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Diffusion-controlled evaporation through a stagnant gas: estimating low vapour pressures from thermogravimetric data

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Abstract

The Langmuir vaporisation relation has been advocated for estimating vapour pressures of low-volatility compounds from thermogravimetric (TG) data. However, this equation is strictly valid only for evaporation into a vacuum. When measurements are conducted at finite pressures, diffusion must to be taken into account. For the situation where the rate of evaporation is controlled by diffusion through a stagnant gas layer, the rate of vaporisation is given by $\mathrm{d}m_\mathrm{A}/\mathrm{d}t = (M_\mathrm{A}S/RT)P_\mathrm{A}D_\mathrm{AB}$. Here $\mathrm{d}m_\mathrm{A}/\mathrm{d}t$ $\mathrm{g\,s^{-1}}$ is the TG-measured rate of mass loss; P_A (Pa) the sample vapour pressure at absolute temperature T (K); R ($\mathrm{J\,mol^{-1}\,K^{-1}}$) the gas constant; D_AB ($\mathrm{m^2\,s^{-1}}$) the diffusion coefficient; M_A ($\mathrm{kg\,kmol^{-1}}$) the molar mass of the vaporising compound; and S (m) a shape factor characteristic of the system geometry. In typical TG set-ups the system geometry takes the form of a partially filled cylindrical sample cup with an inert purge gas sweeping over the top. In this particular case $S = A/z$, where A ($\mathrm{m^2}$) is the cross-sectional surface area and z (m) the depth of the gas-filled part of the sample cup.

Keywords: Vapour pressure; Diffusion; Vaporisation; Evaporation; Thermogravimetry

1. Introduction

Compared to conventional techniques for vapour pressure measurement [1–3], thermogravimetric (TG) methods offer several advantages. 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 necessary for evaluations. As a consequence, several investigators have attempted vapour pressure measurements using thermogravimetry [4–15]. Invariably, measurements were conducted in the presence of a purge gas. Most studies [4,5,7–15] reported a linear relationship between the rate of vaporisation and the vapour pressure at a fixed gas flow rate. With respect to the effect of flow rate, experiences differed. Gückel et al. [4] found that the vaporisation rate from a sample suspended in a fast-flowing purge gas was strongly affected by the flow rate. In contrast, Price and Hawkins [7] stated that small variations in the flow rate of the purge gas did not affect the vaporisation rate of compounds placed in sample cups.

Langmuir [3] derived the following expression for the mass flux of a solid (substance A) evaporating into a vacuum:

$$\frac{\mathrm{d}m_\mathrm{A}}{\mathrm{d}t} = \alpha A\sqrt{\frac{M_\mathrm{A}}{2\pi RT}}P_\mathrm{A} \tag{1}$$

According to Langmuir [3] the vaporisation coefficient α should be close to unity for high molecular

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Nomenclature

A	vaporisation surface area (m^2)
C_A	concentration of compound A ($mol\,m^{-3}$)
D_{AB}	diffusion coefficient ($m^2\,s^{-1}$)
k_c	mass transfer coefficient ($m\,s^{-1}$)
m	sample mass (kg)
M	molar mass ($kg\,kmol^{-1}$)
P_A	vapour pressure of substance A (Pa)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
S	diffusional mass transfer shape factor, Eq. (5) (m)
t	time (s)
T	temperature (K)
z	diffusion path length (m)
z_p	diffusion penetration depth, Eq. (12) (m)

Greek letters

α	Langmuir evaporation constant, Eq. (1)
ϕ	moles (mol)

Subscripts

A	sample compound A
B	inert gas, compound B
IJ	mixture of compounds I and J where I, J $\in$ {A, B, R, S}
R	reference
s	at the sample surface
S	sample
∞	at a distance far removed from sample surface

mass substances. Price and Hawkins [7–9] suggested that Eq. (1) be used for estimating the vapour pressure of low-volatility compounds from thermogravimetric data. They recognised that, when the material volatilises into a flowing gas stream at atmospheric pressure rather than into a vacuum, the vaporisation coefficient α might no longer be equal to unity. Dollimore and co-workers [6,10–15] used this technique to study the vaporisation of a variety of substances. They observed a disturbingly low value for the vaporisation coefficient $\alpha \approx 5.8 \times 10^{-5}$ [10,13]. 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):

$$P_S = P_R\sqrt{\frac{M_R}{M_S}}\left(\frac{(dm/dt)_S}{(dm/dt)_R}\right) \qquad (2)$$

