Thermochimica Acta, 134 (1988) 27–34
Elsevier Science Publishers B.V., Amsterdam

SPECIFIC HEAT ANALYSIS IN 1,1,1-TRICHLOROETHANE

Carlos A. Martin and Gustavo A. Monti

Facultad de Matemàtica, Astronomia y Fisica, Universidad Nacional de Còrdoba, Laprida 854, 5000 Còrdoba, Argentina.

ABSTRACT

The temperature dependence of the specific heat in 1,1,1-Trichloroethane in the low temperature phase ($0 < T < 225$ K) is analysed in a dynamical fashion, approximating the contributions of the acoustic and optic modes by means of the Debye and Einstein models, respectively, and accounting for anharmonicities. A value for the Debye temperature of $(26.9\pm2.6)\mathrm{cm}^{-1}$ is deduced. The analysis also reveals the formation of lattice vacancies, producing values of (5.0 ± 0.3)K for the formation entropy and of (1929 ± 81)K for the formation energy. The excellent description achieved for the specific heat data and the analysis of the values determined for the various parameters, indicate that these are very reasonable ones.

ANALYSIS OF DATA, RESULTS AND DISCUSSION

Methyl cloroform (MCF), also known as 1,1,1-Trichloroethane (CH_3-CCl_3), is a molecular plastic crystal, due to the fact that melting entropies and enthalpies have very low values, as a result of the nearly spherical shape of the constituents molecules. It exhibits various solid-solid phase transitions (1), and it is the purpose of this paper to analyse, as detailed as possible, the temperature dependence of the specific heat (C_p vs T) in phase II ($0 < T < 225$ K).

Phase II is orthorombic (Pnma) with four molecules per

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

primitive unit cell (Z=4) (2,3), therefore producing a total of 96 normal modes of vibration (4). Dispersion of the optic modes across the Brillouin zone will be neglected and it will be assumed that optic modes contribution to the specific heat is well described by Einstein's model (4), while that of the acoustic modes is adequately taken into account by Debye's model (4).

The 96 normal modes may be divided at the Brillouin zone centre, as follows: 72 internal optic (5) normal modes, 21 external optic (5) normal modes, and 3 acoustic. Since the splittings of the internal optic normal modes are very small, as well as the shifts with respect to those of the free molecule (6,7), then the internal optic modes will be taken as four times degenerate of those of the free molecule. These 18 free molecule normal mode frequencies (in cm^{-1}) are: 6 non-degenerate: 2954, 1381, 1012, 524, 343, and 205; and 6 double-degenerate: 3017, 1445, 1087, 720, 863, and 241. The 21 external optic modes may be divided into 9 optic-translatory and 12 optic-rotatory modes. Unfortunately the information about these 21 modes is very scarce, and only 5 of them have been reported at a few temperatures (8,9), and also the 'rotatory character assigned to these measured mode frequencies is not doubt-free. The temperature dependences of these five libratory optic mode frequencies may reasonably well be described by the following linear temperature dependences (in cm^{-1})

$\nu_1=42.0(1-7.09*10^{-4}T)$ $\nu_2=48.2(1-3.58*10^{-4}T)$ $\nu_3=58.1(1-9.78*10^{-4}T)$
$\nu_4=63.0(1-9.63*10^{-4}T)$ $\nu_5=71.8(1-7.32*10^{-4}T)$

It is hoped that, through a careful analysis of the C_p vs T data, to throw some light on the remaining 19 lattice modes: 3 acoustic, 9 optic translatory, and 7 optic rotatory.

As mentioned above, in the approximation that the models due to Debye and Einstein are good enough to account for the acoustic and optic modes, respectively, contributions to the specific heat, we may write (7),

$$C_p = R \underset{\substack{\text{internal}\\ \text{optic}}}{\sum_{j=1}^{18}} \frac{x_j^2\, e^{x_j}}{(e^{x_j}-1)^2} + \frac{R}{4} \underset{\substack{\text{rotatory}\\ \text{optic}}}{\sum_{j=1}^{5}} \frac{1}{(1-c_jT)} \frac{x_j^2\, e^{x_j}}{(e^{x_j}-1)^2} +$$

$$+ \frac{4\,R}{(1-cT)} \frac{x^2\, e^x}{(e^x-1)^2} + \frac{9\,R}{4(1-c_DT)} \frac{T^3}{T_D^3} \int_0^{T_D/T} \frac{x^4\, e^x}{(e^x-1)^2}\, dx \qquad (1)$$

where $x=h\nu/kT$; for the lattice modes a linear temperature dependence, $\nu=\nu_0(1-cT)$, is assumed. The third term in the right-hand-side of Eq. 1 describes, in an average fashion, the contribution of the unknown 16 external optic modes (7 rotatory and 9 translatory). Therefore, unknown quantities are: ν_0, c, T_{0D}, and c_D.

