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# Pressure Dependence of the Thermodynamic Quantities in Phase II of Solid Benzene

**Abstract:** The thermodynamic quantities such as the thermal expansion ($\alpha_p$), isothermal compressibility ($K_T$) and the specific heat ($C_P - C_V$), are predicted at various pressures up to 26 GPa (T = 540 K) in the solid phase II of benzene using volume data from the literature. The Pippard relations are examined using the pressure dependence of $\alpha_p$, $K_T$ and $C_P - C_V$ and the value of the slope dP/dT is deduced for the solid phase II of benzene. The thermodynamic quantities studied here decrease with increasing pressure, as expected, which can be compared with the experimental measurements for the solid phase II of benzene. We find that the Pippard relations are validated within the pressure range considered, in particular, at high pressures for the solid phase II of this molecular crystal.

**Keywords:** thermodynamics quantities, Pippard relations, solid phase II, benzene

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## 1 Introduction

Benzene as one of new high density materials is attractive to study because of technological applications. It is an organic chemical compound ($C_6H_6$) and it shows chemical transformation under pressure [1]. It crystallizes into the solid phase I with four molecules per unit cell below the melting temperature ($T_m$ = 278.5 K) at atmospheric pressure [2]. At 1.2 GPa with increasing temperature up to 373 K, phase I transforms into the phase II [3]. Experimental studies have revealed that the transition from phase II to phase III occurs at 3.56 GPa. As the pressure increases to 14 GPa at room temperature, a fourth phase (phase IV) occurs [4] in benzene. At higher pressures (up to 30 GPa) transformation of benzene to an amorphous hydrogenated carbon has been studied experimentally [5, 6]. At higher temperatures (above about 800 K) with relatively low pressures, polymer phases (polymer 1 and 2) occur in benzene [7]. The pressure–temperature (T–P) phase diagrams of benzene including the solid and liquid phases have been obtained using various experimental techniques [3, 7, 8–10] as also given in Fig. 1. Using the mean field theory, we have also calculated T–P phase diagram of benzene on the basis of the experimental diagram [7] in our recent studies [11, 12].

Thermodynamic quantities can be calculated as functions of temperature and pressure in various phases of benzene, in particular, solid phases of this molecular crystal. Experimental measurements of the thermal expansivity $\alpha_p$ at various pressures in the solid I and melting zones of benzene [13], heat capacity and thermal conductivity for the solid phases I and II [14] have been reported. Molar volumes of solid and liquid phases have been measured as functions of temperature and pressure [15, 16]. Using the experimental data [13, 15], we have calculated the molar volume as a function of temperature [17] and pressure [18] close to the melting point in benzene. We have predicted the pressure dependence of the isothermal compressibility $K_T$ from the vibrational frequencies [19] for the solid phase II of benzene in our recent study [20].

In this study, we calculated the pressure dependence of the thermal expansivity $\alpha_p$, isothermal compressibility $K_T$ and the specific heat $C_P$ in the solid phase II of benzene.

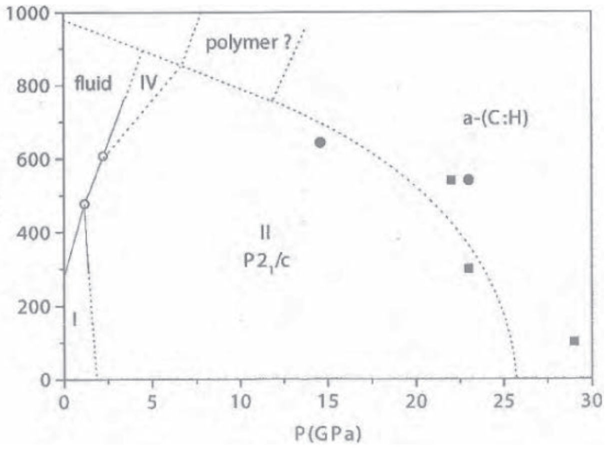

**Fig. 1:** T–P phase diagram of benzene [19]

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They are correlated in this phase according to the Pippard relations [21].

In section 2, we obtain the pressure dependence of these thermodynamic quantities studied here for the solid phase II of benzene. We discuss our results in section 3. Conclusions are given in section 4.

