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Vapor pressure determination by thermogravimetry

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Abstract

A method for measuring the vapor pressures of a wide range of materials using a conventional thermobalance and standard sample holders is described. The equipment is calibrated using pure reference materials of known vapor pressure and exploiting the relationship between volatilization rate and vapor pressure based on the Langmuir equation for free evaporation. Enthalpies of vaporization and sublimation can be determined, in some cases, the melting temperature and enthalpy of fusion can be obtained directly from thermogravimetry. Applications to the study of plasticizers and UV absorbers are described. Poor correlation of experimental results with predicted values obtained by molecular modeling is found. The application of modulated temperature thermogravimetry for the determination of enthalpies of sublimation and vaporization is also explored.

Keywords: Bisphenol-A; Dioctyl phthalate; Modulated temperature thermogravimetry; Sublimation; UV absorber; Vapor pressure; Vaporization

1. Introduction

The tendency of a substance to enter the vapor phase by sublimation (solid → gas) or evaporation (liquid → gas) is defined by its vapor pressure. Knowledge of this parameter is crucially important for a wide variety of materials. For example, the atmospheric accumulation of toxic compounds such as pesticides and pharmaceuticals is highly undesirable therefore it is essential to use compounds with a low vapor pressure [1]. The loss of additives such as plasticizers and UV absorbers from a polymer by diffusion and evaporation from the surface leads to an unwanted reduction in their efficiency [2]. On the other hand, controlled volatilization may be beneficial for the activity of fragrances [3].

On a more fundamental level, the enthalpy of vaporization (ΔH_{vap}) of a substance can be used to calculate its solubility parameter (δ) from the relationship [4]

$$\delta = \sqrt{\frac{\Delta H_{vap} - RT}{V_m}} \quad (1)$$

where V_m is the molar volume.

The solubility parameter concept is useful in predicting whether or not two substances will mix (i.e. when the solubility parameters are similar). Frequently, the enthalpy of vaporization cannot be determined experimentally (e.g. for polymers) and the solubility parameter is calculated using a group contribution approach [5]. In addition, there are various methods for estimating the vapor pressures of materials from their molecular structure [6]. Many of these procedures have been implemented in computer molecular modeling software [7,8].

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Although there are a number of literature compilations of vapor pressure data and enthalpies of sublimation and vaporization [9,10], for many substances, such information is not available and the investigator either has to resort to prediction or direct measurement. As will be demonstrated, molecular modeling often gives unreliable results yet direct measurement using conventional equipment is neither inaccurate nor onerous.

2. Theory

Nesmayanov [11] has reviewed some of the methods for the determination of vapor pressures together with the pressure ranges over which they operate. One of the most popular of these methods is that devised by Knudsen [12,13] which involves the measurement of the rate of loss of molecules of the evaporating substance leaving a small orifice in an otherwise closed cell containing the substance of interest. Wiedemann [14] has described the adaptation of a commercial thermobalance to this technique. Goodrum and Seisel [15] have described using sealed DSC crucibles with laser drilled holes for similar measurements. This approach requires some means of operating the instrument at other than ambient pressure as do the pressure DSC techniques described by Cassel and co-workers [16–19]. Although Emmeneger and Piccand [20] have described a method for vapor pressure measurements using a standard thermobalance operated under ambient pressure, their technique requires a special crucible consisting of a bulb containing the sample fitted with a capillary tube. It would be much more convenient to employ standard instruments and readily available sample holders.

Gückel and et al. [21–24] have measured volatilization rates of pesticides at ambient pressure by isothermal thermogravimetry. Since sublimation and evaporation are zero-order processes, the rate of mass loss of a sample under isothermal conditions due to vaporization should be constant providing that the free surface area does not change [25]. Elder [26] has used the same technique to estimate the vapor pressures of pharmaceutical compounds. Both investigators correlated the rate of mass loss with vapor pressure using the behavior of materials of known vapor pressure as standards. Price and Hawkins [27] have shown that it is possible to use thermogravimetry to determine vapor pressures using the Langmuir equation for free evaporation in vacuo [28]:

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = p\alpha\sqrt{\frac{M}{2\pi RT}} \tag{2}$$

where $-\mathrm{d}m/\mathrm{d}t$ is the rate of mass loss per unit area, p the vapor pressure, M the molecular weight of the effusing vapor, R the gas constant, T the absolute temperature and α is the vaporization coefficient (usually assumed to be 1). Samples are prepared by placing them in parallel-sided crucibles so that a well-defined surface area was achieved. In the case of solid substances, the material is melted first to obtain a flat surface. Measurements can be made under isothermal and linear-rising temperature conditions using an inert atmosphere instrument purge under ambient pressure.

In the case of a material volatilizing into a flowing gas stream at one atmosphere rather than in vacuo, α can no longer be assumed to be unity. Rearranging Eq. (2) gives

$$p = kv \tag{3}$$

where $k = \sqrt{2\pi R}/\alpha$ and $v = (\mathrm{d}m/\mathrm{d}t)\sqrt{T/M}$.

A plot of p vs. v is follows the same trend for a series of compounds with known vapor pressure — regardless of chemical structure — provided that the sample does not associate in the solid, liquid or gas phase allowing the calibration constant k to be determined and thus the vapor pressures of unknown materials to be found [29].

The temperature dependence of the vapor pressure can be described by the Clausius–Clapeyron equation

$$\ln p = B - \frac{\Delta H}{RT} \tag{4}$$

where ΔH is the molar enthalpy of sublimation (ΔH_{sub}) in the case of a solid or the molar enthalpy of vaporization (ΔH_{vap}) in the case of a liquid.

Combining Eqs. (3) and (4),

$$\ln v = B - \frac{\Delta H}{RT} - \ln k \tag{5}$$

Thus the enthalpies of vaporization and sublimation can be found from the slope of a plot of $\ln p$ (or $\ln v$) vs. reciprocal absolute temperature [27]. Although it is desirable to be able to pre-melt solid samples in order

to obtain good vapor pressure data, Price et. al. [29] have shown that temperature-jump methods can be used to estimate ΔH_{sub} and ΔH_{vap} for substances which decompose on melting.

At the melting temperature T_m,

$$\Delta H_{sub}(T_m) = \Delta H_{vap}(T_m) + \Delta H_{fus}(T_m) \quad (6)$$

where ΔH_{fus} is the enthalpy of fusion.

If data can be obtained through the melting region, ΔH_{sub}, ΔH_{vap}, ΔH_{fus} and T_m can be measured directly by thermogravimetry [27]. It is also possible to estimate the boiling temperature (T_b) at normal atmospheric pressure of materials by extrapolating their vapor pressure vs. temperature curve until the pressure is 101 325 Pa. The validity of such predictions should always be questioned since many compounds decompose below their normal boiling temperature.

Over a wider temperature range, Eq. (4) cannot be used to model the vapor pressure curve and the Antoine equation is often used [30,31]:

$$\ln p = A' - \frac{B'}{\theta - C'} \quad (7)$$

where A', B' and C' are constants and θ is the temperature in °C. Furthermore, the enthalpies of sublimation and vaporization show temperature dependence due to the difference in heat capacities of the solid or liquid and the heat capacity of its vapor. This can be expressed by Kirchoff's law:

$$\Delta H(T_0) = \Delta H(T) + \int_{T_0}^{T} \Delta C_p(T)\,dT \quad (8)$$

where T_0 is a common reference temperature (usually 298.15 K) and ΔC_p is the C_p(vapor)–C_p(solid) (for sublimation) or C_p(vapor)–C_p(liquid) (for evaporation). It is often difficult to obtain good quality vapor pressure data over a wide enough temperature range in order to evaluate the temperature dependence of ΔH. Chickos et al. [32] suggest a method for heat capacity corrections to a standard state based upon studies of a wide range of materials. For sublimation and vaporization, they recommend that

$$\Delta H_{sub}(298.15\,K) = \Delta H_{sub}(T) + 0.0320(T - 298.15) \quad (9)$$

$$\Delta H_{vap}(298.15\,K) = \Delta H_{vap}(T) + 0.0540(T - 298.15) \quad (10)$$

when ΔH_{sub} and ΔH_{vap} are measured in kJ mol^{-1} and T is the temperature (K) at which the determination is made. The method of correction is still a "matter of taste or of experience" [33], but the underlying philosophy is always quoting, the temperature at which enthalpies were measured (or correcting them to a standard temperature and the method of correction) is essential for the comparison of thermodynamic data.

