Volume Calculated as a Function of Pressure Near the Melting Point in Solid Hexadecane

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ABSTRACT

We calculate here the volume of solid hexadecane as a function of pressure near the melting point. For this calculation, we analyze the thermal expansivity at constant temperatures of 302 and 325 K in this organic compound.

The volume, which we calculate from the power-law formula for the thermal expansivity, exhibits anomalous behavior close to the melting point in solid hexadecane.

The present calculated values of the volume were compared with the observed data for solid hexadecane in the literature.

Key Words: Volume. Melting Point, Solid Hexadecane.

1. INTRODUCTION

Solid hexadecane is a long chain paraffin solid and exhibits second order phase transformation prior to melting like some other molecular organic compounds /1/. This transition is associated with orientational disorder near the melting temperature /2-4/. In this region the thermodynamic quantities such as the thermal expansivity α_p, isothermal compressibility κ_T and the specific heat C_p diverge. Their critical behaviour can be described by a power-law formula near the melting point in solid hexadecane /1/.

It has been measured experimentally that the premelting energy of n-hexadecane is 5.98 J in the temperature range of 289.035 to 292.438 K /5/. At the triple temperature of T_t^*=291.325K, the experimentally measured values of the specific heat were C_p(solid)=389.994 J/K • mole and C_p(liquid)=506.239 J/K • mole /5/.

As shown in the molecular organic compounds such as benzene, the volume of the solid hexadecane can also exhibit anomalous behaviour near the melting point /1/. In benzene, it has been obtained experimentally that the molar volume exhibits anomalous behaviour near the melting point due to pretransition effects /6, 7/. This has been supported by low frequency Raman spectroscopy in benzene /8, 9/.

In this study, we calculate the pressure dependence of the volume in solid hexadecane close to the melting point. For this calculation, we first analyze the thermal expansivity α_p measured at various pressures near the melting point in solid hexadecane /1/.

2. CALCULATIONS AND RESULTS

In solid hexadecane the thermal expansivity can exhibit critical behaviour close to the melting point. Its

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pressure dependence can be described by a power-law formula

$$\alpha_p = A\,(P-P_m)^{-\gamma} \quad (1)$$

with the critical exponent γ for the thermal expansivity and A is the amplitude. Here P_m is the melting pressure which is close to the critical point /1/.

The pressure dependence of the isothermal compressibility κ_T can be obtained as

$$\kappa_T = A\,(P-P_m)^{-\gamma} / (\partial P_m/\partial T)_V \qquad (2)$$

using the thermodynamic relation

$$\alpha_p / \kappa_T = (\partial P/\partial T)_V\,. \qquad (3)$$

In Eq.(2), $(\partial P_m/\partial T)_V$ denotes the temperature derivative of the melting pressure along the melting line in solid hexadecane.

Equation (2) directly gives the pressure dependence of volume for solid hexadecane by means of the definition of the isothermal compressibility $\kappa_T = -(1/V) / (\partial V/\partial P)_T$, which can be expressed as

$$V_T\,(P) = V_m \exp\left[\frac{1}{(\partial P_m / \partial T)_V}\,\frac{A(P-P_m)^{1-\gamma}}{1-\gamma}\right] \qquad (4)$$

where V_m is the melting volume. Thus, starting from the thermal expansivity α_p (Equation 1), the volume $V_T(P)$ can be calculated as a function of pressure in solid hexadecane close to the melting point.

We first analyzed here the pressure dependence of the thermal expansivity measured at constant temperatures of 302 and 325 K in solid hexadecane /1/. The experimental data for the thermal expansivity was analyzed in the previous work /1/. Here, we reanalyzed the experimental data in both solid and liquid phases of hexadecane for those constant temperatures according to the power-law formula /1/. In a log-log representation Equation (1) can be written as

$$\ln \alpha_p = \ln A - \gamma \ln (P-P_m) \qquad (5)$$

From our analysis, we obtained the values of the critical exponent γ and the amplitude A. Table 1 gives those values of γ and A from our analysis of hexadecane.

Figures 1 and 2 give our plots of $\ln\alpha_p$ against $\ln(P-P_m)$ for the solid and liquid phases, respectively, in solid hexadecane near the melting point for a constant temperature of 302 K. We plot the pressure dependence of the thermal expansivity in a log-log scale for the solid and liquid phases of solid hexadecane near the melting point in Figures 3 and 4, respectively, for a constant temperature of 325 K.

