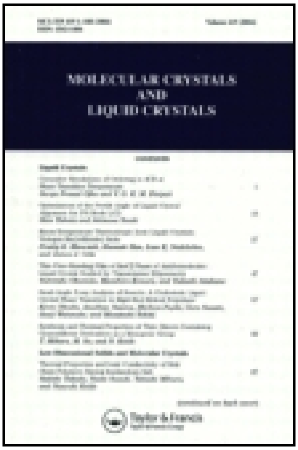

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HIGH-PRESSURE DIFFERENTIAL SCANNING CALORIMETRY INVESTIGATIONS AT LOW TEMPERATURES: SOLID-SOLID PHASE TRANSFORMATIONS OF THE MOLECULAR CRYSTAL T-BUTYL CHLORIDE UP TO 1750 BAR

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ABSTRACT With a high-pressure low-temperature differential scanning calorimeter (d.s.c.) developed by Arntz, measurements were performed on the molecular crystal t-butyl chloride (2-chloro-2-methyl-propane) in the temperature range from about 165 K to 260 K at normal and high pressures up to 1750 bar; so far, high pressure investigations on this substance are unknown. At normal pressure, two solid-solid phase transitions exist, the transition temperatures being 182.8 K ($s_3 \rightarrow s_2$) and 219.2 K ($s_2 \rightarrow s_1$) respectively. With increasing pressure these transition temperatures increase. Additionally a new pressure-induced solid phase s_4 was found above 800 bar; the triple point where the three solid phases s_1, s_2 and s_4 coexist is at about 805 bar and 232 K. Furthermore, the transition enthalpies were determined as a function of pressure along the coexistence lines.

INTRODUCTION In the large group of organic substances with plastic crystalline phases t-buyl chloride is a well-known example. In 1939 the solid rotator phase (s_1) of this substance was found by Baker and Smyth[1] from measurements of the dielectric constant. Since then it has been used for numerous investigations on the mobility of molecules in plastic phases. The aim of the present work was to investigate the thermodynamic behaviour of this plastic crystal under pressure.

EXPERIMENTAL All measurements were performed with a high-pressure low-temperature differential scanning calorimeter (d.s.c.) developed by Arntz. The apparatus and the measuring technique have been described elsewhere[2,3]. Under pressure mercury was used as internal standard. The transition temperatures were taken from heating runs, because the solid-solid transitions of t-butyl chloride supercool. The heating rate under pressure was 0.15 K min^{-1}. T-butyl chloride was obtained from Fluka AG (purity > 99.5%) and was used without further purification.

RESULTS Figure 1 shows the T(p) phase diagram of t-butyl chloride (without melting curve) obtained from the present measurements. At normal pressure t-butyl chloride undergoes two transitions in the solid state. The transition temperatures were determined to be 182.8 K ($s_3 \rightarrow s_2$) and 219.2 K ($s_2 \rightarrow s_1$) respectively (where s_3 is monoclinic or possibly orthorhombic[4], s_2 (plastic)[5] tetragonal[4], s_1 (plastic)[5] face-centered cubic[4]). These values are in

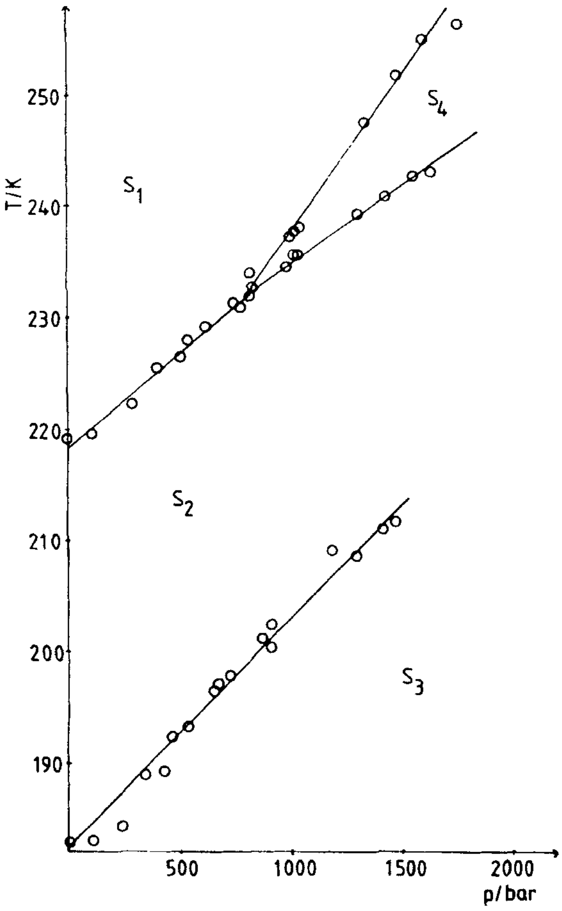

FIGURE 1. T(p) phase diagram of t-butyl chloride (the melting pressure curve is omitted)

good agreement with those reported in literature[4, 6-9]. Above about 800 bar a new pressure-induced solid phase s_4 appears. The triple point where the three solid phases s_1, s_2 and s_4 coexist is at about 805 bar and 232 K. With increasing pressure a shift of the transition temperatures to higher values was observed for all four solid-solid phase transitions. The limits of experimental error in the values of the transition temperatures were ± 0.5 K.

