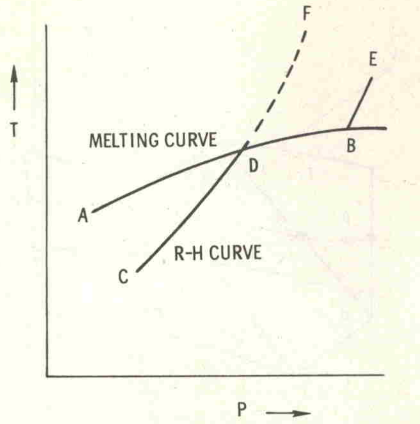

FIG. 33. Temperature–pressure phase diagram and R–H curve.

More direct evidence of melting in shock was sought by Kormer *et al*. (1965b). They constructed melting curves for NaCl and KCl based on a Simon equation and R–H curves from shock data and theoretical equations of state, Fig. 33. For no melting, the calculated R–H curve is *CDF*. For equilibrium melting, the R–H curve is *CDBE*. Temperature was inferred from radiation measurements and was found to follow the equilibrium curve, not the metastable one. They inferred from this that melting occurred under equilibrium conditions. Other workers, e.g., Urtiew and Grover (1971, 1974) and Grover and Urtiew (1974), have encountered serious difficulties in attempting to measure temperature from radiation, so some caution must be exercised in accepting these conclusions as irrefutable.

The discontinuity in dU_s/dU_p reported by Kormer *et al*. (1965a) occurred at a pressure corresponding to point *D* in Fig. 33. No break in slope was found in NaCl. Some further confirmation was provided by Mineev and Savinov (1967), who measured viscosity of Al, Pb, and NaCl as a function of shock pressure by a shock perturbation method. They found that beyond a certain pressure for each material the viscosity decreased quite rapidly. By assuming this to be due to melting, they obtained estimates of the melting pressure. Their values for NaCl fell within the range determined by Kormer *et al*. (1965b).

Belyakov *et al*. (1965, 1967) inferred the existence of shock-induced melting from mechanical effects. While measuring craters produced in lead by flat aluminum disks striking a thick target, they observed that above a critical impact speed the crater changed from a hemispherical to a conical cavity. Assuming this to result from melting, they used the critical impact speed in the shock equations and calculated a melting pressure of approximately 22 GPa. Similar experiments in tin, cadmium, and zinc gave the pressures in Table VII.

In later experiments they used flash x rays of copper cylinders striking lead sheet. The x rays showed the character of the ejecta from the rear of the sheet to change discontinuously at impact speed corresponding to shock pressure of 23 to 25 GPa. A similar experiment with thin foils enabled them to estimate the characteristic melting time. In Fig. 34 *OACE* is an equilibrium R–H curve entering the mixed liquid–solid phase region at *A* and leaving it at *C*. *AB* is the metastable extension of the solid phase Hugoniot. If the shock carries the material to a point *B* in the metastable solid phase, and if the pressure is maintained long enough, the state point of the material will eventually relax back to an equilibrium state, say *D*. If the total shock profile is unchanging in time (which is not possible, but may not be a bad approximation), it will relax along the Rayleigh line, *OBD*, as shown. The resulting shock wave profile will have the general character shown in Fig. 34(b): the pressure will drop from P_B to P_D in a distance Δx or time $\Delta x/U_s$. This time is a measure of the time required to melt under shock conditions. By measuring velocities given to a set of foils by the shock of Fig. 34(b), it is possible to infer the slope of the shock profile (O'Brien and Davis, 1961). Belyakov *et al*. (1967) did this using lead foils and flash x-ray to measure foil motion. They found $\Delta t \simeq 3\times10^{-7}$ s. Many details of their experiment are not given, but it is an interesting experiment and result, to be compared with theory or other experiments in the future.

