

DEPARTMENT OF INORGANIC TECHNOLOGY

LABORATORY WORK

Hydrocarbon separation on micro-porous membranes
Single gas permeance measurement

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1 Introduction

Measuring gas permeation in micro-porous materials is important for determining the separation capabilities of membranes and also to evaluate the effect of mass transport phenomena on the chemical transformations in a micro-porous catalyst pellet. Along with the transport properties the raw information on structural properties of the porous material can be obtained.

The simple tool of unsteady permeation experiment is perfectly suited to get such information in a fast and simple manner. Measurement consists in observing the pressure decrease in constant volume vessel separated by the studied membrane from its surroundings (atmosphere). At the beginning of the experiment the vessel is filled by a pure gas at relatively low pressure (≈ 500 kPa) and is allowed to permeate through the membrane. The time evolution of the pressure inside the vessel is recorded by pressure gauge. From the dependence of $\Delta p(t)$ one can evaluate the permeability (or permeance) and the mean pore diameter. If this measurement is performed for two pure gases the ideal separation factor can be calculated from permeances of this two gases.

1.1 Basic terms in gas separation

Intensity of molar flow (molar flux) $[N L^{-2} T^{-1}]$ This value is defined as the molar flow per unit area of the membrane

$$N = \frac{F}{A}, \quad (1)$$

where A is area perpendicular to the flow direction, F is molar flow $[N T^{-1}]$ defined as

$$\dot{n} \equiv F = \frac{p}{RT} v A, \quad (2)$$

where v is mean stream velocity in $[L T^{-1}]$.

Permeance [$\text{N M}^{-1} \text{T L}^{-1}$] This value is defined as the ratio of the intensity of the molar flow and the pressure difference on both side of the membrane

$$\Pi = \frac{N}{\Delta p} \quad (3)$$

In conventional units the permeance is usually expressed in $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$.

Permeability [$\text{N M}^{-1} \text{T L}^{-2}$] is a value of permeance related to the thickness of the membrane

$$\beta = \frac{\Pi}{\delta} \quad (4)$$

Ideal separation factor is a dimensionless value expressing the ratio of permeances (or permeabilities) of pure gases

$$S_{i,j} = \frac{\Pi_i}{\Pi_j} = \frac{\beta_i}{\beta_j} \quad (5)$$

2 Theoretical part

Permeation of gases through micro-porous solid is a complex phenomena including interactions between the pore wall and diffusing molecules as well as interactions between diffusing molecules themselves. Mechanisms governing the transport of gases in micro-porous media depends of physical properties of the material, experimental conditions and of course on permeating gas.

The micro-porous material can be characterized by the mean pore radius r , porosity ϵ and tortuosity τ . The ratio of ϵ/τ is often expressed as ψ .

Experimental conditions influencing the permeation process are mainly temperature and pressure, which determine the mean free path of the molecule λ

$$\lambda = \frac{RT}{\pi N_A d_m p \sqrt{2}}, \quad (6)$$

where d_m diameter of permeating molecule and N_A is Avogadro constant. The ratio

$$\text{Kn} = \frac{\lambda}{2r}, \quad (7)$$

is called Knudsen number and its value give us the information about the nature of the mass transport mechanism inside the porous structure. Dependence of Knudsen number on pressure and temperature for N_2 in ZSM-5 zeolite is shown in figure 1. For numbers $\text{Kn} > 1$ the Knudsen diffusion is considered to be the dominant contribution to the total flow. For $\text{Kn} < 1$ the combination of viscous and slip flow are dominantly responsible for the diffusion process. The surface diffusion occurs along all previously transport mechanisms and has to be taken into account at low temperatures for polar gases.

As evident from above paragraph total flow of the permeating gas is a linear combination of different types of diffusion processes.

