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Author(s)	Sano, Yukio; Sano, Tomokazu; Nagata, Shinichi
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Yukio Sano, Tomokazu Sano and Shinichi Nagata

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Electronic and ionic contributions to the constant-volume specific heat of carbon tetrachloride shocked at pressures up to 23 GPa

Yukio Sano,[1,a)] Tomokazu Sano,[2] and Shinichi Nagata[3]
[1] *38-10 Shibatani-Cho, Takatsuki, Osaka 569-1025, Japan*
[2] *Department of Manufacturing Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*
[3] *Environmental Biochemistry Division, Research Center for Inland Seas, Kobe University, Kobe 658-0022, Japan*

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For carbon tetrachloride, a temperature Hugoniot at 7–23 GPa and a distribution of the constant-volume specific heat on the Hugoniot $C_V(T)$ at 1057–3275 K are simultaneously estimated from the Walsh–Christian (WC) equation such that the Hugoniot fits well to the existing measured data. The estimated $C_V(T)$ distribution reveals the significance of the contribution of electrons and ions to the specific heat. That is, in contrast to the almost uniform distribution of the specific heat predicted from the Debye equation, the $C_V(T)$ distribution increases significantly with an increase in the Hugoniot temperature due to thermal excitation of electrons at 1057–1500 K (7–10.1 GPa), additional activation of the dimerization reaction at 1500–2350 K (10.1–16 GPa), and also additional activation of the polymerization reaction at 2350–3275 K (16–23 GPa). As an example, evidence is presented that carbon tetrachloride is a semiconductor at 1500 K. The $C_V(T)$ distribution in each temperature range is formulated and a temperature Hugoniot is reevaluated from the WC equation using the specific heat equations formulated. It is confirmed by a good fit of the reevaluated Hugoniot to the existing measured data that the specific heat equations express the $C_V(T)$ distribution appropriately. © *2010 American Institute of Physics*. [doi:10.1063/1.3294963]

I. INTRODUCTION

For carbon tetrachloride, Walsh and Rice[1] reported the onset of opacity at a Hugoniot pressure (the pressure on the Hugoniot) of about 7 GPa and complete opacity at about 17 GPa. Mitchell and Keeler[2] reported the onset of a measurable conductivity at about 7 GPa and a very high conductivity at about 17 GPa. The microwave data of Hawke *et al.*[3] revealed that the mechanism for the conductivity at Hugoniot pressures from 13 to 17 GPa was electronic and ionic. Dick[4] suggested that the observations of both groups might be the result of the dimerization reaction ($2CCl_4 \rightarrow C_2Cl_6 + Cl_2$) in a Hugoniot pressure range of 7–17 GPa and that the molecular rearrangement occurring in the dimerization process could free ions in a sufficient quantity at 7 GPa to produce detectable changes in opacity and conductivity. In order to make a calculation of the degree of the dimerization, Fat'yanov *et al.*[5] performed *ab initio* molecular orbital calculations on isolated molecules (CCl_4, C_2Cl_6, and Cl_2) and estimated the difference in energy between $C_2Cl_6 + Cl_2$ and $2CCl_4$. In addition, Fat'yanov *et al.*[5] estimated the difference between the Hugoniot temperature measured by themselves and that theoretically predicted by Cowperthwaite and Show (CS).[6] Using these difference estimates, Fat'yanov *et al.*[5] found that about 50% of the total amount of CCl_4 could react at 8.1 GPa. Percentages taking part in the reaction are corrected in Sec. IV B.

The conductivity data of Mitchell and Keeler[2] and the microwave data of Hawke[3] suggest that the dimerization reaction begins near 10 GPa and therefore that the contribution of ions to the specific heat is slight at 7–10 GPa. The onset of appreciable thermal activation of the reaction near 10 GPa is confirmed in Sec. IV B.