Once we analyzed the pressure dependence of the thermal expansivity (Equation 5), we were then able to calculate the isothermal compressibility at various pressures close to the melting point in solid hexadecane according to Equation (2).This led us to calculate the pressure dependence of volume for this compound by means of Equation (4). In order to calculate the volume $V_T(P)$ at various pressures, we used the melting volume V_m in Equation (4) as the observed values of 1.305×10^{-3} m^3/kg at 303 K and 1.328×10^{-3} m^3/kg at 323 K /10/. Equivalently, they were 294.930×10^{-6} m^3/mole at 303K and 300.128×10^{-6} m^3/mole at 323 K since one mole of

Table.1

Values of the critical exponent γ for the thermal expansivity α_p and the amplitude A (Equation1) for the solid and liquid phases of hexadecane close to the melting point for constant temperatures indicated.

T (K)	Phases	γ	$A\times10^{-4}$ (MPa/K)
302	Solid	0.54	149.88
	Liquid	1.61	1293.62
325	Solid	0.53	139.73
	Liquid	1.43	833.22

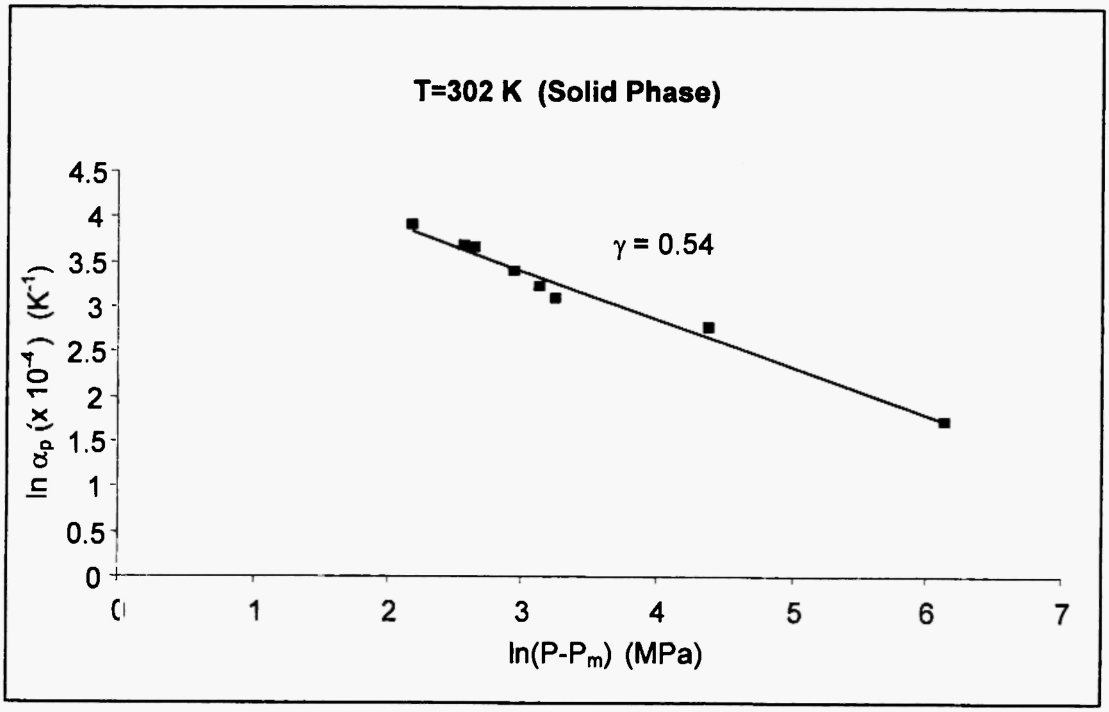

Fig. 1: Thermal expansivity as a function of pressure in a log-log scale near the melting point in the solid phase of hexadecane for a constant temperature of T=302 K according to Equation (5). Observed data are due to Pruzan et al. /1/.

