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Fixed points on the scale of high pressures: The freezing pressure of mercury at 0°C

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Abstract. There is now an increasing tendency to use fixed points, identified by phase changes or polymorphic transitions of pure substances, as a basis for agreement on a practical scale of high pressures, on rather similar lines to the use of fixed points for the definition of the International Practical Scale of Temperature. It was first proposed by Bridgman that the pressures corresponding to the liquid–solid equilibrium of pure mercury at various temperatures offer convenient fixed points in the pressure range up to the order of 20 kb (2000 MN m^{-2}).

The present paper, which is one of a series dealing with investigations of fixed points at the National Physical Laboratory, gives the results of a determination of the freezing pressure of mercury at 0°C, measured directly in terms of the Laboratory's pressure balance standards. The value obtained is 756·92 MN m^{-2} (7569·2 bar, 7718·5 kgf cm^{-2}) with estimated limits of accuracy to $\pm$ 0·12 MN m^{-2}. Comparison with the results of other investigations and possible sources of error are discussed.

1. Introduction

Up to the region of 20 kb high pressures may be measured with considerable accuracy, in absolute terms, using established techniques based on the pressure balance. At higher pressures absolute measurements become increasingly difficult and eventually it is necessary to rely on extrapolation from the absolute scale, based on physical effects which vary smoothly with pressure. An example is the well known manganin electrical resistance gauge. It has now long been recognized that the establishment of a 'practical' scale on these lines is much facilitated by the use of 'fixed points' depending, for example, on phase changes of pure substances and chosen to provide a series of accurately reproducible pressures. The situation is in many respects analogous to the more familiar use of fixed points in defining the International Practical Scale of Temperature.

The application of this concept to the pressure scale owes its initial impetus to the work of P. W. Bridgman who himself performed a vast number of experiments to establish the pressures at which phase changes or polymorphic transitions occur in a wide range of substances. Bridgman's work has subsequently been extended by many others, of whom Drickamer, Kennedy and their co-workers have been especially prominent in recent years (Bridgman 1949, Drickamer 1963, Kennedy and La Mori 1962, Wentorf 1963).

In order that extrapolation based on fixed points may be carried out to the best advantage, it is desirable that any such points which are within the range of absolute instruments such as the pressure balance should be known to the best available accuracy. The object of the present paper and others in this series is to give the results of basic determinations carried out at the National Physical Laboratory, together with sufficient details of the techniques employed to enable these to be reproduced elsewhere.

The first comprehensive study of the freezing pressure of mercury as a function of temperature was carried out by Bridgman (1911) whose results are considered later in this paper (§ 3·3.). The melting line of mercury is of particular significance in that the range of pressure corresponding to temperatures from 0°C up to room temperature practically coincides with the upper half of the pressure range at present accessible to standard designs of pressure balance. The transition at 0°C has been widely used for the local calibration of manganin gauges and other pressure measuring devices. This paper deals in detail with a

recent National Physical Laboratory determination at 0°C, but the techniques, now that they are established, should be applicable with little variation to other temperatures over a moderate range.

2. Experimental method

2.1. *General*

The measurements described in this paper are all based on the identification of the solid–liquid phase transition by means of the change of electrical resistance of the mercury sample. The magnitude of this change—of the order 4 : 1 at 0°C—is such that it can provide an extremely sensitive indication of the proportion of liquid to solid present under any given ambient condition or state of adjustment of the pressure system. This leads to the further advantage that the total quantity of mercury need only be very small, so that volume changes consequent on freezing or melting, which might otherwise affect the equilibrium of the system, are reduced to a completely insignificant level.

