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VOLATILISATION, EVAPORATION AND VAPOUR PRESSURE STUDIES USING A THERMOBALANCE

*D. M. Price**

IPTME, Loughborough University, Loughborough, Leicester LE11 3TU, United Kingdom

Abstract

There is considerable interest in performing volatilisation and evaporation measurements by thermogravimetry. A quick and simple method for determining vapour pressure using a conventional thermobalance and standard sample holders has been developed. These yield meaningful thermodynamic parameters such as the enthalpies of sublimation and vaporisation. Under favourable conditions the melting temperature and enthalpy of fusion of such compounds can be obtained. This technique has been used for the study of dyes, UV absorbers and plasticisers. The use of modulated-temperature programs for such work is also described.

Keywords: bisphenol-A, dioctyl phthalate, evaporation, sublimation, thermogravimetry, vapour pressure

Introduction

The tendency of a substance to enter the vapour phase by sublimation (solid→gas) or evaporation (liquid→gas) is defined by its vapour pressure. Knowledge of this parameter is crucially important for a wide variety of materials. Sublimation and evaporation are zero-order processes, i.e., the rate of mass loss of a sample under isothermal conditions due to vaporisation should be constant providing that its free surface area does not change [1]. Doyle studied this process in 1961, and considered the kinetic analysis of thermogravimetric data with reference to the evaporation of octacyclotetrasiloxane under dry nitrogen as a model zero order process [2]. Based upon earlier studies by Ashcroft and others [3–5], Price and Hawkins [6] showed that it is possible to use thermogravimetry to determine vapour pressures using the Langmuir equation for free evaporation [7]:

$$-\frac{\mathrm{d}m}{\mathrm{d}t}=p\alpha\sqrt{\frac{M}{2\pi RT}} \tag{1}$$

where $-\mathrm{d}m/\mathrm{d}t$ is the rate of mass loss per unit area, p – the vapour pressure, M – the molecular mass of the effusing vapour, R – the gas constant, T – the absolute tempera-

* E-mail: d.m.price@lboro.ac.uk; Fax: +44 1509 223332

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ture and α – the vaporisation coefficient. Normally, this type of study is performed in vacuo, but, by using a calibration procedure based upon measuring the rates of mass loss of substances whose vapour pressures are known, Price and Hawkins have shown that it is possible to estimate the vapour pressures of other materials to good accuracy [6].

This paper summarises the method, which has been developed to carry out these measurements, and validates its use with some data for a plasticizer – dioctyl phthalate. Measurements using stepwise and modulated temperature profiles are also discussed.

Experimental

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 on a TA Instruments TG 2950 with a water-cooled vertical furnace. The thermobalance was calibrated for temperature according to the method of Stewart using indium, tin, bismuth and lead [8]. The magnitude and linearity of the balance response was checked with standard milligram masses. Samples were placed in tared aluminium sample cups (internal diameter: 12.5 mm) of the type used for DSC measurements. 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 or cylindrical platinum crucibles) which form drops with different contact angles can be used to alleviate this problem. Calculations suggest that, even in a ‘worse case’ scenario, curvature of the meniscus has little effect on the data until the sample is nearly exhausted. 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 helium (flow rate: 90 ml min^{-1} into the furnace and 10 ml min^{-1} though the balance assembly). Small variation of gas flow rate did not appear to affect the rate of mass loss. Experiments 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 confirmed that the process followed zero order kinetics (i.e., d*m*/d*t* was constant) and served to check that the free surface area was not changing significantly or that thermal degradation of the sample was not occurring. Experience showed that the rate of mass loss could be resolved down to better than 2.5 mg min^{-1} m^{-2} under isothermal conditions with less sensitivity for continuous heating at moderate heating rates (typically 1–2°C min^{-1}). Doubling the free surface area of the sample (by using two cups) doubled the absolute rate of mass loss.

Theory

Rearranging Eq. (1) gives:

$$p=kv \tag{2}$$

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

A plot of p *vs.* v follows the same trend for a series of compounds with known vapour pressure – regardless of chemical structure – providing that the sample does not associate in the solid, liquid or gas phase. This allows the calibration constant k to be determined and thus the vapour pressures of unknown materials to be found [6].

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

$$\ln p=B-\frac{\Delta H}{RT} \tag{3}$$

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

Combining Eqs (2) and (3):

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

Thus the enthalpies of vaporisation and sublimation can be found from the slope of a plot of ln$p$ (or ln$v$) *vs.* reciprocal absolute temperature [6]. Although it is desirable to be able to pre-melt solid samples in order to obtain good vapour pressure data, Price *et al.* have shown that temperature-jump methods can be used to estimate ΔH_{sub} and ΔH_{vap} for substances, which decompose on melting [9].

