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# Establishment of the mercury fixed point around 0°C using volumetric method

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**Abstract.** The paper describes the determination of melting pressure of mercury around 0°C using the volume method at the National Physical Laboratory. Also described are the details of the experimental set-up and the estimation of the uncertainty in the measurement of pressure. The equilibrium pressure in the flat region of the melting curve over which bulk transformation occurs, is established by increasing/decreasing the pressure. The scatter in the obtained data for equilibrium pressures is within the limit of experimental uncertainty of the measurement of pressure. The average observed value for the melting pressure of mercury at 0·002°C is 756·93 ± 0·25 MPa agreeing well with the reported value of Dadson *et al* [1] and Molinar *et al* [2a, b].

**Keywords.** Freezing pressure; high pressure cell; pressure fixed point; volumetric method.

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## 1. Introduction

In temperature measurement [international practical temperature scale (IPTS–90)], physical effects such as phase transitions in solids or liquids have been used where the temperatures corresponding to these phase transitions are assigned by definition [3]. The defined value of these fixed points is mainly based on the international agreement of reproducible equilibrium states of solids or liquids during phase transition. But since pressure is a derived quantity, the fixed points in pressure refer to the pressure at which a change of phase in a given substance at a specified temperature is observed. However, it is known that during the process of liquid–solid phase transition, the freezing curve follows a curved region at the onset of freezing and then passes through a flat region over which bulk transformation occurs. As the temperature is assigned by definition in this flat region, the accurate measurement of pressure under isothermal condition is one of the most formidable tasks in a pressure metrology laboratory. However, because of lack of international agreements of the measured pressure during the phase transitions, not many reliable and reproducible fixed points are available in pressure metrology [4].

In the low and medium pressure region [0·1 MPa to 1 GPa], pressure can be measured on an absolute scale with sufficient accuracy using the conventional piston cylinder devices [5]. However, at higher pressures, absolute pressure measurement becomes increasingly difficult and it is for this region there is a growing need to study these fixed points. In the pressure region 2·54 GPa, Heydemann [6] has reported the transition pressure of Bi [I–II] using a controlled clearance piston gauge. Even now the transition pressure obtained from this experiment carried out under truly

hydrostatic conditions is considered to be the best value. In the medium pressure range [ < 1 GPa], the determination of a reliable fixed point would not only provide an opportunity to transfer the high accuracy of the piston gauges but could also be used as an indirect method of international intercomparisons of pressure standards.

The liquid metal mercury, because of its easy availability in very pure form, has been the subject of many important researches. Historically the first comprehensive study of the determination of the freezing pressure of the mercury at 0°C was carried out by Bridgman [7]. He observed that this freezing pressure can be used as the fixed point because of its high reproducibility. However, his conception of this fixed point took at least 40 years to re-establish [8]. Since then, there has been a spur of activity in this direction and several standard laboratories have already established or in the process of establishing this pressure fixed point. AIRAPT Task force [4] has recently reviewed the various methods of determination of this fixed point and the value obtained by these methods.

The present paper deals with the determination of the mercury fixed point at 0°C by volume method. The details of the fabrication of the high pressure cell along with the pressure calibration of the strain gauge transducer with reference to the primary standard are discussed. The estimation of the uncertainty of the measured equilibrium pressures taking into account the temperature fluctuation inside the high pressure cell is also described.

## 2. Experimental arrangement

The high pressure cell used for this experiment is essentially similar to the one used earlier at PTB [Germany] [9] but with the modification in the Bridgman seal and pressure line. The material used for the fabrication of this cell is maraging steel. After machining, the heat treatment is conducted in an inert gas environment following the usual procedure. The presence of inert gas during heat treatment has prevented any formation of oxide crust and thus also the change in dimension. After heat treatment, the hardness of the cell is found to be around 60 HRC.