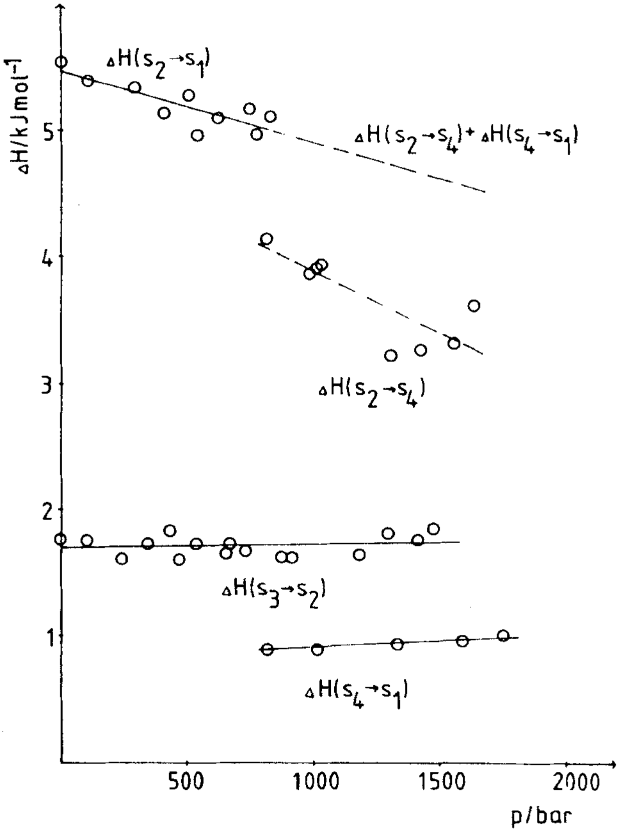

FIGURE 2. Transition enthalpies for the solid-solid transformations of t-butyl chloride as a function of pressure along the coexistence lines

With the d.s.c. method direct measurements of transition enthalpies are possible. Figure 2 shows the transition enthalpies for the solid-solid transformations of t-butyl chloride as a function of pressure along the coexistence lines.

At normal pressure the enthalpy change of the $s_3 \rightarrow s_2$ transition is (1.77 ± 0.02) kJmol^{-1} and is found to be independent of pressure within the limits of experimental accuracy (± 6%) . The transformation of the phase s_2 into the phase s_1 occurs with a transformation enthalpy of (5.55 ± 0.06) kJ mol^{-1} at 1 bar which decreases to a value of (5.0 ± 0.3) kJmol^{-1} at a pressure of 775 bar. The $s_2 \rightarrow s_4$ phase transition enthalpy also decreases with increasing pressure, while the ΔH-value of the $s_4 \rightarrow s_1$ phase transformation increases slightly in the pressure range from 820 to 1750 bar. Between 1050 and 1500 bar the transition enthalpies of these two phase transformations show larger uncertainties (±10%), because the transition traces of these transformations overlap in this range of pressure with the melting trace of mercury (internal standard). The sum of the transition enthalpies $\Delta H(s_2 \rightarrow s_4)$ and $\Delta H(s_4 \rightarrow s_1)$ is also plotted in figure 2. This line gives a continuous plot of the ΔH-values for the $s_2 \rightarrow s_1$ transition. In table 1 transition temperatures and transition enthalpies for the $s_3 \rightarrow s_2$ phase transition of t-butyl chloride are presented as functions of pressure along the coexistence line, and in table 2 the corresponding data for the transitions $s_2 \rightarrow s_1$, $s_2 \rightarrow s_4$ and $s_4 \rightarrow s_1$ are given.

Table 1. Phase transition temperatures T and enthalpies ΔH for the $s_3 \rightarrow s_2$ transition of t-butyl chloride as functions of pressure along the coexistence line

p/bar	T/K	$\Delta H/kJmol^{-1}$
1	182.8	1.77
532	193.3	1.7
919	202.4	1.6
1473	211.7	1.9

Table 2. Phase transition temperatures T and enthalpies ΔH of t-butyl chloride as functions of pressure along the coexistence lines

	T/K			$\Delta H/kJmol^{-1}$		
p/bar	$s_2 \rightarrow s_1$	$s_2 \rightarrow s_4$	$s_4 \rightarrow s_1$	$s_2 \rightarrow s_1$	$s_2 \rightarrow s_4$	$s_4 \rightarrow s_1$
1	219.2	-	-	5.55	-	-
509	226.5	-	-	5.3	-	-
820	-	-	234.0	-	-	0.9
1012	-	235.6	-	-	3.9	-
1337	-	-	247.6	-	-	0.9
1637	-	243.1	-	-	3.6	-

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