



## Method for estimating vapour pressures based on thermogravimetric measurements with a magnetic suspension balance



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### ABSTRACT

In this paper, we report about a fast and straightforward method for estimating vapour pressures of pure liquids from mass loss rates measured with a magnetic suspension balance (MSB). For a measurement, the sample is placed in an open cylinder, attached to the MSB. Nitrogen flows vertically downwards along the sample cylinder to purge all vapour out of the measuring cell of the balance. To determine the total mass transfer of the liquid into the gas phase, the transport process is divided into an internal and an external part. The internal mass transfer takes place inside the sample cylinder and is only based on diffusion while the external mass transfer outside the cylinder consists of diffusion and convection. To describe the external mass transfer, a correlation for the Sherwood number based on numerical data is found. The numerical simulation is validated with experiments using four different alcohols. Furthermore, the influence of the purge gas flow rate and the filling level of the sample cylinder on the evaporation rate are discussed. Lastly, the found equation is tested to calculate vapour pressures of different substances in a range of 100 Pa to 20 kPa. Our results deviate by 10% from literature values. The relative combined expanded uncertainty ( $P = 95.5\%$ ) of the presented method has been calculated to be 12% in the full vapour pressure range considered.

### 1. Introduction and theory

In the last few years, there has been a growing interest in using isothermal thermogravimetric measurements to determine vapour pressures of pure substances. This results from several advantages of the method compared to other methods, such as a short measuring time and a small sample volume.

In most publications, the sample is located in an open cylinder, which is flown around by a purge gas, often nitrogen ( $N_2$ ). The purge gas removes all evaporated vapour away from the sample cylinder. The surrounding pressure is 1 bar and experiments are often carried out under isothermal conditions. The mass loss caused by the evaporation of the sample is measured thermogravimetrically. In literature, two fundamental approaches, which regard diffusion of the sample into the purge gas, exist to calculate the vapour pressure from the evaporation rate. Some authors assume that the vapour concentration of the sample substance at the upper end of the sample cylinder is zero. So the mass transfer only consists of diffusion inside the sample cylinder and the mass transfer outside the sample cylinder is neglected [1–3]. Other authors also take into account the mass transfer around the sample cylinder and regard diffusion as well as convection caused by the pure

gas [4–7].

The total mass transfer depends on many factors such as the filling level of the sample cylinder, the flow pattern around the sample cylinder and the diffusion coefficient of the vapour in the purge gas. Various methods for describing the total mass transfer are proposed. Focke [8] suggests a comparative method, for which a reference substance with known vapour pressure is needed. Beverley et al. [4] develop a gravimetric method to determine evaporation rates of some pure alkanes and ethanol. This development is based on literature values of vapour pressure and variation of the filling level of the sample cylinder and the gas flow rate. Some years later, Rong et al. [6] and Parker and Babas [7] adopt Beverley et al.'s theory and make some modifications and supplements. Both groups introduce an extra transport length above the cylinder where they also consider mass transfer. Parker et al. [7] also suggest a way to consider evaporative cooling.

An interesting approach is proposed by Heym et al. [5], who analyse the evaporation, thermal decomposition and the vapour pressure of ionic liquids [5,9–13]. They report that their method can be used to find the vapour pressure of other substances from the results of thermogravimetric measurements [5]. The measured evaporation rate  $dm/dt$  is a function of the molar mass  $M_s$  of the sample  $s$ , the mass transfer

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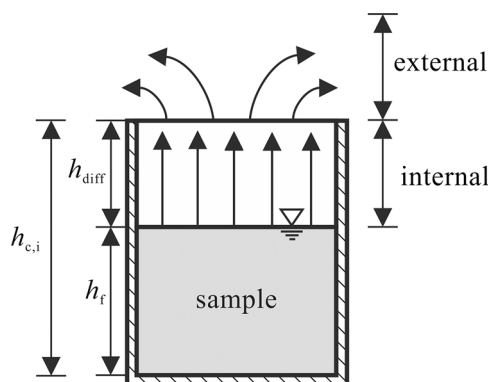


Fig. 1. Schematic drawing of the total mass transfer divided into the internal and the external mass transfer.

coefficient  $\beta$ , the inner cross sectional area of the cylinder  $A_c$ , which is equal to the sample surface, the vapour pressure of the substance  $p_v$ , which is prevailing at the sample surface, the general gas constant  $R$  and the temperature  $T$ .

$$\frac{dm}{dt} = M_s \cdot \beta \cdot A_c \cdot \frac{p_v}{R \cdot T} \quad (1)$$

The mass transfer coefficient  $\beta$  depends on the flow rate of the purge gas, the diffusion coefficient of the vapour in the purge gas and the geometry and the filling level of the sample cylinder. All these parameters are considered by Eq. (2). The mass transfer coefficient  $\beta$  can be calculated from the Sherwood number  $Sh$ , the diffusion coefficient  $D_{s,g}$  of the vapour of the sample  $s$  in the gas  $g$  and a characteristic length  $x$ .

$$\beta = \frac{Sh \cdot D_{s,g}}{x} \quad (2)$$

Heym et al. [5] assume that the mass transfer is only controlled by diffusion inside the sample cylinder and by convection and diffusion outside the cylinder. They divide the total mass transfer into an internal and an external part, see Fig. 1, and develop a correlation for calculating  $Sh$ , which covers both the external and internal mass transfer (Eq. (3)).

