

A fit of the vapours

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INTRODUCTION

The tendency for a substance in the condensed phase (i.e. solid or liquid) to enter the gas phase is described by the material's vapour pressure. This property is important in a wide variety of applications ranging from freeze drying, plant protection and perfumery. The volatility of a substance is of environmental concern with regard to its atmospheric accumulation and dispersal.

In 1997, Mike Hawkins and I gave a poster presentation at the annual Thermal Analysis Conference held at Oxford University deceptively entitled "Calorimetry of two disperse dyes using thermogravimetry" [1]. We described a method for determining the vapour pressure of substances using a conventional thermobalance under an ambient pressure inert atmosphere. The work was subsequently published in *Thermochimica Acta* and has been cited over 50 times since then, most recently in the February edition of this journal [2]. Here I present a personal perspective on the topic and its subsequent development.

METHOD

Evaporation and sublimation are zero order processes in that the rate of mass loss at constant temperature is dependant of the surface area of the material and its vapour pressure [3]. Langmuir studied the evaporation of materials *in vacuo* whereby the relationship between the rate of mass change per unit area (dm/dt) and its vapour pressure (p) is given by [4]:

$$-\frac{dm}{dt} = p\alpha\sqrt{\frac{M}{2\pi RT}} \quad (1)$$

where M is the molecular mass of effusing substance and α is the evaporation coefficient (usually assumed to be unity in vacuum). We proposed a scheme whereby the diffusion of material into a blanketing gas could be accommodated by calibration using materials of known vapour pressure (and ideally similar chemical structure and size) so that the relation simplified to:

$$p = kv \quad (2)$$

where $k = \sqrt{2\pi R}/\alpha$ and $v = dm/dt \sqrt{T/M}$

A plot of the volatilisation rate (v) for a number of compounds against their known vapour pressure (p) is shown in figure 1 – these data have been critically re-evaluated and recalculated from [1] using more precise reference vapour pressures [5-8]. The value of α derived from these data was found to be $1.19 \pm 0.01 \times 10^{-4}$.

DISCUSSION

The approach described above was annexed by Dollimore *et al.* who produced a series of papers amounting to an intellectual land-grab on the technique by re-defining or modifying the calibration protocol [9-23]. However, our original intent was not to measure vapour pressures but to determine the enthalpy of vaporisation (ΔH_{vap}) of dyes and UV absorbers in order to screen them for a solid-state dye diffusion ("Thermosol") process [24-27] since the solubilities in target substrates are governed by the cohesive energy density (δ) [28]:

$$\delta = \sqrt{\frac{\Delta H_{vap} - RT}{V_m}} \quad (3)$$

where V_m is the molar volume.

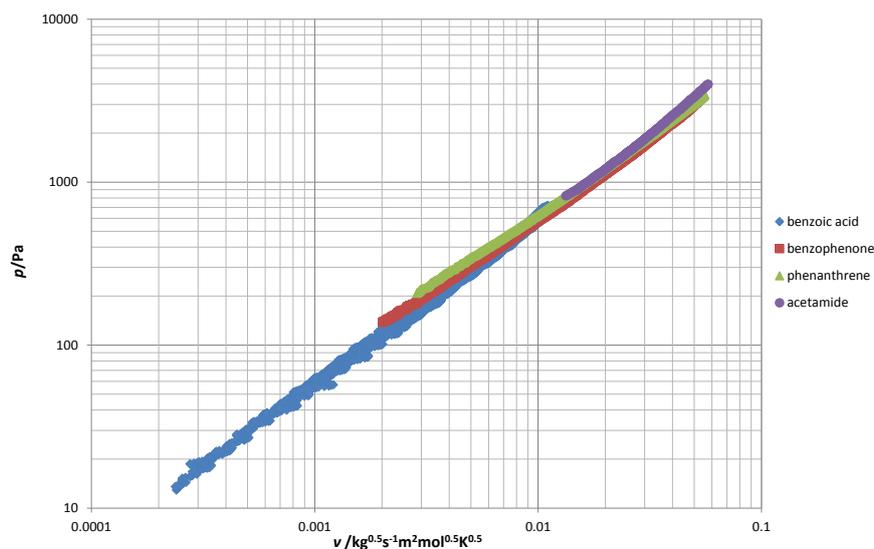


Fig. 1. Calibration curve for benzoic acid, benzophenone, phenanthrene and acetamide according to equation (2).

Cohesive energy densities, enthalpies of fusion and melting temperature were used to establish an operational parameter (“order of merit”) by which the most suitable materials could be prioritised for further testing and unsuitable materials discarded before expensive pilot plant trials were attempted. Unfortunately much of this work remains proprietary information but the vapour pressure data on a series of benzophenone UV absorbers were published in 1999 [29] and the vapour pressure curves of a pair of organophosphate flame retardants were also presented in the same year [30] (or they would have been had not Hurricane Floyd intervened!). Attempts were made to determine the required thermodynamic parameters by molecular modelling but the software employed was found to be highly inaccurate when compared to experimental data [31].

