A REVISED EQUATION FOR ESTIMATING THE VAPOUR PRESSURE OF LOW-VOLATILITY SUBSTANCES FROM ISOTHERMAL TG DATA

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Abstract

Previous investigators have used the Langmuir vaporisation relation to estimate the vapour pressures of low-volatility compounds from thermogravimetric data. However, this equation is strictly valid for evaporation into a vacuum only. For measurements conducted at finite pressures, molecular diffusion must be taken into account. A revised equation is proposed: $dm_A/dt \propto M_A P_A D_{AB}/T$. It is also shown that the proportionality between vapour pressure and vaporisation rate is very general. It arises from the assumptions of ideal gas behaviour, Raoult's law and a negligible concentration of the sample compound far from the sample surface.

Introduction

The vapour pressures of substances of very low volatility can be measured accurately using either torsion effusion, weighing effusion or a combination of these methods [1]. With weighing effusion a sample, placed inside a container with a small hole, is subjected to high vacuum and the rate of mass loss is determined. Knudsen [2] derived the governing equation for this situation. Langmuir [3] considered evaporation, from an isolated solid surface, into a vacuum and obtained an equation similar to that for weighing effusion:

$$P_A = \frac{1}{\alpha}\sqrt{\frac{2\pi RT}{M_A}} n_A \tag{1}$$

Langmuir [3] argued that the 'accommodation coefficient' [3] (or 'vaporisation coefficient' [7, 8]), α, should be close to unity for high molecular mass substances.

Gückel *et al.* [4] described a gravimetric method for determining the rate of evaporation of pesticides. Their data indicated a linear relationship between the rate of vapori-

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sation and the vapour pressure of a substance at a fixed airflow rate. Elder [5] used a thermo-balance to measure the rate of sublimation of pharmaceutical compounds into a stream of nitrogen purge gas. He also observed a linear relationship between vapour pressure and the rate of mass loss under isothermal conditions. In a similar study Aggarwal *et al*. [6] found that the evaporation rate follows the Arrhenius temperature dependence. The apparent energy of activation was shown to approach the enthalpy of vaporization as calculated from the Clausius–Clapeyron equation.

Based on these encouraging results, Price and Hawkins [7–9] formalised a procedure for estimating the vapour pressure, of low-volatility substances, from thermogravimetric data obtained in the presence of an inert purge gas at atmospheric pressure. Their analysis is based on the Langmuir relationship, Eq. (1), rewritten in the following format:

$$P_A = k\varphi \tag{2}$$

where $k = \sqrt{2\pi R}/\alpha$ and $\varphi = \sqrt{T/M_A}\, n_A$.

They noted that, in the case where the material volatilises into a flowing gas stream at one atmosphere rather than into a vacuum, the vaporisation coefficient, α, can no longer be assumed equal to unity. Nevertheless they stated that, for a given experimental set-up, k should be a calibration constant independent of the material being investigated [7]. Dollimore, Alexander and co-workers [10–15] used this technique to study the vaporisation of a variety of substances. However, they questioned the substance independence of the calibration constant k [15]. They regarded another discrepancy as more disturbing: The experimental results yielded an 'unrealistic', very low value for the vaporisation coefficient: $\alpha \approx 5.8 \cdot 10^{-5}$ [10, 13]. They stated: 'Further research should be performed in this direction to critically evaluate the value of α' [10].

In order to overcome these potential problems, they recommend a comparative method based on the ratio of the Langmuir equations for a reference and the sample under investigation [15]. In addition they advise that the reference and sample compounds should melt and evaporate in a similar temperature range and that they should exhibit structural similarities [15].