The high pressure cell consists of three parts—namely the container vessel which is shown schematically in Figure 1(a). The pressure holder and retainer caps are shown in Figures 1(b and c), while the sample holder is indicated in Figure 1(d). In the container vessel, the sample holder is placed inside the cavity of 15 mm in diameter and 200 mm in length [indicated by A]. The cell is pressurized through the port which is located at the bottom of the cavity [indicated by B]. The high pressure seal is essentially a Bridgman seal obtained from the combination of the retainer cap and holder which is provided on the top of the cavity [shown as C]. This sealing materials consist of the O-ring, teflon ring and a wedge ring made of copper. This combination is found to be very effective in preventing any leak from the top cap. Another identical cavity of 8·5 mm in diameter and 200 mm in length is also grooved in the vessel for the temperature measurement [shown as D]. Approximately 10 cc of extraordinary high purity mercury, washed and triple distilled and cleaned specially for use in ultrasonic interferometer manometer [UIM] in the laboratory, is used for this experiment. The sample holder is made from a stainless steel tube which is press fitted inside a copper tube. This soothing copper tube helps in minimizing the temperature gradient along the sample holder. The sample holder is kept vertically and is immersed in the pressure transmitting fluid.

The pressure is generated by a press which is driven by a low pressure assembly.

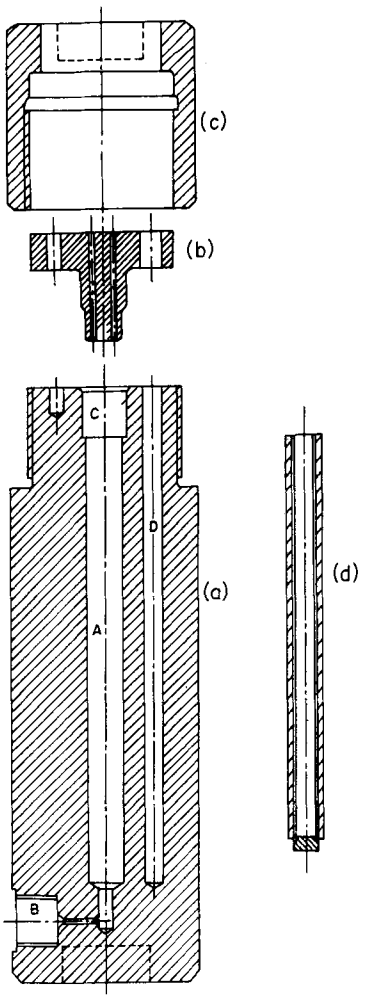


**Figure 1.** Schematic diagrams of different parts of the high pressure cell, a) container vessel—central cavity is for mounting the sample holder and side cavity is for mounting the PRT, b) Pressure holder cap, c) pressure retainer caps—pressure seal is obtained through the Bridgman seal which is formed by the combinations of different o-rings and placed at 45° angular portion of the cap and d) sample holder—stainless steel tube is press fitted inside a copper tube.

A high pressure valve is used to separate the high pressure line from the cell. After generating the desired pressure, this high pressure valve is closed and the slight adjustment of pressure to the desired pressure is carried out by a screw-press. The screw press is separated from the cell by a second high pressure valve. A calibrated strain gauge transducer is used for the continuous pressure measurement. This transducer is connected close to the cell but outside the bath. The pressure transmitting medium in the high pressure line is diethylhexyl sebacate, since this fluid is found to become viscous at low temperature, the low temperature portion consisting of the cell and the high pressure line adjacent to the cell are filled with benzene.

A Tamson temperature bath along with a Neslab cryo-cooler [PBC–75II] attachment is used. The bath is filled with 80% distilled water + 20% ethyleneglycol; ethyleneglycol lowers the freezing point of the mixture. A microprocessor based

temperature controller is used for controlling and monitoring the temperature. This controller uses the mercury contact thermometer as the sensor and the quartz heater as the heating element. The boost heating system continuously adjusts the heating in relation to change in working temperature. The fine adjustment of temperature is done through an auxiliary heater. Any drift in temperature for a particular setting is monitored with the help of a PRT. This PRT is placed close to the high pressure cell and interfaced with the computer for data acquisition. By using a thermocole enclosure, a temperature drift of $\pm 5$ mK is obtained in the bath.

A calibrated 100 ohm PRT is used for the precise temperature measurement in the close vicinity of the mercury. This PRT is encapsulated inside a copper tube of diameter slightly less than 8·5 mm and length of 200 mm and placed at D. The measuring instruments are interfaced through IEEE–488 bus with a PC/AT computer which could monitor and store the data. A complete software is developed to obtain this temperature by first measuring the resistance of PRT taking into account all the possible corrections like the change in the direction of the current, the value of the standard resistance etc. and the temperature is obtained by substituting the resistance value in a well fitted polynomial. The temperatures of the bath as well as the cell are obtained simultaneously.

