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# Gas permeation measurement under defined humidity via constant volume/variable pressure method

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ABSTRACT

Many industrial gas separations in which membrane processes are feasible entail high water vapour contents, as in $CO_2$-separation from flue gas in carbon capture and storage (CCS), or in biogas/natural gas processing. Studying the effect of water vapour on gas permeability through polymeric membranes is essential for materials design and optimization of these membrane applications. In particular, for amine-based $CO_2$ selective facilitated transport membranes, water vapour is necessary for carrier-complex formation (Matsuyama et al., 1996; Deng and Hägg, 2010; Liu et al., 2008; Shishatskiy et al., 2010) [1–4]. But also conventional polymeric membrane materials can vary their permeation behaviour due to water-induced swelling (Potreck, 2009) [5]. Here we describe a simple approach to gas permeability measurement in the presence of water vapour, in the form of a modified constant volume/variable pressure method (pressure increase method).

## 1. Introduction

When water vapour is necessary for proper operation of any polymeric gas separation membrane [1–4], or in general the influence of water vapour activity on membrane performance has to be measured, different permeation measurement principles can be used. The most commonly used method for permeation measurement of humidified gases is based on mixed-gas measurements, where the gas concentrations on the feed and the permeate side are detected by gas chromatography. Often in this type of measurement, a sweep gas is used to generate the needed driving force across the membrane. Detailed descriptions of these method can be found in the literature, for example in [6] (without sweep gas), [7] (with dry sweep gas) and [8] (with humidified sweep gas). The main advantage of this principle is the possibility of multi-gas-mixture measurements, so that the real gas separation process can be simulated. On the other hand, the device setup is expensive, mainly due to the need of a gas-chromatograph. Moreover, the use of a sweep gas on the permeate side can have disadvantages, such as the presence of an additional gas component, and the occurrence of concentration polarisation through the porous substrate layer. In order to get a constant water vapour concentration across the membrane, the sweep gas has to be humidified to a fugacity equal to that in the feed gas mixture. Another possibility of studying the effect of water vapour on the gas permeability of polymeric membranes is the use of a modified constant volume/variable pressure method, which is more or less a simplified time-lag method, as described by Barrer [9]. The main advantages of this principle are the low cost of the device setup and the fact that no sweep gas is necessary for the precise measurement of gas permeation. In this article we present and discuss in detail the implementation of this permeability measurement method.

## 2. Background

### 2.1. General principle of the constant volume/variable pressure method

Generally, an apparatus for gas permeation measurements via constant volume/variable pressure method consists of a membrane test cell, a defined permeate test volume and a vacuum pump, which is connected through a valve to the test volume. For the detection of the feed and the permeate pressure two pressure sensors are additionally needed. Fig. 1 is a simplified description of the device setup. The measurement begins with the evacuation

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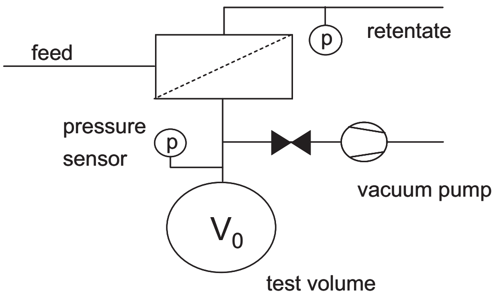

**Fig. 1.** General device setup of a constant volume/variable pressure method test system.

of the test volume by the vacuum pump. After closing the valve, the gas which permeates through the membrane induces a slight pressure increase with time in the test volume on the permeate side. This time-dependent permeate pressure increase at constant feed pressure is illustrated qualitatively in Fig. 2. The gas flux F through the membrane is described by Eq. (3). This equation is formed by placing the ideal equation of state into the general transport equation (Eq. (1)) and subsequently solving the resulting differential equation (Eq. (2)). To obtain the permeability instead of the gas flux, Eq. (4) must be used

$$F = \frac{(dn/dt)}{A(p_F - p_P)} \tag{1}$$

$$\int_{t_1}^{t_2} F\,dt = \int_{p_{perm,1}}^{p_{Perm.,2}} \frac{VV_{STDm}}{ART(p_F - p_P)} dp_P \tag{2}$$

$$F = \frac{VV_{STDm}}{RTA(t_1 - t_0)} \ln\left(\frac{p_F - p_{P,0}}{p_F - p_{P,1}}\right) \tag{3}$$

$$P = \frac{VV_{STDm}L}{RTA(t_1 - t_0)} \ln\left(\frac{p_F - p_{P,0}}{p_F - p_{P,1}}\right) \tag{4}$$

