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# **Determination of External Mass Transfer Coefficients in Dynamic Sorption (DVS) Measurements**

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## **Abstract**

A sorption balance is an instrument used to measure vapor uptake in a sample at controlled temperature and relative humidity. It is most commonly used to determine equilibrium values (sorption isotherms), but is also used for kinetic measurements of transport coefficients. Such measurements can be affected by the external mass transfer resistance in the gas phase around the sample. This paper presents a method to determine the external mass transfer coefficient for a given flow geometry using a water saturated sample, including corrections for temperature changes from evaporative cooling, which is found to have considerable effect on the calculated constant.

**Key words:** mass transfer resistance, sorption balance, kinetics, DVS, mass transfer coefficient.

## **Introduction**

During the last 20 years, commercial sorption balances have emerged as essential instruments for the studies of solid-vapor interaction. These instruments, typically used by the food- and pharmaceutical industry [1-6], flow a gas stream of programmed vapor activity over a sample while measuring the mass of the sample as it absorbs or desorbs the vapor. Most sorption balance studies are primarily designed to yield steady-state values of mass of vapor absorbed/desorbed as a function of the relative vapor pressure, but some studies also evaluate the rate at which equilibrium is reached, often with the aim of evaluating transport properties of the material [7-20]. However, caution has to be exercised when studying sorption kinetics, as the rate of vapor uptake/loss is not only determined by the sample, but also by the resistance of the gas phase through which the vapor reaches/leaves the sample [21, 22].

Compared to other techniques, for example with samples in closed desiccators with saturated salt solutions, sorption balance measurements are relatively rapid as the samples are small and the gas is flowing around the sample. This was

emphasized by the acronym DVS – Dynamic Vapor Sorption – that Surface Measurement Systems used when they launched their first sorption balance [23] (the term DVS is now also used by other producers of such instruments). However, even if a sorption balance measurement is more rapid than other techniques, this does not mean that mass transfer resistances external to the sample are always negligible.

As mentioned above, there are several examples of sorption balance studies in which the measured kinetics of the approach to equilibrium has been used to evaluate the diffusivity in the sample. Neglecting the outer mass transfer resistance can in such cases lead to an underestimation of the diffusivity in the sample for samples with fast diffusion kinetics. For example, Gustavsson and Piculell [21] determined the mass transfer resistance from sorption measurements of thin films of polymer-surfactant complexes, and concluded that the sorption kinetics in their case was completely controlled by external mass transfer over large ranges of experimental conditions. However, only few studies have taken this effect into account. Oliver et al [24] and

Prakash et al. [25] estimated the external mass transfer coefficient by calculating the Sherwood number, while Anderberg and Wadsö [16], Wadsö et al. [26] and Roca et al. [27] performed measurements of the mass transfer resistance related to their experimental setups and subsequently used these values as corrections in dynamic sorption experiments. These measurements were made by eliminating the inner transport of the sample by measuring the mass loss rate from either a wet surface or a water droplet. However, none of these studies have considered that the phase change of the vapor during absorption/desorption is accompanied by a phase change enthalpy, which will cause temperature changes in the sample [28].

A study in which the cooling effect of evaporation was taken into account is that by Kondjoyan and Daudin [29] in which an experimental approach to measure heat and mass transfer coefficients by using two similar wet plaster specimens was developed. One of the bodies has several temperature measurement points and the other body was weighed. From mass change rate and temperature measurements during the constant rate drying period both mean (overall) and local mass and heat transfer coefficients were calculated. Corrections for radiation were applied. However, this study was made with rather large samples in a wind tunnel and is not directly applicable to sorption balances.

In most cases, the temperature change in a sorption balance is small, but there are two cases where it can be significant:

- At the start of a step change in relative humidity (RH), when the mass change rates are high.
- If the mass changes of samples with free water on the surface are studied at low RH, as such samples can have high mass loss rates (constant rate drying) for long periods of time.

As the kinetics of evaporation from wet samples is of interest in the determination of mass transfer

coefficients, this temperature change cannot be ignored in a precise calculation of the external mass transfer resistance. We have therefore investigated the effect of temperature on mass transfer resistance measurements in sorption balances in some detail in the present paper. The objective is to demonstrate a straightforward method to assess the magnitude of the outer transport coefficient of a given experimental setup.

