# Membranes

Ch 17 "Diffusion Mass Transfer in Fluid Systems
2nd Edition, E.L. Cussler, U. Minn.

Membranes separate chemicals using 2 mechanisms

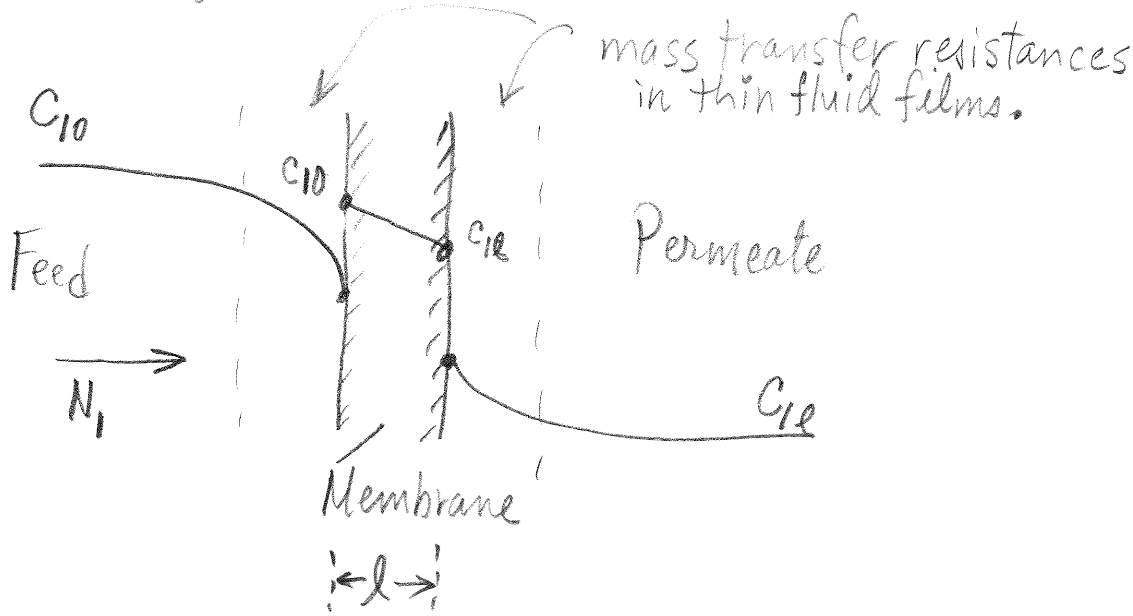
- filtration: where differences in molecular size is the determining factor

- diffusion: where differences in rates of diffusion through a solid membrane is the key factor. Solubility in the membrane is also important.

Main Applications:

- gas separations
- desalinization of sea water
- separations of azeotropic mixtures
- biomedical applications
  + artifical kidney
  + controlled release of drugs.

# Modeling of Diffusive Membrane Transport:




$C_{10}$ = concentration of Species "1" in the Feed bulk.

$c_{10}$ = (lower case 'c'): concentration of species "1" in the membrane on feed-side.

$C_{1\ell}$ = conc. of "1" in the Permeate fluid bulk.

$c_{1\ell}$ = (lower case "c"): conc. of "1" in the membrane on the Permeate-side.

Partitioning: the concentration of "1" in the membrane is related to the fluid concentrations by a <u>partition</u> <u>coefficient</u>, H!

$$\boxed{c_1 = H\, C_1}$$

At steady-state, the flux of "1" is equal in the films and in the membrane. The flux of "1" is equal to:

bulk fluid conc.

$$j_1 = \frac{C_{10} - C_{1\ell}}{\frac{1}{k_1} + \frac{\ell}{\mathcal{D}_{1m} H} + \frac{1}{k_2}}$$

Feed-side film resistance.

Membrane resistance.

Permeate-side film resistance.

