Chem 130A EXAM#3 4/20/05
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Write solutions clearly on separate pages.

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1. Answer true or false and provide your reason concisely.
   a. μ (pure water ice) = μ (pure water liquid) at T = 0 °C and P = 1 atm.
   b. μ (pure water ice) > μ (water) at T = 0 °C and P = 1 atm and ionic strength in the liquid phase = 100 mM NaCl. This is an ice cube melting in salt water.

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2. In some photosynthetic bacteria, light energy is used to pump protons from inside the cell to the outside. Energy harnessed from the flow of protons back into the cell can then drive ATP synthesis according to the following reaction:

   $ADP + P_i \leftarrow (2\,H^+) \rightarrow ATP + H_2O$ $\Delta G° = 31$ kJ/mol

   Two protons are transported to synthesize one ATP molecule; assume all of the energy goes into ATP synthesis and that T = 310 K.

   a. If [ADP] = 100 μm, [ATP] = 1mM, and P_i is in excess, calculate the pH difference between outside and inside the cell that is required for the ATP synthesis reaction to occur spontaneously. (The pH gradient is the only driving force here)
   b. How does this change if the electrical potential inside the cell is 100 mV lower than outside? (Give a quantitative answer)

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3. Let K_s be the equilibrium constant for dissociation of a ligand from a monovalent cell surface receptor as measured on the cell surface. K_d is the equilibrium constant for the same ligand – receptor pair measured in solution.
   a. If K_s is measured to be 30 nM, what fraction of receptors have bound ligand under solution ligand concentrations of 30 nM and 270 nM, respectively? (Assume the solution volume is large enough that surface binding does not change the solution concentration of ligand)
   b. In this experiment the cell surface has a net negative surface charge, σ. If K_s = 30 nm at 150 mM solution ionic strength and 10 nM at 75 mM ionic strength, can you determine if the ligand is charged? (K_d is independent of ionic strength)
   c. If so, what is its sign?
   d. Can you determine its exact charge? If not, what additional information would you need. Write an equation in terms of the relevant parameters to quantify your explanation.

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4. Refer to the miscibility phase diagram for nicotine and water on the board.
   a. Describe what one observes when mixing a 1:1 solution of nicotine and water at 110 °C.
   b. What does the same mixture look like ar 210 °C?
   c. Draw a free energy vs. mole fraction curve for nicotine and water at 110 °C. Label the axes and key features in your curve according to the phase diagram.
   d. Draw the free energy vs mole fraction curve for the system at 210 °C.

Exam 3 Solutions

① (a) True The system is in equilibrium hence $\mu_{water} = \mu_{ice}$

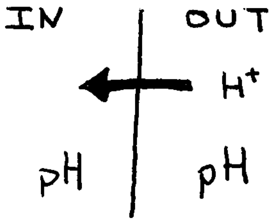
(b) True

$$\mu_{\substack{salt\\water}} = \mu_{\substack{pure\\water}} + RT \ln x_{H_2O}$$

since $x_{H_2O} < 1 \Rightarrow \mu_{\substack{salt\\water}} < \mu_{\substack{pure\\water}}$

②

(a)



$$Q = \frac{[ATP]}{[ADP][P_i]} \underset{\sim}{\overset{\text{if}}{P_i \text{ excess}}} \frac{[ATP]}{[ADP]}$$

$$\underline{\underline{P_i + ADP \rightleftharpoons ATP}}$$

$[P_i] >> [ATP]$ or $[ADP]$

$$\Delta G_{rxn} = \Delta G^\circ + RT \ln Q = 31 \tfrac{kJ}{mol} + (8.314 \tfrac{J}{K\,mol})(310K) \ln\left(\tfrac{1mM}{0.1mM}\right)$$

$$= 36.9 \text{ kJ/mol}$$

$\ln[H^+] = 2.303 \log[H^+] = -2.303\,pH$ since $pH = -\log[H^+]$

$$\Delta\mu_{(in-out)} = RT \ln[H^+]_{in} - RT \ln[H^+]_{out}$$

$$= -2.303\,RT\,(pH_{in} - pH_{out})$$

$$\Delta G_{(in-out)} = 2\,\Delta\mu = -2(2.303)(RT)(\Delta pH)$$

$$\Delta pH \geq 3.1$$

(2b)

$$\mu_{H^+_{in}} = \mu^* + RT \ln [H^+]_{in} + zF\phi_{in}$$

$$\mu_{H^+_{out}} = \mu^* + RT \ln [H^+]_{out} + zF\phi_{out}$$

$$\Delta\mu_{H^+_{in-out}} = -2.303\, RT\, \Delta pH + zF(\phi_{in} - \phi_{out})$$

$\Delta G = n\Delta\mu$

$$\Delta G_{in-out} = -2(2.303)RT\,\Delta pH + 2zF\Delta\phi$$

$$\Delta G_{rxn} + \Delta G_{in-out} < 0$$

$\Delta\phi = 0.1 V$

$$36.9 \frac{kJ}{mol} + 2zF\Delta\phi - 2(2.303)RT\,\Delta pH < 0$$

$$\Delta pH \geq 1.5$$

(3a)

$$LR \rightleftharpoons L + R$$

$$K_s = \frac{[L][R]}{[LR]} = 30 nM$$

$$[R]_{tot} = [R] + [LR]$$

$$\text{Fraction Bound} = \frac{[LR]}{[R]_{tot}} = \frac{[LR]}{[R] + [LR]}$$

$$[R] = \frac{K_s [LR]}{[L]}$$

$\boxed{3a}$ Continued...

