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Note

The measurement of enthalpies of sublimation by thermogravimetry

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The measurement of enthalpies of sublimation, ΔH_{sub}, by direct calorimetry or indirectly by vapour pressure determinations is time-consuming, and frequently requires specialised equipment. Beech and Lintonbon[1] have recently described a rapid method for thermally stable compounds which uses a differential scanning calorimeter. This note reports an equally rapid thermogravimetric method for use with less volatile or less thermally stable substances.

Langmuir[2] showed that the rate of sublimation, *in vacuo*, m, per unit area of substance is related to the vapour pressure, p, by the equation

$$m = \alpha(M/2\pi RT)^{\frac{1}{2}}p$$

where M is the molar mass of the gaseous substance, T is the Kelvin temperature and α is a sublimation coefficient usually assumed to be unity. Application of the Clausius–Clapeyron equation to a sublimation process during which the surface area of the sample is constant, shows that a plot of $\log_{10}[m(T)^{\frac{1}{2}}]$ against $10^3/T$ has a slope of $-0.0522\Delta H_{sub}$, from which ΔH_{sub} may be calculated in kJ.

EXPERIMENTAL

A DuPont Model 950 thermogravimetric analyzer was used to measure the sublimation rate m, but any thermogravimetric equipment with facilities for isothermal and vacuum operation could also be used. Rates of mass loss of a powdered 50–100 mg sample, contained in a platinum boat, were recorded at a series of five or six constant temperatures over a 20–30 degree range. The recordings were made at the maximum ordinate sensitivity of 0.2 mg inch^{-1} for 5–10 min at each temperature until a constant rate was obtained. By choosing the temperature to give low rates of mass loss and low (<2%) overall loss, good straight line Clausius–Clapeyron plots were obtained from which the slopes, calculated by the least squares method, were reproducible to about 5%. Under these low sublimation conditions the sample surface area presumably remains fairly constant. If total losses rose above about 5%, curvature of the plots became apparent.

The materials were mainly of analytical grade and were used without further purification. The anthraquinones were laboratory grade materials which gave no residue on complete sublimation. Benzoic acid was N.B.S. calorimetry standard. Dr. G. Beech of Wolverhampton Polytechnic kindly supplied samples of the acetylacetonates for which analytical data will shortly be published[3]. Analysis of the sublimates showed no evidence of sample decomposition except for a barely detectable amount of Mn^{II} complex formed during the sublimation of $[Mn(acac)_3]$. The reported enthalpy of sublimation for this complex will therefore be a maximum value. A number of compounds such as anthracene, naphthalene, and ferrocene, with established sublimation enthalpies, were too volatile for study by the present method.

RESULTS AND DISCUSSION

The measured sublimation enthalpies are reported in Table I in comparison with literature data. There is fair agreement between the two series of values for the first five compounds, although some variations may be expected from the different temperature ranges of the measurements. In many cases the thermogravimetric method yields results at lower temperatures than the other techniques.

TABLE I

ENTHALPIES OF SUBLIMATION IN kJ mol^{-1}

Compound[a]	ΔH_{sub}	*Temp. range (°K)*	*Literature* ΔH_{sub}	*Lit. temp. range (°K)*	*Ref.*
Anthraquinone	105·9	335–356	112·0	298	4
			127	470–590	3
			106·2	428	5
1,4-Dihydroxyanthraquinone	94·5	324–351	103·6	408	5
1,8-Dihydroxyanthraquinone	96·5	335–356	105·9	405	5
1-Aminoanthraquinone	90·9	361–386	113·8	461	5
Benzoic acid	89·1	299–329	91·5	343–387	6
			100	420–480	3
Thymol	69·0	229–312	91·3	273–313	7
			67·0	420–480	3
$[Sc^{III}(acac)_3]$	97·2	335–361	169	445–555	3
			99·6	389	8
			49·8	377–387	9
$[Cr^{III}(acac)_3]$	85·9	335–356	125	490–595	3
			110·9	397	8
			27·8	389–397	9
$[Mn^{III}(acac)_3]$	117·3[b]	335–356	77·8	383–391	9
$[Fe^{III}(acac)_3]$	114·9	335–356	116	452–535	3
			99·0	391	8
			65·3	378–388	9
			23·4	~ 393	10
$[Co^{III}(acac)_3]$	86·3	335–361	74·9	378–393	9
$[Cu^{II}(acac)_2]$	106·1	335–361	57·3	475–560	3

[a]acac refers to acetylacetonate. [b]Probably a maximum value.

The thermal properties of acetylacetone complexes have recently been studied by Beech and Lintonbon[3]. It seems likely that the sublimation enthalpies reported by Jones *et al.*[9,10] are too low. The remaining data are still not entirely consistent, possibly owing to some temperature dependent vapour phase association of the complex molecules.

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