ChE-402: Diffusion and Mass Transfer

Lecture 12

Intended Learning Outcome

- To analyze diffusion of molecules in porous (nanoporous) materials.
- To revisit the concepts learned, and apply them to understand/predict/design analytical methods used for the measurement of diffusion coefficient.
- If time permits, we will at analyze diffusion of ions under applied electric field.


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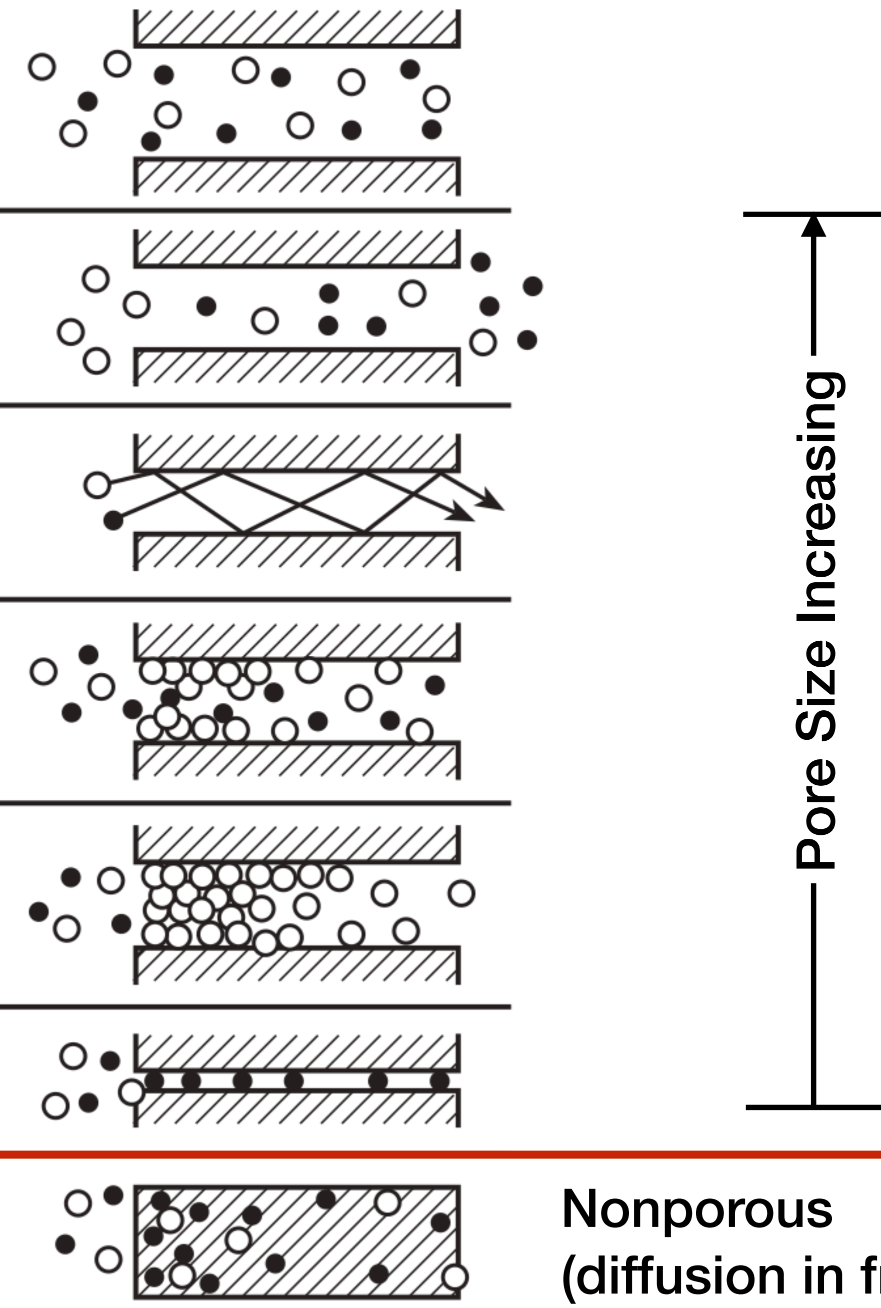
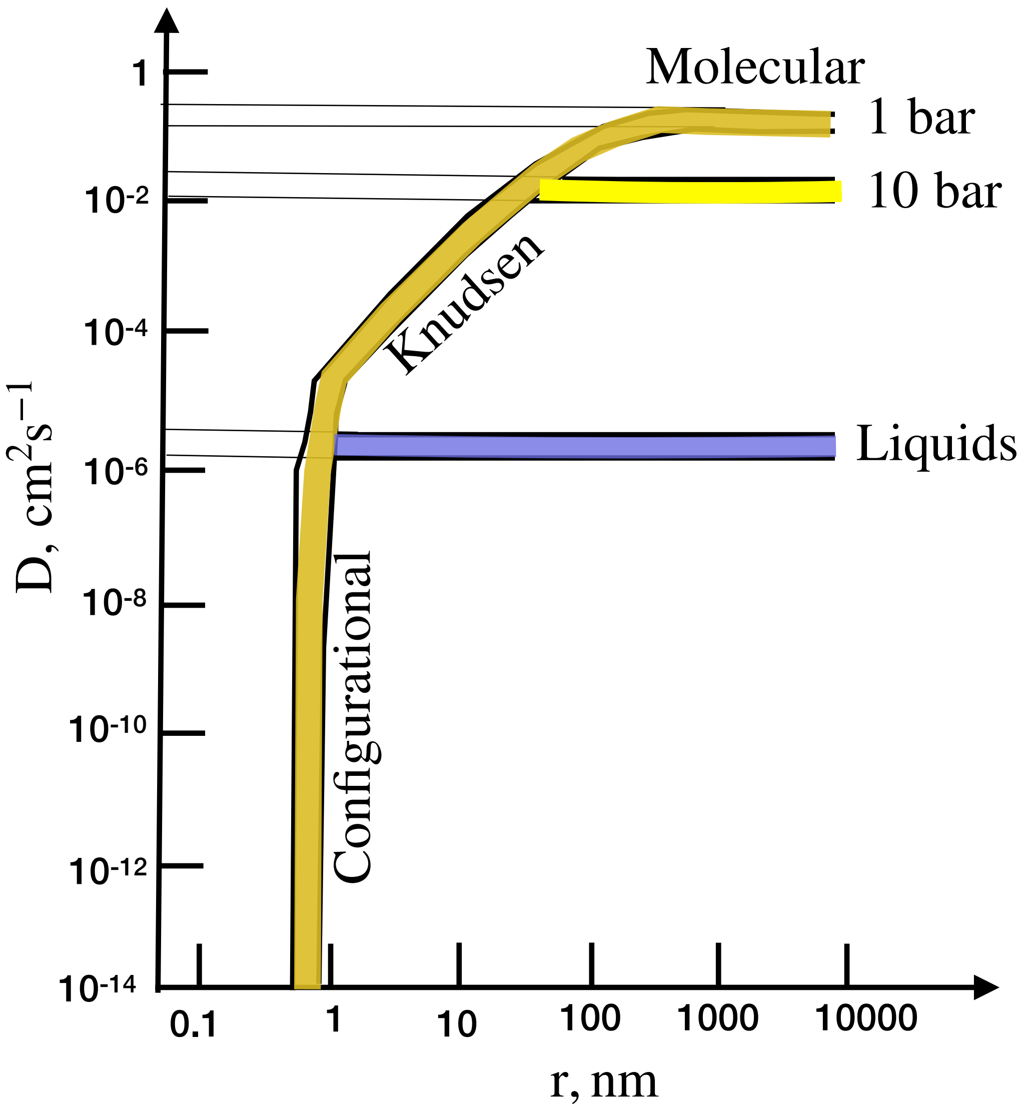
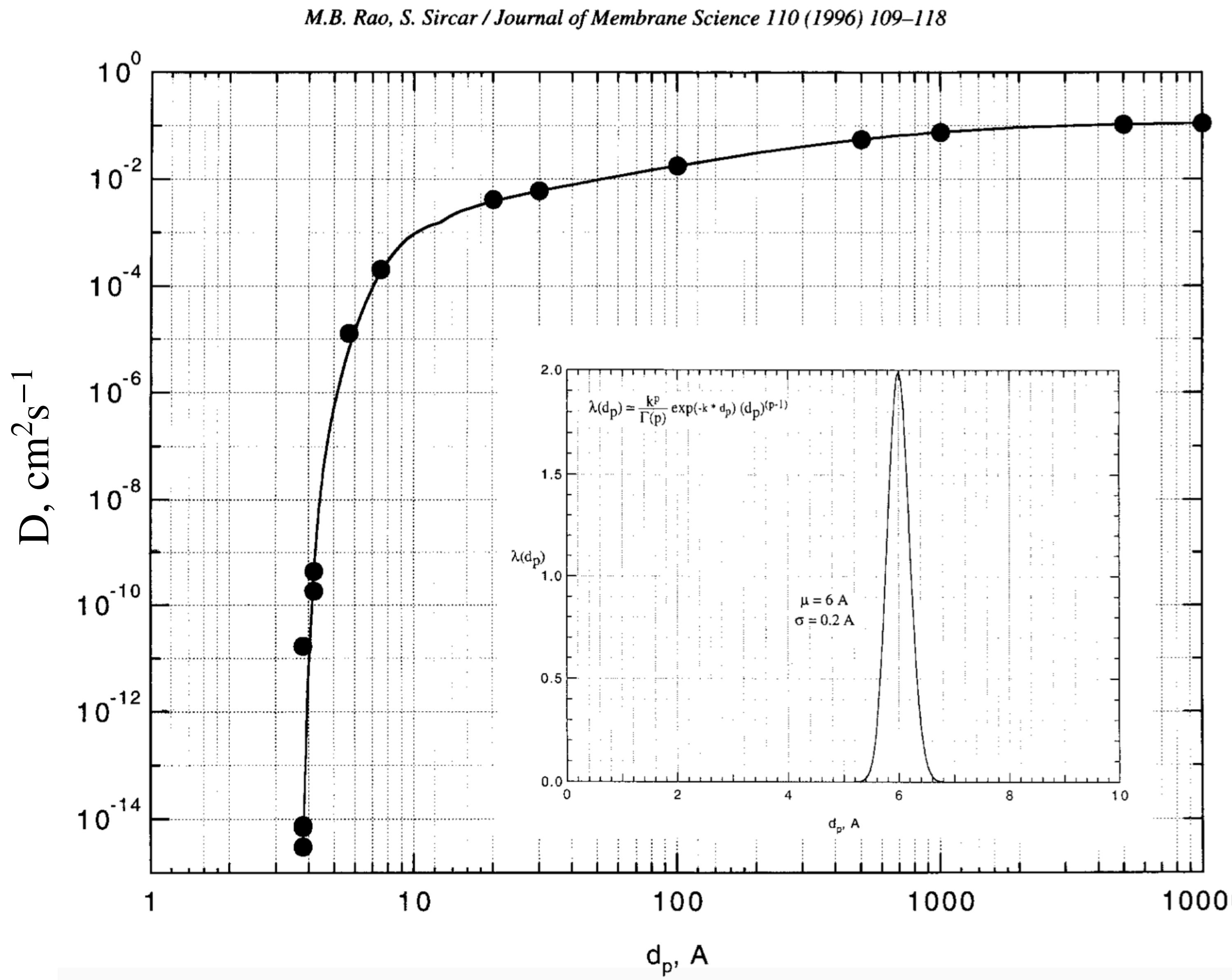
Diffusion in nanoporous materials



