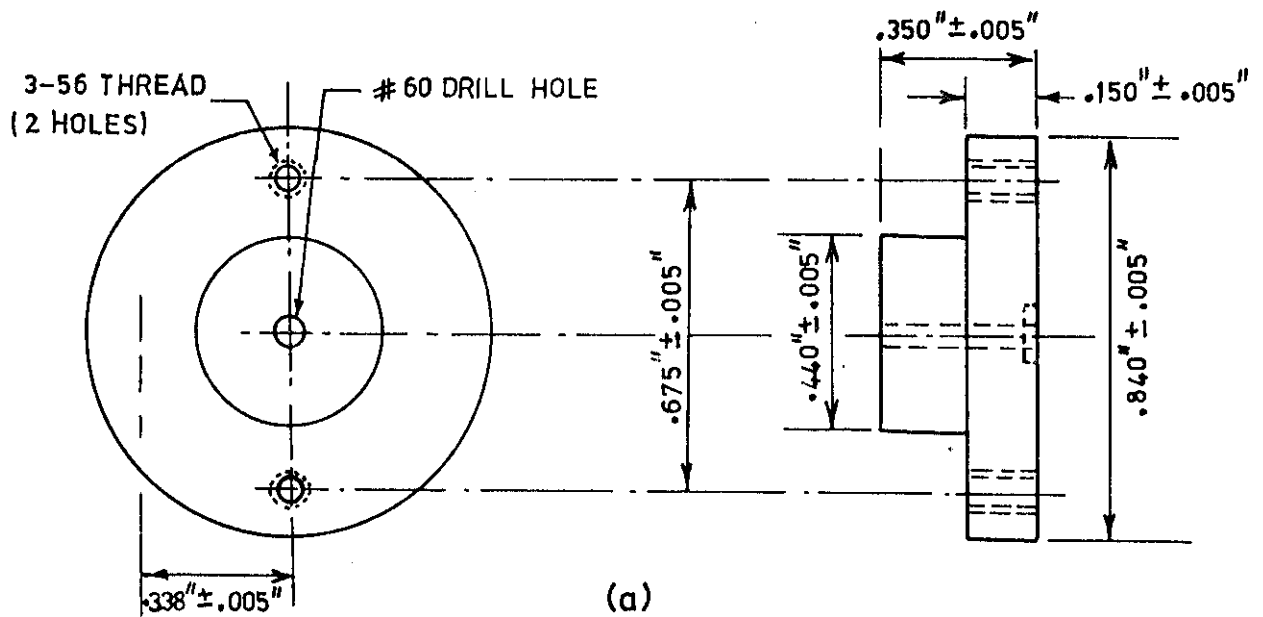


FIGURE 2.16: PISTON PLATE AND PLATE SCREW

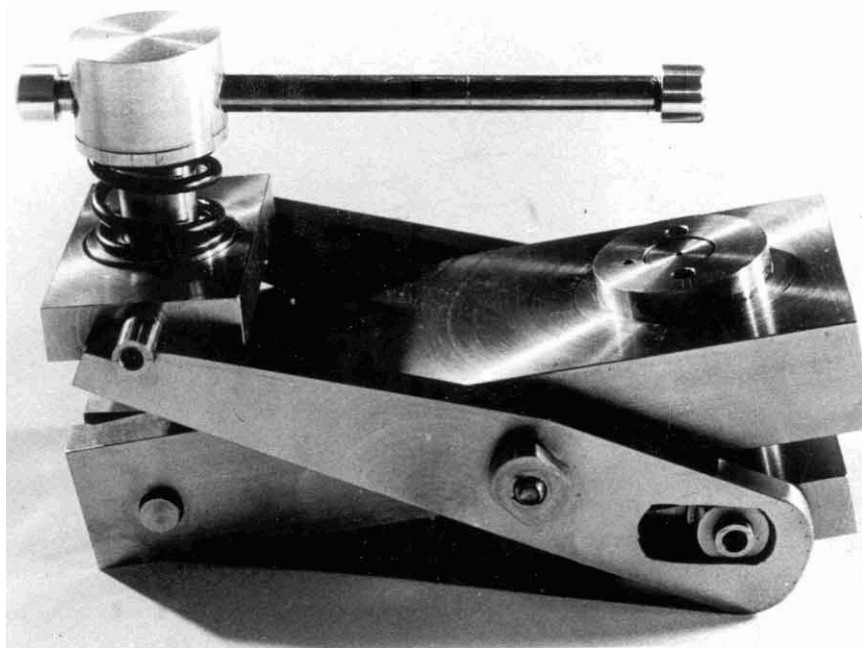


FIGURE 2.17

Photograph of **the** assembled high pressure
X-ray cell

of the moving piston anvil are required for an accurate alignment of the anvil faces.

Thus, by rotating the pressure bolt through known angles (as read on the graduated screw head) force is applied through the pressure bolt plate. The studs of the plate press the lever arms down. The lever arm assembly transmits the pressure to the piston pressure plate. The plate is in contact with the piston containing one of the diamond anvils. This anvil presses against the opposing diamond anvil fixed to the translating plate.

