Project # 4
Measuring Zeolitic Diffusion by Single Crystal Permeation

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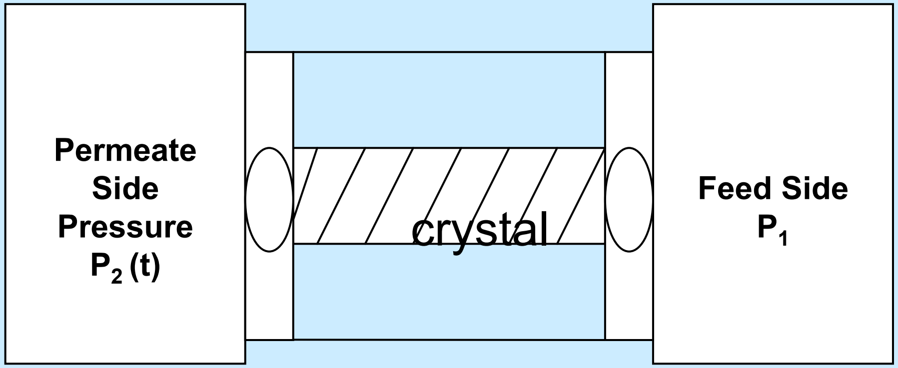
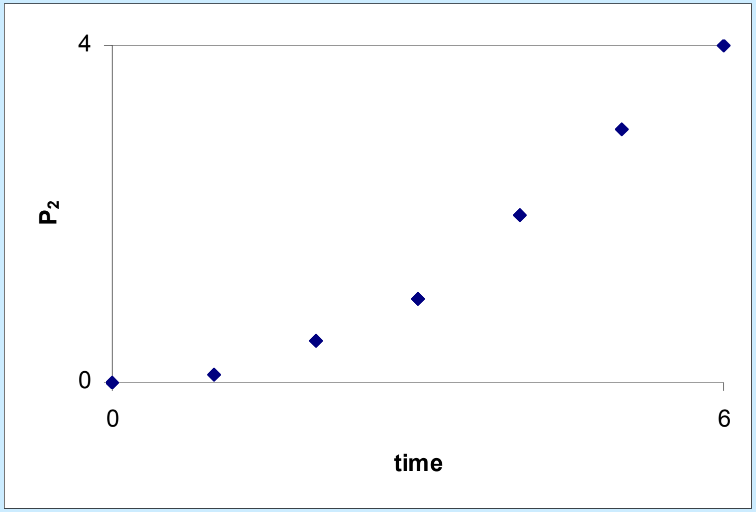
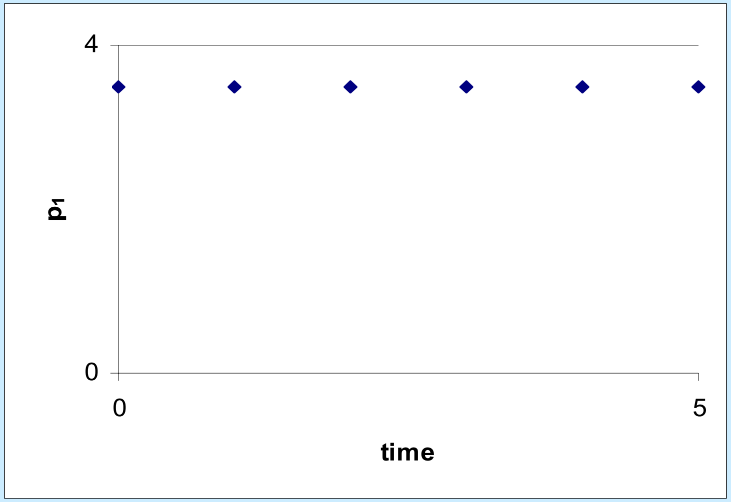
Basic Concept

- Take a large untwinned crystal
- Fabricate a membrane containing the crystal in desired orientation
- Subject the membrane to a concentration gradient
- Monitor the change in a macroscopic property (pressure, concentration) on permeate side
- Analyze data for zeolite diffusivity