Viscous Diffusion	Flow in large pores (>100 nm) or at high pressure
Molecular Diffusion	Diffusion of A in B or B in A
Knudsen Diffusion	Flow in nanopores (2-100 nm)
Surface Diffusion	Flow along surface
Capillary Condensation	$\gamma_{sv} > \gamma_{sl}$
Configurational Diffusion	Flow in nanopores (0.25-2 nm)
Sorption Diffusion	Nonporous (diffusion in free-volume, or lattice gaps)

Diffusion in nanoporous materials





Adapted from
J. Karger, D. M. Ruthven, D. N. Theodorou, Diffusion in Nanoporous Materials

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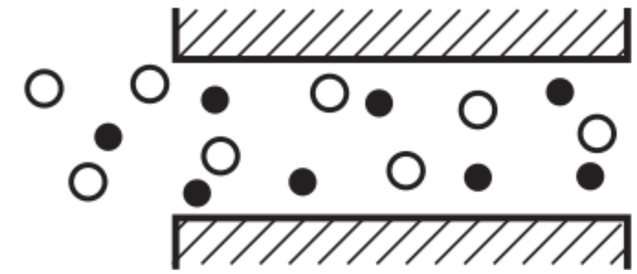
Viscous diffusion

Viscous flow in cylindrical tubes
(when there is a pressure difference between the two ends)



Hagen-Poiseuille equation:

$$v_1 = \frac{d^2 \Delta P_1}{32 \eta_1 l} \qquad N_1 = c_1 v_1 = c_1 \frac{d^2 \Delta P_1}{32 \eta_1 l} = \left(\frac{d^2 c_1 RT}{32 \eta_1} \right) \frac{\Delta c_1}{l}$$

If we have no convection, and only diffusion

$$N_1 = J_1 = D_{vis} \frac{\Delta c_1}{l} \qquad \Rightarrow D_{vis} = \frac{d^2 c_1 RT}{32 \eta_1} = \frac{d^2}{32 \eta_1} P_1$$

Viscous diffusion increases at higher P

<u>Note: This is an approximate treatment; viscous flow is bulk flow (convection can be important)</u>

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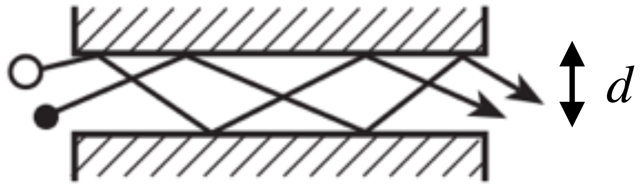
Knudsen diffusion

Occurs when mean free path, l, is larger than d (pore diameter)



$$\text{Knudsen number} = \quad Kn = \frac{l}{d} > 1$$

- For liquids, mean free path is of the order of angstroms, therefore Knudsen transport is not important.
- For gases, mean free path ~ 10-200 nm

Diffusion coefficient derived from the kinetic theory of gases but by replacing l by d

$$D = \frac{1}{3}\bar{v}\,l \quad \Rightarrow \quad D_K = \frac{1}{3}\bar{v}\,d \qquad \bar{v} = \sqrt{\frac{8k_BT}{\pi m}} \qquad D_K = \sqrt{\frac{8k_BTd^2}{9\pi m}}$$

Unlike in viscous flow, the Knudsen diffusion is independent of pressure

Molecular diffusion in pores

Becomes important when more than 1 species is diffusing through the pore

When the pore is too large, the effect of molecular-wall collision becomes negligible and molecular diffusion becomes important

$$D_{AB} = \frac{1.86 * 10^{-3} * T^{1.5} * (1/M_1 + 1/M_2)^{0.5}}{P\sigma_{12}^2\Omega}$$

$$\frac{1}{D} = \frac{1}{D_{\mathrm{K}}} + \frac{1}{D_{\mathrm{AB}}}$$

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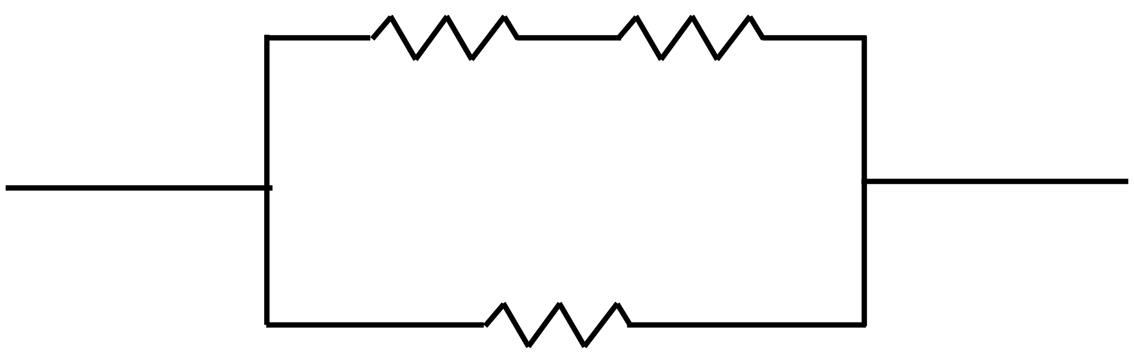
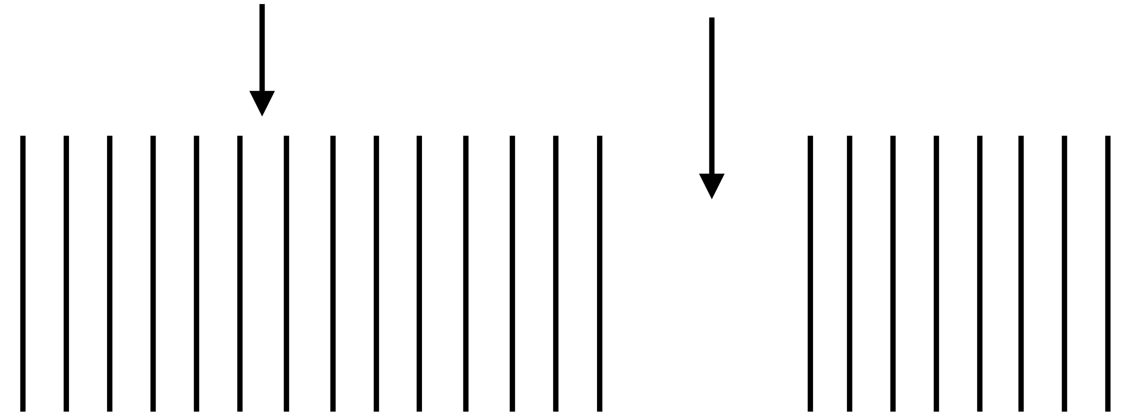
Overall diffusion in pores