Keeler[7] inferred from recovery experiments that above 16 GPa, there might be divergence that indicated a possibility of the polymerization reaction. The inference of Keeler[7] is supported both by the high conductivity of 20 mho/cm at 20 GPa which is derived from the optical data of Yushko[8] and by the fact that hydrocarbons decompose at high pressures and temperatures.[9] The change in the slope of the shock wave velocity-particle velocity (u_s-u_p) curve of Dick[4] at 16 GPa may signal the onset of the polymerization reaction. The divergence[7] is verified in Sec. IV C. If the mechanism for conductivity at Hugoniot pressures above 7 GPa is electronic or electronic and ionic, there should be a contribution of electrons and ions to the specific heat in this pressure range. Furthermore, Keeler[7] inferred from the temperature data of Komer[10] that as a result of thermal excitation of electrons into the conduction band at the high temperatures achieved along the Hugoniot, carbon tetrachloride behaved as an intrinsic semiconductor. This inference is confirmed in Sec. III B.

In this study on carbon tetrachloride, the efficacy of the Debye specific heat equation is first examined by comparing a temperature Hugoniot up to 23 GPa calculated from the Walsh–Christian (WC) equation using the Debye equation with existing measured Hugoniot temperature data.[11–14] Next, a temperature Hugoniot at 7–23 GPa and a distribution of the constant-volume specific heat on the Hugoniot at 1057–3275 K are simultaneously estimated from the WC

[a)] Electronic mail: profeme_ys@yahoo.co.jp.

equation which clarified the significance of the contribution of electrons and ions to the specific heat. Finally, the influences of the endothermic quantity in the dimerization reaction on the temperature Hugoniot and of the polymerization reaction on the pressure Hugoniot are examined, and, as was described above, some results of previous studies are made clearer.

II. CALCULATIONS OF TEMPERATURE HUGONIOTS USING EXISTING CONSTANT-VOLUME SPECIFIC HEAT FUNCTIONS

A. WC equation

The rear of the shock wave front propagating through carbon tetrachloride is assumed to be either in a thermodynamic equilibrium state or in a metastable state. Under this condition, Hugoniot temperature T can be appropriately predicted from the WC equation, which has been applied to metals,[15–18]

$$C_V\frac{dT}{dV}+C_V\frac{\gamma}{V}T=\frac{1}{2}\left[p+(V_0-V)\frac{dp}{dV}\right], \tag{1}$$

where p is the Hugoniot pressure, V is the specific volume, C_V is the specific heat on the Hugoniot, $\gamma \cong \gamma(V)$ from the assumption of Grüneisen,[15] and the subscript 0 refers to an initial state. In addition, an assumption $\gamma(V)/V=\gamma_0/V_0$, which has been used successfully for metals, is made. Errors that are introduced by the assumption into the Hugoniot temperature calculated from Eq. (1) are discussed in Sec. II C.

The pressure Hugoniot $p(V)$ for carbon tetrachloride is obtained using two linear relations measured by Dick,[4] $u_s=1.11+1.67u_p$ for $u_s \leq 4.70$ km/s and $u_s=1.87+1.32u_p$ for $u_s>4.70$ km/s. The Hugoniot has a discontinuity in the slope dp/dV at $V=V_C$, where V_C is the specific volume at $u_s=4.70$ km/s. At this shock front velocity, we have $p=p_C=16.0$ GPa.

B. Existing specific heat equations

Three existing equations are used as equations for the specific heat on the Hugoniot. They are the Dulong and Petit (DP) law, the Debye equation for crystals, and the CS equation for carbon tetrachloride, all of which do not include an electronic contribution term. The DP law is

$$C_V=3Nk, \tag{2}$$

where N is the number of atoms per mol and k is the Boltzmann constant. The Debye equation[16] is given as a function of x [$=\theta/T$; T is temperature and θ is the Debye temperature expressed by $\theta=h\nu_{\max}/k$, where $\nu_{\max}(V)$ is the cutoff frequency] by

$$C_V=3Nk\left[4D-\frac{3x}{e^x-1}\right], \tag{3}$$

where $D(x)$ is the Debye function.[16] The CS equation[6] is given as a function only of temperature T,

TABLE I. Input data for Hugoniot temperature calculations in CCl_4.