Static Single Crystal Membrane Technique





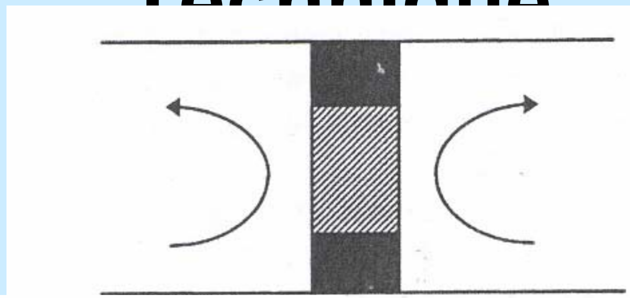


Intercept = f(diffusivity), Slope = f(adsorption constant, micropore diffusivity)

Dynamic Single Crystal Membrane Technique

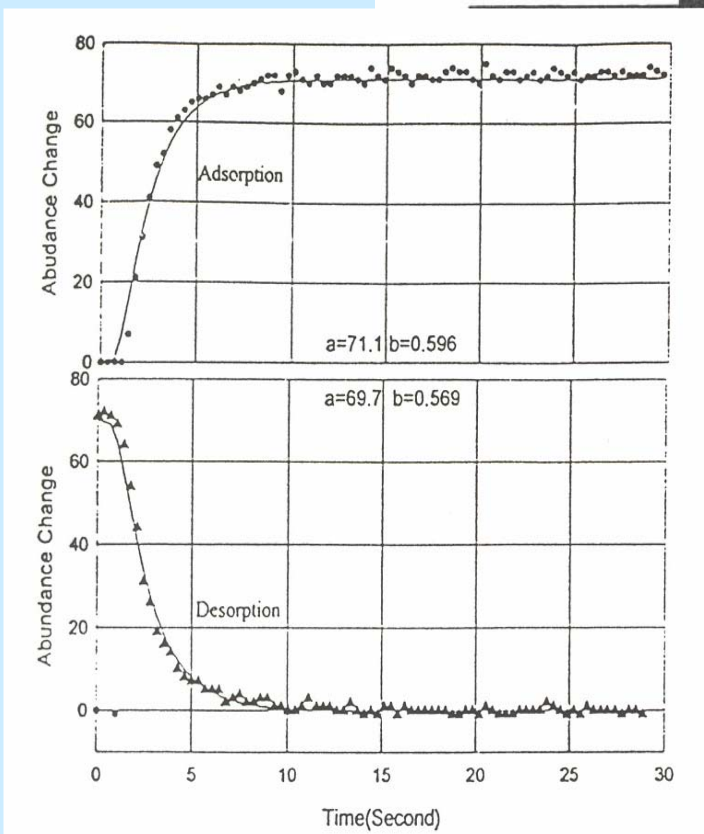
Permeate Side

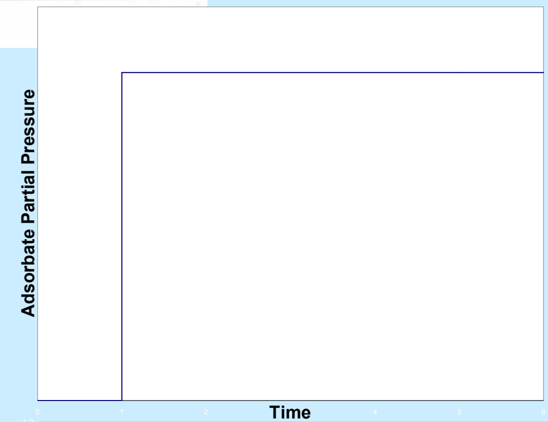
Sweep Gas - He

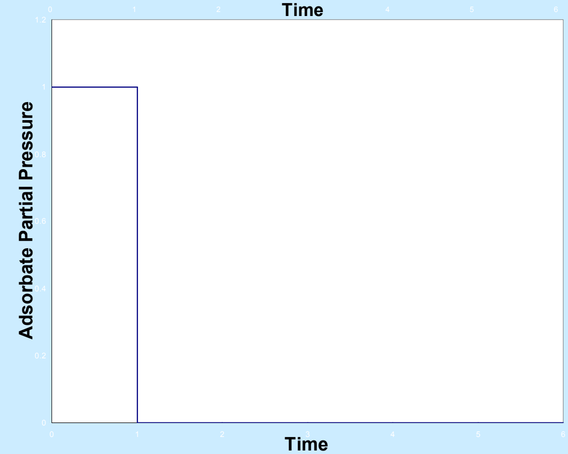


Feed Side

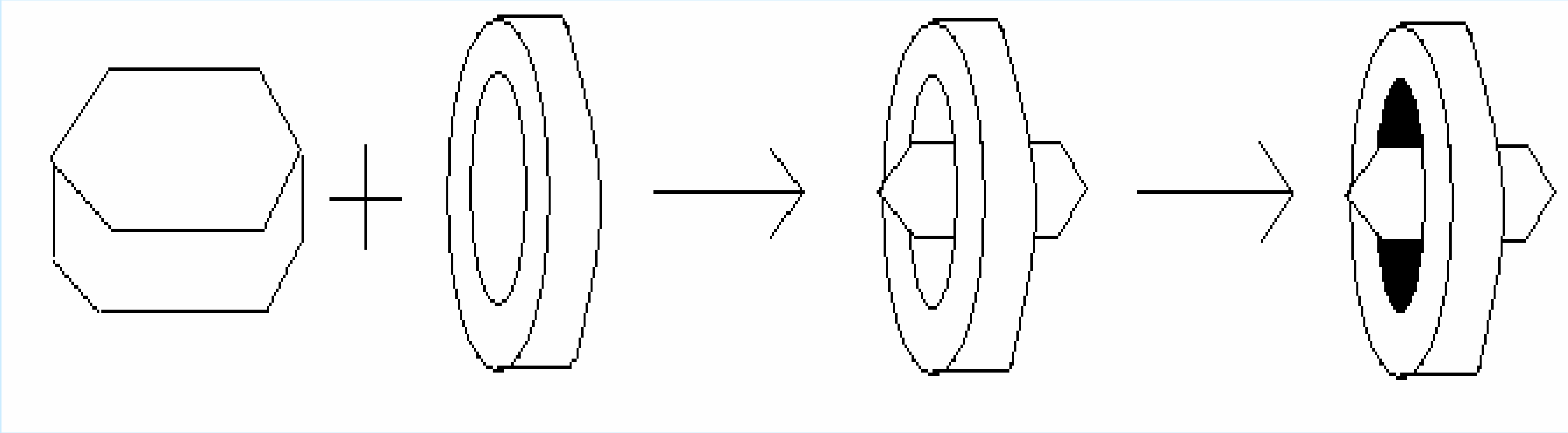
Carrier Gas - He



