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Research Article

# PIPPARD RELATIONS NEAR THE MELTING POINT IN BENZENE

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## ABSTRACT

We calculate here the isothermal compressibility  $\kappa_T$  and the specific heat ( $C_P - C_V$ ) per unit volume as a function of pressure at constant temperatures in the solid and melting zones of benzene. This calculation is performed using the experimental data for the thermal expansivity  $\alpha_p$  from the literature. The experimental data is analyzed using a power-law formula with the critical exponent  $\gamma$  for  $\alpha_p$ . The  $\gamma$  values indicate a second order transformation prior to melting. From the anomalous behavior of the thermodynamic quantities studied in the pressure range, a linear variation of ( $C_P - C_V$ )/V vs.  $\alpha_p$  and also  $\alpha_p$  vs.  $\kappa_T$  is obtained near the melting point in benzene. The slope value of dp/dT=13 MPa/K which we extract from linear plots, is the same as obtained experimentally. Our calculations can be examined with the experimental measurements under the given temperature and pressure conditions near the melting point in benzene.

Keywords: Thermodynamic quantities. Pippard relations. Melting. Benzene.

### 1. INTRODUCTION

Phase transitions in liquids and solids have been the subject of various experimental and theoretical studies mainly by studying solidification and melting<sup>1</sup>. Phase transitions in those materials have been explained using their phase diagrams<sup>2</sup>. Among these composite materials phase transitions in benzene between the liquid and solid phases have been the most experimental studied. Usina various techniques, its phase diagram has been constructed<sup>3-9</sup>. We have also calculated T-P phase diagram of benzene using the mean field theory<sup>10,11</sup> on the basis of the experimental phase diagram<sup>8</sup>.

Crystalline benzene belongs to the plastic crystals and also to the reorientational crystals<sup>4</sup>. Benzene molecules have the reorientational motions around the sixfold axis. On the melting curve between the liquid and solid phase I, a triple point labeled as  $T_1$  exists at the pressure of about 1.4 GPa. At a higher pressure (about 4 GPa) on the transition line between the solid phases I and II, a second triple point ( $T_2$ ), and additionally another triple point  $(T_3)$ , have been reported in previous studies<sup>3,5-</sup> <sup>8,12</sup>. The existence of two new phases, namely III and IV has been reported on the basis of the experimentally studies<sup>8,12</sup>.

The thermodynamic functions such as thermal expansion  $\alpha_p$  , isothermal compressibility

 $\kappa_T$  and the specific heat  $C_P$  can exhibit anomalous behaviour near the melting point, as also observed experimentally in benzene<sup>13</sup>. Under the temperature and pressure conditions, the crystalline environment changes due to molecular orientations and in particular, near the melting point the  $\alpha_{p}$ ,  $\kappa_{T}$  and  $C_{P}$  tend to diverge. This has been observed for the thermal expansivity  $\alpha_{\rm p}$  at various pressures close to the liquid pressure  $p_{L}$  in benzene<sup>13</sup>. The anomalous behaviour of the thermal expansivity  $\alpha_{\rm p}$  as a function of pressure has been described by a power-law formula. We have used the observed data<sup>13</sup> for this divergence behaviour of the  $\alpha_p$  near the melting point to calculate the molar volume at various temperatures<sup>14</sup> and pressure<sup>15</sup>

for benzene in our previous studies. We have also predicted the isothermal compressibility  $\kappa_T$  at various pressures in solid phase II from the measurements of the molar volume<sup>12</sup> and from the observed Raman frequencies<sup>9</sup>, as we have reported recently <sup>16</sup>.

In this study, we analyze the pressure dependence of the thermal expansivity according to a power-law formula for the melting and solid zones in benzene using the experimental data13. This analysis leads calculate the isothermal us to compressibility and the specific heat at various pressures for constant temperatures near the melting point. Variation of the specific heat with the thermal expansivity and also variation of the thermal expansivity with the isothermal compressibility (Pippard relations) are examined near the melting point in benzene.

Below, in section 2 we give our calculations and results. Calculated thermodynamic quantities and the Pippard relations are discussed in section 3. Finally, conclusions are given in section 4.

