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## LETTER TO THE EDITOR

**Pressure and temperature dependence of heat capacity and entropy in condensed matter**

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**Abstract.** In this letter, an attempt has been made to develop a theory to study the heat capacity at constant pressure,  $C_P$ , and the entropy,  $S$ , as a function of pressure at different temperatures. Calculations performed in the case of sodium chloride and liquid methanol are found to be in good agreement with the available data.

To study the pressure dependence of entropy,  $S$ , and the heat capacity at constant pressure,  $C_P$ , in condensed matter, we need the experimental values of these properties as a function of temperature which are easily available in the literature. But, we have been unable to find out the experimental data for  $C_P$  and  $S$  as a function of pressure at different temperatures. However, some theoretical results for  $C_P$  and  $S$  as a function of pressure at different temperatures are available in solids [1, 2] and liquids [3]. Hence, the only course of action left to us is to study the pressure dependence of  $C_P$  and  $S$  at different temperatures by making use of a temperature-dependent equation of state (EOS).

Therefore, the aim of the present letter is to develop the simplest possible relations for  $C_P$  and  $S$  so that these properties can be easily computed as a function of pressure at different temperatures. The calculations done in the case of sodium chloride [1, 2] and liquid methanol [3] are in good agreement with the available theoretical results as shown in tables 1, 2 and 3.

To achieve the desired goal, we start with the well known thermodynamic relations:

$$\left[ \frac{\partial S(P, T)}{\partial P} \right]_T = - \left[ \frac{\partial V(P, T)}{\partial T} \right]_P \quad (1)$$

and

$$\left[ \frac{\partial C_P(P, T)}{\partial P} \right]_T = -T \left[ \frac{\partial^2 V(P, T)}{\partial T^2} \right]_P \quad (2)$$

where the symbols have the usual meaning as defined below. The integration of equations (1) and (2) gives

$$S(P, T) = S(0, T) + \xi V(0, T_A) \left[ \frac{V(P, T)}{V(0, T_A)} - \frac{V(0, T)}{V(0, T_A)} \right] \quad (3)$$

and

$$C_P(P, T) = C_P(0, T) + \xi^2 T \frac{V(0, T_A)}{B_T(0, T_A)} \left[ \frac{V(P, T)}{V(0, T_A)} \frac{B_T(0, T_A)}{B_T(P, T)} - \frac{V(0, T)}{V(0, T_A)} \frac{B_T(0, T_A)}{B_T(0, T)} \right]. \quad (4)$$

In obtaining equations (3) and (4), we have made use of the following relations:

$$-\left[\frac{\partial V(P, T)}{\partial T}\right]_P = \left[\frac{\partial V(P, T)}{\partial P}\right]_T \left[\frac{\partial P}{\partial T}\right]_V = \xi \left[\frac{\partial V(P, T)}{\partial P}\right]_T \quad (5)$$

$$\left[\frac{\partial^2 V(P, T)}{\partial T^2}\right]_P = \xi^2 \left[\frac{\partial^2 V(P, T)}{\partial P^2}\right]_T = \xi^2 \left[\frac{\partial}{\partial P} \left(-\frac{V(P, T)}{B_T(P, T)}\right)_T\right] \quad (6)$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha(P, T) B_T(P, T) = \alpha(0, T_A) B_T(0, T_A) = \xi \quad (7)$$

where equation (7) is given by Kumari and Dass [4].

In equations (1)–(7),  $S$  is the entropy,  $C_P$  is the heat capacity at constant pressure,  $V$  is the volume,  $B_T$  is the isothermal bulk modulus and  $\alpha$  is the coefficient of thermal expansion.

**Table 1.** Variation of heat capacity,  $C_P$  ( $\text{J gm}^{-1} \text{K}^{-1}$ ) with pressure at different temperature (K) in NaCl.