The pressure measurement is carried out by using a SENSOTECH transducer [Model no. UHP/721–02, Range 0–1·03 GPa and the Excitation voltage 10·0 VDC]. The controlling unit of the transducer has signal conditioning and interfacing provisions. The output signal from the signal conditioning unit is interfaced to the computer through a microvoltmeter for direct monitoring the pressure. The transducer is calibrated at different points both before and after completing the experiment.

## 3. Experimental procedure

The volumetric method starts with an initial increase in pressure up to 1 GPa at room temperature and then allowing the pressurized mercury to cool to the isothermal bath temperature near 0°C. During the process of cooling, the pressure will decrease following the freezing curve till it reaches the flat region where it attains the thermodynamically equilibrium state [TES]. Theoretically pressure remains constant in TES provided the temperature is maintained constant. However, because of the inevitable fluctuation of the bath temperature, the pressure in TES is found to fluctuate. The fluctuation in pressure can be minimized by carefully monitoring the bath temperature. Two methods are followed for the determination of the thermodynamic equilibrium pressure. The starting point of both the methods is the attainment of the flat region of the freezing curve where a TES of both the solid and liquid states exist. However the difference between these procedures is the method by which the TES is disturbed and the subsequent readjustment of the equilibrium pressure and temperature is obtained. In the first method, the disturbance is in the form of small increase or decrease in pressure of the pressurized mercury. Because of this disturbance, there will be a change in temperature due to the onset of the freezing of the mercury and the readjustment of the temperature when the system approaches the TES. If the fluctuation of the temperature is limited within the resolution of the pressure measuring devices, the repeated increase and decrease in the pressure would not affect the TES. In the second method, the TES is disturbed by changing the isothermal bath temperature. The system will reestablish its new TES by changing the corresponding pressure. Thus a systematic and selective change

of bath temperature will result in a series of corresponding thermodynamically stable equilibrium pressures forming a part of the mercury melting line which eventually represent the new phase equilibrium after each temperature change. The first method is followed in the present paper.

## 4. Results and discussion

As discussed, the continuous line pressure is measured with a strain gauge transducer which is calibrated with reference to our primary standard. Thirteen different points have been studied both at the beginning and end of the experiment. Special emphasis is laid to the point close to mercury freezing pressure. The primary standard is a controlled clearance piston gauge with different combinations of piston cylinder assemblies in the different ranges and the maximum full scale pressure is 1·4 GPa. This primary standard is characterized following the method described by Sharma *et al* [10a, b]. The cubic root of piston fall rates as a function of jacket pressures for nine different weights, are plotted to calculate the operating jacket pressure [Pj] for each of the weights. The correction terms such as Pj along with the mass of the weight, acceleration due to gravity [$g_{NPL}$], area of the piston etc. are used to compute the measuring pressure for each weights [5, 10]. The detailed measurements of this primary standard show that the overall uncertainty of the measurement of pressure in the region of 757 MPa is within 180 ppm and can be taken as $s_{pc} = \pm 0{\cdot}136$ MPa. For further checking, this strains gauge transducer is calibrated with reference to a fully characterized (Des Granges & Huot) laboratory secondary standard NPL-500 of which the full scale pressure is 500 MPa. Incidentally, this gauge with different piston cylinder assembly is used in the fourth phase of the International comparison in the pressure range 20–100 MPa organized by CCM under BIPM, Paris. The agreement of the deviations of the observed values of Ap from the appropriate least squares best fit straight line is within + 5 ppm in the whole pressure region and the zero pressure effective area (Ao) with respect to the reference value is − 51·5 ppm

