

# Calorimetry of two disperse dyes using thermogravimetry<sup>1</sup>

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## Abstract

A method for studying the volatilisation rate of materials using a conventional thermobalance and standard sample holders is described. This was used to study two dyes; CI Disperse Yellow 54 and CI Disperse Red 60. Using pure reference materials, a relationship between volatilisation rate and vapour pressure based on the Langmuir equation for free evaporation was used to calibrate the system. Thus, the vapour pressures of the dyes could be determined. Heats of sublimation and vaporisation were calculated from a plot of the logarithm of the vapour pressure against reciprocal absolute temperature. Extrapolation of the vapour pressure vs. temperature curve outside the experimentally measured region for Red 60 was made using the melting point and heat of fusion found by DSC. Good agreement was found with literature data. In favourable cases, the melting temperature and heat of fusion can be obtained directly from thermogravimetry. © 1998 Elsevier Science B.V.

*Keywords:* Thermogravimetry; Vapour pressure; Disperse dyes

## 1. Introduction

The behaviour of dyes at elevated temperatures is of particular importance in a number of applications. For example, their performance in thermal-sublimation printing, thermosol dyeing and permanent-press finishing are affected by the tendency of the dye to enter the vapour phase [1–3]. Whilst, it might be advantageous for a dye to possess a high vapour pressure in order to facilitate transfer to the substrate for the purposes of thermal printing, this can also lead to loss of material from the process by volatilisation [4]. There are several strategies for the determination of vapour pressure [5]; these range from direct measurement using a manometer [6], monitoring the gas phase

concentration of the volatile species (by, for example, spectrometry [3,7]), measurement of sample volatilisation by vacuum-effusion (Knudsen cell [8,9]) or transpiration techniques [10,11] to boiling point determination under controlled pressure [12,13].

Gückel and co-workers have measured volatilisation rates of pesticides at ambient pressure by isothermal thermogravimetry [14–17]. Since sublimation and evaporation are zero-order processes, the rate of mass loss of a sample under isothermal conditions due to vaporisation should be constant providing that the free surface area does not change. Their initial studies employed a thermostatically-housed Cahn RG electrobalance purged with a pre-heated air stream. This confirmed that the weight loss was linear with time for these compounds between 15 and 80° and established a double logarithmic relationship between the rate of amount of substance lost per unit area (expressed as mol h<sup>-1</sup> cm<sup>-2</sup>) and the material's vapour pressure [14]. For the same gas flow rate, the calibration factors depended on measuring temperature [16]. Later work

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extended the temperature range by using a thermobalance (Mettler TG-50) [17]. This study correlated the mass loss rate per unit area ( $\text{g h}^{-1} \text{cm}^{-2}$ ) with the vapour pressure over a wide temperature range to derive a similar log-log relationship. More recently, Elder has used the same technique to measure the vapour pressures of pharmaceutical compounds [18].

This study explores the use of thermogravimetry under isothermal and linear rising temperature conditions to determine the vapour pressures of two disperse dyes commonly used in high temperature coloration processes. In addition to this quantity, other thermodynamic parameters (such as heat of fusion and melting temperature) can be derived which leads to the application of the thermogravimetric method for establishing calorimetric properties.

## 2. Experimental

CI Disperse Yellow 54 (2-(3-hydroxy-2-quinolinylidene)-indene-1,3-dione) and CI Disperse Red 60 (1-amino-2-phenoxy-4-hydroxyanthraquinone) (both from BASF) were purified by recrystallisation from acetone. Structure and purity were checked by  $^1\text{H}$  NMR. Melting point, heat capacity and heat of fusion were measured by DSC which also served to confirm that the samples were better than 99% pure. Re-sublimed benzoic acid, acetamide, benzophenone and phenanthrene (Sigma-Aldrich, all >99.99%) were used as received.

