bismuth phase changes at the same load, we determined the pressure increase on heating at a constant press load.

In the second type experiment differential thermocouple techniques were used. Two samples (one of which was mercury in each case) were placed in polyethylene buckets as shown in figure 1 and a thermocouple junction was affixed to each. The thermocouple leads were arranged such that we could measure the e.m.f. of the junction in mercury or in the other junction simultaneously with the difference between the two junctions. We also used as a reference an ice bath junction outside the pressure chamber. The pressure was increased slowly until the mercury L–I transition was observed from the latent heat release causing the temperature of mercury to rise above that of the other sample. The temperature was then slowly increased at constant load, and the thermocouple difference signal referred to the temperature of mercury was observed and the phase changes were noted. We then assumed that the melting curve of mercury proposed by Bogdanov *et al.* (1971) was accurate, at least below about 40 kbar, and that the phase changes of bismuth below 30 kbar were known. From these we determined the value of $\Delta P/\Delta T$ between the mercury and bismuth phases.

3 Results

Figure 2 shows the DTA signal as the mercury and bismuth passed through phase changes at room temperature upon increasing the press load. The Hg L–I and Bi I–II transitions were used in determining the room-temperature pressure calibration.

The shapes of the differential signals at the phase transitions upon changing the temperature at fixed load are shown in figures 3–5. It is noted that the Hg I–L (melting transition) as shown in figure 3a is extremely sharp with a small amount of hysteresis (<2 K) on solidification. After this initial supercooling the temperature rises to the melting value so that the Hg I–L indication is repeatable to $\pm 0{\cdot}2$ K. All the melting signals are similar to that of mercury, provided the samples are pure and do not alloy with the thermocouple or other contact materials. It was noted that the lead samples appeared to alloy with the thermocouple at temperatures above 550°C and that bismuth in a steel container alloyed with the steel above 350°C. This manifested itself as a rounding of the DTA signal and often some spreading of the signal. The solid–solid phase changes are more difficult to analyze. In general there is both supercooling and superheating beyond the equilibrium temperature. This is clear in the Hg I–II signal in figure 3b. In this case it is apparent that the Hg II–I signal is much nearer the equilibrium value than the Hg I–II signal. If the DTA signals are essentially alike on increasing and decreasing temperature one might assume the equilibrium value to be midway between these points. Unfortunately, some transitions show very large hysteresis, particularly at lower temperatures, thus making a precise determination of the equilibrium temperature impossible. The signals in figures 4 and 5 show various bismuth transitions near the triple points on the phase diagram. The thermal arrest signals are not vertical because they are plotted against the temperature measured with the thermocouple recording the temperature of mercury which was changing during the phase transition of bismuth. This is most clearly observed in the bismuth melting signal in figure 5.

In the first type of experiment, in which we measured the several bismuth phase changes and used the room-temperature pressure–load calibration, we determined a pressure increase with heating at constant load of $\Delta P/\Delta T = 0{\cdot}016$ kbar K^{-1} at pressures below 30 kbar. The phase diagram of bismuth above 30 kbar appears to be more inaccurate, for, if we take the phase lines reported by Klement *et al.* (1963b) and Haygarth *et al.* (1969) who used a piston cylinder apparatus, the value of $\Delta P/\Delta T$ suddenly jumps to $0{\cdot}022$ kbar K^{-1} above the IV–V–L triple point. We also find a

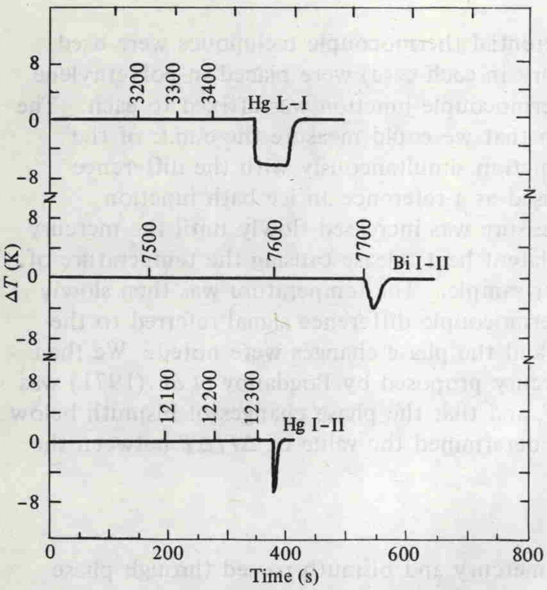

Figure 2. DTA signals upon passing through the Hg L–I, the Bi I–II, and the Hg I–II phase changes at room temperature on increasing the press load. The press load (lb in^{-2}) is indicated by the numbers along the recorder trace.