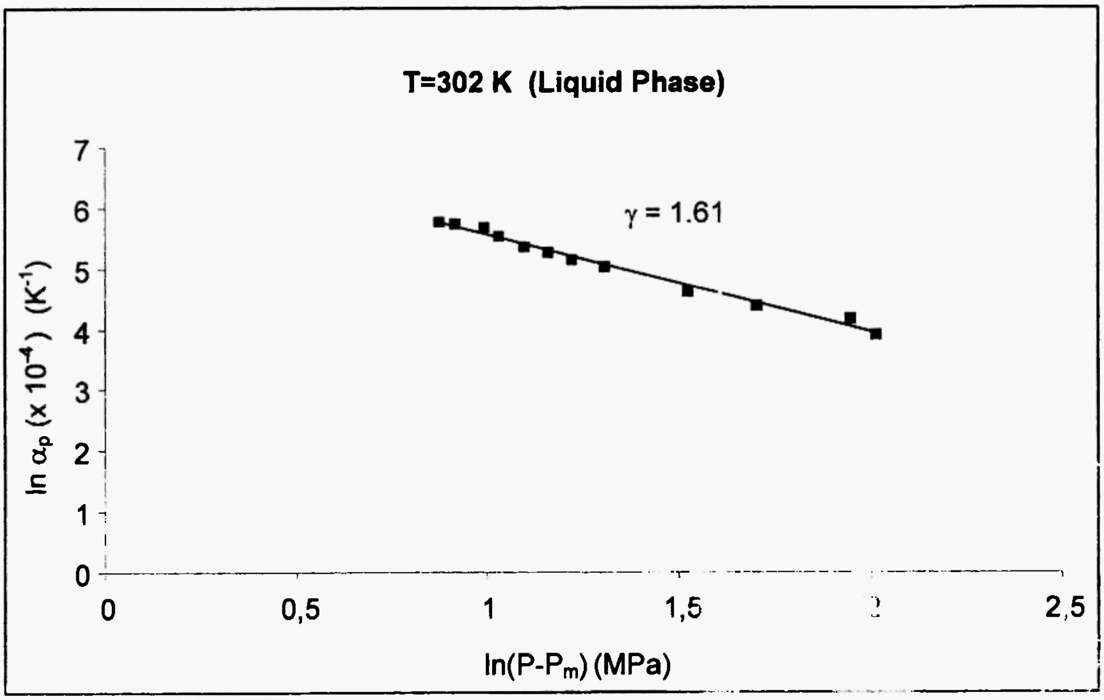

Fig. 2: Thermal expansivity as a function of pressure in a log-log scale near the melting point in the liquid phase of hexadecane for a constant temperature of T=302 K according to Equation (5). Observed data are due to Pruzan et al. /1/.