## 2 Calculations and results

We calculated here the pressure dependence of the isothermal compressibility $K_T$ and of the thermal expansion $\alpha_p$ in phase II of solid benzene at a constant temperature of 540 K. The experimental volume data [19] at various pressures at a constant temperature (540 K) was used for this calculation of $K_T$ and $\alpha_p$ in phase II of solid benzene.

Using a quadratic dependence of the crystal volume V on the pressure,

$$V = a + bP + cP^2 \tag{1}$$

where a, b and c are constants, the pressure dependence of the $K_T$ and $\alpha_p$ were obtained. By fitting Eq. (1) to the experimental V data [19], the coefficients a, b and c were deduced, as given in Table 1. The experimental V vs. P graph is given in Fig. 2. Using the definition of the isothermal compressibility, $K_T = -(1/V)(\partial V/\partial P)_T$, from the functional form of the crystal volume V (Eq. (1)), The pressure dependence of $K_T$ was obtained, as plotted in Fig. 3. Through the thermodynamic relation,

$$\alpha_p / K_T = dP/dT \tag{2}$$

where dP/dT represents the slope of the P-T phase diagram in phase II of solid benzene and using the experimental value of dP/dT = 13 MPa/K [13], the thermal expansion $\alpha_p$ was obtained as a function of pressure (T = 540 K), as also plotted in Fig. 4.

**Table 1:** Values of the coefficients a, b and c which were obtained by fitting Eq. (1) to the experimental V data [19] fot the phase II of solid benzene.

| V (Å³) | a (Å³) | −b (Å³/GPa) | c (Å³/GPa²) |
|---|---|---|---|
| Eq. (1) | 213.87 | 5.73 | 0.12 |

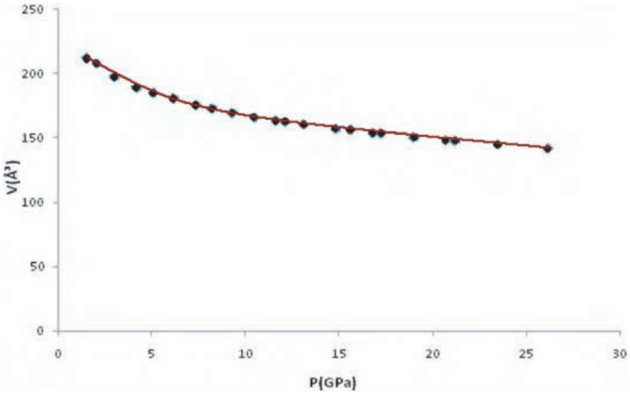

**Fig. 2:** Experimental volume V as a function of pressure at T = 540 K [19] for the phase II of solid benzene.

Also, using the thermodynamic relation,

$$C_p - C_V = VT.\alpha_p^2/K_T \tag{3}$$

the difference in the specific heat can be obtained as a function of pressure (T = 540 K) in phase II of solid benzene. Then, from the pressure dependence of the

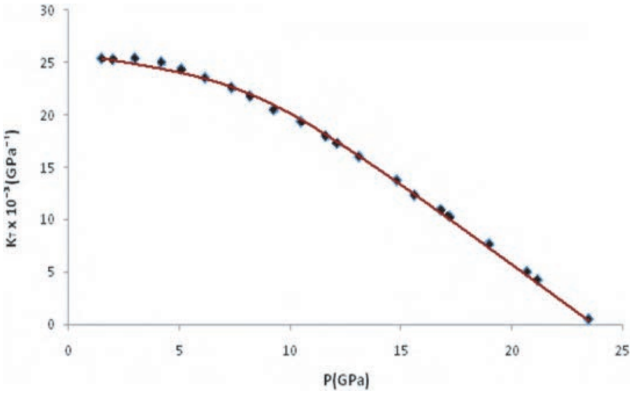

**Fig. 3:** Isothermal compressibility $K_T$ calculated as a function of pressure at T = 540 K for the phase II of solid benzene

