BE 100: BIOENGINEERING FUNDAMENTALS
FALL 2019

Midterm 2

November 27, 2019

1. (23 points) Let's consider a two-dimensional surface comprised of 1 mole of water. Note that the surface is comprised of only one component (i.e., water). For such a two-dimensional system, the surface tension (γ) multiplied by the differential area stretched ($d\underline{a}$) replaces the conventional $P\underline{V}$ work. The Fundamental Equation (i.e., Combined 1st and 2nd Laws) for this two-dimensional system comprised of 1 mole can therefore be written as:

$$dU = \delta Q + \delta W = TdS + \gamma da$$

when considering a closed system. Unlike $P\underline{V}$ work, $\gamma d\underline{a}$ is positive in the Fundamental Equation because performing work on the system (i.e., increasing the energy of the system) corresponds to stretching the surface. Here are the analogous equations in two-dimensions for the molar enthalpy, the molar Helmholtz free energy, and the molar Gibbs free energy:

$$H \equiv U - \gamma a$$
$$A \equiv U - TS$$
$$G \equiv H - TS$$

The molar heat capacity at constant area, C_a, for the surface has been measured, and it is defined as:

$$C_a \equiv \left(\frac{\delta Q}{\partial T} \right)_a$$

This heat capacity can be treated as a known constant in this problem. The same is true for the molar heat capacity at constant surface tension, C_γ, and it is defined as:

$$C_\gamma \equiv \left(\frac{\delta Q}{\partial T} \right)_\gamma$$

The following model represents an equation of state for the surface:

$$\gamma = \frac{\zeta T n}{\underline{a}}$$

where ζ is a known constant, n is the number of moles, $\underline{a}$ is the total area, and T is the absolute temperature.

The surface undergoes a reversible, nonisothermal expansion from (T_1, a_1) to (T_2, a_2). The surface tension of the 1 mole of water during this process was experimentally found to vary according to the following equation:

$$\gamma = \gamma_0 + \beta a$$

where γ_0 and β are constants, while γ and a are the surface tension and molar area, respectively. *Using two distinct overall approaches, derive an expression for the heat transferred to the surface in terms of the variables given as known in the problem statement.*

2. (37 points) Consider two separate experiments. In one experiment, an aqueous mixture containing n* moles of Macromolecule A is put in contact with a negatively charged polymeric scaffold. This scaffold has pores, and water fills the pores. Macromolecule A partitions, or distributes, between the external aqueous solution and the aqueous solution inside the polymeric scaffold. In this experiment, the polymeric scaffold is sitting in a total aqueous solution of $\underline{V}_{tot}$ liters, and $\underline{V}_{ext}$ liters of the $\underline{V}_{tot}$ liters correspond to the volume of the aqueous solution external to the scaffold and not filling the pores of the hydrogel. Macromolecule A is allowed to diffuse between the aqueous solution filling the pores of the polymeric scaffold and the aqueous solution external to the polymeric scaffold at constant temperature and pressure. The temperature and pressure of the aqueous solution inside the polymeric scaffold can be assumed to be equal to the temperature and pressure of the aqueous solution external to the polymeric scaffold at T* Kelvins and P* atm.

The activity coefficient of Macromolecule A in the aqueous solution external to the polymeric scaffold is given by the following expression:

$$\gamma_A = \varepsilon$$

where ε is a parameter that is a known constant at T* Kelvins and P* atm.

The excess Gibbs free energy of the aqueous solution inside the polymeric scaffold is given by:

$$\underline{G}^{ex} = n_A RT ln(\beta) + n_w RT ln(\omega)$$

where n_A and n_w are the moles of Macromolecule A and water, respectively, R is the ideal gas constant, and β and ω are parameters. At T* Kelvins and P* atm, β and ω are known constants.

In another experiment, an aqueous mixture containing n* moles of Macromolecule B is put in contact with a negatively charged polymeric scaffold. This scaffold has pores, and water fills the pores. Macromolecule B partitions, or distributes, between the external aqueous solution and the aqueous solution inside the polymeric scaffold. In this experiment, the polymeric scaffold is sitting in a total aqueous solution of $\underline{V}_{tot}$ liters, and $\underline{V}_{ext}$ liters of the $\underline{V}_{tot}$ liters correspond to the volume of the aqueous solution external to the scaffold and not filling the pores of the hydrogel. Note that n*, $\underline{V}_{tot}$, and $\underline{V}_{ext}$ are the same values between the two experiments. Macromolecule B is allowed to diffuse between the aqueous solution filling the pores of the polymeric scaffold and the aqueous solution external to the polymeric scaffold at constant temperature and pressure. The temperature and pressure of the aqueous solution inside the polymeric scaffold can be assumed to be equal to the temperature and pressure of the aqueous solution external to the polymeric scaffold at T* Kelvins and P* atm.

The activity coefficient of Macromolecule B in the aqueous solution external to the polymeric scaffold is given by the following expression:

$$\gamma_B = \varepsilon$$

where ε is a parameter that is a known constant at T* Kelvins and P* atm, and it's exactly the same as that for Macromolecule A.

The activity coefficient of Macromolecule B in the aqueous solution inside the polymeric scaffold is given by:

$$\gamma = \tau$$

where τ is a parameter, and at T* Kelvins and P* atm, τ is a known constant.