### 2.1.1. *Principle of constant volume/variable pressure method using humidified gases*

In general the permeation rate of water vapour through dense polymeric membrane materials is several orders of magnitudes higher than that of permanent gases which permeate via solution-diffusion mechanism. This is due to the relatively small kinetic diameter of the water molecule (2.6 Å [10]) which leads to high diffusion coefficients and a very high solubility inside the polymer matrix. When a gas stream with constant humidity comes into contact with the membrane surface at the feed side during a pressure increase measurement, the partial pressure equilibrium of the water vapour between feed and permeate side will be achieved very rapidly. Once this equilibrium is reached, only the permanent gas will further permeate through the membrane. The observable pressure increase curve is illustrated in Fig. 3. For calculating the gas flux through the membrane, Eqs. (3) and (4) have to be modified because the driving force inducing permeation of the gas is not the total pressure difference across the membrane anymore. Accordingly, the absolute pressure difference is substituted by the difference in the partial pressures of the gases as shown in Eqs. (4) and (5) [11]. If the partial pressure of water on the feed side is unknown, it can be determined by linear extrapolation of the pressure increase curve as drafted in Fig. 3.

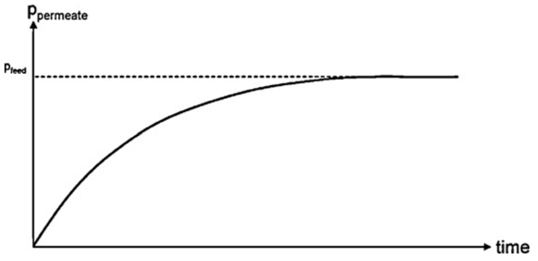

**Fig. 2.** Time-dependent permeate pressure increase at constant feed pressure.

$$F_{gas} = \frac{VV_{STDm}}{RTA(t_1 - t_0)} \ln\left(\frac{(p_F - p_{F,H_2O}) - p_{P,0}}{(p_F - p_{F,H_2O}) - p_{P,1}}\right) \tag{5}$$

$$P_{gas} = \frac{VV_{STDm}L}{RTA(t_1 - t_0)} \ln\left(\frac{(p_F - p_{F,H_2O}) - p_{P,0}}{(p_F - p_{F,H_2O}) - p_{P,1}}\right) \tag{6}$$

The separation factor can be computed as:

$$\alpha_{(gas1/gas2)} = \frac{P_{gas1}}{P_{gas2}} = \left(\frac{F_{gas1}/L}{F_{gas2}/L}\right) \tag{7}$$

### 2.1.2. *Theory of errors*

For the calculation of systematic errors, a method based on the root mean square deviation is used. Eq. (8) shows the main equation for this calculation, where $Z$ is either $F_{gas}$ from Eq. (5), $P_{gas}$ from Eq. (6), or $\alpha$ from Eq. (7). The term $x_i$ stands for each variable $i$ of Eqs. (5), (6) and (7), respectively. Each of these variables has its own uncertainty, which is described by the term $\sigma_{mx_i}$. This uncertainty can be constant or variable, depending of its nature of the variable. Eqs. (A.1)–(A.15), which can be found in Appendix A, list all the partial derivatives of $Z$ with respect to $x_i$.

$$\sigma_{mZ} = \sqrt{\sum_{i=1}^{n}\left(\left(\frac{\partial Z}{\partial x_i}\right)^2 \sigma_{mx_i}^2\right)} \tag{8}$$

For the calculation of flux and permeability two different permeate pressures ($p_{P,0}$ and $p_{P,1}$) are needed. For calculating the systematic error, Eq. (5) or (6) has to be derived with respect to both of these variables. This means that the offset error of the permeate pressure sensor affects the error calculation twice. In order to avoid this problem, the variable $p_{P1}$ must be replaced by the term $p_{P,0} + \Delta p_P$. The new variable $\Delta p_P$ is not affected by the offset error of the permeate pressure sensor any longer. Furthermore the total feed pressure and the feed water vapour pressure are combined in the term $(p_F - p_{H_2O})$.

Additionally, the systematic error in the separation factor $\alpha$ (Eq. (7)), which is a quotient of two single-gas permeabilities, is described by Eq. (11). Here the membrane thickness is cancelled out and thus is not involved in the error calculations.

$$\begin{aligned}\sigma(\alpha_{gas1/gas2}) &= \sqrt{\left(\left(\frac{\partial\alpha}{\partial F_{gas1}}\right)^2 \sigma(F_{gas1})^2 + \left(\frac{\partial\alpha}{\partial F_{gas2}}\right)^2 \sigma(F_{gas2})^2\right)} \\ &= \sqrt{\left(\left(\frac{1}{F_{gas1}}\right)^2 \sigma(F_{gas1})^2 + \left(-\frac{F_{gas1}}{F_{gas2}^2}\right)^2 \sigma(F_{gas2})^2\right)}\end{aligned} \tag{11}$$

## 3. Device set up

### 3.1. *General*

In our experiments we use the device setup shown in Fig. 4. The apparatus consists of a humidification unit and a conventional pressure increase setup which are placed inside an oven (WTB *Binder*) except for the vacuum pump (Varian type *SH-110*). The fresh dry gas flows thereby from the gas bottles through a pressure reducer (5 bars) and through a needle valve which is used to regulate the