Thermochimica Acta, 22 (1978) 371–378

DIFFERENTIAL MICROCALORIMETRY AT HIGH PRESSURE I*

M. KAMPHAUSEN AND G. M. SCHNEIDER
Department of Chemistry, Institute of Physical Chemistry, University of Bochum, Bochum (F.R.G.)

ABSTRACT

A high pressure microcalorimeter based on the differential scanning calorimetry (DSC) principle is described. It was used for the determination of heats of transformation of organic compounds at pressures up to 2300 bar. The accuracy is considered to be ± 1 K for the temperature in the range −20 to +200 °C and to be about ± 5% for the determination of heats of transformation. A high pressure measuring capsule including an internal standard substance is described.

Data are presented for the transition temperatures, the heats of transformation, the volume changes, and the entropy changes of pure heneicosane and hexacosane as a function of pressure, respectively.

INTRODUCTION

A quantitative determination of heats of transformation at high pressure by DTA is very difficult because a sufficiently reproducible calibration is not possible at high pressure[1]. Therefore, differential scanning calorimetry (DSC) is supposed to be a method of much larger accuracy than DTA[2] insofar as the determination of heats of transformation is considered.

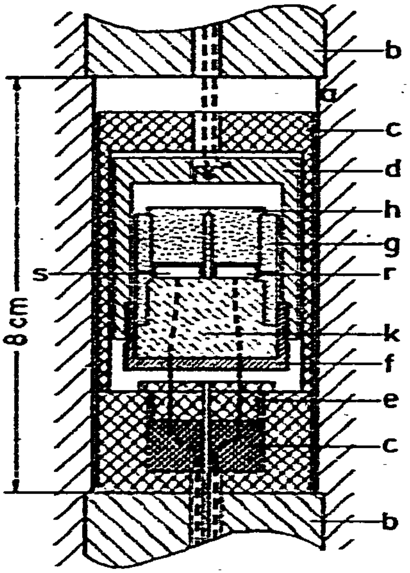
APPARATUS

The high pressure DSC calorimeter and the calibration method have been described elsewhere[3, 4]. Some details may be recalled here. A high pressure DSC measuring head is placed in a cylindrical pressure vessel made of Nimonic 90 and closed by two teflon sealed Bridgman pistons. The pressure is generated by a common pressure supply and is transmitted by purified helium. It is measured by a bourdon tube manometer and two strain gauges and is displayed digitally.

Figure 1 shows details of the measuring head. A modified sample holder of the Perkin-Elmer DSC-1b model is placed into a thermally insulating jacket (c) which works together with the additional heater (d) as an internal thermostat. The surroundings of the two pans (r, s) were stuffed with glass fiber (k) and teflon (g, h) to

---

* Presented at the 2nd Ulm Calorimetry Conference held at the University of Ulm from 24–26 March 1977.



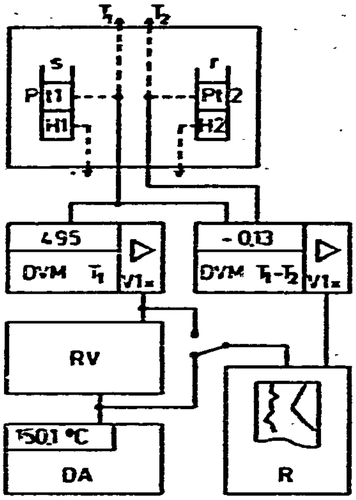


Fig. 1. High pressure DSC measuring head. a = Vessel; b = piston; c = insulating shell (alumina); d = additional heater (connections dashed); e = alumina socket for the sample holder with gilded plugs; f = sample holder base (steel) with gilded pins; g = upper insulater of the sample holder (teflon); h = sample cover (teflon); k = lower insulator of the sample holder (glass fiber); r = reference pan; s = sample pan.

Fig. 2. Schematic diagram of the temperature control unit. s = sample pan; r = reference pan; Pt1, Pt2 = platinum resistors; H1, H2 = heating resistors; DVM T1 = digital display for temperature; DVM T1-T2 = digital display for differential temperature; RV = analog computer; DA = temperature display in °C; R = recorder.

prevent turbulence. The temperature of the two pans is changed simultaneously by two separate heaters in a linear way. During a transformation, an additional power is generated at one pan such that the temperatures of the sample pan (s) and the reference pan (r) will be equal at all times. This power is controlled by a regulator and plotted together with the temperature at the sample pan and together with the pressure by a recorder.