Quality	CCl_4
N (10^{23} mol^{-1})	5×6.02
T_0 (K)	298
V_0 (10^{-3} m^3/kg)	0.631
C_{V0} [J/(kg K)]	803.2 (D)
	810.4 (DP)
γ_0	0.8955 (D)
	0.8876 (DP)
c_0 (m/s)	926
θ_0 (K)	125

$$C_V=C_{V0}+\Delta C_V(T). \tag{4}$$

The value of the specific heat at $T_0=298$ K, C_{V0}, included in the CS equation is 590 J/(kgK) [21.7 cal/(molK)], which was measured under standard conditions.[19] This value is remarkably smaller than the value of 810.4 J/(kgK) calculated from the DP law. Therefore, the CS equation would predict a very low distribution of the specific heat. As for $\Delta C_V(T)$, see Ref. 6.

The $C_V(x)$ function expressed by Eq. (3) is translated into $C_V(V,T)$ using[16]

$$\theta=\theta_0\exp[\gamma_0(V_0-V)/V_0], \tag{5}$$

where $\theta_0=h\nu_{\max}(V_0)/k$, where $\nu_{\max}(V_0)$ is evaluated from $\nu_{\max}(V_0)=[9N/(4\pi V_0)]^{1/3}c_0$, where c_0 is the speed of sound in liquid CCl_4. The value of θ_0 is calculated from $\theta_0=h\nu_{\max}(V_0)/k$ using the value of $\nu_{\max}(V_0)$. The value of C_{V0} is calculated from Eq. (3), where $x=x_0=\theta_0/T_0$. The value of γ_0 is calculated from $\gamma_0=V_0(\partial p/\partial T)_V/C_{V0}$ using the value of $(\partial p/\partial T)_V$ measured under standard conditions (1.14 MPa/K for CCl_4).[19] The values of c_0 adopted and θ_0, C_{V0}, and γ_0 calculated for carbon tetrachloride are listed in Table I.

Three $C_V(T)$ distributions at 298–3275 K calculated from the specific heat equations of DP, Debye, and CS [Eqs. (2)–(4)] are shown in Fig. 1. These distributions are referred to as the DP, Debye, and CS specific heat distributions. The value of the specific heat of Debye $C_{V\mathrm{Debye}}$ at 298 K is only slightly smaller than the value of $3Nk$ [810.4 J/(kgK)]. Thus, there seems to be a thermally stimulated excitation of molecular vibrations at 298 K. The specific heat $C_{V\mathrm{Debye}}$ has a value that is very close to 810.4 J/(kgK) at about 1000 K. On the other hand, the CS specific heat distribution is markedly lower than the $C_{V\mathrm{Debye}}(T)$ distribution. This is presumed to be due to the fact that 590 J/(kgK) [$\ll$810.4 J/(kg K)] was adopted as the value of C_{V0} in the CS equation.

C. Temperature Hugoniots

Errors introduced into the Hugoniot temperatures T by the assumption $\gamma/V=\gamma_0/V_0$ that was applied to γ/V in Eq. (1) are examined qualitatively. In Table II, values of $|dT/dV|$ and T/V are listed for some temperatures T that are calculated using the Debye equation. It is clear from Table II that the errors introduced are not great in the range of $T \geq 500$ K where $|dT/dV| \gg T/V$.

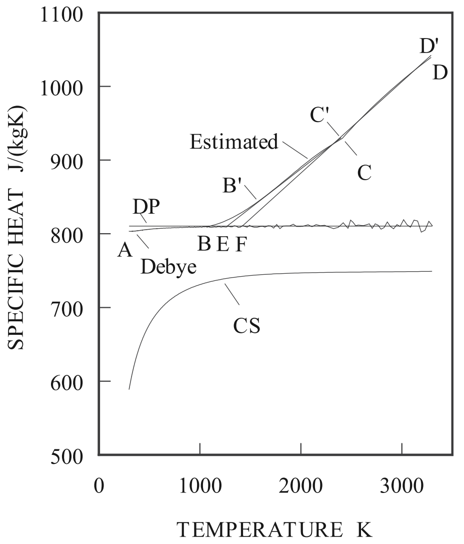

FIG. 1. Three $C_V(T)$ distributions for CCl_4 ranging from 298 to 3275 K that are calculated from the specific heat equations of DP, Debye, and CS. Also shown is a distribution of the constant-volume specific heat on the Hugoniot at 1057–3275 K (curve BB′CD) that is simultaneously determined with the temperature Hugoniot by Eq. (6). The curve BB′ and the straight lines B′C′ and C′D′ are formulated.

