APPENDIX A

THERMODYNAMICALLY CONSISTENT EQUATION OF STATE

The present interest in an equation of state is restricted to describing isotherms and Hugoniots of alpha and epsilon iron. These thermodynamic paths involve very small portions of the equilibrium surface of each phase. In fact, when iron is shocked to a stress of 200 kbar, the total temperature rise is less than 100°K. This temperature rise will displace the Hugoniot stress by less than 3 percent from the isothermal stress at the same volume.

By assuming that the specific heat is constant, simple analytical expressions result which describe the equilibrium alpha and epsilon surfaces. Accurate isothermal compression data have been reported for alpha and epsilon iron in terms of the Murnaghan equation.[33] The equation of state developed below reduces exactly to the Murnaghan equation for isotherms. The accuracy of the calculated Hugoniot, which varies only slightly from the isotherm, is limited principally by the experimental error of ± 2 percent in stress for the measured isotherms.[33]

The choice of the present equation of state rather than that of Andrews[27,28] was made for its simplicity. Andrews' equation of state exists as a deck of computer cards, and ana-lytical expressions describing the equilibrium surfaces are not

readily available. However, Andrews' equation of state does define all of the equilibrium surfaces of alpha and epsilon iron and is more useful than the present equation of state for a variety of problems. Except for the assumptions of constant C_V and constant ratio of Gruneisen parameter to volume for the epsilon phase, the present equation of state and Andrews' equation of state are similar in principle. In practice, the two approaches differ considerably. For example, the present equation of state relies on one set of isothermal compression data to define the equilibrium surfaces while Andrews fitted all the available thermodynamic data to the appropriate derivatives of a Helmholtz potential function to define the surfaces. The two equations of state give values on the Hugoniot for volume and temperature at 130-kbar stress which differ by less than 0.3 percent. The excellent agreement between the equations of state was expected.

A.1. Equilibrium Surfaces

The specific heat at constant volume is assumed constant following the approach suggested by Johnson.[59,60] This approach is sufficient for making accurate predictions along a Hugoniot. These assumptions, along with the isothermal compression data of alpha and epsilon iron, define the equilibrium surfaces for the two phases.

The primary assumption is that the specific heat at constant volume is independent of temperature and volume:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \text{constant} . \qquad (A.1)$$