Both experiments take place at a pH of η, which is close to 7. Macromolecule A and Macromolecule B are the exact same size. However, Macromolecule A has θ carboxylic acid groups (each with a naïve pKa of 4), and Macromolecule B has ψ amines (each with a naïve pKa of 9). *Derive expressions for the net charge of each macromolecule. If you could measure the net charge of Macromolecule B, would you expect the net charge to be equal, more negative, less negative, more positive, or less positive than the predicted expression for Macromolecule B? Please explain.*

Can you qualitatively predict if τ or β is larger? Why or why not? Use equations and words in giving your rationale.

In both experiments, you wait for equilibrium to be achieved at T* Kelvins and P* atm. *Derive an expression for the moles of Macromolecule A encapsulated in the polymeric scaffold at equilibrium. Also derive an expression for the moles of Macromolecule B encapsulated in the polymeric scaffold at equilibrium. Which do you expect to be larger? Please explain qualitatively. Please also explain using the expressions derived for moles encapsulated.*

3. (23 points) You perform an experiment where n_0 moles of a dye are dissolved in $\underline{V}_{w,0}$ liters of water. This solution is then mixed with $\underline{V}_{oil,A}$ liters of type A oil, where the molecular weight of the type A oil is M_A g/mol and its density is ρ_A g/mL. There is no dye originally in the type A oil, but after mixing, the dye distributes between the water phase and the type A oil phase. The concentration of the dye in the type A oil phase after achieving equilibrium at T* Kelvins and P* atm is C_1 mol/L. The $\underline{V}_{w,0}$ liters of water are then removed and put in contact with $\underline{V}_{oil,B}$ liters of type B oil, where the molecular weight of the type B oil is M_B g/mol and its density is ρ_B g/mL. There is also no dye originally in the type B oil, but after mixing, the dye distributes between the water phase and the type B oil phase. The concentration of dye in the aqueous phase after achieving equilibrium at T* Kelvins and P* atm is C_2 mol/L. You know the 1 M standard state of the dye in water at T* Kelvins and P* atm is ψ Joules/mol. Also, the concentration of dye in **every** phase throughout the experiment is very low. *Derive expressions for the 1 M standard state of the dye in the type A oil at T* Kelvins and P* atm <u>and</u> the 1 M standard state of the dye in the type B oil at T* Kelvins and P* atm. Please also derive the infinite-dilution standard state of the dye in the type A oil at T* Kelvins and P* atm <u>and</u> the infinite-dilution standard state of the dye in the type B oil at T* Kelvins and P* atm. Make sure you show your work when connecting the different standard states.*

4. Short answers Part 1

    a. (4 points) A noncharged polymer is added to the left-hand side compartment of a diffusion cell that is filled with permeable water. The molecular weight of the polymer is $M_{w,i}$. Although water can diffuse across the membrane into the right-hand side compartment, the polymer molecules cannot diffuse across the membrane. Assuming that the virial expansion for osmotic pressure applies to this situation and that you only need to consider the expansion to second order (i.e., only consider up to the second virial coefficient, B), make a plot of $\pi/(RT\rho_i)$ vs. ρ_i, where π is the osmotic pressure, R is the ideal gas constant, T is the absolute temperature and ρ_i is the mass of polymer i per volume. Note that these polymer i molecules interact with each other via van der Waals interactions. On the same plot, make a plot for a polymer that has a molecular weight of $M_{w,A}$, where $M_{w,A}$ is greater than $M_{w,i}$. Note that these polymer A molecules interact with each via excluded-volume interactions.

    b. (5 points) Consider a mixture containing three types of molecules (types 1, 2, and 3) at temperature T_0 Kelvins and pressure P_0 atm. The mole fraction of the type 1 molecule is X^* and that of the type 2 molecule is X_0. If you add 1 mole of the type 1 molecule to this mixture, the entropy of the solution decreases by α Joules/Kelvin. The chemical potential of molecule 1 at this composition is known as β Joules/mol. Note that α and β are positive constants. What is the partial molar enthalpy of component 1 at T_0, P_0, and $X_1=X^*$, $X_2=X_0$.

5. Short answers Part 2

   a. (3 points) State the number of independent intensive variables (i.e., the degrees of freedom) for the following scenario. 3 compartments. Compartment 1 (left) has components A, B, C, and D. Compartment 2 (middle) has components A, E, F, and G. Compartment 3 (right) has components E, G, H, and I. As indicated in the picture below, a membrane divides compartments 1 and 2 and only allows component A to diffuse between the two compartments. Also, as indicated in the picture below, a membrane divides compartments 2 and 3 and only allows components E and G to diffuse between the two compartments.

A, B, C, D	A, E, F, G	E, G, H, I
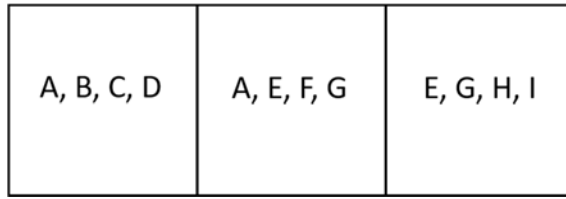
   b. (2 points) What does "CMC" stand for? Please also explain what it represents.

c. (1 point) Consider a two components system comprised of molecules of type 1 and 2. Please write the condition to determine if a homogeneous solution will phase separate.

d. (2 points) Is the following function a state function:

$$f = \frac{\alpha x}{\beta y^2}$$

where α and β are positive constants.

1.