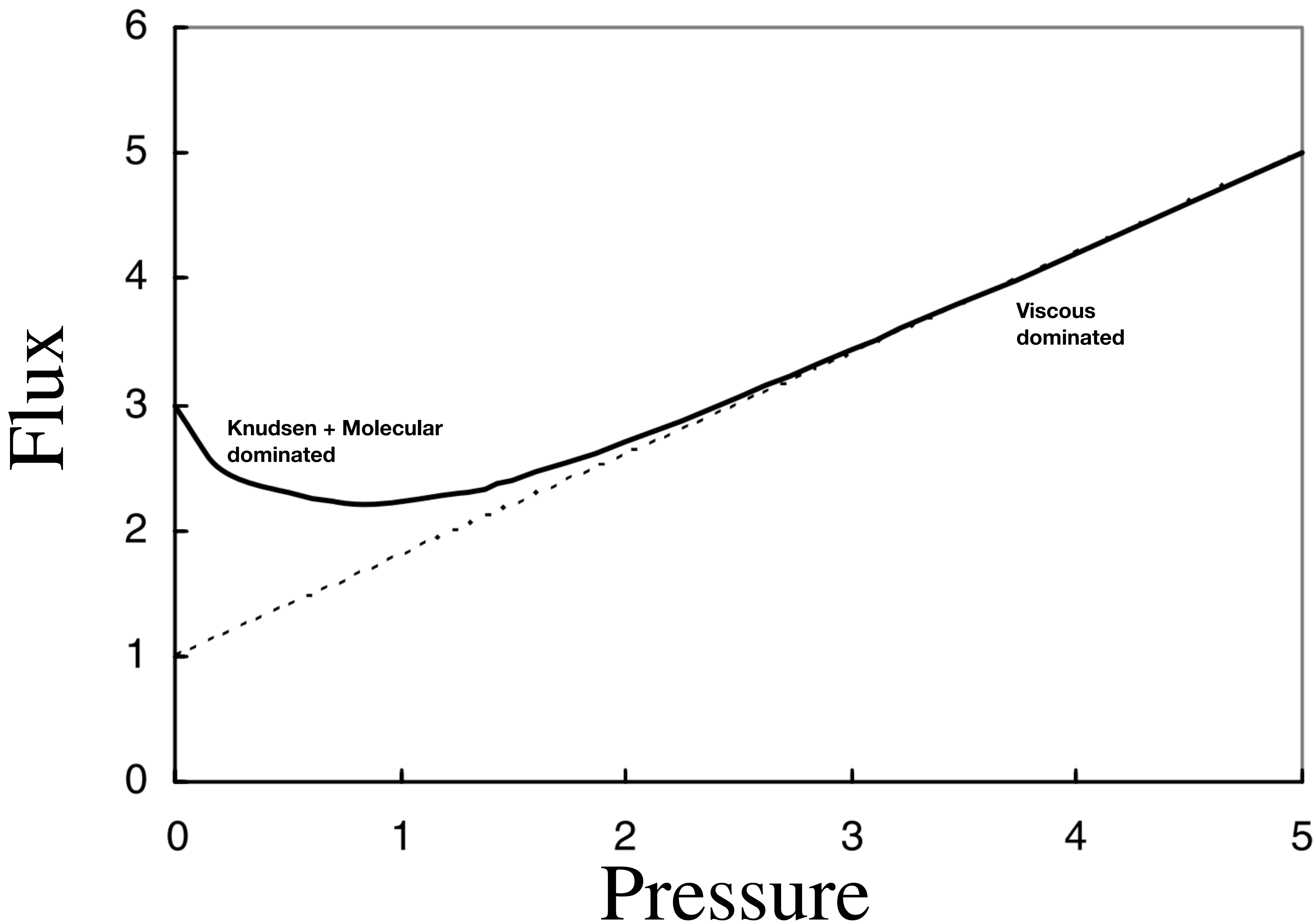
Diffusivity = 1/Resistance

$$\frac{1}{D} = \frac{1}{D_K} + \frac{1}{D_{AB}}$$

$$D_{total} = D_{vis} + D$$



Combination of viscous, Knudsen and molecular diffusion



J. Karger, D. M. Ruthven, D. N. Theodorou, Diffusion in Nanoporous Materials

Relative importance of viscous, Knudsen and molecular diffusion in gaseous diffusion

$$\frac{1}{D} = \frac{1}{D_K} + \frac{1}{D_{AB}}$$

$$D_{total} = D_{vis} + D$$

p (atm)	D_{AB} ($cm^2\,s^{-1}$) Molecular	r (cm)	D_K ($cm^2\,s^{-1}$)	D ($cm^2\,s^{-1}$)[a]	D_{vis} ($cm^2\,s^{-1}$)	D_{total} ($cm^2\,s^{-1}$)	$\frac{D_{vis}}{D_{total}}$
		10^{-6}	0.03		0.0007		
1.0	0.2	10^{-5}	0.3		0.07		
		10^{-4}	3.0		7.0		

$$D_{AB} = \frac{1.86 * 10^{-3} * T^{1.5} * (1/M_1 + 1/M_2)^{0.5}}{P\sigma_{12}^2\Omega}$$

$$D_K = \sqrt{\frac{8k_BTd^2}{9\pi m}}$$

$$D_{vis} = \frac{d^2}{32\eta_1}P_1$$

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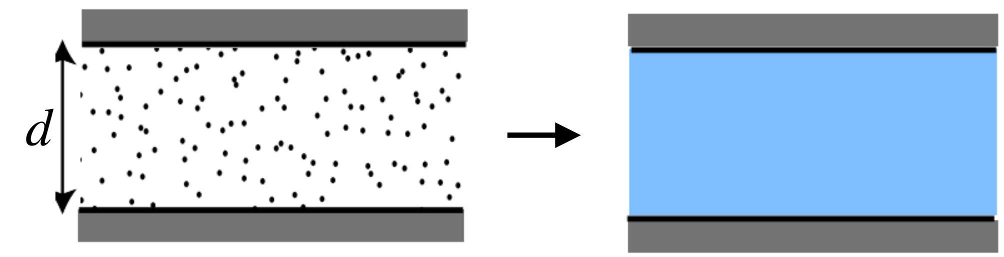
Capillary condensation

Consider two parallel solid surfaces separated by a distance d, which is in contact with vapor reservoir with pressure P_v at temperature T

If d is too large, the liquid-vapor equilibrium will occur at

$$P_v = P_{sat}$$



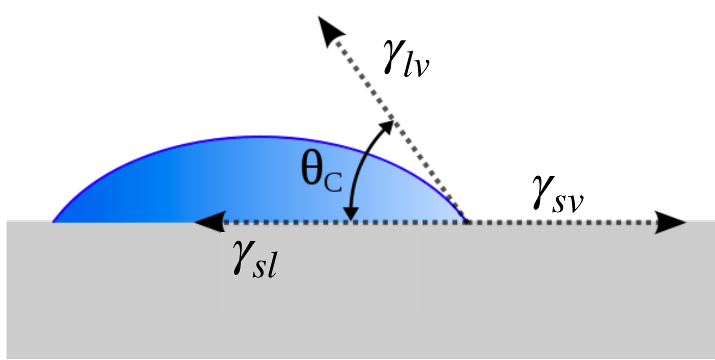
If the surface tension of the dry solid surface is higher than the wet solid surface

$$\gamma_{sv} > \gamma_{sl}$$

then the solid will favor liquid condensation

Young–Dupré equation of partial wetting: $\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl}$

$$0 < \theta < 90$$



Therefore, the solid can successfully stabilize a liquid phase even when

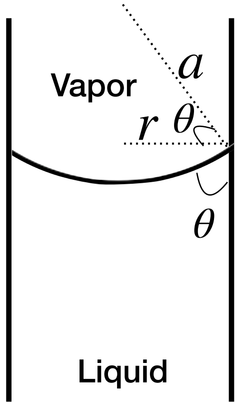
$$P_v < P_{sat} \text{ (flat interface)}$$

Capillary condensation

Kelvin equation: the vapor-pressure in curved interface changes from flat interface

$$P_{sat,curved} = P_{sat,flat} \exp\left(- \frac{2V_l \, \gamma_{lv}}{(r/\cos\theta)RT} \right)$$

$$a = \text{radius of curved interface} = \text{r}/\cos\theta$$



$$\theta = \text{contact angle}$$

$$V_l = \text{liquid molar volume}$$

$$r = \text{radius of tube}$$

- Diffusion in the capillary condensation regime is complicated to follow.
- As soon as a pore fills with condensate, the vapor flux through that pore is cut off and transport then depends on liquid flow driven by capillary forces.
- As a result, the apparent diffusivity is greatly reduced.

