

## VOLATILIZATION, EVAPORATION & VAPOR PRESSURE STUDIES USING A THERMOBALANCE

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### ABSTRACT

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

### 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. Sublimation and evaporation are zero-order processes, i.e. the rate of mass loss of a sample under isothermal conditions due to vaporization should be constant providing that its free surface area does not change (1). Doyle reported 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) have shown that it is possible to use thermogravimetry to determine vapor pressures using the Langmuir equation for free evaporation (7):

$$-\frac{dm}{dt} = p\mathbf{a}\sqrt{\frac{M}{2pRT}} \quad (1)$$

where  $-dm/dt$  is the rate of mass loss per unit area,  $p$  the vapor pressure,  $M$  the molecular weight of the effusing vapor,  $R$  is the gas constant,  $T$  the absolute temperature and  $\mathbf{a}$  is the vaporization coefficient. Normally, this type of study is preformed *in vacuo*, but, by using a calibration procedure based upon measuring the rates of weight loss of standard materials whose vapor pressures are known, Price and Hawkins have shown that it is possible to estimate the vapor pressures of other materials to good accuracy (6).

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

## 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 TGA 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 aluminum 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) can be used to alleviate this problem. Calculations suggest that, even in a “worse case” scenario, this 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<sup>-1</sup> into the furnace and 10 ml min<sup>-1</sup> 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<sup>-1</sup>, 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<sup>-1</sup> m<sup>-2</sup> during continuous heating. An order of magnitude improvement in sensitivity was obtained under isothermal conditions at the expense of longer measurement times. 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  $k = \sqrt{2pR/a}$  and  $v = dm/dt \sqrt{T/M}$

A plot of  $p$  vs.  $v$  follows the same trend for a series of compounds with known vapor 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 vapor pressures of unknown materials to be found (6).

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

$$\ln p = B - \frac{\Delta H}{RT} \quad (3)$$

$\Delta H$  is the molar enthalpy of sublimation ( $\Delta H_{\text{sub}}$ ) in the case of a solid or the molar enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) in the case of a liquid.

Combining Eq. (2) and Eq. (3):

$$\ln v = B - \frac{\Delta H}{RT} - \ln k \quad (4)$$

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

At the melting temperature  $T_m$ :

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

where  $\Delta H_{\text{fus}}$  is the enthalpy of fusion.

If data can be obtained through the melting region,  $\Delta H_{\text{sub}}$ ,  $\Delta H_{\text{vap}}$ ,  $\Delta H_{\text{fus}}$  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 vapor pressure *versus* 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 vapor pressure curve and the Antoine equation is often used (10,11):

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

where  $A'$ ,  $B'$  and  $C'$  are constants and  $q$  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:

$$\Delta H(T_0) = \Delta H(T) + \int_{T_0}^T \Delta C_p(T) dT \quad (7)$$

where  $T_0$  is a common reference temperature (usually 298.15 K) and  $\Delta C_p$  is the  $C_p(\text{vapor}) - C_p(\text{solid})$  (for sublimation) or  $C_p(\text{vapor}) - C_p(\text{liquid})$  (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  $\Delta H$ . 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 vaporization they recommend (12):

$$\Delta H_{\text{sub}}(298.15K) = \Delta H_{\text{sub}}(T) + 0.0320 \cdot (T - 298.15) \quad (8)$$

and

$$\Delta H_{\text{vap}}(298.15\text{K}) = \Delta H_{\text{vap}}(T) + 0.0540 \cdot (T - 298.15) \quad (9)$$

when  $\Delta H_{\text{sub}}$  and  $\Delta H_{\text{vap}}$  are measured in  $\text{kJ mol}^{-1}$  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 vapor pressure of benzoic acid and phenanthrene taken from the literature (14-17). 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 figure 1. The data was extrapolated outside of the measured region using Eq. (6). The measurements show good agreement with literature data on this material (18-21).