At the melting temperature T_m:

$$\Delta H_{sub}(T_m)=\Delta H_{vap}(T_m)+\Delta H_{fus}(T_m) \tag{5}$$

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 [6]. It is also possible to estimate the boiling temperature (T_b) at normal atmospheric pressure of materials by extrapolating their vapour pressure *vs.* temperature curve until the pressure is 101325 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 vapour pressure curve and the Antoine equation is often used [10, 11]:

$$\ln(p)=A'-\frac{B'}{(\theta-C')} \tag{6}$$

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

$$\Delta H(T_0)=\Delta H(T)+\int_{T_0}^{T}\Delta C_p(T)\mathrm{d}T \tag{7}$$

where T_0 is a common reference temperature (usually 298.15 K) and ΔC_p is the C_p(vapour)–C_p(solid) (for sublimation) or C_p(vapour)–C_p(liquid) (for evaporation). It is often difficult to obtain good quality vapour pressure data over a wide enough temperature range in order to evaluate the temperature dependence of ΔH. Chickos *et al.* suggest a method for heat capacity corrections to a standard state based upon studies of a wide range of materials. For sublimation and vaporisation they recommend [12]:

$$\Delta H_{sub}(298.15\ \mathrm{K})=\Delta H_{sub}(T)+0.0320(T-298.15) \tag{8}$$

and

$$\Delta H_{vap}(298.15\ \mathrm{K})=\Delta H_{vap}(T)+0.0540(T-298.15) \tag{9}$$

when ΔH_{sub} and ΔH_{vap} are measured in kJ mol^{-1} and T is the temperature (in K) at which the determination is made. The method of correction is still a 'matter of taste or of experience' [13], but the underlying philosophy of 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.

Results and discussion

A calibration curve obtained using benzoic acid and phenanthrene was constructed using values for the vapour pressures of benzoic acid and phenanthrene taken from the literature [14–17] (Fig. 1). Once the apparatus had been calibrated in this way, the vapour pressures of unknown materials could be measured. Vapour pressure data for dioctyl phthalate measured by thermogravimetry are shown in Fig. 2. The data was extrapolated outside of the measured region using Eq. (6). The measurements are in good agreement with literature data on this material [18–21].

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 vapour pressure data. However, the enthalpies of sublimation and vaporisation can still be found by the temperature-jump technique described by Flynn and Dickens [22]. The rates of mass loss are 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:

$$\Delta H_{\text{sub}} = R\ln\left[\frac{(\text{d}m/\text{d}t)(T_1)\sqrt{T_1}}{(\text{d}m/\text{d}t)(T_2)\sqrt{T_2}}\right]\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{10}$$

Note that it is no longer necessary to know the molecular mass of the vaporising 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 ma-