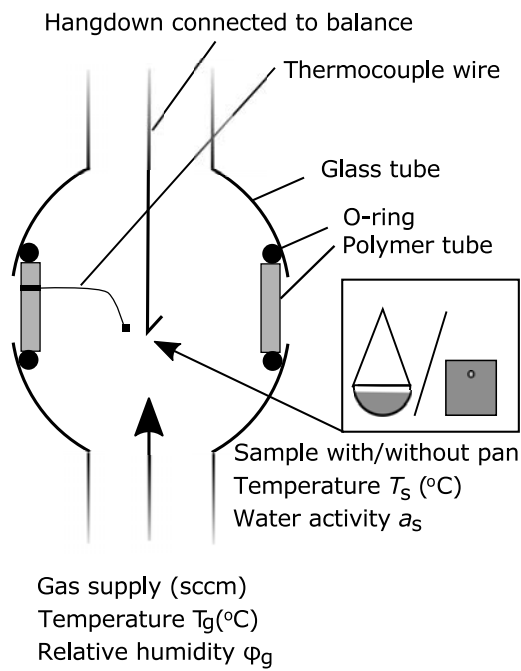
## Theory and methodology

### *Flow pattern and transport equations*

When a fluid flows around a stationary object, a layer of gas around the object surface is slowed down due to wall effects and the gas at the surface is essentially still. This is termed a boundary layer, through which any transport occurs by diffusion rather than convection. The thickness of such a layer depends on the shape of the object, the gas velocity and the viscosity of the fluid. [22]

In a sorption balance, the gas is a combination of a carrier gas (typically nitrogen) and a vapor (typically water vapor). The aim of having a flow of gas is to make it easier for the vapor to be exchanged between the gas and the sample. However, the boundary layer formed around the sorption balance sample in the gas stream still leads to an external mass transfer resistance for the moisture to reach or leave the sample. If this external resistance is not much smaller than that of the internal resistance of the sample, any measurements of moisture transport rate into or out of the sample will be affected by the boundary layer. As the gas flow patterns can be quite different in different sorption balances and around different sample geometries, we expect the mass transfer resistances for different sorption balance cases to be different. The method presented can be used for any setup based on gravimetric vapor sorption.

Figure 1 shows the setup in the DVS 1000 instrument (Surface Measurement Systems Ltd) that we have used. A gas stream with temperature  $T_g$  and the RH ( $\phi_g$ ) flows from under the sample,



**Figure 1:** Schematic of the experimental setup in the investigated sorption balance. Dry and water-saturated nitrogen gas is mixed to the set relative humidity  $\phi_g$  and supplied to the sample, which is hanging from a metal hangdown connected to a balance.

which is suspended from a hangdown connected to a balance. The sample may be placed in a pan or mounted directly on the hangdown; its temperature is  $T_s$  and its water activity is  $a_s$ . We here use water activity as a measure of the state of a material, while RH is the state of the gas phase; the numerical values of water activity and RH at normal temperature and pressure are equal at equilibrium for the present purposes [30]. The transport of vapor from the sample through the boundary layer is governed by the following formulation of Fick's law, in which  $D_v$  ( $\text{m}^2 \cdot \text{s}^{-1}$ ) is the diffusivity of the vapor in the carrier gas, and  $v$  ( $\text{g} \cdot \text{m}^{-3}$ ) is the vapor content:

$$\frac{dm}{dt} = -D_v \cdot \frac{A}{\delta} \cdot \Delta v. \quad (1)$$

Here,  $\Delta v$  is the vapor content difference between the gas at the surface of the sample and the surroundings,  $A$  ( $\text{m}^2$ ) is the total surface area of the sample, and  $\delta$  (m) is the thickness of the boundary layer. The latter is the average thickness of still gas that would give the same resistance to diffusion as the boundary layer does. The mass change rate on

the left hand side of Eq. 1 equals the mass transport rate, in units of  $\text{g} \cdot \text{s}^{-1}$ . For a sample of a given geometry and a certain boundary layer thickness, the effect of the boundary layer can be expressed as a mass transfer coefficient  $k_v$  ( $\text{m} \cdot \text{s}^{-1}$ ):

$$k_v = \frac{D_v}{\delta}. \quad (2)$$

This mass transfer coefficient is an overall coefficient reflecting the fact that the vapor molecules have to diffuse through the gas phase of the boundary layer. It is an average value for the entire sample, as both the gradient and the thickness of the stagnant phase around the sample may be non-uniform.

