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A NEW METHOD FOR THE MEASUREMENT OF ENTHALPIES OF SUBLIMATION USING DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The enthalpies of sublimation of naphthalene, benzoic acid and phenanthrene have been determined by isothermal operation of a DSC, coupled to a vacuum system. The results obtained by this method are in excellent agreement with those reported in the literature from established procedures. The precision obtained was found to be dependent on the rate of sublimation. This paper describes the experimental procedure, calibration, the corrections applied and comparison of the results, mainly with those obtained by dynamic experiments in DSC.

INTRODUCTION

Beech and Lintonbon [1] and Holdiness [2] reported the use of differential scanning calorimetry for the measurement of heats of sublimation within 15 and 5%, respectively, of the accepted literature values for substances such as naphthalene or benzoic acid.

The method of Beech and Holdiness consists of heating a sample contained in a capsule with a pinhole in the cover. Since for most of the cases the experimental temperature range was above the melting point, the measurement actually involves the vaporization of the sample and additional data for the heat of fusion were necessary in order to calculate the heat of sublimation. In addition it is not possible to assign the values of heat of sublimation obtained to a particular temperature. In this work we report a new method for the reliable measurement of heats of sublimation at one fixed temperature using a differential scanning calorimeter. The method is valid for instruments operating under the power compensation principle because the experiments are isothermal and the energy required to maintain

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the sample and reference at the same temperature is simultaneously recorded while the endothermal effect of the sublimation is manifested when the pressure is reduced.

EXPERIMENTAL

The substances used in this work are naphthalene (Merck) purified by zone melting (its purity was determined by DSC as 99.98 mol%); benzoic acid (39i from NBS) with a purity certificate of 99.997 mol%; and phenanthrene (Eastman) purified by sublimation (slight decomposition was observed during the fusion but the purity was estimated as better than 99.5 mol%).

The calorimeter was a Perkin–Elmer DSC-1B coupled to a vacuum system consisting of a mechanical pump, one pressure regulator (Gilmont C-2200-D), three bellow vacuum valves and one Pirani gauge (Balzers TPR-010). A digital multimeter (HP-3478A) controlled by an HP-85B microcomputer was connected to the calorimeter for automatic data collection.

In this system the residual pressure could be controlled between 0.5 and 3 kPa. The lowest temperature attainable for good power compensation response is 323 K if room temperature is maintained at 293 K. Beyond these limits the pilot light turns off.

Sublimation cells were constructed using conventional aluminium sample pans. Covers with a sublimation hole (diameter 4.6 mm) were made from copper foil (thickness 0.15 mm). The cover was carefully bonded to the pan using a small amount of epoxy resin. The diameter of the hole was chosen as the most suitable, after several trials.

The rate of the sublimation process must be controlled by a good choice of the experimental temperature and residual pressure. If the sublimation is too slow, flat and large calorimetric curves are obtained and the baseline extrapolation may be inaccurate. Alternatively, if the sublimation is too fast, high and narrow ballistic curves are produced and non-reliable power compensation response from the calorimeter is observed. A sublimation rate of 1×10^{-5} g s^{-1} for samples of about 5 mg and calorimetric sensitivity of 33.5 mJ s^{-1} was found most convenient.

In a typical experiment the procedure was as follows: the samples were placed in the sublimation cells and then carefully melted by the proximity of a small soldering iron; immediately thereafter the cells were cooled over a metallic block in order to prevent decomposition. The sample-containing cells were weighed on an electronic microbalance (Sartorius 7704), placed in the sample holder assembly using an empty sublimation cell as reference. The working temperature was chosen and thermal equilibrium was allowed to be reached and recorded for a few minutes. The valve to the vacuum

TABLE 1

Experimental results of enthalpy of sublimation

Experiment	$\Delta_{sub}H_m^\ominus$ (kJ mol^{-1})		
	Naphthalene [a] at 323 K	Benzoic acid [b] at 335 K	Phenanthrene [b] at 350 K
1	70.23	87.61	87.7
2	70.63	87.66	85.9
3	71.18	87.41	86.3
4	70.83	87.66	88.5
5	71.12	87.81	88.0
6	70.40	87.38	86.0
7	70.53	87.50	88.2
8	70.97	87.17	85.9
9	71.25	86.64	86.9
10	71.39	87.71	88.6
Mean	70.85 ± 0.39 [c]	87.45 ± 0.34	87.24 ± 1.1

[a] Residual pressure = 3 kPa.

[b] Residual pressure = 50 Pa.