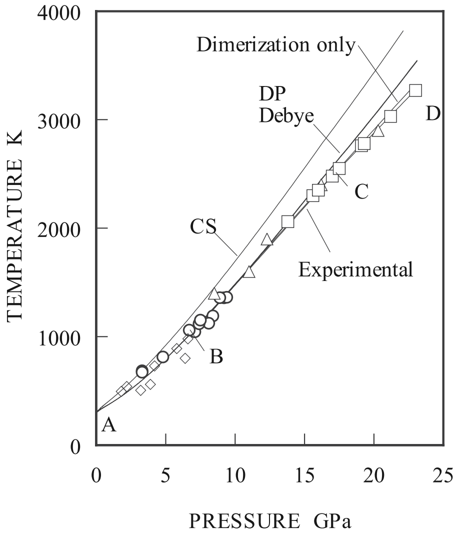

FIG. 2. Three $T(p)$ Hugoniots for CCl_4 at Hugoniot pressures up to about 23 GPa, calculated from the WC equation using the specific heat equations of DP, Debye, and CS. Circles and lozenges are the Hugoniot temperature data measured by Fat'yanov *et al.* (Ref. 13) and Sato *et al.* (Ref. 14) using time-resolved two-band infrared radiometry, respectively, and triangles and squares are those measured by Voskoboinikov *et al.* (Ref. 11) and Dolgoborodov *et al.* (Ref. 12) using optical pyrometry, respectively. Also shown is an experimental temperature Hugoniot $T_{ex}(p)$, the curve BCD [$p_B=7$ GPa and $T_B=1057$ K at the point B, $p_C=16$ GPa and $T_C=2350$ K at the point C, and $p_D=23$ GPa and $T_D=3275$ K at the point D] that fits to the measured data of three group of Fat'yanov *et al.*, Voskoboinikov *et al.*, and Dolgoborodov *et al.* A hypothetical temperature Hugoniot at 16–23 GPa calculated assuming that only the dimerization reaction occurs is also shown.

Figure 2 shows three temperature Hugoniots $T(p)$ of DP, Debye, and CS at Hugoniot pressures up to about 23 GPa calculated from the WC equation using the DP, Debye, and CS equations. Despite that there is a small difference between the DP and Debye specific heat distributions below about 1000 K, both temperature Hugoniots coincide well in the whole range up to 23 GPa. This coincidence indicates that the Hugoniot temperature is not sensitive to the specific heat. Since the CS specific heat distribution is remarkably lower than the DP and Debye distributions, nevertheless, the temperature Hugoniot of CS is considerably higher than the other two Hugoniots.

The Hugoniot temperature data for carbon tetrachloride that were measured by Fat'yanov *et al.*[13] with an uncertainty of 2.5%–3% except for the lowest temperature that was accurate to ±4.5%, by Voskoboinikov *et al.*,[11] by Dolgoborodov *et al.*,[12] and by Sato *et al.* (2–6.6 GPa)[14] are plotted in Fig. 2. The temperature Hugoniot of Debye fits the measured data well up to about $p_B=7$ GPa ($T_B=1057$), indicating that the Debye specific heat equation is efficient up to 7 GPa, that is, we have $C_V(V,T) \cong C_{V\text{Debye}}$ for $298 \leq T < 1057$ K.

TABLE II. Values of $|dT/dV|$ and T/V(K kg/m^3) for CCl_4 calculated from the WC equation using the Debye equation for the specific heat.

