Read Chapter 14 (at least Sections 14.1, 14.2, and 14.3) and Chapter 3, answer the following problems, and indicate with whom you worked: _____.

(1) Do problems 2.17, 2.18, 2.19, 13.7, 13.14, and 14.2 in Bard and Faulkner (B&F).
Answers:
Problem 2.17. **No, because it prefers to be highly charged in aqueous solution and thus it would partition into the aqueous phase and not remain in the non-aqueous solvent that is immiscible with water. However, with long greasy alkyl chains, i.e. the C_{20} groups, the molecule will stay soluble – at least the tails will – and the charged head group will approach the aqueous phase to chelate the ion in solution, and thus yes.**

Problem 2.18. **Well, Section 2.4.4 discussed potentiometric gas-sensing electrodes, and the gases, e.g. O_2, are uncharged.** (The Clark electrode is not a good example because it is not potentiometric.) **Thus, it is feasible.** However, you cannot have an electrode that detects potential changes based on Equation (2.4.2) because it has a z_i factor in front; uncharged species have z_i = 0; also, then this reaction is not due to redox chemistry but simply concentration differences and so direct potentiometric measurements of uncharged species are not as clear, except that Section 2.4.4 describes some.

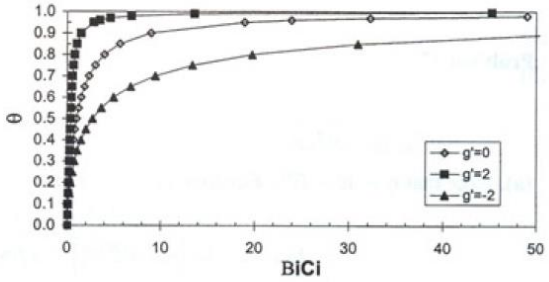
Problem 2.19. $\boldsymbol{E = \frac{RT}{4F}\ln\left(\frac{p_a c_{eg}^{O^{2-}}}{p_{eg} c_a^{O^{2-}}}\right) = \frac{RT}{4F}\ln\left(\frac{p_a}{p_{eg}}\right)}$, but T was not specified. In the text, the temperature where these solid electrolyzes operate was reported to be 500 – 1000 °C (773.15 – 1273.15 K) and so any temperature in that range would have been acceptable. Thus, because $E = (4.9606 \cdot 10^{-5})T \log\left(\frac{0.21 \cdot 1 \text{ atm}}{0.01 \text{ atm}}\right) = (6.5590 \cdot 10^{-5})T$, E = [0.0507, 0.0835] V = **[50.7, 83.5] mV**

Problem 13.14 The Frumkin isotherm accounts for interactions between the adsorbates, either attractive ($g' > 0$) or repulsive ($g' < 0$). Equation (13.5.14) describes the Frumkin isotherm.

$$\beta_i C_i = \frac{\theta}{1-\theta} \exp\left[-g'\theta\right] \quad (1)$$

The dimensionless term $\beta_i C_i$ describes the concentration effects. The most direct way to calculate the isotherm is to calculate $\beta_i C_i$ for a range of θ. The isotherm is a plot of θ versus $\beta_i C_i$. The appended spreadsheet shows the responses for g' of 2, 0, and -2. For $g' = 0$, the isotherm is Langmerian, and on the plot this is the central data set. When $g' = 2$, the interactions are attractive and the adsorbed layer is formed at lower $\beta_i C_i$. Conversely, for $g' = -2$, the interactions are repulsive and higher $\beta_i C_i$ is required to drive monolayer formation.

θ	θ/(1−θ)	BiCi (g'=0)	BiCi (g'=2)	BiCi (g'=-2)
0.00	0	0	0	0
0.05	0.052632	0.052632	0.047623	0.058167
0.10	0.111111	0.111111	0.09097	0.135711
0.15	0.176471	0.176471	0.130733	0.23821
0.20	0.25	0.25	0.16758	0.372956
0.25	0.333333	0.333333	0.202177	0.549574
0.30	0.428571	0.428571	0.235205	0.780908
0.35	0.538462	0.538462	0.267392	1.084328
0.40	0.666667	0.666667	0.299553	1.483694
0.45	0.818182	0.818182	0.332648	2.012403
0.50	1	1	0.367879	2.718282
0.55	1.222222	1.222222	0.406842	3.671758
0.60	1.5	1.5	0.451791	4.980175
0.65	1.857143	1.857143	0.50613	6.814408
0.70	2.333333	2.333333	0.575393	9.462133
0.75	3	3	0.66939	13.44507
0.80	4	4	0.807586	19.81213
0.85	5.666667	5.666667	1.035207	31.01904
0.90	9	9	1.48769	54.44683
0.95	19	19	2.841804	127.032
0.96	24	24	3.518567	163.703
0.97	32.33333	32.33333	4.646428	224.9996
0.98	49	49	6.902063	347.867
0.99	99	99	13.66885	717.0316
0.997	332.3333	332.3333	45.2471	2440.94