A deficiency of the Langmuir expression is that it cannot account for the effect of gas flow rate observed by Gückel et al. [4], at least not in an explicit way. In fact, because it neglects the effect of mass diffusion, the Langmuir equation is actually invalid for describing evaporation at finite pressures [16]. Unfortunately, this flaw also invalidates the comparative method proposed by Phang et al. [15,16]. In this paper a revised vaporisation equation is derived for the situation where the rate of vaporisation is diffusion-limited. The situation where mass transfer by convection enhances the rate of vaporisation was dealt with in [16].

2. Theory

Thermogravimetric experiments that involve evaporation of a liquid or solid sample (compound A) through a stagnant surrounding layer of an inert gas B are considered. The objective is to calculate the steady-state mass loss subject to the following simplifying assumptions:

1. *Ideal gases*. All the vapours behave as ideal gases. The solubility of compound A in the gas B follows Raoult’s law.
2. *Concentration of the sample substance A in the gas phase*. The concentration of A assumes a constant value at the sample surface that equals the equilibrium concentration at the prevailing temperature and pressure. Far away from the sample surface the concentration becomes negligible.
3. *Gas solubility*. It is assumed that the carrier gas is insoluble in the sample liquid/solid.
4. *Quasi-isothermal conditions*. The thermogravimetric experiment is conducted under isothermal steady-state conditions. Alternatively the temperature is ramped up linearly under quasi-isothermal conditions. This implies a temperature scan rate that is very slow compared to the rates of diffusion and convection such that the mass loss rate at any given temperature also corresponds to that of the corresponding isothermal experiment at steady-state conditions.

5. *Pseudo-steady-state conditions*. Vaporisation leads to a loss of sample and in reality one is dealing with a moving boundary problem. It is assumed that the condensed phase boundary regression is sufficiently slow to have a negligible effect on the instantaneous diffusion path-length, i.e. pseudo-steady-state conditions prevail.
6. *Constant physical properties*. All relevant physical properties, e.g. the diffusion coefficient D_{AB}, are concentration-independent. The mole fraction of compound A everywhere 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.
7. *No chemical reaction occurs*. The possibility of association of sample molecules in the gas phase is not considered.
8. *Equimolar counterdiffusion*. In practice the difference between the two extreme diffusion situations, cf. equimolar counterdiffusion of A and B and diffusion of A through stagnant B are usually very small, and a good estimate of the molar flux is often obtained using either condition [17]. Here the former assumption is used as it involves simpler mathematics.
9. *Negligible convective transport*. The rate of mass transport is limited by a diffusion mechanism and not by the flow rate of the inert purge gas B.

Consider first the case of diffusion into an infinite or a semi-infinite medium. When assumptions 6–9 apply, Fick's second law of diffusion governs the mass transport in the gas phase [17,18]

$$\frac{\partial C_A}{\partial t} = D_{AB}\,\nabla^2 C_A \qquad (3)$$

This equation must be solved taking the system geometry and boundary conditions into account. The evaporation rate can then be calculated from the concentration gradient at the sample surface. In practice it is conventional to express this flux in terms of an empirical parameter, the mass transfer coefficient k_c, as follows [17,18]:

$$\frac{d\phi_A}{dt} = k_c A(C_{A,s} - C_{A,\infty}) \qquad (4)$$

For pure diffusion the steady-state mass transfer coefficient is a function of geometry only and can be expressed in terms of shape factors [19]:

$$k_c = D_{AB}\frac{S}{A} \qquad (5)$$

Shape factors have been tabulated for many geometries, e.g. by Hahne and Grigull [20] for the analogous case of heat transfer by conduction. Eq. (4) can be rewritten as

