relationship, we will assume $F(v)$ is well known and use the Hugoniot for liquids[3] ($u_1=1.2$ and $u_2=1.7$) to calculate it.

DEPENDENCE OF CALCULATED SHOCK TEMPERATURE ON $(\partial p/\partial T)_v$ AND C_v

Let T_H denote temperature on a Hugoniot curve and T_s denote temperature on an isentrope. Then Eq. (4) relating the temperatures at a volume v_1 on the Hugoniot centered at ($p_0=0$, v_0, T_0) and on the isentrope through ($p_0=0$, v_0, T_0) can be written formally as

$$T_H(v_1, b, C_v)=T_s(v_1, b) + (2C_v)^{-1}\int_{v_0}^{v_1}[\exp b(v-v_1)]F(v)\,dv, \tag{5}$$

with $T_s(v_1, b)=T_0\exp b(v_0-v_1)$. We will use Eq. (5) to determine the qualitative dependence of shock temperature on $(\partial p/\partial T)_v$ and C_v. Partial differentiation of Eq. (5) with respect to $(\partial p/\partial T)_v$ and use of the identity $C_v[\partial b/\partial(\partial p/\partial T)_v]=1$ leads to the equation

$$\frac{\partial T_H}{\partial(\partial p/\partial T)_v}=\frac{T_s(v_0-v_1)}{C_v}+\frac{I}{2C_v^2}, \tag{6}$$

where

$$I=\int_{v_0}^{v_1}(v-v_1)\,[\exp b(v-v_1)]F(v)\,dv.$$

The integral I must be positive since $T_H>T_s$ and $(v-v_1)\geq 0$. Thus $\partial T_H/\partial(\partial p/\partial T)_v>0$ and the slope of the T_H vs $(\partial p/\partial T)_v$ curve is positive. An increase in $(\partial p/\partial T)_v$ in a Walsh–Christian temperature calculation will produce an increase in shock temperature, but a decrease in $(\partial p/\partial T)_v$ will produce a decrease in shock temperature. Partial differentiation of Eq. (5) with respect to C_v and use of the identity $\partial b/\partial C_v=-b/C_v$ leads to the equation,

$$\frac{\partial T_H}{\partial C_v}=-\left[b\,\frac{\partial T_H}{\partial(\partial p/\partial T)_v}+\frac{T_H-T_s}{C_v}\right]. \tag{7}$$

Thus $\partial T_H/\partial C_v<0$ since $\partial T_H/\partial(\partial p/\partial T)_v>0$, and the slope of the T_H vs C_v curve is negative. In contrast to the former case, an increase in C_v will produce a decrease in shock temperature in a Walsh–Christian calculation, but a decrease in C_v will produce an increase in shock temperature.

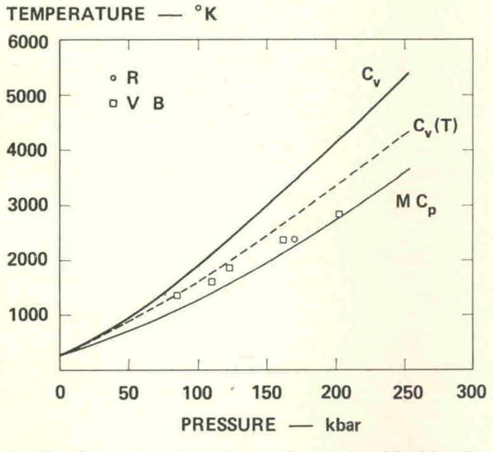

FIG. 1. Shock temperature for carbon tetrachloride. Comparison of calculated values with those obtained experimentally by the "brightness" method. The circle was obtained by Ramsay and the squares by Voskoboinikov and Bogomolov. The line C_v was calculated in the present work using the Walsh–Christian method (constant C_v). The line MC_p was calculated by Mader also using the Walsh–Christian method but using C_p for the value of C_v. The dashed line $C_v(T)$ was calculated in the present work using C_v as a function of temperature. The input data for the calculations are in Table I. For constant C_v the shock temperature at 150 kbar agrees with that calculated by Dick.[13]

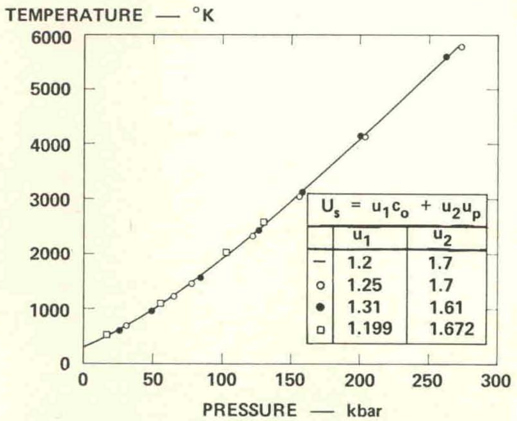

FIG. 2. Shock temperature for carbon tetrachloride. Sensitivity of the calculated temperatures to the form of the Hugoniot. u_1, u_2=1.2, 1.7 (Ref. 3); 1.25, 1.7 (this work, arbitrary variation of u_1); 1.31, 1.61 (Ref. 7); and 1.199, 1.672. (Recalculated from Ref. 13 by R. D. Dick). The other input data are in Table I.