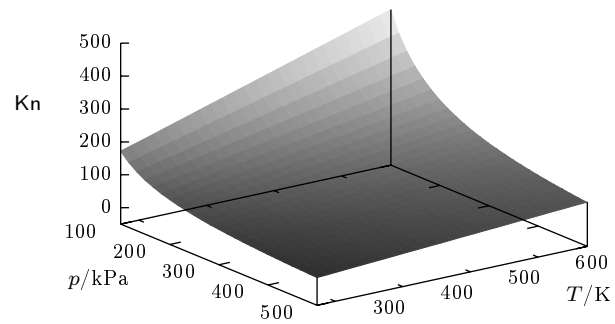


Figure 1: Knudsen number in ZSM-5 zeolite ($2r = d_p = 5.5 \cdot 10^{-10} \text{m}$) as a function of p and T for N_2 ($d_m = 3 \cdot 10^{-10} \text{m}$).

2.1 Knudsen diffusion

Knudsen diffusion take place in system where the pore diameter is comparable to the molecule mean free path of diffusing gas and thus the collisions of type molecule-wall predominates over molecule-molecule collisions. The Knudsen regime of flow occurs typically when Kn becomes larger than 10. The flow generated by Knudsen diffusion can be written as

$$N_K = -\frac{2r\epsilon}{3RT} \sqrt{\frac{8RT}{\pi M}} \frac{dp}{dx} = -D_K \frac{dp}{dx}, \quad (8)$$

where ϵ is membrane porosity, r the pore radius, M the molar mass of gas and x is axial coordinate in membrane layer. If only the Knudsen regime is assumed two gases will permeate through a membrane at ratio $\sqrt{M_i/M_j}$.

2.2 Viscous flow

Viscous (Poiseuille) flow occurs when the mean free path of molecules of diffusing gas is smaller than the pore diameter and the momentum is shared predominately by more often happening molecule-molecule collisions. Poiseuille flow is represented by following relationship

$$N_P = -\frac{r^2\epsilon}{8\eta RT} p \frac{dp}{dx} = -D_P p \frac{dp}{dx}, \quad (9)$$

where η is gas dynamic viscosity. As can be seen from equation 9 in the viscous flow regime we observe poor separation abilities.

2.3 Slip flow

This kind of transitional transport mechanism is supposed to take place on the boundary between Knudsen and viscous flow ($\text{Kn} \approx 0.1$) and is described by following equation

$$N_S = -\frac{\pi}{4} \frac{\text{Kn}^{-1}}{1 + \text{Kn}^{-1}} \frac{dp}{dx} = -D_S \frac{dp}{dx}, \quad (10)$$

The nature of slip flow is a combination of bulk flow (viscous) and of flow of independent molecules.

2.4 Surface diffusion

Surface diffusion can occur in parallel with Knudsen diffusion. Gas molecules are adsorbed on the pore walls of the membrane and migrate along the surface. Surface diffusion increases the permeability of the components adsorbing more strongly to the membrane pores. At the same time, the effective pore diameter is reduced. Consequently, transport of non adsorbing components is reduced and selectivity is increased.

3 Experimental

The permeation measurement apparatus is shown in figure 2. The single gas permeation measurements will be carried out at room temperature. The apparatus consist of three different pressure vessels, and the active volume is set using valves V1, V2 and V3. The three pressure detectors measure the pressure in the interior of the apparatus (p_1), at the outlet side of the apparatus (p_2) and the difference of pressures between p_1 and p_2 (Δp). During the measurement the gas passes through the membrane and the decrease of the pressure (p_1) will be recorded as function of time.