Note that  $k_v$  is given on a “per meter squared” basis, as is the convention for mass transfer coefficients. As it is often difficult to assess the surface area of a sample in a sorption balance, we can usually only measure  $A \cdot k_v$ . We have therefore defined a *sample mass transfer coefficient*  $K_v$  ( $\text{m}^3 \cdot \text{s}^{-1}$ ):

$$K_v = A \cdot k_v. \quad (3)$$

By measuring  $K_v$  for a sample in a sorption balance it is possible to assess the influence of the boundary layer on a kinetic sorption measurement. Note that this approach is suitable for samples with negligible shrinkage/swelling; for samples undergoing large surface area changes,  $k_v$  will be more constant than  $K_v$  during a measurement series, and may be evaluated if the surface area changes are known. In the two measurement series made in this work,  $K_v$  was constant.

The vapor content at a sample surface is the water activity at the surface times the saturation vapor content at the surface temperature, while the gas vapor content is the RH times the saturation vapor content of the gas. As the saturation vapor content is a function of the temperature, Eq. 1 can be written:

$$\frac{dm}{dt} = -K_v [a_s \cdot v_{sat}(T_s) - \phi_g \cdot v_{sat}(T_g)]. \quad (4)$$

For the purpose of this study,  $D_v$  is considered constant, as its dependence on temperature is about six times smaller than that of  $v_{\text{sat}}$  at room temperature [31]. As the aim of the present study is to determine  $K_v$ , we make measurements of sample temperature  $T_s$  and mass change rate  $dm/dt$  with a wet sample ( $a_s=1.00$ ) at a fixed gas phase temperature  $T_g$  at different RHs. However, the temperature of the sample could not be measured at the same time as the sample is being weighed, so a separate measurement of temperature (no weighing) has to be made. It is important that the samples used in both measurements are similar and placed in similar positions in the sorption balance.

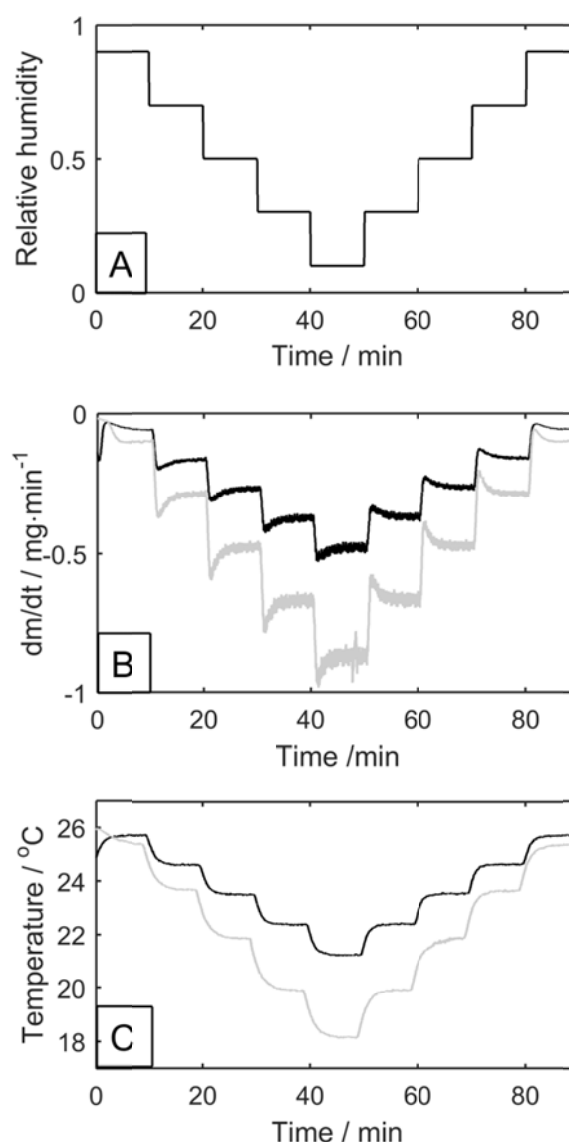
### Experimental procedure

The studied sorption balance was a DVS-1000 from Surface Measurements Systems with a gas flow rate of  $100 \text{ cm}^3 \cdot \text{min}^{-1}$  past the sample. This corresponds to a gas velocity of about  $2 \text{ mm} \cdot \text{s}^{-1}$ . Two types of samples were used: a glass pan of inner diameter 8.6 mm with a droplet of water and an  $8 \times 9 \text{ mm}$  two-layer wet cotton cloth. The two geometries were chosen to represent two experimental setups - with and without a pan. The pan measurement mimics the most common type of sample setup in DVS instruments, while the hanging cotton cloth geometry would be a better choice for diffusivity measurements. Both sample types were subjected to an RH program of  $0.9 - 0.7 - 0.5 - 0.3 - 0.1 - 0.3 - 0.5 - 0.7 - 0.9$  at a measured gas temperature  $T_g$  of  $26.2^\circ\text{C}$  with 10 minutes on each RH level.

