Vapour permeation measurements with free-standing nanomembranes

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Fig. SM1. Photograph of the high-vacuum permeation setup. To navigate the reader, some of the system components are indicated similar to Fig. 1.
Fig. SM2. (a) Helium ion micrograph of the calibration nanoaperture. It was drilled in a 100-nm-thick silicon nitride window (Silson Ltd.) by a focused helium ion beam [1]. The area of the opening is determined from the image to be 19400 nm$^2$. The gas transmission probability $\alpha$ is calculated using the approximation for short circular ducts as follows [2]:

$$\alpha = \frac{1}{1 + \frac{3l}{8r}}; \quad \frac{l'}{l} = 1 + \frac{1}{3 + \frac{3l}{7r}}$$

where $l$ is the length of the duct, and $r$ is the radius. Deducing the effective $r$ from the area of the aperture, one obtains $\alpha$ equal to 0.62.

(b) Helium ion micrograph of the nanohole which was placed into the membrane cell to verify the equality between the sample and the reference inlets. Its area equals to 18300 nm$^2$ and the transmission probability is obtained to be 0.61. The two apertures were compared by recording QMS signals for different gases as a function of applied feed pressure. The discrepancy in corresponding intensity/flow rate slopes was found to be less than 10% indicating the accuracy of the system.

Fig. SM3. QMS response as a function of the gas flow rates. The measurements were done with the aperture depicted in Fig. SM2a upon increasing the upstream pressure. The flow rate is determined in accordance with the above described gas transmission probability.
Fig. SM4. Schematic of the sample assembly. The fixture is analogous to that used in [3]. A nanomembrane is suspended over a holey silicon nitride window and is kept tightly by van der Waals forces [4]. The silicon chip is fixed onto a copper disc with an epoxy glue, and the leak-tight connection is achieved by securing the disc between two conflat flanges. The reference nanoaperture is mounted alike.

Fig. SM5. Water coverage as a function of relative pressure. \( \theta_{\text{mono}} \) and \( \theta_{\text{multi}} \) were calculated within the developed model for the indicated values of \( L_0 \). \( \theta_{\text{total}} \) stands for the total surface coverage, i.e. \( \theta_{\text{mono}} + \theta_{\text{multi}} \).
Table SM1. System components. Designations are identical to those shown in Fig. 1.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Description</th>
<th>Supplier</th>
<th>Model</th>
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<tr>
<td><strong>Vacuum Pumps</strong></td>
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<tr>
<td>RP1</td>
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<td>Edwards, UK</td>
<td>RV8 (&gt;10 years old)</td>
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<td>Chemical Resistant Scroll Pump</td>
<td>Edwards, UK</td>
<td>nXDS15iC (brand new)</td>
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<td>TURBOVAC TMP-150 (&gt;10 years old)</td>
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<td>Pfeiffer Vacuum Technology AG, Germany</td>
<td>HiPace 80 (brand new) MVP 015-4 (brand new)</td>
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<td>Quadrupole Mass Spectrometer</td>
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</table>
Solution of the Eqs. 10 and 11

1) Rearranging

\[ \frac{n_0 L^3}{L_0^2} = \frac{x}{2(1-x)}, \]

one obtains:

\[ L = \left( \frac{L_0^2}{2(1-x)} \right)^{\frac{1}{3}} = \left( \frac{L_0}{2y} \right)^{\frac{1}{3}}, \]

where \( y = x/(1-x) \).

2) The equation

\[ \frac{n_0 + n_0 L^2 L}{L_0} = \frac{x}{(1-x)} \]

can be written in the form

\[ L^3 - L^2 = L_0 \left( \frac{x}{(1-x)} - 1 \right) = L_0^2 (y - 1), \]

where \( y = x/(1-x) \).