Measurement of diffusion coefficients

How would you measure diffusion coefficient for your material, system, etc?

Motivation:

1) **Sometime we want to measure the diffusion coefficient in film (sensor, membranes, evaporation, catalyst, ion-exchange membrane in fuel cell, batteries, skin grafts, etc.)**

2) **Sometime, we want to measure the diffusion coefficient in nanoporous materials in powder form (catalyst, adsorbents, etc.; e.g. zeolites, MOFs, activated carbon, carbon nanotube, etc.)**

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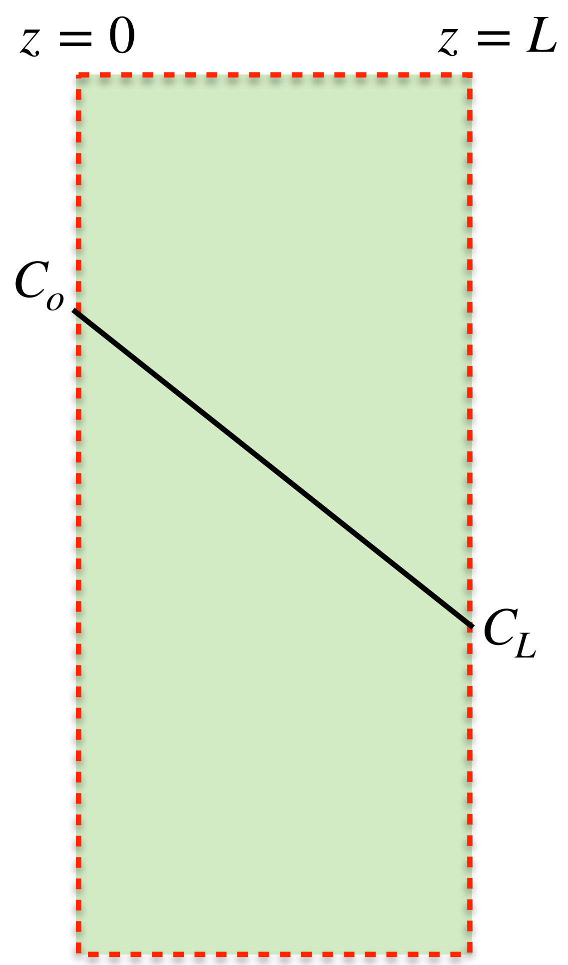
Diffusion across a thin porous film

$$C = C_0 + (C_L - C_0)\frac{z}{L}$$

$$J = -D\frac{dC}{dz} = D\frac{(C_0 - C_L)}{L} \;=\; constant$$

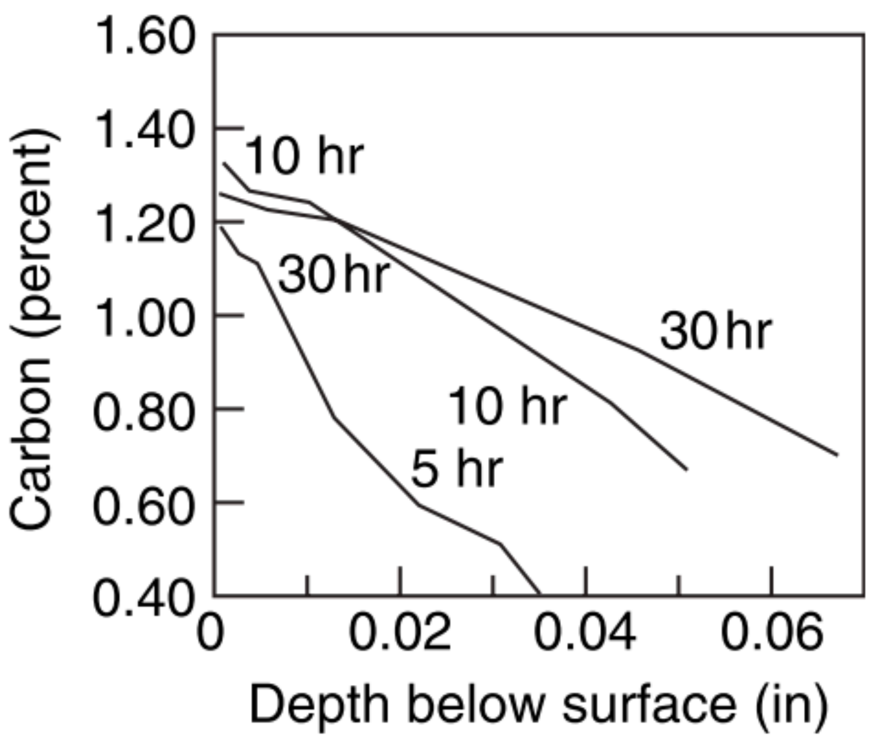
Fix the concentrations on both sides.

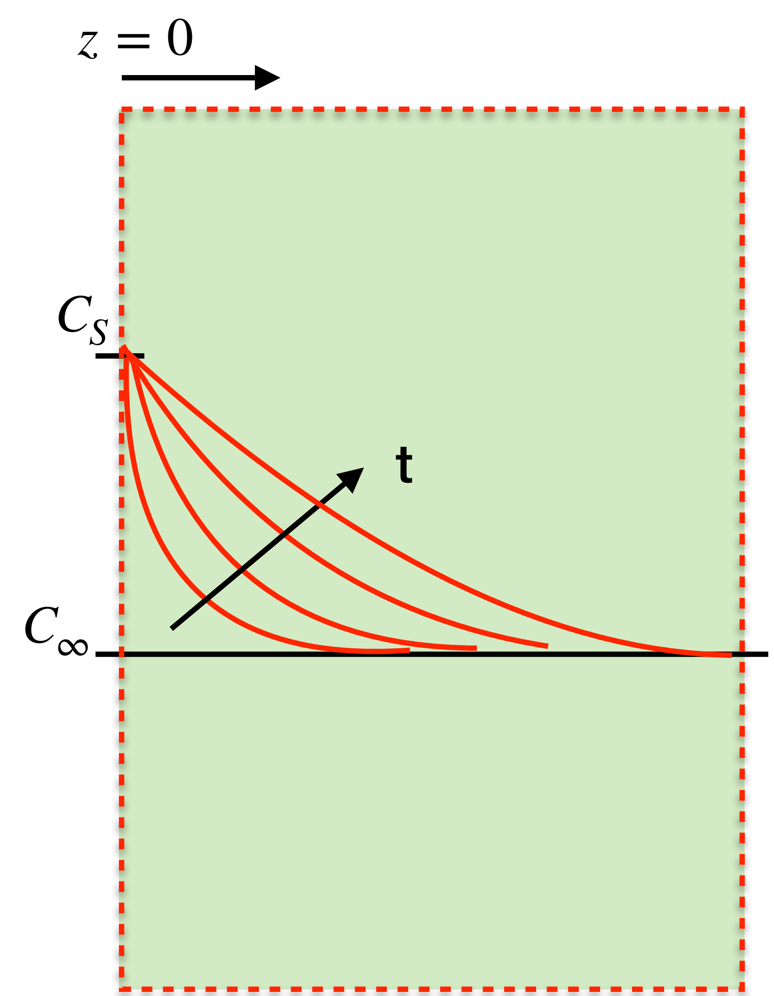
Measure the flux.