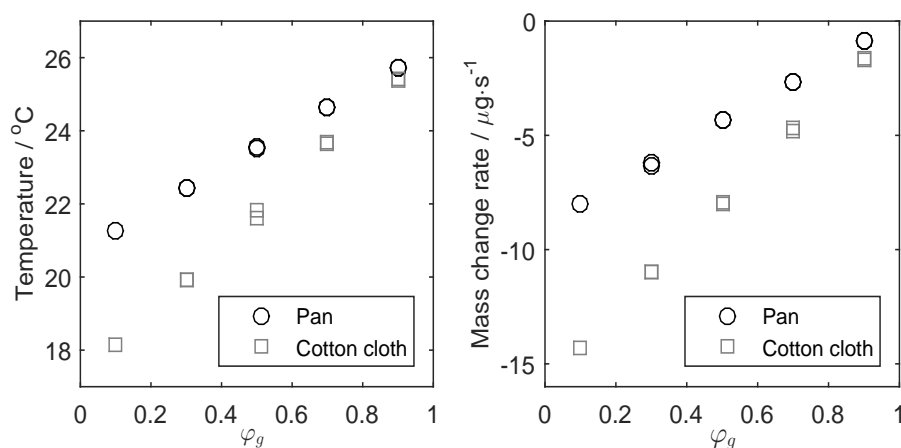
To be able to insert the thermocouple while still having the samples in the same position during the mass change rate and temperature measurements, a small modification had to be made to the sorption balance: a 20 mm polymer tube was added between the upper and lower part of the sorption balance where the sample is positioned (Fig. 1). The tube was sealed with O-rings and was used both for the mass and temperature measurements.

For the temperature measurements, an insulated thin-wire (diameter  $76 \mu\text{m}$ ) copper/constantan thermocouple was inserted into the water in the

pan or sewn in between the cotton layers to ensure good thermal contact. In the case of the pan, it was still hanging in the balance hang-down when the temperature was measured; the cotton sample was hanging on the thermocouple wire and was placed in a similar position as for the mass measurement but adjusting the thermocouple wires. The temperature was logged by a serial TC-08 (Pico Technology). The temperature measurement was verified against a calibrated Pt100 precision thermometer.



**Figure 2:** Raw data from DVS 1000 measurements on a freely hanging wet cotton sample (gray) and water in a pan (black), showing a) the RH program b) the mass change rate, and c) the resulting sample temperatures.



**Figure 3:** Evaluated temperature and mass change rate at the ends of each RH-step in Fig. 2 for the pan (circles) and the cotton cloth (squares).

## Results and discussion

### Steady state rates and temperatures

The results of the measurements can be seen in Fig. 2. The upper plot (Fig. 2A) shows how the RH of the sorption balance was programmed, while Figs. 2B and 2C depict the resulting evaporation rate and temperature, respectively. The results show that the evaporation rate and temperature at the end of each RH-level had reached constant (steady-state) values, as the corresponding values for decreasing and increasing RH-levels are similar. This is more clearly shown in Fig. 3, which displays the end values of each 10-minute step. These values are used in the calculations below. The initial, unsteady state rates of evaporation are not within the scope of this article.

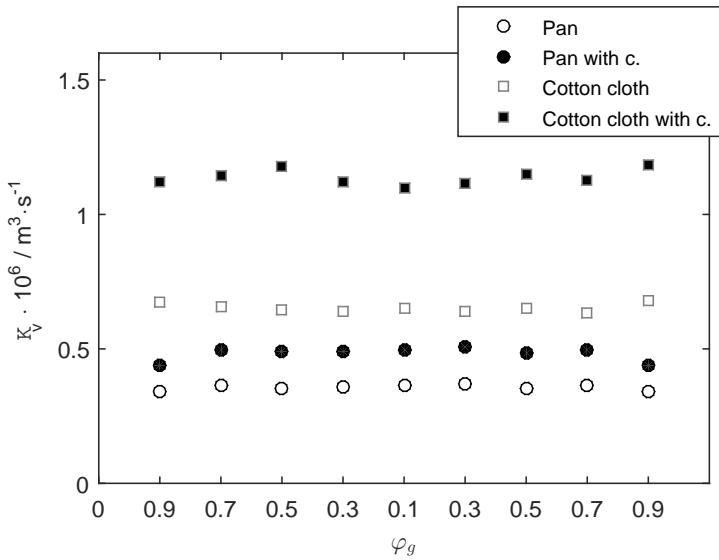
From Figs. 2C and 3, it is clear that even at the low air velocities used in the present measurements, the sample temperature is significantly lowered from the surrounding temperature. This affects the vapor content gradient around the sample; the effect of a 5 K temperature drop at a 25 °C surface with a water activity of 1.0 is a vapor content change from 23.0 to 17.3  $\text{g}\cdot\text{m}^{-3}$ , a decrease of about 25%. Considering Eq. 4, such a change will lead to a significant underestimation of the external transport coefficient if the temperature change is not taken into account.

