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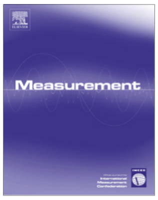

Calibration of a novel instrument for the investigation of small permeation fluxes of gases through membranes

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ABSTRACT

In this study the calibration and the determination of the sensitivity and reproducibility of a permeation measurement equipment are presented. It is showed that the calibration constant describing the relationship between the material current entering a vacuum chamber through a membrane and the pressure increase over the base pressure in this chamber is dependent on the type of gas used but independent of the membrane temperature. The reproducibility of the calibration constant is approx. ±13%, which can be accepted as the reproducibility of the equipment. The results indicate that the minimum material current required for the determination of the transport parameters in a mounted membrane is in the range of 10^{-11} $\lfloor \mathrm{mol\,s^{-1}} \rfloor$ and the maximum measurable permeating current is 5 orders of magnitude higher than this. Using various mountable membrane thicknesses this means that the transport properties of a wide range of materials can be investigated with the equipment.

1. Introduction

The investigation of gas permeation through different membranes is of great interest. There are a lot of industrial processes based on the permeation properties of inorganic membranes such as gas purification or separation (e.g. [1–7]). As it is possible to deposit thin metallic layers (such as palladium or palladium alloys) on highly permeable and relatively cheap polymeric membranes mechanically supporting the thin layers (e.g. [8,9]), the permeation properties of metallic as well as polymeric materials are of interest. Despite the interest in the permeation through different materials and the processes involved in the permeation, there are numerous questions left. First of all it is important to acquire reproducible and accurate data concerning the transport of gasses in different materials. Another interesting question is the role of the surface or surface processes e.g. the effect of surface contaminants (such as an oxide layer on a metal surface) and different layers and treatments on the transport properties of a material. In order to study the effect of surface contaminants and transport properties of metals with low hydrogen permeability a new high sensitivity instrument was constructed and described earlier [10]. As a new instrument raises a number of questions concerning its calibration, sensitivity or the reproducibility of the measured data, the present study tries to address these issues.

In case of a high vacuum chamber pumped continuously, the achieved base pressure is the result of a dynamic equilibrium between the pumping speed of the high vacuum pump and the desorption speed of the contaminants from the wall of the chamber. After reaching this dynamic equilibrium, additional material (e.g. due to permeation through a membrane) entering the chamber causes the pressure to rise. In case of pressures lower than approx. 10^{-3} mbar, turbomolecular pumps generally have a constant pumping speed (e.g. [11]), meaning that in case of a

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material current (J [mol s^{-1}]) entering into a vacuum chamber in dynamic equilibrium (e.g. permeation through a membrane), the pressure increase (Δp [mbar]) in the chamber is expected to be linearly proportional to the material flux entering the chamber (temperature is kept constant) [10]:

$$J = k \cdot \Delta p \tag{1}$$

where k $\lfloor \text{mol s}^{-1}\ \text{mbar}^{-1} \rfloor$ is the proportionality constant. As this constant is not expected to vary with time if other parameters are kept constant, a similar relationship can be assumed to the amount of the permeated material (Q [mol]) with the integration of Eq. (1):

$$Q = \int J\, dt = k \int \Delta p\, dt \tag{2}$$

The equations presented are the underlying fundamentals of the permeation measurement equipment described earlier [10]. The proportionality constant k is vital as it determines the sensitivity and shows the reproducibility of the measurements. It can be assumed, that k is dependent on the temperature and the type of permeating gas.

2. Materials and methods

2.1. Samples and permeant gases

The measurements reported here were conducted through a 0.1 ± 0.02 mm thick polytetrafluoroethylene (PTFE) membrane with a density of 2.1–2.2 g cm^{-3} (KOLOFOL Ltd., Hungary). As PTFE is chemically resistant, heat resistant, readily available and relatively cheap and has good mechanical properties and a relatively high reported permeability to gases [12,13], it is a suitable material to carry out the experiments required for the calibration of the permeation measurement equipment.

The following high purity gases were supplied by Messer Hungarogáz Ltd. (Hungary) and used as permeants: He (99.996%), H_2 (99.999%), N_2 (99.995%), Ar (99.9995%) and CO_2 (99.995%).

2.2. Permeation measurement system

As the newly built permeation measurement equipment was described in detail elsewhere [10], only a brief description is given here. The system consists of a high vacuum chamber (base pressure approx. $7 \cdot 10^{-9}$ mbar) separated by the membrane under investigation from a gastight high pressure chamber with a known volume of $4.84 \pm 0.24\ cm^3$ (Fig. 1). The membrane is supported by a plate covered by a fine stainless steel mesh and holes drilled in it, in order to let through the permeated gas. The role of this plate is to prevent the rupture of the investigated membrane caused by the pressure difference between the vacuum chamber and the high pressure chamber. The mounting system was tested with metal and polymeric membranes of different thicknesses between 10 μm and 125 μm in order to provide a gastight mounting which does not cause ruptures and maintains the active surface (the part of the surface which plays a role in the permeation) of the membranes.

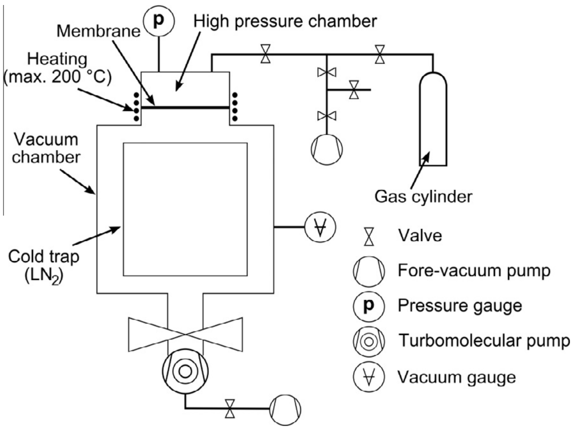

Fig. 1. The scheme of the high sensitivity permeation measurement setup for the investigation of permeation properties of membranes from [10].

The vacuum chamber is pumped by a turbomolecular pump and a rotary vane pump. The pressure of the chamber is measured with a hot cathode ionization gauge (MKS 909AR, MKS Instruments Inc. USA). The high pressure chamber is connected to a gas system through which any arbitrary type of gas can be introduced into the chamber and its pressure registered with the aid of an industrial pressure transmitter (Swagelok, USA). The investigated membranes can be heated from the outside to 50–200 °C.

The turbomolecular pump and the vacuum chamber can be separated with a valve. If the built in liquid nitrogen cold trap is filled, it is possible to make integral (static method) measurements with even higher sensitivity than dynamic method measurements [10]. Although measurements made according to the static method present a way to conduct more sensitive measurements, they have a drawback as the highest measurable permeating material current is very limited. As a PTFE membrane was chosen to calibrate the equipment, the relatively high amount of permeating gas rendered the application of the static method impractical.

2.3. Calibration of the instrument

In order to determine the calibration constant k (Eqs. (1) and (2)), the material current entering the chamber through the PTFE membrane and the resulting pressure increase had to be measured. The process of a calibration measurement at room temperature with H_2 gas is shown in Fig. 2. Initially before each measurement, the membrane was empty of permeant, the temperature was held constant and the pressure in the vacuum chamber reached the dynamic equilibrium corresponding to the base pressure of the chamber at the given temperature. After the permeating gas is first introduced to the high pressure chamber its pressure is kept constant. As the permeating flux starts to build up, the pressure in the vacuum chamber increases. Reaching the steady-state permeation, a new dynamic equilibrium pressure is achieved in the vacuum