Thermogravimetric measurement of evaporation: Data analysis based on the Stefan tube

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A B S T R A C T

Commercial thermogravimetric analyzers (TGA) can precisely measure the evaporation of liquids from an open pot. Analysis of this data to determine vapour pressure has often been based on the Langmuir equation for evaporation in a vacuum. These methods are flawed, since they cannot account correctly for the effects of ambient air. We formulate an improved model for evaporation in a TGA, based on the Stefan tube. It incorporates these effects explicitly. We demonstrate its validity by determining accurate vapour pressures for pure liquids, without using a reference sample. Calculated values typically agree with literature data to within a few per cent, over a range of vapour pressures from 60 Pa to 30 kPa. A weakness of thermogravimetric determination of vapour pressure has been that its accuracy depends on the end correction. Our data analysis avoids this problem. Also, the air flow rate and the end effect are shown to act separately on evaporation. Accurate results depend on correctly accounting for both. Finally, a simple heat balance is used to account for the effect of evaporative cooling.

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1. Introduction

Evaporation is a key step in many natural and man-made processes. Examples include: the fates of organic aerosols in the atmosphere [1] or oil spills on the sea [2], spin coating of polymers [3] and the spray drying of flavours [4]. Evaporation is challenging to measure and model, because mass transfer and heat transfer are tightly coupled [5].

The thermogravimetric analyzer (TGA) is an attractive basis for studying evaporation, as the instrument is extremely accurate, robust and easy to use. Measuring vapour pressure using evaporation in a TGA has been discussed and implemented many times; see, for example, references [6–11]. However, the data analysis has often been based on the Langmuir equation [10,11] for evaporation in a vacuum. Its use is unsatisfactory, as the effect of the ambient air is not taken into account explicitly. This point seems to have been first made by Pieterse and Focke [8]. Later, Rong et al. [9] came to the same conclusion, independently. The latter based their data analysis on that of Beverley et al. [12], who determined vapour pressures using the evaporation of millilitre samples of liquid from an open cylindrical tube.

Taking a broader perspective, we note that the appropriate analysis has been available for more than a century: it is that of the Stefan tube [13], which is an experimental setup corresponding exactly to that of Beverley et al. [12]. The Stefan tube and TGA have traditionally had different goals: the TGA has been used to determine the vapour pressure with given gas phase diffusion coefficient, whereas the Stefan tube has been used to do the reverse. However, this difference is arbitrary, since the same theory underlies the two methods. It shows that only the product of the vapour pressure and the gas phase diffusion coefficient can be determined [8,13,14].

2. Theory

Following Rong et al. [9], we base our analysis on that of Beverly et al. (abbreviated as BCF, here). Their analysis is similar to that given fifty years ago by Lee and Wilke for the determination of gas phase diffusion coefficients using the Stefan tube [14].

Fig. 1 shows the relevant lengths for evaporation of a liquid from a cylindrical pot.

The evaporating liquid must diffuse through a length $h = i + e$, which varies with the amount of liquid left in the pot. Note that the end effect, e, may be positive or negative [14], depending on the configuration and the air flow rate.

Both Pieterse and Focke [8] and Barantoni and Cozzani [6] ignored the end effect. So, implicitly, they assume that it is negligible compared to the depth of free space above the liquid, i. In other words, they assume that $i + e = i$ is a good approximation. However, Lee and Wilke [14] showed that even in a long tube,

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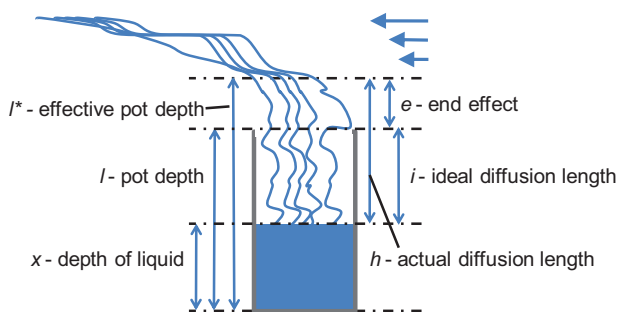*E-mail address:* alan.parker@firmenich.com (A. Parker).

Fig. 1. Relevant lengths during evaporation of a liquid from a pot.

where i is many centimetres, end corrections can be significant. Therefore, in a TGA, where i is only a few millimetres, it is essential to incorporate the end effect into the data treatment. Rong et al. [9] treated e as an unknown and determined it using a nonlinear fit. Here we show first how to determine e using a linear fit and second how to determine the vapour pressure, or diffusion coefficient, without the need to determine e.