### Sample mass transfer coefficients

Figure 4 shows the external mass transport coefficient calculated for each corresponding RH from Eq. 4 and the data in Fig. 3. For the freely hanging cotton cloth, the  $K_v$  values calculated without considering temperature changes (empty circles) are approximately 40% lower than the temperature-corrected transfer coefficients (filled circles), confirming the impact temperature changes can have on kinetic measurements. The cooling effect on the pan is smaller, as the mass transfer is lower. This is likely due to both the smaller area of the water droplet and that the water surface in the pan is positioned at a right angle to the direction of the gas flow, in contrast to the fully exposed cotton sample.

As  $K_v$  describes the diffusion rate through the stagnant layer, it is expected to be independent of changes in vapor content. The slight deviations of  $K_v$  in the pan at higher gas humidity can be explained by the smaller mass-flows and temperature differences measured, leading to a higher sensitivity to measurement errors. For example, a measurement error of  $\pm 0.1$  °C in  $T_g$  leads to under 1% error in  $K_v$  below an RH of 0.3, but the same error at a an RH of 0.9 is 6-9%. Therefore, the  $K_v$  values measured with the highest RH of the gas stream are more uncertain.

For the cotton cloth measurements, the area of the sample is known ( $1.4\cdot 10^{-4}$   $\text{m}^2$ ) and we can



**Figure 4:** Sample mass transfer coefficients ( $K_v$ ) for the pan (circles) and cotton cloth (squares) evaluated by Eq. 4 from the measurements with DVS 1000. The filled dots are calculated from the measured temperatures (with correction), while the empty ones are the results without temperature corrections.

therefore calculate  $k_v$ . At 10-70% RH, the mean  $k_v$  is about  $8 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$ . This is within the range of literature data from various DVS-instruments, which spans from  $3.7 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$  [21],  $4.7 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$  [26] and  $8.2 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$  [27] to  $17 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$  [32]. The latter three values were obtained by methods similar to the one presented here, but without compensation for evaporative cooling, while reference [21] used the results from samples for which the internal resistance was negligible. All values above were recalculated to  $k_v$ , that is, a diffusion coefficient per area with vapor content  $v$  ( $\text{g} \cdot \text{m}^{-3}$ ) as potential.

Our results indicate that both the uncorrected and the corrected  $K_v$  are rather constant as a function of the relative humidity, mass loss rate and temperature depression of the sample. For the corrected  $K_v$  this is an indication that the assumptions we made are realistic. However, for the uncorrected  $K_v$  it may seem odd that it does not approach the value of the corrected  $K_v$  as the RH increases and the temperature depression of the sample goes towards zero, but it should not, as is shown below. The uncorrected  $K_v$  and the  $K_v$  corrected for the temperature depression of the sample for a certain measurement can be written as follows:

$$K_v^{corr} = \frac{q_m}{v_{sat}(T_s) - v_{sat}(T_g) \cdot \phi} \quad (5)$$

$$K_v^{uncorr} = \frac{q_m}{v_{sat}(T_g) - v_{sat}(T_g) \cdot \phi} \quad (6)$$

Here,  $q_m$  is the mass flow rate ( $\text{g s}^{-1}$ ), i.e.  $dm/dt$  in Eqs. 1 and 4. The ratio of these two expressions is

$$r = \frac{v_{sat}(T_g) - v_{sat}(T_g) \cdot \phi}{v_{sat}(T_s) - v_{sat}(T_g) \cdot \phi} \quad (7)$$

