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Simultaneous measurements of enthalpies of sublimation and vapour pressures. Application to the polyols derived from neopentane

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Abstract

A high sensitivity calorimeter coupled to a high vacuum system is described. This calorimetric device allows the simultaneous measurement of enthalpies of sublimation and vapour pressures of compounds of low volatility by means of the Knudsen effusion method. Calibration was carried out using naphthalene as standard reference material. As a first measurement we determined the enthalpies of sublimation and the vapour pressures of neopentyl glycol in both crystalline and plastic solid phases. The results obtained were: $\Delta H = 841$ J g^{-1} and $P_{\text{sat}} = 6.6$ Pa at 311.3 K (crystalline phase) and $\Delta H = 725$ J g^{-1} and $P_{\text{sat}} = 15.4$ Pa at 318.6 K (plastic phase), with estimated errors of 5% and 7% for ΔH and P_{sat}, respectively.

Keywords: Effusion; Heat of sublimation; Neopentyl glycol; Plastic crystal; Vapour pressure

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1. Introduction

For several years we have been interested in the thermodynamic and structural characterization of polyols derived from neopentane, which show a plastic mesophase (plastic crystals) [1–4]. The molecule of these compounds is always tetrahedral, with a C atom bonded to the groups CH_3, CH_2OH, NO_2 and NH_2. Our purpose is to study the influence of these groups on the properties of the different plastic crystals.

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In this work we describe a sublimation calorimetric system, constructed by us, as applied to measure the vapour pressures and sublimation enthalpies of compounds of low vapour pressure (<100 Pa). Energies of intermolecular interaction between the molecules in the solid phase, depending on the structure, size and polarity of the molecules, can be related to the enthalpy of sublimation. Limited information about the enthalpy of sublimation and vapour pressure of the above mentioned polyols is found in the literature. We have found results only for pentaerythritol [5,6]. The knowledge of these values can allow us to determine the contribution of hydrogen bonds, which are always present in this type of compound, to the cohesive energy of the lattice [7].

The enthalpy of sublimation can be obtained by a direct measurement or from the derivative of the vapour pressure as a function of temperature [8]. The disadvantage of the latter indirect method is that the experimental error in vapour pressures is enhanced by differentiation.

In this study we have measured the enthalpy of sublimation by means of a calorimetric system (direct method) using a Knudsen effusion cell. Simultaneously, vapour pressures have been determined from the rates of effusion. The effusion Knudsen method is the most suitable for compounds with low volatility [8] such as the polyols in our study.

2. Experimental

2.1. Calorimetric set-up

The calorimeter used in these measurements is a new design based on that we have already used widely [9]. It comprises a cylindrical block of copper (65 mm in diameter and 54 mm high) in which are placed, in the bottom of two symmetrical holes (12.2 mm diameter and 30 mm deep), two thermoelectric modules (Melcor FC06-32-06L) connected in opposition. Thus we measure a differential signal between two identical Knudsen effusion cells (stainless-steel cylinders, 11.9 mm and 12.1 mm in internal and external diameter and 25 mm high) placed on these thermopiles, using a small quantity of Apiezon L grease to assure good thermal contact. One of these cells contains the sample for sublimation and the other one holds a reference substance (SiC) to equilibrate the heat capacity values. The sublimation rate can be regulated by use of different effusion orifices. The aluminium sheet used in this work has a thickness $L = 0.15$ mm and an orifice diameter $d = 0.45$ mm. A cover with a hole of diameter 1 mm is screwed to the cell. A Viton O-ring serves to seal the cylinders.

The temperature is measured with a Pt-100 calibrated probe placed at the axis of the block. The block is heated by an electrical resistance surrounding it. The temperature of the calorimeter is controlled by means of an electronic system with a resolution of 0.05 K.

The thermopiles show high sensitivity to changes in temperature ($k_H = 409$ mV W^{-1} at 311 K, determined in calibration by the Joule effect) [10]. The upper usable temperature limit is 400 K. Another type of thermoelectric sensor (TNO WS-21 HT) with smaller sensitivity ($\approx$100 mV W^{-1} at room temperature) could be used in order to extend this limit to 473 K [1].

We acquire the differential signal ΔT (without amplification) with a Keithley 181 nanovoltmeter (10 nV resolution). The temperature T is measured with an HP 3478A microvoltmeter (1 mΩ resolution). Numerical data acquisition is performed via the IEEE-488 interface with a sampling period of 10 s.