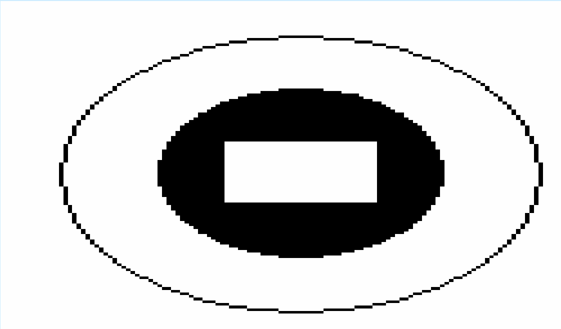




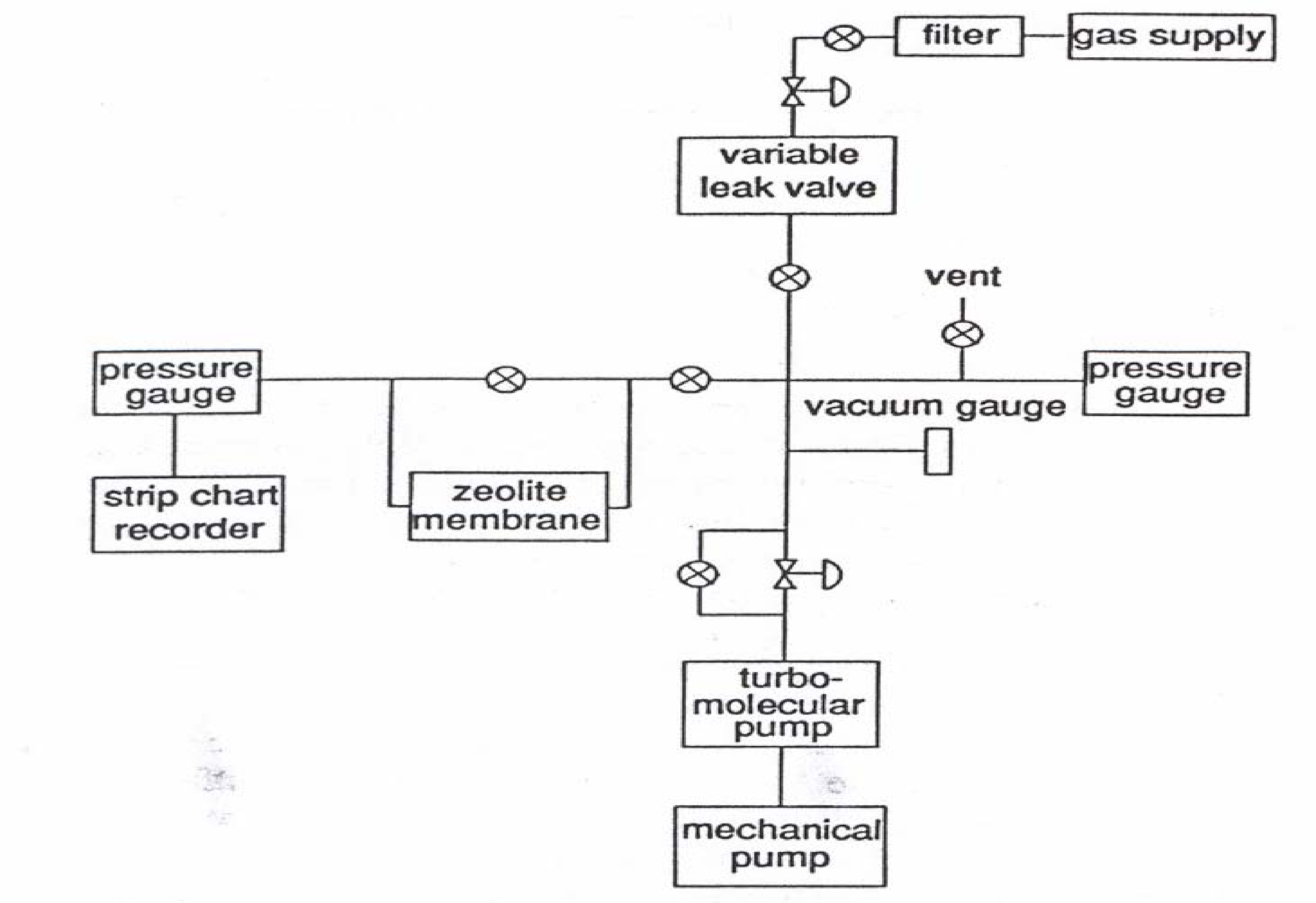
Membrane Fabrication Schematics



Silicalite crystal **Aluminum disk** **Crystal mounting in the disk** **Curing and filing**

