temperature is given by the equation

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

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°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[12] 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[13] observed a break in the p–v Hugoniot and is also the region where Mader[8] calculated that significant amounts of decomposition of CCl_4 into C_2Cl_6 and 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[14] using their own equation of state, and with the shock temperatures at 86 kbar calculated by Campbell, Davis, and Travis[15] and Mader.[16]

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
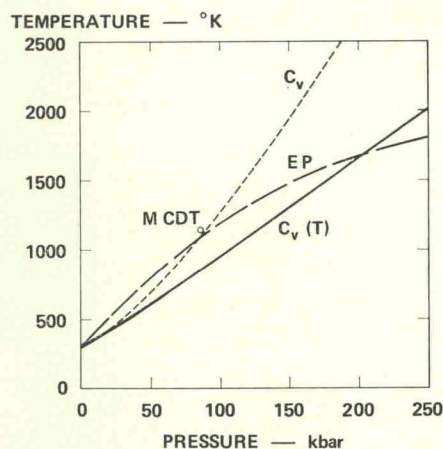

FIG. 4. Shock temperature for nitromethane. The point M CDT was obtained by Mader using the Walsh–Christian method (constant C_v), but using C_p for the value of C_v. The point M CDT was also obtained by Campbell, Davis, and Travis using the "ideal gas equation of state." The line C_v was calculated 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 $g^{-1} \cdot deg^{-1}$ which differs significantly from the literature value[2] of 0.29 cal $g^{-1} \cdot deg^{-1}$. Moreover, it has been pointed out by Jacobs[17] 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 $g^{-1} \cdot deg^{-1}$ which greatly exceeds the classical maximum of ~ 0.7 cal $g^{-1} \cdot deg^{-1}$ 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 Δe 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.[2b]

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
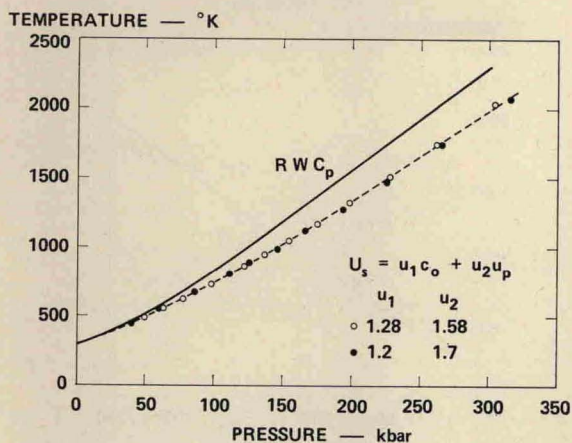
FIG. 5. Shock temperature for water. Comparison of the constant C_v model with the Rice–Walsh constant C_p model. The shock temperatures calculated using the constant C_v model are not sensitive to the form of the Hugoniot. $u_1, u_2 = 1.28, 1.58$ (personal communication from R. W. Woolfolk); 1.2, 1.7 (Ref. 3). The other input data are in Table I.

pressure only. From the analysis of the dependence of calculated shock temperature on $(\partial p/\partial T)_v$ and C_v, we conclude that the shock temperature will be very sensitive to the value chosen for C_v. The observed difference between the present results and those obtained by Rice and Walsh is therefore regarded as not significant.

The inapplicability of the $C_v(T)$ model to water at low pressures is yet another example of water being an anomalous liquid. Specifically, the model is not valid since the value of C_v has its classical value at atmospheric pressure and temperatures where the O–H vibrations are not fully excited. It is for this reason that shock temperatures calculated by Duvall[18] using Eq. (1), the C_v model and standard conditions for the lower limits of integration are lower than those calculated by Walsh and Rice.[19] A similar calculation with the $C_v(T)$ model would give even lower values of shock temperature. Similarly to Rice and Walsh, the integration of Eq. (1) is started from a point on the Hugoniot above atmospheric pressure. As shown in Table I, the point selected was ($p_H = 10$ kbar, $v = 0.819$ cc g^{-1}, $T_H = 323°$K).

CONCLUSIONS

When compared with the Walsh–Christian method, the present method for calculating shock temperatures takes better account of the properties of liquids and the greater dependence of shock temperature on C_v than on $(\partial p/\partial T)_v$. It is therefore considered to be an improvement on the Walsh–Christian method and will yield more realistic values of shock temperature in liquid explosives. This conclusion is substantiated by the improved agreement between the calculated and experimental temperatures for carbon tetrachloride, but account must be taken of the inapplicability of the model to water in the low pressure region. Thus the $C_v(T)$ model is expected to be better for nonassociated liquids than associated liquids. An improvement of the present model must include the variation of $(\partial p/\partial T)_v$ and a better method for calculating the variation of C_v for associated liquids.

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$$U_s = u_1 c_0 - [(u_1 - 1) c_0 / \exp(u_3 u_p / c_0)] + u_2 u_p$$

with u_3 as a constant as a better form of the Hugoniot curve. This form has the advantage that it satisfies the limiting condition $U_s = c_0$ when $u_p = 0$. However the linear form is used for convenience since values of shock temperature calculated with $u_3 = \infty$ have been found[7] to be not significantly different from those calculated with $u_3 = 1$ and $u_3 = 10$.
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