2.2. Vacuum system

A stainless-steel cylindrical chamber (300 mm in diameter and 150 mm high) is coupled to a vacuum system consisting of a mechanical rotatory pump (primary vacuum) and a turbomolecular pump (type 5150 with CFF 450 turbo, flow rate 140 l s^{-1}). This system allows us to reach a vacuum of $< 10^{-4}$ Pa (high vacuum system). The pressure inside the chamber is measured with a CFA 212 gauge (Pirani scale 0.5–2000 Pa, Penning scale 10^{-4} to 0.1 Pa). The calorimeter is placed inside the chamber and isolated from its base with a ceramic material. A scheme of the calorimetric set-up coupled to the vacuum system is given in Fig. 1.

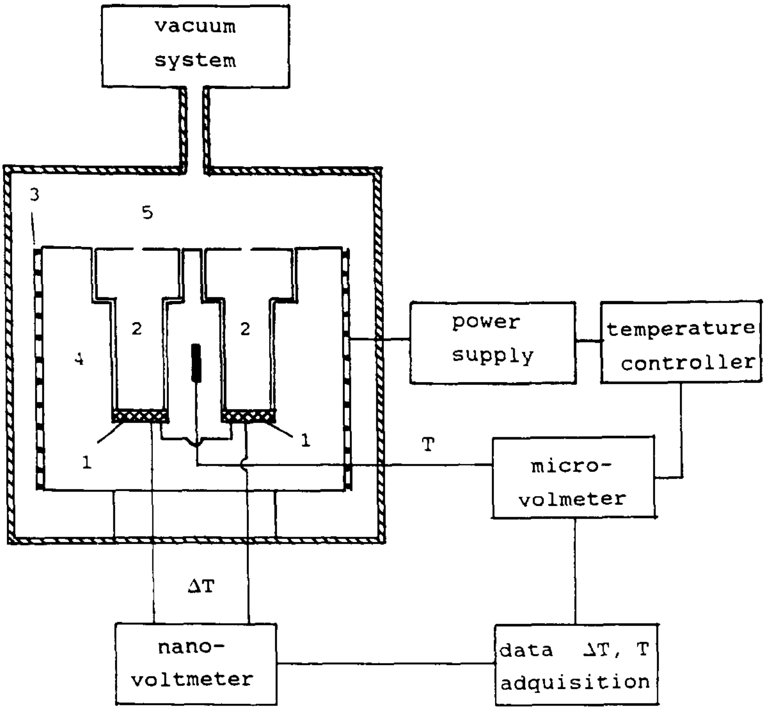

Fig. 1. Scheme of the calorimetric set-up: 1, thermoelectric modules; 2, Knudsen effusion cells; 3, electrical resistance; 4, calorimeter; 5, stainless-steel vacuum chamber.

2.3. Procedure

Working in isothermal mode, a mass of substance between 50 and 250 mg (depending on the sublimation rate) is placed in the sample cell and introduced into the calorimeter. The measurement is finished when the sample mass has completely effused. The masses are determined with a resolution of 0.01 mg. The sublimation process is detected as an endothermic differential signal. Approximately 30 min after the beginning of the sublimation, we observe in the thermogram a constant value of the calorimetric signal (stationary isothermal period). When the substance has completely evaporated, this signal decreases quickly to zero. The pressure in the chamber is practically constant 3 min after the start of the sublimation. Taking into account that the minimum time of measurement is ≈ 3 h, we accept that the effusion rate remains constant during the experiment. The thermal signal obtained in the first 30 min (dynamic period) is caused by the start-up of the vacuum system and is much amplified because of the high sensitivity of the thermopiles. In the early measurements we tried to eliminate this effect on the signal by sealing the effusion orifice with a plug located by a rod. Unfortunately, the contact between the cover of the effusion cell and the stopper seal caused displacement of the base-line of the thermogram. Finally, taking into account that this displacement was not repeatable, we decided to keep the effusion cell open and to stop the measurement when the sample mass had completely sublimed. The enthalpy of sublimation is obtained from the area of the thermogram in the stationary period, that is, when the effect of the start-up of the vacuum system has disappeared. The zero value of the signal obtained when all the mass has been evaporated confirms that the effect detected in the stationary period is due only to the sublimation process, taking into account that our measurements are of differential form. This kind of procedure has also been used by Sabbah et al. [11].

In order to obtain a more accurate value of the calibration constant k_H, we used the sublimation process of naphthalene at 311.3 and 318.6 K (the temperature of the measurements). This compound is recommended by IUPAC as a standard reference material at 298.15 K [12], but it has been widely studied and accurate values at different temperatures can be found in the literature [13,14]. The calibration was performed with the same experimental conditions as for the measurements (temperature, pressure in the sublimation chamber, effusion orifice diameter). The reproducibility in the areas taken from the thermogram was $\approx 2\%$. We applied Eq. (1) to determine the values of the enthalpy of sublimation ΔH from those of the measured heat ΔE [15].

$$\Delta H = \Delta E + \delta\Delta H = \Delta E + (1 - P_i/P_{\text{sat}})RT \qquad (1)$$

where P_i is the pressure in the chamber during the sublimation process, P_{sat} is the vapour pressure at temperature T and R is the ideal gas constant.