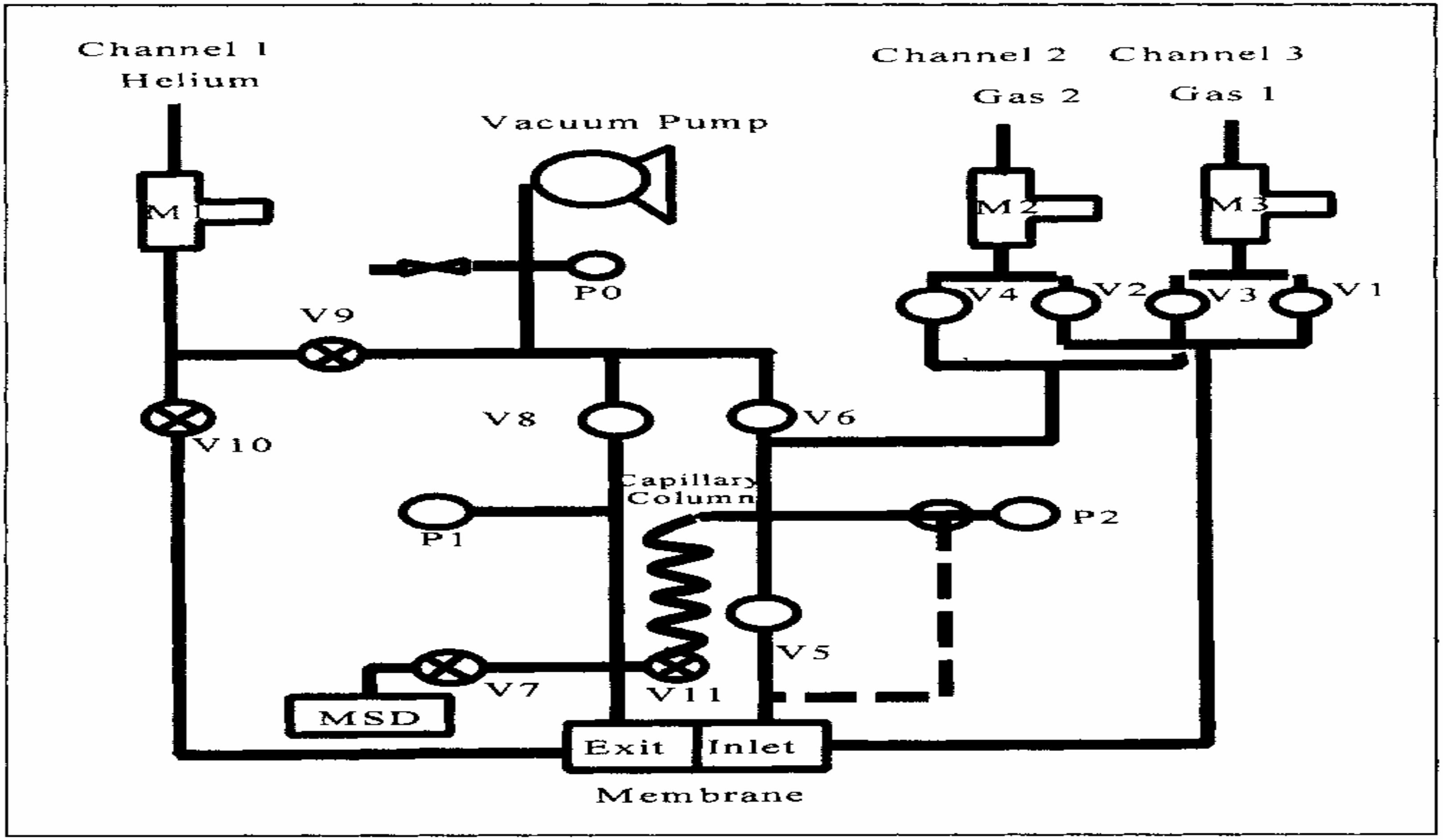


Top view



Static SCM experimental setup

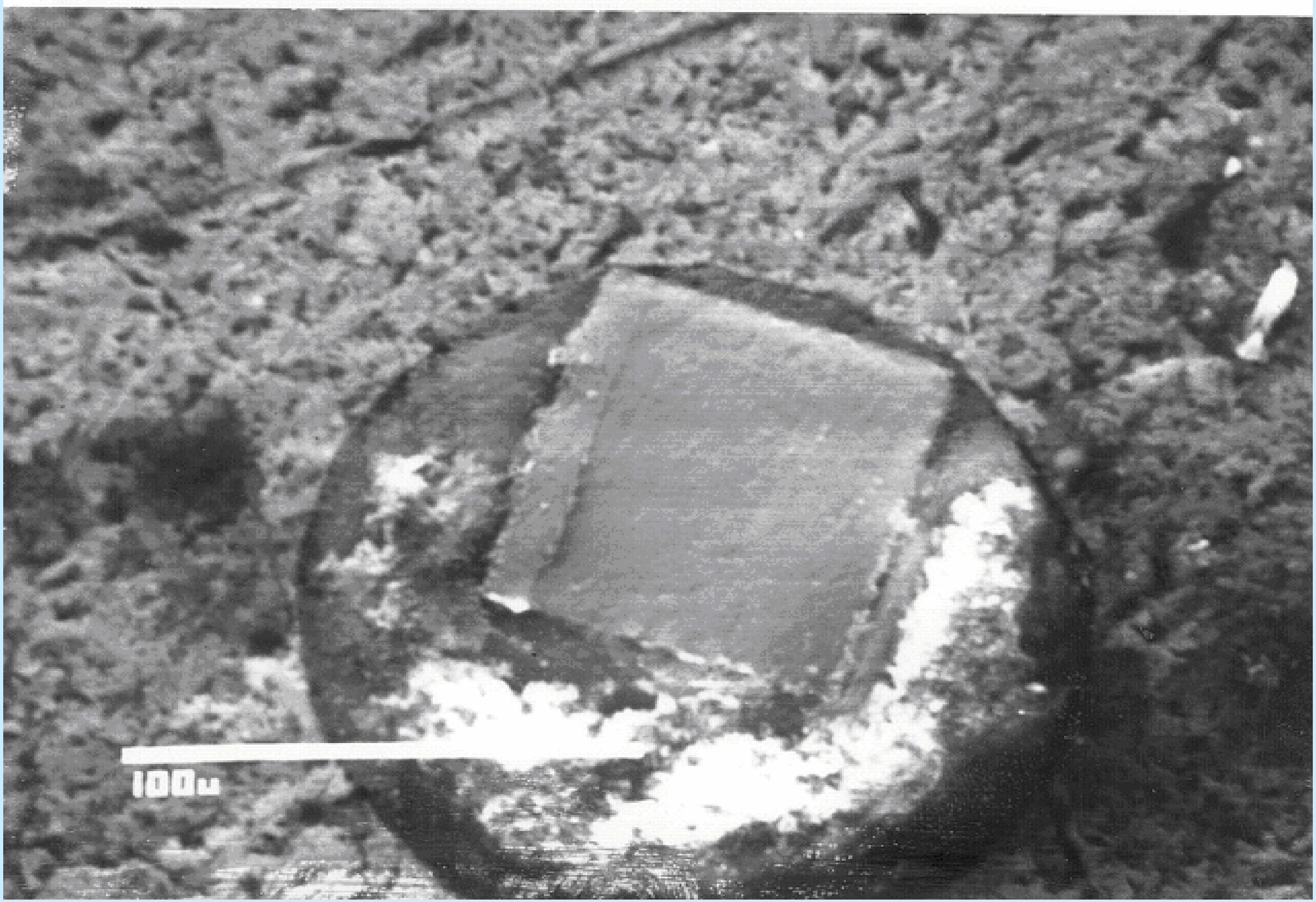
Dynamic SCM Experimental Setup



Systems Studied

- **Adsorbent – Silicallite (100x100x300 μm)**
- **Adsorbates - n-Alkanes (dynamic), normal and branched alkanes (static), aromatics (static) & inert gases (static)**
- **Partial pressure of adsorbates – 0 to 10 torr**
- **Temperatures – 303K to 343K**

SEM of SCM



Experimental Procedure for Dynamic SCM

- Check the structural integrity of membrane by exposing to TEA (kinetic dia = 7.4Å) at 18 torr. No TEA should be detected on the outlet side.

