

temperature is given by the equation

$$C_v(T) = C_v(298) + \Delta C_v^0(T), \quad (10)$$

where  $C_v(298)$  is the specific heat of the liquid at 298°K, and  $\Delta C_v^0(T)$  is the increase in  $C_v(T)$  from 298 to  $T^\circ\text{K}$  as calculated with the Einstein function for a molecule considered to be in the ideal gas state.

The assumptions for  $(\partial p/\partial T)_v$  and  $C_v(T)$  together with the Hugoniot curve implicitly define the state variables in the volume range spanned by the Hugoniot curve. Integrating along lines of constant volume from the Hugoniot gives the following expressions for temperature and energy,

$$T = T_H + (\partial T/\partial p)_v (p - p_H),$$

$$e = e_H + \int_{T_H}^T C_v(T) dT,$$

where  $T_H$  is obtained by integrating Eq. (1) with a Runge-Kutta technique and  $e_H$  is given by the Hugoniot equation  $e_H = e_0 + \frac{1}{2}p(v_0 - v)$ .

#### SHOCK TEMPERATURE CALCULATIONS WITH $C_v(T)$

Shock temperatures were calculated for carbon tetrachloride, nitromethane, and water.

##### Carbon Tetrachloride

The shock temperature of carbon tetrachloride was calculated using  $C_v(T)$  and other input data given in Table I. The results, shown in Fig. 1, show better agreement with the experimental measurements than do the temperatures calculated using the constant value of  $C_v$ . Although Mader<sup>12</sup> obtained better agreement with the experimental results above 150 kbar using the Walsh-Christian method, he used the value of  $C_p$  for  $C_v$ .

The experimentally observed temperatures start to diverge from those calculated using  $C_v(T)$  at pressures above about 150 kbar. This is the region in which Dick<sup>13</sup> observed a break in the  $p$ - $v$  Hugoniot and is also the region where Mader<sup>8</sup> calculated that significant amounts of decomposition of  $\text{CCl}_4$  into  $\text{C}_2\text{Cl}_6$  and  $\text{Cl}_2$  take place.

##### Nitromethane

The results of the shock temperature calculations with both the constant  $C_v$  and  $C_v(T)$  models are shown in Fig. 4. They are compared with those calculated by Enig and Petrone<sup>14</sup> using their own equation of state, and with the shock temperatures at 86 kbar calculated by Campbell, Davis, and Travis<sup>15</sup> and Mader.<sup>16</sup>

It is of interest to discuss reasons why the temperatures calculated with the  $C_v(T)$  model are considered to be more realistic than those calculated with the other methods. As mentioned earlier, the constant

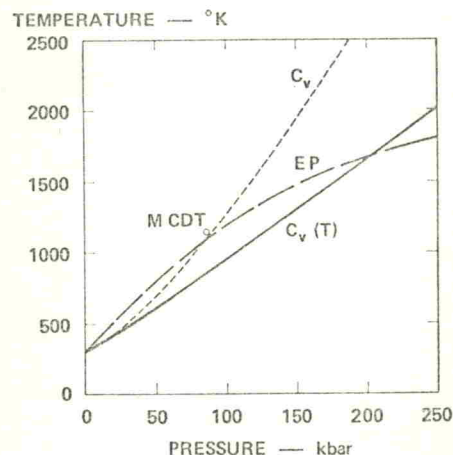


Fig. 4. Shock temperature for nitromethane. The point *M CDT* was obtained by Mader using the Walsh-Christian method (constant  $C_v$ ), but using  $C_p$  for the value of  $C_v$ . The point *M CDT* was also obtained by Campbell, Davis, and Travis using the "ideal gas equation of state." The line  $C_v$  was calculated in the present work using the Walsh-Christian method, and the line  $C_v(T)$  was calculated in the present work using  $C_v$  as a function of temperature. The line *EP* was calculated by Enig and Petrone who used another equation of state. The input data for the present calculations are in Table I.

$C_v$  model ignores the excitation of molecular vibrations; it thereby underestimates the value of  $C_v$  along the Hugoniot curve, and gives an overestimate of shock temperature. Calculation of  $C_v$  at 298°K with the Enig-Petrone equation of state gives a value of 0.24 cal  $\text{g}^{-1}\cdot\text{deg}^{-1}$  which differs significantly from the literature value<sup>2</sup> of 0.29 cal  $\text{g}^{-1}\cdot\text{deg}^{-1}$ . Moreover, it has been pointed out by Jacobs<sup>17</sup> that their equation of state predicts high values for  $C_v$  at higher temperatures. For example, at 2000°K,  $C_v$  is increasing rapidly and has already attained a value of 2 cal  $\text{g}^{-1}\cdot\text{deg}^{-1}$  which greatly exceeds the classical maximum of  $\sim 0.7$  cal  $\text{g}^{-1}\cdot\text{deg}^{-1}$  given by the generalized Dulong and Petit expression  $3nR/M$  for a solid of molecular weight  $M$  containing  $n$  atoms per molecule. Campbell, Davis, and Travis have calculated a shock temperature of 1140°K at 86 kbar using the expression  $T = 300 + \Delta e/C_v$ , where  $\Delta e$  is given by the Hugoniot equation. However, the calculation ignores the forces of interaction between the molecules and uses the value of  $C_p$  for  $C_v$ . It should be noted that use of the value of  $C_v$  in the calculation gives a value of 1450°K. Mader calculated a value of 1168°K at 86 kbar using the Walsh-Christian method with a constant  $C_v$ . The agreement with the value calculated by Campbell, Davis, and Travis can be explained by the fact that the value of  $C_p$  and a high value of  $(\partial p/\partial T)_v$  were used in the calculation.<sup>2b</sup>

##### Water

The results of calculations using the Walsh-Christian method are shown in Fig. 5. The results are compared with those calculated by Rice and Walsh who assumed  $C_p$  to be constant and  $C_p/(\partial v/\partial T)_p$  to be a function of