$$\frac{d\phi_A}{dt} = D_{AB}S(C_{A,s} - C_{A,\infty}) \qquad (6)$$

Assumptions 1 and 2 imply that $C_{A,\infty}$ equals zero and that $C_{A,s} = P_A/RT$. It follows that

$$\frac{d\phi_A}{dt} = \left(\frac{S}{RT}\right) P_A D_{AB} \qquad (7)$$

Since the concentration of the sample compound in the gas phase is very low, the mass loss rate of sample compound A, as measured by TG, is related to the molar rate loss as

$$\frac{dm_A}{dt} = M_A\frac{d\phi_A}{dt} = \left(\frac{M_A S}{RT}\right) P_A D_{AB} \qquad (8)$$

Eq. (8) is the general form for the TG-measured vaporisation rate at finite pressures when mass transfer is limited by diffusion through a stagnant gas. Several comments are in order at this point: First, since Eq. (7) does not contain the molar mass in the argument, the vaporisation process is fundamentally a molar rather than a mass-based rate process. Secondly, the proportionality between vapour pressure and vaporisation rate arises from the combination of assumptions 1 and 2, i.e. that Raoult's law gives the gas phase surface concentration of A and that the purge gas is free from A as impurity. Thirdly, the TG experiment yields the product of $D_{AB}P_A$, and separate knowledge of the diffusion coefficient is therefore required in order to extract the vapour pressure. Finally, Eq. (8) applies to any sample shape. Thus, provided the conditions guarantee a constant sample shape and size, any experimental set-up can in principle be used to determine vapour pressures.

In practice it is common in TG to study evaporation from a cylindrical sample cup maintained at a constant temperature and pressure [5–15]. Fig. 1 illustrates this experimental set-up. The sample cup shape is idealised as a cylindrical tube. The cup is partially filled with the sample liquid (or compressed solid) A. Inert gas B (e.g. nitrogen) flows rapidly across the open end of the tube, sweeping away any molecules of A emerging from the cup. This justifies the assumption that the concentration of vapour A equals zero at the top of the pan. Mass transfer in this system thus corresponds to one-dimensional diffusion through a stagnant gas layer. The steady-state solution of Eq. (3) as applied to this problem yields a linear concentration profile. At isothermal conditions the steady-state flux is given by [18]

$$\frac{d\phi_A}{dt} \approx \frac{AD_{AB}P_A}{zRT} \tag{9}$$

Comparison of this result with Eq. (7) shows that the form factor for the partially filled sample cup set-up is given by

$$S = \frac{A}{z} \tag{10}$$

Here A is the area of the cylinder and z the height of the tube occupied by gas. Note that the form factor changes during the TG experiment: as the sample becomes depleted the diffusion path-length z increases.

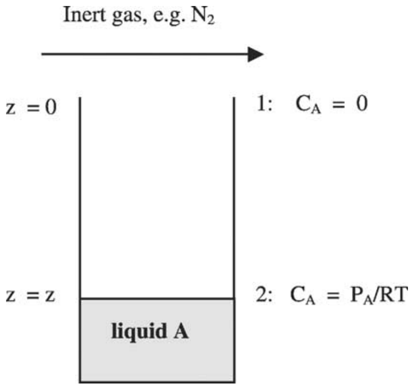

Fig. 1. Schematic of the experimental TG set-up utilising a partially filled sample cup. The sample compound diffuses through the gas region inside the pan. Sample molecules are swept away by the purge gas flowing over the top when they emerge from the cup.

