$C_v(T)$ 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 $C_v(T)$ 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[1] 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[2] 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[3] and Ramsay.[4]

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.[5] 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

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

with the equation

$$de = -\tfrac{1}{2}pdv + \tfrac{1}{2}(v_0 - v)dp, \quad (3)$$

obtained by differentiating the Hugoniot equation

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

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

$$b = (\partial p/\partial e)_v = (\partial p/\partial T)_v/C_v$$

and

$$F(v) = p + (v_0 - v)(dp/dv).$$

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

TABLE I. Input data for shock temperature calculations.

Quantity	Units	Carbon tetrachloride	Ref.	Nitromethane	Ref.	Water	Ref.
$(\partial p/\partial T)_v$	10^7 dyn $cm^{-2} \cdot deg^{-1}$	1.14	9	1.637[f]	2c	4.04	h
Sound speed	10^5 cm sec^{-1}	0.926[e]	d	1.30	2c	1.48	h
Specific volume at $p=0$	cc g^{-1}	0.631	9	0.884	2c	1.002	h
Temp. at $p=0$ and $v=v_0$	°K	298		298		293	
First volume point on Hugoniot[a]	cc g^{-1}	0.631		0.884		0.819	
Temp. at first volume point on Hugoniot	°K	298		298		323	
Molecular wt	g mol^{-1}	153.84		61		18.02	
C_v (constant)	cal $mol^{-1} \cdot deg^{-1}$	21.7	9	17.8	2c	14.07	h
C_v fit:[b]			e		g		
B		−75 415.8		1.23375×10^6			
C		−2 109.31		−9956.86			
D		8.10247		17.3573			
E		$−8.64548 \times 10^{-4}$		8.09421×10^{-3}			
F		1.12516×10^{-7}		$−2.24624 \times 10^{-6}$			

[a] Integration starts from the first volume point on the Hugoniot and the volume increment is −0.01 cc g^{-1}.
[b] $C_v(T)$ is given by C_v (constant) $+(B/T^2)+(C/T)+D+E \times T+F \times T^2$.
[e] Sound speed calculated from the data in Ref. 9 is 0.922×10^5 cm sec^{-1}.
[d] Handbook of Chemistry and Physics (Chemical Rubber, Cleveland, Ohio, 1968–1969), 49th ed., p. E-38.
[e] JANAF Thermochemical Tables (Dow Chemical, Midland, Mich., 1961).
[f] Calculated from $(\partial p/\partial T)_v = \alpha C_v c_0^2/v_0 C_v$ where α 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).
[h] N. E. Dorsey, Properties of Ordinary Water Substance (Reinhold, New York, 1940).

constants, and U_s, u_p, and c_0 denote shock velocity, particle velocity, and sound speed in unshocked material.[6] 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[1] and for nitromethane by Mader[8] 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[3,4] (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

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).

p (kbar)	v (cc g^{-1})	T Eq. (4) Trapezoidal (°K)	T Eq. (1) Runge–Kutta (°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