The vapour pressure is determined from the sublimation rate dm/dt by means of the equation of Knudsen molecular effusion [7,8]

$$P_{\text{sat}} = \frac{(2\pi RT/M)^{1/2}\, dm/dt}{k_P} \qquad (2)$$

where M is the molar mass and k_P is a constant depending on geometrical factors. This last constant is equal to SW, where S is the surface of the effusion orifice and W is the Clausing factor [16]. Taking into account the difficulty in measurement of S owing to the small orifice diameter, we used the values of the vapour pressure of naphthalene, as widely reported [17,18], for determination of the constant k_P. The reproducibility of our values of $\mathrm{d}m/\mathrm{d}t$ varied between 2% and 3%.

2.4. *Materials*

The polyol we studied, neopentyl glycol (NPG; $(CH_3)_2C(CH_2OH)_2$, $M = 104.15$ g mol^{-1}), was obtained from Aldrich (purity 99%). We submitted NPG to a drying process by melting. The transition in the solid state between the crystalline and plastic phases of NPG takes place at 314.6 K, with an enthalpy change of $\Delta H_{s \to p} = 122.6$ J g^{-1} [19].

The determination of the enthalpies of sublimation and the vapour pressures in the crystalline and plastic phases was performed at 311.3 and 318.6 K respectively.

The naphthalene used in the calibration was obtained from Aldrich (scintillation grade, 99 + %) and was subjected to additional purification by sublimation at 315 K.

3. Calibration

We determined the calibration constants k_H and k_P, making five sublimation measurements of naphthalene at each temperature. The masses ranged between 50 and 300 mg. The sublimation time t varied between 3 and 20 h. No dependence of this time on the effusion rate was observed. This fact confirms the above assumption that the dynamic period of the thermogram has no significant influence on $\mathrm{d}m/\mathrm{d}t$.

3.1. *Calibration at* T = *311.3 K*

The average value of $\mathrm{d}m/\mathrm{d}t$ was 48.7 mg h^{-1}. The inlet pressure in the sublimation chamber (P_i) was 5.0 mPa. The vapour pressure of naphthalene was 37.83 Pa (the values of the vapour pressure of naphthalene were obtained by interpolation from those in Ref. [17]). The enthalpy of sublimation was 562.4 J g^{-1} [13]. The correction term $\delta\Delta H$ was 20.2 J g^{-1}. With these values, we obtained $k_H = 405$ mV W^{-1}.

3.2. *Calibration at* T = *318.6 K*

The corresponding values at this temperature were: $\mathrm{d}m/\mathrm{d}t = 89.8$ mg h^{-1}; $P_i = 10$ mPa; vapour pressure of naphthalene = 71.70 Pa [17]; enthalpy of sublimation = 561.3 J g^{-1} [13]; $\delta\Delta H = 20.6$ J g^{-1}; $k_H = 394$ mV W^{-1}.

The values of k_H are of the same order as those determined in calibration by means of the Joule effect [10]. The discrepancies of 1% and 5% at 311.3 and 318.6 K respectively can be explained taking into account that the experimental conditions are different (crucibles, vacuum and thermal effect used in the calibration).

At 318.6 K, $\mathrm{d}m/\mathrm{d}t$ is within the limit of effusion rates recommended [8]. In order to determine k_P accurately, we measured $\mathrm{d}m/\mathrm{d}t$ at 296.0 K, obtaining a value of 11.5 mg h^{-1}. Taking into account the vapour pressure of naphthalene at this temperature (8.94 Pa [17]) we obtained $k_P = 126 \times 10^{-3}$ mm^2 as the average value of the measurements performed at 311.3 and 296.0 K. This result agrees with that calculated using the Clausing factor: $SW = 127 \times 10^{-3}$ mm^2, with $W = 0.800$ for $2L/d = 0.666$ [16].

4. Results and discussion

As an example, we present in Fig. 2 a thermogram corresponding to the sublimation of NPG at 318.6 K. Five measurements were carried out at each temperature. The average results are included in Table 1.

Taking into account the reproducibility of the values of $\mathrm{d}m/\mathrm{d}t$ and of the thermogram area, as well as the influence that the temperature resolution has on the calibration values (mainly on the vapour pressure of naphthalene), we estimate errors of 5% and 7% in the results for enthalpy and pressure respectively.