#### 2. CALCULATIONS AND RESULTS

We analyzed the pressure dependence of the thermal expansion  $\alpha_p$  in the solids and melting zones of benzene according to a power-law formula,

$$\alpha_{p} = A(p-p_{L})-\gamma$$
 (1)

In Eq. (1),  $\gamma$  is the critical exponent for the thermal expansion  $\alpha_p$  and A is the amplitude.  $p_L$  represents the liquid pressure ( the pressure between the solid and melting zones of benzene ). In this analysis, we used the experimental data for the thermal expansion at various pressures close to the melting zone in benzene at constant temperatures of 268, 302, 325 and 355K<sup>13</sup>. Table 1 gives the values of  $\gamma$  and A for the pressure ranges indicated according to Eq.(1).

As given in Table 1, we obtained  $\gamma_s = 0.3$  for the solid zone and  $\gamma_m = 1.6$  for the melting zone as the values of the critical exponent for the thermal expansion, as also obtained previously <sup>13</sup>. Using the approximate relation <sup>13</sup>

$$\frac{\alpha_p}{\kappa_T} = \left(\frac{\partial p}{\partial T}\right)_S \tag{2}$$

close to the melting point, the pressure dependence of the isothermal compressibility  $\kappa_T$  can be written as

$$\kappa_T = \frac{1}{\left(\frac{\partial p}{\partial T}\right)_S} A(p_t - p)^{-\gamma} \qquad (3)$$

In Eq.(3),  $p_t(=p_L)$  is the transition pressure and  $(\partial p / \partial T)_s$  is the slope of the pressuretemperature (p-T) transition line at a constant entropy S. Its experimental value can be taken as  $dp_r/dT = (\partial p / \partial T)_s = 13$ MPa/K for benzene [13]. Using the definition

$$\frac{dp_t}{dT} = \frac{p - p_t}{T - T_t} \tag{4}$$

close to the melting line in benzene, the temperature dependence of the thermal expansion  $\alpha_p$  can be obtained from Eq.(1) as

$$\propto_p (T) = A \left(\frac{dp_t}{dT}\right)^{-\gamma} (T - T_t)^{-\gamma}$$
(5)

Similarly, the temperature dependence of the isothermal compressibility  $\kappa_T$  can be obtained from Eq.(3) as

$$\kappa_T = A \left(\frac{dp_t}{dT}\right)^{-(\gamma+1)} \left(T - T_t\right)^{-\gamma} \tag{6}$$

We plot the isothermal compressibility  $\kappa_T$  as a function of pressure (p-p<sub>L</sub>) at constant temperatures of 268, 302, 325 and 355K in the melting zone and solid phase in Figs.(1) and (2), respectively for benzene.

The temperature and pressure dependence of the specific heat can also be obtained for both melting and solid zones in benzene. Using the thermodynamics relation

$$C_p = C_V + TV\alpha_p (\frac{\partial p}{\partial T})_5 \qquad (7)$$

we calculated the pressure dependence of  $(C_p - C_V)/V$  for the melting zone and solid phase in benzene, as plotted in Figs. (3) and (4), respectively. Plots were obtained for constant temperatures of 268, 302, 325 and

355K, as before. Values for  $(C_p - C_v)/V$ were obtained from the pressure dependence of the thermal expansivity  $\alpha_p$ (Eq.1) with a constant  $(\partial p / \partial T)_s$  value for benzene.

We then constructed the Pippard relations given by

$$C_p = TV\left(\frac{dv}{dT}\right)\alpha_p + T\left(\frac{dS}{dT}\right) \qquad (8)$$

and

$$\alpha_p = \left(\frac{dp}{dT}\right) \kappa_T + \left(\frac{1}{V}\right) \left(\frac{dV}{dT}\right) \tag{9}$$

for the melting and solid phases of benzene. By using the pressure dependence of the specific heat and of the thermal expansion, we established here the first Pippard relation (Eq.8) for constant temperatures of 268, 302, 325 and 355K Fig. 5 gives  $(C_v - C_v)/V$  vs.  $V\alpha_p$ for constant temperatures of 268 and 302K for both solid and melting phases of benzene. This plot is given in Fig.6 for T=325 and 355 K for both regions studied here. Table 2 gives the values of the slope dp/dT which were deduced from Eq. (8) for the melting zone and solid phase of benzene.