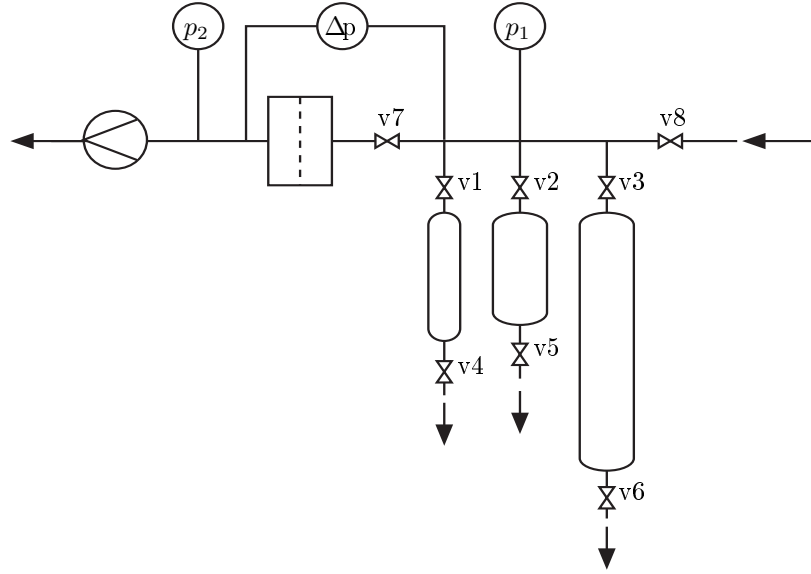


Figure 2: Experimental apparatus for unsteady permeation experiments. Valves v1 to v3 are destined to set the volume of the vessel, valve v8 serve for filling up the apparatus by chosen gas and valve v7 is used to open the interior volume to the atmosphere (through the membrane).

4 Treatment of data from single gas permeance measurement

In our calculations we will consider only Knudsen diffusion and viscous flow to participate to the total flow of the permeating gas.

As mentioned above, permeance of gas is defined as ratio of intensity of molar flow N and the pressure gradient Δp over the membrane

$$\Pi = \frac{N}{\Delta p}, \quad (11)$$

where $\Delta p = p_1(t) - p_2$, $p_1(t)$ is in our case pressure inside the vessel and p_2 is atmospheric pressure. In following text we omit (t) for simplicity. Material balance of permeation apparatus (figure 3) is as follows

$$\frac{dn_1}{dt} = -AN, \quad (12)$$

where A is membrane cross section area and N is the intensity of molar flow. For ideal gas we can write

$$\frac{dp_1}{dt} = -\frac{ART}{V}N = QN. \quad (13)$$

It is obvious that

$$\frac{dp_1}{dt} = \frac{d\Delta p}{dt}. \quad (14)$$

Data obtained on the experimental apparatus are in the form of time dependence of pressure p_1 (see figure 3). To obtain the value of N from equation 13 it is necessary to evaluate the derivative dp_1/dt . This goal could be achieved by several ways:

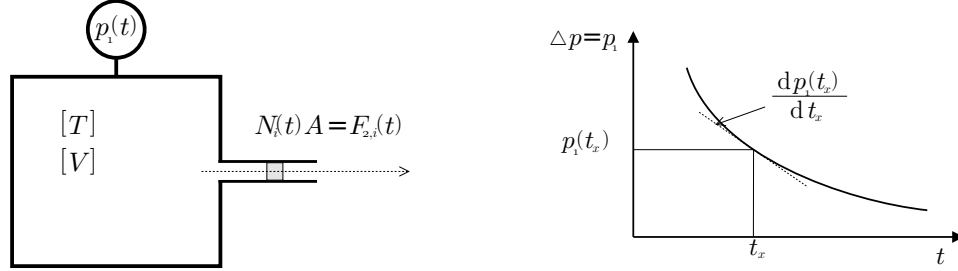


Figure 3: A schematic picture of the permeation apparatus (left) and a typical output from permeance measurement (right).

Numerical differentiation Numerical derivation of obtained data can be done by using following relationship

$$\frac{dp_1}{dt} = \frac{d\Delta p}{dt} \approx \frac{p_{1,(t+\Delta t)} - p_{1,(t)}}{\Delta t}. \quad (15)$$

This approach often fails because of the limited number precision of pressure gauge. This effect has an more pronounced impact specially at lower pressure differences or slower pressure decrease (see figure 4). This inconvenience hampers the use of equation 15.

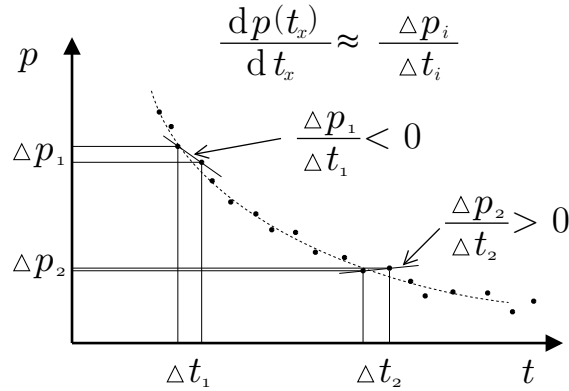


Figure 4: A schematic picture of the numerical evaluation of dp/dt .