[c] Uncertainties represent one standard deviation.

controller was then opened and the sublimation process started. After about eight minutes, the final baseline was approached.

RESULTS

Enthalpies of sublimation were calculated by integration of the calorimetric curves using Simpson's method with about 125 points. Additional experiments were performed in order to evaluate the thermal effect of expansion, which was found to be negligible relative to the thermal effect of sublimation. Corrections were applied for the mass loss that occurs between the time that the cell is weighed and the time at which the sublimation is started; this correction is in reality most significant in the case of naphthalene. A further correction factor of 1.058 ± 0.002 was applied to the total energy; this factor is based on the reported enthalpy of fusion [3] of high purity indium of 3283 ± 7 J mol^{-1}; no significant deviations of this factor were observed during our experiments.

DISCUSSION

In order to make a fair comparison of our results with the accepted values reported in the literature, we have corrected them from the experimental

TABLE 2

Enthalpies of sublimation for naphthalene

Reference	Method	T (K)	$\Delta_{\text{sub}}H_{\text{m}}^{\ominus}(T)$ (kJ mol^{-1})	$\Delta_{\text{sub}}H_{\text{m}}^{\ominus}$(298.15 K) (kJ mol^{-1})
6	Calorimetry			72.1 ± 0.3
7	Calorimetry			73.0 ± 0.3
8	Calorimetry			73.2 ± 1
9	Diaphragm manometer			72.5 ± 0.2
10	Diaphragm manometer			72.5 ± 0.1
4	Torsion-effusion	267.88	74.4 ± 0.5	72.6 ± 0.6
11	Effusion	278	73.93 ± 0.29	72.8 ± 0.3
12	Recommended value			72.5 ± 0.25
1	DSC	355–490	78 ± 2	
2	DSC	Not specified	72.59 ± 0.42	
This work	DSC	323	70.85 ± 0.39	72.32 ± 0.40

temperature T to 298.15 K, using the temperature coefficients of the enthalpy of sublimation, $\Delta C_{\text{p}} = C_{\text{p}}(\text{g}) - C_{\text{p}}(\text{s})$ [4,5] as: naphthalene, -59 ± 5 J K^{-1} mol^{-1}; benzoic acid, -48 ± 5 J K^{-1} mol^{-1}; phenanthrene, -73 ± 25 J K^{-1} mol^{-1}. The results of this work and those from other workers are collected in Tables 2, 3 and 4 for comparison. These tables show an excellent agreement between our results and those in the literature (both calorimetric

TABLE 3

Enthalpies of sublimation for benzoic acid

Reference	Method	T (K)	$\Delta_{\text{sub}}H_{\text{m}}^{\ominus}(T)$ (kJ mol^{-1})	$\Delta_{\text{sub}}H_{\text{m}}^{\ominus}$(298.15 K) (kJ mol^{-1})
6	Calorimetry			89.5 ± 0.2
13	Calorimetry			89.7 ± 0.6
14	Calorimetry	360	86.18 ± 0.33	88.83 ± 0.42
5	Diaphragm manometer	353.15	89.45 ± 0.05	92.106 ± 0.250
15	Thermal conductivity manometer	304	88.1 ± 0.2	
16	Mass loss effusion	313	92.5 ± 0.5	
10	Effusion	303.4	90.35 ± 0.13	90.6 ± 0.2
12	Recommended value	298.15		89.7 ± 0.5
1	DSC	420–480	100 ± 5	
2	DSC	Not specified	89.5 ± 0.4	
This work	DSC	335	87.45 ± 0.34	89.23 ± 0.95

TABLE 4

Enthalpies of sublimation for phenanthrene

Reference	Method	T (K)	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}(T)$ (kJ mol^{-1})	$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\ominus}$ (298.15 K) (kJ mol^{-1})
6	Calorimetry	298.15		89.5 ± 0.17
4	Torsion-effusion	325.03	90.5 ± 1	92.5 ± 2
17	Knudsen-effusion	315	90.6 ± 1.2	
18	Knudsen-effusion	317	86.9 ± 0.8	
This work	DSC	350	87.2 ± 1.1	90.9 ± 1.7

and from vapour pressure measurement). Nevertheless it is clear that no comparison is possible with the DSC values obtained by other workers by dynamic experiments. For example, the value of 78 ± 2 kJ mol^{-1} reported for naphthalene by Beech and Lintonbon [1] is excessively high if we consider that the mean temperature of measurement was 422 K (the same is valid for benzoic acid).

In conclusion, high precision values for the enthalpy of sublimation can be obtained when the isothermal method described above is used.

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