| $P$    |        |        |        |        |        |        | $P$    |          |          |          |
|--------|--------|--------|--------|--------|--------|--------|--------|----------|----------|----------|
| (kbar) | 298.15 | 373.15 | 473.15 | 573.15 | 673.15 | 773.15 | (kbar) | 300      | 550      | 800      |
| 0      | (0.86) | (0.89) | (0.92) | (0.95) | (0.97) | (1.00) | 0      | [0.8412] | [0.9043] | [0.9481] |
| 10     | 0.85   | 0.878  | 0.903  | 0.927  | 0.939  | 0.939  | 2      | 0.8392   | 0.8994   | 0.9379   |
|        | (0.85) | (0.87) | (0.90) | (0.92) | (0.95) | (0.97) |        | [0.8384] | [0.8979] | [0.9368] |
| 20     | 0.845  | 0.870  | 0.892  | 0.912  | 0.919  | 0.933  | 4      | 0.8375   | 0.8950   | 0.9287   |
|        | (0.84) | (0.86) | (0.89) | (0.91) | (0.93) | (0.95) |        | [0.8358] | [0.8922] | [0.9271] |
| 30     | 0.841  | 0.864  | 0.884  | 0.901  | 0.905  | 0.915  | 6      | 0.8358   | 0.8909   | 0.9204   |
|        | (0.84) | (0.86) | (0.88) | (0.91) | (0.92) | (0.94) |        | [0.8335] | [0.8872] | [0.9189] |
| 40     | 0.837  | 0.860  | 0.877  | 0.893  | 0.895  | 0.902  | 8      | 0.8343   | 0.8872   | 0.9130   |
|        | (0.83) | (0.85) | (0.87) | (0.89) | (0.91) | (0.93) |        | [0.8314] | [0.8827] | [0.9117] |
| 50     | 0.835  | 0.856  | 0.873  | 0.887  | 0.887  | 0.893  | 10     | 0.8329   | 0.8838   | 0.9062   |
|        | (0.83) | (0.85) | (0.87) | (0.89) | (0.90) | (0.92) |        | [0.8294] | [0.8787] | [0.9054] |
| 100    | 0.827  | 0.846  | 0.860  | 0.870  | 0.866  | 0.868  |        |          |          |          |

Results in parentheses ( ) are taken from [1] and [ ] are taken from [2].

To obtain the value of  $V(P, T)/V(0, T_A)$  and  $B_T(P, T)/B_T(0, T_A)$ , we use the following relations [5–7].

$$\frac{V(P, T)}{V(0, T_A)} = [(1 + \beta) \exp\{Z(P - P_{th})\} - \beta]^{-1/\eta} \quad (8)$$

and

$$\frac{B_T(P, T)}{B_T(0, T_A)} = 1 + \beta[1 - \exp\{-Z(P - P_{th})\}] \quad (9)$$

where  $\beta = B'_T(0, T_A)/B_T(0, T_A)Z$  and  $\eta = B'_T(0, T_A) + B_T(0, T_A)Z$ . In equations (8) and (9),  $Z$  is a pressure and temperature independent parameter,  $B'_T$  is the first pressure derivative of  $B_T$  and  $P_{th} = \xi(T - T_A)$  is the thermal pressure which is used to convert an isothermal EOS into a temperature dependent EOS [5]. Further, putting  $P = 0$  in equations (8) and (9), we can also obtain the value of  $V(0, T)/V(0, T_A)$  and  $B_T(0, T)/B_T(0, T_A)$ .

It is clear from the above discussion that the computation of  $C_P$  and  $S$  as a function of pressure at different temperatures is possible only when the values of  $B_T(0, T)$ ,  $B'_T(0, T)$ ,  $Z$  and  $\alpha(0, T_A)$  become known along with the value of  $V(0, T_A)$ . In the case of sodium chloride,  $B_T(0, T_A) = 240.14$  kbar,  $B'_T(0, T_A) = 4.54$  and  $Z = 1.236 \times 10^{-3} \text{ kbar}^{-1}$

**Table 2.** Variation of heat capacity  $C_P$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) as a function of pressure at different temperature in liquid methanol.

| $P$<br>(kbar) | 298.15 K |       | 313.15 K |       | 333.15 K |       |
|---------------|----------|-------|----------|-------|----------|-------|
|               | [3]      | Calc. | [3]      | Calc. | [3]      | Calc. |
| 0.001         | 81.18    | 81.18 | 84.36    | 84.36 | 89.50    | 89.50 |
| 0.005         | 81.16    | 81.08 | 84.34    | 84.21 | 89.46    | 89.16 |
| 0.01          | 81.13    | 81.00 | 84.30    | 84.07 | 89.42    | 88.83 |
| 0.025         | 81.05    | 80.74 | 84.21    | 83.65 | 89.29    | 87.49 |
| 0.05          | 80.92    | 80.33 | 84.06    | 83.00 | 89.09    | 86.46 |
| 0.1           | 80.67    | 79.58 | 83.79    | 81.84 | 88.72    | 84.02 |
| 0.2           | 80.23    | 78.34 | 83.32    | 79.96 | 88.09    | 80.38 |
| 0.3           | 79.86    | 77.34 | 82.93    | 78.52 | 87.58    | 77.78 |
| 0.4           | 79.52    | 76.52 | 82.59    | 77.37 | 87.15    | 74.85 |
| 0.5           | 79.22    | 75.84 | 82.29    | 76.43 | 86.78    | 74.35 |
| 0.6           | 78.95    | 75.26 | 82.03    | 75.66 | 86.45    | 73.15 |
| 0.7           | 78.70    | 74.26 | 81.79    | 75.01 | 86.16    | 72.18 |
| 0.8           | 78.47    | 74.33 | 81.57    | 74.45 | 85.89    | 71.37 |
| 0.9           | 78.25    | 73.96 | 81.37    | 73.98 | 85.66    | 70.69 |
| 1.0           | 78.06    | 73.63 | 81.19    | 73.56 | 85.44    | 70.11 |