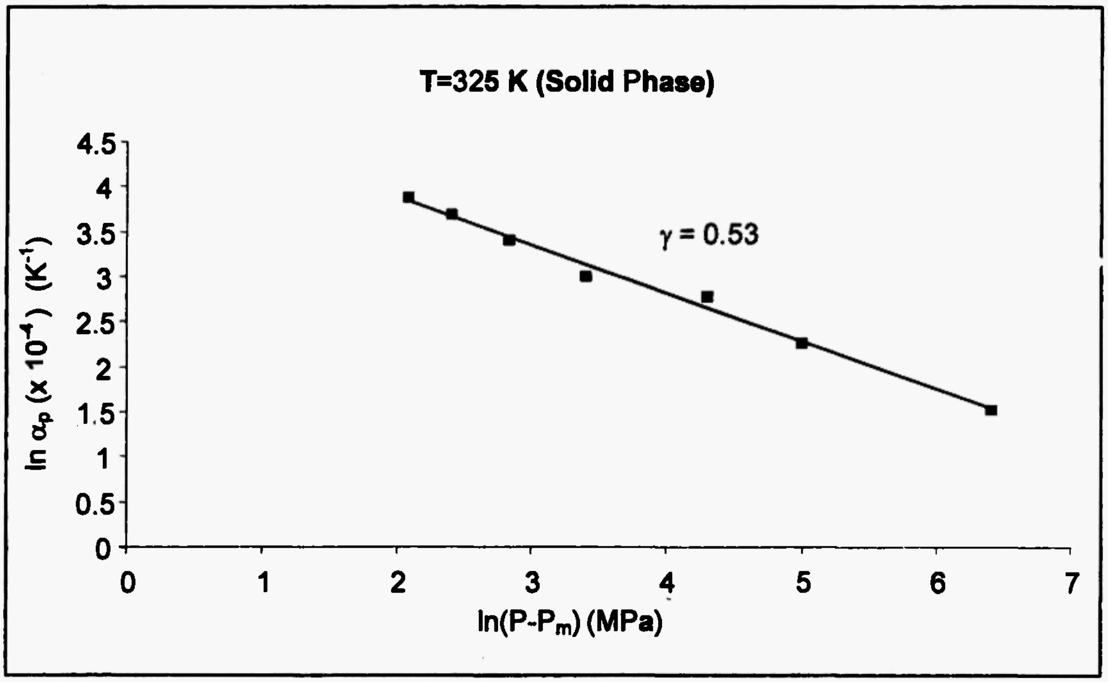

Fig. 3: Thermal expansivity as a function of pressure in a log-log scale near the melting point in the solid phase of hexadecane for a constant temperature of T=325 K according to Equation (5). Observed data are due to Pruzan et al. /1/.

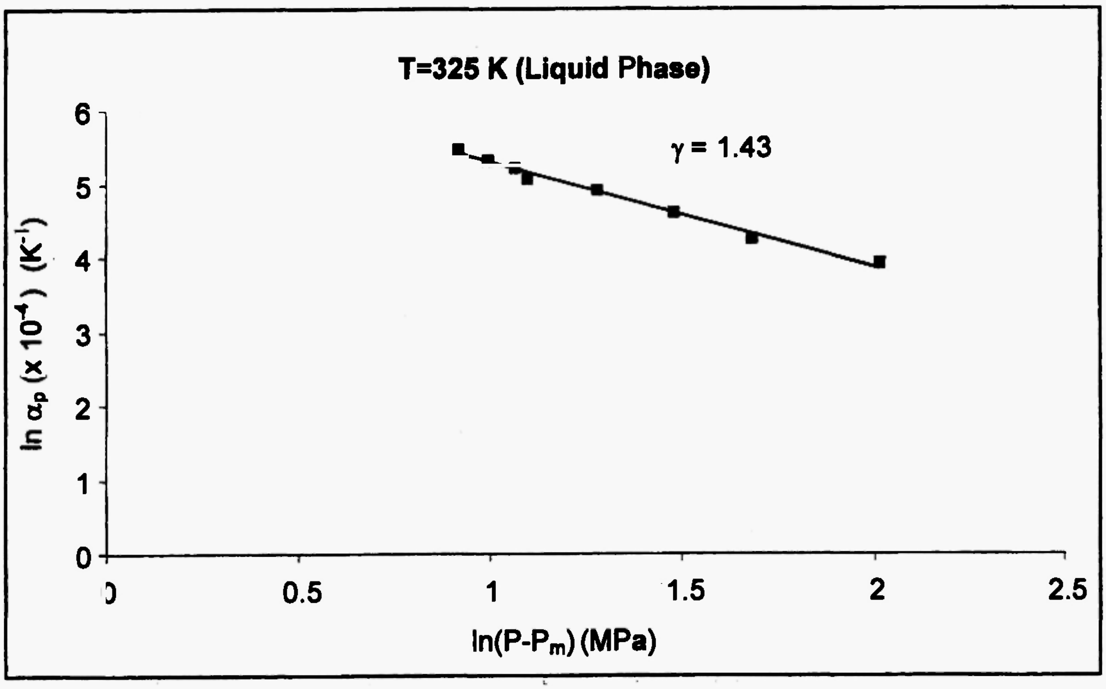

Fig. 4: Thermal expansivity as a function of pressure in a log-log scale near the melting point in the liquid phase of hexadecane for a constant temperature of T=325 K according to Equation (5). Observed data are due to Pruzan et al. /1/.