It is possible to measure sonic velocity in the shocked state. A shock or rarefaction can be made to follow the primary shock in a flyer plate experiment by making the plate thin and backing it with a material of higher or lower impedance. Reflection from this rear surface sends the required wave into previously shocked material (see, for example, Barker and Hollenbach, 1974). If shocked material is in an elastic–plastic state, a second shock should travel at bulk wave velocity ($\sqrt{k/\rho}$), whereas a rarefaction should have elastic wave speed $\sqrt{(k+\frac{4}{3}\mu)/\rho}$. An alternative is to produce a disturbance in the shock wave which spreads laterally across the shock front. By measuring its progress in a known time, lateral rarefaction velocity can be determined (Al'tshuler *et al*., 1960). Comparison of measured values with predictions from equations of state provides a clue to the state of shocked material. If rarefaction velocities appear to be bulk rather than elastic, the liquid state is suggested. Hord (1975) has measured lateral rarefaction velocities in shock-loaded iron at 180 GPa. He concludes that it has not melted at this pressure.

Asay and Hayes (1975) measured velocity of an overtaking rarefaction in initially porous aluminum for shock pressures between 0.6 and 11 GPa. The temperature

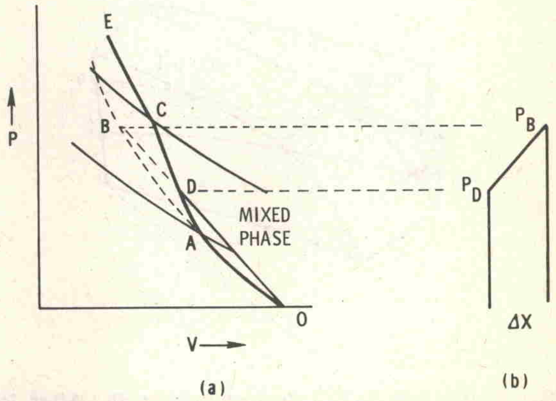

FIG. 34. (a) R–H curves in the mixed phase region. (b) Wave profile from metastable melting.

produced in a shock wave of given pressure is increased in an initially porous material, relative to the solid, so that melting may be expected at a lower pressure. In Asay's experiments, melting was estimated from equation of state calculations to occur at 7.5 GPa. A discontinuity in rarefaction velocity was found at 7.0 GPa, and this was taken as evidence of the onset of melting. The work of Grady *et al.* (1975) suggests that the change would have been observed even if partial melting occurred. This might result from inhomogeneity of temperature distribution in the porous material.

B. Bismuth

The phase diagram of bismuth (Fig. 26) has been mapped out in static measurements and some aspects of it are controversial. Nevertheless, the Bi I–II and I–liquid boundaries are well established. A shock wave with initial temperature $T_0 \gtrsim 435$ K crosses the boundary between solid and liquid. Since $V_{\text{liq}} - V_{\text{solid}} < 0$ along this boundary, such a shock wave should be double, like those produced by polymorphic transitions. If such a wave is observed, melting is inferred; otherwise not. Duff and Minshall (1957) did one such experiment on polycrystalline bismuth, using pins to detect free surface motion, observed no double wave at the melting line, and inferred that no melting had occurred. They did find a second shock wave at higher pressures which they assumed to arise from crossing the metastable phase I–phase II boundary.

In a series of three papers, Johnson *et al.* (1974), Asay (1974), and Hayes (1975) have given a detailed analysis of the wave structure to be expected for various initial temperatures and final pressures and have compared these with a careful set of experiments. Expectations can be summarized most easily with reference to Figs. 35 and 36 taken from Johnson *et al.* (1974). These are scale drawings of the $P-V-T$ surface in bismuth showing phases I, II, and liquid. Figure 35 is the equilibrium surface; Fig. 36 is frozen, i.e., it is drawn assuming that melting cannot occur. In Fig. 35 are drawn two R–H curves $oabcdp$ and $\hat{o}\hat{c}\hat{d}\hat{p}\hat{e}$. The lower one is for an initial temperature of 400 K. Compression from zero pressure at $\hat{o}$ to $\hat{p}$ in phase II would occur in two shocks: the first from $\hat{o}$ to $\hat{c}$, the second from $\hat{c}$ to $\hat{p}$. The upper R–H curve is for an initial temperature of 493 K. Compression to p in phase II would be via a shock from o to a, a compression fan from a to b, since the R–H curve is convex upward there (Duvall, 1962), and a final shock from b to p. The line segment between I–II and the liquid–I region represents the triple point. If melting were not to occur, Fig. 36 applies, and for both initial temperatures a double shock occurs. These two compression processes are illustrated in the wave profile calculations shown in Fig. 37 for a final compression of about 2.1 GPa. The experimentally observed wave profile is shown in Fig. 37 by the dotted curve, which fits neither calculated curve. The experimental record terminated before the final pressure was reached. It was inferred from the leveling off of the