Transient diffusion across a semi-infinite slab

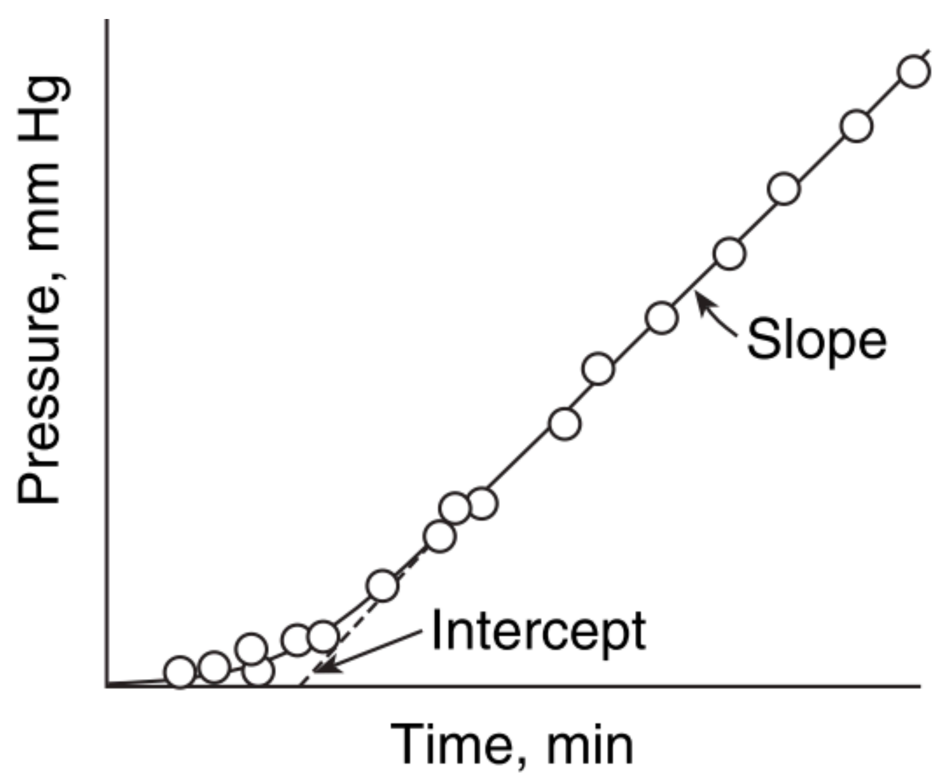
$$\frac{C - C_S}{C_\infty - C_S} = erf\,\zeta = \frac{2}{\sqrt{\pi}}\int_0^{\zeta} \exp(-s^2)ds \qquad \zeta = \frac{z}{\sqrt{4Dt}}$$

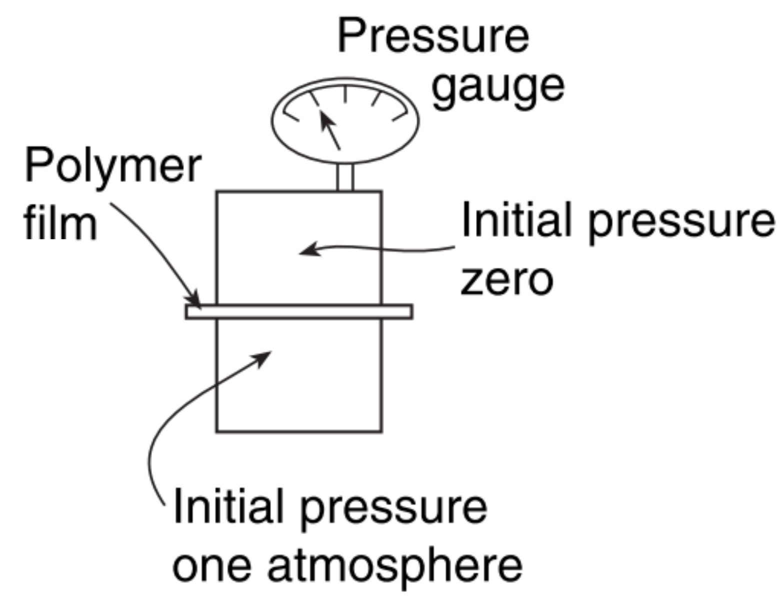




Diffusion across a dense polymeric film

Fix the concentrations on both sides.
Measure the flux.





$$p = \left\{ \frac{ARTp_0}{Vl} \right\} (H\,D) \left[t - \frac{l^2}{6D} \right]$$

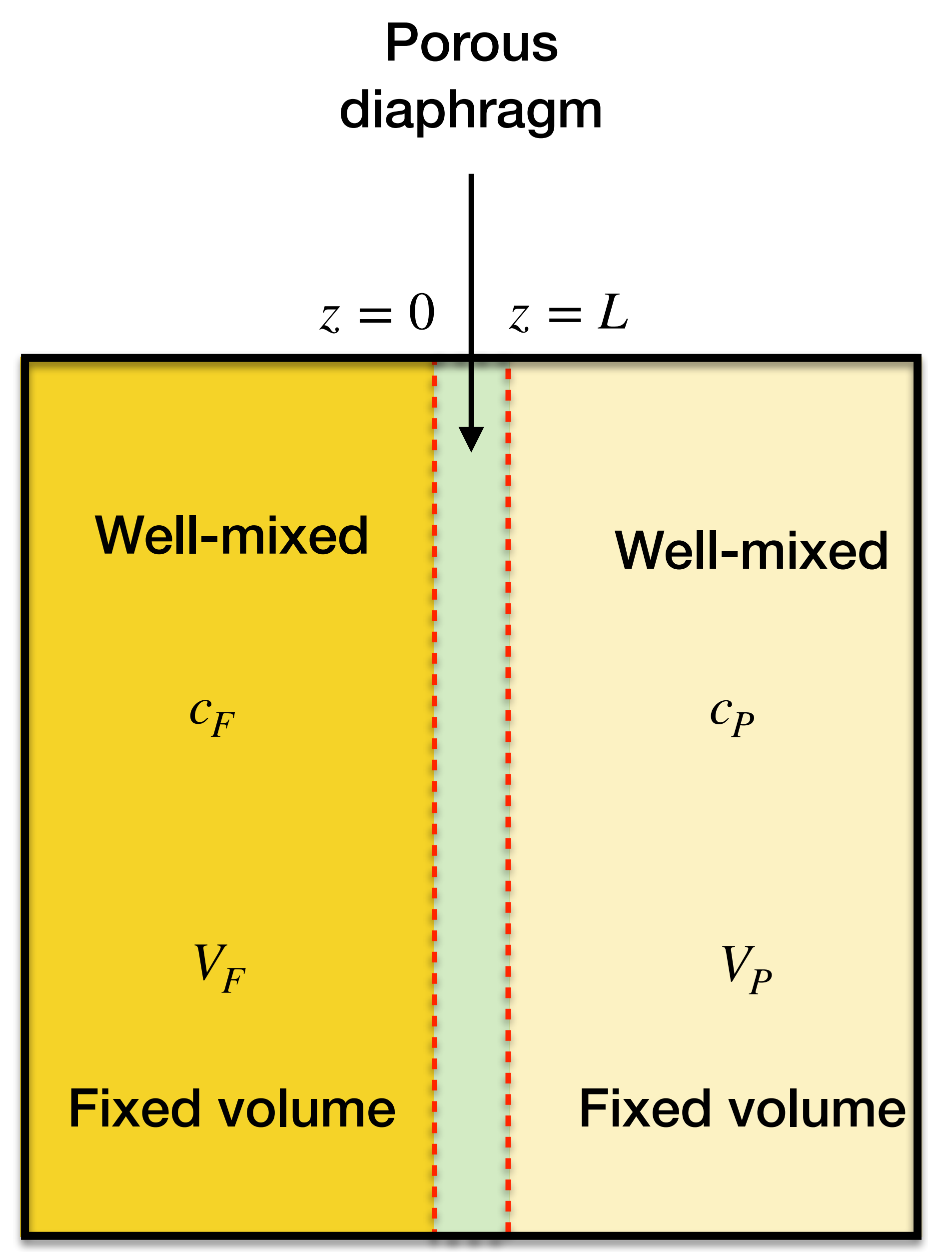
Diaphragm-cell to measure diffusion coefficient

