# $C_v(T)$ Equation of State for Liquids. Calculation of the Shock Temperature of Carbon Tetrachloride, Nitromethane, and Water in the 100-kbar Region\*

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The  $C_v(T)$  model for calculating shock temperature in liquids is presented as an extension of the Walsh-Christian model for metals. The model is based on an analysis showing shock temperature to be more sensitive to variations in  $C_v$  than in  $(\partial p/\partial T)_v$ , and it takes account of the temperature dependence of  $C_v$ . Measured shock temperatures for carbon tetrachloride are compared with calculated values as a test of the constant  $C_v$  and  $C_v(T)$  models. The constant  $C_v$  model overestimates shock temperature and is inappropriate to polyatomic liquids. The agreement obtained with the  $C_r(T)$  model suggests that it will be valuable for calculating more realistic values of temperature in shock initiation studies of liquids in the neighborhood of 100 kbar.

## INTRODUCTION

Since pressure-volume-temperature (p-v-T) equations of state of liquids in the kilobar regime are not known, calculation of shock temperature is important in shock-initiation studies of liquid explosives. Use of the method developed by Walsh and Christian<sup>1</sup> for metals is limited, because it is based on thermodynamic assumptions that are inappropriate for polyatomic liquids. The assumptions of constant specific heat at constant volume  $C_v$ , with a value equal to the specific heat at constant pressure  $C_p$ , are adequate for describing metals, but inadequate for describing molecular liquids with internal degrees of vibrational freedom. For such liquids under normal conditions,  $C_v$  is a function of temperature, and there is a significant difference<sup>2</sup> between the values of  $C_p$  and  $C_v$ . Thus the object of the present work is to develop a more realistic model for calculating shock temperature in liquids.

This paper attempts to take into account the differences between liquids and metals in formulating the  $C_v(T)$  model for liquids from the Walsh-Christian model for metals. The formulation is based on a variational analysis that shows that calculated shock temperature is more sensitive to changes in  $C_v$  than changes in  $(\partial p/\partial T)_v$  and also on the assumption that differences in the vibrational excitation of a molecule in the liquid and gaseous phase can be neglected. The  $C_v$  and  $C_v(T)$ models together with the Hugoniot curve define the p-v-T and internal energy-volume-temperature (e-v-T)equations of state in the volume range spanned by the Hugoniot.

Shock temperatures for various liquids were calculated using both the constant  $C_v$  and the  $C_v(T)$ models, and the values for carbon tetrachloride were compared with the brightness temperatures measured by Voskoboinikov and Bogomolov<sup>3</sup> and Ramsay.<sup>4</sup>

# THE WALSH-CHRISTIAN METHOD OF CALCULATING SHOCK TEMPERATURES

The thermodynamics of the Walsh-Christian model with  $C_{v}$  and  $(\partial p/\partial T)_{v}$  regarded as constants have been

discussed by Cowperthwaite.<sup>5</sup> Their method of calculating shock temperature is to integrate the following differential equation along the Hugoniot curve,

$$dT/dv + T(\partial p/\partial e)_v = (2C_v)^{-1} [p + (v_0 - v) (dp/dv)], \quad (1)$$

where e denotes specific energy and the subscript 0 denotes unshocked material. Equation (1) is derived by combining the differential form of the (e-v-T) equation of state

$$de = C_v dT + [T(\partial p/\partial T)_v - p]dv$$
<sup>(2)</sup>

with the equation

$$de = -\frac{1}{2}\rho dv + \frac{1}{2}(v_0 - v)d\rho, \qquad (3)$$

obtained by differentiating the Hugoniot equation

 $e-e_0=\frac{1}{2}(p+p_0)(v_0-v)$ 

and neglecting the initial pressure  $p_0$  with respect to the shock pressure p.

With the assumptions of constant  $C_v$  and constant  $(\partial p/\partial T)_v$ , Eq. (1) is integrated from an initial condition  $(T_0, v_0)$  to give the following expression for shock temperature,

$$T = T_0 \exp[b(v_0 - v)] + \exp(-bv/2C_v)$$

$$\times \int_{v_0}^{v} [\exp(bv)] F(v) dv, \quad (4)$$

where for simplicity we set

and

$$b = (\partial p / \partial e)_{v} = (\partial p / \partial T)_{v} / C_{v}$$

$$F(r) = b + (r - r) (db / dr)$$

$$F(v) = p + (v_0 - v) \left( \frac{dp}{dv} \right).$$

Thus calculation of shock temperature requires a knowledge of  $C_v$ ,  $(\partial p/\partial T)_v$ , and the function F(v) along the Hugoniot curve. The values chosen for  $C_v$  and  $(\partial p/\partial T)_v$  are those measured under standard conditions, and F(v) is calculated from experimental shock wave data.

