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**Note**

# The measurement of sublimation enthalpies by differential scanning calorimetry

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Heats of vaporisation and sublimation are usually obtained from measurements of vapour pressures or mass loss, or from rates of transpiration. These methods are all time-consuming and, since they are indirect, may lead to inaccuracies[1]. A small number of direct measurements have been made using conventional calorimetry[2].

Differential scanning calorimetry (DSC) has been used with considerable success in the measurement of enthalpies of phase transformations and of chemical decompositions[3], but it has so far failed to produce reproducible and accurate results for sublimation enthalpies[4]. It is thought that this is due to the condensation of evolved material on to cooler parts of the sample holder assembly.

We have attempted to overcome this difficulty by minimising temperature gradients within the sample pan such that re-condensation of the sample has been virtually eliminated.

## EXPERIMENTAL

A Perkin-Elmer differential scanning calorimeter (DSC-1B) was used for this work. Samples ($<5$ mg) were placed in aluminium pans and the space between the pan and a domed aluminium cover was filled with fine aluminium powder. The cover was pierced to permit the evolved material to escape. It was important to ensure that the three metal components were in intimate contact to minimise temperature gradients.

The sample enclosure was purged with nitrogen gas throughout the experiments. The heat of fusion of ferrocene was determined by the use of sealed volatile-sample pans.

Heating rates were chosen between 8 and 32 $K \cdot min^{-1}$. The higher rates sometimes aided the separation of fusion and vaporisation. Uncertainties are expressed as standard deviations of the mean.

## RESULTS AND DISCUSSION

A number of compounds which appeared to have well-defined thermochemical properties were studied. With the exception of ferrocene and anthracene, each of

TABLE I

HEATS OF FUSION, VAPORISATION, AND SUBLIMATION

| *Compound* | *Heating rate* $(K \cdot min^{-1})$ | $\Delta H_{fus}$ | $\Delta H_v$ $(kJ \cdot mol^{-1})$ | $\Delta H_{sub}$ | *Temp. range of vaporisation (K)* | *Literature value,* $\Delta H_{sub}$ $(kJ \cdot mol^{-1})$ | *Quoted temp. or temp. range of literature value measurement (K)* |
|---|---|---|---|---|---|---|---|
| Benzoic acid | 8, 16, 32 | | | 100 ±5 | 420–480 | 91.5[5] | 343–387 |
| | | | | | | 89.1[6] | 299–329 |
| Anthraquinone | 32 | | | 127 ±3 | 470–590 | 112.0[7] | 298 |
| Phthalic anhydride | 16 | | | 81 ±1(.5) | 390–470 | 88.7[8] | 303–333 |
| Thymol | 16 | 20.5 ±0.6 | 46.5 ±3.0 | 67.0 ±3 | 420–480 | 91.3[9] | 273–313 |
| | | | | | | 69.0[6] | 299–312 |
| Ferrocene | 16, 32 | 18.5 ±0.1 | 65.5 ±2 | 84 ±2 | 385–455 | 73.4[10] | 298 |
| | | | | | | 85.3[11] | 298 |
| Anthracene | 16 | | | 126 ±4 | 420–540 | 97.6[12] | 338–353 |
| | | | | | | 98.6[13] | 342–359 |
| Naphthalene | 16 | 18.9 ±0.2 | 59 ±2 | 78 ±2 | 355–490 | 62.0[14] | 298 |
| | | | | | | 72.7[15] | 298 |
| 8-Hydroxy quinoline | 16 | 22.1 ±0.4 | 68 ±3 | 90 ±4 | 355–450 | 109[16] | 308–328 |

the compounds melted prior to vaporisation. In Table I heats of fusion ($\Delta H_{fus}$) vaporisation ($\Delta H_v$) and sublimation ($\Delta H_{sub}$) are shown and the latter compared with previously established values.

The results obtained were in general within ±15% of the literature values with the exception of those of thymol and of anthracene. In the case of thymol the more recent unpublished result[6] is in close agreement with that reported here. The high result obtained for anthracene may be due to the facile crystallisation of this compound from the vapour phase.

The enthalpy changes reported here were obtained in the temperature ranges quoted in Table I. It is possible to correct these to a standard temperature by various empirical methods[17].

This modified method of sample enclosure has extended the usefulness of differential scanning calorimetry to yield heats of vaporisation and sublimation of moderate accuracy. One of the main advantages of the technique is the rapidity with which such results may be obtained.

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