Chemistry 24b
Spring Quarter 2004
Instructor: Richard Roberts

Lecture 3&4
Date: April 2 & 5

Passive Transport Across Membranes

Neutral Solutes

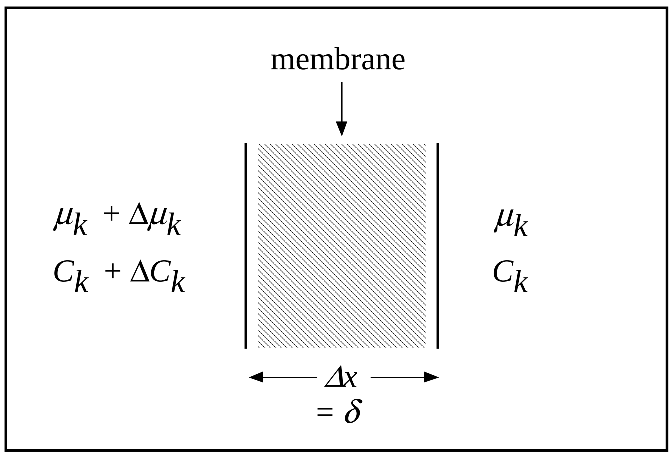

Figure 2-1

General Equation

$$J_k = -\lambda_k C_k \left(\frac{1}{N_A}\right)\frac{d\mu_k}{dx} \quad \text{moles / cm}^2\text{ / sec}$$

where $\lambda \equiv$ mobility

Take an imaginary boundary inside a membrane.

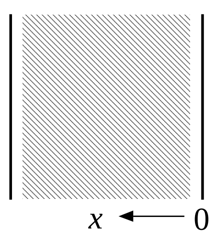

Figure 2-2

We may write:

$$J_k^m(x) = -\lambda_k^m C_k^m(x) \frac{1}{N_A} \frac{d\mu_k^m(x)}{dx} \equiv \text{ flux of species } k \text{ at point } x \text{ in the membrane}$$

$$= -\lambda_k^m C_k^m(x) \frac{1}{N_A} RT \frac{1}{C_k^m} \frac{dC_k^m(x)}{dx}$$

$$= -\lambda_k^m k_B T \frac{dC_k^m(x)}{dx}$$

Invoke the steady state approximation and assume that there is no accumulation of solute at each boundary. Then $J_k^m(x)$ = constant for every point x in the membrane, and if λ_k^m is independent of x, $\frac{dC_k^m(x)}{dx}$ must be constant across the membrane as well for each species.

We shall of course assume that the concentrations all remained outside the membrane so that

$$C_k(x=0) \quad \text{and} \quad C_k(x+\Delta x) \quad \text{are} \quad C_k \quad \text{and} \quad C_k + \Delta C_k$$

on the right and left boundaries, respectively.

Define the partition coefficient such that

$$C_k^m = k_k^p C_k$$

where $k_k^p \equiv$ partition coefficient for kth species

$\equiv$ equilibrium distribution coefficient

Then at the two membrane boundaries

$$C_k^m(x=0) = k_k^p C_k(x=0)$$

$$C_k^m(x+\Delta x) = k_k^p C_k(x+\Delta x) = k_k^p C_k(x=0) + k_k^p \Delta C_k$$

Substituting into the flux equation:

$$
\begin{aligned}
J_k^m(x) &= -\lambda_k^m k_B T \frac{dC_k^m(x)}{dx} \\
&= -\lambda_k^m k_B T \frac{\Delta C_k^m}{\Delta x} \\
&= -\lambda_k^m k_B T \frac{C_k^m(x=\Delta x) - C_k^m(x=0)}{\Delta x} \\
&= -\lambda_k^m k_B T \;\; k_k^p \frac{\Delta C_k}{\Delta x} \\
&= -\lambda_k^m k_B T \;\; k_k^p \frac{1}{\delta} \Delta C_k \\
&= -p_k^m \Delta C_k
\end{aligned}
$$

where $p_k^m \equiv$ permeability coefficient of species k

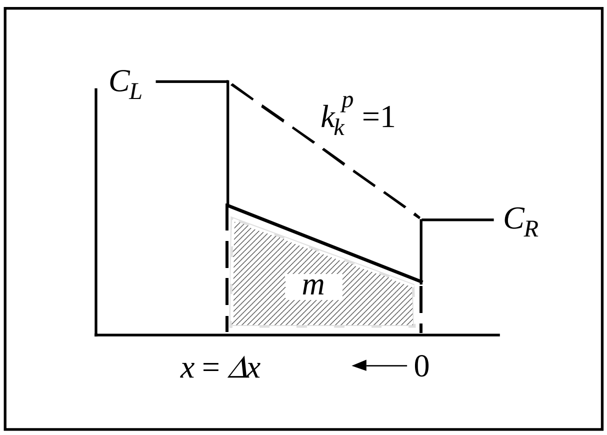

Figure 2-3

Water Transport Across Membranes

(This has been an active field in biophysics for many years!)