**Table 3.** Variation of entropy ( $\text{J mol}^{-1} \text{K}^{-1}$ ) as a function of pressure at different temperature in liquid methanol.

| $P$<br>(kbar) | 298.15 K |        | 313.15 K |        | 333.15 K |        |
|---------------|----------|--------|----------|--------|----------|--------|
|               | [3]      | Calc.  | [3]      | Calc.  | [3]      | Calc.  |
| 0.001         | 128.08   | 128.08 | 132.08   | 132.08 | 137.24   | 137.24 |
| 0.005         | 128.06   | 128.06 | 132.06   | 132.05 | 137.21   | 137.20 |
| 0.01          | 128.04   | 128.03 | 132.04   | 132.02 | 137.19   | 137.16 |
| 0.025         | 127.96   | 127.97 | 131.96   | 131.94 | 137.10   | 137.03 |
| 0.05          | 127.84   | 127.86 | 131.84   | 131.80 | 136.97   | 136.84 |
| 0.1           | 127.61   | 127.65 | 131.59   | 131.55 | 136.70   | 136.48 |
| 0.2           | 127.18   | 127.27 | 131.14   | 131.09 | 135.21   | 135.86 |
| 0.3           | 126.77   | 126.92 | 130.71   | 130.69 | 135.76   | 135.34 |
| 0.4           | 126.39   | 126.61 | 130.31   | 130.33 | 134.34   | 134.89 |
| 0.5           | 126.03   | 126.33 | 129.93   | 130.01 | 137.94   | 134.49 |
| 0.6           | 125.68   | 126.07 | 129.58   | 129.72 | 134.57   | 134.14 |
| 0.7           | 125.35   | 125.83 | 129.23   | 129.45 | 133.21   | 133.82 |
| 0.8           | 125.03   | 125.60 | 129.91   | 129.20 | 133.53   | 133.53 |
| 0.9           | 124.73   | 125.39 | 128.59   | 128.97 | 133.54   | 133.26 |
| 1.0           | 124.43   | 125.19 | 128.75   | 128.75 | 133.22   | 133.02 |

are taken from [6] whereas the values of  $V(0, T_A) = 0.4374 \text{ cm}^3 \text{ g}^{-1}$  and  $\alpha(0, T_A) = 11.752 \times 10^{-5} \text{ K}^{-1}$  are taken from the literature. On the other hand,  $B_T(0, T_A) = 7.85 \text{ kbar}$ ,  $B'_T(0, T_A) = 10.73$  and  $Z = 0.166 \text{ kbar}^{-1}$  are obtained [7] in the case of methanol by fitting the volume compression data given in [3] whereas the values of  $\alpha(0, T_A) = 12.06 \times 10^{-4} \text{ K}^{-1}$  and  $V(0, T_A) = 40.92 \text{ cm}^3 \text{ mol}^{-1}$  are also taken from [3].

The computed values of  $C_P$  as a function of pressure at different temperatures in the case of sodium chloride are compared in table 1 whereas those in the case of methanol are compared in table 2. Further, the calculated values of  $S$  as a function of pressure at different

temperatures are compared in table 3 in the case of methanol. The overall agreement is very good in both the substances.

The following points are worth noting:

(1) The relations developed here for  $C_p$  and  $S$  to study these as a function of pressure at different temperature are independent of a particular EOS. Therefore, the relations are general in nature and a non-inverted EOS like Birch–Murnaghan [8] or universal [9] can also be used to give the values of  $C_p$  and  $S$  as a function of pressure.

(2) The relations for  $C_p$  and  $S$  are developed on a simple assumption as given in equation (7) and have been found to be good working relations for a sufficient pressure and temperature region [5].

(3) The present calculated results for  $C_p$  and  $S$  are in very good agreement with the values reported by other workers as shown in tables 1–3. Moreover  $C_p$  and  $S$  are found to increase with rising temperature and decrease with increasing pressure.

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