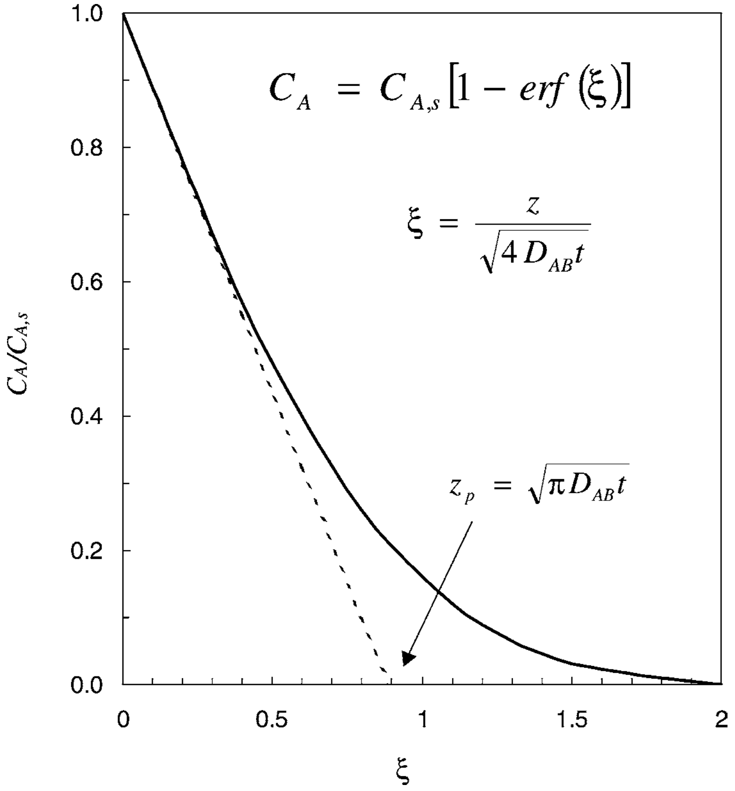

Fig. 2. The dimensionless concentration profile for diffusion into a semi-infinite one-dimensional medium.

When the isothermal TG experiment commences, the system is not necessarily at steady state. This will be the case, for example, immediately following a temperature jump from ambient to the measurement conditions. Valid steady-state measurements can only be made once a characteristic delay time has elapsed. A conservative estimate of the required equilibration time can be obtained as follows. Consider transient diffusion into a tube of infinite length. It is assumed that the concentration of A is initially zero everywhere inside the tube. At time $t = 0$, the concentration at the bottomend of the tube is suddenly increased to $C_{A,s}$. Solution of Eq. (6) yields the concentration profile mathematically described by the error function [17,18], and shown in Fig. 2:

$$C_A = C_{A,s}\left[1 - \operatorname{erf}\left(\frac{z}{\sqrt{4D_{AB}t}}\right)\right] \tag{11}$$

Fig. 2 also shows, as a straight line, the tangent of the concentration profile at the sample surface, i.e. at $z = 0$. It intersects the $C_A = 0$ level at a distance along the tube of

$$z_p = \sqrt{\pi D_{AB} t} \tag{12}$$

The distance z_p is called the penetration depth [17]. Owing to the linear steady-state concentration profile in a tube of finite length, this tangent line also corresponds to the steady-state concentration profile for a tube with a length corresponding to the penetration depth z_p. Thus Eq. (12) provides a conservative estimate for the time required to achieve equilibrium in a tube with a finite depth of z_p.