<u>one approach</u>

$\delta Q_{rev} = T dS$ Eq. (1)   since the process is reversible

Expand dS in terms of dT and da as given (T_1, a_1) and (T_2, a_2)

$$dS = \left(\frac{\partial S}{\partial T}\right)_a dT + \left(\frac{\partial S}{\partial a}\right)_T da \quad \text{Eq.(2)}$$

Combining Eqs. (1) and (2)

$$\delta Q_{rev} = T \left[\left(\frac{\partial S}{\partial T}\right)_a dT + \left(\frac{\partial S}{\partial a}\right)_T da\right] \quad \text{Eq.(3)}$$

$$\delta Q_{rev} = T \left(\frac{\partial S}{\partial T}\right)_a dT + T \left(\frac{\partial S}{\partial a}\right)_T da \quad \text{Eq.(4)}$$

Let's first get $\left(\frac{\partial S}{\partial T}\right)_a$ and $\left(\frac{\partial S}{\partial a}\right)_T$ in terms of measurable quantities

$$\delta Q = T dS$$

$$\left(\frac{\delta Q}{\partial T}\right)_a = T \left(\frac{\partial S}{\partial T}\right)_a \quad \text{Eq (5)}$$

$$\left(\frac{\partial S}{\partial T}\right)_a = \frac{1}{T} \left(\frac{\delta Q}{\partial T}\right)_a \quad \text{Eq.(6)}$$

$$\left(\frac{\partial S}{\partial T}\right)_a = \frac{C_a}{T} \quad \text{Eq. (7)}$$

Combining Eqs. (4) and (7)

$$\delta Q_{rev} = T \frac{C_a}{T} dT + T \left(\frac{\partial S}{\partial a}\right)_T da \quad \text{Eq (8)}$$

$$\delta Q_{rev} = C_a\, dT + T\left(\frac{\partial S}{\partial a}\right)_T da \qquad Eq\,(9)$$

Since $A \equiv U - TS$

$$dA = dU - TdS - SdT \qquad Eq.\,(10)$$

Given

$$dU = TdS + \gamma da \qquad Eq.\,(11)$$

Combining Eqs. (10) and (11)

$$dA = TdS + \gamma da - TdS - SdT$$

$$dA = -SdT + \gamma da \qquad Eq.\,(12)$$

Using Maxwell Reciprocity

$$\left(\frac{\partial(-S)}{\partial a}\right)_T = \left(\frac{\partial \gamma}{\partial T}\right)_a$$

$$\left(\frac{\partial S}{\partial a}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_a \qquad Eq.\,(13)$$

Combining Eqs. (9) and (13)

$$\delta Q_{rev} = C_a\, dT - T\left(\frac{\partial \gamma}{\partial T}\right)_a da \qquad Eq.\,(14)$$

Let's evaluate $\left(\frac{\partial \gamma}{\partial T}\right)_a$ using the equation of state

$$\gamma = \frac{\zeta T n}{\underline{a}} \cdot \frac{\frac{1}{n}}{\frac{1}{n}} \qquad Eq.\,(15)$$

$$\gamma = \frac{\zeta T}{a} \qquad Eq.\,(16)$$

$$\left(\frac{\partial \gamma}{\partial T}\right)_a = \frac{\zeta}{a} \qquad Eq.\,(17)$$

Combining Eqs. (14) and (17)

$$\delta Q_{rev} = C_a\, dT - \frac{\gamma T}{a}\, da \qquad Eq\ (18)$$

Combining Eqs. (16) and (18)

$$\delta Q_{rev} = C_a\, dT - \gamma\, da \qquad Eq\ (19)$$

Since heat is path dependent, we need to consider the actual path in evaluating Eq. (19)

We are given how γ varies with a for the process

$$\gamma = \gamma_0 + \beta a \qquad Eq.\ (20)$$

Combining Eqs. (19) and (20):

$$\delta Q_{rev} = \underbrace{C_a\, dT}_{\substack{\text{can now} \\ \text{do this} \\ \text{integral} \\ \text{from } T_1 \text{ to } T_2}} - \underbrace{(\gamma_0 + \beta a)\, da}_{\substack{\text{can now do this} \\ \text{integral from } a_1 \\ \text{to } a_2}} \qquad Eq.\ (21)$$

$$\int \delta Q_{rev} = Q_{rev} = \int_{T_1}^{T_2} C_a\, dT - \int_{a_1}^{a_2} (\gamma_0 + \beta a)\, da \qquad Eq.\ (22)$$

$$Q_{rev} = C_a\,(T_2 - T_1) - \gamma_0 \int_{a_1}^{a_2} da - \beta \int_{a_1}^{a_2} a\, da \qquad Eq.\ (23)$$

$$Q_{rev} = C_a\,(T_2 - T_1) - \gamma_0 (a_2 - a_1) - \beta \left[\frac{a^2}{2}\right]_{a_1}^{a_2} \qquad Eq\ (24)$$

$$Q_{rev} = C_a\,(T_2 - T_1) - \gamma_0 (a_2 - a_1) - \frac{\beta}{2}\left[(a_2)^2 - (a_1)^2\right] \qquad Eq\ (25)$$

another approach

$$dU = \delta Q + \delta W \quad \text{Eq (26)}$$

$$\Delta U = Q + W \quad \text{Eq. (27)}$$

$$Q = \Delta U - W \quad \text{Eq. (28)}$$

Since the process occurs reversibly, subscript Q and W with "rev"

$$Q_{rev} = \Delta U - W_{rev} \quad \text{Eq. (29)}$$

For work, I need to follow the actual path. This path is reversible and given by Eq. (20)