Polynomial representation of data The other way is to represent measured data by adequately chosen polynomial function

$$p_1(t) = \sum_{i=1}^{n_p} a_i t^{i-1}, \quad (16)$$

where n_p is the number of parameters. The derivative dp_1/dt is then calculated using following formula

$$\frac{dp_1}{dt} = \frac{d\Delta p}{dt} = \sum_{i=1}^{n_p} (i-1) a_i t^{i-2}. \quad (17)$$

The advantage of this approach is its simplicity and fast application. The disadvantage is the fact, that by using an empirical formula (equation 16) we introduce uncertainty¹ and by deriving this “uncertain” approximation (equation 17) we enhance this error by order of magnitude.

Using a representative ("real") model The most effort end time consuming approach is also the best. We derive a model, which represent the gas transport mechanism in porous media and derived relationship $\Delta p = f(t)$ will be used to represent measured data. This approach is described in following section.

4.1 Model of Knudsen diffusion and viscous (Poiseuille) flow

By solving differential equation 8 for membrane of thickness δ we obtain

$$N_K = -\frac{D_K}{\delta} (p_2 - p_1) = \Pi_K \Delta p, \quad (18)$$

where the parameter $\Pi_K = D_K/\delta$. We keep in mind that we choose in the first paragraph $\Delta p = p_1 - p_2$ and thus the minus sign in equation 18 disappear.

By integration of equation 9 over a membrane of thickness δ we obtain

$$N_P = -\frac{D_P}{2\delta} (p_2^2 - p_1^2) = \frac{\Pi_P}{2} (p_1^2 - p_2^2) \quad (19)$$

where the last therm $(p_1^2 - p_2^2)$ can be transformed as follows

$$N_P = \frac{\Pi_P}{2} (p_1 - p_2)(p_1 + p_2) = \Pi_P \left(\frac{\Delta p^2}{2} + p_2 \Delta p \right) \quad (20)$$

This two above mentioned mechanism of gas transport occurs in parallel and their contribution to the total flow can be represented by their linear combination

$$N = N_P + N_K = \Pi_P \left(\frac{\Delta p^2}{2} + p_2 \Delta p \right) + \Pi_K \Delta p \quad (21)$$

From equation 11 and equation 23 one can evaluate the permeance as function of the pressure difference

$$\Pi = \frac{1}{2} \Pi_P \Delta p + \Pi_P p_2 + \Pi_K \quad (22)$$

¹In other words we are not describing the exact nature of the diffusion process.

4.2 Solution of Knudsen and Poiseuille model - obtaining parameters Π_K and Π_P

By substituting N in equation 13 by equation 21 we obtain

$$\frac{d\Delta p}{dt} = Q\left(\frac{1}{2}\Pi_P\Delta p^2 + (\Pi_P p_2 + \Pi_K)\Delta p\right) \quad (23)$$

The solution of differential equation 23 is as follows (after subsequent evaluation of Δp)

$$\Delta p = 2K \frac{\exp\{KQt + C_1\}}{\Pi_P - \Pi_P \exp\{KQt + C_1\}}, \quad (24)$$

where $K = \Pi_P p_2 + \Pi_K$. The adjustable parameters are K , Π_P and C_1 . Their estimation can be obtained from nonlinear regression procedure of experimental data, i.e. by nonlinear fit of $\Delta p(t)$ data by equation 24. This task is quite complicated because of strong correlation between unknown parameters. To avoid unsuccessful convergence of nonlinear estimation procedure, we have to rearrange the equation 24 in following way

$$\Delta p = L \frac{\exp\{KQt + C_1\}}{1 - \exp\{KQt + C_1\}}, \quad (25)$$

where

$$L = 2(p_2 + \Pi_K/\Pi_P) \quad (26)$$

For nonlinear regression it is primordial to choose "good" initial estimates of fitted parameters. For parameter L we use the ratio Π_K/Π_P as initial estimate. This ratio can be expressed from 8 and 9 as

$$\Pi_K/\Pi_P = \frac{32}{3} \frac{\eta}{r} \sqrt{\frac{2RT}{\pi M}}. \quad (27)$$

For temperature around 298.15 K this ratio is approximately equal to

$$\Pi_K/\Pi_P(298 \text{ K}) = 635.6 \frac{\eta}{r\sqrt{M}} \quad (28)$$

This equation provide the initial estimate of parameter L (through equation 26)

The initial estimate of C_1 parameter is given by

$$C_1 = \ln\left(\frac{\Delta p^0}{\Delta p^0 + L}\right), \quad (29)$$

where Δp^0 is the initial pressure difference.