$$t_{\text{equilibrium}} \approx \frac{z^2}{\pi D_{AB}} \tag{13}$$

Table 1
The mass loss of methylparaben evaporating into air

Temperature T (K)	Vapour pressure P (kPa)	Diffusion coefficient D_{AB} (10^6 m^2 s^{-1})	Estimated pan depth z (mm)	Mass loss rate[a] dm/dt (μg s^{-1})		
				Experimental	Predicted	Error (%)
446	1.28	14.00	2.76	7.93	8.40	5.9
447	1.34	14.05	2.77	8.31	8.82	6.1
448	1.42	14.11	2.79	8.69	9.25	6.4
449	1.49	14.16	2.80	9.06	9.69	7.0
450	1.57	14.22	2.82	9.48	10.15	7.1
451	1.65	14.28	2.84	9.88	10.62	7.5
452	1.73	14.33	2.86	10.32	11.11	7.7
453	1.82	14.39	2.88	10.79	11.61	7.6
454	1.91	14.44	2.90	11.21	12.13	8.2
455	2.01	14.50	2.92	11.68	12.66	8.3
456	2.11	14.55	2.94	12.16	13.20	8.6
457	2.21	14.61	2.96	12.68	13.76	8.6
458	2.32	14.67	2.99	13.16	14.34	9.0
459	2.43	14.72	3.01	13.69	14.93	9.0
460	2.54	14.78	3.04	14.21	15.53	9.3
461	2.66	14.83	3.07	14.76	16.14	9.4
462	2.79	14.89	3.09	15.33	16.78	9.5
463	2.92	14.95	3.12	15.90	17.42	9.6
464	3.05	15.00	3.15	16.49	18.08	9.6
465	3.19	15.06	3.19	17.13	18.75	9.4
466	3.34	15.12	3.22	17.75	19.43	9.5
467	3.49	15.17	3.25	18.37	20.12	9.6
468	3.64	15.23	3.29	19.08	20.83	9.1
469	3.80	15.29	3.32	19.67	21.55	9.6
470	3.97	15.34	3.36	20.35	22.28	9.5
471	4.14	15.40	3.40	21.00	23.02	9.6
472	4.32	15.46	3.44	21.67	23.77	9.7
473	4.51	15.52	3.48	22.38	24.53	9.6

[a] The experimental thermogravimetric evaporation rates reported of Phang et al. [15] are compared with the values predicted by Eq. (14).

3. Comparison with literature experimental data

Phang et al. [15] have reported detailed TG measurements for methylparaben. Their data was obtained using dynamic scanning conditions (scan rate: 20 °C min^{-1}) and an airflow rate of 100 ml min^{-1}. These data were used to test the validity of the revised vaporisation rate (Eq. (8)), as applied to a cylindrical sample cup. This was done as follows: From the data provided in [10], the pan dimensions were estimated as 3.48 mm tall with a diameter of 6.34 mm. The initial sample mass was 87 mg. The density of methylparaben was arbitrarily assumed to equal 1.0 g cm^{-3}. By integrating the given mass loss rates, using Simpson's rule, the amount of material remaining was estimated. This allowed the estimation of the pan depth at each temperature. The vapour phase diffusion coefficients for methylparaben were estimated using the empirical Fuller method [21]. Sample calculations performed using an Excel Spreadsheet are reported in Table 1.

The predicted and experimental thermogravimetric mass loss rates are compared in Fig. 3. The theoretical predictions for diffusion in a tube show reasonable agreement at low temperatures. However, at the higher measurement temperatures the predicted values are up to 10% higher than the experimental data.

Price and Hawkins [7] found that the mass loss rates measured at a scan rate of 1 °C/min were similar to those measured under isothermal conditions. However, the data of Phang et al. [15] were obtained using a much higher scanning rate of 20 °C/min. How can one be sure that this rate was not too high to ensure pseudo-steady-state conditions? With methylparaben as sample substance at 200 °C, the diffusion coefficient is estimated at $1.55 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$. If it evaporates from a pan with a depth of 4 mm, Eq. (13) predicts $t_{\mathrm{equilibrium}} \approx 0.33\,\mathrm{s}$. Thus, in this case, equilibrium is established relatively fast. The reported [15] mass loss rate at this temperature was ca. 1.34 mg min^{-1}. Thus it is calculated that, in the time interval required to establish equilibrium, the following changes occurred: temperature changed by 0.11 °C, vapour pressure by less than 0.5% and the diffusion path-length by about 0.26 μm (if a density of ca. 1.0 g cm^{-3} is assumed). These changes are sufficiently small to indicate that, despite dynamic measurement conditions, the assumptions of quasi-isothermal and pseudo-steady-state conditions are essentially valid.

