

THERMODYNAMIC PROPERTIES OF LIQUID CARBON

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Abstract—It is known that carbon is vaporized to a mixture of molecular species such as C_1 , C_2 , C_3 , etc., and the larger polyatomic species have an increasingly important effect on thermodynamic properties at higher temperatures and pressures. Though little is presently known about the vapor species above C_5 , in some estimates it is usually known that C_3 species are dominant at a relative condition. To make up for the lack in experimental data for liquid carbon, the thermodynamic properties of liquid carbon are calculated over a wide range of temperature from the triple point to the critical point, by using the significant liquid structure model which has been successfully applied to many liquids.

Key Words—Molar volume, vapor pressure, entropy, enthalpy, critical point.

1. INTRODUCTION

For carbon to be used in high temperature missile and space applications a knowledge of the various thermodynamic properties of solid-liquid-vapor is required, however experimental information on the properties of liquid carbon is little, because of the difficulties of experimenting under the condition of extremely high temperature and pressure. The temperature and vapor pressure at its triple point were estimated as 4226 K and 103 atm from the LANG grade of graphite[1], furthermore its critical temperature and pressure were calculated to be 7020 K and 7863 atm.

The volumetric change at the melting point, ΔV_m , obtained by Clapeyron's equation[2] was shown to be quite large compared with common liquids and it was observed that the sign of liquid volume difference (ΔV_l) in the transition from graphite to liquid was changed as shown in the phase diagram. So it can be thought that the structure of liquid carbon might be changed to long chain molecules as proposed by Pitzer and Clementi[3].

Carbon is known to vaporize to a mixture of molecular species such as C_1 , C_2 , C_3 , etc.[4-6], and it is now believed that the contributions of the larger polyatomic species become increasingly important at higher temperature and pressure. Little is presently known about the vapor species above C_5 , however such knowledge is essential for some estimates based on recent theoretical calculations[3, 7-10] and experimental evidence[4-6] relating to the vapor phase at the higher temperature. Pitzer and Clementi pointed out that by molecular orbital theory C_5 and C_7 were the most abundant species at a low temperature, and a high temperature region in a saturated vapor pressure. But it is usually known that C_3 species are dominant[5, 11-13] in the relatively low temperature region.

Here, we intended to calculate the various thermodynamic properties of liquid carbon by using the significant liquid structure model which has been successfully applied to various liquids[14-16].

Based on the above facts, we construct the liquid state partition function dividing it into the solid-like part and

the gas-like part as is usually done in the significant liquid structure theory. The solid-like partition functions were considered as if the gaseous states were composed of C_1 , C_2 , and C_3 species in the form of an ideal gas, because of little experimental data for calculating the larger species.

From the constructed partition function, various thermodynamic properties including the critical constants of liquid carbon were predicted.

2. PARTITION FUNCTION

The description of liquid carbon requires several terms in the conventional partition function. The total partition function is written as

$$f_N = f_s^{(V_s/V)N} \cdot f_g^{(V-V_s/V)N} \quad (1)$$

Here, f_s and f_g are the partition functions of the solid-like and gas-like structures, respectively. V , V_s , and N are the molar liquid volume, the molar volume of the solid-like structure, and number of C_1 molecules, respectively.

In representing the solid-like partition function, we assumed that there were typically only the three spectroscopic modes, which were one stretching mode and two bending modes by totally averaging all molecules.

Thus the solid-like partition function is represented as follows.

$$f_s = e^{E_s/RT} \cdot f_{\text{deg}} \cdot (f_{\text{bend}})^2 \cdot (f_{\text{st}}) \quad (2)$$

Here, E_s is the sublimation energy of each carbon species and the degeneracy term, f_{deg} , is given as

$$f_{\text{deg}} = \prod_{i=1}^3 \left(1 + n \frac{V - V_s}{V_s} e^{-\frac{aE_{si}V_s}{(V - V_s)RT}} \right) \frac{\chi_i}{i} \quad (3)$$

Here, i and χ_i are integers representing the carbon species and its mole fraction, respectively, and a and n are the dimensionless proportionality constants.

From mass spectrometric experiments[4–6, 12] and other theoretical studies[3, 7], the gas-like partition function of each gaseous species, $f_{g,i}$, is represented as,

$$f_i = (2\pi m_i kT)^{3/2} / h^3 \cdot f(T) \cdot (V - V_i) \cdot \chi_i \quad (4)$$

$$f_{y_i} = \frac{(f_i)^{n_i}}{n_i!} \quad (5)$$

Also the gas-like partition function was divided as follows.

$$f_{g_i} = f_{tr,i} \cdot f_{rot,i} \cdot f_{vib,i} \cdot f_{corr,i} \cdot f_{elec,i} \quad (6)$$

where $f_{tr,i}$, $f_{rot,i}$, $f_{vib,i}$, $f_{corr,i}$ and $f_{elec,i}$ are the translational, rotational, vibrational, correlational, and electronic partition function, respectively, and $f(T)$ represents the remaining terms except the translational partition function.