Values of Π_K and Π_P are then computed from parameters obtained from nonlinear regression by following relationships

$$\Pi_K = K\left(1 - \frac{2p_2}{L}\right) \quad (30)$$

$$\Pi_P = 2\frac{K}{L} \quad (31)$$

The flux is then evaluated from equation 21 using parameters 30 and 31

$$N = \frac{K}{L}\Delta p^2 + K\Delta p. \quad (32)$$

The permeance as function of pressure difference is then calculated from equation 22

$$\Pi = \frac{K}{L}\Delta p + K. \quad (33)$$

4.3 Calculation procedure and some recommendations

1. Fitting of measured data
 - (a) Find suitable input parameters, such as viscosity, molar mass and membrane area. Physical properties for some gases can be found in table 1
 - (b) Estimate initial values of parameters of equation 24 using relationships described in previous section
 - (c) Perform a nonlinear fit using one of provided programs (Octave or Matlab), or use your own program (recommended!)
 - (d) If the fit is successful (calculated parameters are "reasonable"), then evaluate desired parameters. If the non-linear procedure fails, try a new fit with different initial estimates (i.e. different initial estimation of mean pore radius or different value of Π_p)
2. Display results
 - (a) Display relative deviation of fitted values (Δp_c) from experimental values (Δp_e)
 - (b) Display permeance dependence on Δp , (equation 33)
 - (c) Display ratio of $S_{i/j} = \Pi_i(\Delta p)/\Pi_j(\Delta p)$ (ideal separation factor), where subscripts i and j correspond to two different gases
3. Final remarks for report writing
 - (a) If you provide a value (result or input), write corresponding units along the number (i.e. for Boltzmann constant $k_B = 1.3806503 \cdot 10^{-23} \text{m}^2 \text{kg s}^{-2}$). Number without units is ... is a number without units (useless)!
 - (b) Do not make copy of whole text or whole images from un-cited sources (no CTRL+c - CTRL+v). If you want to copy a whole image, you have to ask the author. Better way is to draw your own picture and cite the original in the reference section or your report. Also use your own words instead of "hard-copying" of somebody else's text. This is a base of scientific work and also of the scientific "etiquette"

Gas	Molar mass/(mol kg ⁻¹)	$\eta(293 \text{ K})/(\text{Pa s})$	$\eta(298 \text{ K})/(\text{Pa s})$
H ₂	2.02 · 10 ⁻³	9.9843 · 10 ⁻⁶	9.0837 · 10 ⁻⁶
He	4.00 · 10 ⁻³	19.526 · 10 ⁻⁶	19.742 · 10 ⁻⁶
CH ₄	16.04 · 10 ⁻³	10.887 · 10 ⁻⁶	11.042 · 10 ⁻⁶
N ₂	28.01 · 10 ⁻³	17.283 · 10 ⁻⁶	17.512 · 10 ⁻⁶

Table 1: Dynamic viscosity (η) and molar mass of measured gases.

References

- [1] Roy, S., Raju, R., Chuang, H., Cruden, B., Meyyappan, M., *J. Appl. Phys.*, **93** (2003) 4870
- [2] Fott, P. and Petrini, G., *Appl. Cat.*, **2** (1981) 367
- [3] Rutherford, S., and Do, D., *Ind. Eng. Chem. Res.*, **38** (1999) 565

