10/22/99

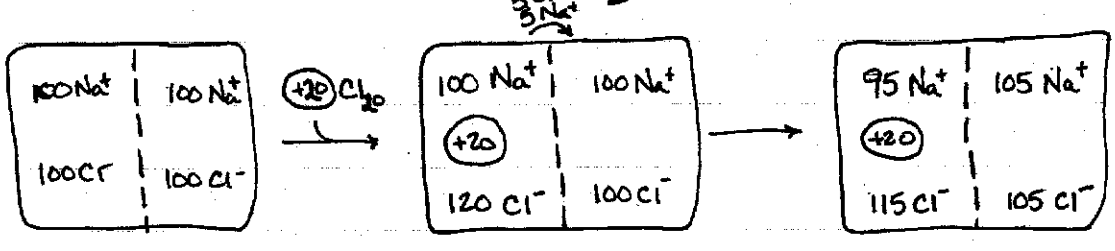
EXAM NEXT THURSDAY
OCTOBER 28, 7:00P-9:00P
LGRT 103

REVIEW IN-CLASS
WED OCTOBER 27
(I will NOT be available Thurs!)

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).

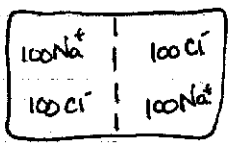
Have to move together → WHY?



EQUILIB — NOT EQUILIB — SOMETHING LIKE THIS OUGHT TO OCCUR

Cl⁻ happier
Na⁺ less happy
} Overall: happier

Let's do the math



INITIAL

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

BUT:

$$\mu_{NaCl} = \mu^{\circ}_{NaCl} + RT \ln C_{Na^+} C_{Cl^-}$$

$$\mu^{\text{inside}}_{NaCl} = \mu^{\circ}_{NaCl} + RT \ln C^{IN}_{Na^+} C^{IN}_{Cl^-} = \mu^{\circ}_{NaCl} + RT \ln C^{OUT}_{Na^+} C^{OUT}_{Cl^-} = \mu^{\text{outside}}_{NaCl}$$

$$\ln C^{IN}_{Na^+} C^{IN}_{Cl^-} = \ln C^{OUT}_{Na^+} C^{IN}_{Cl}$$

$$C^{IN}_{Na^+} C^{IN}_{Cl^-} = C^{OUT}_{Na^+} C^{OUT}_{Cl^-}$$

CHARGE NEUTRALITY

OUTSIDE

$$C_{Na^+}^{OUT} = C_{Cl^-}^{OUT} \Rightarrow C$$

INSIDE

$$z_m C_m + C_{Na^+}^{IN} = C_{Cl^-}^{IN}$$

$$C_{Na^+}^{IN} C_{Cl^-}^{IN} = C_{Na^+}^{OUT} C_{Cl^-}^{OUT}$$

$$C_{Cl^-}^{IN} = \frac{C_{Na^+}^{OUT} C_{Cl^-}^{OUT}}{C_{Na^+}^{IN}} = \frac{C^2}{C_{Na^+}^{IN}}$$

$$\frac{C^2}{C_{Na^+}^{IN}} = z_m C_m + C_{Na^+}^{IN}$$

let $x = C_{Na^+}$ inside

$$\frac{C^2}{x} = z_m C_m + x$$

$$x^2 + z_m C_m x - C^2 = 0$$

$$\therefore \quad x = \frac{-z_m C_m + \sqrt{(z_m C_m)^2 - 4C^2}}{2} = C_{Na^+}^{OUT}$$

$$\frac{C_{Na^+(IN)}}{C_{Na^+(OUT)}} = \frac{x}{C} = -\frac{z_m C_m}{2C} + \sqrt{\left(\frac{z_m C_m}{2C}\right)^2 + 1}$$

So, $\frac{C_{Na^+}^{IN}}{C_{Na^+}^{OUT}} < 1.0$

FOR EXAMPLE GIVEN

So $C_{Na^+}^{IN} \neq C_{Na^+}^{OUT}$

and $C_{Cl^-}^{IN} \neq C_{Cl^-}^{OUT}$

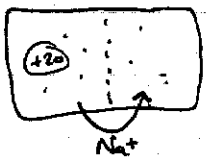
Why? They're supposed to reach equilibrium!