Thermogravimetry was performed using a TA Instruments model 951 TGA. The thermobalance was calibrated for temperature according to the method of Stewart, using indium, tin, bismuth and lead [19]. The magnitude and linearity of the balance response was checked with standard milligramme masses. Samples were placed in tared aluminium sample cups (i.d.: 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. 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. The furnace was purged with dry, oxygen-free nitrogen (flow rate:  $100 \text{ ml min}^{-1}$ ). 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, or on continuous heating at  $1^\circ\text{C min}^{-1}$ . Experience showed that the rate of mass loss could be resolved down to ca.  $25 \text{ mg min}^{-1} \text{m}^{-2}$  during continuous heating. An order of magnitude improvement was obtained under isothermal conditions at the expense of longer measurement times. Isothermal measurements also served to confirm that the sample's mass decreased in a linear fashion with time and that thermal degradation was not occurring. When two sample cups were used (i.e. twice the sample surface area) the absolute rate of mass loss (in  $\text{mg min}^{-1}$ ) was doubled.

## 3. Theory

Analysis of the thermogravimetric data is based on the Langmuir equation for evaporation in vacuo [20]:

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

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  $\alpha$  is the vaporisation coefficient (usually assumed to be 1).

In the case of a material volatilising into a flowing gas stream at one atmosphere rather than a vacuum,  $\alpha$  can no longer be assumed to be unity. Therefore, rearranging the above gives

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

where  $k$  can be evaluated by calibration with substances of known vapour pressure and  $v$  is  $(dm/dt)\sqrt{T/M}$ .

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

$$\frac{d(\ln p)}{dT} = \frac{\Delta H}{RT^2} \quad (3)$$

where  $\Delta H$  is the molar heat of sublimation ( $\Delta H_{\text{sub}}$ ) for the solid or heat of vaporisation ( $\Delta H_{\text{vap}}$ ) for the liquid.

At the melting temperature  $T_m$ :

$$\Delta H_{\text{sub}}(T_m) = \Delta H_{\text{vap}}(T_m) + \Delta H_{\text{fus}}(T_m) \quad (4)$$

where  $\Delta H_{\text{fus}}$  is the heat of fusion. Below this temperature the heat of sublimation is given according to Kirchoff's law:

$$\Delta H_{\text{sub}}(T) = \Delta H_{\text{sub}}(T_m) + \int_T^{T_m} \Delta C_p(T) dT \quad (5)$$

where  $\Delta C_p(T)$  is the difference in heat capacities of the solid and vapour. However, 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  $\Delta H_{\text{sub}}$ . Even in cases where this has been done  $\Delta C_p(T)$  is small and its contribution can be neglected for all but the most precise work. Thus for practical purposes, and over limited temperature range,  $\Delta H$  may be considered constant; thus Eq. (3) may be written in the form:

$$\ln p = B - \frac{\Delta H}{RT} \quad (6)$$

combining this with Eq. (2) gives:

$$\ln v = B' - \frac{\Delta H}{RT} \quad (7)$$

thus, the heats of vaporisation and sublimation can be found directly from the rate of mass loss obtained by

thermogravimetry providing the molecular weight of the vaporising species is known [21].

#### 4. Results and discussion

Plots of vapour pressure ( $p$ ) against  $v$  for benzoic acid, acetamide, benzophenone and phenanthrene are shown in Fig. 1. The vapour pressures were interpolated from data in [22–27]. Corresponding heats of sublimation and vaporisation were calculated from the slope of plots of  $\log(v)$  vs.  $1/T$  (Table 1). Both acetamide and benzoic acid gave lower heats of vaporisation than given in the literature. This is attributed to the association of molecules in the gas phase which would reduce its effective pressure since this depends on the number rather than mass of molecules present. Calis-Van Ginkel et al. have discussed how absolute vapour pressure determinations (using a torsion-effusion technique) can be combined with weighing measurements to study the association in the gas phase for formic, acetic, propanoic and butanoic acids [28]. Our measurements suggest that benzoic acid sublimates almost exclusively as the monomer – which is in agreement with the studies of De Kruif and Blok [25] – but that some association occurs for material