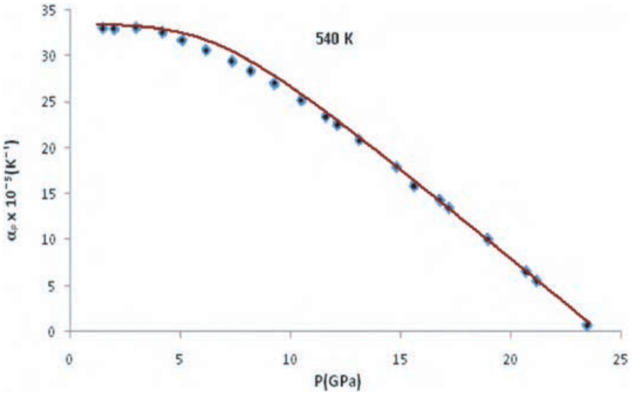

**Fig. 4:** Thermal expansion $\alpha_p$ calculated according to Eq. (2) as a function of pressure (T = 540 K) for the phase II of solid benzene.

thermodynamic quantities $K_T$, $\alpha_p$ and $C_p - C_V$, the Pippard relations can be established according to

$$C_p = (dP/dT)\ V\ T\ \alpha_p + T\ (dS/dT) \qquad (4)$$

and,

$$\alpha_p = (dP/dT)\ K_T + (1/V)(dV/dT) \qquad (5)$$

for the phase II of solid benzene.

In this study, we calculated the pressure dependence of the $C_p - C_V$ using the $\alpha_p$ and $K_T$ values according to Eq. (3) for the phase II of solid benzene. This was done at a constant temperature of T = 540 K as before Fig. 5 gives $C_p - C_V$ plotted as a function of pressure at T = 540 K in phase II of solid benzene. We then examined the Pippard relations using the pressure dependence of the $\alpha_p$, $K_T$, and $C_p - C_V$ according to Eqs. (4) and (5), which are plotted in Figs. 6 and 7, respectively, for the phase II of solid benzene (T = 540 K). From a linear plot of $C_p - C_V$ vs. V $\alpha_p$ (Eq. (4)), we obtained the values of the slope dP/dT and the intercept dS/dT (Eq. (4)) in the phase II of solid benzene (T = 540 K). Table 2 gives our values of the slope and intercept which were obtained from Eqs. (4) and (5) for the phase II of solid benzene.

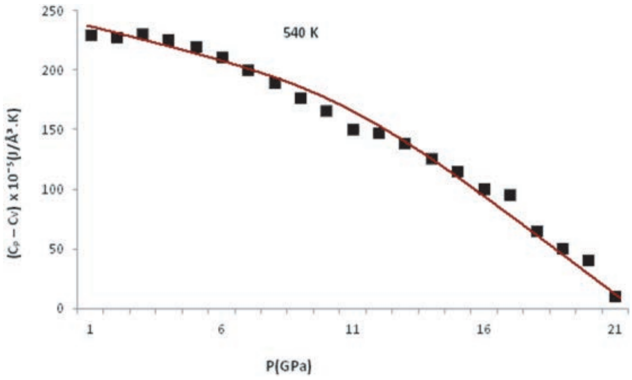

**Fig. 5:** Specific heat ($C_p - C_V$) calculated as a function of pressure (T = 540 K) according to Eq. (3) for the phase II of solid benzene.

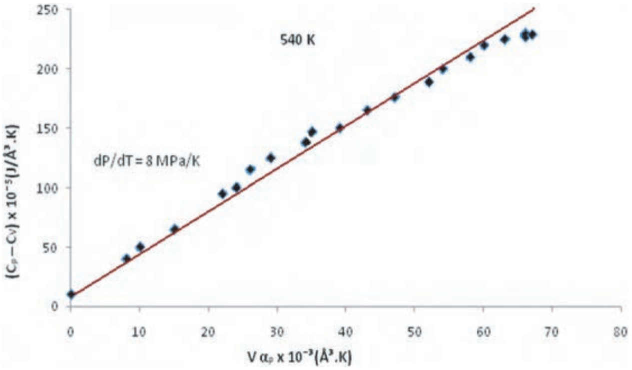

**Fig. 6:** A plot of $C_p - C_V$ against $V\alpha_p$ at various pressures (T = 540 K) according to the Pippard relation (Eq. (4)) for the phase II of solid benzene.