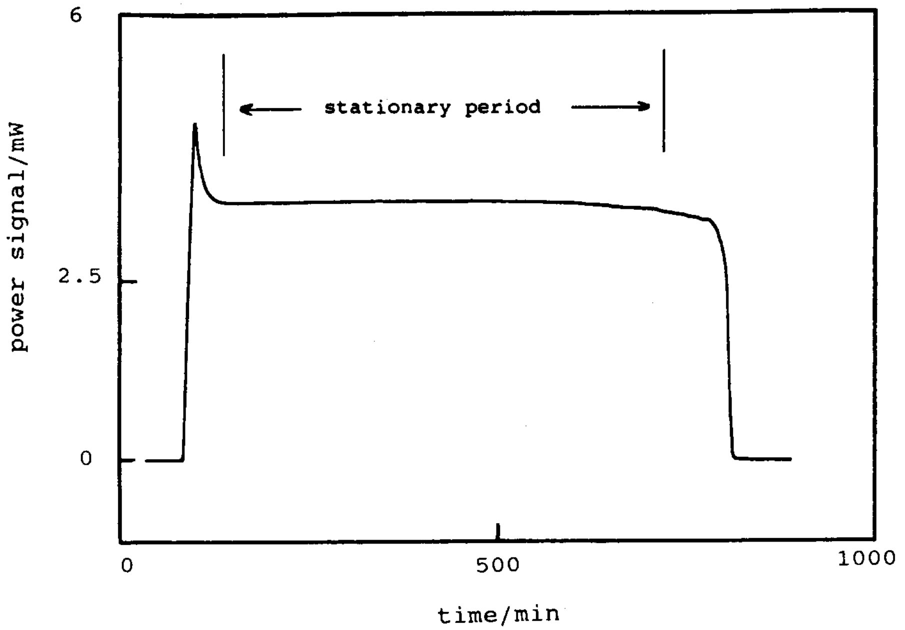

Fig. 2. Thermogram corresponding to sublimation of 210.80 mg of NPG at 318.6 K.

Table 1
Results of enthalpy of sublimation and vapour pressure of NPG at 311.3 and 318.6 K

	$T = 311.3$ K	$T = 318.6$ K
t (h)	12–17	4–12
(dm/dt) (mg h^{-1})	7.5	17.5
P_i (Pa)	2.0×10^{-3}	4.5×10^{-3}
ΔE (J g^{-1})	816	700
ΔH (J g^{-1})	841	725
P_{sat} (Pa)	6.6	15.4

The enthalpies of sublimation of the solid and the plastic phases can be related by the expression

$$\Delta H\ (318.6\ \mathrm{K}) = \Delta H\ (311.3\ \mathrm{K}) + \int_{311.3\ \mathrm{K}}^{314.6\ \mathrm{K}} [C_P(\mathrm{g}) - C_P(\mathrm{s})]\mathrm{d}T - \Delta H_{\mathrm{s}\to\mathrm{p}} + \int_{314.6\ \mathrm{K}}^{318.6\ \mathrm{K}} [C_P(\mathrm{g}) - C_P(\mathrm{p})]\mathrm{d}T \qquad (3)$$

where C_P is the heat capacity of the solid (s), plastic (p) and gas (g) phases. Taking into account that the integral limits are very close, we assume that Eq. (3) may be rewritten in the form

$$\Delta H\ (318.6\ \mathrm{K}) = \Delta H\ (311.3\ \mathrm{K}) - \Delta H_{\mathrm{s}\to\mathrm{p}} \qquad (4)$$

From the values of Table 1 we obtain a difference between the enthalpies of sublimation of the solid and plastic phases of 116 J g^{-1}. The difference between this value and that corresponding to the transition from solid to plastic phase (122.6 J g^{-1}) determined by DSC [19] is 5% and so, taking into account the error estimated for ΔH measurements, we can conclude that the two results are in agreement.

5. Conclusions

We have designed and constructed a calorimetric system in order to carry out simultaneous measurements of enthalpies of sublimation and vapour pressures of compounds of low volatility. The high sensitivity of the thermoelectric modules used in our calorimeter makes it possible to detect small thermal effects. Thus measurements at very low effusion rates, the most suitable in order to approach thermodynamic equilibrium, can be realized. The results from the first measurements allow us to expect an accuracy of 5% in enthalpy and 7% in pressure values for compounds showing volatility similar to that of the materials studied in the present work.

We have determined for neopentyl glycol (NPG) $\Delta H = 841$ J g^{-1}, $P_{sat} = 6.6$ Pa at 311.3 K (crystalline phase) and $\Delta H = 725$ J g^{-1}, $P_{sat} = 15.4$ Pa at 318.6 K (plastic phase).

The purpose of our future research will be to apply this calorimetric system to plastic crystals derived from neopentane in order to elucidate the influence that different groups in the molecule have on the lattice energy.

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