TEMPERATURE MEASUREMENT

Fig. 2 is a schematic diagram of the temperature control equipment. The temperature is measured by two platinum resistors (Pt1, Pt2) at the bottom of the pans (s, r). The values of the voltage drops corresponding with the temperatures of the pans are displayed digitally (DVM T1) or they are converted to °C by an analog computer (RV) and plotted by a recorder. Additionally the difference of the voltage drops may be displayed and recorded in order to be used as an additional check.

HIGH PRESSURE MEASURING CAPSULE

The procedure of calibrating the apparatus has been reported elsewhere[3,4]. In

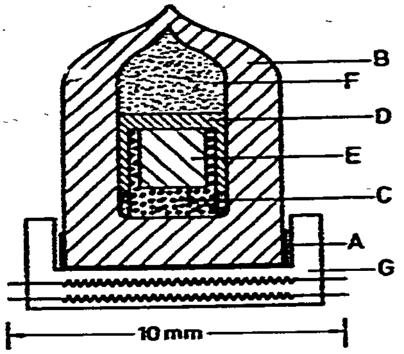


Fig. 3. High pressure DSC measuring capsule. A = aluminium pan; B = indium cell; C = teflon cover; D = inner cell; E = gallium; F = substance under test; G = sample holder.

order to prevent the pressure transmitting noble gas from being dissolved in the substance of the sample, a closed well was developed. Figure 3 shows this well the wall of which is capable to transmit the pressure without rupture. It was found that capsules of indium (B) are suitable for this purpose. A second smaller well of molybdenum (D) with a teflon cover (C) including highly purified gallium (E) is placed into the indium capsule. Because the transition temperatures and enthalpies of gallium are well known[5], gallium is suitable as an internal standard substance. Using this standard the accuracy is considered to be ± 0.5 to 1 K for the temperature and 3 to 5% for the determination of heats of transformation.

SUBSTANCES

The two substances heneicosane and hexacosane were obtained from Lachat Chemicals Inc., Mequon, WI, U.S.A. The purity was controlled by g.l.c. and found to be better than 99%.

RESULTS

In Fig. 4, five original DSC peaks obtained experimentally are presented for heneicosane at 1, 500, 1 000, 1 500, and 2 000 bar. In the upper part of Fig. 4 the DSC peaks corresponding to the phase transformations are plotted, in the lower part the corresponding temperature versus time curves are given. At pressures up to 1.5 kbar two peaks exist. The greater peak corresponds to the melting of s_I and the smaller one to a solid–solid transformation $s_{II} \rightarrow s_I$ that has been attributed to a rotational transition[6]. Only one single peak is found at 2.0 kbar corresponding to the melting of the solid s_{II}.

The transition temperatures and the enthalpies of transformation such as determined from the experimental DSC peaks are plotted versus pressure in Figs. 5 and 6.

The phase diagrams of Fig. 5 are in good agreement with measurements of

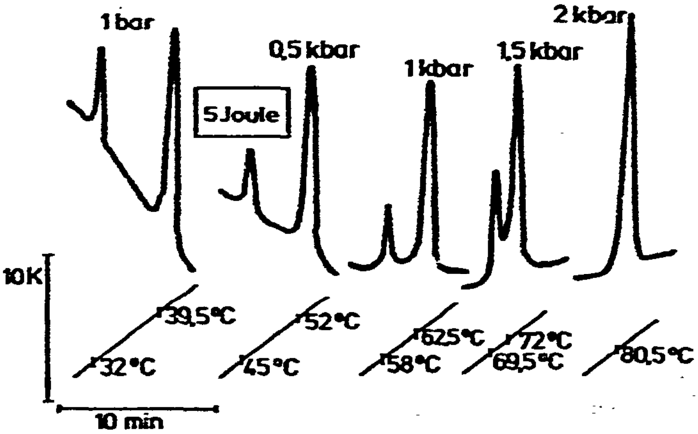


Fig. 4. DSC peaks of heneicosane at different pressures (see text).