You have to worry about a difference in the hydrostatic pressure across the membrane, in addition to the activity difference, i.e.,

$$\frac{\Delta P}{\Delta x} \text{ in addition to } \frac{\Delta \ln x_s}{\Delta x}$$

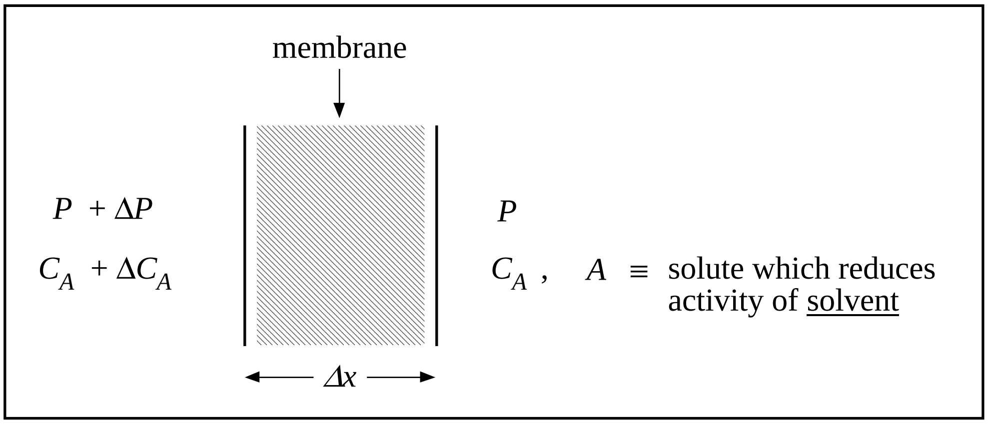

Figure 2-4

Start with the Magic Formula

$$J_s^m = \text{ water flux across the membrane}$$

$$= -\lambda_s^m C_s^m \frac{1}{N_A} \frac{d\mu_s^m}{dx}$$

As before, assume the driving force is constant across each imaginary boundary within the membrane.

Then

$$J_s^m = -\lambda_s^m C_s^m \frac{1}{N_A} \frac{\mu_s^m(x=\Delta x) - \mu_s^m(x=0)}{\delta}$$

Now

$$\mu_s^m(x=0) = \mu_s(x=0) = \mu_s^0(P) + RT \ln x_s \quad \text{and}$$

$$\mu_s^m(x=\Delta x) = \mu_s(x=\Delta x) = \mu_s^0(P+\Delta P) + RT \ln x_s'$$

Therefore

$$\mu_s^m(x=\Delta x)-\mu_s^m(x=0) = \mu_s^0(P+\Delta P)-\mu_s^0(P)+RT\ln x_s'-RT\ln x_s$$
$$= \left(\frac{\partial \mu_s^0}{\partial P}\right)\Delta P + RT\,\Delta \ln x_s$$
$$= \overline{V}_s^*\Delta P - RT\overline{V}_s^*\Delta C_A\,, \quad \overline{V}_s^* = \text{ average molar volume of solvent}$$

Therefore

$$J_s^m = -\lambda_s^m C_s^m \frac{1}{N_A}\frac{1}{\delta}\left(\overline{V}_s^*\Delta P - RT\overline{V}_s^*\Delta C_A\right)$$
$$\cong -\lambda_s^m k_s^p \overline{C}_s \frac{1}{N_A\delta}\,\overline{V}_s^*\left(\Delta P - RT\,\Delta C_A\right)$$
$$\cong -\lambda_s^m k_s^p \frac{1}{N_A\delta}\left(\Delta P - RT\,\Delta C_A\right) \qquad \text{as} \quad \overline{C}\,\overline{V}_s^* \cong 1 \quad \text{for dilute solutions}$$

Note at equilibrium $J_s^m = 0$ so that $\Delta P = RT\,\Delta C_A = \pi$ as expected.