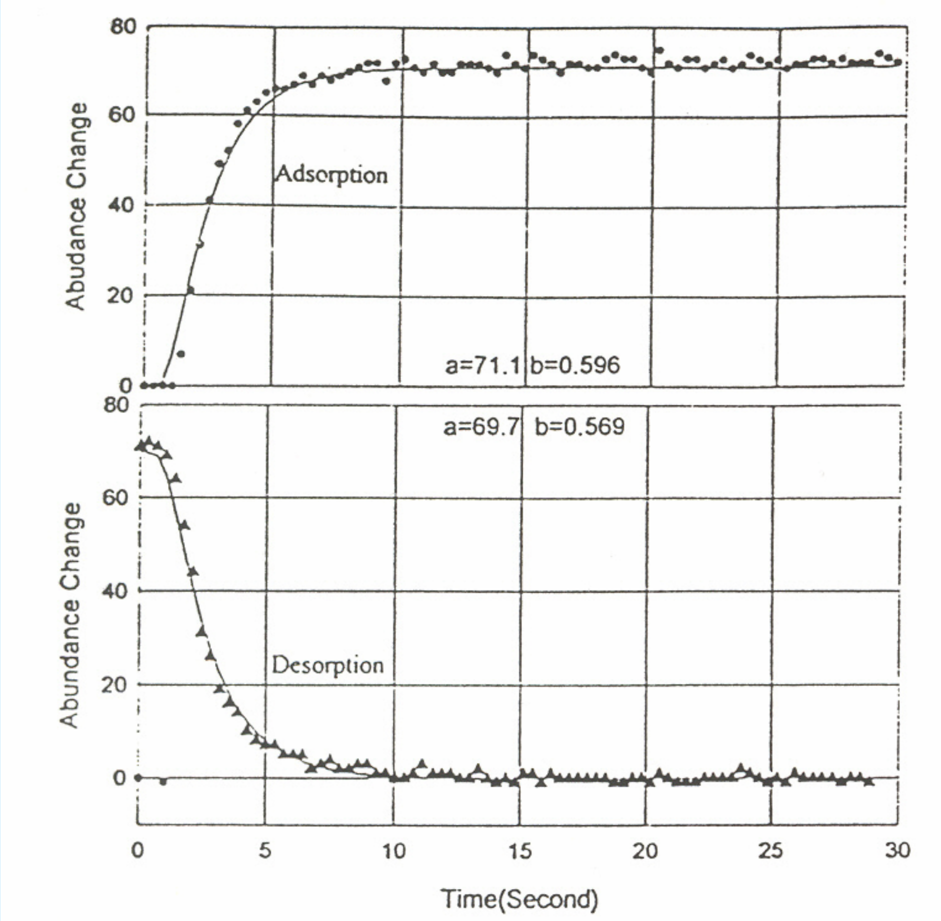
- Activate the membrane under vacuum and at 200°C for 8 hours.

- Expose the inlet side to flowing adsorbate at desired pressure. Outlet side helium flow is at 15 torr.

- Use mass selective detector to continuously monitor the ions with the largest fraction (m/z ratio) in helium carrier gas at the outlet side.

- Use transient or steady state response to calculate diffusivity.

Experimental and Predicted MSD Response Curves



Typical MSD response curves for adsorption and desorption and their best curve fits

Steady-State Analysis

$$J = -D_t \frac{dq}{dx} \rightarrow D_t = D_0 * \frac{d \ln P}{d \ln q} \rightarrow J = -D_0 q \frac{d \ln P}{dx}$$

$$q = \rho_{\text{solid}} * n + \epsilon * \rho_{\text{gas}}, \rightarrow d\psi = n * d \ln P$$

$$\downarrow$$

$$J_{ss} * dx = -D_0 * \left(\rho_{\text{solid}} * d\psi + \epsilon * \frac{P}{RT} * d \ln P \right).$$