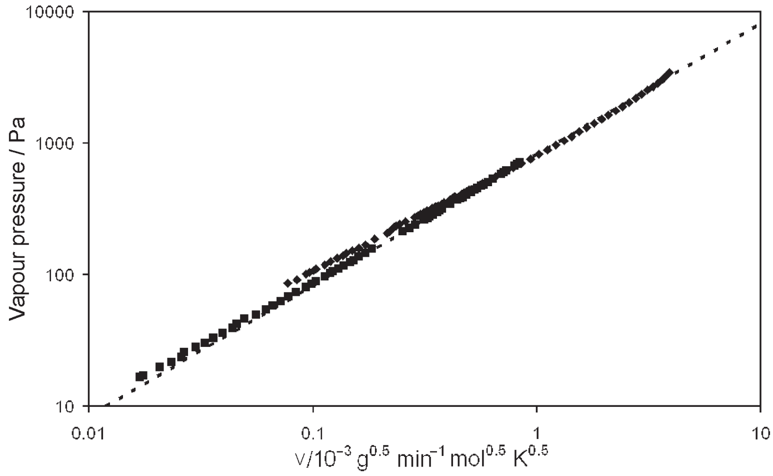

Fig. 1 Calibration curve using ■ – benzoic acid and ◆ – phenanthrene

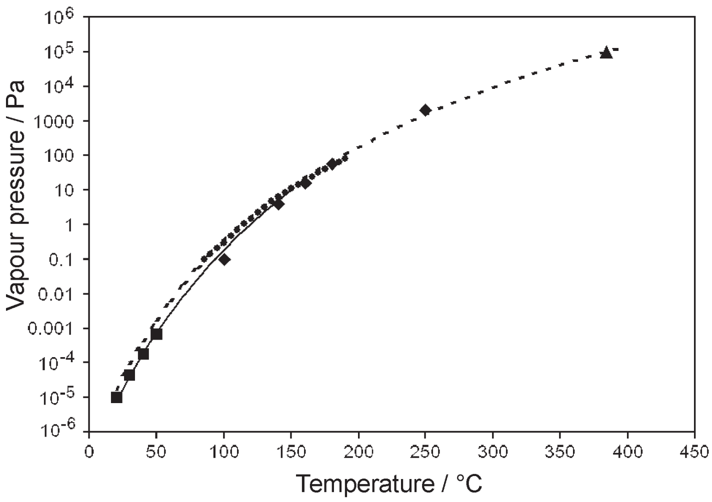

Fig. 2 Vapour pressure data for dioctyl phthalate (● – measured, ◆ – Wilson [18], ▲ – Weast and Grasselli (19), ■ – Davis *et al.* [20], solid line — Tang and Munckelwitz [21], broken line - - - fit of measured data to Eq. (6))

trix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) [9]. The error in this type of determination amounts to about ±7%.

An alternative approach is to use modulated temperature thermogravimetry whereby a sinusoidal heating rate is used instead of a conventional linear rise in temperature [23]. Using a modified form of the equations described by Blaine and Hahn [23], the enthalpies of sublimation or vaporisation can be found from:

$$\Delta H = \frac{R(T^2 - A^2)L}{2A} \tag{11}$$

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

In order to investigate this approach, a sample of bisphenol-A was measured under such conditions. The temperature program consisted of an underlying linear rise of 1°C min^{-1} with a superimposed 5°C modulation of period 300 s (Fig. 3). Pooled data from duplicate determinations gave ΔH_{vap}=103.1±2.8 kJ mol^{-1} at 174.5°C. Transpiration measurements gave ΔH_{sub}=141.9±1.3 kJ mol^{-1} at 92.3°C [13]. Differential scanning calorimetry of bisphenol-A determined its melting temperature (T_m) to be 156.9±0.1°C with an enthalpy of fusion of 31.0±1.1 kJ mol^{-1} in good agreement with the values reported in the literature [24–25]. 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±2.8 kJ mol^{-1} and $\Delta H_{sub}(T_m)$=139.9±1.3 kJ mol^{-1}, the difference between these two values

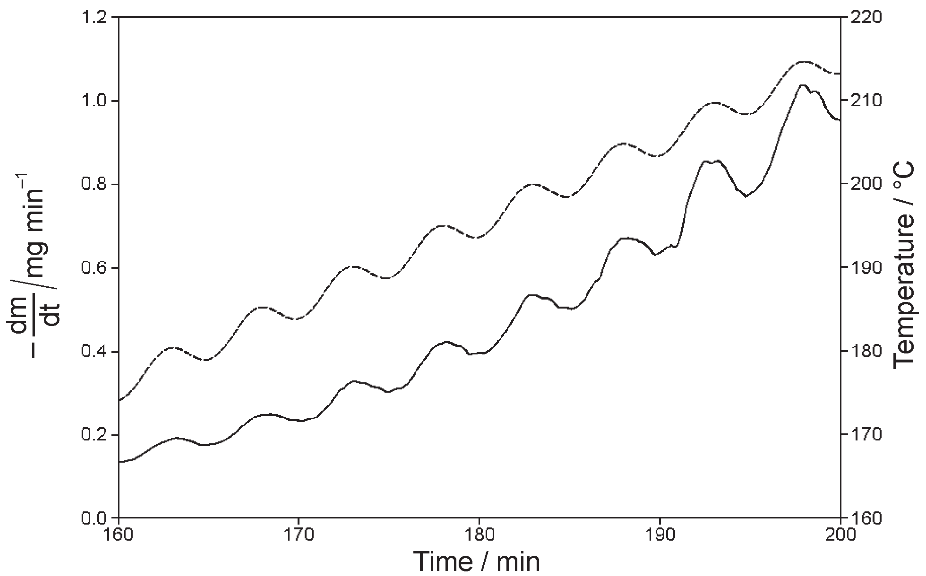

Fig. 3 Raw data from modulated temperature thermogravimetry of bisphenol-A (solid line: –d*m*/d*t*, broken line: temperature)

(35.8±4.1 kJ mol^{-1}) being in good agreement with the enthalpy of fusion determined directly by calorimetry.

Conclusions

This paper shows that it is possible to obtain accurate vapour pressure data by thermogravimetry. Once a calibration chart has been developed then it is possible to determine the vapour pressures of a number of samples very quickly. More sophisticated temperature programs such as temperature-jump and modulated temperature profiles can be used to obtain enthalpies of sublimation and vaporisation to good accuracy.

* * *

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