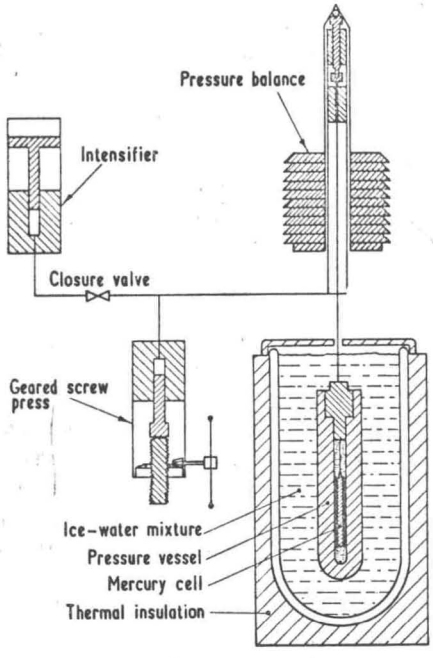

Figure 1. General arrangement of pressure system.

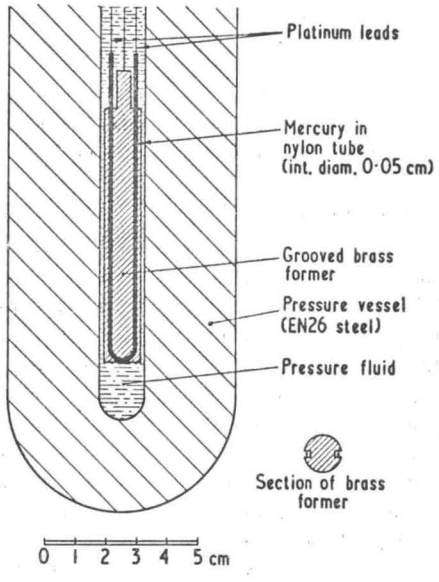

Figure 2. Details of mercury cell.

The general arrangement of the apparatus is shown in figure 1 and an enlarged outline of the mercury cell in figure 2. The pressure in the system was generated by an intensifier capable of producing steady pressures up to 10 000 bar, combined with a highly geared screw press for fine adjustments. The pressure transmitting fluid used was oil of specification DTD 822A, having a kinematic viscosity varying from about 60 to 25 cs over the range 0–20°C at 1 atm. In order to avoid undesirable time effects in pressure transmission the lengths of all connecting lines were reduced to a minimum. The pressure vessel containing the mercury cell was of EN 26 steel, with a ratio of external to internal diameter of about 5 : 1, fitted with ceramic-insulated electrical leads.

The ambient temperature during the measurements was within the range 18–21°C.

2.2. *Design of mercury cell*

The final design of the mercury cell was reached after trials of several other designs. Initially experiments were made with cells fabricated from Perspex and containing a

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°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 $3{\cdot}0 \pm 0{\cdot}1 \times 10^{-7}$ 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.

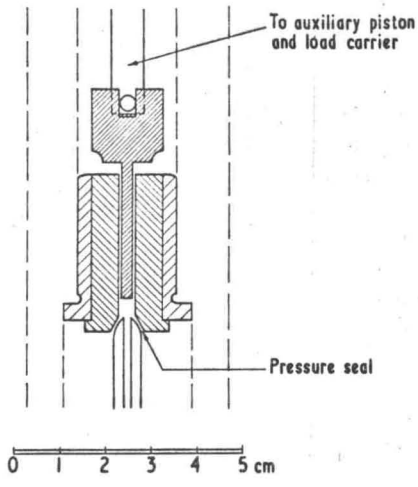

Figure 3. Diagram of piston–cylinder assembly.

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

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 $\pm 0{\cdot}1 \times 10^{-7}$ 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 $\pm$ 0·7 bar.

Apart from occasional runs, the temperature of the ice bath during measurements was kept within the range $\pm$ 0·002°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.