We also obtained the thermal expansion  $\alpha_{\rm p}$ function the as а of isothermal compressibility  $\kappa_T$  according to the second Pippard relation (Eq. 9). Fig.(7) gives a plot of  $\alpha_p$  vs.  $\kappa_T$  for constant temperatures of 268 and 355K in the melting zone of benzene. Similar plot is also given in Fig. 8 for constant temperatures of 302 and 325 in the melting zone of benzene. We also have our plot of  $\alpha_p$  vs.  $\kappa_T$  for constant temperatures of 268, 302 and 355K in the solid phase of benzene in Fig. 9. Table 2 gives the values of the slope dp/dT which were deduced from Eq. (9) for both melting and solid phases of benzene.

# 3. DISCUSSION

The pressure dependence of the thermal expansion  $\alpha_p$  was analyzed here according to a power-law formula (Eq. 1) using the experimental data<sup>13</sup> for the melting and solid zones of benzene. Values of the critical exponent  $\gamma$  for the thermal expansion  $\alpha_p$  which we obtained, were 0.3 and 1.6 for the

solid and melting zones respectively, as obtained by Pruzan et al. [13]. Using the  $\gamma$ and A values (Table 1), we calculated the temperature and pressure dependences of the isothermal compressibility  $\kappa_T$ , those of the specific heat,  $(C_p-C_V)/V$  for the solid and melting phases of benzene. The isothermal compressibility  $\kappa_T$  and the specific heat decrease as the temperature and pressure increase in both melting and solid phases of benzene, as shown in our plots.

As we calculated here, the isothermal compressibility (Fig. 1) and the specific heat (Fig. 3) diverge as the melting point is approached in the melting zone of benzene. divergence behaviour This of the thermodynamic quantities, which was described by a power-law formula (Eqs. 1 and 3) can be considered as a second order transformation prior to melting, as also pointed out by Pruzan et al. [13]. In the solid zone, there is not such a strong divergence (Figs. 2 and 4), as seen in the melting zone. This can be stated in terms of the values of the critical exponent  $\gamma$  for the thermal expansivity in both zones ( $\gamma$ =1.6 in the melting zone and  $\gamma=1.3$  in the solid zone) of benzene. We note that the critical exponent  $\gamma$  also describes the anomalous behaviour of the isothermal compressibility and the specific heat near the melting point in benzene. This indicates that the  $\gamma$  values which we obtained from our analysis of the observed  $\alpha_p$  vs. p-p<sub>L</sub> data [13], describe a second order transition.

We also examined in this study whether the Pippard relations are valid in the melting and solid zones near the melting point in benzene. From our plots of  $(C_p-C_V)/V$  vs.  $\alpha_p$ (Figs. 5 and 6) and  $\alpha_p$  vs.  $\kappa_T$  (Figs. 7 and 8), we see that they are all linear as expected from Eqs.(8) and (9), and that they are all parallel to each other. This means that the slope value of dp/dT = 13 MPa/K was found as the experimental one13 which we used initially to calculate the isothermal compressibility from the thermal expansion (Eq. 1) This also shows that the specific heat varies linearly with the thermal expansivity near the melting point in benzene. In the same manner, the thermal expansivity varies linearly with the isothermal compressibility near the melting point in this molecular crystal. For those linear

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variations we obtained, the pressure dependence of the thermodynamic quantities was considered at constant temperatures (T=268, 302, 325 and 355K). In fact, in regard to the same slope value (dp/dT = 13 MPa/K) which we obtained, those linear variations are independent of temperature near the melting pressure ( $p_L$ ) of benzene.

The experimental measurements can be carried for out the isothermal compressibility and the specific heat at various pressures in the same pressure interval as performed for the thermal expansivity (at constant temperatures of 268, 302, 325 and 355K) near the melting point in benzene. This then compares with our calculations for the pressure dependence the thermodynamic of quantities studied here and also the validity of the Pippard relations is examined near the melting point in benzene.