The temperature dependence of the specific heat in MCF has been measured a number of times (1,2,11-13). In two of these investigations (11,12) a solid-solid phase transition is reported to occur at about 205 K whose reproducibility has not been achieved by other authors (1,2,13,14). Additionally, at other temperatures, the data of the various authors show systematic departures among themselves. In view of this situation it was decided to use the data reported in Table 1 of Ref. 13 on the temperature range $0 < T < 225$ K , and depicted in Fig. 1. It is clear that for temperatures above ≃ 160 K an additional contribution to the specific heat, not accounted for in Eq. 1, appears. The origin of this contribution is uncertain, although various causes may be proposed. First, the solid phase in the temperature interval $225 < T < 243 \simeq$ melting point is known as the "rotator phase" (12), as deduced from dielectric constant

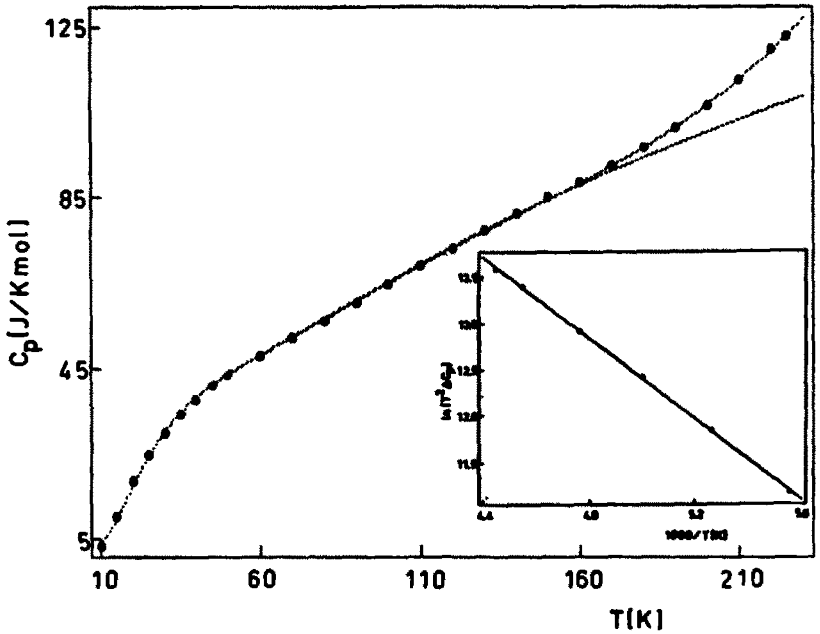

Fig.1: Selected values for C_p vs T data (full circles) in Methylchloroform taken from Ref. 13. The dotted line depicts the C_p vs T calculated by adding Eqs. 1 and 2. Full circles in the insert correspond to experimental data from which the produced values by Eq. 1 have been substracted out; the dotted line depicts Eq. 2. As may be seen the description of the data over the whole temperature range is excellent.

measurements, because the molecules of MFC show as much freedom of orientation as that existing in the liquid. The increase in the dielectric constant below ≃ 225 K may be attributed to a progressive onset of such molecular reorientations. Second, in a similar compound (Trichlorofluoromethane - CCl_3F) (15) Schottky point defects (lattice vacancies) have been shown to make a significant contribution to the temperature dependence of the specific heat. Third, anomalies in the specific heat are also produced by what is known as a Schottky anomaly (16), which is produced in an essentially two level energy system. Unfortunately, these three mechanisms produce, in the low temperature limit, the same functional temperature dependence of their contributions to the specific heat (16-18), i.e.

$$\Delta C = A\ R\ \left(\frac{E}{k\ T}\right)^2\ e^{-E/kT} \qquad (2)$$

where A is a constant which may take different values for each mechanism: $A=e^{S/k}$ for vacancies (S=formation entropy per vacancy, k=Boltzmann constant; a vacancy must be understood in the sense that a lattice site which should otherwise be occupied by a whole molecule, is empty), and E is the formation energy per vacancy; A=3 in the case of a rigid rotator, and E is the energy of first excited level of the rotator; and A=1 (Schottky anomaly) in the case of a non-degenerate two level energy system separated by E.