To obtain a number fraction of each species n_i , the following equations are available.

$$\sum_{i=1}^3 n_i \cdot i = N \frac{V - V_s}{V} \quad (7)$$

$$\sum_{i=1}^3 \chi_i = 1. \quad (8)$$

From the above two equations

$$n_i = N \frac{\chi_i}{i} \cdot \frac{V - V_s}{V}. \quad (9)$$

Thus, the total gas-like partition function is represented as,

$$f_{g_i}^{(V-V_s/V)N} = \frac{\{(2\pi m_i kT)^{3/2} / h^3 \cdot f(T) \cdot (V - V_i) \cdot \chi_i\}^{(V-V_s/V) \cdot (N/n_i)}}{\left(N \frac{\chi_i}{i} \cdot \frac{V - V_s}{V}\right)!} \quad (10)$$

$$= \{(2\pi m_i kT)^{3/2} / h^3 \cdot f(T) \cdot e \cdot V \cdot i / N\}^{(V-V_s/V) \cdot (N/n_i)}. \quad (11)$$

Now, in constructing the gas-like partition function for each species, its electronic terms are effective, for it exists in the very high temperature region, so it is represented as follows.

(a) *For the monomer*

$$f_{g,1} = f_{tr,1} \cdot f_{elec,1}^{[17,18]} \quad (12)$$

$$f_{tr,1} = (2\pi m_1 kT)^{3/2} / h^3 \cdot \frac{eV}{N} \quad (13)$$

$$f_{elec,1} = \sum_{i=0}^{12} g_{1,i} \bar{e}^{-h\nu_{1,i}/kT}, \quad (14)$$

where $g_{1,i}$ and $\nu_{1,i}$ are the effective statistical weight and the electronic level of the C_1 molecule.

$$f_{g,2} = f_{tr,2} \cdot f_{rot,2} \cdot f_{vib,2} \cdot f_{corr,2}^{[19,20]} \cdot f_{elec,2}^{[17,18]} \quad (15)$$

$$f_{tr,2} = (2\pi m_2 kT)^{3/2} / h^3 \cdot \frac{eV}{N/2} \quad (16)$$

$$f_{rot,2} = \frac{8\pi^2 I_2 kT}{2h^2} \quad (17)$$

$$f_{vib,2} = \frac{1}{1 - \bar{e}^{h\nu_2/kT}} \quad (18)$$

$$f_{corr,2} = 1 + \frac{kT}{\bar{B}} \left(\frac{\bar{D}}{\bar{B}}\right) + \frac{1}{e^{\beta h\nu} - 1} \left(\frac{\bar{\alpha}}{\bar{B}}\right) + \frac{2\beta h\nu}{(e^{\beta h\nu} - 1)^2} X_e + \dots \quad (19)$$

$$f_{elec,2} = 1 + \sum_{i=1}^9 g_{2,i} \bar{e}^{h\nu_{2,i}/kT}, \quad (20)$$

where \bar{B} , \bar{D} , $\bar{\alpha}$, and X_e are the rotational constant, the centrifugal distortion constant, the rotation-vibration coupling constant, and the anharmonicity constant, respectively, whose values are listed in Table 1.

(c) *For the trimer*

$$f_{g,3} = f_{tr,3} \cdot f_{st,3} \cdot f_{bend-rot}^{[21-23]} \cdot f_{elec,3}^{[17,18]} \quad (21)$$

$$f_{tr,3} = (2\pi m_3 kT)^{3/2} / h^3 \cdot \frac{eV}{N/3} \quad (22)$$

$$f_{st,3} = \prod_{i=1}^2 \frac{1}{(1 - \bar{e}^{h\nu_{3,i}/kT})} \quad (23)$$

$$f_{bend-rot} = \frac{8\pi^2}{h^4} (2\pi kT)^2 \frac{m_1^2}{3} \gamma^4 \times \int_0^\pi \exp(-\beta V(\theta)) \sin \theta \, d\theta \quad (24)$$

$$= 0.0542997^2 \int_0^\pi \exp\left\{-\frac{214.87}{T}\right\} \times [\theta^2 + 0.63439\theta^4] \sin \theta \, d\theta \quad (25)$$