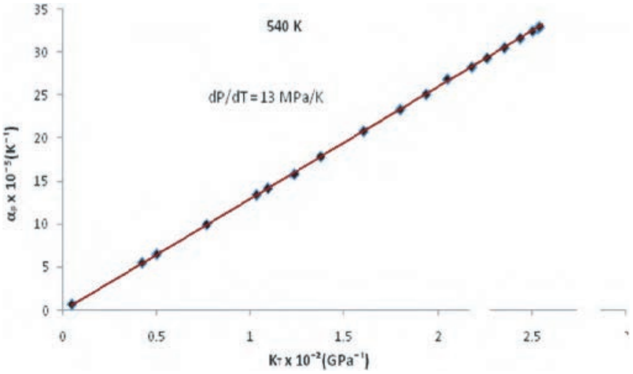

**Fig. 7:** A plot of $\alpha_p$ against $K_T$ at various pressures (T = 540 K) according to the Pippard relation (Eq. (5)) for the phase II of solid benzene.

## 3 Discussion

We calculated the pressure dependence of the isothermal compressibility $K_T$, thermal expansion $\alpha_p$ and the specific heat ($C_p - C_V$) for the phase II of solid benzene at T = 540 K. For this calculation, the experimental volume (V) data [19] was used. As shown in Figs. 3–5, $K_T$, $\alpha_p$, and $C_p - C_V$ decrease as the pressure increases at 540 K in the phase II of solid benzene.

**Table 2:** Values of the slope dP/dT and the intercept according to the relations within the pressure intervals indicated for the phase II of solid benzene.

| Pippard Relations | dP/dT (MPa/K) | (dS/dT) × $10^{-3}$ (J/Å³.K²) | (1/V)(dV/dT) × $10^{-3}$ ($K^{-1}$) | Pressure Interval (GPa) |
|---|---|---|---|---|
| $C_p - C_V$ vs. V $\alpha_p$ (Eq. 4) | 8 | 8.4 | – | $13.1 \le P \le 26.2$ |
| $\alpha_p$ vs. $K_T$ (Eq. 5) | 13 | – | 6.7 | $1.5 \le P \le 26.2$ |

**Table 3:** Values of the volume (Eq. (1)), variation of the volume (Eq. (5)) and entropy (Eq. (4)) with temperature, and the slope dP/dT (Eq. (7)) at constant pressures indicated (T = 540 K) for the solid II of benzene.

| P (GPa) | V (Å³) | dV/dT (Å³/K) | (dS/dT) × 10⁻³ (J/Å³.K²) | dP/dT (MPa/K) |
|---|---|---|---|---|
| 13.1 | 159.40 | 1.068 | 8.4 | 12.7 |
| 26.2 | 146.11 | 0.979 | 8.4 | 13.9 |

We also examined here the Pippard relations (Eqs. (4) and (5)) as linear variations of $C_p$ vs. $V\alpha_p$ (Eq. (4)) and $\alpha_p$ vs. $K_T$ (Eq. (5)), which we plotted in Figs. 6 and 7, respectively. In Fig. 6 our plot was $C_p - C_V$ vs. $V\alpha_p$ where $C_V$ corresponds to T(dS/dT) in Eq. (4). In this plot, the slope value was dP/dT = 8 MPa/K in the pressure interval studied (Table 2). We obtained the value of dP/dT = 13 MPa/K from our plot of $\alpha_p$ vs. $K_T$ (Fig. 7), as also given in the Table 2 with a small intercept value of (1/V)(dV/dT).

Since the pressure dependence of the thermal expansion $\alpha_p$ was calculated using the experimental value of dP/dT = 13 MPa/K [13] from the isothermal compressibility $K_T$ according to Eq. (2), we should get the same value for the slope dP/dT from a plot of $\alpha_p$ vs. $K_T$ (Eq. (5)), as given in Fig. 7. This value of 13 MPa/K is valid for all the pressure range studied, $1.5 \leq P(\text{GPa}) \leq 26.2$. For our plot of $C_p - C_V$ vs. $V\alpha_p$, the slope value of 8 MPa/K is smaller than the experimental value of 13 MPa within the pressure interval where the solid phase II becomes stable.