T	$\lvert dT/dV\rvert$ ($\times 10^6$)	T/V ($\times 10^6$)
298	0.42	0.47
336	0.60	0.61
500	3.6	1.1
1000	17	2.6
1500	33	4.1
2000	51	5.7
2500	35	7.3
3000	46	9.1

III. ESTIMATE OF THE SPECIFIC HEATS ON THE HUGONIOT

A. Calculation of the specific heat using existing measured Hugoniot temperature data

The experimental data on conductivity of Mitchell and Keeler[2] indicate the onset of thermal excitation of electrons at $p_B=7$ GPa. In the 1057–3275 K (7–23 GPa) range, where the Debye specific heat equation is inefficient, the specific heat on the Hugoniot $C_V(T)$ is estimated from the following equation, which is transformed from Eq. (1),

$$C_V = \frac{[p + (V_0 - V)dp/dV]/2}{(dT/dp)(dp/dV) + \gamma T/V}, \tag{6}$$

where $T(p)$ is the experimental temperature Hugoniot $T_{ex}(p)$ function between 7 and 23 GPa that fits the existing measured Hugoniot temperature data (see Fig. 2).[11–14] The function $T(p)$ is continuous at $p=p_C$. The function $C_V(T)$ is also continuous at $T=T_C$, where T_C is the Hugoniot temperature at $p=p_C$. Under the assumption of $\gamma=(\gamma_0/V_0)V$, the function $\gamma(V)$ is continuous at $V=V_C$. As was described in the preceding section, on the other hand, the pressure Hugoniot function $p(V)$ has a discontinuity in the derivative dp/dV at $V=V_C$. With these conditions on continuity, Eq. (6) indicates that the derivative of $T(p)$, dT/dp, is discontinuous at $p=p_C$. The discontinuity in dT/dp at $p=p_C$ is also suggested by the measured data.[11–14] To this end, the function $T(p)$ is formulated by two different equations. One is a quartic equation for $7 \leq p \leq 16$ GPa, while the other is a quadratic equation for $16 < p \leq 23$ GPa,

$$T = a_4 p^4 + a_3 p^3 + a_2 p^2 + a_1 p + a_0 \quad (7 \leq p \leq 16 \text{ GPa}), \tag{7a}$$

$$T = b_2 p^2 + b_1 p + b_0 \quad (16 < p \leq 23 \text{ GPa}), \tag{7b}$$

where $T_C = 2350$ at $p_C = 16$ and $T_D = 3275$ K at $p_D = 23$ GPa.

Under one condition that an estimated temperature Hugoniot fits the measured data[11–14] and two conditions that an estimated distribution of the specific heat has a value close to 810.4 J/(kgK) at the point B in Fig. 1 and the curves BC and CD in Fig. 1 connect at the point C, the $C_V(T)$ function and Eqs. (7a) and (7b) are simultaneously determined by Eq. (6). Temperature measurements as well as theoretical estimation both contain some error due to the assumptions in the measurement method and/or uncertainty in the values in the material properties for calculation. However, if the difference in the Hugoniot temperature values between several measurements is not large, agreements obtained by the comparison between theory and experiments can be stated as a proposal to model the thermal properties of carbon tetrachloride under shock compression.

Figure 1 shows a distribution of the specific heat $C_V(T)$ (curve BB′CD) for $1057 \leq T \leq 3275$ K that is estimated with Eq. (6). In this temperature range, no large errors are caused in the calculation of C_V by the assumption $\gamma = (\gamma_0 / V_0) V$ (see Table II) and the endothermic effect is not large (see Sec. IV B). In the region from 1057 to 1500 K ($p = 10.1$ GPa and $T = 1500$ K at the point B′), the contribution of ions to the specific heat is negligible,[2,3] so that the electronic contribution is substantially expressed by $C_{Ve} = C_V - 3Nk$. As is shown in the curve BB′, the electronic specific heat increases gradually largely with an increase in T. The value of the ratio $C_{Ve}/3Nk$ at 1500 K is about 0.041. This value is considerably smaller than the value of the ratio of about 0.21 at the same temperature for iron,[15] indicating that carbon tetrachloride is a semiconductor. That is, as a result of thermal excitation of electrons into the conduction band by the high Hugoniot temperatures, carbon tetrachloride behaves as an intrinsic semiconductor in this temperature range.[7] As is shown in the curve B′C, the contribution of electrons and ions C_{Veid} increases significantly from 1500 to 2350 K, suggesting that electrons are more excited and the percentage of the dimerization reaction increases with increasing T.[2,3] The rate of increase in the contribution of electrons and ions C_{Veip} from 2350 to 3275 K (the slope of the curve CD) is a little larger than that of increase in the contribution to C_{Veid} from 1500 to 2350 K (the slope of the curve B′C). The reason for this is that the polymerization reaction begins to be appreciably activated near 16 GPa and the percentage of the reaction increases with increasing T.[7]