$$W_{rev} = \int_{a_1}^{a_2} \gamma \, da \quad \text{Eq. (30)}$$

Sub Eq. (20) into Eq. (30)

$$W_{rev} = \int_{a_1}^{a_2} (\gamma_0 + \beta a) \, da \quad \text{Eq. (31)}$$

$$W_{rev} = \gamma_0 \int_{a_1}^{a_2} da + \beta \int_{a_1}^{a_2} a \, da \quad \text{Eq (32)}$$

$$W_{rev} = \gamma_0 (a_2 - a_1) + \beta \left[\frac{a^2}{2} \right]_{a_1}^{a_2} \quad \text{Eq (33)}$$

$$W_{rev} = \gamma_0 (a_2 - a_1) + \frac{\beta}{2} \left[(a_2)^2 - (a_1)^2 \right] \quad \text{Eq (34)}$$

We now need ΔU for this process. I will choose a reversible, isothermal path followed by a reversible, constant area path.

$$(T_1, a_1) \longrightarrow (T_1, a_2) \longrightarrow (T_2, a_2)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_a dT + \left(\frac{\partial U}{\partial a}\right)_T da \quad Eq. (35)$$

$$\Downarrow \qquad\qquad\qquad \Downarrow$$
$$0 \qquad\qquad\qquad 0$$

when isothermal   when constant area

$$\Delta U = \int_{a_1}^{a_2} \left(\frac{\partial U}{\partial a}\right)_T da + \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_a dT \quad Eq. (36)$$

isothermal step   constant area step

Need an expression for $\left(\frac{\partial U}{\partial a}\right)_T$ in terms of measurable properties

$$dU = TdS + \gamma da \quad Eq. (37)$$

$$\left(\frac{\partial U}{\partial a}\right)_T = T\left(\frac{\partial S}{\partial a}\right)_T + \gamma \quad Eq. (38)$$

Combining Eqs. (13), (17), and (38)

$$\left(\frac{\partial U}{\partial a}\right)_T = -\frac{ST}{a} + \gamma \quad Eq. (39)$$

Combining Eqs. (16) and (39)

$$\left(\frac{\partial U}{\partial a}\right)_T = -\gamma + \gamma = 0 \quad Eq. (40)$$

Combining Eqs. (36) and (40)

$$\Delta U = \int_{a_1}^{a_2} (0) da + \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_a dT \quad Eq. (41)$$

$$\Delta U = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_a dT \quad Eq. (42)$$

Need an expression for $\left(\frac{\partial U}{\partial T}\right)_a$ in terms of measurable properties

$$dU = \delta Q + \gamma \, da \quad \text{Eq (43)}$$

$$\left(\frac{\partial U}{\partial T}\right)_a = \left(\frac{\delta Q}{\partial T}\right)_a + \gamma \left(\frac{\partial a}{\partial T}\right)_a \quad \text{Eq (44)}$$

$$\Downarrow$$
$$0$$

$$\left(\frac{\partial U}{\partial T}\right)_a = \left(\frac{\delta Q}{\partial T}\right)_a \quad \text{Eq. (45)}$$

$$\left(\frac{\partial U}{\partial T}\right)_a = C_a \quad \text{Eq (46)}$$

Combining Eqs. (42) and (46):

$$\Delta U = \int_{T_1}^{T_2} C_a \, dT \quad \text{Eq. (47)}$$

$$\Delta U = C_a (T_2 - T_1) \quad \text{Eq (48)}$$

Combining Eqs. (29), (34), and (48)

$$Q_{rev} = C_a (T_2 - T_1) - \gamma_0 (a_2 - a_1) - \frac{\beta}{2} \left[(a_2)^2 - (a_1)^2 \right] \quad \boxed{\begin{array}{l} \text{Same} \\ \text{as Eq (25)} \end{array}}$$

2.

Let's derive the net charge of Macromolecule A

let $X_i^{\ominus}$ be the deprotonated carboxylic acid group

Using the Henderson-Hasselbalch equation

$$pH = pKa + \log\left(\frac{[X_i^{\ominus}]}{[HX_i]}\right) \quad Eq. (1)$$

$$\frac{[X_i^{\ominus}]}{[HX_i]} = 10^{pH-pKa} \quad Eq. (2)$$

$$[HX_i] = \frac{[X_i^{\ominus}]}{10^{pH-pKa}} \cdot \frac{10^{pKa-pH}}{10^{pKa-pH}} \quad Eq. (3)$$

$$[HX_i] = 10^{pKa-pH} [X_i^{\ominus}] \quad Eq. (4)$$

Let's say we have $1 \frac{mol}{L}$ of Macromolecule A

$$[X_i^{\ominus}] + [HX_i] = (\ominus)\left(1 \frac{mol}{L}\right) \quad Eq. (5)$$

Combining Eqs. (4) and (5):

$$[X_i^{\ominus}]\left(1 + 10^{pKa-pH}\right) = (\ominus)\left(1 \frac{mol}{L}\right) \quad Eq. (6)$$

$$[X_i^{\ominus}] = \frac{\ominus \frac{mol}{L}}{1 + 10^{pKa-pH}} \quad Eq. (7)$$

$$\frac{\text{charge}}{\text{macromolecule}} = \frac{[X_i^{\ominus}] \frac{\text{mol } X_i^{\ominus}}{L} \cdot \frac{N_A \text{ molecules of } X_i^{\ominus}}{\text{mol } X_i^{\ominus}} \cdot \frac{(-1e) \text{ electronic charge}}{1 \text{ molecule of } X_i^{\ominus}}}{1 \frac{\text{mol macromolecule}}{L} \cdot \frac{N_A \text{ macromolecules}}{\text{mol macromolecule}}} \qquad Eq. (8)$$

$$\frac{\text{charge}}{\text{macromolecule}} = (-1e)[X_i^{\ominus}] \qquad Eq. (9)$$