For relatively "thick" membranes (10-100 μm), the membrane resistance dominates. The flux is,

$$\boxed{j_1 = \frac{\mathcal{D}_{1m} H}{\ell} (C_{10} - C_{1\ell})}$$

$j_1$ is proportional to $\mathcal{D}_{1m}$, $H$, $1/\ell$

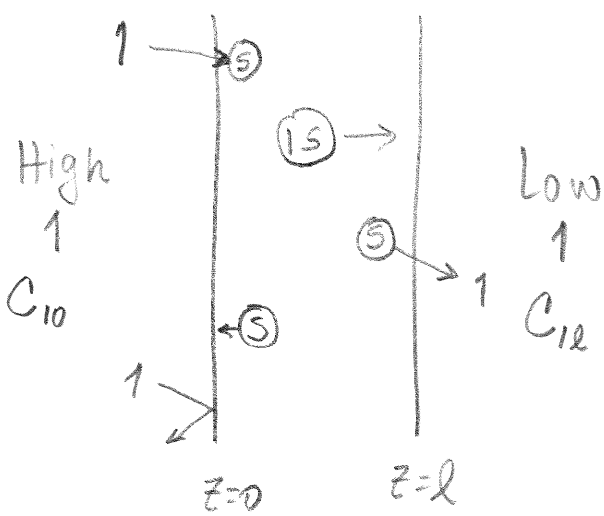
diffusivity in membrane (not very selective)

Solubility in membrane (very selective)

membrane thickness (governs rates of diffusion).

# Facilitated Diffusion Across Membranes:

Some membrane can be fabricated to contain "mobile carriers" that facilitate (greatly accelerate) the rate of diffusion. The solute of interest "reacts" with high selectivity (to the exclusion of other solutes) with the mobile carrier.




1. Solute 1 "reacts" with carrier, forming a "complex". 1S
2. Complex diffuses across membrane
3. Complex releases 1
4. carrier diffuses across membrane to High 1 side.
5. Uncomplexed solute diffuses at a slow rate due to low solubility.

Mon 4/17/06

Experimental Observations:

1. Solute flux is much larger + selective than expected based on normal membrane mechanisms (solubility-diffusion).
2. Flux of solute increases as concentration difference increases, up to a point, and then is constant as solute conc. increases. (insufficient carriers available!)

3. Fluxes can be strongly coupled when 2 or more solutes react competitively (or cooperatively) with carriers.

Biological systems (cells) utilize facilitated diffusion. Proteins often act as the "carrier"!

Equations for Facilitated Diffusion.

We assume that solute and carrier are constantly reacting within the membrane:

$$(\text{solute}, 1) + (\text{carrier}, s) \rightleftharpoons (\text{complex}, 1s)$$

At steady-state, the diffusion equations for each species in the membrane is:

solute 1: $$0 = \mathcal{D} \frac{d^2 c_1}{dz^2} - r_{1s} \quad (1)$$

carriers: $$0 = \mathcal{D} \frac{d^2 c_s}{dz^2} - r_{1s} \quad (2)$$

complex 1s: $$0 = \mathcal{D} \frac{d^2 c_{1s}}{dz^2} + r_{1s} \quad (3)$$

note: dilute assumption for 1, s, and 1s

where $r_{1s}$ is the rate of formation of complex within the membrane. For simplicity, $\mathcal{D}$ is assumed to be the same for 1, s, and 1s !

BC1 $\quad z=0 \quad c_1 = H\,C_{10}$

BC2 $\quad z=\ell \quad c_1 = H\,C_{1\ell}$

also $\quad \dfrac{1}{\ell}\displaystyle\int_0^\ell (c_s + c_{1s})\,dz = \bar{c}$ ⟨ average carrier concentration in the membrane

We require 3 more BCs or constraints to solve this system of equations!

<u>Fast Reaction Case:</u> reaction rate >> diffusion rate.

In this case, an equilibrium is established everywhere in the membrane,

$$c_{1s} = K\,c_1 c_s$$

where K is a reaction equilibrium constant.
(association)

Also,

BC3 $\quad z=0 \quad , \; J_s^* + J_{1s}^* = 0$ or $-\mathcal{D}\left(\dfrac{dc_s}{dz} + \dfrac{dc_{1s}}{dz}\right) = 0$

BC4 $\quad z=\ell \quad$ " $\quad$ "

We can learn about the behavior of the carrier / complex in the membrane by adding eqns ② and ③,

$$
\begin{array}{rl}
 & 0 = \mathcal{D}\dfrac{d^2 c_s}{dz^2} - r_{1s} \\
+ & 0 = \mathcal{D}\dfrac{d^2 c_{1s}}{dz^2} + r_{1s} \\
\hline
 & 0 = \mathcal{D}\left(\dfrac{d^2 c_s}{dz^2} + \dfrac{d^2 c_{1s}}{dz^2}\right)
\end{array}
$$

integrate once $\quad \dfrac{dc_s}{dz} + \dfrac{dc_{1s}}{dz} = A_1$ (a constant)

but using BC3 we see that $\boxed{A_1 = 0}$

Integrating again,

$$c_s + c_{1s} = A_2 \text{ (another constant).}$$

Now using the condition $\frac{1}{l}\int_0^l (c_s + c_{1s})\, dz = \bar{c}$

We find that $A_2 = \bar{c}$

Therefore $\boxed{c_s + c_{1s} = \bar{c}}$ everywhere in the membrane!