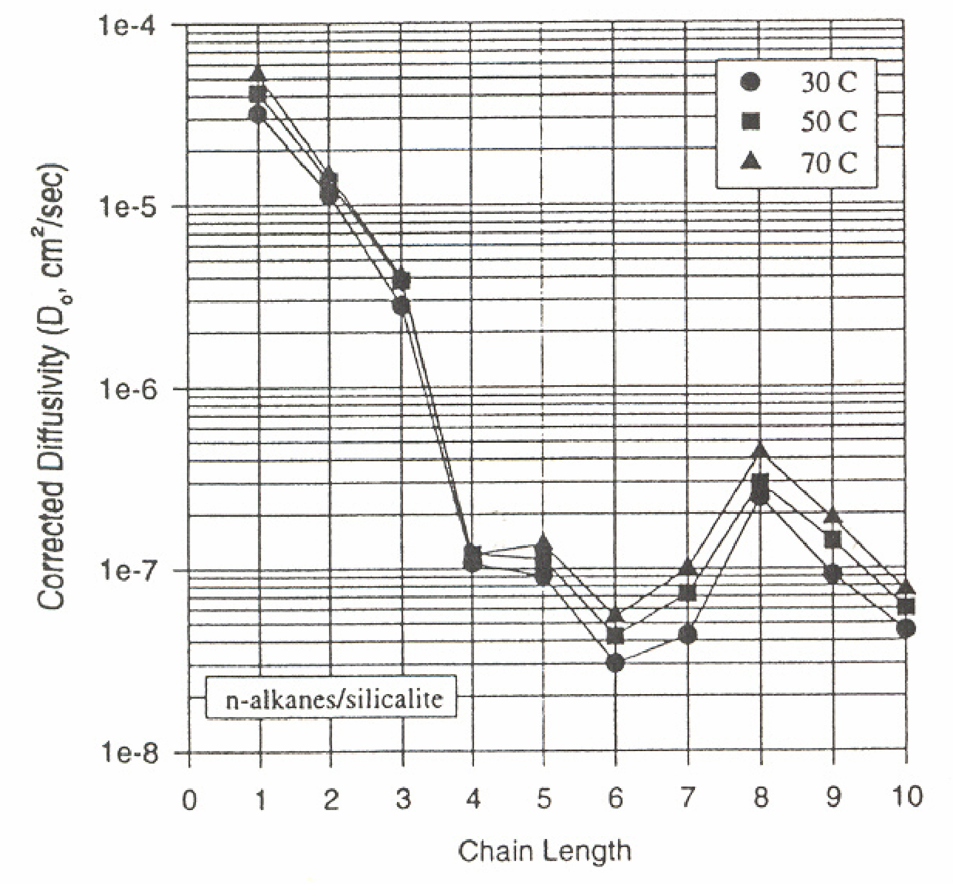
$$\downarrow$$

$$J_{ss} * L = D_0 \left(\rho_{\text{solid}} * \psi_{\text{inlet}} + \epsilon * \frac{P_{\text{inlet}}}{RT} \right)$$

$$J_{ss} = \frac{Q}{A}$$

$$D_0 = \frac{Q * L}{A \left(\rho_{\text{solid}} * \psi_{\text{inlet}} + \epsilon * \frac{P_{\text{inlet}}}{RT} \right)}.$$

C_1-C_{10} Diffusivities in Silicalite



Corrected diffusivities from SCM steady-state measurements for n-alkanes

Strengths

- External mass transfer resistances are eliminated such as axial dispersion, bed diffusion and macropore diffusion.
- The length of diffusion path may be accurately known.
- In principle, diffusion along different paths may be measured.

Requirements

- Crystal should be large and untwinned
- Mounting, Sealing and Polishing a crystal presents formidable difficulties (success rate ~ 5 – 10 %)
- Activation temperature is rather low (~200°C) because epoxy degrades at higher temperatures
- The flux coming across the membrane is rather small (10^{-10} mol/sec). A highly accurate measurement system is needed on the permeate side

Requirements (Continued)

- Good and accurate equilibrium data are necessary. Otherwise calculated diffusivity values may be grossly in error.
- One still needs to make some assumption about how diffusivity varies with the loading.
- Measurements at high temperature and pressure are not possible due to membrane rupture possibilities.

Experimental Plan

- Zeolite Materials – A, X, MFI and Ferrierite – Large crystals
- Adsorbates – To be decided jointly by the Group
- Measure pure component equilibrium
- Measure pure component permeation
- Measure or predict mixture equilibrium data
- Measure mixture permeation