A key assumption, in both the Knudsen and Langmuir derivations, is that the vapour pressure is so low that the actual rate of evaporation of the substance is independent of the presence of vapour around it, i.e. collisions between the vapour molecules do not occur at all. This implies that, when an individual molecule leaves the surface of the sample, it never returns. The derivation presented by Langmuir [3] makes this very clear. However, at atmospheric pressures, collisions between sample molecules and inert gas molecules are inevitable: the mean free path in air at ambient conditions is of the order of $8 \cdot 10^{-8}$ m. This length scale is much shorter than typical sample and equipment dimensions and, as a consequence, diffusion cannot be neglected. Thus vaporisation under these conditions will be lower than predicted by the Langmuir equation owing to the return to and re-absorption of molecules on the sample surface.

Thermogravimetric methods potentially have considerable advantages compared to the conventional methods for determining vapour pressures. These include the relatively small amounts of substance that are sufficient for measurements, the simplicity of the experimental set-up and the short experimental times that are neces-

sary for evaluations. Thus it is of interest to reconsider the theoretical basis of the methods developed by the pioneers [4–15].

Price and Hawkins [7] observed that small variations in the flow rate of the purge gas did not affect the rate of vaporisation of a sample placed in an aluminium sample cup. This observation is consistent with mass transport limited by diffusion through a stagnant medium, i.e. the inert gas. In contrast, Gückel *et al*. [4] found that the vaporisation rate from a sample suspended in a fast flowing gas was strongly affected by the flow rate. This implies that forced convection controlled the mass transfer. In this paper a modified vaporisation equation is derived on the basis of convective mass transport for an isolated sample suspended in a flowing gas stream. The analogy between heat and mass transfer is invoked to facilitate calculations. The revised vaporisation theory is applied to the experimental results obtained by Gückel *et al*. [4] and Dollimore, Alexander and co-workers [15].

Theory

Consider the evaporation of compound A when an inert gas B flows past the sample. The objective is to calculate the steady state mass loss from the isolated sample body. The following simplifying assumptions are made:

- Constant physical properties. All physical properties, including the diffusion coefficient, D_{AB}, are assumed concentration independent. The mole fraction of compound A anywhere in the purge gas is so low that the physical properties of the gas mixture are essentially identical to those of the pure purge gas.
- No chemical reaction occurs. The possibility of association of sample molecules in the gas phase is not considered.
- Gas solubility. It is assumed that the carrier gas is insoluble in the sample liquid/solid.
- Isothermal conditions. The thermogravimetric experiment is conducted under steady state isothermal conditions.
- Sample dimensions. The sample has well-defined dimensions with a characteristic length scale denoted by L. The size of the sample substance is assumed small compared to dimensions of the experimental cavity.
- Steady state conditions. In reality vaporisation leads to a loss of sample volume and strictly speaking one is dealing with a moving boundary problem. It is assumed that the boundary regression is so slow that a pseudo-steady state assumption is valid.
- Ideal gases. All the vapours behave as ideal gases.
- Concentration of the sample substance A in the gas. The approaching purge gas does not contain compound A as an impurity. At the sample surface the concentration of compound A equals the equilibrium concentration at the prevailing temperature and pressure and is calculated from Raoult's law.
- Convective mass transport. The flow rate of the inert purge gas B is sufficiently fast to control the rate of mass transfer into the inert gas stream.
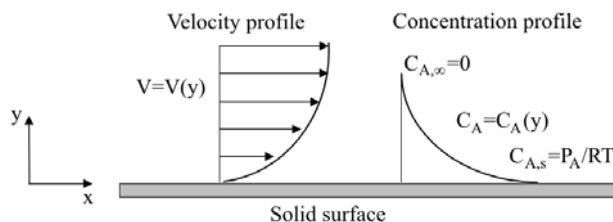
Fig. 1 Concentration and velocity profiles for flow past a solid surface. The solid is composed of low-vapour pressure substance A that sublimes into the inert gas

Figure 1 illustrates the evaporation of substance A into an inert gas stream flowing past its surface. When there is no chemical reaction occurring and the density and diffusion coefficient are assumed constant, the differential equation that describes the mass transfer takes the following form:

$$\frac{\partial C_A}{\partial t} + \overline{\mathbf{v}} \bullet \nabla C_A = D_{AB} \nabla^2 C_A \tag{3}$$