Combining Eqs. (7) and (9)

$$\frac{\text{charge}}{\text{macromolecule}} = (-1e)\frac{\theta \cdot \frac{\text{mol}}{L}}{1 + 10^{4-n}} \qquad Eq. (10) \leftarrow \begin{array}{l}\text{charge per molecule}\\\text{of Macromolecule A}\end{array}$$

Let's derive the net charge of Macromolecule B

Let $HX_2^{\oplus}$ be the protonated amine group

Using the Henderson–Hasselbalch equation

$$pH = pKa + \log\left(\frac{[X_2]}{[HX_2^{\oplus}]}\right) \qquad Eq. (11)$$

$$\frac{[X_2]}{[HX_2^{\oplus}]} = 10^{pH-pKa} \qquad Eq. (12)$$

$$[X_2] = 10^{pH-pKa}[HX_2^{\oplus}] \qquad Eq. (13)$$

Let's say we have $1 \frac{\text{mol}}{L}$ of Macromolecule B

$$[X_2] + [HX_2^{\oplus}] = (\psi)\left(1 \frac{\text{mol}}{L}\right) \qquad Eq. (14)$$

Combining Eqs. (13) and (14):

$$[HX_2^\oplus]\left(10^{pH-pka}+1\right)=(\psi)\left(1\,\frac{mol}{L}\right) \quad Eq.\,(15)$$

$$[HX_2^\oplus]=\frac{\psi\,\frac{mol}{L}}{1+10^{pH-pka}} \quad Eq\,(16)$$

$$\frac{charge}{macromolecule}=\frac{[HX_2^\oplus]\,\frac{mol\,HX_2^\oplus}{L}\cdot\frac{N_A\,molecules\,of\,HX_2^\oplus}{mol\,HX_2^\oplus}\cdot\frac{(+1e)\,electronic\,charge}{1\,molecule\,of\,HX_2^\oplus}}{1\,\frac{mol\,macromolecule}{L}\cdot\frac{N_A\,macromolecules}{mol\,macromolecule}} \quad Eq.\,(17)$$

$$\frac{charge}{macromolecule}=(+1e)\,[HX_2^\oplus] \quad Eq\,(18)$$

Combining Eqs. (16) and (18)

$$\frac{charge}{macromolecule}=(+1e)\,\frac{\psi\,\frac{mol}{L}}{1+10^{\,\eta-9}} \quad Eq.\,(19) \leftarrow \begin{array}{l}charge\,per\,molecule\\of\,Macromolecule\,B\end{array}$$

If I could measure the net charge of Macromolecule B, I would expect the net charge to be less positive since it is unfavorable for multiple positive charges to be next to each other. I know it is positive vs. negative since amines are either neutral or positive when protonated.

$\mu^{ex}_{A,ext}$ = excess chemical potential of Macromolecule A in the aqueous solution external to the polymeric scaffold

$\mu^{ex}_{A,in}$ = excess chemical potential of Macromolecule A in the aqueous solution inside the polymeric scaffold

Similar notations will be used for $\mu^{ex}_{B,ext}$ and $\mu^{ex}_{B,in}$

$$\mu^{ex}_{A,ext} = RT \ln \varepsilon \qquad Eq. (8)$$

$$\mu^{ex}_{A,in} = \left(\frac{\partial G^{ex}}{\partial n_A} \right)_{T,P,n_w} \qquad Eq. (9)$$

$$\mu^{ex}_{A,in} = RT \ln \beta \qquad Eq. (10)$$

$$\mu^{ex}_{B,ext} = RT \ln \varepsilon \qquad Eq. (11)$$

$$\mu^{ex}_{B,in} = RT \ln \tau \qquad Eq (12)$$

I would predict that $\mu^{ex}_{B,in} < \mu^{ex}_{A,in}$ since Macromolecule B is positively charged and Macromolecule A is negatively charged, while the scaffold is negatively charged. In other words, B would be attracted to the scaffold, while A would be repelled. Excluded-volume interactions would be the same since the macromolecules are the same size. Due to the favorable interaction, $\mu^{ex}_{B,in}$ would be lower since the free energy would be more favorable. In fact, I would expect $\mu^{ex}_{B,in}$ to be negative while $\mu^{ex}_{A,in}$ would be positive.