It should be noted that Doyle [34] considered the kinetic analysis of thermogravimetric data in 1961 with reference to the evaporation of octacylotetrasiloxane under dry nitrogen as a model zero order process. Ashcroft [35] has described the use of the Langmuir method for enthalpy of sublimation determinations in vacuo. Gulbransen and Brassart [36] employed the same approach for determining the vapor pressure of silicon using a high temperature vacuum thermobalance. Therefore, this type of study is hardly original but its routine application under more familiar conditions is still novel.

3. Experimental

The structure and sources of the UV absorbers described can be found in Ref. [37]. Technical grade *bis*(2-ethylhexyl)phthalate (commonly known as "dioctyl phthalate") was obtained from Exxon Chemicals. Re-sublimed benzoic acid and phenanthrene (Sigma–Aldrich, >99.99%) were used as received. A purified sample of bisphenol-A (4,4′-dihydroxydiphenyl-2,2-propane) was kindly supplied by Dr. Sergey Verevkin (University of Rostock).

Measurements were carried out using thermobalances made by TA Instruments. Two models of instrument were used: an older TGA 951 with a horizontal furnace and a more modern TGA 2950 with a water-cooled vertical furnace. The latter was used for measurements on dioctyl phthalate and the modulated temperature experiments described below. Both thermobalances were calibrated for temperature according to the method of Stewart [38] using indium, tin, bismuth and lead. The magnitude and linearity of the balance response was checked with standard milligram masses. Samples were placed in tared aluminum sample cups (internal diameter: 12.5 mm) of the type used for

DSC measurements.[1] The cup was filled completely with material which was then melted so that a known sample surface area was obtained. Liquid samples could be measured directly, although the formation of a curved meniscus meant that the free surface of evaporation was less well defined. In this case, pans with a larger surface area and/or made of a different material (such as the lids of stainless steel pressure resistant pans[2] or cylindrical platinum crucibles[3]) could be used to alleviate this problem. The sample thermocouple was kept as close as possible to the surface of the specimen in order to accurately record its temperature without interfering with the operation of the balance. Measurements were made under nitrogen for the TGA 951 (flow rate: 100 ml min^{-1}) and helium for the TGA 2950 (flow rate: 90 ml min^{-1} into the furnace and 10 ml min^{-1} through the balance assembly). Small variation of gas flow rate did not appear to affect the rate of mass loss. Measurements were carried out either under isothermal conditions at increasing temperatures, on continuous heating at 1°C min^{-1} or using modulated temperature programs described below. Observation of the rate of mass loss at a constant temperature served to check that the free surface area was not changing significantly and that thermal degradation of the sample was not occurring. Experience showed that the rate of mass loss could be resolved down to better than 25 mg min^{-1} m^{-2} during continuous heating. An order of magnitude improvement was obtained under isothermal conditions at the expense of longer measurement times.

Differential scanning calorimetry was performed using a TA Instruments 2920 DSC under nitrogen in order to determine the purity, melting temperatures and enthalpies of fusion of the UV absorbers and the sample of bisphenol-A. Samples were encapsulated in hermetically sealed aluminum pans in order to prevent loss of material. The instrument was calibrated for temperature and heat flow response according to the melting points and enthalpies of fusion of pure gallium, indium, tin and bismuth under the same conditions used to study the materials under investigation.

[1] Part number 900786.901 from TA Instruments, New Castle, DE.

[2] Part number 319-0218 from Perkin Elmer, Norwalk, CT.

[3] Part number 952018-906 from TA Instruments, New Castle, DE.