Equations (1) and (4) were used to calculate shock temperature with a computer (and the input data given in Table I). The equation for a Hugoniot curve used in the calculations is  $U_s = u_1 c_0 + u_2 u_p$ , where  $u_1$  and  $u_2$  are

Quantity	Units	Carbon tetrachloride	Ref.	Nitromethane	Ref.	Water	Ref.
$(\partial p/\partial T)_v$	10 <sup>7</sup> dyn cm <sup>-2</sup> ·deg <sup>-1</sup>	1.14	9	1.6371	2c	4.04	h
Sound speed Specific volume at $p=0$	10 <sup>5</sup> cm sec <sup>-1</sup> cc g <sup>-1</sup>	0.926° 0.631	d 9	1.30 0.884	2c 2c	1.48 1.002	h h
Temp. at $p=0$ and $v=v_0$	°K	298		298		293	
First volume point on Hugoniot <sup>a</sup>	cc g <sup>-1</sup>	0.631		0.884		0.819	
Temp. at first volume point on Hugoniot	°K	298		298		323	
Molecular wt	g mol <sup>-1</sup>	153.84		61		18.02	
$C_v$ (constant) $C_v$ fit: <sup>b</sup>	cal mol <sup>-1</sup> · deg <sup>-1</sup>	21.7	9 e	17.8	2c g	14.07	h
B C D E F		$\begin{array}{r} -75 \ 415.8 \\ -2 \ 109.31 \\ 8.10247 \\ -8.64548 \times 10^{-4} \\ 1.12516 \times 10^{-7} \end{array}$		$\begin{array}{r} 1.23375 \times 10^{6} \\ -9956.86 \\ 17.3573 \\ 8.09421 \times 10^{-3} \\ -2.24624 \times 10^{-6} \end{array}$			

TABLE I. Input data for shock temperature calcu
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<sup>8</sup> Integration starts from the first volume point on the Hugoniot and

the volume increment is  $-0.01 \text{ cc } g^{-1}$ . <sup>b</sup>  $C_{\psi}(T)$  is given by  $C_{\psi}$  (constant) +  $(B/T^2)$  + (C/T) + D +  $E \times T$  +  $F \times T^2$ .  $^{\rm c}$  Sound speed calculated from the data in Ref. 9 is  $0.922 \times 10^{5} \rm ~cm~sec^{-1}.$ d Handbook of Chemistry and Physics (Chemical Rubber, Cleveland, Ohio,

1968-1969), 49th ed., p. E-38. JANAF Thermochemical Tables (Dow Chemical, Midland, Mich.,

constants, and  $U_s$ ,  $u_p$ , and  $c_0$  denote shock velocity, particle velocity, and sound speed in unshocked material.<sup>6</sup> Equation (1) was integrated step by step with a Runge-Kutta program written by S. P. Gill, and the integral in Eq. (4) was evaluated with a program based on a trapezoidal approximation written by B. Y. Lew. As expected, both methods of calculation are found to be consistent. Shock temperatures for carbon tetrachloride calculated with the Runge-Kutta scheme are in excellent agreement with those calculated with the trapezoidal method as shown in Table II. In addition, shock temperatures calculated for copper by Walsh and Christian<sup>1</sup> and for nitromethane by Mader<sup>8</sup> are in good agreement with our values calculated with the same input data and the trapezoidal method.

However, comparison of calculated shock temperatures of carbon tetrachloride with experimental brightness temperatures<sup>3,4</sup> (Fig. 1) demonstrates the inadequacy of applying the Walsh-Christian method to liquids. The poor agreement between the calculated and experimental results indicates that the Walsh-Christian method gives an upper estimate for shock temperature in liquids. Our extension of their method to liquids will take into consideration the sensitivity of calculated

1961).

<sup>f</sup> Calculated from  $(\partial p/\partial T)_v = \alpha C_v c_0^2 / v_0 C_v$  where  $\alpha$  is the coefficient of expansion.

g J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp, and G. Waddington, J. Am. Chem. Soc. 76, 4791 (1954).

<sup>h</sup> N. E. Dorsey, Properties of Ordinary Water Substance (Reinhold, New York, 1940).

shock temperature to choice of the parameters F(v),  $(\partial p/\partial T)_v$ , and  $C_v$ . But since calculations for carbon tetrachloride (Fig. 2) show that the shock temperature vs shock pressure relationship is insensitive to changes of the order of 10% in the constants in the  $U_s$  vs  $u_p$ 

TABLE II. Comparison of shock temperatures for carbon tetrachloride calculated from Eq. (4) by trapezoidal evaluation of the integral and shock temperatures calculated by a Runge-Kutta integration of Eq. (1).

