**Equilibrium Dialysis**

But this time start with NaCl on both sides at equilibrium. Then add a positively charged protein (no direct binding - only distant charge effects).

Let's do the math

**Initial**

\[
\begin{array}{cc}
100 \text{Na}^+ & 100 \text{Cl}^- \\
100 \text{Na}^+ & 100 \text{Cl}^- \\
\end{array}
\]

\[
\begin{array}{cc}
95 \text{Na}^+ & 105 \text{Cl}^- \\
45 \text{Cl}^- & 115 \text{Cl}^- \\
\end{array}
\]

Examine the NaCl on both sides. Have to move together → WHY?

EQUILIB \quad \text{NOT EQUILIB}

Require \( \mu_{\text{NaCl}} \) (inside) = \( \mu_{\text{NaCl}} \) (outside)

\[
\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^0 + RT \ln C_{\text{Na}^+} C_{\text{Cl}^-}
\]

\[
\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^0 + RT \ln C_{\text{Na}^+} C_{\text{Cl}^-} = \mu_{\text{NaCl}}^0 + RT \ln C_{\text{Na}^+} C_{\text{Cl}^-} \cdot \mu_{\text{NaCl}}
\]

\[
\ln C_{\text{Na}^+} C_{\text{Cl}^-} = \ln C_{\text{Na}^+} C_{\text{Cl}^-}
\]

\[
C_{\text{Na}^+} C_{\text{Cl}^-} = C_{\text{Na}^+} C_{\text{Cl}^-}
\]

Exam next Thursday
October 28, 7:00p-9:00p
LGRT 103

Review in-class
Wed October 27
(I will not be available Thurs!)
**CHARGE NEUTRALITY**

**OUTSIDE**
\[ C_{Na^+}^{\text{out}} = C_{Cl^-}^{\text{out}} \Rightarrow C \]

**INSIDE**
\[ Z_m C_m + C_{Na^+}^{\text{in}} = C_{Cl^-}^{\text{in}} \]

\[
\begin{align*}
C_{Na^+}^{\text{in}} & = C_{Na^+}^{\text{out}} C_{Cl^-}^{\text{out}} \\
& = \frac{C_{Na^+}^{\text{out}} C_{Cl^-}^{\text{out}}}{C_{Na^+}^{\text{in}}} = \frac{C^2}{C_{Na^+}^{\text{in}}} \\
& = \frac{C^2}{Z_m C_m + C_{Na^+}^{\text{in}}} \\
& \quad \text{(let } x = C_{Na^+}^{\text{in}} \text{ inside)} \\
\Rightarrow \quad \frac{C^2}{x} & = Z_m C_m + x \\
\Rightarrow \quad x^2 + Z_m C_m x - C^2 & = 0 \\
\Rightarrow \quad x & = -\frac{Z_m C_m}{2} + \frac{\sqrt{(Z_m C_m)^2 - 4C^2}}{2} = C_{Na^+}^{\text{out}} \\
\frac{C_{Na^+}^{\text{in}}}{C_{Na^+}^{\text{out}}} & = \frac{x}{C} = -\frac{Z_m C_m}{2C} + \frac{\sqrt{(\frac{Z_m C_m}{2C})^2 + 1}}{C_{Na^+}^{\text{out}}} \leq 1.0
\end{align*}
\]

So, \( \frac{C_{Na^+}^{\text{in}}}{C_{Na^+}^{\text{out}}} < 1.0 \) for example given
So \[ C_{\text{Na}^+}^{\text{IN}} = C_{\text{Na}^+}^{\text{OUT}} \]

and \[ C_{\text{Cl}^-}^{\text{IN}} = C_{\text{Cl}^-}^{\text{OUT}} \]

Why? They're supposed to reach equilibrium!

Yes, but real requirement is that at equilibrium,
\[ \mu_{\text{NaCl}} \text{ (outside)} = \mu_{\text{NaCl}} \text{ (inside)} \]

We can say that with respect to \( \mu_{\text{Na}^+} \) and \( \Delta G_{\text{Na}^+} \),
there is an extra (electrical) component to \( \Delta G \).