B. Expressions for $C_V(T)$

For $1057 \leq T \leq 1500$ K, where the dimerization reaction is inactive (see Sec. IV B), the specific heat on the Hugoniot of carbon tetrachloride $C_V(T)$ is formulated based on the relation $C_V = C_{V\text{harm}} + C_{V\text{anharm}} + C_{Ve}$, where $C_{V\text{harm}}$ is the harmonic phonon specific heat, which is expressed by $C_{V\text{harm}} = C_{V\text{Debye}}$, $C_{V\text{anharm}}$ is the anharmonic specific heat, and C_{Ve} is the conduction-electronic specific heat. As seen in Fig. 1, we have $C_{V\text{harm}} + C_{V\text{anharm}} \cong 3Nk$ above 1057 K. The electronic contribution $C_{Ve}(T)$ that increases gradually largely with an increase in T from 1057 to 1500 K, which is shown by the curve BB′ in Fig. 1, suggests that the number of conduction-electrons increases gradually largely. The contribution $C_{Ve}(T)$ is approximated by a quadratic equation $CV_e = \Gamma_{12} T^2 + \Gamma_{11} T$. In this temperature range, the specific heat $C_V(T)$ is expressed by

$$C_V = 3Nk + C_{Ve} \quad (1057 \leq T < 1500 \text{ K}). \tag{8a}$$

We obtain $\Gamma_{12} = 2.393 \times 10^{-5}$ J/(kg K^3) and $\Gamma_{11} = -2.531 \times 10^{-2}$ J/(kg K^2) from $C_V = 3Nk$ at 1057 and $C_V = 826.3$ J/(kg K) at 1500 K. The electronic specific heat $C_{Ve}(V, T)$ is expressed by $C_{Ve} = \Gamma(V) T$ where $\Gamma(V)$ is evaluated from $\Gamma(V) = \Gamma_{12} T + \Gamma_{11}$.

For $1500 \leq T \leq T_D$ K, where the dimerization reaction or the mixed dimerization and polymerization one are active (see Sec. IV B), the specific heat on the Hugoniot is formulated based on the relation $C_V = 3Nk + C_{Vei}$, where C_{Vei} represents the contribution of electrons and ions. The curve B′C is approximated to a straight line B′C′ [$C_V = 928$ J/(kg K) at 2350 K]. With the linear approximation, the electronic and ionic contribution C_{Veid} is expressed by $C_{Veid} = \Gamma_2 (T\text{-}T_E)$ [$\Gamma_2 = 1.197 \times 10^{-1}$ J/(kg K^2) and $T_E = 1367$ K], where Γ_2 is the slope of the line B′C′ and T_E is the Hugoniot temperature at the point E in Fig. 1, the point at which the extension line of the line B′C′ intersects with line $C_V = 3Nk$. Thus, the specific heat $C_V(T)$ is expressed by

$$C_V = 3Nk + C_{Veip} \quad (1500 \leq T < T_C \text{ K}). \tag{8b}$$

The curve CD is approximated to a straight line C′D′ [$C_V = 1050$ J/(kg K) at 3275 K]. With this approximation, C_{Veip} is expressed by $C_{Veip} = \Gamma_3 (T - T_F)$ [$\Gamma_3 = 1.319 \times 10^{-1}$ J/(kg K^2) and $T_F = 1458$ K], where Γ_3 is the slope of the line C′D′ and T_F is the Hugoniot temperature at the point F, the point where the extension line of the line C′D′ intersects with the line $C_{Ve} = 3Nk$. Thus, the $C_V(T)$ is

$$C_V = 3Nk + C_{Veid} \quad (T_C \leq T \leq T_D \text{ K}). \tag{8c}$$

A temperature Hugoniot $T_{\text{ex}}(p)$ ranging from 7 to 23 GPa is re-evaluated from Eq. (1) using Eqs. (8a)–(8c). The re-evaluated Hugoniot coincides well with that expressed by Eqs. (7a) and (7b), which was determined together with the $C_V(T)$ function from Eq. (6), indicating that Eqs. (8a)–(8c) are a set of equations which appropriately express the $C_V(T)$ distribution for $1057 \leq T \leq 3275$ K.