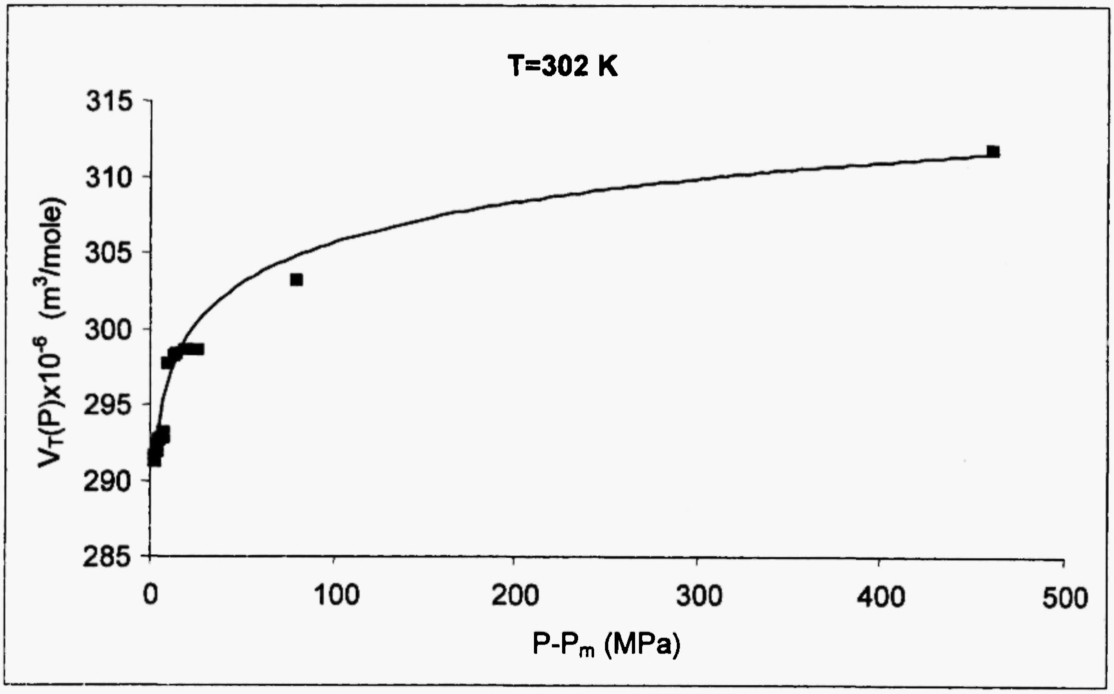

Fig. 5: Volume calculated at various pressures close to the melting point in solid hexadecane for a constant temperature of T=302 K according to Equation (4).

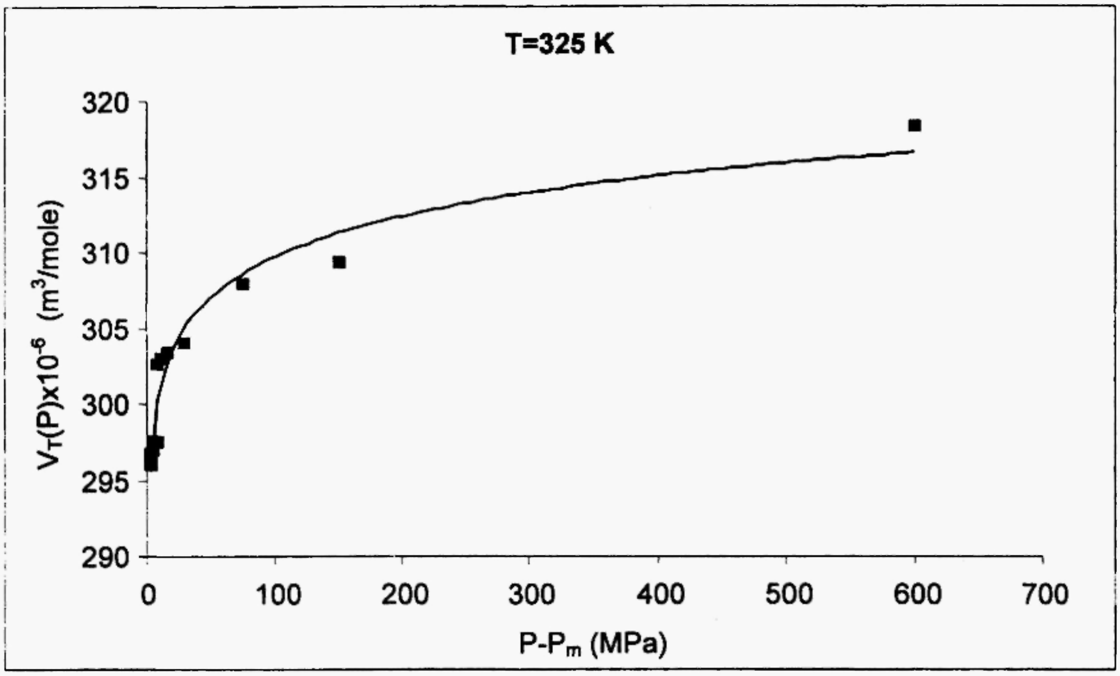

Fig. 6: Volume calculated at various pressures close to the melting point in solid hexadecane for a constant temperature of T=325 K according to Equation (4).