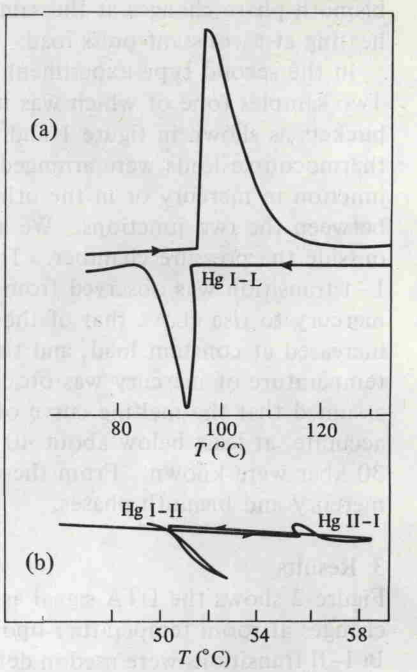

Figure 3. DTA signals at (a) the Hg I–L and (b) the Hg II–I phase transitions on increasing and decreasing the temperature near 47 kbar.

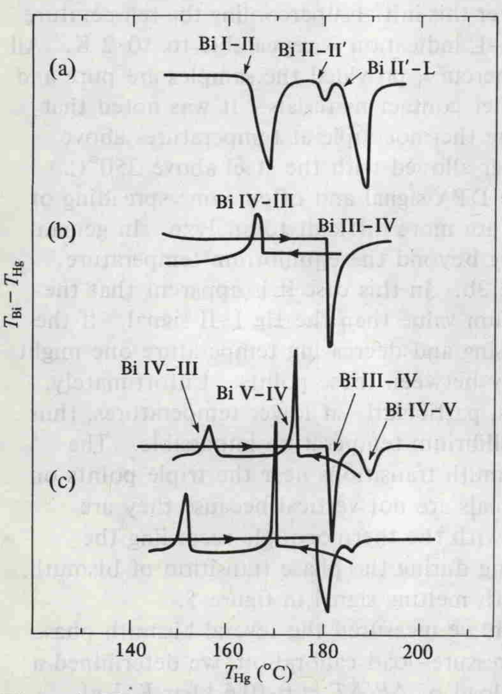

Figure 4. DTA signals at the phase changes of bismuth: (a) near 19 kbar, showing the presence of the II′ phase; (b) near 36 kbar—note the types of hysteresis in this transition; and (c) 50·9 and 51·3 kbar, just below the III–IV–V triple point.

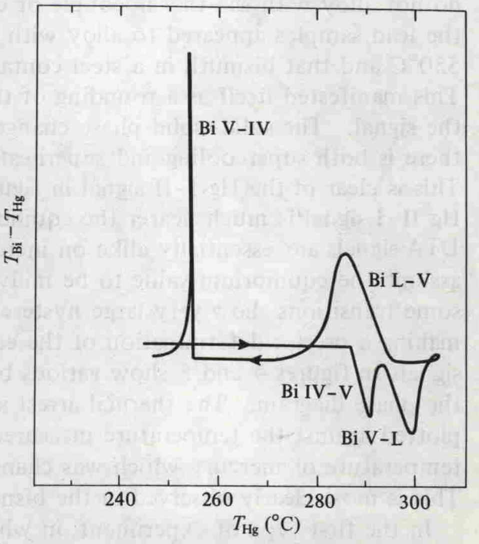

Figure 5. DTA signals near the Bi IV–V–L triple point. Note that the nature of the IV–V and V–IV transitions is the same as that shown in figure 4. The melting signal is not vertical because the temperature at the mercury junction is changing while the bismuth is going through the phase change.