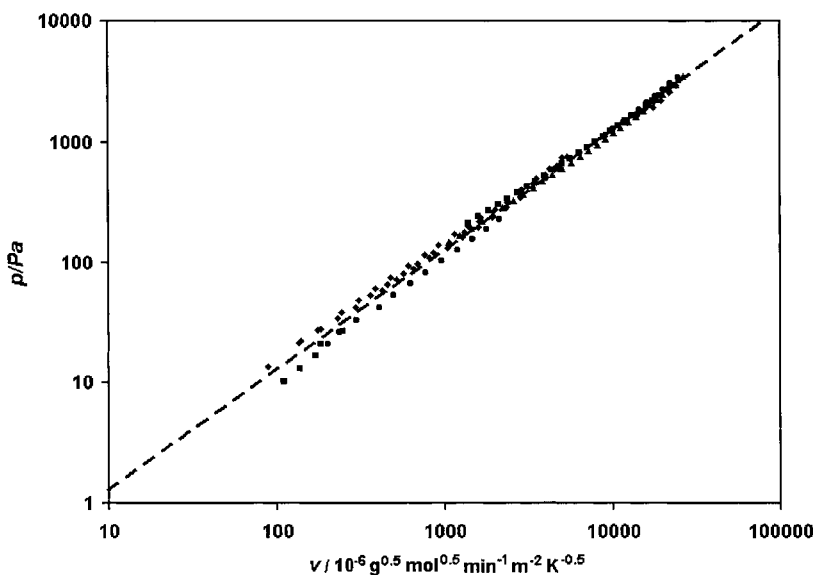


Fig. 1. Calibration curve showing relationship between volatilisation rate ( $v = (dm/dt)\sqrt{[T/M]}$ ) and vapour pressure ( $p$ ), for benzoic acid ( $\blacklozenge$ ), benzophenone ( $\blacktriangle$ ), phenanthrene ( $\blacksquare$ ) and acetamide ( $\bullet$ ). 90% of original data omitted for clarity. Dashed line indicates linear trend.

Table 1  
Heats of sublimation and vaporisation for calibration substances

Substance	$\Delta H_{\text{sub}}$ (kJ mol <sup>-1</sup> )		$\Delta H_{\text{vap}}$ (kJ mol <sup>-1</sup> )	
	This work	Literature	This work	Literature
acetamide	78.5±0.3	77.8 [22]	53.2±0.4	58 <sup>a</sup> [23,24]
benzoic acid	87.5±0.4 <sup>b</sup>	86–90 [25]	55±6 <sup>b</sup>	66–69 [25]
benzophenone	not measured	92–95 [26]	63.9±0.2	62 <sup>a</sup> [23,24]
phenanthrene	92±1	85–92 [27]	63.1±0.1	59 <sup>a</sup> [23,24]

<sup>a</sup> denotes value calculated from vapour pressure data.

<sup>b</sup> denotes mean of three determinations.