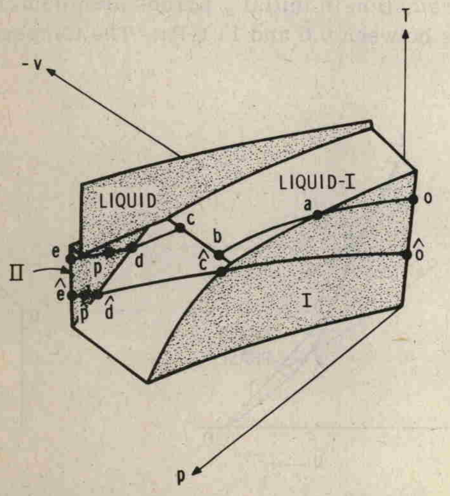

FIG. 35. Equilibrium $P-V-T$ surface in bismuth. After Johnson *et al.* (1974). Two R–H curves for initial temperatures of 400 and 493 K are shown.

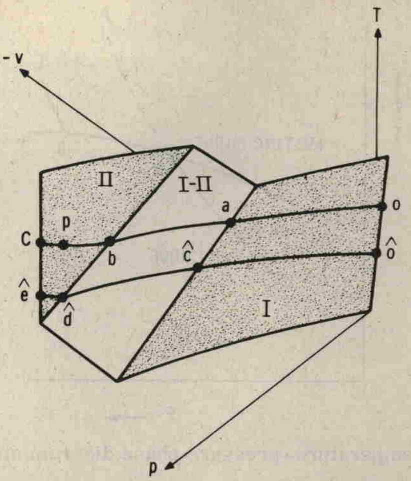

FIG. 36. Metastable $P-V-T$ surface in Bi I→Bi II bismuth in the absence of melting. After Johnson *et al.* (1974). Two R–H curves for initial temperature of 400 and 493 K are shown.

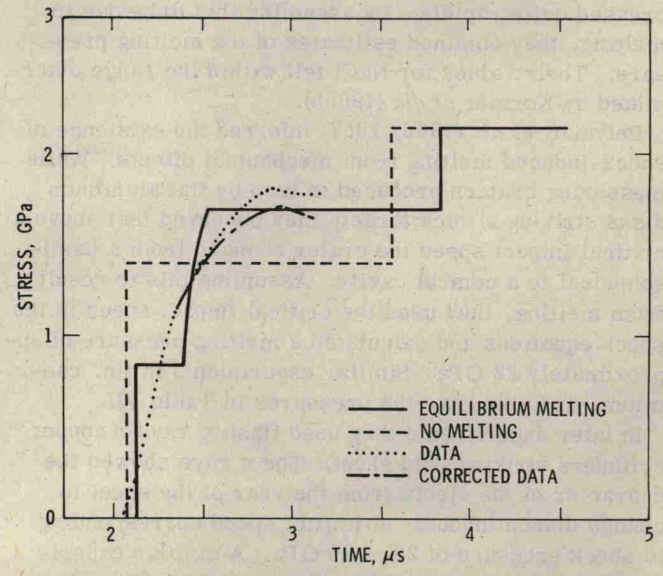

FIG. 37. Calculated and experimentally observed wave profiles for bismuth shock loaded at 2.1 GPa, at an initial temperature of 493 K. After Johnson *et al.* (1974).