At a solid surface the fluid velocity vanishes and the mass transfer rate is by molecular diffusion only:

$$N_A = -D_{AB} \frac{d(C_A - C_{A,\infty})}{dy}\bigg|_{y=0} \tag{4}$$

It is convenient to lump the effects of geometry, fluid flow patterns and boundary conditions on the rate of mass transport into an empirical parameter, the mass transfer coefficient, defined as follows:

$$N_A = k_c(C_{A,\,s} - C_{A,\,\infty}) = k_c C_{A,s} \tag{5}$$

The last part of this expression follows from the assumption that the concentration of the sample species is negligible far away from the sample. Under conditions in which the ideal gas law applies, the surface molar concentration is given by Raoult's law as:

$$C_{A,s} = \frac{P_A}{RT} \tag{6}$$

Since the concentration of the sample compound in the gas phase is very low, the mass flux is related to the molar flux:

$$n_A = N_A M_A \tag{7}$$

Combining Eqs (5) to (7) and rearranging yields the revised vaporisation equation:

$$P_A = \left(\frac{RT}{k_c M_A}\right) n_A \tag{8}$$

Comparing Eq. (8) with Eq. (1) provides an expression for the Langmuir vaporisation 'constant', α, at finite pressures

$$\alpha = k_{\mathrm{c}} \sqrt{\frac{2\pi M_{\mathrm{A}}}{RT}} \tag{9}$$

Note that Eq. (8) shows that the vapour pressure, P_{A}, is actually proportional to the molar flux rather than the mass flux ($N_{\mathrm{A}} = n_{\mathrm{A}}/M_{\mathrm{A}}$). P_{A} is also inversely proportional to the mass transfer coefficient, k_{c}. The latter depends on factors such as sample geometry, the presence or absence of fluid flow, etc.

Dimensionless parameters are commonly used to correlate experimental mass and heat transport data as well as theoretical results. In dimensionless form the mass transfer coefficient is termed the Sherwood number. Formally it is obtained by combining Eqs (4) and (5).

$$Sh = \frac{k_{\mathrm{c}} L}{D_{\mathrm{AB}}} = \frac{\left[\dfrac{\mathrm{d}}{\mathrm{d}y}(C_{\mathrm{A}} - C_{\mathrm{A},\infty})\right]_{y=0}}{\left[\dfrac{C_{\mathrm{A,s}} - C_{\mathrm{A},\infty}}{L}\right]} \tag{10}$$

Note that the Sherwood number also incorporates a characteristic length scale for the geometry under consideration (e.g. in the case of mass transport from a sphere, the length scale is defined by the diameter, $L=d$).

Implicit in Eq. (10) is the solution of differential Eq. (3) subject to specified boundary and initial conditions in the context of the sample geometry, flow conditions, etc. Alternatively, Sherwood numbers can be obtained empirically by correlating extensive experimental data. For steady-state convective mass transfer the Sherwood number is a function of the mass transport Fourier number, the Reynolds number and the Schmidt number:

$$Sh = Sh(Fo,\ Re,\ Sc,\ geometry) \tag{11}$$

The Fourier number is a dimensionless time. The Reynolds number ($Re = vL/\nu$) quantifies the relative importance of inertia and viscous forces in the flow field [16]. The Schmidt number provides an indication of the relative thickness of the hydrodynamic boundary layer to the concentration boundary layer [18]. It is defined as the ratio of the molecular diffusivity of momentum to the molecular diffusivity of mass: $Sc = \nu/D_{\mathrm{AB}}$.