Monovalent indicates only 1 ligand can bind per receptor molecule.

$$\text{Fraction Bound} = \frac{[LR]}{\frac{K_s[LR]}{[L]} + [LR]} = \frac{[L]}{K_s + [L]}$$

assume

$$[L]_{tot} = [L]$$

$$[L] = 30nM$$

$$\text{Fraction Bound} = \frac{30nM}{30nM + 30nM} = 0.5$$

$$[L] = 270nM$$

$$\text{Fraction Bound} = \frac{270nM}{30nM + 270nM} = 0.9$$

$\boxed{3b}$

e.g. $I_1 = 150nM$ $K_{s_1} = 30nM$

$I_2 = 75nM$ $K_{s_2} = 10nM$

The dissociation constant is lower at lower ionic strength, because the electric field is shielded less effectively. Yes we can determine the ligands charge

$\boxed{3c}$ The ligand must be positively charged.

$\boxed{3d}$ $RT \ln K_s + zF\Phi_o$

$$K_s = K_d e^{-\frac{zF\Phi_o}{RT}}$$

$$\frac{K_{s_1}}{K_{s_2}} = e^{-zF(\Phi_{o_1} - \Phi_{o_2})/RT}$$

$$z = \frac{RT}{F\Delta\Phi_o} \ln \frac{K_{s_2}}{K_{s_1}}$$

$\Delta\Phi_o = \Phi_{o_1} - \Phi_{o_2} < 0$

$\ln \frac{K_{s_2}}{K_{s_1}} < 0$ $\Rightarrow$ $z > 0$

we need ε, T, and σ to find z

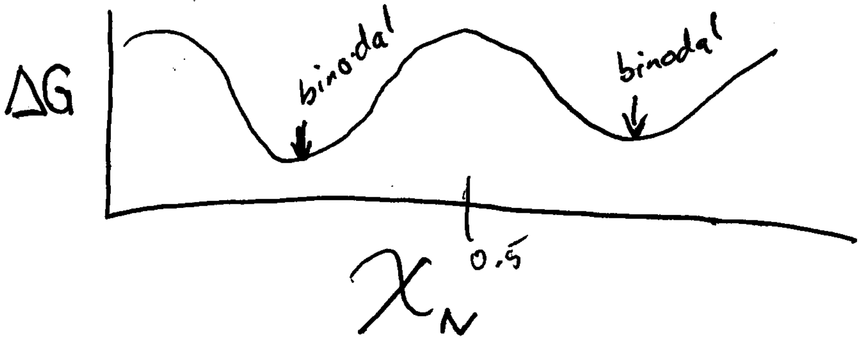
$$\Phi_o = \frac{\sigma\varepsilon}{L_D}$$

$$L_D = \sqrt{\frac{k_b T \varepsilon}{2Ie}}$$

④ (a) You're going to observe phase separation! One phase will be of high $\chi_{nicotine}$ and the other phase will be of low $\chi_{nicotine}$ (thus high χ_{H_2O}).

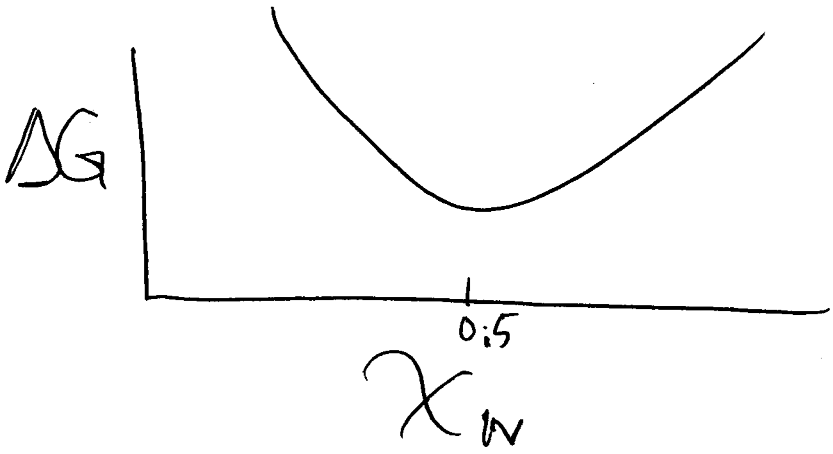
(b) The conditions are above critical point where there will be only one phase.

(c)



110°C

(d)



210°C