Problem 13.7. The number of moles of Z that absorbed to the electrode are 1.0 x 10^{-9} mol cm^{-2} x 100 cm^2 = 1 x 10^{-7} mol. This represents a loss of molecules from the solution, and a concentration loss of (10^{-7} mol / 0.05 L) = 2 x 10^{-6} M. This means the new concentration is (1 x 10^{-4} – 2 x 10^{-6}) = 0.98 x 10^{-4} M. The absorbance is calculated using the Beer–Lambert law as $A = \varepsilon c\ell = \varepsilon$(0.98 x 10^{-4})(1.00) = (0.98 x 10^{-4})ε. From the start of the problem, A = 0.500 for c = 1.00 x 10^{-4} in a 1 cm pathlength cuvette and thus, ε = 0.500/((1.00 x 10^{-4})(1.00)) = 5000 M^{-1} cm^{-1}. Therefore, A_{final} = (0.98 x 10^{-4})(5000) = **0.49**, and so a loss in absorbance of 0.01 which is entirely detectable by any commercial ultraviolet–visible spectrophotometer. The only catch is you need to put a 10 x 10 cm^2 electrode in the cuvette which will be challenging.

Problem 14.2 The curve in Figure 14.3.4b is almost identical in shape to the theoretical curve in Figure 14.3.4a, consistent with only adsorbed O electroactive. The relationship between peak current, i_p, and surface coverage, Γ^*_O, is given by equation (14.3.22).

$$i_p = \frac{\alpha F^2 A v \Gamma^*_O}{2.718RT} \qquad (14.3.22)$$

To account for n other than 1, the equation is modified as follows, consistent with the usual cluster of nF/RT.

$$i_p = \frac{\alpha n F^2 A v \Gamma^*_O}{2.718RT} \qquad (1)$$

It is given that $n = 2$, $A = 0.017\ cm^2$, and $v = 0.1\ V/s$. From Figure 14.3.4b, $i_p = 2.2 \times 10^{-7}\ A$. Assume $\alpha = 0.5$ and $T = 298\ K$.

$$i_p = \frac{\alpha n F^2 A v \Gamma^*_O}{2.718RT} \qquad (2)$$

$$\begin{aligned} \Gamma^*_O &= \frac{i_p 2.718RT}{\alpha n F^2 A v} \qquad (3) \\ &= \frac{2.2 \times 10^{-7}\ A \times 2.718}{0.5 \times 2 \times 96485 C/mole \times 38.92 V^{-1} \times 0.017\ cm^2 \times 0.1\ V/s} \\ &= 9.37 \times 10^{-11}\ mole/cm^2 \\ &= 9.37 \times 10^{-11}\ mole/cm^2 \times 6.02 \times 10^{23}\ molecules/mole \\ &= 5.64 \times 10^{13}\ molecules/cm^2 \end{aligned}$$

This corresponds to $1.77 \times 10^{-14}\ cm^2 = 177\ Å^2$ per molecule, well below a compact monolayer.

Cutting this graph out, weighing it, and using mass to solve this problem was completely reasonable. In fact, I preferred that. Thus, your answer may be off somewhat, but a number in the ballpark of that reported here suffices.

(2) In Naegeli, Redepenning, & Anson, *Journal of Physical Chemistry*, 1986, 90, 6227 (see class website), redox-active molecules are embedded in Nafion-coated electrodes and their formal potentials are measured.

a. Based on Figure 2, answer the following:
    i. Why are the potentials called formal potentials and not standard potentials?

Answer: **Because activity must be used and not concentration.** That is, the electrolyte, solvent, etc. make the solution non-ideal.

ii. Explain why the formal potential for the reduction of the redox-active molecules in solution at a bare electrode becomes slightly more negative as the concentration of LiCl is increased?
Answer: **Activity; the activity coefficient for species that are more highly charged is smaller and so for a reduction event for these molecules, the reduced species is less positively charged and so has a smaller charge and thus larger activity coefficient. The Nernst equation has the reduced species in the numerator of the reaction quotient and so the numerator is larger than the denominator. Thus, the activity coefficient factor will be negative (i.e. -0.5916 mV (log γ_r/γ_o)) and so the reduction potentials will become slightly more negative as the salt concentration increases, and this is what was observed.**

iii. When a Nafion-coated electrode is used, explain the cause of the LiCl concentration dependence to the formal potentials? (Assume that the Nafion was presoaked in an aqueous electrolyte containing a high concentration of LiCl in a large beaker.)
Answer: **Donnan potentials due to $[Li^+] \approx 1$ in Nafion, as counterions to the sulfonate groups, and generally $[Li^+]$ in solution being smaller.** Notice that at ~ 1M LiCl, the formal potentials in solution are nearly equal to the formal potentials in the membrane, and this is because under that condition the Donnan potential is ~0 V.