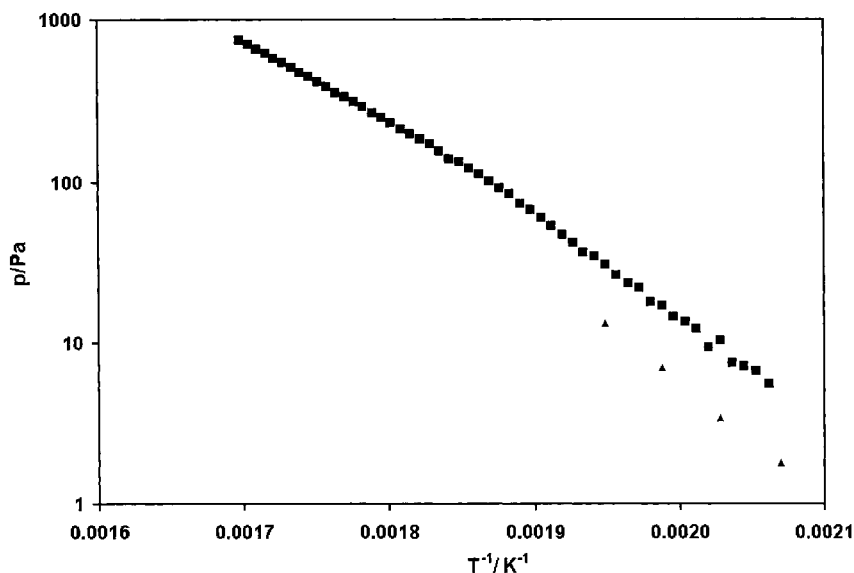


Fig. 2. Vapour pressure data for CI Disperse Yellow 54 (■ this work, ▲ McDowell [6]).

evaporating from the melt. The results for acetamide lead to similar conclusions.

Using Eq. (2) it is possible to relate the rate of mass loss to vapour pressure. Using the data for benzophenone, phenanthrene, solid benzoic acid and solid acetamide we find that  $p = 0.1274v$  with a correlation coefficient  $R^2$  of 0.998 where  $v$  is expressed as the rate of mass loss per unit area (mg min<sup>-1</sup> m<sup>-2</sup>) multiplied by the square root of the absolute temperature ( $K$ ) divided by the square root of the molecular weight (g mol<sup>-1</sup>). Thus, providing the same experimental conditions are used, it is possible to find the vapour pressure of other non-associating materials.

McDowell's spectroscopic studies of disperse dyes in the gas phase showed no evidence for association

[7]; therefore their vapour pressures could be calculated with confidence. A plot of  $\log(p)$  against reciprocal absolute temperature for Yellow 54 is shown in Fig. 2. McDowell reported lower values for the vapour pressure in the range 210–240°C [7]. This may be attributed to differences in the purity of the sample, which can also exist in two tautomeric forms. The heats of sublimation ( $\Delta H_{\text{sub}}$ ) and vaporisation  $\Delta H_{\text{vap}}$  were obtained from the slope of the plot below and above the melting region respectively. The heat of sublimation (125.2±0.4 kJ mol<sup>-1</sup>) is comparable with that calculated from the vapour pressure data of McDowell (139 kJ mol<sup>-1</sup>) [7]. The heat of vaporisation was found to be 94.1±0.1 kJ mol<sup>-1</sup>, the difference between  $\Delta H_{\text{sub}}$  and  $\Delta H_{\text{vap}}$  being