Let's call it \( \Rightarrow ZFV \)

Now \[ \Delta G = \frac{a_{\text{Na}^+}^{\text{IN}}}{a_{\text{Na}^+}^{\text{OUT}}} + ZFV = 0 \]

\[ \Delta G = RT \ln \frac{a_{\text{Na}^+}^{\text{IN}}}{a_{\text{Na}^+}^{\text{OUT}}} + ZFV = 0 \]

\[ V = -\frac{RT}{ZF} \ln \frac{a_{\text{Na}^+}^{\text{IN}}}{a_{\text{Na}^+}^{\text{OUT}}} \approx -\frac{RT}{ZF} \frac{C_{\text{Na}^+}^{\text{IN}}}{C_{\text{Na}^+}^{\text{OUT}}} \]

\[ C_{\text{Na}^+}^{\text{OUT}} > C_{\text{Na}^+}^{\text{IN}} \quad C_{\text{Cl}^-}^{\text{OUT}} < C_{\text{Cl}^-}^{\text{IN}} \]
Surfaces, Membranes

A surface is 2-dimensional (unlike a solution, which is 3D)

Conc is \( \text{mol/cm}^2 \) instead of \( \text{mol/cm}^3 \)

\( \frac{F}{\text{length}} \) instead of \( \frac{F}{\text{area}} \) \( \Rightarrow \) \( \frac{J}{\text{m}^2} \) instead of \( \frac{J}{\text{m}^3} \)

Surface free energy is \( \frac{J}{\text{m}^2} \) instead of \( \frac{J}{\text{m}^3} \)

Increased surface tension is equivalent to increasing the energetic price to create a surface.

So liquids with very high surface tension form drops readily (a sphere has the lowest surface volume) despite the fact that gravity disfavors drops.

E.g. Mercury 487 mN m\(^{-1}\) little balls everywhere
Water 72 mN m\(^{-1}\)
Acetone 24 mN m\(^{-1}\) ever seen acetone bead up? - No.
Ethanol too
Molecular Interpretation

Some solutes in a liquid will raise the surface tension. Others will lower it. What's happening?

1) Solutes which raise the surface tension will distribute away from the surface (so as to not raise the overall free energy)

2) Solutes which lower the surface tension will concentrate at the surface (so as to lower the overall free energy)

Examples of (2) $\rightarrow$ surfactants, detergents.

What happens?

Pure water $\rightarrow$ air

water molecules at interface are
unsatisfied.

$\Rightarrow$ Cost to form a surface

Water + Detergent $\rightarrow$ air

Nonpolar tails want to get away from the water (why?)

So they line up at interface

Not so bad... i.e. lowers energy of the surface
Vapor Pressure and Surface Tension

Net transfer of water from small drops to big

WHY? How?

Surface tension \rightarrow \text{Vapor Pressure}

\text{liquid} \rightarrow \text{gas}

\text{REMINDER} \quad \left(\frac{\partial G}{\partial A}\right)_{\text{PT}}

\text{Used to have: } \Delta G = -S \Delta T + V \Delta P + \mu_{\text{H}_2\text{O}} \Delta n_{\text{H}_2\text{O}}

\text{Now: } \Delta G = -S \Delta T + V \Delta P + \gamma \Delta A + \mu_{\text{H}_2\text{O}} \Delta n_{\text{H}_2\text{O}}

\text{Surface tension} \rightarrow \left(\frac{\partial G}{\partial A}\right)_{\text{PT}}

\text{So we ultimately have to worry about...}

\text{TOTAL CHEMICAL POTENTIAL}

\downarrow

\text{Surface tension}

\text{electrical potential}

\text{chemical potential}

(centrifugal) gravitational potential \rightarrow \text{either earth's or centrifuge-equivalent}