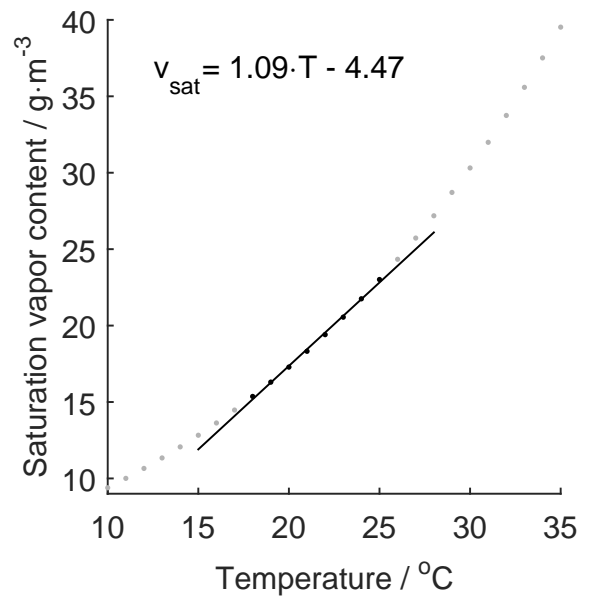
As seen in Fig. 5, the saturation vapor content is approximately a linear function of temperature in the small temperature interval where we are working ( $a$  and  $n$  are constants, cf. Fig. 5):

$$v_{sat} = aT + n \quad (8)$$

From our measurements (Fig. 4) we find that the wet surface temperature is an approximately linear function of the relative humidity:

$$T_s = b \cdot \phi + m \quad (9)$$

where  $b$  and  $m$  are constants with approximate values of 9.1 and 17 for the cotton cloth sample. Entering Eqs. 8 and 9 into Eq. 7 and noting that  $T_g$  can be calculated from Eq. 9 with  $\phi=1$ , gives:



**Figure 5:** The saturation vapor content  $v_{sat}$  ( $\text{g m}^{-3}$ ) of water vapor, including a linearization of the data between 18 and 25 °C.



$$r = \frac{ab + am + n}{am + n}. \quad (10)$$

For our measurement with a cotton cloth this ratio is 0.65, which agrees well with the ratio between the uncorrected and corrected  $K_v$  in figure 4. The constant error is an effect of the local linearity of the saturation water pressure and the wet sample temperature.

### **Mass transfer correlations**

Above we have calculated the mass transfer coefficient for a flat plate geometry and found it ( $k_v$ ) to be about  $8 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$ . It is of some interest to compare this value with one calculated from the corresponding flat plate correlation [22]:

$$Sh_x = \frac{k_v L}{D_v} 0.646 Re_x^{1/2} Sc^{1/3}. \quad (11)$$

The result is about  $2 \cdot 10^{-3}$ , which is about 75% lower than the measured value, although of the same order of magnitude. This is possibly partly due to the limited extension of the sample width, as Eq. 11 is derived for an infinitely wide plate. However, the main discrepancy between the correlation and the actual case is that the correlation assumes that the plate is placed in an infinite volume of flowing fluid, while in the DVS the flow geometry around the sample is quite restricted. This would limit the usefulness of corresponding correlations for other sample geometries (spheres, cylinders etc.) as well. For the most common experimental setup, where the sample is placed in a pan, further errors might be introduced, since the pan itself affects the flow around the sample. We believe that - for DVS measurements - measured mass transfer coefficients can be more accurate than those based on common correlations.

### **Applications and limitations**

By mimicking a sample in shape and using a water saturated surface, an approximate external sample mass transfer coefficient  $K_v$  can be calculated from the measured  $T$ -depression and  $dm/dt$ . The coefficient is specific for the instrument, flow rate

and mounting used, as the direction of the gas flow and sample geometry will affect the thickness of the boundary layer.

A difficulty with the present approach lies in mounting the sample identically for the mass-loss and temperature measurements. There is also the risk of underestimating the temperature depression due to the conductivity of the thermocouple, but this can be minimized by using thin thermocouple wires.

The heat transfer Biot number [33] is  $< 0.1$  for our cotton case, so the temperature gradient through the thickness of the sample is negligible. The temperature measurement is therefore not dependent on where in the cross section the sensor is mounted. However, the temperature field in flow direction in the wet samples may be inhomogeneous as the vaporization rate is highest at the leading edge of a flat object like the textile, and this part will then be at a slightly lower temperature than the rest of the sample. Nonetheless, we believe that this is a second order effect compared to the changes from using the correction. The moisture concentration field will not have the same problem in either of the tested cases as the equilibration of liquid water or in a textile will be very quick.

