

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. Accurate enthalpies of vaporization and sublimation can be determined, thus allowing the melting temperature and enthalpy of fusion to be obtained directly from thermogravimetry. Applications to the study of flame-retardants and UV absorbers are described. Poor correlation of experimental results with data generated from molecular modeling is found. The application of Modulated-Temperature Thermogravimetry for the determination of enthalpies of sublimation and vaporization is also explored.

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 UV absorbers and flame retardants from a substrate by evaporation leads to an unwanted reduction in their efficiency (2). On the other hand, controlled volatilization may be beneficial for the activity of fragrances (3). Although there are a number of literature compilations of vapor pressure data and enthalpies of sublimation and vaporization (4,5), for many materials, such information is not available and the investigator either has to resort to measurement or prediction using methods described by Lyman *et. al.* (6). The latter approach has been incorporated into in computer molecular modeling software (7).

Nesmeyanov has reviewed some of the methods for the determination of vapor pressures together with the pressure ranges over which they operate (8). One of the most popular of these methods is that devised by Knudsen (9,10) 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 has described the adaptation of a commercial thermobalance to this technique (11). Goodrum and Seisel have described using sealed DSC crucibles with laser drilled holes for similar measurements (12). This approach requires some means of operating the

instrument at other than ambient pressure as do the pressure DSC techniques described by Cassel and others (13-15). It would be much more convenient to employ standard instruments and readily available sample holders.

As will be demonstrated, molecular modeling often gives unreliable results yet direct measurement using conventional equipment is neither inaccurate nor onerous.

EXPERIMENTAL

Price and Hawkins (16) have shown that it is possible to use thermogravimetry to determine vapor pressures using the Langmuir equation for free evaporation *in vacuo* (17) :

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

where $-dm/dt$ is the rate of mass loss per unit area, p the vapour pressure, M the molecular weight of the effusing vapour, R is the gas constant, T the absolute temperature and \mathbf{a} is the vaporization coefficient (usually assumed to be 1). Samples were prepared by placing them in standard open DSC pans so that a well-defined surface area could be achieved¹. In the case of solid substances, the material was melted first to obtain a flat surface. Measurements were carried out with a TA Instruments 951 TGA under isothermal and linear-rising temperature conditions using an inert atmosphere purge at 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:

$$p = kv \quad (3)$$

where $k = \sqrt{2pR}/\mathbf{a}$ and $v = dm/dt \sqrt{T/M}$

A plot of p vs. v is co-linear for a series of compounds of known vapor pressure allowing the calibration constant k to be determined and thus the vapor pressures of unknown materials to be found (figure 1).

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

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

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.

¹ Part number 900786.901 from TA Instruments Inc., New Castle, Delaware, USA

Combining Eq. (3) and Eq. (4):

$$\ln v = B - \frac{\Delta H}{RT} - \ln k \quad (5)$$

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 [16]. 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 ΔH_{sub} and ΔH_{vap} for substances which decompose on melting [18].

At the melting temperature T_m :

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

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 (16). Vapor pressures outside the region determined by direct measurement can be obtained by extrapolation using the formula:

$$p(T) = p(T_m) \exp \left\{ \frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right\} \quad (7)$$

where $p(T_m)$ is the vapor pressure at the melting temperature and ΔH is the enthalpy of sublimation (if $T < T_m$) or vaporization (if $T > T_m$). It is also possible to estimate the boiling temperature (T_b) at normal atmospheric pressure of these materials by extrapolating the vapor pressure *versus* temperature curve until the pressure is 101325 Pa although their thermal stability at such temperatures should be questioned.

RESULTS & DISCUSSION

Figure 2 shows a plot of $\ln p$ vs. $1/T$ for 2,4,4'-trihydroxybenzophenone, a UV absorber. The melting temperature ($209 \pm 5^\circ\text{C}$) and enthalpy of fusion (31 ± 3 kJ/mol) can be found directly from thermogravimetry. These results compare favorably with those determined by DSC ($198.5 \pm 0.5^\circ\text{C}$ & 34 ± 1 kJ/mol respectively).

Table 1 lists measured enthalpies of vaporization and estimated boiling points obtained from measurements of the vapor pressures of a series of UV absorbers (18). Alongside the data are given the calculated values obtained using a commercial molecular modeling package (7). Correlation coefficients between the experimental and predicted values were 0.877 for ΔH_{vap} and -0.058 for T_b . Although the results of molecular modeling depend on the chosen method (in this case from reference (6)), these findings suggest that the predicted values are not reliable guides to actual behavior.

Vapor pressure data for two flame retardants: tris(1-chloro-2-propyl)phosphate ($TCPP = \text{CH}_2\text{Cl}(\text{CH}_2\text{CHO})_3\text{PO}$), and tris(1,3-dichloro-2-propyl)phosphate ($TDCP = ((\text{CH}_2\text{Cl})_2\text{CHO})_3\text{PO}$) are co-plotted in figure 3. The data was extrapolated outside of the measured region using Eq. (4). Despite the uncertainties inherent in such a procedure, "order of magnitude" values are valuable for engineering calculations for purification by distillation under reduced pressure and are certainly an improvement on estimation.