4. Results and discussion

At typical calibration curve obtained using benzoic acid and phenanthrene is shown in Fig. 1 using values for the vapor pressure of benzoic acid and phenanthrene taken from the literature [10,39–41]. Plots of p vs. v are linear for both compounds and lie on the same trend line. Due to the wide range of values shown, the data are plotted on a log–log scale although from Eq. (3) there is a linear relationship between the two parameters, from which k is found. The original work employed benzophenone and acetamide as additional calibration materials and showed that only in cases where chemical association of the vaporizing species occurs does the simple relationship between p and v break down [27]. Once the apparatus has been calibrated in this way, the vapor pressures of unknown materials can be measured. Vapor pressure data for dioctyl phthalate measured by thermogravimetry are shown in Fig. 2. The data were extrapolated outside of the measured region using Eq. (7). The measurements show good agreement with literature data on this material [42–45].

Over a more narrow temperature range, Eq. (4) can be used to estimate the enthalpies of vaporization and sublimation. Fig. 3 shows a plot of $\ln p$ vs. $1/T$ for 2,4,4′-trihydroxybenzophenone, a common UV absorber. The slopes of the plots above and below the melting temperature represent the enthalpy of vaporization and enthalpy of fusion of the compound. The intercept of two lines occurs at the melting temperature (209 ± 5°C) and enthalpy of fusion (30 ± 3 kJ mol^{-1}) can be found from the difference between ΔH_{sub} and ΔH_{vap} according to Eq. (6). These values compare favorably with those determined by DSC (198.5 ± 0.5°C and 34 ± 1 kJ mol^{-1}, respectively) [37].

Table 1 lists measured enthalpies of vaporization and estimated boiling points obtained from measurements of the vapor pressures of a series of UV absorbers [37]. The enthalpies of vaporization have been corrected to 25°C (298.15 K) according to Eq. (9). Alongside the data are given the calculated values obtained using a commercial molecular modeling package [8]. Correlation coefficients between the experimental and predicted values were 0.784 for ΔH_{vap} and −0.058 for T_b. Although the outcome of molecular modeling depends on the chosen method (in

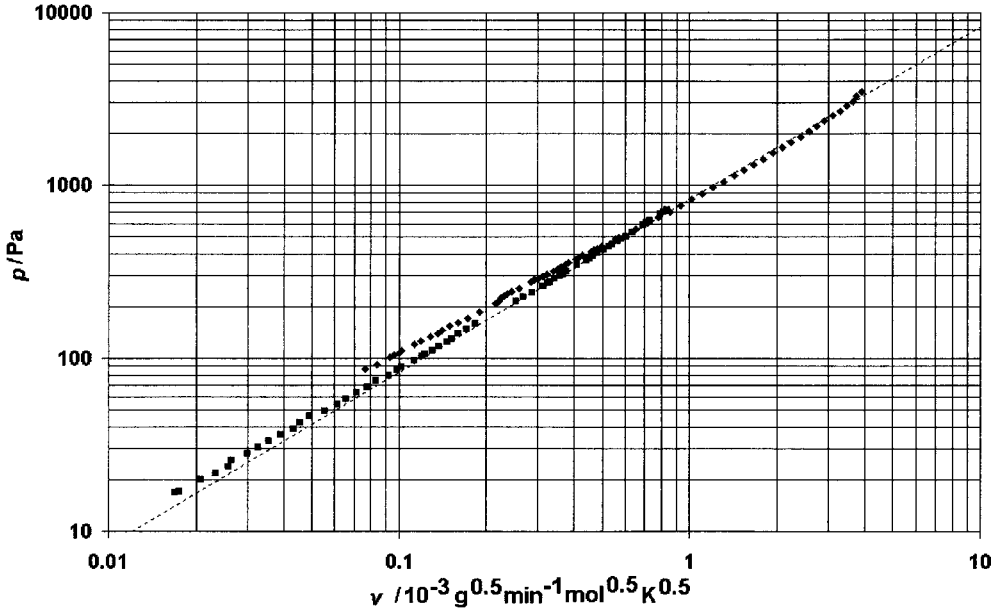

Fig. 1. Calibration curve using benzoic acid (■) and phenanthrene (◆).

this case from Ref. [6]), the results suggest that direct measurement is better than prediction.

