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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.

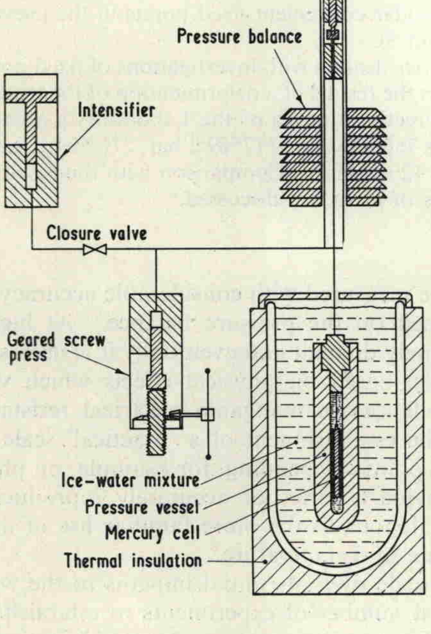

Figure 1. General arrangement of pressure system.

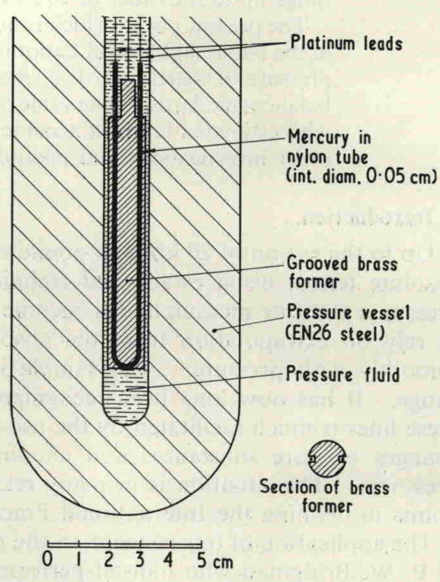

Figure 2. Details of mercury cell.

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