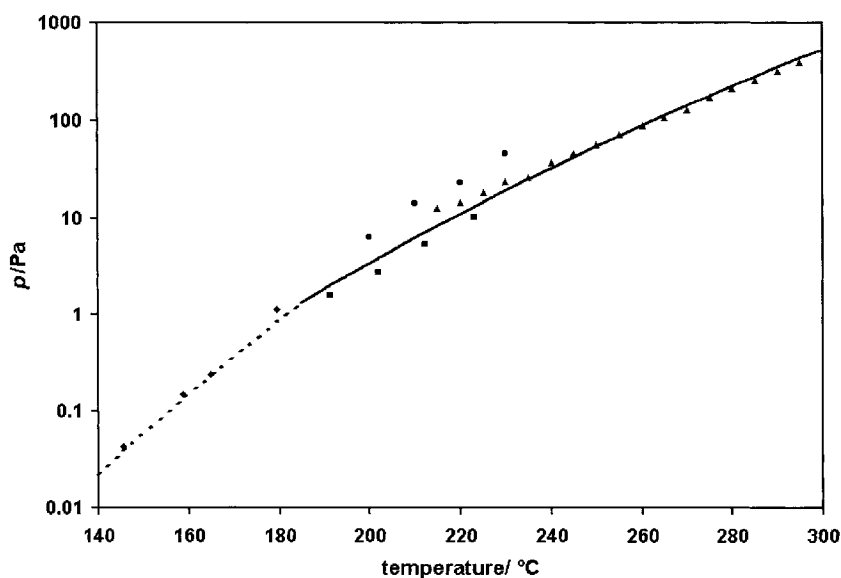


Fig. 3. Vapour pressure data for CI Disperse Red 60 (■ isothermal measurements, ▲ made at  $1^{\circ}\text{C min}^{-1}$ ). Solid line indicates fit to Clausius–Clapeyron equation, dashed line indicates extrapolation of this curve into the solid state. Sublimation data of Macnab [29] (◆) and vaporisation data of McDowell [7] (●) shown for comparison.

$31.1 \pm 0.5 \text{ kJ mol}^{-1}$  – consistent with that measured by DSC ( $31.59 \text{ kJ mol}^{-1}$ ). Extrapolation of the linear regions of the  $\log(p)$  vs.  $1/T$  plots allowed the melting temperature to be estimated from the thermogravimetric data. This value ( $267.5^{\circ}\text{C}$ ) was also in excellent agreement with that obtained by DSC ( $267.8^{\circ}\text{C}$ ), indicating that this technique is capable of providing accurate calorimetric information. The vapour pressure of Yellow 54 at its melting temperature is 136 Pa. Similar studies on other materials of interest confirmed these findings, and showed that melting temperatures and heats of fusion could be calculated for substances which gave poorly defined DSC traces.

A comparison of experimental results (from continuous-heating and isothermal measurements) and literature data for Red 60 is shown in Fig. 3 [7,29]. The heat of vaporisation was found to be  $114.1 \pm 0.2 \text{ kJ mol}^{-1}$ , compared to McDowell's value of  $128 \text{ kJ mol}^{-1}$ . No reliable measurements could be made in the solid state for this compound since the rate of mass loss was too small. However, an approximation for the vapour pressure in this region was obtained by taking into account its melting temperature ( $185.0^{\circ}\text{C}$ ) and heat of fusion ( $30.14 \text{ kJ mol}^{-1}$ ) measured by DSC and extrapolating the data according to

relationship.

$$p(T) = p(T_m) \exp \left\{ \frac{-\Delta H_{\text{sub}}}{R} \left( \frac{1}{T} - \frac{1}{T_m} \right) \right\} \quad (8)$$

where  $p(T_m)$  is the vapour pressure at the melting temperature ( $1.31 \text{ Pa}$  at  $185.0^{\circ}\text{C}$ ) – obtained by extrapolation of the vapour pressure data in the melt – and  $\Delta H_{\text{sub}}$  is the heat of sublimation from Eq. (4) ( $144.2 \text{ kJ mol}^{-1}$ ).

It is also possible to estimate the boiling point at normal atmospheric pressure of these materials by extrapolating the vapour pressure vs. temperature curve until the pressure is  $101325 \text{ Pa}$ . For Yellow 54 and Red 60, the normal boiling temperatures were found to be  $518.3$  and  $460.8^{\circ}\text{C}$  respectively – although the thermal stability of these compounds at such temperatures is questionable.

## 5. Conclusions

This work shows that, accurate estimates of vapour pressures can be derived from thermogravimetry after calibration with substances of known vapour pressure under the same conditions providing that the mole-

cular weight of the substance in the vapour phase is known. Linear rising temperature conditions afford a rapid means of measurement, although increased sensitivity can be obtained by performing isothermal experiments; these also serve to confirm the validity of results. Heats of vaporisation can be calculated from the temperature dependence of the vapour pressure. If the material has sufficient vapour pressure in the solid state its heat of sublimation can be found in the same manner, thus the heat of fusion calculated by difference. In such cases, its melting temperature can be obtained too. Studies of two disperse dyes indicates that thermogravimetry is capable of providing accurate calorimetric information.

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