solid hexadecane ($C_{16}H_{34}$) is $226x10^{-3}$ kg. Figures 5 and 6 give our plots of the volume $V_T(P)$ as functions of pressure for constant temperatures of T=302 K and T=325 K, respectively, near the melting point in solid hexadecane.

3. DISCUSSION

In order to calculate the volume as a function of pressure, we started here by analyzing the experimental data for the thermal expansivity α_p near the melting point in solid hexadecane, as stated above. From our analysis of the thermal expansivity α_p according to a power-law formula (Equation 1) or in the log-log scale (Equation 5), we obtained the value of γ=0.5 as the critical exponent for α_p in the solid phase of hexadecane. In the liquid phase our values of γ=1.6 (T=302 K) and γ=1.4 (T=325 K) are close to each other in hexadecane, as given in Table 1.

From their analysis of the thermal expansivity data, Pruzan *et al.* /1/ have obtained the values of 0.7 and 1.9 for the solid and liquid phases of hexadecane, respectively, near the melting point. Those exponent values for the solid phase can be compared with the expected value of ½ due to theoretical models /11, 12/. On the basis of the quasiharmonic theory, a model developed for alkali halides near the melting point also estimates the exponent value of ½, which agrees with the experimental data for NaCl /13, 14/, as also pointed out previously /1/.

On the other hand, our γ values for the liquid phase in hexadecane can be compared with an effective exponent greater than 1 to describe the critical behaviour of the thermal expansivity due to surface melting model of Lipowsky and Speth /15, 16/. Regarding the impurity effects, it has been interpreted that for the liquid phases observed in molecular organic compounds the exponents of the power-law are close to the value of 2 /1/. Consequently, our values of the critical exponent γ indicate that the critical behaviour of the thermal expansivity α_p is considerably different in the solid and liquid phases of hexadecane near the melting point.

Using our γ values in the pressure regions of the solid and liquid phases of hexadecane, the volume values were calculated according to Equation (4) and they were plotted as a function of pressure, as given in Figures 5 and 6 for constant temperatures of 302 and 325 K, respectively. These graphs show that the volume increases as the pressure increases above the melting point for both constant temperatures. Near the melting point, the volume exhibits anomalous behaviour, which can be described by a power-law formula, according to Equation (4). Above the pressures of P-P_m=100 MPa, the pressure dependence of the volume can be described analytically in solid hexadecane. This anomalous behaviour of the volume is directly related to the critical behaviour of the thermal expansivity α_p measured for solid hexadecane /1/. So, the critical behaviour of α_p or of the other thermodynamic quantities (isothermal compressibility κ_T and the specific heat C_p) may be affected by a) short time measurement compared to the slow thermal equilibration in the molecular organic compounds b) temperature inhomogeneity in the cell c) surface melting, as also pointed out by Pruzan *et al.* /1/. Besides, impurities may cause continuous large variations in the thermodynamic quantities near the melting point in solid hexadecane. Thus, in order to observe large variations in the thermodynamic quantities in a small melting zone, purified hexadecane should be used experimentally /5/. This then makes it possible to describe the critical behaviour of the thermodynamic quantities by a power-law formula in solid hexadecane or in general molecular organic compounds near the melting point.

4. CONCLUSIONS

We studied here the pressure dependence of volume of solid hexadecane near the melting point by analyzing the experimental data for the thermal expansivity in this organic compound. The anomalous behaviour of volume was obtained for constant temperatures of 302 and 325 K in solid hexadecane close to the melting point.

This anomalous behavior can be compared with the experimental measurements of the volume at various pressures near the melting point in solid hexadecane for constant temperatures studied here.

Anomalous behaviour can also be examined on the basis of the experimental measurements of the volume at various temperatures for some constant pressures near the melting point in solid hexadecane.

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