#### 4. CONCLUSIONS

Analysis of the thermal expansivity was performed at various pressures for constant temperatures near the melting point in benzene according to a power-law formula. Using the values of the critical exponent for the thermal expansivity, the pressure dependence of the isothermal compressibility and the specific heat was calculated near the melting point in this molecular crystal. It was found that the thermodynamic quantities diverge near the melting point. The Pippard relations were also constructed in the pressure range at constant temperatures, which gave the same dp/dT value, as obtained experimentally.

Our results give an evidence that anomalous behavior of the thermodynamic quantities can be considered as a second order transformation prior to the melting in benzene, as pointed out earlier workers.

# Table 1: Values of the critical exponent $\gamma$ for the thermal expansion $\alpha_p$ and the amplitude A, according to Eq. (1) for the melting and solid zones of benzene

Pressure range p-p∟ (MPa)	γ	A [(MPa) <sup>y</sup> /K]
1.1	1.6	741.9
4.7	1.6	455.2
7	1.6	552.1
15.3	0.3	21.3
17.4	0.3	21.4
249.9	0.3	22.8
139.9	0.3	22.8
62	0.3	21.5

Table 2: Values of the slope dp/dT which were extracted from the first Pippard relation (Eq. 8) and the second Pippard relation (Eq. 9) for the melting and solid phases of benzene for constant temperatures indicated here

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Т(К)	dp/dT (MPa/K) Eq.(8)	dp/dT (MPa/K) Eq.(9), Melting Zone	dp/dT (MPa/K) Eq.(9), Solid Phase
268	12.8	12.6	13.1
302	13	12.9	13.2
325	13	13	14.5
355	13	13.5	13







Fig. 2: Isothermal compressibility  $\kappa_T$  as a function of pressure for constant temperatures indicated in the solid phase of benzene according to Eq. (3) using the experimental data<sup>1</sup>.











Fig. 5: The specific heat as a function of the thermal expansion in the melting and solid zones of benzene according to the first Pippard relation (Eq. 8) for constant temperatures of 268 and 302K. dp/dT is the slope obtained from Eq. (8).







Fig. 7: The thermal expansion  $\alpha_p$  as a function of the isothermal compressibility  $\kappa_T$  in the melting zone of benzene for constant temperatures of 268 and 355K according to the second Pippard relation (Eq. 9). dp/dT gives the slope value obtained from Eq. (9).







Fig. 9: The thermal expansion α<sub>p</sub> as a function of the isothermal compressibility κ<sub>T</sub> in the solid zone of benzene for constant temperatures of 268, 302 and 355K according to the second Pippard relation (Eq. 9). dp/dT gives the slope value obtained from Eq. (9).

#### REFERENCES

- 1. Boyer LL. Phase Trans. 1985;5:1.
- Ubbelohde AR. The Molten State of Matter, John Wiley and Sons, Chichester (1978).
- 3. Bridgman PW. J Chem Phys. 1941;9:794.
- 4. Andrew ER and Eades RG. Proc Royal Soc. 1953;218A: 537.
- 5. Piermarini GJ, Mighell AD, Weir CE and Block S. Science. 1969; 169:1250.
- 6. Block S, Weir CE and Piermarini GT. Science. 1970; 169:586.
- 7. Akella J and Kennedy GJ. J Chem Phys. 1971;55:793.
- 8. Cansell F, Fabre D and Petitet CP. J Chem Phys. 1993;99:7300.
- 9. Ciabini L, Gorelli FA, Santoro M, Bini R, Schettino V and Mezouar M. Phys Rev. B 2005;72:094108.
- 10. Şen S and Yurtseven H. J Optoelectronics and Adv Mater Symposia. 2009;1(3):517-520.
- 11. Şen S and Yurtseven H. Int J Trans. Phenomena. 2011;12:319.
- 12. Thiery MM and. Leger JM. J Chem Phys. 1988;89:4255.
- 13. Pruzan Ph, Liebenberg DH and Mills RL. J Phys Chem Solids. 1986;47:949.
- 14. Yurtseven H and Ünsal T. High Temp Mater Proc. 2007;26:365.
- 15. Yurtseven H and Ünsal T. Tsinghua Sci and Tech. 2007;12:624.
- 16. Yurtseven H, Rașitoğlu B and Kilit E. J Mol Struc. 2011;993:428.