Next, we can examine the total flux of Solute, $J_1^* + J_{1S}^*$!

Add Eqns 1 + 3

$$0 = \mathcal{D} \frac{d^2 c_1}{dz^2} - r_{1S}$$

$$+ \quad 0 = \mathcal{D} \frac{d^2 c_{1S}}{dz^2} + r_{1S}$$

$$0 = \mathcal{D} \left( \frac{d^2 c_1}{dz^2} + \frac{d^2 c_{1S}}{dz^2} \right) \qquad (4)$$

We need to relate $c_{1S}$ to $c_1$ and other constant properties in the membrane.

$$\left. \begin{array}{l} c_{1S} = K c_1 c_S \\ c_S + c_{1S} = \bar{c} \end{array} \right\} \text{ everywhere in the membrane!}$$

$$c_S = \bar{c} - c_{1S}.$$

$$c_{1S} = K c_1 c_S$$

$$c_{1S} = K c_1 (\bar{c} - c_{1S}) \quad \text{or}$$

$$c_{1S} (1 + K c_1) = K c_1 \bar{c} \quad \text{or}$$

$$c_{1S} = \frac{K c_1 \bar{c}}{(1 + K c_1)}$$

Eqn. 4 becomes.

$$0 = \mathcal{D}\left(\frac{d^2 c_1}{dz^2} + \frac{d^2}{dz^2}\left(\frac{Kc_1\bar{c}}{(1+Kc_1)}\right)\right)$$

This equation can be restated as.

$$0 = \frac{d}{dz}\left[\mathcal{D}\left(\frac{dc_1}{dz} + \frac{d}{dz}\left(\frac{Kc_1\bar{c}}{1+Kc_1}\right)\right]\right. \quad (5)$$

If $d/dz$ of the [ ] term is 0, then the [ ] term is constant in the membrane. The [ ] term is just $-(J_1^* + J_{1s}^*)$, the total flux of Solute 1!

(5) is integrated Once to give,

$$-(J_1^* + J_{1s}^*) = \mathcal{D}\left[\frac{dc_1}{dz} + \frac{d}{dz}\left(\frac{Kc_1\bar{c}}{1+Kc_1}\right)\right]$$

Separating variables and integrating

$$-\int_0^l (J_1^* + J_{1s}^*)\, dz = \mathcal{D}\int_{c_1 = Hc_{10}}^{c_1 = Hc_{1l}} \left(dc_1 + d\left(\frac{Kc_1\bar{c}}{1+Kc_1}\right)\right)$$

$$-(J_1^* + J_{1s}^*)\,\ell = \mathcal{D}\left[ (HC_{1\ell} - HC_{10}) + \frac{\bar{c}KHC_{1\ell}}{1+KHC_{1\ell}} - \frac{\bar{c}KHC_{10}}{1+KHC_{10}} \right]$$

$$= \mathcal{D}H(C_{1\ell} - C_{10}) +$$

$$\mathcal{D}H\left(\frac{\bar{c}(1+KHC_{10})KC_{1\ell} - \bar{c}(1+KHC_{1\ell})KC_{10}}{(1+KHC_{1\ell})(1+KHC_{10})}\right)$$

This simplifies to:

flux due to uncomplexed solute

$$\boxed{J_1^* + J_{1s}^* = \frac{\mathcal{D}H}{\ell}(C_{10} - C_{1\ell}) + \frac{\mathcal{D}H}{\ell}\left[\frac{K\bar{c}}{(1+HKC_{10})(1+HKC_{1\ell})}\right](C_{10} - C_{1\ell})}$$

flux due to complexed solute
(most important)

Limiting Cases:

- dilute solute, $C_{10}, C_{1\ell}$ v. small.

$$\boxed{J_1^* + J_{1s}^* = \frac{DHK\bar{c}}{\ell}(C_{10} - C_{1\ell})}$$

facilitation factor

• Large $C_{10} \to C_{12} = 0$

$$\boxed{J_1^* + J_{1s}^* = \frac{\mathcal{D}\bar{c}}{l}}$$

achieves a constant flux - as observed

Wed 4/19/06