IV. CALCULATION RESULTS

A. Experimental temperature Hugoniots

An experimental temperature Hugoniot $T_{\text{ex}}(p)$ at 7–23 GPa (curve BCD) is shown in Fig. 2. The slope dT_{ex}/dp is somewhat smaller at 16–23 GPa than at 7–16 GPa. The reason for this difference is clarified in Sec. IV C. The deviation of the Hugoniot $T_{\text{ex}}(p)$ from the Hugoniot of Debye $T_{\text{Debye}}(p)$, $\Delta T(p) [= T_{\text{Debye}}(p) - T_{\text{ex}}(p)]$, is very small at 7–10.1

GPa (1057–1500 K), is slightly larger at 10.1–16 GPa (1500–2350 K), and becomes large at 16–23 GPa (2350–3275 K).

B. Endothermic effect

The difference between the specific internal energy on the temperature Hugoniot of Debye E_{Debye} and that on the experimental temperature Hugoniot E_{ex}, $\Delta E(V)$, is expressed by $\Delta E = E_{\mathrm{Debye}} - E_{\mathrm{ex}}$. If both the differences ΔE and ΔT [see the preceding section] are assumed to be caused only by the endothermic quantity in the dimerization reaction, it is found from $\mathrm{CCl_4} \rightarrow (1/2)\mathrm{C_2Cl_6} + (1/2)\mathrm{Cl_2} - 9.15$ (kcal/mol) that the percentage of the reaction x is expressed by $x = (\Delta E/9.15) \times 100$.[5] Calculations of x performed using $\Delta E = C_V \Delta T$ indicate $x=0.9$ at $p=10.1$, $x=25$ at $p=16$, and $x=100\%$ at $p=23$ GPa. Thus, for $p<10.1$ GPa, the dimerization reaction is inactive.[2,3] In addition, the quantities of specific internal energy $(E_{\mathrm{ex}} - E_0)$ are estimated from the Rankine–Hugoniot jump condition for energy $E_{\mathrm{ex}} - E_0 = (p + p_0)(V_0 - V)/2$: They are 85.0 at $p=16$ and 132 kcal/mol at $p=23$ GPa. We obtain inequalities $2.3(9.15 \times 0.25) \leqslant 85$ at $p=16$ and $9.15 \leqslant 132$ kcal/mol at $p=23$ GPa, meaning that for $7 < p \leq 23$ GPa, the influence of the endothermic quantity on the difference ΔT is not large and therefore the influence of the endothermic quantity is only slightly involved in the measured Hugoniot temperature data.[11–13]

C. Influences of the polymerization reaction

Under the assumption that only the dimerization reaction occurs at 2350–3275 K, a temperature Hugoniot ranging from 16 to 23 GPa is calculated from Eq. (1) using a linear $C_V(T)$ function (a straight line B′C′D″ in Fig. 1), where the point D″ (not shown here) is a point on an extension line of the line B′C′ in Fig. 1 at 3275 K. The calculated Hugoniot deviates only slightly from the experimental temperature Hugoniot with an increase in the Hugoniot pressure from 16 to 23 GPa and has a maximum difference of about 8 K at 23 GPa. Thus, the influence of the difference in value between C_{Veip} and C_{Veid} on the temperature Hugoniot is slight.