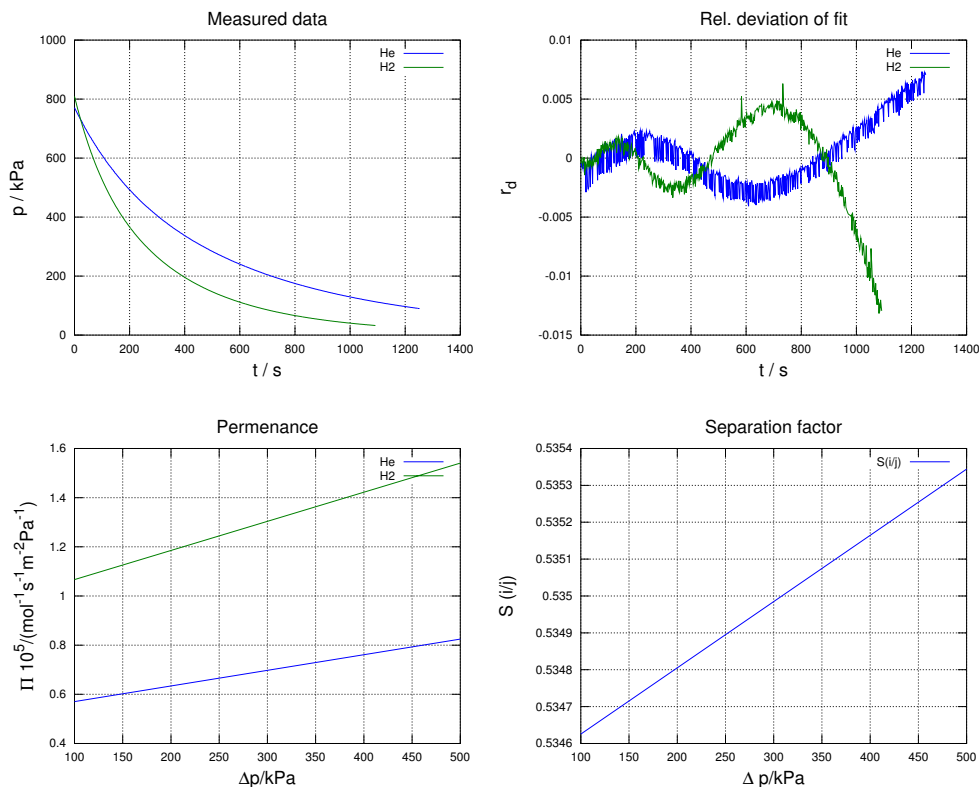


Figure 5: Measured data ($\Delta p(t)$), relative deviation of fit ($r_d = (\Delta p_c - \Delta p_e) / \Delta p_e$), permeance and ideal separation factor of CH₄ and H₂ as function of pressure difference on titanosilicate membrane.

A Example of Octave program for nonlinear fit

```
%% This program calculates the coefficients p() resulting from
%% non-linear regression fit of data (data.txt) by function F

T = 298.15;           % Temperature [K]
R = 8.314;           % Universal gas constant [J/mol/K]
V = 0.544e-3;        % Apparatus volume [m3]
A = 0.7274635e-4;    % Membrane area (membrane type K) [m2]
eta= 11.042e-6;      % Gas dynamic viscosity (CH4) [Pa.s]
Mw = 16e-3;          % Molar mass (CH4) [kg/mol]
rp = 1e-7;           % Mean pore radius estimate [m]
val= dlmread('data.txt'); % Read input data from file
y = val(:,2)*1e3-val(:,4)*1e3; % Independent variables
x = val(:,1);        % Dependent variable
[npts,trash] = size(x); % Read n. of points [npts]
Q = -R*T*A/V;        % Q constant
```

```

%% Intial estimates
p2 = sum(val(:,4))*1e3/npts;          % Mean atmospheric pressure [Pa]
dp0= (val(1,2) - val(1,4))*1e3;      % Initial pressure difference [Pa]
%% L
pin(1) = 2*p2 + 32*eta/(2*rp)*sqrt(2*R*T/(3.1415926*Mw));
%% K
pin(2) = pin(1)*1.0e-11;
%% C
pin(3) = log(dp0/(dp0+pin(1)));
%% -----
ndf      = (npts - 3);                % N. deg. of freedom
wt        = ones(size(x));           % Weights
niter     = 100;                     % Max. num. of iteration for non-lin. fit
stol      = 1e-9;                    % Tolerance (stop. criterion)
%
%% Function to fit
F = @(x,p)(p(1).*(exp(p(2).*Q.*x(:,1) + p(3))./( 1 - exp(p(2).*Q.*x(:,1) + p(3)))));
%% This is the Octave fitting routine for explanation read:
%% http://octave.sourceforge.net/optim/function/leasqr.html
%% [f,p,cvg,iter,corp,covp,covr,stdresid,Z,r2]=
%%                                     leasqr(x,y,pin,F,{stol,niter,wt,dp,dFdp,options})
dFdp = 'dfdp';
dp = [1e-6; 1.e-6; 1.e-6];
[f,p,kvg,iter,corp,covp,covr,stdresid,Z,r2] = leasqr(x, y, pin, F,stol,niter,wt,dp,dFdp);

%% RESULTS
fprintf('L      = %12.4e\n', p(1));
fprintf('K      = %12.4e\n', p(2));
fprintf('C      = %12.4e\n', p(3));
fprintf('iter = %4i\n', iter);
fprintf('ndf   = %4i\n', ndf);
fprintf('WSSR = %12.4e\n', sqrt(sum((f(:)-y(:)).^2)./ndf));
fprintf('PIk   = %12.4e\n', p(2).*(1-2*p2./p(1)));
fprintf('PIp   = %12.4e\n', p(2)/p(1));
fprintf('rp    = %12.4e\n', (32/2)/(p(1)-2*p2)*eta*sqrt(2*R*T/3.1415926/Mw));