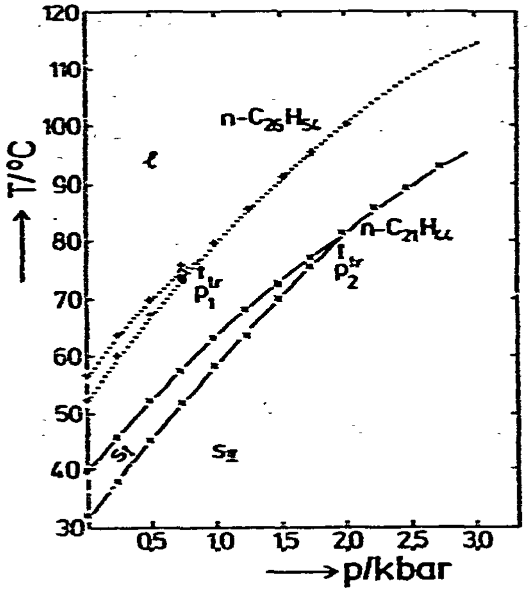
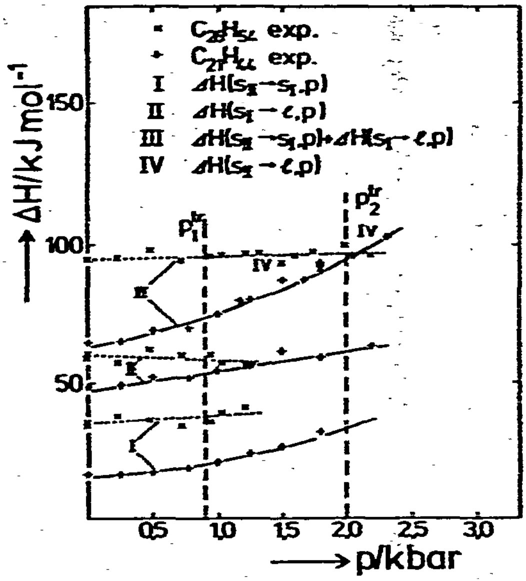


Fig. 5. $T(p)$ phase diagrams of heneicosane (x) and hexacosane (+).

Würflinger[1] for heneicosane and of Koppitz[7] for hexacosane. The triple point of heneicosane was found to be (2000 ± 100) bar and (80.5 ± 1.5)°C in accordance with Würflinger[1]. The triple point of hexacosane, however, was found to be situated at (870 ± 50) bar and (76.7 ± 1.5)°C that is about 130 bar and 1 K lower than reported in ref. 7. The lower accuracy in the neighbourhood of the triple point is caused by increasing difficulties in separating the two overlapping peaks of melting and of the rotational transition.

In Fig. 6, the enthalpies of melting (II = $s_I \rightarrow l$, IV = $s_{II} \rightarrow l$), of the rotational transition (I = $s_{II} \rightarrow s_I$) and of the sum (III) of I and II are plotted as functions of pressure for heneicosane as well as for hexacosane. Whereas all these enthalpy



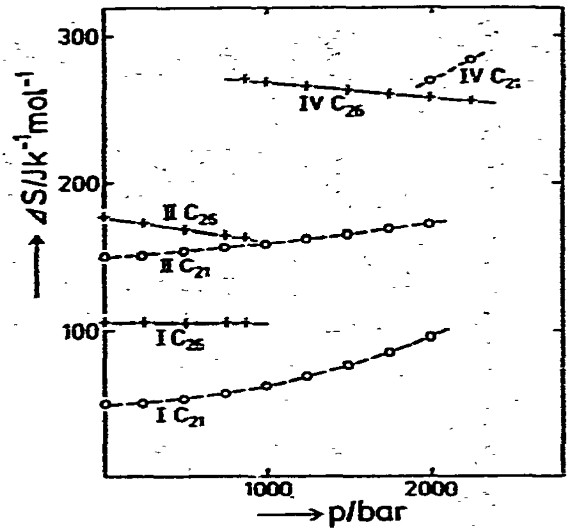


Fig. 6. Enthalpies of transformation ΔH of heneicosane (+) and hexacosane (×) as a function of pressure along the coexistence curve.