$$D = \frac{1}{\beta t} \ln\left(\frac{c_{F0} - c_{P0}}{c_F - c_P}\right)$$

$$\beta = \frac{AH}{L}\left(\frac{1}{V_F} + \frac{1}{V_P}\right)$$

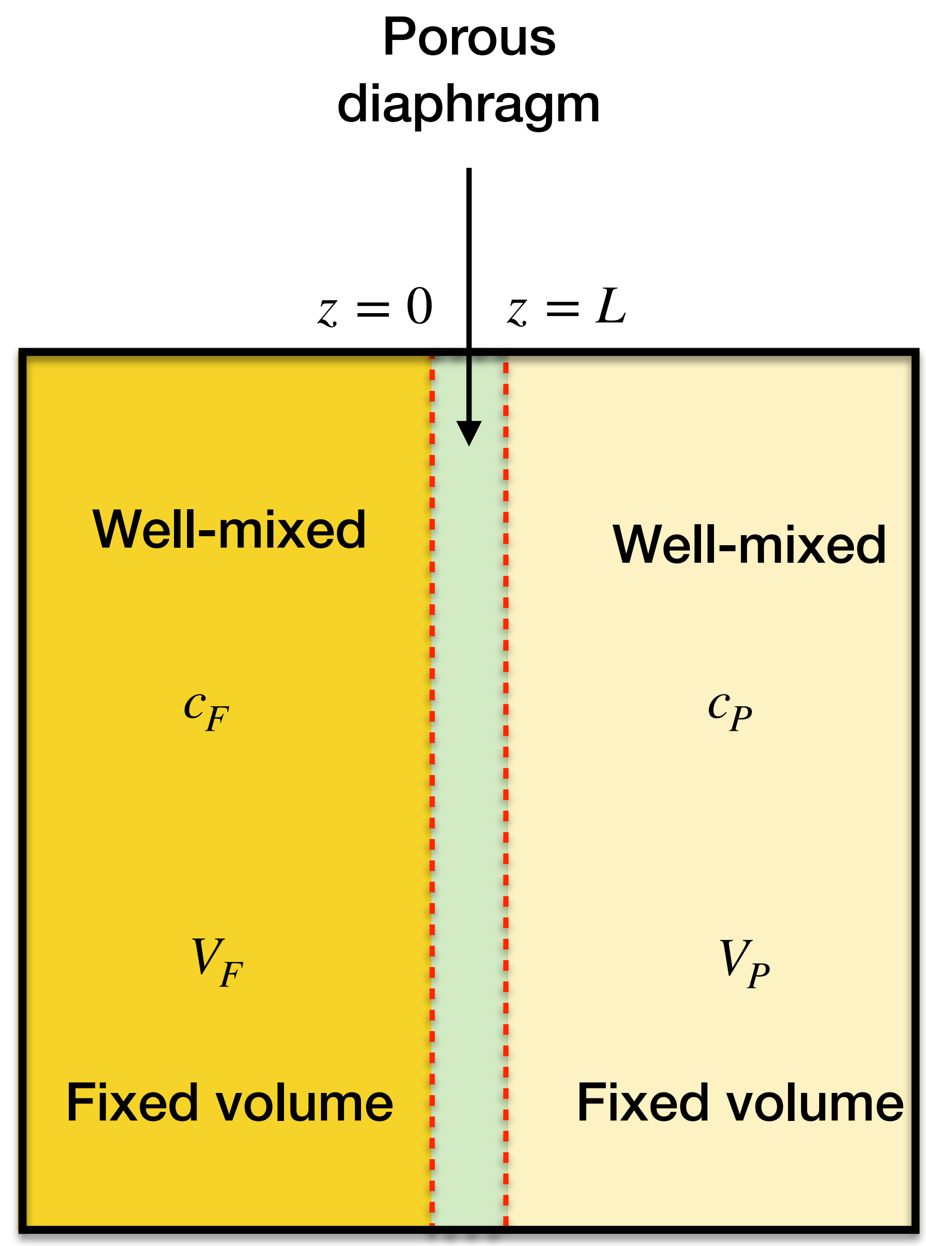
Measure the initial concentration in both sides.
Measure the final concentration in both sides.

$\text{Cross} - \text{sectional area} = \text{A}$



Diaphragm-cell with large well-mixed reservoirs (quasi steady-state)

$\text{Cross} - \text{sectional area} = \text{A}$



Define your system - Diaphragm and reservoirs

2 boundary and 2 initial conditions:

$$t = 0 \quad c = c_{F0} \text{ in left reservoir} \qquad t > 0 \quad c = c_F \; at \; z = 0$$
$$c = c_{P0} \text{ in right reservoir} \qquad c = c_P \; at \; z = L$$

Quasi steady-state assumption

- **Mass stored in reservoir is >> mass in diaphragm**
- **Change in concentration in reservoir is extremely slow**
- **Diaphragm is at quasi steady-state**

$$J_{z=0} = J_{z=L} = -D\frac{dc}{dz} = DH\frac{(c_F - c_P)}{L}$$

where c_F and c_P are functions of time

Diaphragm-cell with large well-mixed reservoirs (quasi steady-state)

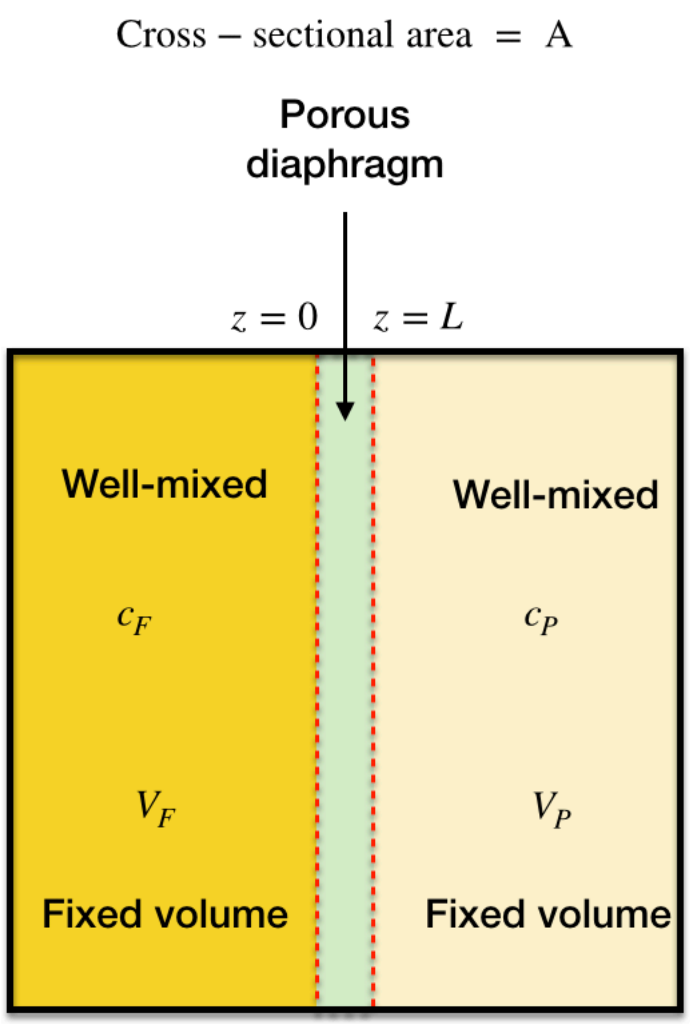
Reservoirs

$$\overset{o}{Accumulation} * dV = \overset{o}{Flux}\,|_{in} * dA - \overset{o}{Flux}\,|_{out} * dA + \overset{o}{Generation} * dV - \overset{o}{Consumption} * dV$$

Left reservoir

$$V_F \frac{dc_F}{dt} = 0 - AJ\,|_{z=0} + 0 - 0$$

$$V_F \frac{dc_F}{dt} = -AJ\,|_{z=0} \qquad = -AHD\frac{(c_F - c_P)}{L} \qquad \Rightarrow J_{z=0} = DH\frac{(c_F - c_P)}{L}$$



Right reservoir

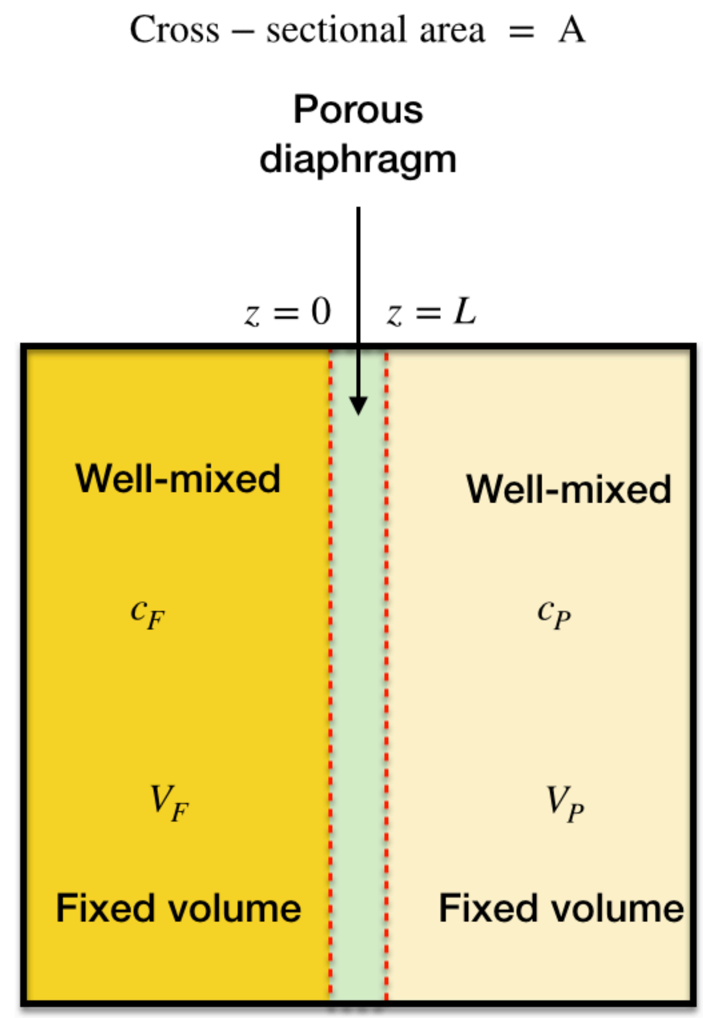
$$V_P \frac{dc_P}{dt} = AJ\,|_{z=L} - 0 + 0 - 0$$

$$V_P \frac{dc_P}{dt} = AJ\,|_{z=L} = AHD\frac{(c_F - c_P)}{L}$$

Case of a diaphragm-cell

$$V_F \frac{dc_F}{dt} = -AHD\frac{(c_F - c_P)}{L} \qquad V_P \frac{dc_P}{dt} = AHD\frac{(c_F - c_P)}{L}$$

$$\Rightarrow \frac{dc_F}{dt} = -\frac{AHD}{L}\frac{(c_F - c_P)}{V_F} \qquad \Rightarrow \frac{dc_P}{dt} = \frac{AHD}{L}\frac{(c_F - c_P)}{V_P}$$



Overall we have two coupled partial differential equations, 2 boundary and 2 initial conditions

The equations look similar. We can reduce them to a single partial differential equation by subtraction from each other.