The equation

$$-\frac{C_v(\partial T_H/\partial C_v)}{(\partial p/\partial T)_v[\partial T_H/\partial(\partial p/\partial T)_v]}=1 + \frac{T_H-T_s}{b[T_s(v_0-v_1)+I/2C_v]}, \tag{8}$$

obtained by rearranging Eq. (7), is convenient for making a more quantitative estimate of the dependence of shock temperature on $(\partial p/\partial T)_v$ and C_v. Let $\Delta T_H(\delta C_v)$ and $\Delta T_H[\delta(\partial p/\partial T)_v]$ denote the change in shock temperature produced by a small decrease in C_v and a small increase in $(\partial p/\partial T)_v$. Then if second- and higher-order terms are neglected, Eq. (8) can be written as

$$-\frac{\Delta T_H(\delta C_v)}{\Delta T_H[\delta(\partial p/\partial T)_v]}=1+\frac{T_H-T_s}{b[T_s(v_0-v_1)+I/2C_v]}. \tag{9}$$

The right-hand side of Eq. (9) has been evaluated along the Hugoniot curve, and the left-hand side has been calculated for a 10% increase in $(\partial p/\partial T)_v$ and a 10% decrease in C_v. The results of these calculations are given in Table III and Fig. 3. At a given shock pressure, shock temperature is more sensitive to changes in C_v

TABLE III. Sensitivity of the shock temperature of carbon tetrachloride to the values of C_v and $(\partial p/\partial T)_v$.[a]

					$\frac{\Delta T_H(\delta C_v)}{\Delta T_H[\delta(\partial p/\partial T)_v]}$	
p (kbar)	v (cc g^{-1})	$bT_s(v_0-v_1)$ (deg)	$bI/2C_v$ (deg)	T_H-T_s (deg)	Calc. analytically	Obs. empirically
0	0.631	0	0	0	...	...
29	0.431	169	98	223	1.8	2.4
49	0.401	207	150	515	2.4	3.4
73	0.381	233	208	978	3.2	4.5
113	0.361	262	274	1696	4.1	5.7
144	0.351	277	300	2354	5.1	7.0
188	0.341	292	328	3335	6.4	8.3
253	0.331	308	347	4853	8.4	9.7

[a] Input data used; see Table I.

than to changes in $(\partial p/\partial T)_v$, and this sensitivity increases with pressure along the Hugoniot curve.

THE $C_v(T)$ MODEL

The assumptions concerning the variations of C_v and $(\partial p/\partial T)_v$ along the Hugoniot curve, necessary for calculating shock temperature with Eq. (1), should be compatible with the known properties of liquids. For example, under normal conditions of atmospheric pressure and room temperature C_v for carbon tetrachloride increases with temperature as does the coefficient $(\partial p/\partial T)_v$.[9] Moreover, other properties of liquids in the kilobar region are known from the classical high-pressure work of Bridgman.[10] Of particular interest is his investigation of the previously advanced hypothesis that liquids can adequately be described by a van der Waals' type (p–v–T) equation of state; namely, that $(\partial p/\partial T)_v$ is a function of volume only, or equivalently, that C_v is a function of temperature only. The hypothesis was found to hold well at low and moderate pressures, but to break down at high pressures where $(\partial p/\partial T)_v$ was found to decrease with increasing temperature at constant volume. For temperatures below 450°K, C_v for 18 liquids was found to be insensitive to pressure below 100 kbar.

A logical extension of the Walsh–Christian model for calculating shock temperature in initiation studies of liquids below 100 kbar would be based on the assumptions that $(\partial p/\partial T)_v$ is a function of volume and that C_v is a function of temperature. The present work, however, assumes that $(\partial p/\partial T)_v$ is a constant and that C_v is a function of temperature, i.e., $C_v(T)$. These assumptions are reasonable since our variational analysis shows C_v to be a more important parameter than $(\partial p/\partial T)_v$ in shock temperature calculations, and also because we have a better understanding of the dependence of $C_v(T)$ on temperature than of $(\partial p/\partial T)_v$ on volume. Specifically, constancy of $(\partial p/\partial T)_v$ is retained because calculated shock temperature is relatively insensitive to its variation (Fig. 3), because the increase and subsequent decrease of $(\partial p/\partial T)_v$ with increasing pressure will tend to cancel, and because we have little insight as to the variation of $(\partial p/\partial T)_v$ along the Hugoniot curve. On the other hand, the specific heat is assumed to be a function of temperature because calculated shock temperature is sensitive to C_v, and because we expect C_v to increase with increasing pressure along the Hugoniot curve as internal molecular vibrations become more excited. The dependence of $C_v(T)$ on temperature is based on the additional assumption that internal molecular vibrations are essentially unaffected by the forces of interaction among the molecules. This approximation has also been used by Davies and Matheson.[11] Then the increase in $C_v(T)$ above room temperature is due primarily to the increase in the vibrational heat capacity as the vibrations become more classical. The functional dependence of $C_v(T)$ on

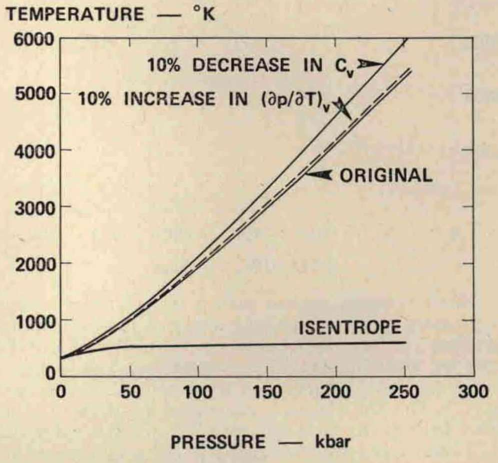

FIG. 3. Shock temperature of carbon tetrachloride. Sensitivity of the calculated temperatures to the values used for C_v and $(\partial p/\partial T)_v$. The original input data are in Table I.