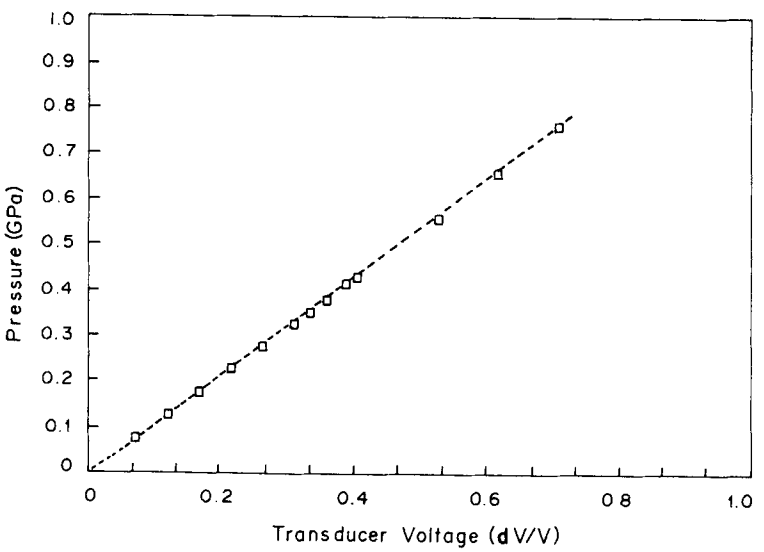


**Figure 2.** Pressure calibration of the strain gauge transducer—the relative output voltage is plotted with pressure.

and the deviation of the pressure distortion coefficient from the reference value is $-0{\cdot}47 \times 10^{-6}\,\mathrm{MPa}^{-1}$ [11]. The estimated uncertainty of our measurement in Ao is $\pm 74$ p pm and thus agreement is well with our estimated uncertainty.

Figure 2 shows the calibration curve where the measured pressure is plotted against the relative change in voltage ($dV/V$). At least four different readings are taken to obtain the average reading for each pressure. The long term stability of the strain gauge transducer is studied systematically. In a span of roughly 3 months, there is absolutely no change in the calibration factors except the zero shift which is always taken into account before each measurement. The calibrated pressures with the relative change of the voltage are best fitted with a polynomial of second order,

$$P = A + B(dV/V) + C(dV/V)^2,$$

where $P$ is expressed in MPa. $A = 1{\cdot}9325$, $B = 990{\cdot}1863$ and $C = 57{\cdot}1575$, standard deviation ($s_r$) $= \pm 0{\cdot}143$ MPa. Following Sharma *et al* [12], we estimated the uncertainty of the pressure measurement by this transducer ($s_{senso}$) as $\pm 0{\cdot}151$ MPa.

The measurements of temperature inside the cell are carried out at that pressurized condition with all the other apparatus remained unchanged and after attaining the TES. Usually just before the determination of the plateau as discussed in experimental procedure, an equal time interval is given to measure the fluctuation in temperature and thereby the drift of the cell temperature from the bath temperature is obtained. The uncertainty of the temperature measurements can be calculated from this fluctuation of the temperature. From figure 3, it is clear that although the bath temperature is kept at 0°C but the temperature inside the high pressure cell is 0·002°C with a fluctuation of $\pm 0{\cdot}5$ mK. Thus the thermal mass of the cell helps in the reduction of the temperature fluctuation in the cell, but it increases the average temperature of the cell from that of the bath temperature. From the earlier data [2,9] of melting line of mercury at different temperatures and around 0°C, it can be shown that the shift in temperature by an amount 0·002°C from 0°C, will give rise to a change in

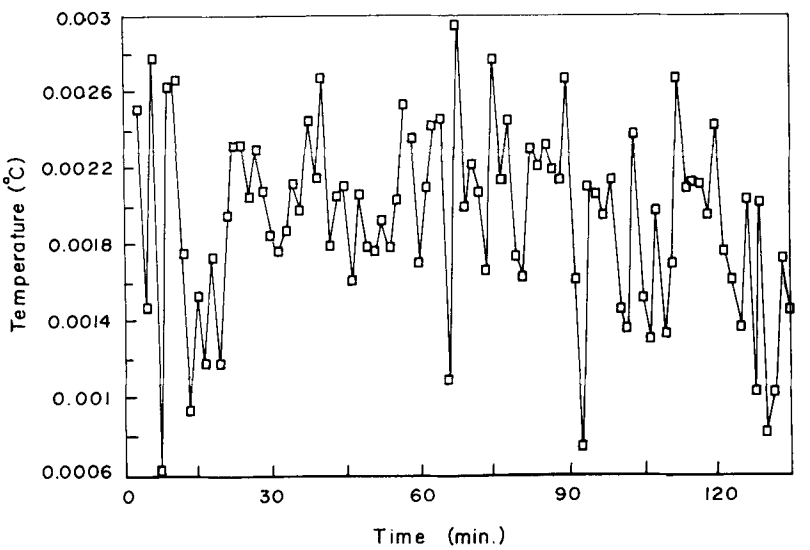


**Figure 3.** The fluctuations in the measured temperature with time—a systematic drift of about 0·002°C from the bath temperature is observed with a fluctuation of $\pm 0{\cdot}0005$°C.