$$f_{elec,3} = \sum_{i=0}^2 g_{3,i} \bar{e}^{h\nu_{3,i}/kT}, \quad (26)$$

Table 1. Parameter and experimental values used in the calculations

E_s	; 121151(cal/mol), θ ; 340.28($^{\circ}$ K), a ; 0.006766, n ; 10.2115,
V_s	; 7.72(cc/mol)
$g_{1,i}^a$ ($i = 1, 12$)	; 1, 3, 5, 5, 1, 5, 9, 3, 15, 34, 99, 401
$v_{1,i}^a$ ($i = 1, 12$)	; 0, 16.4, 43.5, 10194, 21648, 33735, 50360, 61982, 64090, 70000, 75000, 85000
v^b	; 1854.71
\bar{b}^c	; 1.81984
\bar{D}^c	; 6.92×10^{-6}
$\bar{\alpha}^c$; 0.01765
χ_e^c	; 7.1925×10^{-3}
v_i^a ($i = 1, 2$)	; 1230, 2040
$g_{3,i}^a$ ($i = 1, 3$)	; 1, 2, 1
$v_{3,i}^a$ ($i = 1, 3$)	; 1300, 550, 2200

$g_{2,1}$ and $v_{2,i}$ are taken from ref. 17, 35 and 36.

a; from ref. 18, b; from ref. 26, c; from ref. 19, 31 to 34.

d; from ref. 6 and 37

Where E_s is obtained by producing the sublimation energy and molefraction of each carbon species.

where the other symbols used in above equations have their usual statistical and quantum mechanical significance, and their parametric values are listed in Table 1.

3. RESULTS AND DISCUSSION

Common liquids exhibit an approximately 10% volumetric expansion at their melting points, but carbon shows a large volumetric expansion, approximately 50% from Bundy's data[24]. It is therefore apparent that the structure of carbon is changed on melting. Not that the graphite becomes liquid by the introduction of vacancies into the solid-like structure of the simple graphite lattice, but that it has its liquid properties by the introduction of vacancies into another type of lattice structure by changing the structure. From such a point of view, the long chain model proposed by Pitzer and Clementi can explain the volumetric change of liquid carbon well. Consequently the observed phenomenon[24-27] that the volume of liquid carbon suddenly diminished at a pressure of about 80Kb was not simply thought of as compression due to the effect of pressure but rather that the solid-like structure was itself changed to a denser structure. The positional degeneracy due to the movement of kinetic segments is ignored in this calculation because it is too small to effect the thermodynamical properties.

In constructing the gas-like partition function, it is reasonable to take the gas-like molecules as C_1 , C_2 , C_3 ,

etc. because the $—C\equiv C—C\equiv C—C\equiv C—$ structure is highly unstable.

(a) Molar volume and vapor pressure

For the calculation of molar volume and vapor pressure, the relationship[14] between the Helmholtz free energy and molar volume is used. To draw the common tangent to the points corresponding to the liquid and vapor phases for liquid carbon, we first construct the partition function for each species and then calculate the free energy. From this free energy the mole fraction of each gaseous species was obtained and the total gas-like partition function finally constructed. From this totally constructed partition function the vapor pressure is given by the slope of the common tangent, and the abscissae of two points indicate the molar volumes of liquid and vapor respectively. To find out the common tangent at a given temperature, the iterative Newtonian method is used.

The calculated results are shown in Figs. 1 and 2.

(b) Entropy

The entropy is calculated from

$$S = \left\{ \frac{\partial}{\partial T} (kT \ln f_N) \right\}_V \quad (27)$$

and the results are shown in Fig. 3.

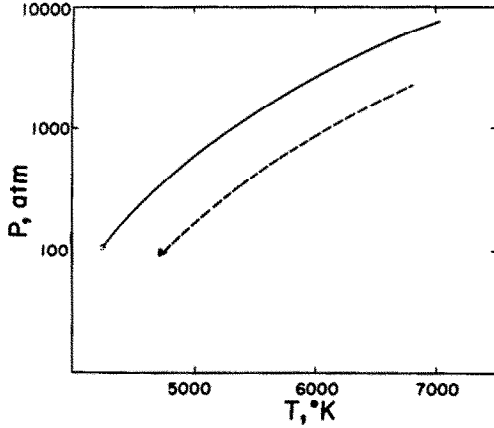


Fig. 1. Vapor pressure of liquid carbon as a function of temperature; continuous line, our work; dashed line, total vapor pressure of all the vapor species[27].

(c) *Enthalpy*

The enthalpy of the liquid is related to the partition function by the equation.

$$H = kT^2 \left(\frac{\partial \ln f_N}{\partial T} \right)_V + VKT \left(\frac{\partial \ln f_N}{\partial V} \right)_T \quad (28)$$

and the results are shown in Fig. 4.

(d) *Critical constants*

Critical temperature, T_c , critical pressure, P_c , and critical volume, V_c are calculated from the partition function by using the usual iteration technique.

$$\left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (29)$$

in conjunction with the expression $P = -(\partial A / \partial V)_T$. The calculated results are summarized in Table 2.