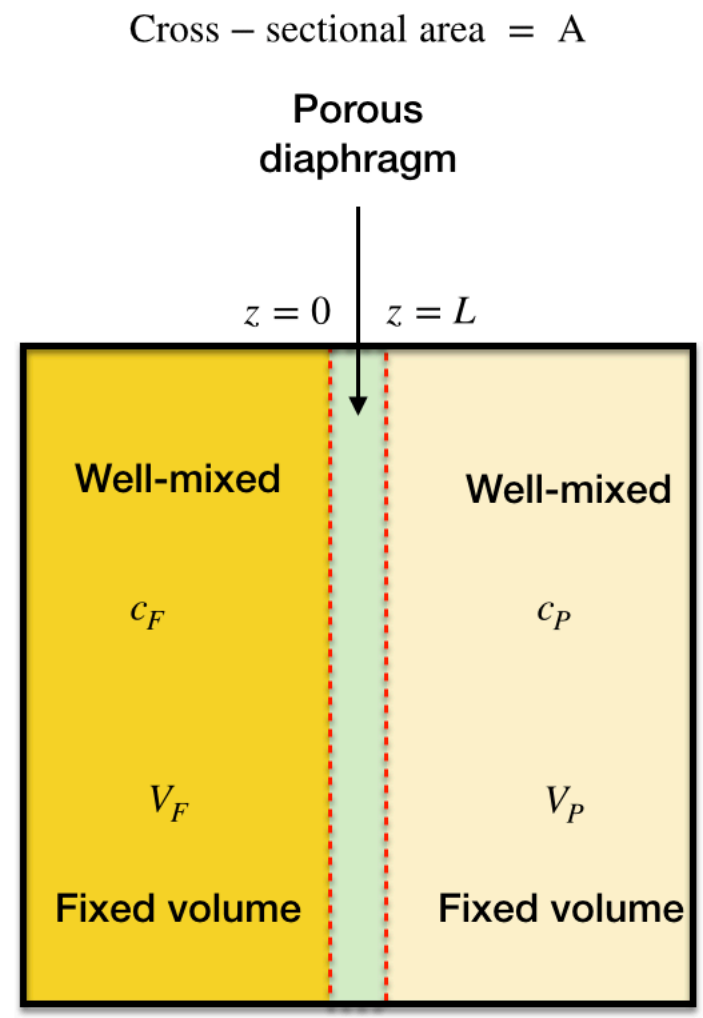
Subtracting right from left

$$\frac{d}{dt}(c_F - c_P) = -\frac{AH}{L}\left(\frac{1}{V_F} + \frac{1}{V_P}\right)D(c_F - c_P)$$

$$\frac{d}{dt}(c_F - c_P) = -\beta D(c_F - c_P) \qquad \beta = \frac{AH}{L}\left(\frac{1}{V_F} + \frac{1}{V_P}\right)$$

Case of a diaphragm-cell

$$\frac{d}{dt}(c_F - c_P) = -\beta D(c_F - c_P) \qquad \beta = \frac{AH}{L}\left(\frac{1}{V_F} + \frac{1}{V_P}\right)$$



Solution

$$\ln(c_F - c_P) = -\beta Dt \; + \; constant$$

Two initial conditions can be rearranged as one:

$t = 0 \quad c = c_{F0}$ in left reservoir

$\qquad\quad c = c_{P0}$ in right reservoir

$$(c_F - c_P)\,|_{t=0} = (c_{F0} - c_{P0})$$

After applying initial condition

$$\frac{c_F - c_P}{c_{F0} - c_{P0}} = \exp(-\beta Dt) \qquad D = \frac{1}{\beta t}\ln\left(\frac{c_{F0} - c_{P0}}{c_F - c_P}\right)$$

Diffusion for strong electrolytes

Table 6.1-1 *Diffusion coefficients of ions in water at 25 °C*

Cation	*D*	Anion	*D*
H^+	9.31	OH^-	5.28
Li^+	1.03	F^-	1.47
Na^+	1.33	Cl^-	2.03
K^+	1.96	Br^-	2.08
Rb^+	2.07	I^-	2.05
Cs^+	2.06	NO_3^-	1.90
Ag^+	1.65	CH_3COO^-	1.09
NH_4^+	1.96	$CH_3CH_2COO^-$	0.95
$N(C_4H_9)_4^+$	0.52	$B(C_6H_5)_4^-$	0.53
Ca^{2+}	0.79	SO_4^{2-}	1.06
Mg^{2+}	0.71	CO_3^{2-}	0.92
La^{3+}	0.62	$Fe(CN)_6^{3-}$	0.98

Note: Values at infinite dilution in 10^{-5} cm^2/sec. Calculated from data of Robinson and Stokes (1960).

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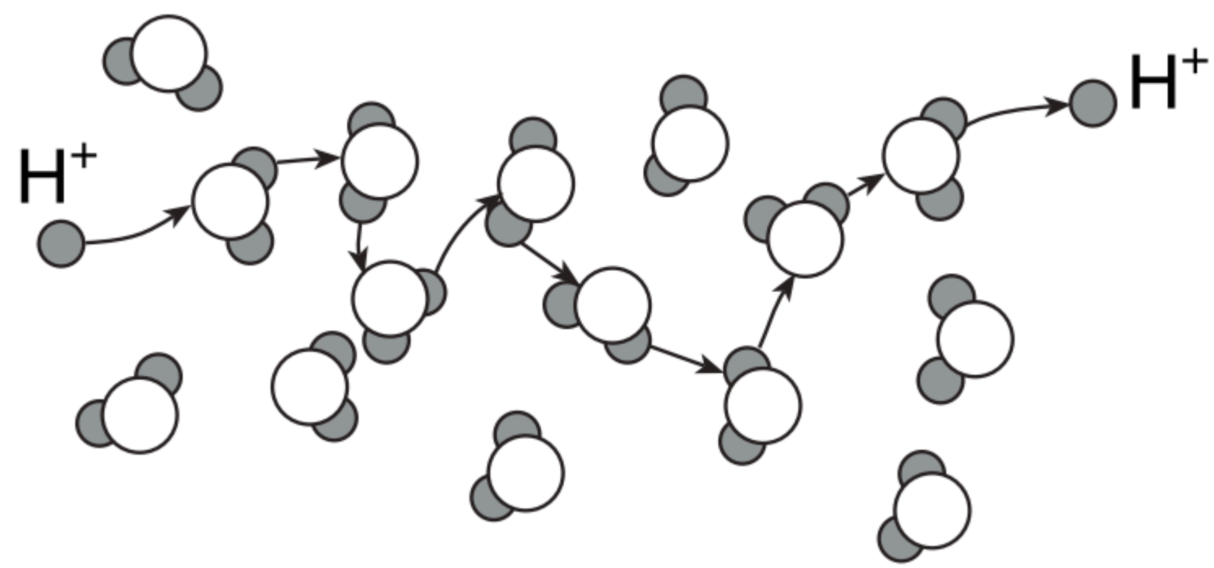
Special case for diffusion of protons