This cubic equation can be solved using the Cardano formula. For simplicity, we denote

\[ k = L_0^2 (y - 1) \]

and obtain:

\[ L^3 - L^2 - k = 0, \]

which corresponds to a general form

\[ L^3 + aL^2 + bL + c = 0 \]

with the coefficients \( a = -1, b = 0 \) and \( c = -k \).

Substituting with \( L = z - a/3 \), we obtain the depressed cubic, where the quadratic term equals to zero:

\[ \left( z - \frac{a}{3} \right)^3 + a \left( z - \frac{a}{3} \right)^2 + b \left( z - \frac{a}{3} \right) + c = 0 \]

\[ \left( z - \frac{a}{3} \right) \left( z^2 - \frac{2a}{3}z + \frac{a^2}{9} \right) + a \left( z^2 - \frac{2a}{3}z + \frac{a^2}{9} \right) + bz - \frac{1}{3}ab + c = 0 \]

\[ \left( z^3 - \frac{2}{3}az^2 + \frac{a^2}{9}z - \frac{a^2}{3}z + \frac{1}{27}a^3 \right) + \left( az^2 - \frac{2}{3}a^2z + \frac{a^3}{9} \right) + bz - \frac{1}{3}ab + c = 0 \]

\[ z^3 + \left( -\frac{2}{3}a - \frac{1}{3}a + a \right) z^2 + \left( \frac{1}{9}a^2 + \frac{2}{3}a^2 - \frac{2}{3}a^2 + b \right) z + \left( -\frac{1}{27}a^3 + \frac{1}{9}a^3 - \frac{1}{3}ab + c \right) = 0 \]

\[ z^3 + \left( -\frac{1}{3}a^2 + b \right) z + \left( \frac{2}{27}a^3 - \frac{1}{3}ab + c \right) = 0 \]
Inserting the coefficients leads to:

\[ z^3 - \frac{1}{3}z - \frac{2}{27} - k = 0, \]

where \( p = -\frac{1}{3} \) and \( q = -\frac{2}{27} - k \).

Now, one can calculate the discriminant:

\[
D = \left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3 = \frac{q^2}{4} + \frac{p^3}{27} = \left(\frac{-27 - k}{2}\right)^2 + \left(\frac{-3}{3}\right)^3 = \left(\frac{-2 - 27k}{2}\right)^2 + \left(\frac{-3}{3}\right)^3
\]

\[
= \left(\frac{-2 - 27k}{54}\right)^2 + \left(\frac{-1}{9}\right)^3 = \frac{4 - 108k + 729k^2}{2916} - \frac{1}{729} = \frac{4 - 108k + 729k^2}{2916} - \frac{4}{2916}
\]

\[
= \frac{729k^2 - 108k}{2916} = \frac{27k^2 - 4k}{108}
\]

Using the Cardano formula

\[
z = \sqrt[3]{\frac{-q}{2} + \sqrt{\left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3}} + \sqrt[3]{\frac{-q}{2} - \sqrt{\left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3}}
\]

we obtain:

\[
z = \sqrt[3]{\frac{2 + 27k}{54} + \frac{27k^2 - 4k}{108}} + \sqrt[3]{\frac{2 + 27k}{54} - \frac{27k^2 - 4k}{108}}
\]

Undoing the substitution \( L = z + 1/3 \), \( L \) is expressed as

\[
L = \sqrt[3]{\frac{2 + 27k}{54} + \frac{27k^2 - 4k}{108}} + \sqrt[3]{\frac{2 + 27k}{54} - \frac{27k^2 - 4k}{108}} + \frac{1}{3}
\]

where \( k = L_0^2(y - 1) \).

The final solution is written as following:

\[
L = \sqrt[3]{\frac{2 + 27L_0^2(y - 1)}{54} + \frac{27L_0^4(y - 1)^2 - 4L_0^2(y - 1)}{108}} + \sqrt[3]{\frac{2 + 27L_0^2(y - 1)}{54} - \frac{27L_0^4(y - 1)^2 - 4L_0^2(y - 1)}{108}} + \frac{1}{3}
\]
References