Fig. 7. Entropies of transformation ΔS of heneicosane (O) and hexacosane (+) as a function of pressure along the coexistence curve.

changes increase with pressure for heneicosane, the corresponding values of hexacosane are nearly independent of pressure.

From the enthalpies of transformation the changes of entropy ΔS during a phase transition were calculated according to

$\Delta S^i = \Delta H^i / T^i$ where i = I, II, and IV.

The results are plotted in Fig. 7 as functions of pressure for both alkanes, respectively. Using the Clapeyron equation

$$\left(\frac{dp}{dT}\right)^i_{\mathrm{coex}} = \frac{\Delta H^i}{T^i \Delta V^i} \quad \text{where i = I, II, and IV}$$

it is also possible to calculate the volume changes ΔV^i during the phase transitions from the experimental data. From the accuracy of the transition temperatures (about ± 1 K) an error of about 14% for $(dp/dT)^i_{\mathrm{coex}}$ and one of about 20% for the ΔV^i values was estimated. Thus, the ΔV^i values are only suitable for estimations as long as directly measured data are not available. All ΔV^i values decrease with increasing pressure except those of the rotational transition of heneicosane where ΔV^I increases. Although the limits of experimental error are great, they cannot explain this surprising effect. A possible explanation is that the lattice of the crystal is more widened by the rotational transition than it is compressed by the pressure increase. Besides the same effect was also found by Nelson et al.[8] for the rotational transitions of pentadecane and tetracosane from much more accurate pVT measurements.

TABLE 1

$T, \Delta H, \Delta S$, AND ΔV FOR PHASE TRANSITIONS IN HENEICOSANE AND HEXACOSANE AS FUNCTIONS OF PRESSURE: COEFFICIENTS OF THE POLYNOMIALS $X = A + Bp/\text{bar} + Cp^2/\text{bar}^2$

Function X	*Accuracy*	$I = s_{II} \rightarrow s_I$			$II = s_I \rightarrow l$			$IV = s_{II} \rightarrow l$		
		A	$B10^3$	$C10^6$	*A*	$B10^3$	$C10^6$	*A*	$B10^3$	$C10^6$
Heneicosane										
$T(p)$(°C)	1 K	31.67	27.58	−1.95	39.46	25.57	−2.54	28.15	34.20	−4.0
$\Delta H(p)$(kJ mol^{-1})	5%, 7%[a]	15.3	2.36	3.5	47.1	6.43	0.29	62.4	8.79	3.8
$\Delta S(p)$(JK^{-1} mol^{-1})	5%, 7%[a]	50.1	4.54	9.39	150.7	8.20	1.44	155.5	58.6	0
$\Delta V(p)$(cm^3 mol^{-1})	20%	13.1	2.59	0	38.6	− 5.91	0	73.6	−12.3	0
Validity range			1–2000 bar			1–2000 bar			2000–2300 bar	
Hexacosane										
$T(p)$(°C)	1 K	52.21	31.69	−4.12	56.38	29.34	−6.91	54.15	27.81	−2.79
$\Delta H(p)$(kJ mol^{-1})	5%, 7%[a]	34.8	2.7	0	59.2	− 1.8	0	94.0	1.1	0
$\Delta S(p)$(JK^{-1} mol^{-1})	5%, 7%[a]	106.8	− 0.778	0	179	−16.9	0	280.6	−10.9	0
$\Delta V(p)$(cm^3 mol^{-1})	20%	33.9	− 9.08	0	52.6	−28.2	0	76.7	−16.7	0
Validity range			1–870 bar			1–870 bar			870–2300 bar	

[a] The accuracy of the ΔH and ΔS values about 400 bar below the triple point and of these values in column I is 7% because the DSC peaks overlap and the accuracy decrease the more the smaller the peaks are.

All values of T^i, ΔH^i, ΔS^i, and ΔV^i as functions of pressure have been adjusted to polynomials of the form

$$X = A + Bp + Cp^2$$

The values of A, B and C obtained by least square fitting are summarized in Table 1 together with the accuracy obtained and the range of validity of the approximations.