$$Sh = \left( \frac{1}{Sh_{int}} + \frac{1}{Sh_{ext}} \right)^{-1} \quad (3)$$

The internal Sherwood number  $Sh_{int}$  can be derived from the characteristic length  $x$ , the internal height of the sample cylinder  $h_{c,i}$  and the filling level of the cylinder  $h_f$ . The length between the sample surface and the upper end of the sample cylinder is the diffusion length  $h_{diff}$ .

$$Sh_{int} = \frac{x}{h_{c,i} - h_f} \quad (4)$$

The external Sherwood number  $Sh_{ext}$  describes the mass transfer outside the sample cylinder. The basis of this equation is a commonly used equation to describe the mass transfer caused by forced convection, see Eq. (5). Heym et al. calculate the mass transfer for a crossflow of a gas around a cylinder. Therefore they set the parameters  $c$  and  $d$  to  $c = 1/2$  and  $d = 1/3$  [5,14]. Furthermore, they determine the parameters  $a$  and  $b$  by means of a numerical simulation study by varying the influence parameters of the mass transfer coefficient.

$$Sh_{ext} = a + b \cdot Re^c \cdot Sc^d \quad (5)$$

The Reynolds number and the Schmidt number are defined as:

$$Re = \frac{u \cdot x}{\nu_g} \quad (6)$$

$$Sc = \frac{\nu_g}{D_{s,g}} \quad (7)$$

Herein,  $u$  is the inflow velocity and  $\nu_g$  the kinematic viscosity of the purge gas.

Since the parameters determined by Heym et al. [5] are only valid for their specific setup, i.e. a sample cylinder in a cross-flow, the parameters in Eq. (5) have to be determined again for the new setup. The geometry of the here-used MSB is different compared to the apparatus used by Heym et al. [5]. The purge gas flows vertically through the cylindrical measuring cell alongside the sample cylinder. The sample evaporates only through the open top of the cylinder and no mass is transferred through the other surfaces. Therefore the parameters  $a$ ,  $b$ ,  $c$  and  $d$  have to be determined for this geometry. The inner radius of the sample cylinder was chosen as characteristic length  $x$ . To determine the parameters for the calculation of  $Sh_{ext}$  (Eq. (5)), an own numerical simulation study for the used setup was performed. In general, a numerical simulation study has several advantages: Results can be obtained faster than with experiments and solutions of the numerical computations can be visualised. Furthermore, influence parameters can be varied in a larger range compared to experiments. Finally, the vapour pressure of a pure liquid can be calculated with the following equation:

$$p_v = \frac{dm}{dt} \cdot \frac{R \cdot T}{M_s \cdot \beta \cdot A_{c,i}} = \frac{dm}{dt} \cdot \frac{R \cdot T \cdot x}{M_s \cdot \left( \frac{1}{Sh_{int}} + \frac{1}{Sh_{ext}} \right)^{-1} \cdot D_{s,g} \cdot A_{c,i}} \quad (8)$$

This equation is only valid under the following assumptions: isothermal conditions (no evaporative cooling), constant physical properties of the sample and the gas, the gas is not soluble in the liquid, no chemical reactions and ideal gas behaviour. Furthermore, the inert gas is free of impurities and at the sample surface the vapour pressure of the sample is prevailing.

Since not all diffusion coefficients needed are available, they have to be calculated with a suitable method. Poling et al. [15] discuss several methods to estimate diffusion coefficients. They figure out that the method developed by Fuller et al. [16] yields the smallest average error. So they recommend this equation to estimate gas diffusion coefficients at low pressures. Tang et al. [17] compare diffusion coefficients of organic compounds calculated with Fuller et al.'s method to experimental diffusion coefficients. They also conclude that the equation is suitable for the estimation of diffusion coefficients. We chose to calculate the diffusion coefficient with the method by Fuller et al. [16]:

$$D_{s,g} = \frac{10^{-3} \cdot T^{1.75} \cdot \left( \frac{1}{M_s} + \frac{1}{M_g} \right)^{0.5}}{p \cdot \left[ \left( \sum_s \nu_{i,s} \right)^{1/3} + \left( \sum_g \nu_{i,g} \right)^{1/3} \right]^2} \quad (9)$$

Herein, the binary diffusion coefficient  $D_{s,g}$  is obtained in  $\text{cm}^2/\text{s}$ , when the temperature  $T$  is inserted in K, the molar mass of the sample  $M_s$  and the gas  $M_g$  in  $\text{g/mol}$ , the ambient pressure  $p$  in atm and if the special atomic diffusion volumes  $\nu_i$  are determined with data from Table 1. For substances with an aromatic or heterocyclic ring, such for cyclohexane, a value has to be subtracted from the diffusion volume. The authors note an average deviation of the calculated diffusion coefficients from literature values of about 4% [16].

Table 1  
Special atomic diffusion volumes provided by Fuller et al. [16].

Atomic and structural diffusion volume increments	Diffusion volumes of simple molecules		
C	16.5	N <sub>2</sub>	17.9
H	1.98	He	2.88
O	5.48	Air	20.1
Aromatic or heterocyclic rings			-20.2

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