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Press calibration at elevated temperatures

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Abstract. The pressure increase upon heating an internal liquid cell in a pyrophyllite pressure chamber within a multi-anvil press was determined by simultaneously measuring the phase diagrams of bismuth and mercury to 55 kbar and comparing them with the established phase diagrams. The shapes of the differential thermal analysis signals are used to establish equilibrium values of the phase lines. Phase diagrams for thallium, tin, indium, and lead are reported.

1 Introduction

For the past several years we have struggled with the problem of how to measure pressure accurately in an internally heated pressure chamber within a multi-anvil pressure cell. Some of these problems have been reviewed earlier by Decker *et al.* (1972). Even if one has a means of calibrating the pressure versus load using fixed point phase transitions, one does not know the pressure at higher temperatures because of thermal expansion of the pressure cell on heating. Experiments which attempt to measure the pressure dependence of melting curves and diffusion measurements at high pressure, to mention two, would be greatly improved by a means of determining the pressure at elevated temperatures. Earlier attempts by Decker and Vanfleet (1965), Mitra *et al.* (1967), and Millet and Decker (1969) assumed a Simon's equation for the melting curve; the pressure calibration was adjusted to cause the melting curve to take this form. Various arguments were given to justify a certain pressure and temperature dependence of the pressure correction. A second approach by Young (1969) involved measuring the lattice parameter of NaCl at high pressure and elevated temperatures and obtaining the pressure from a theoretical equation of state by Decker (1965). This method did show pressure changes with heating, but only for a pressure cell of the material and construction of that used for x-ray work. It is not clear how to interpret these results for an internally heated liquid cell for example. A third attempt by Candland *et al.* (1972) consisted of measuring the resistance of a Manganin wire over a range of pressure and temperature in a liquid medium within a large-volume pressure cell. The results were interpreted by extrapolating the Manganin room-temperature pressure calibration to higher temperatures with the use of the measurements of Wang (1967) to 250°C and 4 kbar as a guide to the extrapolation. The major drawback to this approach is the large extrapolation which makes the results rather uncertain.

In the present experiment, we determine the pressures from a knowledge of certain fairly well studied phase diagrams. One can use either two materials and measure transitions between their phases at elevated pressures, or a single substance, such as bismuth, with several phases. The philosophy is very simple. If one knows $P(T)$ along two lines in P, T space, then maintaining a constant load one raises the temperature crossing these two known lines at T_1 and T_2 and from the known relations one has also P_1 and P_2 so a pressure versus temperature increase is measured of value $(P_2 - P_1)/(T_2 - T_1)$.

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2 Experimental procedure

We simultaneously measured the phase diagrams of mercury with bismuth, thallium, tin, and lead, as well as the phase diagram of bismuth alone. Two types of samples were used, both of them in a hydrostatic liquid environment in which the phase changes are sharp and distinct. In the first case about 100 mg of bismuth was placed in a boron nitride cup (4.7 mm diameter and 4 mm deep) and a thermocouple was embedded in the bismuth while molten. This was placed in a thin-wall Inconel can, 6.3 mm inside diameter and 2.4 cm long, which was filled with petroleum ether and capped at each end with polyethylene plugs. Electrical current was sent through the can causing the temperature to rise slowly (between 0.1 and 1 K s⁻¹) while observing the thermal arrest as the bismuth underwent phase transitions. This was repeated at many constant loads. The pressure at each phase change was determined from the measured temperature on the assumption that the phase diagram of bismuth is known. This last assumption is likely to be quite valid for the measurements of Tikhomirova *et al.* (1966) in liquid systems below about 30 kbar. The temperatures were determined from the e.m.f. of the Chromel-Alumel thermocouple and corrected for the effects of pressure by averaging the measurements of Getting and Kennedy (1970) and Hanneman *et al.* (1971). This correction to the e.m.f. due to pressure on the thermocouple junction is less than 1.2 K at any point in this experiment and is small enough not to contribute more than a 0.1 kbar error at any pressure. The thermocouples were calibrated at atmospheric pressure against the melting points of indium, tin, lead, and zinc. To get the pressure increase with heating we took the pressure at room temperature, 26°C, from a calibration against load—determined from a fixed-point calibration with the phase changes Hg L-I, Bi I-II, and Tl I-II taken as a 12.6, 25.6, and 38 kbar respectively—all measured on increasing pressure only. From this pressure at room temperature and that at the

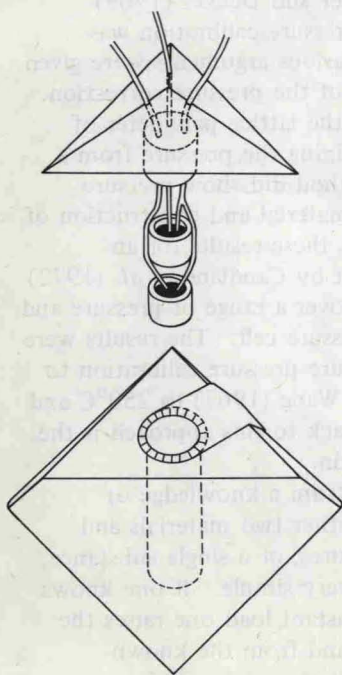


Figure 1. A diagram of the pressure cell. A pyrophyllite cube, 2.45 cm along an edge, contains a liquid-filled chamber into which the specimens are inserted. The specimens are in polyethylene cups. The wires entering through the edges of the cube are thermocouple wires.