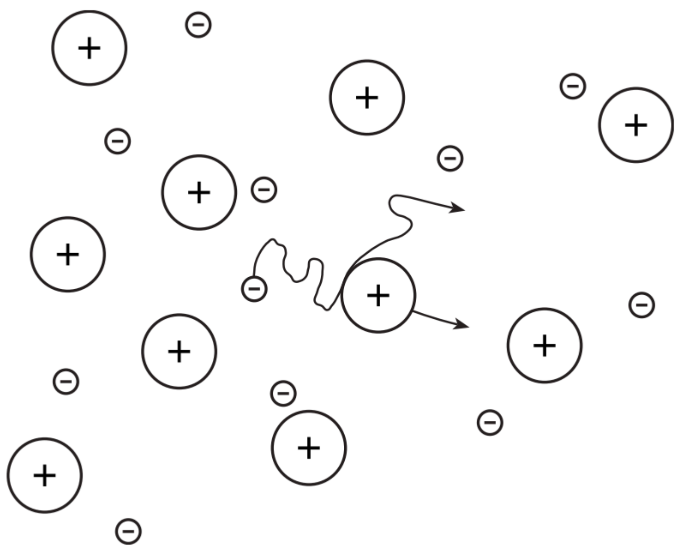


Grotthus mechanism

Coupled diffusion of ions in dilute solution

$$\begin{pmatrix}\text{ion}\\ \text{velocity}\end{pmatrix} = \begin{pmatrix}\text{ion}\\ \text{mobility}\end{pmatrix}\begin{pmatrix}\text{chemical} & + & \text{electrical}\\ \text{forces} & & \text{forces}\end{pmatrix}$$

$$v_i = -u_i(\nabla\mu_i + z_i F\nabla\psi)$$



$\mathrm{u_i}$ = representation of ion mobility $= \dfrac{1}{6\pi\eta \mathrm{r}} = \dfrac{1}{\mathrm{f}}$

$\mathrm{z_i}$ = charge on ion

F = Faraday constant = $\mathrm{eN_A}$

$\nabla\psi$ = electrostatic potential gradient

Coupled diffusion of ions in dilute solution

$$v_i = - u_i(\nabla \mu_i + z_i F \nabla \psi)$$

$$\Rightarrow v_i = - u_i\left(\frac{RT}{c_i} \nabla c_i + z_i F \nabla \psi\right)$$

$$\Rightarrow c_i v_i = - u_i RT\left(\nabla c_i + z_i c_i \frac{F \nabla \psi}{RT}\right)$$

$$\Rightarrow J_i = - u_i RT\left(\nabla c_i + z_i c_i \frac{F \nabla \psi}{RT}\right)$$

$$\boxed{\begin{aligned} \mu_i &= \mu_{i,0} + RT \ln \frac{P_i}{P} \\ \mu_i &= \mu_{i,0} + RT \ln \frac{c_i}{c} \\ \nabla \mu_i &= RT \nabla \ln c_i = \frac{RT}{c_i} \nabla c_i \end{aligned}}$$

$$N_i = c_i v_i$$

In the absence of convective flux (dilute solution)

$$J_i = N_i = c_i v_i$$

Coupled diffusion of ions in dilute solution

$$\Rightarrow\ J_i = -u_i RT\left(\nabla c_i + z_i c_i \frac{F\nabla\psi}{RT}\right)$$

$$\mathrm{u_i} = \text{ion mobility} = \frac{1}{6\pi\eta \mathrm{r}} = \frac{1}{\mathrm{f}}$$

$$\mathrm{u_i RT} = \frac{\mathrm{RT}}{6\pi\eta \mathrm{r}} = \frac{\mathrm{RT}}{\mathrm{f}} = \mathrm{D_i}$$

$$\Rightarrow\ J_i = -D_i\left(\nabla c_i + z_i c_i \frac{F\nabla\psi}{RT}\right)$$

Nernst-Plank Equation

Exercise problem 1

Helium/Argon mixture is diffusing through a 100 nm pore at 1 bar and 25 ºC. Report $D_{molecular}$, D_K and D_{vis} for helium at 1 bar and 10 bar. Calculate D_{total} at 1 and 10 bar pressures.

$D_{He,Ar} = 0.7\ cm^2 s^{-1}$ at 1 bar

$$D_K = \sqrt{\frac{8k_B T d^2}{9\pi m}}$$

$$D_{vis} = \frac{d^2}{32\eta_1} P_1$$

$$\eta_{He} = 2 * 10^{-5}\ \text{Pa s}$$

Exercise problem 2:
Capillary condensation

Water at 25 ºC and 1 bar has a vapor pressure of 23.8 torr. Calculate the equilibrium vapor pressure in a capillary with diameter of 2 nm.

$$\gamma_{lv} \;=\; \text{surface tension} \;=\; 0.072 \text{ N/m}$$

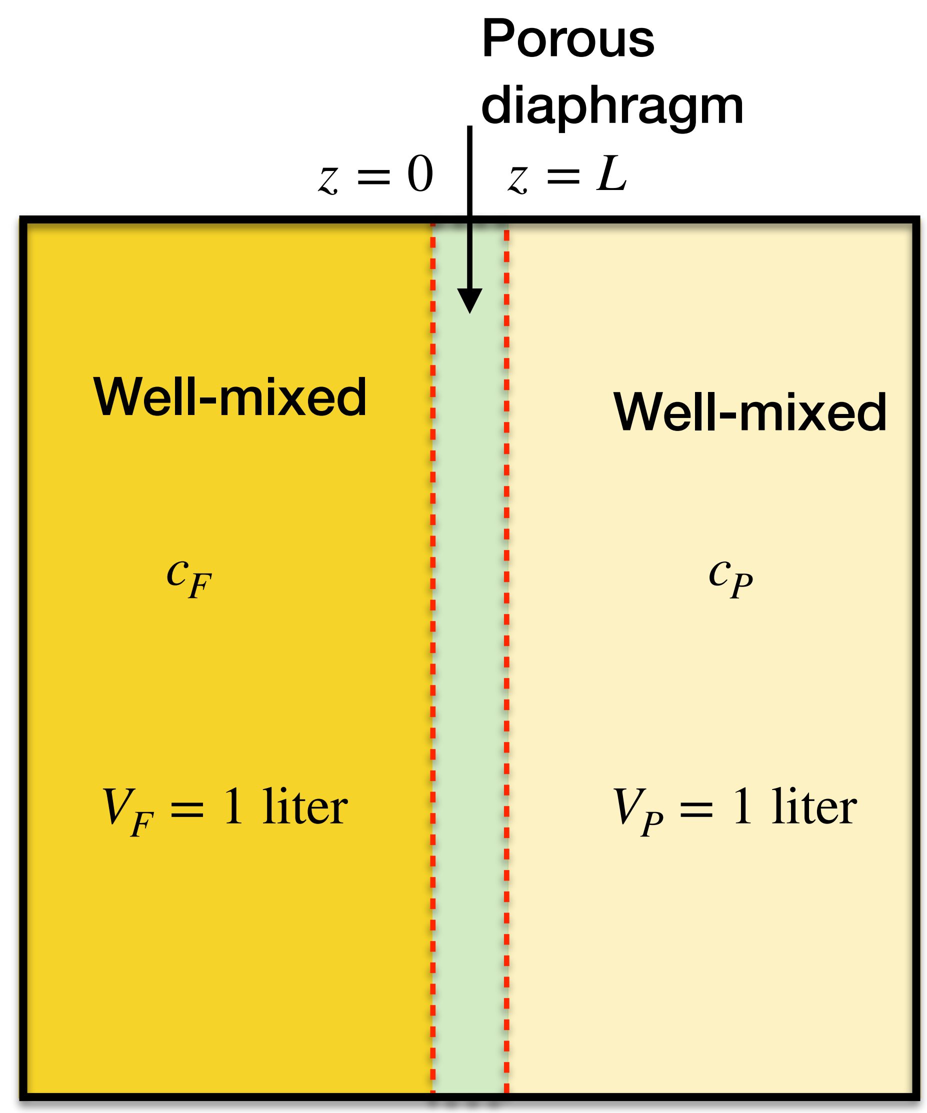
$$\theta \;=\; \text{contact angle} \;=\; 30 \text{ degree}$$

$$V_l \;=\; \text{molar volume} = 0.018/1000 \text{ m}^3\text{/mole}$$

Exercise problem 3

An electrochemical cell is composed of an ion-selective membrane which separates two well-mixed compartments filled with electrolytes. You are working as a process engineer, and need to screen a newly launch membrane. To do this you decide to place the membrane in cell such that:

$$t = 0,\ c_{F0} = 1\ \mathrm{M}$$
$$c_{P0} = 0\ \mathrm{M}$$



$$A = 1\ m^2 \qquad L = 100\ \mu m$$
$$H = 0.1\ \frac{M}{M}$$

Calculate the diffusion coefficient for a membrane if

$$@\, t = 1\ \mathrm{hr},\ (\mathrm{c_F} - \mathrm{c_P}) = 0.5\ \mathrm{M}$$

Compare above with the diffusion coefficient for another membrane when

$$t = 1\ \mathrm{hr},\ (\mathrm{c_F} - \mathrm{c_P}) = 0.25\ \mathrm{M}$$

$$D = \frac{1}{\beta t} \ln\left(\frac{c_{F0} - c_{P0}}{c_F - c_P}\right) \qquad \beta = \frac{AH}{L}\left(\frac{1}{V_F} + \frac{1}{V_P}\right)$$