BCF write their key equation for the evaporation rate as:

$$-\frac{dm}{dt} = \frac{MADPz}{RT} \times \frac{1}{h}\left(1 - \frac{D}{D + hF/X}\right) \qquad (1)$$

where:

m = mass of sample
M = evaporating molecule's molecular weight
A = cross sectional area of the pot
D = evaporating molecule's diffusion coefficient in air
P = vapour pressure of the evaporating molecule
R = universal gas constant
T = absolute temperature
h = actual diffusion length, see Fig. 1
F = volumetric flow rate of air at the mouth of the pot
X = area through which air flow occurs above the pot
z = correction factor for the enhanced evaporation rate at high vapour pressures, due to Stefan flow.

The correction factor is given by:

$$z = \frac{P_{atm}}{P}\ln\left(\frac{1}{1 - (P/P_{atm})}\right) \qquad (2)$$

with P_{atm} = atmospheric pressure. At a relative vapour pressure of 0.1 ($\sim$10 kPa under ambient conditions), the correction increases the evaporation rate by about 5%, whereas at a relative vapour pressure of 0.3 the increase is 19%. When the vapour pressure is known to be low, it is reasonable to neglect this correction. However, in a TGA quite high vapour pressures are easily attained, so it is better to include the correction in the data analysis, as a matter of course.

BCF did not discuss how to use the z-correction to determine the vapour pressure. In Eq. (2), z is calculated from the vapour pressure, whereas the reverse process is needed if the vapour pressure is the unknown. Further, the vapour pressure, P, cannot be determined separately from z. Only their product, the apparent vapour pressure, $P = Pz$, can be computed. We want to calculate the true vapour pressure, P, from the measured P. Call the required correction factor z. We calculate it by fitting a power law series to the correction factor in Eq. (2) as a function of the apparent vapour pressure:

$$P = P'z' = P'\left(1 - 0.5P' + 0.166P'^2 - 0.037P'^3\right) \qquad (3)$$

This equation is accurate to within 0.1% over the range of vapour pressures studied here. We use it in our standard measurement protocol, described below. We assume that the atmospheric

pressure is exactly one atmosphere. For measurements where the correction is significant, accuracy might be further improved by using the true barometric pressure at the time of the experiment.

The last term in the BCF equation accounts for the effect of the air flow over the mouth of the pot on the evaporation rate. We name this factor Q. It is given by:

$$Q = \left(1 - \frac{D}{D + hF/X}\right) \qquad (4)$$

Q expresses how far the vapour in the air next to the sample is from equilibrium with the evaporating liquid. Two limits exist:

■ When the air flow rate, F, is very low, then Q is close to zero, so the rate of evaporation is very low. This result is intuitive: when there is no flow, the air at the mouth of the pot is saturated in vapour, in equilibrium with the gas just above the liquid surface, so there is zero net evaporation.
■ When the air flow rate is very high, Q is close to one. In this limit, the evaporation occurs as though the vapour at the mouth of the tube was in contact with vapour-free air.

In summary:

■ When Q is zero, the sample is at equilibrium with the vapour above it and the net evaporation rate is zero.
■ When Q is one, the sample is as far from equilibrium as possible and the evaporation rate is maximal.

We now rewrite Eq. (4) in a clearer form, using the appropriate dimensionless group. A Peclet number, Pe, expresses the balance between the effects of diffusion and convection (flow). It is given by:

$$Pe = \frac{vl}{D} \qquad (5)$$

Where v is a velocity, l is a characteristic length and D is the evaporating molecule's gas phase diffusion coefficient. Rewriting Eq. (4) in terms of the Peclet number:

$$Q = \left(1 - \frac{D}{D + hF/X}\right) = \frac{Pe}{Pe + 1} \qquad (6)$$

Fig. 2 shows how Q varies with the Peclet number.

Thus, the flow regimes reflect our remarks above and determine the two limits:

■ When the Peclet number is much greater than one, i.e. when convection dominates, Q is one, so no correction is required. This regime occurs at high air flow rate.
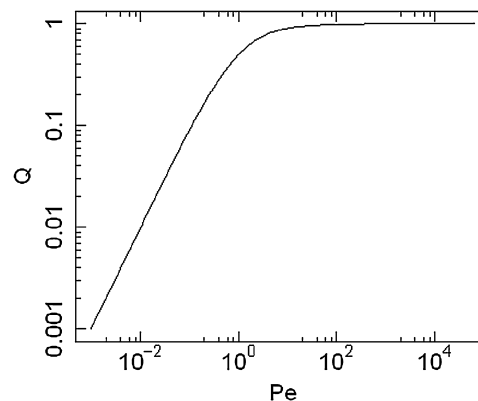

Fig. 2. Influence of the Peclet number on Q, the correction factor for the effect of air flow rate on the rate of evaporation.