Yes, but real requirement is that at equilibrium,

$$\mu_{NaCl}\,(\text{outside}) = \mu_{NaCl}\,(\text{inside})$$

We can say that with respect to μ_{Na^+} and ΔG_{Na^+} there is an extra (electrical) component to ΔG.

Let's call it → ZFV

Now 

At equilibrium there is no driving force

$$\Delta G = 0$$

$$\Delta \bar{G} = RT \ln \frac{a_{Na^+(in)}}{a_{Na^+(out)}} + ZFV = 0$$

$$V = \frac{-RT}{ZF} \ln \frac{a_{Na^+(in)}}{a_{Na^+(out)}} \approx -\frac{RT}{ZF} \frac{C_{Na^+(in)}}{C_{Na^+(out)}}$$

$$C_{Na^+}^{OUT} > C_{Na^+}^{IN} \qquad C_{Cl^-}^{OUT} < C_{Cl^-}^{IN}$$

Surfaces, Membranes

↳ including any interface between two surfaces

A Surface is 2-Dimensional (unlike a solution, which is 3D)

Conc is $\frac{mol}{cm^2}$ instead of $\frac{mol}{cm^3}$

Surface Tension

- Surf pressure is $\frac{F}{length}$ instead of $\frac{F}{area}$ $\Rightarrow$ ($\frac{J}{m^2}$ instead $\frac{J}{m^3}$)
- Surface free energy is $\frac{J}{m^2}$ instead of $\frac{J}{m^3}$

T, P

surface area

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

∴ liquids with very high surface tension form drops readily (a sphere has the lowest $\frac{surface}{volume}$) 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 also...~~

Ethanol too

Molecular Interpretation

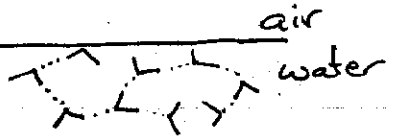
Some solutes in a liquid will raise the surface tension. Others will lower it (of the solution) → What's happening?

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

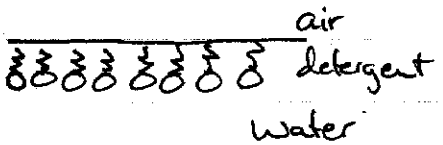
2) Solutes which lower the surface tension will concentrate at the surface (so as to <u>lower</u> the overall free energy)

<u>Examples of (2)</u> → <u>surfactants</u>, detergents.
What happens?

<u>Pure water</u>
water molecules at interface are <u>unsatisfied</u>.
∴ <u>Cost</u> to form a surface



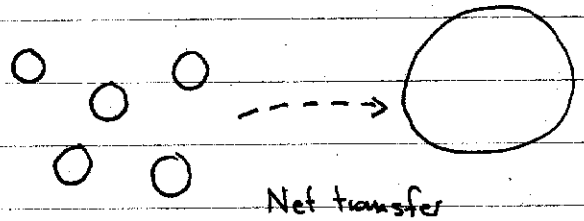
<u>Water + Detergent</u>



Nonpolar tails want to get away from the water (why?)
So they line up at interface

Not so bad.... ie. lowers energy of the surface

Vapor Pressure and Surface Tension



Net transfer of water from small drops to big

WHY? How?

- Surface tension
- Vapor Pressure: liquid $\rightleftharpoons$ gas

Remember: $\left(\frac{\partial G}{\partial n}\right)_{P,T}$

Used to have: $\partial G = -S\,\partial T + V\partial P + \mu_{H_2O}\,\partial n_{H_2O}$

Now: $\partial G = -S\,\partial T + V\partial P + \gamma\partial A + \mu_{H_2O}\,\partial n_{H_2O}$

surface tension $\Rightarrow \left(\frac{\partial G}{\partial A}\right)_{P,T}$

So we ultimately have to worry about

TOTAL CHEMICAL POTENTIAL

- Surface tension
- electrical potential
- chemical potential
- (centrifugal) gravitational potential → either earth's or centrifuge-equivalent