IV. CONSTRUCTION OF (e-p-v) EQUATION OF STATE

The limited number of experimental Hugoniot points and the restricted range of data along the atmospheric isobar prohibit the construction of an equation of state solely from experimental data. It is important, however, to use both shock wave and static data to indicate the most appropriate form of the (e-p-v) equation of state. A graphic fit of Hugoniot data in the 200-kbar regime, without the three points from shots 12,326 and 12,496 that indicate crossing Hugoniot curves, suggests a linear dependence of internal energy on pressure along lines of constant volume-isochores; static data show that the partial derivative $(\partial e/\partial p)_v$ varies along the atmospheric isobar. Thus, the (e-p-v) data were fitted to the form

$$e = pf(v) + g(v) \tag{11}$$

with $(\partial e/\partial p)_v = f(v) > 0$ everywhere in the region of interest.

Additional properties of this model follow from thermodynamic relationships. The relationship between specific heat at constant pressure C_p and specific heat at constant volume C_v is

$$C_p = C_v\left[1 + T(\partial v/\partial T)_p/f(v)\right] \tag{12}$$

and C_v is constant along an isentrope, since

$$\left(\frac{\partial C_v}{\partial T}\right)_s = \left(\frac{\partial^2 e}{\partial p^2}\right)_v \left(\frac{\partial p}{\partial T}\right)_v^2 = 0 \tag{13}$$

The equation for a Hugoniot curve centered at $(p_o = 0, v_o)$ is

$$p\left[f(v) - \tfrac{1}{2}(v_o - v)\right] = g(v_o) - g(v) \tag{14}$$

the differential equation for an isentrope is

$$\left(\frac{\partial p}{\partial v}\right)_s = -\frac{p(1 + df/dv) + dg/dv}{f(v)} \tag{15}$$

and the equation[9] obtained by formal integration of Eq. 15 shows that the first derivative of g(v) must be positive, i.e., $dg/dv > 0$. The rapid increase of pressure along an isentrope indicates that the (e-p-v) relationship will satisfy the mechanical stability condition $(\partial p/\partial v)_s < 0$ if f(v) satisfies the condition $(1 + df/dv) > 0$.

Values of $f(v)$ in the specific volume range $0.994 < v < 1.35$ cc/g along the atmospheric isobar were calculated with the identity,

$$f(v) = -C_p \left(\frac{\partial v}{\partial p}\right)_s \left(\frac{\partial T}{\partial v}\right)_p \qquad (16)$$

The values of C_p and $(\partial v/\partial T)_p$ were determined experimentally. The values of $(\partial p/\partial v)_s$ were calculated from the sound velocity data of McSkimin[10], which were extrapolated to cover the range of initial temperatures used in the shock experiments. Values of $f(v)$ in the volume range $0.515 < v < 0.55$ cc/g were taken to be the slopes of (e-p) isochores calculated from the Hugoniot curves. Values of $f(v)$ in the intermediate range were assumed to lie on a smooth curve because values of $(\partial e/\partial p)_v$ calculated in the neighborhood of 0.54 cc/g were approximately equal to the value calculated at 0.994 cc/g. Least squares fits of the data give the following expressions for $f(v)$:

$f(v) = -23.055 + 23.134v$ if $v \geq 1.152$ cc/g

$f(v) = 60.502 - 121.866v + 62.916v^2$ if $0.9693 \leq v \leq 1.152$ cc/g

$f(v) = 1.3822 + 0.108v$ if $v \leq 0.9693$ cc/g

where the constants are given to a number of decimal places for computation.

Since $h = e = g(v)$ when $p = 0$, the measured enthalpies at atmospheric pressure give values of $g(v)$ in the volume range $0.985 \leq v \leq 1.66$ cc/g. A linear least squares fit for $g(v)$ in this volume range is given by the expression

$$g(v) = -16.107 + 15.517v.$$

For values of volume less than 0.985 cc/g, fits for $g(v)$ were generated by patching together the high pressure Hugoniot data and the atmospheric data so as to satisfy the condition $dg/dv > 0$. The best least squares fits for $g(v)$ with a slight discontinuity in the slope at $v = 1.01316$ cc/g are:

$g(v) = 2408.116 + 7566.432v - 7949.11v^2 + 2787.845v^3$ if $v \leq 1.0136$ cc/g

$g(v) = -16.107 + 15.517v$ if $v \geq 1.0136$ cc/g