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

## DEPENDENCE OF CALCULATED SHOCK TEMPERATURE ON $(\partial p / \partial T)_*$ AND $C_*$

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

$$T_{H}(v_{1}, b, C_{v}) = T_{s}(v_{1}, b) + (2C_{v})^{-1} \int_{v_{0}}^{v_{1}} [\exp b(v - v_{1})] F(v) dv, \quad (5)$$

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

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

The integral I must be positive since  $T_H > T_s$  and  $(v-v_1) \ge 0$ . 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



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.<sup>13</sup>



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.

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,

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

The equation

$$-\frac{C_{v}(\partial T_{H}/\partial C_{v})}{(\partial p/\partial T)_{v}[\partial T_{H}/\partial(\partial p/\partial T)_{v}]} = 1$$
$$+\frac{T_{H}-T_{s}}{b[T_{s}(v_{0}-v_{1})+I/2C_{v}]}, \quad (8)$$

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 higherorder terms are neglected, Eq. (8) can be written as

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

	¢ (kbar)	7 (cc g <sup>-1</sup> )	$bT_s(v_0-v_1)$ (deg)	bI/2C <sub>v</sub> (deg)	$T_H - T_s$ (deg)	$\frac{\Delta T_H(\delta C_v)}{\Delta T_H[\delta(\partial p/\partial T)_v]}$		
						Calc. analytically	Obs. empirically	
	0	0.631	0	0	0	See		in g
	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	

TABLE III. Sensitivity of the shock temperature of carbon tetrachloride to the values of  $C_v$  and  $(\partial p/\partial T)_{v,a}$ 

<sup>a</sup> 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  $(\partial p/\partial T)_{p}$  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  $C_n$  for carbon tetrachloride increases with temperature as does the coefficient  $(\partial p/\partial T)_{v}$ .<sup>9</sup> Moreover, other properties of liquids in the kilobar region are known from the classical high-pressure work of Bridgman.<sup>10</sup> 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  $(\partial p/\partial T)_{*}$  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, 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  $(\partial p/\partial T)_*$  is a function of volume and that  $C_*$ is a function of temperature. The present work, however, assumes that  $(\partial p/\partial T)_*$  is a constant and that  $C_*$  is a function of temperature, i.e.,  $C_*(T)$ . These assumptions are reasonable since our variational analysis shows  $C_*$ to be a more important parameter than  $(\partial p/\partial T)_*$  in shock temperature calculations, and also because we have a better understanding of the dependence of  $C_*(T)$  on temperature than of  $(\partial p/\partial T)_*$  on volume. Specifically, constancy of  $(\partial p/\partial T)_*$  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.<sup>11</sup> 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



F1G. 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.