If the material cannot be prepared as a specimen with a well-defined surface area, then it is not possible to use this technique to obtain reliable vapor pressure data. However, the enthalpies of sublimation and vaporization can still be found by the temperature-jump technique described by Flynn and Dickens [46]. An example of this is shown in Fig. 4 for benzoic acid. Measurements were carried out under stepwise-isothermal conditions of 15 min dwell time at 5°C increments. Excursions in the rate of mass loss occur during

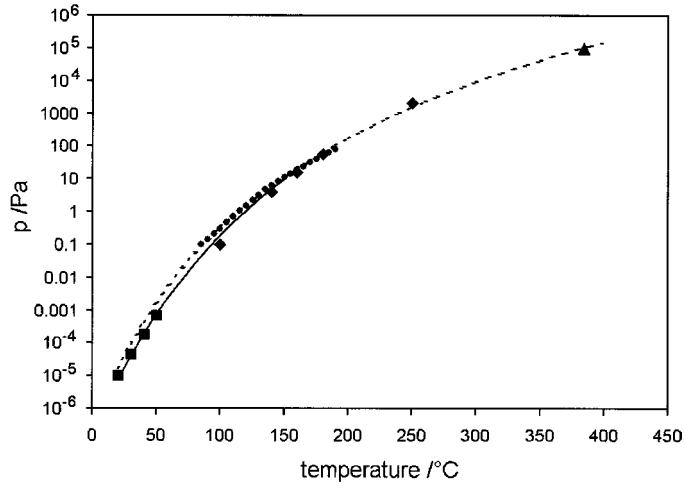

Fig. 2. Vapor pressure data for dioctyl phthalate ((●) measured, (◆) Wilson [42], (▲) Weast and Grasselli [43], (■) Davis et al. [44], solid line: Tang and Muckelwitz, broken line: fit of measured data to Eq. (7)).

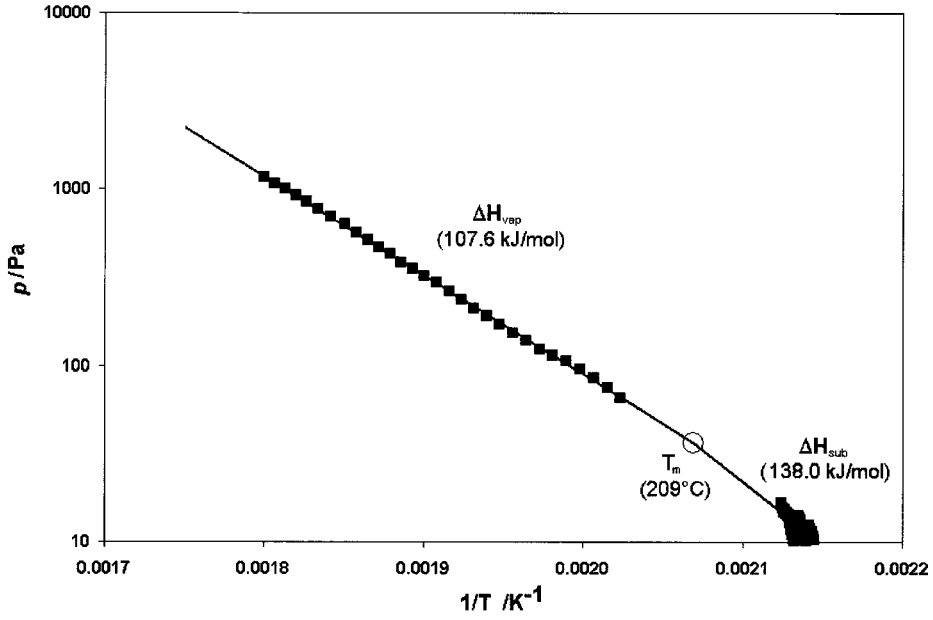

Fig. 3. Calculation of melting point and enthalpy of fusion from vapor pressure data for 2,4,4′-trihydroxybenzophenone.