Accordingly,

$$RT \ln \tau < RT \ln \beta$$

and $\tau < \beta$

Now for the last part of the problem

At constant T^* and P^* and at equilibrium

$$\mu_{A,ext} = \mu_{A,in} \qquad Eq.(13)$$

$$G_A^{IM} + RT \ln C_{A,ext} + RT \ln \varepsilon = G_A^{IM} + RT \ln C_{A,in} + RT \ln \beta \qquad Eq(14)$$

↙ equal since at same T^* and P^*
and also A in water for both

$$RT \ln \left(\frac{C_{A,ext}}{C_{A,in}} \right) = RT \ln \left(\frac{\beta}{\varepsilon} \right) \qquad Eq.(15)$$

$$C_{A,ext} = \frac{\beta}{\varepsilon} C_{A,in} \qquad Eq.(16)$$

Doing a mole balance on Macromolecule A

$$n^* = C_{A,ext} \underline{V}_{ext} + C_{A,in} (\underline{V}_{tot} - \underline{V}_{ext}) \qquad Eq.(17)$$

Combining Eqs. (16) and (17)

$$n^* = \frac{\beta}{\varepsilon} \underline{V}_{ext} C_{A,in} + (\underline{V}_{tot} - \underline{V}_{ext}) C_{A,in} \qquad Eq(18)$$

$$C_{A,in} = \frac{n^*}{\frac{\beta}{\varepsilon} \underline{V}_{ext} + \underline{V}_{tot} - \underline{V}_{ext}} \qquad Eq(19)$$

$$C_{A,in} = \frac{n^*}{\underline{V}_{tot} + \underline{V}_{ext}\left(\frac{\beta}{\varepsilon} - 1\right)} \qquad Eq\ (20)$$

$$\text{moles of A encapsulated} = C_{A,in}\left[\underline{V}_{tot} - \underline{V}_{ext}\right] \qquad Eq.\ (21)$$

Combining Eqs. (20) and (21):

$$\text{moles of A encapsulated} = \left[\frac{n^*}{\underline{V}_{tot} + \underline{V}_{ext}\left(\frac{\beta}{\varepsilon} - 1\right)}\right]\left[\underline{V}_{tot} - \underline{V}_{ext}\right] \qquad Eq\ (22)$$

At constant T^* and P^* <u>and</u> at equilibrium

$$\mu_{B,ext} = \mu_{B,in} \qquad Eq.\ (23)$$

$$G_B^{IM} + RT\ln C_{B,ext} + RT\ln\varepsilon = G_B^{IM} + RT\ln C_{B,in} + RT\ln\tau \qquad Eq\ (24)$$

↖ equal since at same T^* and P^*)

<u>and</u> also B in water for both

$$RT\ln\left(\frac{C_{B,ext}}{C_{B,in}}\right) = RT\ln\left(\frac{\tau}{\varepsilon}\right) \qquad Eq.\ (25)$$

$$C_{B,ext} = \frac{\tau}{\varepsilon}C_{B,in} \qquad Eq\ (26)$$

Doing a mole balance on Macromolecule B

$$n^* = C_{B,ext} \underline{V}_{ext} + C_{B,in} (\underline{V}_{tot} - \underline{V}_{ext}) \quad Eq.(27)$$

Combining Eqs. (26) and (27)

$$n^* = \frac{\tau}{\varepsilon} C_{B,in} \underline{V}_{ext} + (\underline{V}_{tot} - \underline{V}_{ext}) C_{B,in} \quad Eq.(28)$$

$$C_{B,in} = \frac{n^*}{\underline{V}_{tot} + \underline{V}_{ext}\left(\frac{\tau}{\varepsilon} - 1\right)} \quad Eq.(29)$$

$$\text{moles of B encapsulated} = C_{B,in} \left[\underline{V}_{tot} - \underline{V}_{ext}\right] \quad Eq.(30)$$

Combining Eqs. (29) and (30):

$$\text{moles of B encapsulated} = \left[\frac{n^*}{\underline{V}_{tot} + \underline{V}_{ext}\left(\frac{\tau}{\varepsilon} - 1\right)}\right] \left[\underline{V}_{tot} - \underline{V}_{ext}\right] \quad Eq.(31)$$

I expect more moles of B to be encapsulated since B experiences attractive electrostatic interactions with the scaffold while A experiences repulsive electrostatic interactions.

This can also be seen when comparing Eqs. (22) and (31). The only difference between the 2 equations is β and τ. Since we already discussed $\tau < \beta$, then $\left(\underline{V}_{tot} - \underline{V}_{ext} + \frac{\beta}{\varepsilon} \underline{V}_{ext}\right)$ is greater than $\left(\underline{V}_{tot} - \underline{V}_{ext} + \frac{\tau}{\varepsilon} \underline{V}_{ext}\right)$. Since the terms in parentheses are in the denominator, it follows that moles of A encapsulated is less than moles of B encapsulated.

3.

At constant T^* and P^* and at equil

$$\mu_{D,w} = \mu_{D,O_A} \quad Eq.(1)$$

Each phase is an ideal solution since the conc of dye in every phase is low.

$$G_{D,w}^{IM} + RT \ln C_{D,W_1} = G_{D,O_A}^{IM} + RT \ln C_{D,O_A} \quad Eq.(2)$$

$$G_{D,w}^{IM} = \Psi \quad Eq.(3)$$

$$C_{D,O_A} = C_1 \quad Eq.(4)$$

Combining Eqs. (2)-(4):

$$\Psi + RT \ln C_{D,W_1} = G_{D,O_A}^{IM} + RT \ln C_1 \quad Eq.(5)$$

$$G_{D,O_A}^{IM} = \Psi + RT (\ln C_{D,W_1} - \ln C_1) \quad Eq.(6)$$

$$G_{D,O_A}^{IM} = \Psi + RT \ln \left(\frac{C_{D,W_1}}{C_1} \right) \quad Eq.(7)$$

Do a mole balance on dye in this first extraction

$$n_0 = C_{D,W_1} \underline{V}_{w,0} + C_1 \underline{V}_{oil,A} \quad Eq.(8)$$

$$C_{D,W_1} = \frac{n_0 - C_1 \underline{V}_{oil,A}}{\underline{V}_{w,0}} \quad Eq.(9)$$

