

$C_v(T)$ 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 Christian¹ 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 difference² 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 Bogomolov³ 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

$$de = -\frac{1}{2}p dv + \frac{1}{2}(v_0 - v)dp, \quad (3)$$

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

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

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