From the slight influence on the temperature Hugoniot found above, it is inferred that the discontinuity in dp/dV at V_C and the decrease in $|dp/dV|$ are caused by the polymerization reaction and that the decrease is the main cause of the somewhat smaller slope of the experimental temperature Hugoniot at 16–23 GPa. The decrease may be due to the difference in the pressure Hugoniot between the products from the polymerization reaction and those from the dimerization reaction. To examine the validity of the above inference, a hypothetical temperature Hugoniot for $p \geq 16$ GPa is calculated using a hypothetical pressure Hugoniot that is transformed using $u_s = 1.11 + 1.67 u_p$ as $p(V)$ for $V \leq V_C$, in addition to the linear $C_V(T)$ function (the line B′C′D″ in Fig. 1), and is shown in Fig. 2. The Hugoniot, which is calculated assuming that only the dimerization reaction occurs, increases almost linearly and deviates gradually, but more sharply from the experimental temperature Hugoniot than in the above case where only the difference in value between C_{Veip} and C_{Veid} was taken into consideration. The difference at 23 GPa in this case is about 54 K. Figure 2 further shows that the temperature Hugoniot composed of the curve BC and the hypothetical Hugoniot rises linearly over 7–23 GPa. The validity of the above inference is verified by the linear rise in this pressure range.

V. CONCLUSIONS

For carbon tetrachloride, it was clarified that the distribution of the specific heat on the Hugoniot differed significantly from that of Debye due to thermal excitation of electrons at 1057–1500 K (7–10.1 GPa), additional activation of the dimerization reaction at 1500–2350 K (10.1–16 GPa), and further additional activation of the polymerization reaction at 2350–3275 K (16–23 GPa). The distribution was formulated in each of the three temperature ranges. An experimental temperature Hugoniot was evaluated at 7–23 GPa from the WC equation using the specific heat equations formulated. The Hugoniot fits well to the existing measured data.

[1] J. M. Walsh and M. H. Rice, J. Chem. Phys. **26**, 815 (1957).
[2] A. C. Mitchell and R. N. Keeler, Rev. Sci. Instrum. **39**, 513 (1968).
[3] R. S. Hawke, A. C. Mitchell, and R. N. Keeler, Rev. Sci. Instrum. **40**, 632 (1969).
[4] R. D. Dick, J. Chem. Phys. **52**, 6021 (1970).
[5] O. V. Fat'yanov, T. Ogura, M. F. Nicol, K. G. Nakamura, and K. Kondo, Appl. Phys. Lett. **77**, 960 (2000).
[6] M. Cowperthwaite and R. Shaw, J. Chem. Phys. **53**, 555 (1970).
[7] R. N. Keeler, *Proceedings of the International School of Physics*, in Course XLVIII in Physics of High Energy Density, edited by P. Caldrirola and H. Knoepfel (Academic, New York, 1971), p. 106.
[8] K. B. Yushko, G. V. Krishkevich, and S. B. Kormer, JETP Lett. **7**, 12 (1968).
[9] W. J. Nellis, F. H. Ree, R. J. Trainor, A. C. Mitchell, and M. B. Boslough, J. Chem. Phys. **80**, 2789 (1984).
[10] S. B. Komer, Usp. Fiziol. Nauk **94**, 641 (1964) [Sov. Phys. Usp. **11**, 229 (1968)].
[11] I. M. Voskoboinikov, V. M. Bogomolov, A. N. Afanasenkov, and V. N. Shevelev, Dokl. Akad. Nauk SSSR **182**, 807 (1968); Sov. Phys. Dokl. **13**, 1026 (1969).
[12] A. Yu Dolgoborodov, I. M. Voskoboinikov, and I. K. Tolstov, Khimicheskaya Fizika **10**, 679 (1991); Sov. J. Chem. Phys. **10**, 1036 (1992).
[13] O. V. Fat'yanov, T. Ogura, M. F. Nicol, and K. Kondo, in *Shock Waves in Condensed Matter-1999*, edited by M. D. Furnish, L. C. Chhabildas, and R. S. Hixson (AIP, New York, 2000), p. 959.
[14] A. Sato, S. Oguchi, and K. G. Nakamura, Chem. Phys. Lett. **445**, 28 (2007).
[15] Y. Sano and T. Sano, Phys. Rev. B **69**, 144201 (2004).
[16] Y. Sano and A. Abe, J. Appl. Phys. **89**, 105 (2001).
[17] T. Sano and Y. Sano, J. Appl. Phys. **90**, 3754 (2001).
[18] T. Sano and Y. Sano, J. Appl. Phys. **90**, 5576 (2001).
[19] D. Harrison and E. A. Moelwyn-Hughes, Proc. R. Soc. London **A239**, 230 (1957).