

capillary channel based largely on a design suggested by Bridgman (1953). Cells of this form did not, however, prove successful and showed a tendency to fracture after exposure to the required pressures. Eventually it was decided to try the simple expedient of holding the mercury in a length of plastic tubing, arranged as a vertical U-tube, with fine wire electrodes at the ends. This arrangement proved very successful, the final form consisting of a U-shaped loop of nylon capillary tube of nominal internal diameter 0.05 cm and length about 30 cm held in grooves in a cylindrical brass block almost filling the cavity in the pressure vessel. The capillary was filled with mercury to within about 3 cm of the ends, the remainder being filled with oil communicating with that in the pressure vessel. With this arrangement the mercury pressure will always be highest at the lower end of the U-tube, owing to the effect of the hydrostatic head, thus ensuring that freezing will commence at the lowest point. In these circumstances there is little danger of electrical contact being lost through loss of continuity in the mercury thread and in practice this only happened on very rare occasions. The electrical leads were of the purest available platinum. The purpose of the brass block was to reduce the volume of oil in the pressure system and to minimize thermal disturbances arising from adjustments to the pressure system.

Purified mercury from two different sources (see § 3.1) was used in the final measurements. In order to check for possible contamination of the mercury as a result of contact with the platinum leads under pressure, samples which had been submitted to a long series of measurements were subjected to spectrographic analysis at the National Chemical Laboratory, using controls of pure mercury from the same original source. These tests, which were capable of detecting a few parts per million impurity, were completely negative.

2.3. Constant temperature bath

The constant temperature bath was based on the type used at the National Physical Laboratory for the calibration of precision thermometers at the ice point, the ice-water mixture being contained in a Dewar flask which in turn was enclosed in a thermally insulated container. In the region of 0°C the freezing pressure of mercury is known to vary by about 200 bar per degree and the maintenance of steady and accurately reproducible temperature conditions is thus of primary importance. The temperature of the bath was checked periodically by a calibrated platinum resistance thermometer supplemented by sensitive mercury thermometers, calibrated against the Laboratory's standards, for routine monitoring of the bath temperature during measurements. With few exceptions this was found to remain within the limits of $\pm 0.002^\circ\text{C}$ during the relevant periods.

Subsidiary experiments were carried out at atmospheric pressure, but with the apparatus otherwise unchanged, to determine the *difference* between the temperature of the bath and that of the interior of the pressure vessel, using a pair of small platinum resistance thermometers of the pattern due to Barber (1955). On the average, the temperature of the bath was about -0.001°C , while that of the interior of the pressure vessel exceeded that of the bath by about 0.0005 deg c. In view of the fact that the temperature *inside* the vessel was not measured during the actual experimental runs, it was decided not to attempt to correct individual readings for temperature variation but to make appropriate allowance for these variations in the final estimation of the limits of error. This aspect is discussed further in §3.2.

2.4. Pressure measurement

The pressure measurements were all carried out by the direct use of one of the Laboratory's standard pressure balances covering the range up to the region of 8000 bar. The effective areas of the piston-cylinder assemblies used and their variation with applied pressure were determined by the similarity method and other procedures developed at the National Physical Laboratory, which have been fully described elsewhere (Dadson 1955, 1958, Dadson, Greig and Horner 1965). These assemblies were of the simple pattern shown diagrammatically in figure 3 in which the effective area A_P at the applied pressure P (bar) is given in terms of the area at zero applied pressure by the expression $A_P = A_0(1 + \lambda P)$,

where λ has the value $3.0 \pm 0.1 \times 10^{-7}$ per bar. In order to achieve the optimum sensitivity the balance was always operated with the piston and load system in a state of free rotation. The standard corrections were applied to account for the small difference of level between the piston-cylinder assembly and the mercury cell.

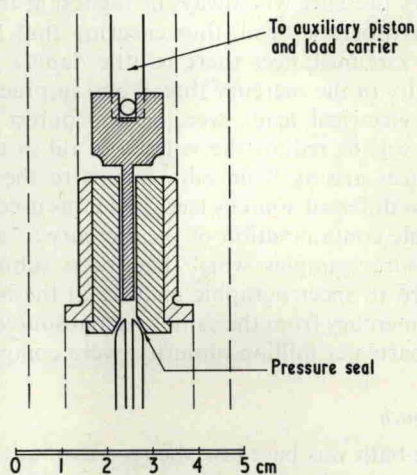


Figure 3. Diagram of piston-cylinder assembly.

2.5. Electrical resistance measurement

The electrical resistance of the mercury sample was determined by measuring the potential difference across it with a fixed value of direct current. A recording potentiometer was used to measure the approximate fraction of mercury frozen at the start of each experimental run, this being replaced by a sensitive dial potentiometer and galvanometer arrangement for the final observations. The normal direct current through the mercury was about 0.5 mA, but this was increased by a factor of 2 for a limited series of measurements in order to check whether the heating effect was appreciable. This, however, produced no significant change in the observed freezing pressure, indicating that such effects were unimportant.

2.6. Observational procedure

In view of the strong dependence of the freezing pressure upon temperature it is essential that departures from equilibrium, such as variations in the fluid pressure, are kept to a minimum while the critical measurements are being made. The procedure adopted for the manipulation of the pressure system and the recognition of the transition point is thus of particular importance.

With the ice bath set up for a sufficient time for temperature stability to be reached, the pressure on the mercury cell was first slowly increased until the fraction of mercury frozen reached the desired value as indicated by the recording potentiometer, the load on the pressure balance being adjusted to approximately the correct value for equilibrium. The combination of pressure vessel, pressure balance and screw press (figure 1) was then isolated from the remainder of the pressure system and the dial potentiometer and galvanometer brought into operation. The load on the pressure balance was then adjusted in small steps until the exact equilibrium point was found. Since the pressure balance in its undisturbed state