each temperature-jump due to disturbance of the instrument. In addition, it can be seen that the rates of mass loss are not constant during each isothermal segment due to changing surface area of the specimen. In order to account for this, the rates of mass loss were determined at the point of the temperature-jump between isothermal plateaus by linear extrapolation. This gives dm/dt at two temperatures (T_1 and T_2) from which ΔH_{sub} may be obtained:

$$\Delta H_{sub} = R\left[\ln\left(\frac{(dm/dt)(T_1)\sqrt{T_1}}{(dm/dt)(T_2)\sqrt{T_2}}\right)\right]\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \quad (11)$$

Note that it is no longer necessary to know the mass of the vaporizing species provided that it does not change significantly during the change in temperature. This method has been used to measure the enthalpies of sublimation of a series of isomers of dihydroxybenzoic acid for studies into the mechanism of matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) [29]. The error in this type of determination amounts to about ±7%.

Finally, the potential of modulated temperature thermogravimetry [47] was investigated as a means of accurately determining the enthalpies

Table 1
Measured [37] and calculated (this work) enthalpies of vaporization (corrected to 25°C) and normal boiling temperatures of UV stabilizers

Compound	Measured		Calculated	
	ΔH_{vap} 25°C (kJ mol^{-1})	T_b (°C)	ΔH_{vap} (kJ mol^{-1})	T_b (°C)
2,4,4′-Trihydroxybenzophenone	119.56	413.5	172.7	396.3
2,4-Dihydroxy-4′-methoxybenzophenone	112.17	382.3	151.0	368.4
2,2′-Dihydroxy-4-methoxybenzophenone	89.18	354.3	151.0	368.4
2,2′,4,4′-Tetrahydroxybenzophenone	161.17	329.7	202.5	436.2
2-Hydroxy-4,4′-dimethoxybenzophenone	91.66	388.2	129.2	346.9
2,2′-Dihydroxy-4,4′-dimethoxybenzophenone	106.14	372.0	159.0	383.0
2-Hydroxy-4,4′-diethoxybenzophenone	108.92	364.1	139.1	372.4
2-Hydroxy-4-butoxy-4′-methoxybenzophenone	102.11	393.0	144.0	384.9
2-Hydroxy-4,4′-dibutoxybenzophenone	104.41	421.9	158.9	421.5

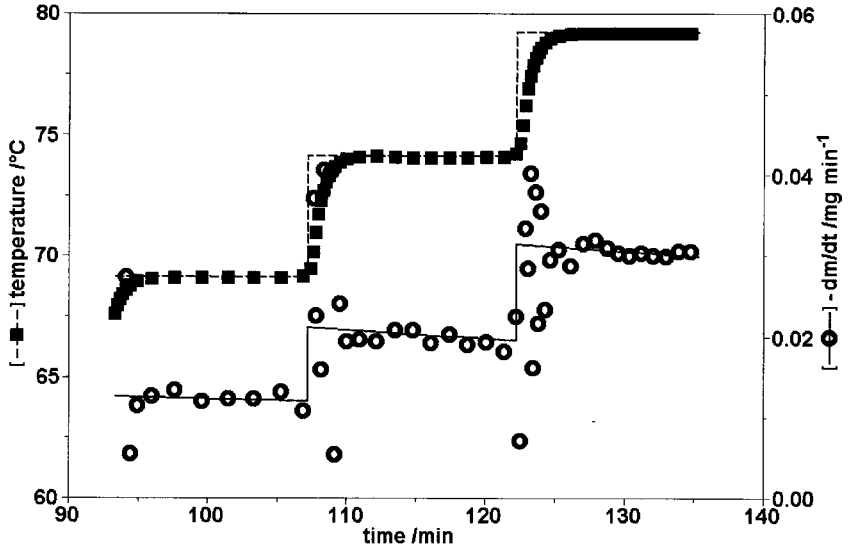

Fig. 4. Temperature (■) and rate of mass loss (○) vs. time for benzoic acid during a temperature-jump experiment. Solid and broken lines indicate constructions used to determine average temperatures and rates of mass loss, respectively, over each temperature-jump.