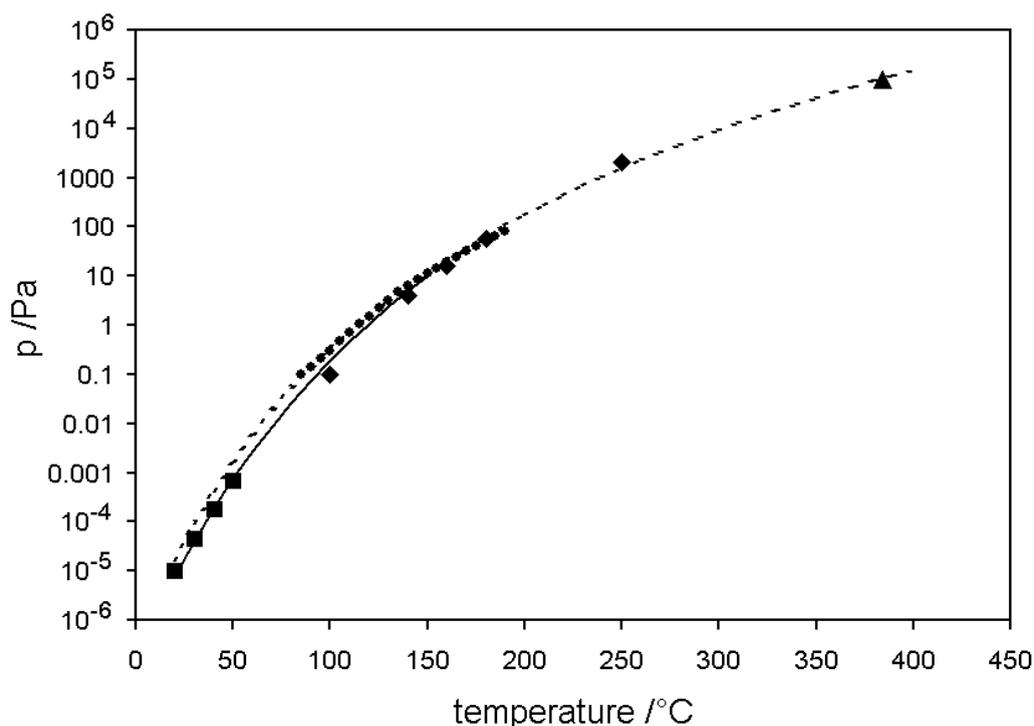


Figure 1. Vapor pressure data for dioctyl phthalate (● measured, ◆ Wilson (18), ○ Weast & Grasselli (19), ■ Davis *et al.* (20), solid line = Tang and Munckelwitz (21), broken line = fit of measured data to Eq. 6)

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

(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  $\Delta H_{sub}$  may be obtained:

$$\Delta H_{sub} = R \ln \left[ \frac{\left\{ \frac{dm}{dt}(T_1)\sqrt{T_1} \right\}}{\left\{ \frac{dm}{dt}(T_2)\sqrt{T_2} \right\}} \right] \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (10)$$

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) (9). The error in this type of determination amounts to about  $\pm 7\%$ .

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 vaporization can be found from:

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

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  $1^\circ\text{C}/\text{min}$  with a superimposed  $5^\circ\text{C}$  modulation of period 300s. Pooled data from duplicate determinations gave  $\Delta H_{vap} = 103.1 \pm 2.8 \text{ kJ mol}^{-1}$  at  $174.5^\circ\text{C}$ . Transpiration measurements gave  $\Delta H_{sub} = 141.9 \pm 1.3 \text{ kJ mol}^{-1}$  at  $92.3^\circ\text{C}$  (13). Differential scanning calorimetry of bisphenol-A determined its melting temperature to be  $156.9 \pm 0.1^\circ\text{C}$  with an enthalpy of fusion of  $31.0 \pm 1.1 \text{ kJ mol}^{-1}$  in good agreement with the values reported in the literature (24-25). Using the factors in Eq. (9) and (10) it is possible to correct these values to  $156.9^\circ\text{C}$ . This gives  $\Delta H_{vap}(T_m) = 104.1 \pm 2.8 \text{ kJ mol}^{-1}$  and  $\Delta H_{sub}(T_m) = 139.9 \pm 1.3 \text{ kJ mol}^{-1}$ , the difference between these two values ( $35.8 \pm 4.1 \text{ kJ mol}^{-1}$ ) being the same as the enthalpy of fusion determined directly by calorimetry (within the limits experimental error).

