Passive Transport Across Membranes

Neutral Solutes

\[ J_k = -\lambda_k C_k \left( \frac{1}{N_A} \right) \frac{d\mu_k}{dx} \] moles / cm² / sec

where \( \lambda \equiv \text{mobility} \)

Take an imaginary boundary inside a membrane.
We may write:

\[ J^m_k(x) = -\lambda^m_k C^m_k(x) \frac{1}{N_A} \frac{d\mu^m_k(x)}{dx} = \text{flux of species } k \text{ at point } x \text{ in the membrane} \]

\[ = -\lambda^m_k C^m_k(x) \frac{1}{N_A} RT \frac{1}{C^m_k(x)} \frac{dC^m_k(x)}{dx} \]

\[ = -\lambda^m_k k_B T \frac{dC^m_k(x)}{dx} \]

Invoke the steady state approximation and assume that there is no accumulation of solute at each boundary. Then \( J^m_k(x) \) = constant for every point \( x \) in the membrane, and if \( \lambda^m_k \) is independent of \( x \), \( \frac{dC^m_k(x)}{dx} \) 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

\[ C_k(x = 0) \text{ and } C_k(x + \Delta x) \text{ are } C_k \text{ and } C_k + \Delta C_k \]

on the right and left boundaries, respectively.

Define the partition coefficient such that

\[ C^m_k = k^p_k C_k \]

where \( k^p_k \equiv \text{partition coefficient for } k\text{th species} \]

\[ \equiv \text{equilibrium distribution coefficient} \]

Then at the two membrane boundaries

\[ C^m_k(x = 0) = k^p_k C_k(x = 0) \]

\[ C^m_k(x + \Delta x) = k^p_k C_k(x + \Delta x) = k^p_k C_k(x = 0) + k^p_k \Delta C_k \]
Substituting into the flux equation:

\[ J_k^m (x) = -\lambda_k^m k_BT \frac{dC_k^m (x)}{dx} \]

\[ = -\lambda_k^m k_BT \frac{\Delta C_k^m}{\Delta x} \]

\[ = -\lambda_k^m k_BT C_k^m (x = \Delta x) - C_k^m (x = 0) \]

\[ = -\lambda_k^m k_BT k_k^p \frac{\Delta C_k}{\Delta x} \]

\[ = -\lambda_k^m k_BT k_k^p \frac{1}{\delta} \Delta C_k \]

\[ = -p_k^m \Delta C_k \]

where \( p_k^m \) = 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.,

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

![Diagram of water transport across a membrane](image)

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

\[ \mu_s^m(x = 0) = \mu_s(x = 0) = \mu_s^0(P) + RT \ln x_s \]

and

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

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

Therefore

\[
J_s^m = -\lambda_s^m C_s \frac{1}{N_A} \left( \bar{V}_s^* \Delta P - RT \bar{V}_s^* \Delta C_A \right) \\
\equiv -\lambda_s^m k_p C_s \frac{1}{N_A \delta} \bar{V}_s^* \left( \Delta P - RT \Delta C_A \right) \\
\equiv -\lambda_s^m k_p \frac{1}{N_A \delta} \left( \Delta P - RT \Delta C_A \right) \quad \text{as } \bar{C} \bar{V}_s^* \equiv 1 \text{ for dilute solutions}
\]

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

**Electrodiffusion (Diffusion of Ions Across Membranes)**

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

where \( \bar{\mu}_k^m(x) = \bar{\mu}_k^0 + RT \ln C_k^m(x) + z_k F \Phi_k^m(x) \)

Now

\[
\frac{d\bar{\mu}_k^m(x)}{dx} = \frac{RT}{C_k^m} \frac{dC_k^m}{dx} + z_k F \frac{d\Phi_k^m(x)}{dx}
\]

Assume a steady state with:

1. linear concentration gradient
2. constant potential gradient

over the region of the membrane (\( \Delta x \)).
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
\[ J_k^m(x) = -\lambda_k^m C_k^m \left( \frac{k_BT}{C_k} k_k^p \frac{\Delta C_k}{\Delta x} + \frac{z_k F}{N_A} \frac{\Delta \Phi}{\Delta x} \right) \]
\[ = -\frac{\lambda_k^m k_k^p k_BT}{\delta} \left( \Delta C_k + \frac{z_k F}{RT} \frac{\Delta \Phi}{C_k} \right) \]
where \( \frac{\lambda_k^m k_k^p k_BT}{\delta} = P_k^m \) and \( C_k = \text{center of membrane} \)

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 \( \Delta \Phi \).

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

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 net 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,
or \[- \sum_{k=1}^{n} z_k P_k^m \Delta C_k - \frac{F}{RT} \sum_{k=1}^{n} z_k^2 P_k^m \bar{C}_k \Delta \Phi = 0\]

or \[\Delta \Phi = - \frac{RT}{F} \frac{\sum_{k=1}^{n} z_k P_k^m \Delta C_k}{\sum_{k=1}^{n} z_k^2 P_k^m \bar{C}_k}\] (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 $K^+$.

\[\text{Figure 2-5}\]

**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 $K^+$.