of sublimation and vaporization of benzoic acid. A rising saw-tooth temperature profile was applied to the sample by raising the oven temperature by 4°C at 2°C min^{-1} followed by cooling at 1°C min^{-1} over 2°C. Fig. 5 shows the raw temperature and rate of mass loss vs. time profiles. Melting of the specimen is seen as a disturbance in the modulation of the rate of mass loss between 110 and 120°C — despite this being below the melting point (122.3°C) of benzoic acid. One might assume that this is due to poor temperature

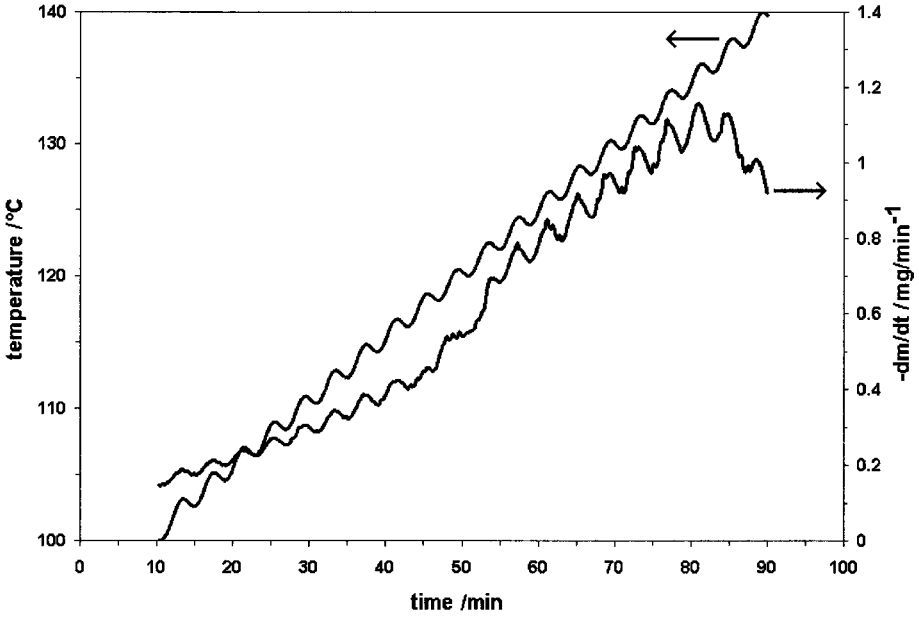

Fig. 5. Raw data for benzoic acid heated under a modulated temperature program.

calibration of the instrument or temperature gradients within the furnace but the same effect is observed for temperature-jump measurements as discussed below. There is also a drop off in $-\mathrm{d}m/\mathrm{d}t$ above 130°C due to exhaustion of the specimen.

Using a modified form of the equations described by Blaine and Hahn [47], the enthalpies of sublimation or vaporization can be found from

$$\Delta H = \frac{R(T^2 - A^2)L}{2A} \tag{12}$$

where T is the average temperature over one modulation, A is half of the amplitude of the temperature modulation and L is the amplitude of $\ln v$.

Benzoic acid has been extensively used as a standard for combustion and adiabatic calorimetry and has been recommended by IUPAC as a calibration and test material for enthalpy of sublimation measurements [48]. De Kruif and Blok [39] have reviewed the literature data for this material and provides a table of vapor pressures over a wide temperature range from which the enthalpy of sublimation can be calculated. The collected data from two temperature-jump experiments and a modulated temperature experiment on benzoic acid are shown in Fig. 6 along with values from De Kruif and Blok. Although, the results exhibit some scatter, the mean values of ΔH_{sub} and ΔH_{vap} (90.8 ± 0.6 and $67 \pm 2\,\mathrm{kJ\,mol^{-1}}$, respectively) from modulated temperature thermogravimetry are in good agreement with those in the literature (86–90 and 66–69 kJ $\mathrm{mol^{-1}}$ [39]). Again, in the region between 110 and 120°C, a fall in ΔH is observed. Although, this might suggest improper temperature calibration, the occurrence of this effect in both types of experiment (repeated on different instruments under different conditions) is unexpected. An alternative explanation is that melting of the surface of the specimen occurs before the bulk of the sample leading to a lower value of ΔH. Whatever the reason for this discrepancy, experience has shown that although data may be unreliable near the melting region of the substance under investigation, its melting temperature and enthalpy of fusion can be reliably estimated by extrapolation using data from the solid and liquid state.