## CONCLUSIONS

This paper shows that it is possible to obtain accurate vapor pressure data by thermogravimetry. Once a calibration chart has been developed then it is possible to determine the vapor 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 vaporization to good accuracy.

## REFERENCES

1. D. Dollimore; *Thermochim. Acta* **1999** 340-341 19.
2. C.D. Doyle; *J. Appl. Polym. Sci.* **1961** 5(15) 285.
3. S.J. Ashcroft; *Thermochim. Acta* **1972** 2 512.
4. E.A. Gulbransen, F.A. Brassart; in: *Microweighing in Vacuum and Controlled Environments*, A.W. Czanderna and S.P. Wolsky (eds.), Elsevier, Amsterdam 1980, p. 324.
5. J.P. Elder; *J. Thermal Anal.* **1997** 49 897.
6. D.M. Price and M.. Hawkins, *Thermochim. Acta* **1998** 315 19.
7. I. Langmuir, *Phys. Rev.* **1913** 2 329.
8. L.N. Stewart; in H.G. McAdie (Ed.), *Proc. 3<sup>rd</sup> Toronto Symp. Thermal Anal., Chemical Institute of Canada*, Toronto 1969, p. 205.
9. D.M. Price, S. Bashir and P.R. Derrick; *Thermochim. Acta* **1999** 327 167.
10. C. Antoine; *Compt. Rend.* **1888** 107 681.
11. S.H. Fishtine; *Ind. Eng. Chem.* **1963** 55 20.
12. J.S. Chickos; S. Hosseini, D.G. Hesse and J.F. Liebman; *Struct. Chem.* **1993** 4 271.
13. S.P. Verevkin; *personal communication*.
14. T.E. Jordan; *Vapor Pressure of Organic Compounds*, Interscience Publishers, New York 1954.
15. C.G. De Kruif and J.G. Blok; *J. Chem. Thermodyn.* **1982** 14 201.
16. G.W.C. Kaye and T.H. Laby; *Tables of Physical & Chemical Constants, 14th edition*, Longman, London 1973.
17. C.G. De Kruif; *J. Chem. Thermodyn.* **1980** 12 243.
18. A.S. Wilson; *Plasticisers, Principles & Practice*, The Institute of Materials, London 1995.
19. R.C. Weast and J.G. Grasselli; *CRC Handbook of Data on Organic Compounds, 2<sup>nd</sup> Ed.*, CRC Press, Boca Raton FL. 1989.
20. E.J. Davis, P. Ravindran and A.K. Ray; *Chem. Eng. Commun.* **1980** 5 251.
21. I.N. Tang and H.R. Munkelwitz; *J. Colloid. Interface Sci.* **1989** 141 1519.
22. J.H. Flynn and B. Dickens; *Thermochim. Acta*, **1976** 15 1.
23. R.L. Blaine and B.K. Hahn; *J. Thermal Anal.* **1998** 54 695.
24. D. Wzrzykowska-Stankiewicz and A. Szafranski; *Wiss. Z. TH Leuna-Merseburg*, **1975** 17 265.
25. N.V. Novoselova, L.Ya. Tsvetkova, I.B. Rabinovich, E.M. Moseeva and L.A. Faminskaya; *Zhur. Fiz. Khim.*, **1985** 59 604.