From Planck's equation for a phase transition i

$$(\mathrm{d}\Delta H/\mathrm{d}p)^{i}_{\mathrm{coex}} = \Delta C^{i}_{p}(\mathrm{d}T/\mathrm{d}p)^{i}_{\mathrm{coex}} + \Delta V^{i} - T^{i} \cdot (\partial \Delta V^{i}/\partial T)_{p}$$

(where i = I and II) the change of the heat capacity at constant pressure ΔC^i_p can be calculated when $(\mathrm{d}\Delta H/\mathrm{d}p)^i_{\mathrm{coex}}$, $(\mathrm{d}T/\mathrm{d}p)^i_{\mathrm{coex}}$, ΔV^i and $(\partial \Delta V^i/\partial T)_p$ are known. Here, the first and the second term are available from the experimental data of the present paper whereas values of ΔV^i as a function of temperature at atmospheric pressure were measured by Templin[9] for hexacosane. From these data ΔC^i_p of hexacosane was calculated to be

$$\Delta C^{I}_{p} = C_p(\mathrm{s_I}) - C_p(\mathrm{s_{II}}) = (2.1 \pm 1.4)\ \mathrm{J\,g^{-1}\,K^{-1}} = (790 \pm 500)\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

for the rotational transition I and to be

$$\Delta C^{II}_{p} = C_p(\mathrm{l}) - C_p(\mathrm{s_I}) = -(2.3 \pm 1.5)\ \mathrm{J\,g^{-1}\,K^{-1}} = -(840 \pm 500)\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

for the melting II of solid s_I at atmospheric pressure. Although the limits of error are great because of the reasons discussed above the sign of the ΔC^i_p values is correct. A surprising result follows from these findings: The heat capacity of the solid rotator phase $C_p(\mathrm{s_I})$ is larger than that of the liquid phase $C_p(\mathrm{l})$. This effect was also found by Messerly et al.[10] for heptadecane, pentadecane, and tridecane. It may be explained by the same arguments used for the discussion of the exceptionally great lattice expansion in the rotational phase: Rather complicated motions of the molecules in the solid phase, which were recently reported by Strobl et al.[11-13] for tritriacontane, very probably occur in a similar way in all rotator phases of the other alkanes up to the triple point.

In order to continue the investigations, the enthalpy changes during the phase transitions in liquid crystals such as EBBA have been recently measured up to 2.5 kbar in the same apparatus by Sandrock[14] whereas a new low-temperature high-pressure microcalorimeter is being developed by Arntz[15].

ACKNOWLEDGMENTS

Financial support of the Deutsche Forschungsgemeinschaft DFG and of the Verband der Chemischen Industrie (Fonds der Chemischen Industrie) is gratefully acknowledged.

REFERENCES

1 A. Würflinger and G. M. Schneider, *Ber. Bunsenges. Phys. Chem.*, 77 (1973) 121.
2 E. S. Watson, M. J. O'Neill, J. Justin and N. Brenner, *Anal. Chem.*, 36 (1964) 1233.
3 M. Kamphausen, *Rev. Sci. Instrum.*, 46 (1975) 668.
4 M. Kamphausen, *Dissertation*, University of Bochum, F.R.G., 1976.
5 P. W. Bridgman, *Phys. Rev.*, 48 (1935) 901.
6 W. R. Turner, *Ind. Eng. Chem. Prod. Res. Devel.*, 10 (1971) 238.
7 B. Koppitz, *Diplomarbeit*, University of Bochum, F.R.G., 1973.
8 R. R. Nelson, W. Webb and J. A. Dixon, *J. Chem. Phys.*, 33 (1960) 1756.
9 P. R. Templin, *Ind. Eng. Chem.*, 48 (1956) 154.
10 J. F. Messerly, G. B. Guthrie, S. S. Todd and H. L. Finke, *J. Chem. Eng. Data*, 12 (1967) 338.
11 G. Strobl, B. Even, E. W. Fischer and W. Piesczek, *J. Chem. Phys.*, 61 (1974) 5257.
12 W. Piesczek, G. Strobl and K. Malzahn, *Acta Crystallogr.*, B30 (1974) 1278.
13 B. Even, E. W. Fischer, W. Piesczek and G. Strobl, *J. Chem. Phys.*, 61 (1974) 5265.
14 R. Sandrock, *Diplomarbeit*, University of Bochum, 1977.
15 H. Arntz, *Dissertation*, University of Bochum, in preparation.