Heat transfer has received more attention than mass transfer owing to its greater importance in engineering applications. Thus many more empirical correlations and analytical solutions were developed for heat transfer than for mass transport. Fortunately there is a very convenient analogy between mass and heat transport [16]. This is important; as it allows one apply solutions obtained for heat transfer to the corresponding mass transfer situation. For convective heat transfer the corresponding equation is:

$$Nu = Nu(Fo,\ Re,\ Pr,\ geometry) \tag{12}$$

The analogy between heat and mass transfer allows us one to obtain Eq. (11) by simply replacing *Nu* with *Sh* and *Pr* with *Sc* in Eq. (12). Eliminating k_c in Eq. (8) using Eq. (10) yields:

$$P_A = \left(\frac{LRT}{Sh D_{AB}} \right) N_A \qquad (13)$$

Equation (13), c.f. Eq. (8), is the general form for the vaporisation rate at finite pressures. Note that, fundamentally, the proportionality between vapour pressure and vaporisation rate arises from the assumptions that the gas-phase surface concentration of A is given by Raoult's law and that the purge gas is free from A as impurity. These equations have general validity for all experimental conditions including transient and steady state vaporisation conditions. Thus, provided the experimental conditions guarantee a constant value for k_c, any experimental set-up can in principle be used to determine vapour pressures.

However, it is obvious that particular experimental conditions will be easier to control and will be conducive to more accurate measurement of vapour pressures. Two situations of particular interest are those associated with forced convective mass transfer and steady-state diffusion through a stagnant gas. For the steady-state diffusion the Sherwood number assumes a constant value characteristic of the diffusion geometry, e.g. $Sh=Sh_D$. In the former case typical correlations for the Sherwood number may take the form:

$$Sh = aRe^b Sc^{1/3} \qquad (14)$$

The important point to be made here is that the vapour pressure cannot be measured independent of the diffusion coefficient with the thermogravimetric method, i.e. for steady-state diffusion into a stagnant fluid:

$$P_A D_{AB} = \left(\frac{LRT}{Sh_D} \right) N_A \qquad (15)$$

Equation (15) shows that the experiments in actual fact yield estimates for the product of the diffusion coefficient and vapour pressure under the prevailing conditions. Thus extraction of vapour pressure values from experimental data requires knowledge of the diffusion coefficient.

A similar conclusion holds true for measurements done under forced convection conditions. Here the Schmidt number dependence of the mass transfer coefficient must be taken into account when the relative vaporisation rates between different molecules are considered:

$$P_A D_{AB}^{2/3} \propto T N_A \qquad (16)$$

Interestingly, there is mutual temperature compensation between the gas kinematic viscosity and that of the diffusion coefficient. Figure 2 shows that the temperature dependence of the kinematic viscosity of typical purge gases is the same as that expected for gaseous diffusion coefficients, i.e. $\nu \propto T^{7/4}$. The straight lines in Fig. 2
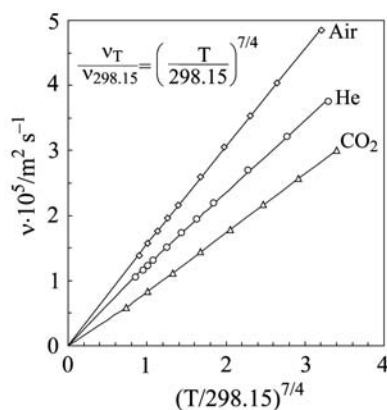
Fig. 2 The temperature dependence of the kinematic viscosity of gases. The solid
markers indicate data values from [16]

suggest that, for practical purposes, the Schmidt number may be taken as constant
over wide temperature ranges.

Comparison with literature experimental data

Forced convection experiments

When convective mass transfer conditions apply, the inert gas flow rate affects the
rate of vaporisation. This is what Gückel *et al*. [4] observed in their experiments.
They measured the isothermal vaporisation rates of several substances with known
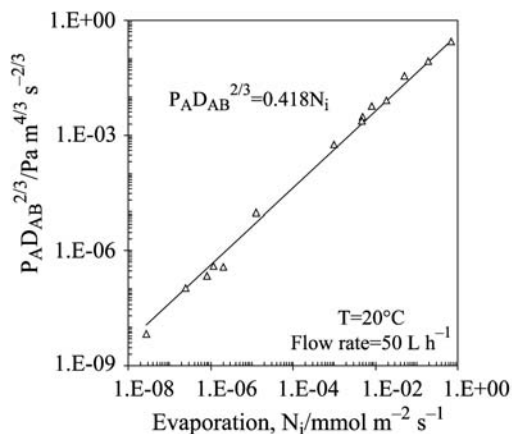

