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## $C_{i}(T)$ 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

. 18

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  $C_x$  and the  $C_r(T)$ models, and the values for carbon tetrachloride were compared with the brightness temperatures measured by Voskoboinikov and Bogomolov<sup>3</sup> and Ramsav.<sup>4</sup>

## THE WALSH-CHRISTIAN METHOD OF CALCULATING SHOCK TEMPERATURES

The thermodynamics of the Walsh-Christian model with  $C_*$  and  $(\partial p/\partial T)_*$  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

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

with the equation

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

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

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

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