b. Based on Figure 4, where the ordinate axis should be labeled "fraction of protonated molecule s," answer the following:
   i. What is the approximate pK_a of $[Ru^{II}(NH_3)_5(pz\text{-}H^+)]^{3+}$, where pz is pyrazine and pz-H is protonated pz?
   Answer: **~2.4 based on the diagram**, but 2.5 from the text. Both answers, or anything close, are fine.

   ii. Why does $[Ru^{II}(NH_3)_5(pz\text{-}H^+)]^{3+}$ not deprotonate when it is incorporated into Nafion and the pH is varied? (Assume that the Nafion was presoaked in an aqueous electrolyte containing a high concentration of HCl in a large beaker.)
   Answer: **Because over this pH range, only acid was added to the solution and so the only cations in the system are protons. Thus, there is no way for any significant amount of protons to equilibrate out of the Nafion membrane due to charge neutrality requirements.** That is, when a proton diffuses out down its concentration gradient, only a proton can diffuse in (no net change). Also, the fixed sulfonates cannot diffuse out with the protons and no other cations can diffuse into the membrane. A Donnan potential results.

   iii. If the pH of the solution changed to 11 using NaOH, and the beaker is large, will $[Ru^{II}(NH_3)_5(pz\text{-}H^+)]^{3+}$ in Nafion deprotonate? Explain why or why not?

Answer: **Yes, because Na^+ can diffuse into the membrane concomitant with proton diffusion out to establish equilibrium between the phases.**

(3) At steady-state, a human neuron has the following approximate distribution of ions across its cell membrane:

	Inside (mM)	Outside (mM)	Relative permeability
K^+	100	10	100
Na^+	10	100	1
Cl^-	10	100	10

Based on this information, answer the following:

a. What is the resting potential of the membrane at physiological temperature (i.e. 98.6 °F)?
Answer: Using the GHHK equation at exactly 37 °C, which is 310.15 K,
$E = \frac{RT}{F}\ln\left(\frac{\left(p_{K^+}c_{K^+}^{out}\right)+\left(p_{Na^+}c_{Na^+}^{out}\right)+\left(p_{Cl^-}c_{Cl^-}^{in}\right)}{\left(p_{K^+}c_{K^+}^{in}\right)+\left(p_{Na^+}c_{Na^+}^{in}\right)+\left(p_{Cl^-}c_{Cl^-}^{out}\right)}\right) = 0.06154\log\left(\frac{100(0.01)+1(0.1)+10(0.01)}{100(0.1)+1(0.01)+10(0.1)}\right) =$
$= 0.06154\log\left(\frac{1+0.1+0.1}{10+0.01+1}\right) = 0.06154\log\left(\frac{1.2}{11.01}\right) = 0.06154\log\left(\frac{1.2}{11.01}\right) = -0.05924 \approx$
–59 mV. Check out GHHK here: http://www.nernstgoldman.physiology.arizona.edu/!

b. When a nerve is stimulated by an action potential, voltage-sensitive sodium channels open up (wide) and the cell depolarizes to roughly +40 mV. However, due to charge neutrality, the concentrations of Na^+ inside and outside of the cell change very little, and the small flux of sodium simply charges the membrane like a capacitor. What is the relative permeability of Na^+ that caused this depolarization?
Answer:
$0.040 = 0.06154\log\left(\frac{1+p(0.1)+0.1}{10+p(0.01)+1}\right) = 0.06154\log\left(\frac{0.1p+1.1}{0.01p+11}\right)$, and so
$4.4666 = \frac{0.1p+1.1}{0.01p+11}$, and so
$0.044666p + 49.132 = 0.1p + 1.1$, and so
$0.055334p = -48.032$, and so $\boldsymbol{p_{Na^+}}$ **= 868**

c. This depolarization causes the Na^+ channels (from part b) to close and another channel to open. If this results in a membrane potential that is slightly more negative than the resting potential (from part a), *could* the chloride *and/or* potassium channel have opened up (wide)? Explain your answer.
Answer: **Both *could* have opened up (wide). This is because if $\boldsymbol{p_{Cl^-}}$ becomes very large, the membrane potential is dominated by the Cl^- term which makes the membrane potential more negative than the answer for part a**; $E = 0.06154\log\left(\frac{c_{Cl^-}^{in}}{c_{Cl^-}^{out}}\right) = 0.06154\log\left(\frac{0.01}{0.1}\right) = -0.06154$ V. **The exact same logic holds for K^+**; $E = 0.06154\log\left(\frac{c_{K^+}^{out}}{c_{K^+}^{in}}\right) = 0.06154\log\left(\frac{0.01}{0.1}\right) = -0.06154$ V. Physiologically, only K^+ channels open up (wide) due to this depolarization, but that was not what this problem was asking.