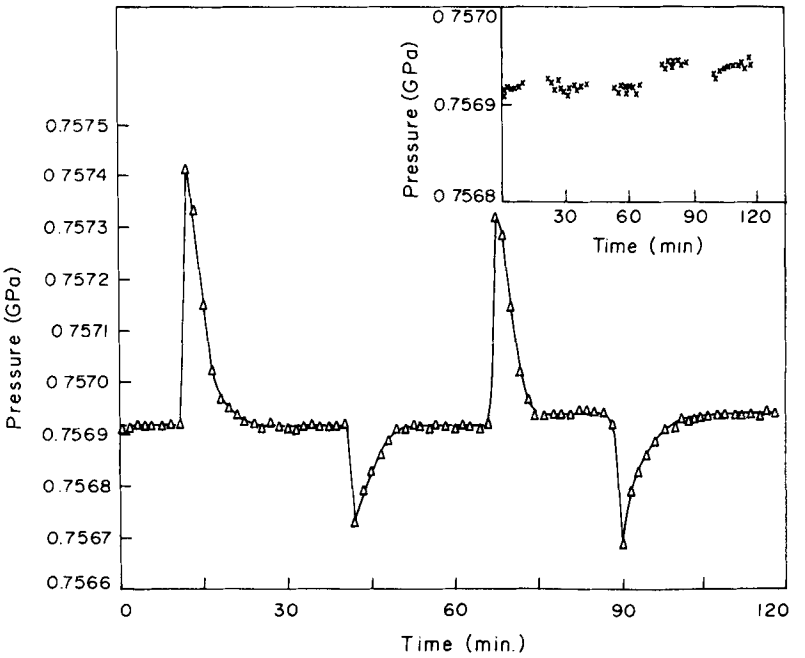


**Figure 4.** Readjustment of the liquid–solid phase equilibrium pressure at a temperature of 0·002°C after disturbance of the phase equilibrium by a sudden change in pressure. Inset shows pressure equilibrium points in the extended scale.

pressure of 0·04 MPa. While the random error [$s_{temp}$] of $\pm 0{\cdot}5$ mK in the bath temperature corresponds to a pressure of $\pm 0{\cdot}001$ MPa.

Figure 4 shows the equilibrium pressure versus time plot obtained at that temperature 0·002°C. The inset of figure 4 shows the thermodynamically equilibrium pressure points which are obtained by deleting the portions of increase or decrease in pressure. This shows that the equilibrium pressure changes with disturbances although thermodynamically it is assumed to be constant. In our earlier paper on the effect of liquid phase on the triple point pressure of argon [13], we have discussed about this change of equilibrium pressure with disturbances. Based on it, the average value of pressure is obtained by taking the mean of these equilibrium pressure points. Therefore, the average equilibrium pressure turns out to be 756·93 MPa with a random uncertainty ($s_{rl}$) of $\pm 0{\cdot}01$ MPa.

The total uncertainty of the measurement of pressure ($s_p$) is carried out by the usual method [1, 14]

$$s_p = (s_{pc}^2 + s_r^2 + s_{senso}^2 + s_{temp}^2 + s_{rl}^2)^{1/2}$$

and this gives $s_p = \pm 0{\cdot}25$ MPa. Therefore, the measured pressure at 0·002°C is $756{\cdot}93 \pm 0{\cdot}25$ MPa. It may be pointed out that the reported value of the freezing pressure at 0°C by Dadson *et al* [1] is $756{\cdot}92 \pm 0{\cdot}12$ and Molinar *et al* [2] is $756{\cdot}84 \pm 0{\cdot}16$ and the average value reported by Bean *et al* [4] is $756{\cdot}95 \pm 0{\cdot}21$. Thus the obtained value is clearly in agreement with the reported value. However, the total uncertainty of the measurement of pressure is slightly higher than the reported uncertainty [1, 2, 4]. This limitation is coming from the uncertainty of the measurement of pressure by transducers which can be improved by using directly a piston gauge/pressure multiplier.

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