As further confirmation of this technique, a sample of bisphenol-A was measured under a modulated temperature program. For these experiments, a sinusoidal heating rate was used. This consisted of an underlying linear rise of $1\,^{\circ}\mathrm{C\,min^{-1}}$ with a superimposed 5°C modulation of period 300 s. Pooled data from duplicate determinations gave $\Delta H_{\mathrm{vap}} = 103.1 \pm 2.8\,\mathrm{kJ\,mol^{-1}}$ at 174.5°C. Transpiration measurements

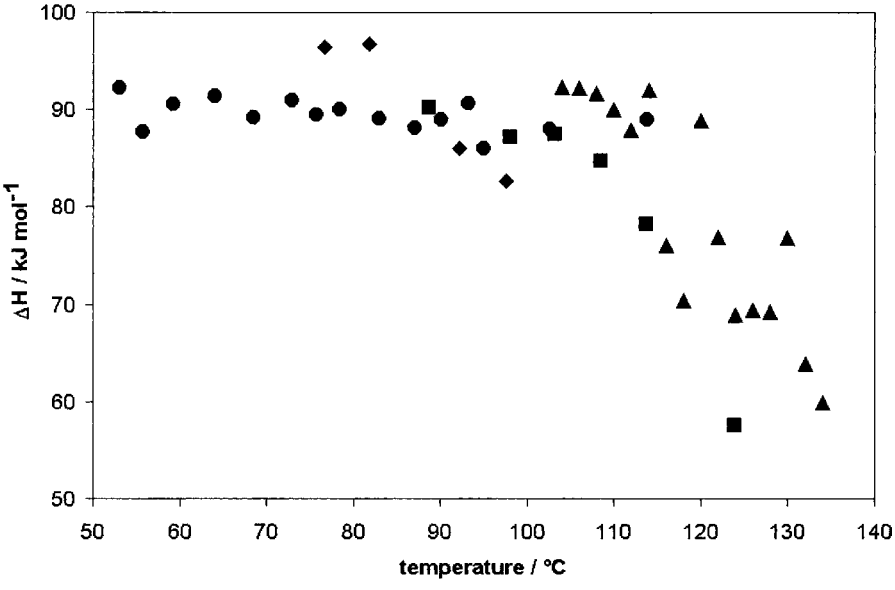

Fig. 6. Enthalpies of sublimation and vaporization derived from temperature jump (◆, ■) and modulated temperature (▲) experiments on benzoic acid. Literature data from De Kruif and Blok [39] are shown (●).

gave $\Delta H_{sub} = 141.9 \pm 1.3\,kJ\,mol^{-1}$ at 92.3°C [33]. Differential scanning calorimetry of bisphenol-A gave a melting temperature of 156.9 ± 0.1°C and an enthalpy of fusion of $31.0 \pm 1.1\,kJ\,mol^{-1}$ in good agreement with the values reported in the literature [49,50]. Using the factors in Eqs. (9) and (10) it is possible to correct these values to 156.9°C. This gives $\Delta H_{vap}(T_m) = 104.1 \pm 2.8\,kJ\,mol^{-1}$ and $\Delta H_{sub}(T_m) = 139.9 \pm 1.3\,kJ\,mol^{-1}$, the difference between these two values ($35.8 \pm 4.1\,kJ\,mol^{-1}$) being within the experimental error of the value determined directly by calorimetry.

5. Conclusions

This paper shows that it is possible to obtain accurate and meaningful thermodynamic data using a standard thermobalance and readily available materials. Once a calibration chart has been developed then it is possible to determine the vapor pressures of a number of samples very quickly. In cases where the compounds are not amenable to direct measurement, useful data can still be obtained using more sophisticated temperature programs.

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