Fig. 3 Recalculated calibration curve for forced convection mass transfer data obtained
by Gückel *et al*. [4] for 14 compounds including linear alcohols, glycerine and
various pesticides. The data is consistent with a direct proportionality between
$P_i D_{iB}^{2/3}$ and N_i

vapour pressures at 20°C and ambient pressure using gravimetry [4]. The procedure was as follows: a thin coating of the compound to be tested was applied to a roughened glass slide. The sample plate was suspended vertically from one arm of a highly accurate electric balance inside a glass tube. A continuous dry air current was passed through the tube at a constant flow rate, e.g. 50 L h^{-1}. Gückel *et al.* [4] measured the vaporisation rate of 14 compounds with known vapour pressures and proposed a power law relationship between the vapour pressure and the molar vaporisation rate:

$$P_A = cN_A^e \tag{17}$$

Their data have been re-plotted in Fig. 3. As suggested by Eq. (16), the experimental data show a direct proportionality between $P_A D_{AB}^{2/3}$ and N_A at a constant temperature.

Diffusion through a stagnant gas medium

Price and Hawkins [7] observed that small variations in the flow rate of the purge gas did not affect the rate of vaporisation from samples pans. This observation is consistent with mass transport limited by diffusion through a stagnant medium, i.e. the inert gas.

In thermogravimetric analysis the overall mass loss rate is recorded:

$$\frac{dm_A}{dt} = An_A = AN_A M_A \tag{18}$$

Owing to the difficulties involved in controlling sample geometry, it is not easy to make absolute measurements in commercial thermo-balances. Instead, reference compounds are used to establish appropriate calibration curves. In order to 'address the problem of the non-ideal vaporization coefficient', Phang *et al.* [15] proposed a comparative method based on the Langmuir relationship, Eq. (1):

$$P_S = P_R \sqrt{\frac{M_R}{M_S}} \left(\frac{(dm/dt)_S}{(dm/dt)_R} \right) \tag{19}$$

However, according to Eqs (15) and (18) the correct relationship, for diffusion into a stagnant gas layer and, provided the Sherwood number remains constant during the experiment, is in fact:

$$P_S = P_R \left(\frac{D_{RB}}{D_{SB}} \right) \left(\frac{M_R}{M_S} \right) \left(\frac{(dm/dt)_S}{(dm/dt)_R} \right) \tag{20}$$

Note that the comparisons are made at the same temperature and that identical Sh_D values are assumed to apply for both reference and sample experiments. Table 1 details revised vapour pressure data for ethylparaben calculated from their experimental data using methylparaben as reference compound. Diffusion coefficients were estimated using Fuller's method [17]. Note that use of Eq. (20) instead of (19) suggests a constant 2.1% upward revision for the vapour pressure data of ethylparaben as reported by Phang *et al.* [15]. The fact that the correction is small is attributed to the sensible advice offered by

Phang *et al*. [15] with respect to sample and reference compounds that they should 'melt and evaporate within a similar temperature range and exhibit structural similarities'.

Table 1 Physical properties of methylparaben and ethylparaben. The Antoine vapour pressure constants[*] for ethylparaben were recalculated from the experimental data of Phang *et al.* [15] using Eq. (20). The temperature ranged from 446 to 473 K. Diffusion coefficients were estimated using Fuller's method [17]

Property	Methylparaben (reference)	Ethylparaben (sample)
Molar mass	152.15	166.18
$D_{AB} \cdot 10^5 / m^2\ s^{-1}$ at 446 K	1.38	1.29
A	5.2366	5.1014
B	1159.34	1159.26
C	−220.03	−219.79