We can also interpret for the pressure interval studied our value of the variation of the entropy with the temperature, dS/dT, which was obtained as the intercept of the $C_p - C_V$ vs. $V\alpha_p$ plot (Fig. 6). For the pressures between 13 and 26 GPa, the dS/dT value (Table 2) will increase as the pressure decreases which indicates that the orientational disorder takes place close to the phase I in the solid II phase of benzene. With decreasing pressure, the thermodynamic quantities of $C_p - C_V$, $\alpha_p$, and $K_T$ will increase, as shown in Figs. 3–5. Using the variation of entropy and volume with the temperature, dS/dT and dV/dT, respectively the thermodynamic Clausius–Clapeyron relation expressed as

$$dP/dT = \Delta S/\Delta V \tag{6}$$

can be examined for the solid phase II of benzene. In Eq. (6) ΔS and ΔV represent the differences of entropy and molar volume, respectively. By expressing Eq. (6) in terms of the variations of entropy and volume with the temperature as,

$$dP/dT = (dS/dT)/(dV/dT) \tag{7}$$

the slope dP/dT can be calculated in the pressure range (Table 2) of benzene solid II. We calculated here dP/dT at the lower and upper limits of the pressure for the plots of $C_p - C_V$ vs. $V\alpha_p$ (Eq. (4)) and $\alpha_p$ vs. $K_T$ (Eq. (5)) using the values of dS/dT and (1/V)(dV/dT) as given in the Table 2. The volume values were deduced using Eq. (1) with the coefficients a, b and c (Table 1). We give in the Table 3 the values of V, dV/dT, dS/dT (Table 2) and dP/dT calculated according to Eq. (7) for constant pressures (lower and upper limits) as indicated. The dP/dT value is nearly 13 MPa (K as obtained from our plot of $C_p - C_V$ vs. $V\alpha_p$ (Eq. (4)) in the pressure range studied, which is the same as the experimental value. This shows that on the basis of the Clasius–Clapeyron equation (Eq. (6)), the validity of the first Pippard relation of $C_p - C_V$ vs. $V\alpha_p$ (Eq. (4)) is restricted to higher pressures above 13.1 up to 26.2 GPa (Fig. 6) in the solid phase II of benzene. Although the second Pippard relation of $\alpha_p$ vs. $K_T$ (Eq. (5)) is valid in all the pressure region ($1.5 \leq P(\text{GPa}) \leq 26.2$) with the slope value of dP/dT = 13 MPa/K (Table 2), this experimental value was used initially to calculate the $\alpha_p$ and $K_T$, as pointed out earlier. So that the first Pippard relation ($C_p - C_V$ vs. $V\alpha_p$) should be examined carefully since it has limitations, as shown here for the solid phase II of benzene.

The pressure dependence of the isothermal compressibility $K_T$, thermal expansion $\alpha_p$ and the specific heat $C_p$, was calculated by analyzing the experimental volume V [19] at various pressures (T = 540 K) according to Eq. (1), as stated above. This cubic crystal equation of state describes adequately the thermodynamic behavior of reorientational crystalline benzene in solid phase II, as also used previously for the solid phase I of benzene near the melting point [15]. This then leads to the proportionality between the thermal expansion and the isothermal compressibility tensors in the monoclinic benzene (phase II) at high pressures as in the orthorombic benzene (phase I) at high temperatures [22]. Variation of the specific heat with the pressure is somehow different from that dependence of the thermal expansion and the isothermal compressibility in the solid phase II of benzene, as studied here.

Our calculated values of $\alpha_p$, $K_T$ and $C_P - C_V$ can be compared with the experimental measurements of those thermodynamic quantities at various pressures (between 1.5 and 26.2 GPa at a constant temperature of 540 K for the solid phase II of benzene. This then examines our method of calculating the thermodynamic functions using the volume data for the solid phase II of this molecular crystal.

## 4 Conclusions

We studied here the pressure dependence of isothermal compressibility, thermal expansion and the specific heat at a constant temperature (T = 540 K) in phase II of solid benzene using the experimental data for volume. The Pippard relations were constructed in the pressure intervals studied and the slope dP/dT was deduced for the phase II of solid benzene. Our results show that this method of calculating the thermodynamic quantities is adequate for the phase II of solid benzene, which can be applied to the other phases of this molecular crystal and also to the various organic molecular systems.

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