```

B Matlab program for nonlinear fit

```

%% This program calculates the coefficients p() resulting from
%% non-linear regression fit of data (data.txt) by function F

```

```

T = 298.15;          % Temperature [K]
R = 8.314;           % Universal gas constant [J/mol/K]
V = 0.544e-3;        % Apparatus volume [m3]
A = 0.7274635e-4;    % Membrane area (membrane type K) [m2]
eta= 11.042e-6;      % Gas dynamic viscosity (CH4) [Pa.s]
Mw = 16e-3;          % Molar mass (CH4) [kg/mol]

```

```

rp = 1e-5;          % Mean pore radius estimate [m]
val= dlmread('data.txt');          % Read data from file
y = val(:,2)*1e3-val(:,4)*1e3;      % Independent variables
x = val(:,1);          % Dependent variable
[npts,trash] = size(x);          % Read n. of points [npts]
Q = -R*T*A/V;          % Q constant

%%Nonlinear least squares regression
%% Intial estimates
p2 = sum(val(:,4))*1e3/npts;          % Mean atmospheric pressure [Pa]
dp0= (val(1,2) - val(1,4))*1e3;      % Initial pressure difference [Pa]
%% L
pin(1) = 2*p2 + 32*eta/(2*rp)*sqrt(2*R*T/(3.1415926*Mw));
%% K
pin(2) = pin(1)*1.0e-11;
%% C
pin(3) = log(dp0/(dp0+pin(1)));
%% N. deg. of freedom
ndf = (npts - 3);
stol = 1e-9;          % Tolerance (stop. criterion)
%
%% Function to fit, F(<pars. to evaluate>,<independet var.>)
F = @(p, x)(p(1).*(exp(p(2).*Q.*x(:,1) + p(3))./(1 - exp(p(2).*Q.*x(:,1) + p(3)))));

%% This is the Matlab fitting routine for explanation read:
%% http://www.mathworks.com/help/toolbox/stats/nlinfit.html
%%
[p,r,J,covp,wssr] = nlinfit(x,y,F,pin);

%% RESULTS
fprintf('L = %12.4e\n',p(1));
fprintf('K = %12.4e\n',p(2));
fprintf('C = %12.4e\n',p(3));
fprintf('ndf = %4i\n', ndf);
fprintf('WSSR = %12.4e\n', sqrt(wssr));
fprintf('PIk = %12.4e\n', p(2).*(1-2*p2./p(1)));
fprintf('PIp = %12.4e\n', p(2)/p(1));
fprintf('rp = %12.4e\n', (32/2)/(p(1)-2*p2)*eta*sqrt(2*R*T/3.1415926/Mw));

```