	a la ser a	1.1.1.1.1.1	Т	Т			
			Eq. (4)	Eq. (1)			
þ		υ	Trapezoidal Runge-Kutta				
	(kbar)	(cc g <sup>-1</sup> )	(°K)	(°K)			
	0	0.631	298	298			
	29	0.431	661	662			
	49	0.401	980	980			
	73	0.381	1401	1402			
	113	0.361	2198	2198			
	144	0.351	2866	2867			
	188	0.341	3857	3857			
	253	0.331	5385	5386			

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  $C_v$ 

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

$$C_{v}(T) = C_{v}(298) + \Delta C_{v}^{0}(T), \qquad (10)$$

where  $C_{\nu}(298)$  is the specific heat of the liquid at 298°K, and  $\Delta C_{\nu}^{0}(T)$  is the increase in  $C_{\nu}(T)$  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<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  $C_{\nu}(T)$  at pressures above about 150 kbar. This is the region in which Dick<sup>13</sup> observed a break in the  $p-\nu$  Hugoniot and is also the region where Mader<sup>8</sup> calculated that significant amounts of decomposition of CCl<sub>4</sub> into C<sub>2</sub>Cl<sub>6</sub> and Cl<sub>2</sub> 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<sub>v</sub> 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<sup>2</sup> of 0.29 cal g<sup>-1</sup>·deg<sup>-1</sup>. 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<sub>v</sub> is increasing rapidly and has already attained a value of 2 cal g<sup>-1</sup>·deg<sup>-1</sup> which greatly exceeds the classical maximum of  $\sim 0.7$  cal g<sup>-1</sup>·deg<sup>-1</sup> 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  $C_p$ . 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



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  $C_{\nu}$ . 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<sup>18</sup> using Eq. (1), the  $C_{*}$  model and standard conditions for the lower limits of integration are lower than those calculated by Walsh and Rice.<sup>19</sup> 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  $(p_H = 10 \text{ kbar}, v = 0.819 \text{ cc g}^{-1},$  $T_H = 323^{\circ} \text{K}$ ).

#### 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  $C_{\mu}$ for associated liquids.

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<sup>1</sup> J. M. Walsh and R. H. Christian, Phys. Rev. 97, 1544 (1955). <sup>2</sup> (a) J. W. Enig and F. J. Petrone, Phys. Fluids 8, 769 (1965). (b) C. L. Mader, Phys. Fluids 8, 771 (1965). (c) B. O. Reese,

L. B. Seely, R. Shaw, and D. Tegg, J. Chem. Eng. Data 15, 140 (1970)

<sup>8</sup> I. M. Voskoboinikov and B. M. Bogomolov, ZhETF Pis. Red. 7, 338 (1968).

<sup>4</sup> Personal communication from C. L. Mader re experiments by Ramsay

<sup>5</sup> M. Cowperthwaite, Am. J. Phys. 34, 1025 (1966). <sup>6</sup>S. J. Jacobs has suggested

 $U_{s} = u_{1}c_{0} - \left[ (u_{1}-1)c_{0} / \exp(u_{3}u_{p}/c_{0}) \right] + u_{2}u_{p}$ 

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 found7 to be not significantly different from those calculated with  $u_3 = 1$  and  $u_3 = 10$ .

<sup>7</sup> Stanford Research Institute Project 4051 Technical Progress Report 69-2 (Semiannual), "Sensitivity Fundamentals," October 1969.

8 C. L. Mader (personal cummunication).

<sup>9</sup> D. Harrison and E. A. Moelwyn-Hughes, Proc. Roy. Soc.

(London) A239, 230 (1957). <sup>10</sup> P. W. Bridgman, *The Physics of High Pressure* (Bell, London, 1958), pp. 127-142.

<sup>11</sup>D. B. Davies and A. J. Matheson, Discussions Faraday Soc. 43, 216 (1967)

<sup>12</sup> C. L. Mader, Los Alamos Scientific Laboratory of the University of California, Los Alamos, N.M., Rept. No. LA-2900.

<sup>13</sup> R. D. Dick, Los Alamos Scientific Laboratory of the University of California, Los Alamos, N.M., Rept. LA-3915.
<sup>14</sup> J. W. Enig and T. J. Petrone, Phys. Fluids 9, 398 (1966).
<sup>15</sup> A. W. Campbell, W. C. Davis, and J. R. Travis, Phys. Fluids

4, 498 (1961).

<sup>16</sup> C. L. Mader, quoted in Ref. 19.

<sup>17</sup> S. J. Jacobs (personal communication).
<sup>18</sup> G. E. Duvall, "Equations of State of Liquids and Calculations of Waste Heat," Stanford Research Institute Project PAU-4900, 6 November 1966, Spec. Tech. Rept. No. 3.
<sup>19</sup> M. H. Rice and J. M. Walsh, J. Chem. Phys. 26, 824 (1957).