Combining Eqs. (8) and (9):

$$G_{D,O_A}^{IM} = \Psi + RT \ln \left(\frac{n_0 - C_1 \underline{V}_{oil,A}}{C_1 \underline{V}_{w,0}} \right) \quad Eq.(10)$$

At constant T^* and P^* <u>and</u> at equil

$\mu_{D,W} = \mu_{D,OB}$ Eq. (11)

$G_{D,W}^{IM} + RT \ln C_{D,W_2} = G_{D,OB}^{IM} + RT \ln C_{D,OB}$ Eq. (12)

Each phase is an ideal solution since the conc of dye in every phase is low

$C_{D,W_2} = C_2$ Eq. (13)

Combining Eqs. (3), (12), and (13)

$\Psi + RT \ln C_2 = G_{D,OB}^{IM} + RT \ln C_{D,OB}$ Eq. (14)

$G_{D,OB}^{IM} = \Psi + RT(\ln C_2 - \ln C_{D,OB})$ Eq. (15)

$G_{D,OB}^{IM} = \Psi + RT \ln \left(\dfrac{C_2}{C_{D,OB}} \right)$ Eq. (16)

Do a mole balance on dye in the second extraction

$C_{D,W_1} \underline{V}_{w,o} = C_2 \underline{V}_{w,o} + C_{D,OB} \underline{V}_{oil,B}$ Eq. (17)

$C_{D,OB} = \dfrac{(C_{D,W_1} - C_2) \underline{V}_{w,o}}{\underline{V}_{oil,B}}$ Eq (18)

Combining Eqs. (9) and (18)

$$C_{D,OB} = \dfrac{\left(\dfrac{n_o - C_1 \underline{V}_{oil,A}}{\underline{V}_{w,o}} - C_2 \right) \underline{V}_{w,o}}{\underline{V}_{oil,B}} = \dfrac{n_o - C_1 \underline{V}_{oil,A} - C_2 \underline{V}_{w,o}}{\underline{V}_{oil,B}}$$ Eq. (19)

Combining Eqs. (16) and (19)

$$G_{D,OB}^{IM} = \Psi + RT \ln \left(\dfrac{C_2 \underline{V}_{oil,B}}{n_o - C_1 \underline{V}_{oil,A} - C_2 \underline{V}_{w,o}} \right)$$ Eq. (20)

Now to derive an expression that relates G_D^∞ and G_D^{IM}

$$\mu_{D,o}^{id} = G_{D,o}^\infty + RT \ln X_{D,o} = G_{D,o}^\infty + RT \ln \left(\frac{n_{D,o}}{n_{D,o} + n_{oil}} \right) \quad Eq \ (21)$$

Since the solution is very dilute

$$n_{oil} >> n_{D,o} \quad Eq \ (22)$$

and

$$\mu_{D,o}^{id} = G_{D,o}^\infty + RT \ln \left(\frac{n_{D,o}}{n_{oil}} \right) \quad Eq \ (23)$$

Now to estimate the molar volume of oil (can be A or B)

$$\frac{1}{\rho_o} \frac{mL \ oil}{g \ oil} \times \frac{L \ oil}{10^3 mL \ oil} \times \frac{M_{w,o} \ g \ oil}{1 \ mole \ oil} = \frac{M_{w,o}}{1000 \ \rho_o} \frac{L \ oil}{mol \ oil} \quad Eq. \ (24)$$

$$\mu_{D,o}^{id} = G_{D,o}^\infty + RT \ln \left(\frac{n_{D,o} \frac{M_{w,o}}{1000 \rho_o} \frac{L \ oil}{mol \ oil}}{n_{oil} \frac{M_{w,o}}{1000 \rho_o} \frac{L \ oil}{mol \ oil}} \right) \quad Eq \ (25)$$

$$n_{oil} \frac{M_{w,o}}{1000 \rho_o} \frac{L \ oil}{mol \ oil} \approx \underline{V} \equiv total \ volume \quad Eq. \ (26) \ since \ mostly \ oil$$

$$\mu_{D,o}^{id} = G_{D,o}^\infty + RT \ln \left(\frac{n_{D,o}}{\underline{V}} \times \frac{M_{w,o}}{1000 \rho_o} \frac{L \ oil}{mol \ oil} \right) \quad Eq \ (27)$$

$$\mu_{D,o}^{id} = G_{D,o}^\infty + RT \ln \left(C_{D,o} \times \frac{M_{w,o}}{1000 \rho_o} \frac{L \ oil}{mol \ oil} \cdot \frac{1M \ dye}{1M \ dye} \right) \quad Eq \ (28)$$

$$\mu_{D,o}^{id} = G_{D,o}^\infty + RT \ln \left((1M \ dye) \left(\frac{M_{w,o}}{1000 \rho_o} \frac{L \ oil}{mol \ oil} \right) \right) + RT \ln \left(\frac{C_{D,o}}{1M \ dye} \right) \quad Eq \ (29)$$

Comparing Eq. (29) with $\mu_{D,o}^{id} = G_{D,o}^{IM} + RT \ln C_{D,o}$

We conclude that

$$G_{D,o}^{IM} = G_{D,o}^\infty + RT \ln \left[(1M \ dye) \left(\frac{M_{w,o}}{1000 \rho_o} \frac{L \ oil}{mol \ oil} \right) \right] \quad Eq. \ (30)$$