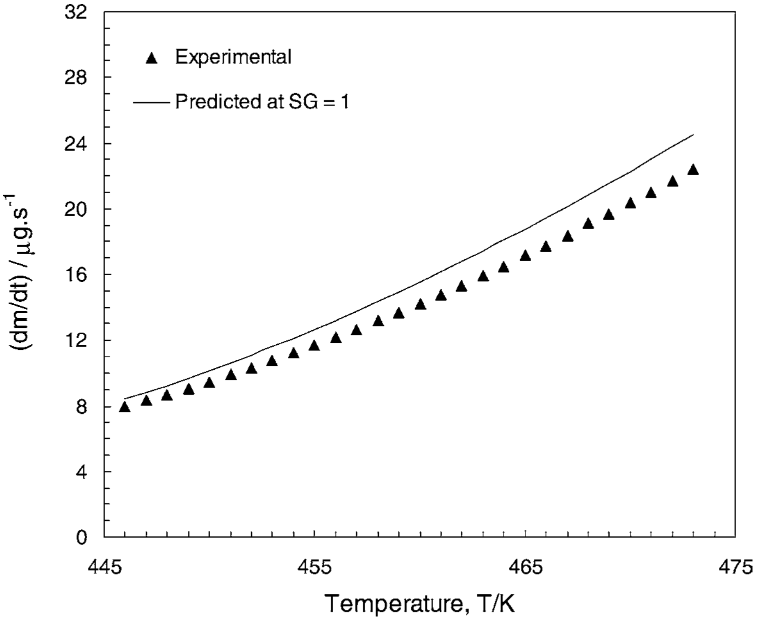

Fig. 3. Comparison of experimentally determined [15] and theoretically predicted (Eq. (14)) TG evaporation rates for methylparaben.

The difference between theory and experiment can therefore not be attributed to deviations from this condition.

4. Discussion and conclusions

The final equation that describes the vaporisation mass loss rate for diffusion-limited evaporation from a partially filled cylindrical cup is

$$\frac{\mathrm{d}m_\mathrm{A}}{\mathrm{d}t} = \left(\frac{M_\mathrm{A} A}{zRT}\right) P_\mathrm{A} D_\mathrm{AB} \qquad (14)$$

Unlike the Langmuir relation, Eq. (14) 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.

Comparison of Eqs. (1) and (14) provides the following expression for the Langmuir evaporation "constant" at finite pressures:

$$\alpha = \frac{D_\mathrm{AB}}{z}\sqrt{\frac{2\pi M_\mathrm{A}}{RT}} \qquad (15)$$

It is clear that α is not substance-independent and can therefore not be viewed as a calibration constant. This confirms the fears expressed by Phang et al. [15]. References [10,13] reported an average value for the Langmuir evaporation "constant", for measurements conducted with methylparaben, of $\alpha \approx 5.8 \times 10^{-5}$ and expressed surprise at the large, unexpected deviation from unity. Using SI units and the following parameter values for the methylparaben experiment at 473 K, $D_\mathrm{AB} = 1.55 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$, $M_\mathrm{A} = 0.15214\,\mathrm{kg\,mol^{-1}}$ and $z = 0.002\,\mathrm{m}$; Eq. (15) predicts $\alpha \approx 4.8 \times 10^{-5}$, a value that is in the right ballpark.

Eq. (14) is valid for steady-state isothermal mass loss measurements. However, an approximate analysis suggests that the equilibration time for shallow pans is very fast and that mass loss measurements obtained under dynamic conditions can provide pseudo-steady-state mass loss values even when scan rates of 20 °C min^{-1} are used. However, it will always be prudent to check whether this applies to a new sample by ensuring that TG-measured vaporisation rates are independent of the temperature scan rate.

From Eq. (13) the following revised equation for the comparative method is obtained:

$$P_\mathrm{S} = P_\mathrm{R}\left(\frac{z_\mathrm{S}}{z_\mathrm{R}}\right)\left(\frac{D_\mathrm{RB}}{D_\mathrm{SB}}\right)\left(\frac{M_\mathrm{R}}{M_\mathrm{S}}\right)\left(\frac{(\mathrm{d}m/\mathrm{d}t)_\mathrm{S}}{(\mathrm{d}m/\mathrm{d}t)_\mathrm{R}}\right) \qquad (16)$$

Note that it assumes that comparisons are made at the same temperature and that identical sample cups are used. This equation differs substantially from the one proposed by Phang et al. [15]. Thus, using the Langmuir equation in ratio format unfortunately did not overcome its inherent deficiencies with respect to applying it to measurements conducted at finite pressures.

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