2.3 The anvils, their alignment and their use in the gasketed configuration

Each anvil is a brilliant cut gem quality stone (approximately $\frac{1}{3}$ 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 (figure 2.15), 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 piston plate could be used for several experiments without any visible sign of indentation.

The anvils were used in a gasketed configuration as shown in figure 2.18. Inconel and waspaloy which were often used as gaskets^{3,22} were found to be unsuitable for containing the fluid sample at the relatively low pressures of interest in our study. After trying out various metals like lead and nickel, it was finally

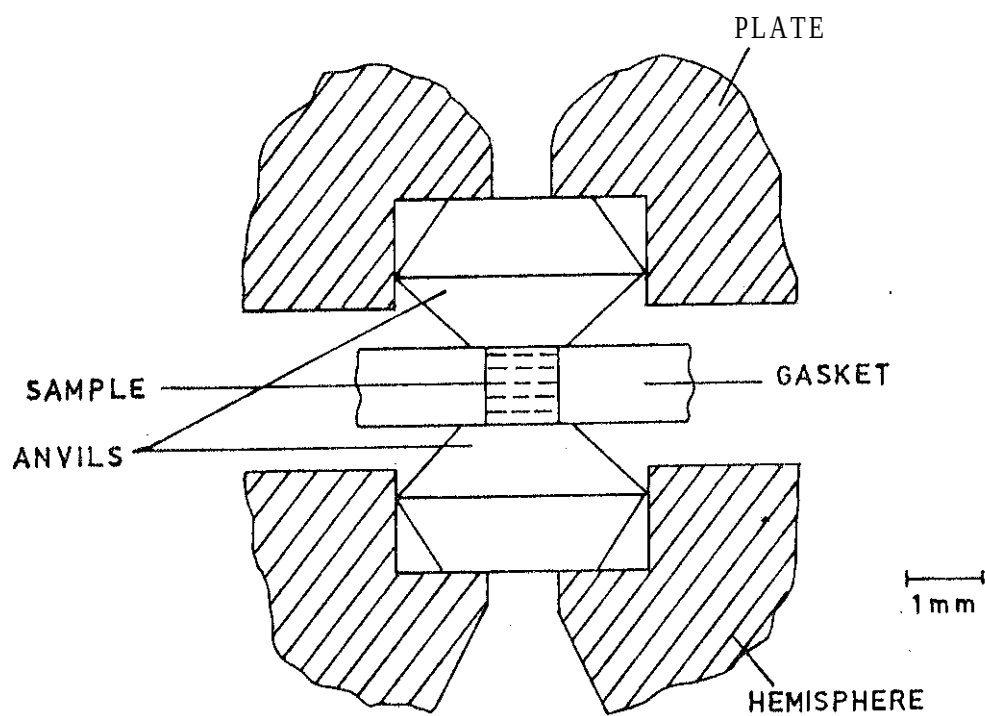


FIGURE 2.18

**Sample encapsulated in aluminium gasket between
diamond anvils.**

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.

- (i) The liquid crystal sample is maintained under hydrostatic conditions for long periods of time without any pressure leaks, and
- (ii) 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 gaskets were 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 X-ray beam.

2.4 Pressure and 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 a 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 in the gasket hole and observing their melting temperature. Since the melting points of these compounds are known, a calibration graph could 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.

a) Transition temperature determination: At any fixed pressure, the transition temperatures were determined 'in situ' in the following manner. The temperature of the sample was varied slowly, at the rate of approximately 1 to 2°C per minute. This rate is the same as that used in the temperature calibration experiment described

earlier. Light from a laser (Spectra Physics 2 mW) was made to fall on the sample. The transmitted light intensity was monitored by a photocell (Motorola, USA, MRD 300) whose output was fed to the Y axis of a high sensitivity XY recorder (Riken Denshi F43P). The temperature of the sample as measured by the thermocouple was fed to the X axis of the recorder. There was an abrupt change in intensity during a phase transition. The transition temperature at any pressure could be reproduced to an accuracy of $\pm 0.2^\circ\text{C}$.

b) 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.²³ This was refined to a greater precision by Piermarini et al.²⁴ 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 dependant 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 $0.36 \text{ \AA}^a$ per kbar.³ Thus, even with the best commercially available monochromator system, one cannot determine pressure variations to an accuracy of better than ± 300 bars. This accuracy is not adequate since, as already stated in the introduction (2.1), we are interested in fine variations of pressure. Hence, an indirect but nevertheless accurate method was employed. At 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 the differential thermal analysis (DTA) 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 bars.

The efficacy of the method will be self-evident in

the next chapter wherein we discuss the use of the cell to study the pressure variation of the smectic A layer spacing of 4'-n-octyloxy-4-cyanobiphenyl (8 OCB), a compound which shows the re-entrant behaviour under elevated pressures.²⁵

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