The C_p vs T data were therefore analysed by adding Eqs. 1 and 2 and fitting the parametres ν_o, c, T_{oD}, c_D, A, and E, according to the least-squares procedure developed by Deming (19).The following comments and discussion are in order. First, it was found that the standard deviation for c_D was larger than the value determined for c_D itself, therefore hereafter c_D was taken zero, i.e. $T_D=T_{oD}$. Carrying the fitting the following values were determined for the parameters:

$T_D=(26.9\pm81)cm^{-1}$ $\nu_o=(60.7\pm0.6)cm^{-1}$ $c=(10.17\pm0.30)10cm^{-1}K^{-1}$
$\ln(A)=(5.0\pm0.3)$ $E/k=(1929\pm81)K$

The fit produced by these parameters when substituted into Eqs. 1 and 2 is depicted in Fig. 1. As may be seen the description provided for the data is excellent. The value deduced for the Debye temperature turned out to be somewhat lower as compared with those obtained in similar compounds (15,20), i.e. $(71.1\pm1.9)cm^{-1}$ and $(72.5\pm1.0)cm^{-1}$ for Methylchloride (CH_3Cl) and Trichlorofluoromethane (CCl_3F), respectively. However, these differences arise from the fact that the three compounds have different number of molecules (Z) per unit cell, i.e. Z=1,2, and 4 for CCl_3F, CH_3Cl and MFC, respectively, since roughly speaking the larger (more massive) the unit cell is, the smaller the acoustic frequencies are. Therefore, the value determined for T_D may be considered as a reasonable one. The value for ν_o is, roughly speaking, the arithmetic mean of the 16 unknown external optic modes, therefore making it impossible to say anything more about this besides the fact that it has a reasonable value as well as its temperature dependence given by c.

The value determined for ln(A) rules out the rigid rotator and the Schottky anomaly mechanisms as responsibles of the high temperature ($160 < T < 225$ K) anomalous behaviour of the C_p vs T data, leaving only that due to vacancy formation, whose characteristic formation parameters are $S/k=(5.0\pm0.3)$ and $E/k=(1929\pm81)$ K. These values satisfy the experimentally found correlation indicating that $S\ T_m=B\ E$, where B is a constant and T_m is the melting temperature (21). In organic compounds similar to the present one the values for B fall in the range $0.5 \leq B \leq 0.7$; substituting the obtained values for E/k and S/k and taking $T_m=243.1$ K (13) a value of 0.63 is produced for B, therefore providing additional support to the above given interpretation that the extra mechanism contributing to C_p in the high temperature range is that due to vacancies. The value deduced for E/k compares well with those reported by other authors (22-24), which employ Nuclear Magnetic Resonance (NMR) and/or Nuclear Quadrupolar Resonance (NQR) techniques, spanning the range 1860-2170 K, although there is not agreement as to what the physical process involved is (reorientations of the methyl group, reorientations of the molecule as a whole, or a high mobility of the molecules such as that to be expected near the melting point or for those molecules near to a lattice vacancy). The above analysis of C_p vs T shows that an additional mechanism, i.e. lattice vacancies, not accounted for previous NMR-NQR investigations in the temperature range $T < 225$, is present. It may be mentioned that vacancy formation and migration do affect the NMR and NQR parametres (25,26), producing behaviours similar to those reported in Refs. 22-24. However, the elucidation of this point must await further experimental NMR-NQR work (particularly temperature dependences of the absorption lineshapes for H and Cl, and relaxation data for H and Cl), as well as a careful theoretical interpretation of these measurements.

ACKNOWLEDGMENTS

Partial financial support provided by Consejo de Investigaciones Cientificas y Tècnicas (CONICET), and by Consejo de Investigaciones Cientificas y Tecnològicas de la Provincia de Còrdoba (CONICOR), is gratefully acknowledged.

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