

acts as a barostat as regards the pressure in its neighbourhood, each small change of load rapidly produces a corresponding change of pressure. In practice steps of about 0.1 bar were adopted. A pressure step of this magnitude on either side of the equilibrium point was found to give rise almost instantaneously to a recognizable drift of electrical resistance, corresponding to a slow increase or decrease in the fraction of mercury frozen according to the direction of the pressure change.

3. Results of measurements

3.1. Mean value and effects of certain variables

The final series of measurements, carried out when the techniques described above were considered thoroughly established, consisted of 74 individual observations of the freezing pressure. Two mercury cell assemblies were used, with mercury from two different sources. One sample was taken from the stock of purified mercury maintained for use in the Laboratory's primary standard barometers, the precise origin of which is not now on record. The other sample was taken from the supply of specially purified mercury which had been used in a recent National Physical Laboratory determination of the density of mercury (Cook 1961). This mercury originated from the Cordero Mine, McDermitt, Nevada, U.S.A., and was obtained under the auspices of the National Bureau of Standards, Washington. There was no recognizable difference in behaviour between the two samples. There was also no significant dependence of the freezing pressure on the fraction of the mercury frozen in the equilibrium condition, which was varied between about 0.2 and 0.8 during the series. The control experiments in which the normal direct current through the mercury sample was increased about two-fold gave no evidence of any systematic effect on the freezing pressure due to heating with the values of current used.

The mean value of the complete final series of 74 measurements is given below in SI† units and on the scale defined by the bar, kilobar (kb) etc. now widely used in high pressure technology. For convenience of comparison with earlier published values the conversions to other units formerly in common use are also given.

SI units	756.92 MN m ⁻²
bar scale	7569.2 bar
conventional kilogram force per square centimetre	7718.5 kgf cm ⁻²
conventional pound force per square inch	109 782 lbf in ⁻²
international atmospheres	7470.2 atm

3.2. Dispersion and estimated errors

The systematic and random errors in the present determination are fairly easily differentiated. The only systematic errors likely to be of any importance are those resulting from (i) a possible systematic error in the effective area of the pressure balance, and (ii) a possible systematic departure of the temperature of the mercury cell from the desired value of exactly 0°C.

The distortion coefficient λ of the piston-cylinder assembly is considered to be known to within $\pm 0.1 \times 10^{-7}$ per bar (Dadson *et al.* 1965). Allowing for the small uncertainty—within about 1 part in 10^5 —in the absolute values of the effective areas of the Laboratory's standard pressure balances at low pressures, this corresponds, in the region of 7500 bar, to an uncertainty in the pressure measurement of within ± 0.7 bar.

Apart from occasional runs, the temperature of the ice bath during measurements was kept within the range $\pm 0.002^\circ\text{C}$, with an overall average of -0.001°C , thus showing a

† The SI (Système Internationale) scale of units now recommended internationally is that in which the fundamental units of length, mass and time are the metre, kilogramme and second and in which the basic unit of pressure is the newton per square metre (N m⁻²), 'newton' being the name given to the unit of force, i.e. that force which will give to a mass of 1 kg an acceleration of 1 m sec⁻².

tendency to remain slightly below the desired value. The special series of measurements conducted at atmospheric pressure to determine the difference between the temperature of the interior of the pressure vessel and that of the bath indicated, however, that in general the temperature in the vessel slightly exceeded that of the bath. This difference, averaging about 0.0005 degc with a range of from -0.0005 to $+0.0010$ °c, thus tended to offset the error in the temperature of the bath itself. It was finally concluded that any *systematic* departure of the temperature of the interior of the pressure vessel from the desired value 0 °c was unlikely to exceed ± 0.001 degc, corresponding to an equivalent error in the measurement of the freezing pressure of the mercury of about ± 0.2 bar.

The total systematic error may therefore be taken to be within the limits ± 1 bar.

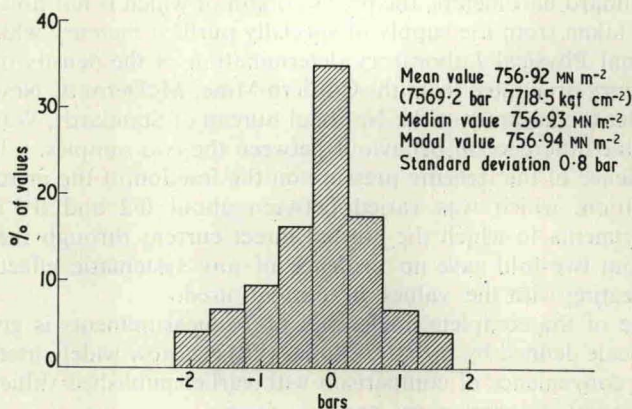


Figure 4. Dispersion of results (74 measurements).

The random dispersion of the whole series of results is shown in the histogram in figure 4. The distribution is reasonably symmetrical and a fair approximation to a normal distribution having a standard deviation of about 0.8 bar. The median and modal values, 756.93 and 756.94 MN m^{-2} respectively, lie very close to the mean. Since, other things being equal, a variation in the temperature of the mercury cell will undoubtedly entail a variation in the freezing pressure, the effects of temperature dispersion may be regarded as included in the total dispersion observed, the remaining dispersion arising from minor departures from equilibrium of the pressure system with possibly other small unidentified effects. The observed standard deviation corresponds to a standard error of the mean of about 0.1 bar, or an uncertainty of about ± 0.2 bar on the basis of 95% confidence limits.

We consider it reasonable therefore to attach to the mean value stated above a total uncertainty of ± 1.2 bar.

3.3. Comparison with former published results†

The first considerable investigation of the freezing pressure of mercury as a function of temperature was that of Bridgman (1911) whose measurements covered the temperature range from about -20 to $+21$ °c. He adopted both the electrical resistance change and the volume change methods, arriving at a final value for 0 °c of 7640 kgf cm^{-2} . This value is thus about 1% low compared with the more recent determinations. It may be of interest to observe, although this may be mere coincidence, that Bridgman's electrical resistance data obtained in 1909, to which he attributed less accuracy than his later work in 1911, gave

† For ease of comparison with other published results the unit kgf cm^{-2} is used throughout this discussion ($1 \text{ kgf cm}^{-2} = 9.80665 \times 10^4 \text{ N m}^{-2} = 0.980665 \text{ bar}$).