One of the difficulties with the original approach was the requirement that the substance under investigation could be fused in the sample crucible in order to prepare a well-defined surface. Many materials of interest were suspected to degrade on melting; therefore temperature-jump thermogravimetry was employed in order to circumvent this requirement [32]. Again, this work was directed at using easily-measured thermodynamic properties to predict behaviour in (this case) Matrix Assisted Laser Desorption Ionisation. Modulated temperature thermogravimetry was also explored as an equivalent methodology to step-wise heating [33].

For brief period, the author enjoyed acting as a consultant for other workers keen to use this technique on materials of interest to them. Good agreement of the thermogravimetric data with vapour pressure measurements by transpiration techniques was obtained [34] and the vapour pressures of fragrance ingredients were determined [35].

Meanwhile, there were growing concerns amongst the occupation forces that the simple calibration method required to extract vapour pressure data was in some way flawed as the evaporation coefficient (α) appeared to be alarmingly small (of the order of 10^{-4} - 10^{-5}) [11,18]. They proposed a comparative method whereby a material of known, but similar structure and volatility, was run against the target compound so that a variable calibration “constant” could be employed. An alternative analysis developed by Focke [36,37] and extended by Cozzani [38] which considered diffusion through the locally stagnant atmosphere above the surface of the specimen to derive the following expression relating the rate of mass change per unit area to its vapour pressure (p):

$$-\frac{dm}{dt} = pD \left(\frac{M}{zRT} \right) \quad (4)$$

where D is the diffusion coefficient for the material into the surface layer of thickness z .

Comparison of this relationship with the original Langmuir equation provides a correspondence between the evaporation coefficient (α) and the diffusivity (D):

$$\alpha = \frac{D}{z} \sqrt{\frac{2\pi M}{RT}} \quad (5)$$

Which would support the conjecture that a universal calibration cannot be applied since the evaporation coefficient would be substance dependent. Using an arbitrary value of 2 mm for z in equation (4) with the data shown in figure 1 does suggest that different materials have different diffusivities (table 1), although there seems to be little dependence on temperature since a plot of $-dm/dt$ vs. pM/zRT appears to be fairly linear for each compound (figure 2).

Table 1. Diffusion coefficients according to equation (4), $z=2\times 10^{-3}$ m.

Substance	Diffusion coefficient ($\times 10^9/\text{m}^2\text{s}^{-1}$)
Benzoic acid	1.60 ± 0.01
Benzophenone	1.39 ± 0.05
Phenanthrene	1.36 ± 0.06
Acetamide	2.12 ± 0.03

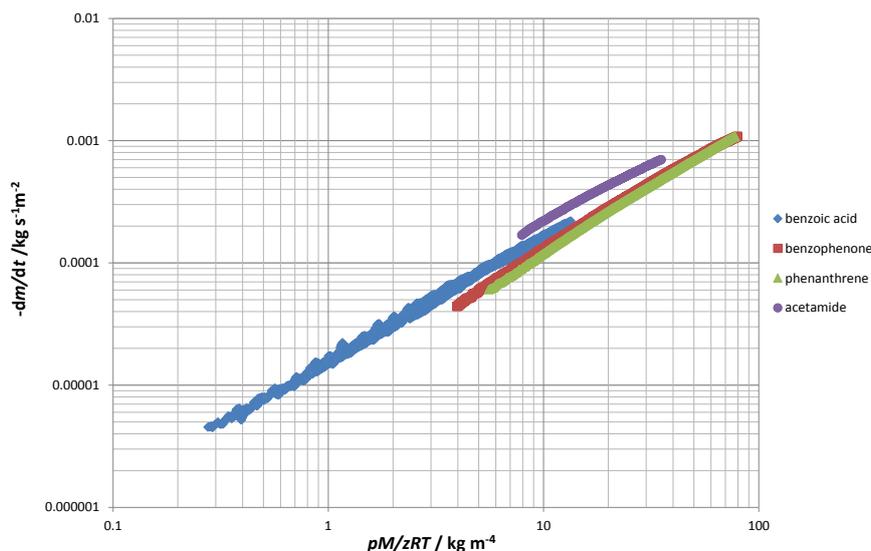


Fig. 2. Data for benzoic acid, benzophenone, phenanthrene and acetamide re-plotted according to equation (4).

Verevkin *et al.* argued that introducing a plethora of additional (but ill defined) parameters into the data treatment makes it too complex for the reliable estimation of the enthalpy of vaporisation for extremely low-volatility compounds and that an extended study of the vaporisation coefficient is still highly required [39]. Nevertheless, some careful experimental work by Veechio has shown that the Langmuir equation approach can be used to determine enthalpies of vaporisation provided that measurements are made over a limited temperature range [40-49]. Thus useful parameters can be obtained for fragrances, drugs and pesticides. Since the transport of condensable materials through vacuum pumps and pipework is of current interest to the author, I am particularly pleased to find that TGA is being used to determine the vapour pressures of materials used for semiconductor manufacture [50].

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