Electrodiffusion (Diffusion of Ions Across Membranes)

$$J_k^m(x) = -\lambda_k^m C_k^m(x)\frac{1}{N_A}\frac{d\overline{\mu}_k^m(x)}{dx}$$

where $\overline{\mu}_k^m(x) = \overline{\mu}_k^{0\,m} + RT\ln C_k^m(x) + z_k F\Phi^m(x)$

Now

$$\frac{d\overline{\mu}_k(x)}{dx} = \frac{RT}{C_k^m}\frac{dC_k^m}{dx} + z_k F\frac{d\Phi^m(x)}{dx}$$

Assume a steady state with:

(1) linear concentration gradient

(2) constant potential gradient

over the region of the membrane (Δx).

Then

$$\frac{dC_k^m(x)}{dx} = k_k^p \frac{dC_k}{dx} = k_k^p \frac{\Delta C_k}{\Delta x} \quad \text{and}$$

$$\frac{d\Phi^m(x)}{dx} = \frac{\Delta\Phi}{\Delta x}$$

so that

$$J_k^m(x) = -\lambda_k^m C_k^m \left(\frac{k_B T}{C_k^m} k_k^p \frac{\Delta C_k}{\Delta x} + \frac{z_k F}{N_A} \frac{\Delta\Phi}{\Delta x} \right)$$

$$= -\frac{\lambda_k^m k_k^p k_B T}{\delta} \left(\Delta C_k + \frac{z_k F}{RT} \overline{C}_k \Delta\Phi \right)$$

where $\quad \dfrac{\lambda_k^m k_k^p k_B T}{\delta} = P_k^m \quad$ and $\quad \overline{C}_k =$ center of membrane

for each ionic species.

Consider Two Types of Membranes

(1) If a membrane is permeable to only one ionic species, say *k*, then without any external electrical connection, no electric current can flow (hence no flux in this case). Thus, $J_k = 0$ and we can solve for $\Delta\Phi$.

$$\Delta\Phi = \frac{-RT}{z_k F}\left[\frac{\Delta C_k}{\overline{C}_k}\right] \quad \text{or more exactly}$$

$$\frac{-RT}{z_k F} \ln \frac{C_L}{C_R} = \Phi_L - \Phi_R \quad \text{(Gibbs - Donnan potential)}$$

(2) If, on the other hand, a membrane is permeable to a variety of ions present, each with its own permeability coefficient, then the condition of no <u>net</u> electric current flow gives the following

$$\sum_{k=1}^{n} z_k J_k^m = 0 \ , \quad \text{for all ions}$$

In this case, ionic fluxes are possible,

$$\text{or} \quad -\sum_{k=1}^{n} z_k P_k^m \Delta C_k - \frac{F}{RT}\sum_{k=1}^{n} z_k^2 P_k^m \overline{C}_k \Delta\Phi = 0$$

$$\text{or} \quad \Delta\Phi = -\frac{RT}{F}\,\frac{\sum_{k=1}^{n} z_k P_k^m \Delta C_k}{\sum_{k=1}^{n} z_k^2 P_k^m \overline{C}_k} \qquad \text{(steady state potential)}$$

This is the approximate Goldman equation.

Biological Membranes

For biological membranes, the ionic permeability of many ions is small, so a few ions dominate. Therefore, you need to sum over the principal ions whose permeabilities and conductances across the membrane are significant .

Resting Nerve

Only the permeability of K^+ is significant, so $\Delta\Phi \approx$ Gibbs-Donnan potential applied to K^+.

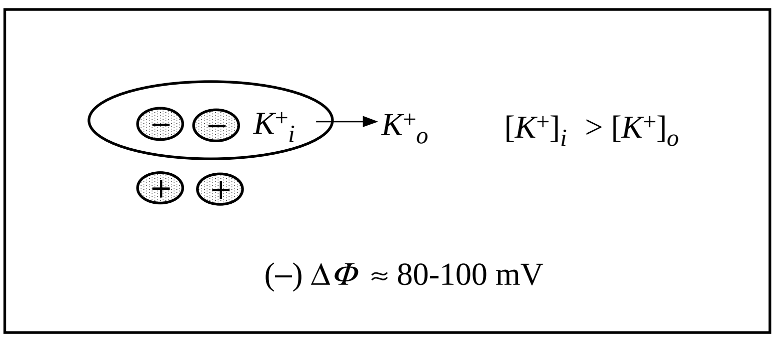

Figure 2-5

Excited Nerve

The permeabilities of K^+ and Na^+ are significant. During impulse transmission, changes occur in the membrane so that the conductances of both K^+ and Na^+ are important. A transient point is reached where the Na^+ permeability coefficient or conductance is much greater than that for K^+.