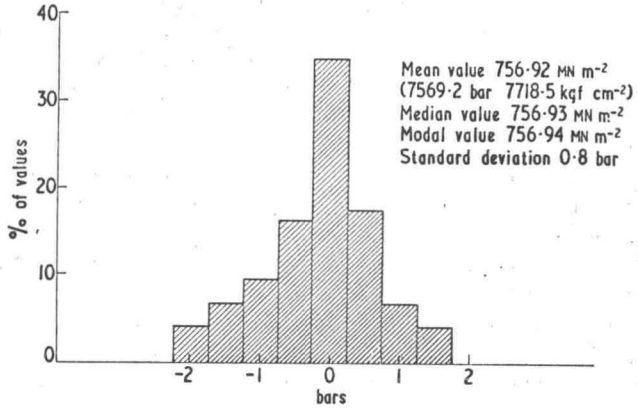

Figure 4. Dispersion of results (74 measurements).

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 kgf cm^{-2} = 9·806 65 × 10^4 N m^{-2} = 0·980 665 bar).

the value 7730 kgf cm^{-2}, which is much closer to the later results. Babb (1963) has recently discussed a possible revision of the scale based on Bridgman's work.

Johnson and Newhall (1953), using the volume change method, arrived at a value of 7717 kgf cm^{-2}, but with the rather wide limits of accuracy of $\pm$ 53 kgf cm^{-2}. More recently Newhall, Abbot and Dunn (1963) have followed a similar method with improved techniques and give the value 7715·6 kgf cm^{-2} with estimated limits of error or about $\pm$ 4 kgf cm^{-2}. This value, however, appears to rest on a single complete measurement and no information as to the dispersion within a series of measurements is given. A rather surprising feature of the measurement technique is the high running temperature of the pressure balance piston, quoted as between 35 and 50°C, compared with the ambient temperature, stated to be in the range 21·5–23·0°C. No explanation of the increased piston temperature is given. It is of interest to note that these authors attempted initially to use the method of electrical resistance change but were unable to obtain satisfactory results. They attribute this in part to sluggishness in the freezing and melting of the mercury and time delays in pressure transmission through the connecting lines. This result is not in accordance with our experience in the present investigation.

In several papers from 1955 onwards Zhokhovskii and his associates (1955, 1957, 1958; 1959) have reported determinations of the dependence of the freezing pressure of mercury on temperature, with a view to establishing this relationship in numerical form as a basis for a pressure scale. In their last paper (Zhokhovskii *et al.* 1959) they extend the scale to 25 000 kgf cm^{-2}. The experimental value 7715 kgf cm^{-2} originally stated for 0°C (Zhokhovskii 1955) is based on measurements at the temperature 0·035°C using a pressure balance. No precise limits of error, or evidence as to the dispersion of the data on which this result is based, are given. Zhokhovskii *et al.* have fitted their data over the whole range up to 25 000 kgf cm^{-2} to a function, based on the Simon equation, which corresponds at 0°C to the smoothed value 7719 kgf cm^{-2}. They observe that their representation is in good agreement with earlier work by Michels, Wassenaar and Blaisse (1942) covering the range from 0 to 3000 kgf cm^{-2}. The process of fitting the large number of experimental points given by Zhokhovskii *et al.* by a smooth mathematical function should considerably reduce the effects of random errors, and this may provide reasons for preferring their smoothed value for 0°C to the individual experimental result for that temperature. The smoothed value, 7719 kgf cm^{-2}, is in striking agreement with the result 7718·5 kgf cm^{-2} given by the present investigation and the above argument suggests that this agreement may have an important measure of significance.

4. Conclusion

Measurements of the freezing pressure of mercury at 0°C have been carried out by the direct use of calibrated pressure balances, and have yielded a value in close agreement with the smoothed value for that temperature corresponding to the melting formula adopted by Zhokhovskii *et al.* The technique used, depending on observation of the phase change by the change in electrical resistance, proved very successful and has the advantage of requiring only a very small volume of mercury so that disturbances to equilibrium arising from volume changes in the system are reduced to negligible proportions. This technique may well prove the most suitable for practical applications of the fixed point such as the calibration of manganin resistance, or other secondary gauges. It is expected that further measurements will be carried out at other temperatures in due course.

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