[*]Antoine equation: $\log_{10}P = A - B/(C+T)$

Discussion and conclusions

The final equation that describes the vaporisation mass loss rate, as measured in a thermogravimetric experiment, is:

$$\frac{dm_A}{dt} = \left(\frac{ASh}{LRT}\right) M_A P_A D_{AB} \tag{21}$$

Unlike the Langmuir relation, Eq. (21) shows that the vaporisation rate, expressed in terms of the molar flux, is independent of the molecular mass of the sample. It also shows that knowledge of the diffusion coefficient is required in order to extract the vapour pressure from experimental thermogravimetric data. At first glance this may seem unfortunate. However, the quantity $P_A D_{AB}$ has practical importance as it quantifies the vapour release rate under quiescent conditions. On the other hand, knowledge of the vapour pressure is important as it provides an estimate of the maximum vapour phase concentration of an impurity via the relation: $C_A = P_A/RT$. Thus both the product $P_A D_{AB}$ and the vapour pressure are relevant for practical situations where the release of volatiles such as pesticides [4], perfumes [6] and volatile corrosion inhibitors [19] occur.

Another important point is that relationship (21) is based on the assumption that the surface vapour concentration is given by Raoult's law: $C_A = P_A/RT$. This also assumes ideal gas behaviour. However, at low pressures the behaviour of real vapours is more adequately described by the truncated virial equation of state [20]. When the vapour mole fraction is negligible, e.g. $y_A < 0.0001$, the following expression for the gas phase concentration is obtained:

$$C_A \approx \frac{P_A}{RT} \exp\left[\frac{(P - P_A)(\bar{V}_A + B_{BB} - 2B_{AB})}{RT}\right] \tag{22}$$

Using the second virial coefficients reported by Dymond and Smith [21], the correction factor on the right hand side of Eq. (22) for the dodecane–nitrogen system amount to 1.024 at 300 K and 1.0025 at 400 K. While these corrections are relatively small, they do indicate limitations on the accuracy that can be achieved using Eq. (21).

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List of symbols

A	vaporisation surface area	m^2
a	constant in Eq. (14)	–
B	second virial coefficient	$m^3\,mol^{-1}$
b	coefficient in Eq. (14)	–
C_A	concentration of compound A	$mol\,m^{-3}$

D_{AB}	diffusion coefficient	$m^2\,s^{-1}$
d	diameter	m
e	constant in Eq. (17)	–
Fo	Fourier number $(D_{AB}t/L^2)$	–
k	constant in Eq. (2)	–
k_c	mass transfer coefficientm	s^{-1}
L	sample geometry characteristic length	m
M	molar mass	$kg\,kmol^{-1}$
m	sample mass	kg
N_A	molar flux of compound A	$mol\,m^{-2}\,s^{-1}$
n_A	mass flux of compound A	$kg\,m^{-2}\,s^{-1}$
Nu	Nusselt number	–
P_A	vapour pressure of substance A	Pa
P	pressure	Pa
Pr	Prandtl number	–
R	universal gas constant	$J\,mol^{-1}\,K^{-1}$
Re	Reynolds number (vL/v)	–
Sc	Schmidt number (v/D_{AB})	–
Sh	Sherwood number (k_cL/D_{AB})	–
Sh_D	Sherwood number for diffusion in a stagnant medium	
T	temperature	K
t	time	s
$\bar{V}$	molar volume of saturated liquid	$m^3\,mol^{-1}$
v	velocity	$m\,s^{-1}$
$\bar{v}$	velocity vector	$m\,s^{-1}$
x	lateral distance	m
y	normal distance	m
y_A	mole fraction component A	–

Subscripts

A	compound A
AB	mixture of compounds A and B
B	compound B
S	sample
R	reference
s	at the surface
∞	at a distance far removed from sample surface

Greek symbols

α	Langmuir evaporation constant, Eq. (1)	
φ	scaled mass flux $(\varphi = \sqrt{T/M_A}\,n_A)$ (Eq. (2))	
v	knematic viscosity	m^2/s