The main problem in applying these values is most probably that it is difficult to make a wet sample that behaves exactly like the sample we are interested in. For example, a polymer film will not hold as much water as a textile and could therefore not be used as a wet sample, and the polymer film can, e.g., be slightly bent, while the wet sample of a textile is more flat. We do not know how accurate our values are, but believe that they are good enough to be used to assess the influence of external mass transfer resistance on a kinetic measurement of a material's transport properties.

### **Using measured $K_v$**

If kinetic measurements have been made with the aim of calculating transport properties of a material and it is of interest to know if the external mass transfer will influence the result, we need to

be able to compare  $K_v$  ( $\text{m}^3\text{s}^{-1}$ ) to the sample diffusivity  $D_c$  ( $\text{m}^2\text{s}^{-1}$ ). However, this is a non-trivial task as these two coefficients are given with different transport potentials. The diffusivity  $D_c$  is given with moisture concentration  $c$  (g water per  $\text{m}^3$  material) as potential, while the mass transfer coefficient is given with the vapor content  $v$  (g water vapor per  $\text{m}^3$  of gas). This is natural, as the two processes quantified by these two coefficients take place in different locations:  $D_c$  in the material and  $K_v$  in the gas phase. When these two coefficients are used together one of them must be recalculated to the other's potential. Normally this is made by recalculating  $K_v$  to  $K_c$  and then comparing  $K_c$  to the  $D_c$  of the sample.

To calculate  $K_c$  from  $K_v$ , start with writing Fick's law for the same case, using the two potentials:

$$q_m = K_v \Delta v \quad (12)$$

$$q_m = K_c \Delta c \quad (13)$$

As the two formulations of Fick's law are written for the same case, the mass flows are the same, and

$$K_c = K_v \cdot \frac{\Delta v}{\Delta c} \quad (14)$$

The recalculation coefficient is the inverse of the slope of the sorption isotherm divided by the saturation vapor content  $v_{\text{sat}}$  ( $\text{g m}^{-3}$ ) and multiplied by the density of the material  $\rho$  ( $\text{g m}^{-3}$ ):

$$\frac{\Delta c}{\Delta v} = \frac{\Delta u}{\Delta \varphi} \cdot \frac{\rho}{v_{\text{sat}}} \quad (15)$$

Here,  $u$  (g water per g dry material) is the moisture content and  $\varphi$  is the RH. From here, the procedure is different depending on whether the sample area is known or not.

#### Known sample area

If the sample area is known,  $k_c$  can be calculated by dividing  $K_c$  by the sample area (Eq. 3). It is then possible to compute the mass transfer Biot number  $\text{Bi}_m$ , which is the ratio between the internal and the external resistances to mass transport:

$$\text{Bi}_m = \frac{k_c L}{D_c} \quad (16)$$

Here,  $L$  (m) is half the thickness of the material sample. A commonly used criterion is that if  $\text{Bi}_m < 0.1$ , the external resistance governs a process [34, 35]. If  $\text{Bi}_m$  is over 50 the effect of the external resistance is negligible when evaluating a diffusivity from mass changes after step changes in RH. The Biot number is also used in the solution to Fick's law for the mass change of a plate (slab) following a step change in the external conditions, when there is an influence of the external resistance (cf. Eq. 4.53 in reference [36]).

As an example, consider a case where kinetic measurements are made at 20 °C with a sample with  $D_c = 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ,  $\rho = 10^6 \text{ g m}^{-3}$  and  $\Delta u / \Delta \varphi = 0.1$  in the same instrument and with the same area of the sample that we used in our cotton cloth measurements, i.e., with  $k_v = 8 \cdot 10^{-3} \text{ m s}^{-1}$ . The mass transfer coefficient with concentration as potential is then

$$k_c = k_v \frac{\Delta \varphi}{\Delta u} \cdot \frac{v_{\text{sat}}}{\rho} = 8 \cdot 10^{-3} \cdot 0.1 \cdot \frac{17.3}{10^6} \approx 1.4 \cdot 10^{-8} \text{ m s}^{-1}$$

And the mass transfer Biot number is

$$\text{Bi}_m = \frac{1.4 \cdot 10^{-8} \cdot L}{10^{-12}}$$

In this case the Biot number is 50, 10 and 0.1 for samples of thicknesses 7 mm, 1.4 mm and 14  $\mu\text{m}$  ( $L$  is half thickness), demonstrating how the external mass transfer resistance becomes negligible for thick samples. If the Biot number is significantly higher than 0.1, but under 50, sample diffusivity may be calculated using solutions to Fick's law that includes the influence of external mass transfer, for example Eq. 4.53 in reference [36].