Finally, the potential of "Modulated-Temperature Thermogravimetry" (20) was investigated as a means of accurately determining the properties 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 followed by a cooling at 1°C/min over 2°C. Figure 4 shows the raw temperature and rate of mass loss vs. time profiles. Using a modified form of the equations described by Blaine and Hahn [20] the enthalpies of sublimation or vaporization can be found from:

$$\Delta H = \frac{R(T^2 - A^2)L}{2A} \quad (8)$$

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

Whilst the results shown in figure 5 exhibit some scatter, the mean values of ΔH_{sub} and ΔH_{vap} (90.8 ± 0.6 & 67 ± 2 kJ/mol respectively) are in good agreement with those in the literature (86-90 and 66-69 kJ/mol) (21). Further work is required in order to fully explore this approach.

CONCLUSIONS

This paper demonstrates 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. Computer modeling of thermodynamic properties was shown to lead to erroneous predictions. In cases where the compounds are not amenable to complete analysis, useful data can still be obtained using more sophisticated temperature programs such as temperature-jump or modulated-temperature profiles.

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Table 1. Measured (19) and calculated (*this work*) enthalpies of vaporization and normal boiling temperatures of UV stabilizers (see text).

Compound	measured		calculated	
	ΔH_{vap} (kJ/mol)	T_b (°C)	ΔH_{vap} (kJ/mol)	T_b (°C)
2,4,4'-trihydroxybenzophenone	107.6	413.5	172.7	396.3
2,4-dihydroxy-4'-methoxybenzophenone	102.7	382.3	151.0	368.4
2,2'-dihydroxy-4-methoxybenzophenone	81.8	354.3	151.0	368.4
2,2',4,4'-tetrahydroxybenzophenone	150.5	329.7	202.5	436.2
2-hydroxy-4,4'-dimethoxybenzophenone	83.5	388.2	129.2	346.9
2,2'-dihydroxy-4,4'-dimethoxybenzophenone	96.9	372.0	159.0	383.0
2-hydroxy-4,4'-diethoxybenzophenone	100.2	364.1	139.1	372.4
2-hydroxy-4-butoxy-4'-methoxybenzophenone	92.6	393.0	144.0	384.9
2-hydroxy-4,4'-dibutoxybenzophenone	94.0	421.9	158.9	421.5

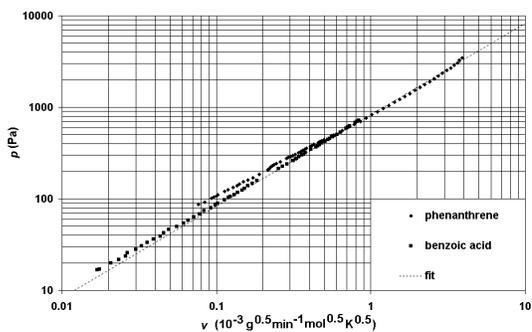


Figure 1. Calibration curve using benzoic acid and phenanthrene.

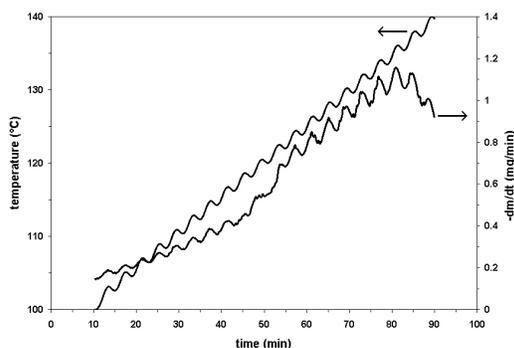


Figure 4. Raw data for benzoic acid heated under a modulated temperature program.

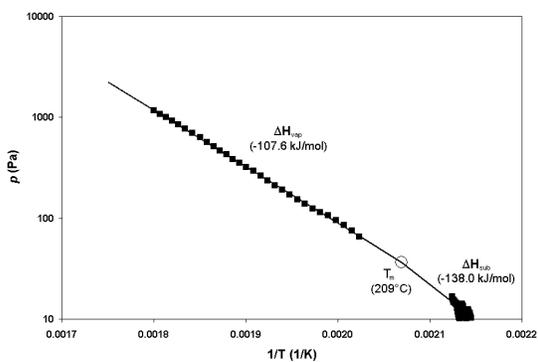


Figure 2. Calculation of melting point and enthalpy of fusion from vapor pressure data for 2,4,4'-trihydroxybenzophenone.

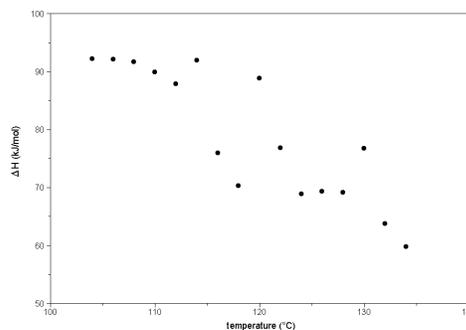


Figure 5. Enthalpies of sublimation and vaporization derived from data in figure 4.

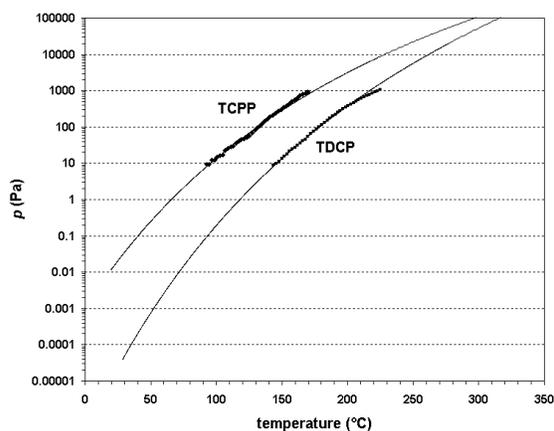


Figure 3. Vapor pressure data for two flame retardants.