Rearranging Eq. (30)

$$G_{D,O}^{\infty} = G_{D,O}^{IM} - RT \ln \left[(1M\,dye) \left(\frac{Mw,o}{1000\,\rho_o} \cdot \frac{L\,oil}{mol\,oil} \right) \right] \qquad Eq\,(31)$$

Therefore,

$$G_{D,OA}^{\infty} = G_{D,OA}^{IM} - RT \ln \left[(1M\,dye) \left(\frac{M_A}{1000\,\rho_A} \cdot \frac{L\,oil\,A}{mol\,oil\,A} \right) \right] \qquad Eq.\,(32)$$

and

$$G_{D,OB}^{\infty} = G_{D,OB}^{IM} - RT \ln \left[(1M\,dye) \left(\frac{M_B}{1000\,\rho_B} \cdot \frac{L\,oil\,B}{mol\,oil\,B} \right) \right] \qquad Eq.\,(33)$$

where $G_{D,OA}^{IM}$ is given by Eq. (10)
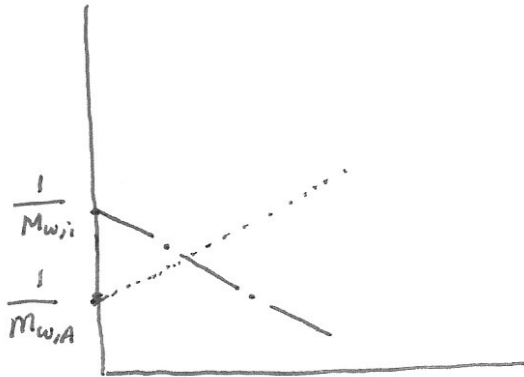
and $G_{D,OB}^{IM}$ is given by Eq (20)

4.

a.

$$\frac{\pi}{\rho_i RT} = \frac{1}{M_{w,i}} + B_i \rho_i$$

$$\frac{\pi}{\rho_A RT} = \frac{1}{M_{w,A}} + B_A \rho_A$$

$\dfrac{\pi}{\rho_i RT}$

or

$\dfrac{\pi}{\rho_A RT}$

$\dfrac{1}{M_{w,i}}$

$\dfrac{1}{M_{w,A}}$

ρ_i or ρ_A

b.

$$\left(\frac{\partial \underline{S}}{\partial n_1}\right)_{T_0, P_0, n_2, n_3} = -\alpha$$

$$\mu_1 = \left(\frac{\partial \underline{G}}{\partial n_1}\right)_{T_0, P_0, n_2, n_3} = \beta$$

$$\underline{G} \equiv \underline{H} - T\underline{S}$$

$$\left(\frac{\partial \underline{G}}{\partial n_1}\right)_{T_0, P_0, n_2, n_3} = \left(\frac{\partial \underline{H}}{\partial n_1}\right)_{T_0, P_0, n_2, n_3} - T_0 \left(\frac{\partial \underline{S}}{\partial n_1}\right)_{T_0, P_0, n_2, n_3}$$

$$\beta = \overline{H}_1 - T_0(-\alpha)$$

$$\overline{H}_1 = \beta - \alpha T_0$$

5.

a.

The Gibbs phase rule does _not_ apply.

For Compartment 1, we have $(c+1) = 4+1 = 5$ intensive variables

For Compartment 2, we have $(c+1) = 4+1 = 5$ intensive variables

For Compartment 3, we have $(c+1) = 4+1 = 5$ intensive variables

We start out with 15 intensive variables.

We now need to look at the equilibrium conditions which correspond to constraints on these variables

Thermal Equil. $\quad T^{(1)} = T^{(2)}$

$$T^{(2)} = T^{(3)}$$

Diffusional Equil $\quad \mu_A^{(1)} = \mu_A^{(2)}$

$$\mu_E^{(2)} = \mu_E^{(3)}$$

$$\mu_G^{(2)} = \mu_G^{(3)}$$

$\left.\right\}$ 5 constraints

$$\mathcal{L} = 15 - 5 = 10$$

b. CMC stands for the critical micelle concentration.

The CMC is the concentration of surfactant at which any additional amount of surfactant that is added goes to forming micelles and/or adding to micelles. It does not add to the free monomer population.

c.

$$\left(\frac{\partial^2 G}{\partial X_1^2}\right)_{T,P}\Bigg|_{X_1 = X_{1,eq}} < 0$$

$\overset{or}{=}$

$$\left(\frac{\partial^2 G}{\partial X_2^2}\right)_{T,P}\Bigg|_{X_2 = X_{2,eq}} < 0$$

d. Need to check if $\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x$ equals $\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial}{\partial x}\left(\frac{\alpha}{\beta}xy^{-2}\right)\right)_y\right)_x \overset{?}{=} \left(\frac{\partial}{\partial x}\left(\frac{\partial}{\partial y}\left(\frac{\alpha}{\beta}xy^{-2}\right)\right)_x\right)_y$$

$$\left(\frac{\partial}{\partial y}\left(\frac{\alpha}{\beta}y^{-2}\right)\right)_x \overset{?}{=} \left(\frac{\partial}{\partial x}\left(\frac{-2\alpha}{\beta}xy^{-3}\right)\right)_y$$

$$-\frac{2\alpha}{\beta}y^{-3} = -\frac{2\alpha}{\beta}y^{-3}$$

So f is a state function