(e) *Parametric values*

In this work five typical parameters, shown in Table 1, were used and determined by using common tech-

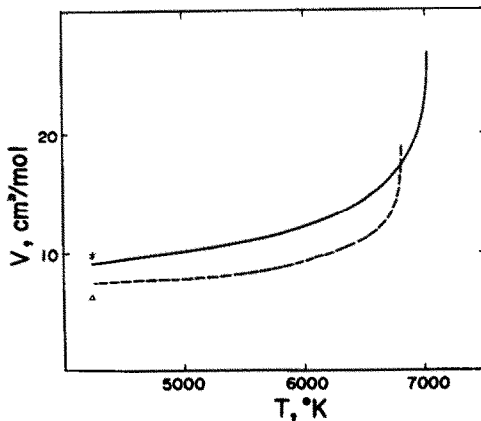


Fig. 2. Volume of liquid carbon as a function of temperature; continuous line, our work; dashed line, liquid volume obtained by liquid density[27].

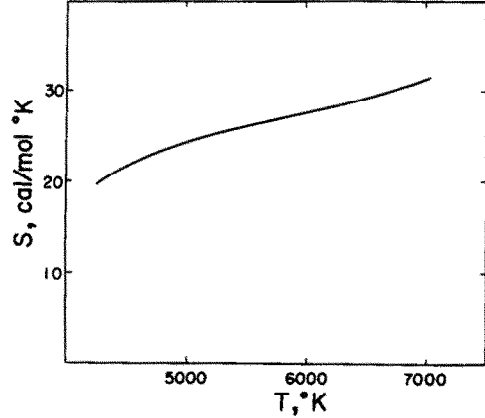


Fig. 3. Entropy of liquid carbon as a function of temperature.

niques[28] except V_s which was obtained from the structure proposed by Pitzer and Clementi together with the assumption that in long chain structures an interchain distance is obtained by extrapolation to 4020 K of the longitudinal thermal expansion data in Mantell[29]. The values obtained were still much greater than that estimated from the solid density[27, 29] at the triple point, so it was conclusively thought that at high pressures carbon might have a denser structure than that proposed by Pitzer and Clementi.

In fixing another parameter, θ , its value for the solid-like structure in the liquid has assumed that the Einstein partition function[30] might be simply represented by three modes by approximately averaging the two bending modes and one stretching mode at a sufficiently high temperature, and which were given by the relation

$$f_{\text{Einstein}} = f_{\text{bend}} \cdot f_{\text{st}} = \left(\frac{1}{1 - e^{-h\nu_{b1}/kT}} \right) \cdot \left(\frac{1}{1 - e^{-h\nu_{st}/kT}} \right) \quad (30)$$

$$\approx \left(\frac{1}{1 - e^{-h\nu_{av}/kT}} \right) \quad (31)$$

$$\equiv \frac{1}{(1 - e^{-\theta/T})^3} \quad (32)$$

Here, $\theta = h\nu_{av}/k$ is the Einstein characteristic temperature, and ν_{b1} , ν_{b2} , ν_{st} , and ν_{av} are the frequencies of the two bending modes, the stretching mode, and of the totally averaged one, respectively.

4. CONCLUSION

In several aspects, it is accepted that the structure of liquid carbon may be changed to the structure of a long chain polymer upon melting. Being vacancies and long chained molecules in an equilibrium state the gas-like molecules in the liquid could be taken as the C_1 , C_2 , and C_3 molecules from the chain entering the vacancy.

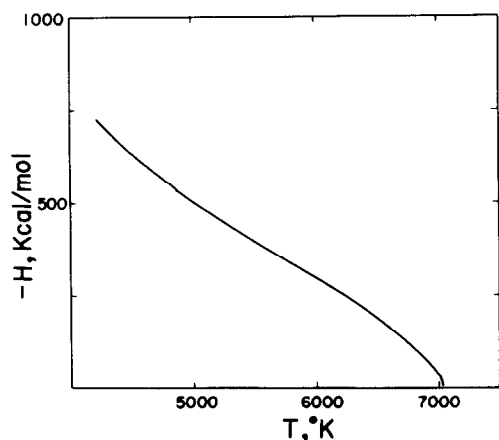


Fig. 4. Enthalpy of liquid carbon as a function of temperature.

Table 2. Critical constants of liquid carbon

	T_c °K	ρ_c atm	V_c cm ³ /mol
Our Work	7020.5	7863	26.62
Others ⁽²⁴⁾	6810	2200	18.8

From such a point of view, we represent the total partition function as the product of the solid-like partition function having the various degeneracies and the gas-like partition function being composed by its various compositions in its gaseous state.

Considering the various terms affecting the total partition function, we predict many thermodynamic properties of liquid carbon using the significant liquid structure model concept.

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