#### Unknown sample area

If our sample used for  $K_v$ -measurement does not have a well-defined area, we can still use  $K_v$  to make an analysis of whether the external mass transfer resistance governs a sorption step. Assume

that the internal mass transfer resistances are negligible. Then Fick's law and mass conservation gives:

$$q_m = K_v(v_g - v_s)$$

$$\frac{dv_s}{dt} = \frac{q_m v_{sat}}{m_0} \cdot \frac{d\phi}{du}$$

Here,  $v_g$  is the vapor content of the gas,  $v_s$  is the vapor content in equilibrium with the sample moisture content, and  $m_0$  is the dry sample mass at the start of the measurement. A step change in the gas vapor content from  $v_i$  to  $v_g$ , has the following solution:

$$\frac{v_s(t) - v_i}{v_g - v_i} = 1 - \exp(-\beta t), \quad (17)$$

where:

$$\beta = \frac{K_v v_{sat}}{m_0} \cdot \frac{d\phi}{du} \quad (18)$$

As we have assumed that the sorption isotherm is locally linear, changes in vapor content are proportional to changes in mass, and we may write Eq. 17 as:

$$E = 1 - \exp(-\beta t), \quad (19)$$

where  $E$  is the extent of mass change, i.e., how far the process has proceeded on a scale from 0 to 1.

Equations 18 and 19 give that if the external mass transfer coefficient governs the mass change rate for a case with a mass transfer coefficient  $K_v$ ,  $E$  is only governed by the sorption isotherm of the sample, as  $v_{sat}/m_0 \cdot d\phi/du$  is the inverse of how much moisture a sample takes up per change in vapor content. This has, for example, been experimentally demonstrated by Gustavsson and Piculell [21]: They found that the characteristic time ( $1/\beta$ ) for the exponential water uptake of thin samples was proportional to the slope of the sorption isotherm over a wide range of RHs. So, if we have measured  $K_v$  and then measure on a sample with the same geometry, we can compare our measured result with the result of a calculation with Eq. 19. If these results are similar, then there

is no information about the internal mass transfer in our measurement; but if the measured mass change rate significantly slower, there is information on the sample sorption kinetics in the results.

## Conclusions

External mass transfer coefficients for vapor transport between a wet sample and a surrounding flowing gas phase were measured. This was done by recording the temperature of and the mass transport from surfaces with a constant water activity of 1.0 at various relative humidity of the surrounding gas phase. Evaporative cooling was found to lead to considerable temperature changes, and consequently vapor content changes, on the studied wet surfaces. This affected the calculated external diffusion coefficient considerably. The external mass transfer coefficient needs to be taken into account when kinetic studies are made in sorption balances, either by showing that its influence is negligible ( $Bi_m \leq 0.1$ ) or by including it in sample diffusivity calculations.

## Nomenclature

$\beta$	Rate constant ( $s^{-1}$ )
$\delta$	Boundary layer thickness (m)
$\phi_g$	Relative humidity of gas phase
$\rho$	Density ( $g \cdot m^{-3}$ )
$v$	Vapor content ( $g \cdot m^{-3}$ )
$v_{sat}$	Saturation vapor content ( $g \cdot m^{-3}$ )
$A$	Sample area ( $m^2$ )
$a_s$	Water activity of sample
$Bi_m$	Mass transfer Biot number
$c$	Moisture concentration ( $g \cdot m^{-3}$ )
$D_c$	Mass diffusivity ( $m^2 \cdot s^{-1}$ )
$D_v$	Mass diffusivity ( $m^2 \cdot s^{-1}$ )
$E$	Extent of mass change
$k_v$	External mass transfer coefficient ( $m \cdot s^{-1}$ )
$k_c$	External mass transfer coefficient ( $m \cdot s^{-1}$ )
$K_v$	Sample external mass transfer coefficient ( $m^3 \cdot s^{-1}$ )
$L$	Half sample thickness (m)
$m$	Mass (g)
$q_m$	Mass flow rate ( $g \cdot s^{-1}$ )
$T_s$	Sample temperature ( $^{\circ}C$ )
$T_g$	Gas (surroundings) temperature ( $^{\circ}C$ )
$t$	Time (s)
$u$	Moisture content ( $g \cdot g^{-1}$ )

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