Chem 471 (1999) Exam #2 **Name**. ________________________________

Work independently. Do not look at others' exams.
Do not allow your exam responses to be shared.

1. (30 points) Circle ALL correct answers, or fill in the blank, as appropriate.

If two aqueous solutions containing different nonvolatile solutes exhibit exactly the same vapor pressure at the same temperature, the activities of water in the two solutions (**are identical** / **might be different**) .

Are identical (Chapt 5, Prob 16)

The path which produces the maximum work is (**reversible** / **irreversible**).

reversible

The activity coefficients of ions in aqueous solution are typically (**equal to zero / greater than zero / less than zero**).

Ouch! This should have read "Less than one / etc" Correct answer would have been: Less than one

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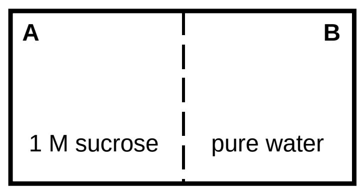
A system contains a solution (in water) of 1 M sucrose separated from pure water by a membrane permeable only to water (see diagram at right).



Which of the following statements are is/true:

the activity of water on side A equals the activity of water on side B
the activity of water on side A is less than the activity of water on side B
the activity of sucrose on side A equals the activity of sucrose on side B
the activity of water on side A equals the activity of sucrose on side A

(Chapt 5, Prob 28) **activity of water on side A equals the activity of water on side B** or **activity of water on side A is less than the activity of water on side B**

For the transfer of a small amount of water through the membrane from side A to side B (at constant T and P), ΔG is (**less than zero** / **equal to zero / greater than zero**).

(Chapt 5, Prob 28) **equal to zero** or **greater than zero**, depending on how you answered above

For the transfer of a small amount of water through the membrane from side A to side B (at constant T and P), ΔH is (**less than zero** / **equal to zero / greater than zero**).

(Chapt 5, Prob 28) **equal to zero**

For the transfer of a small amount of water through the membrane from side A to side B (at constant T and P), ΔS is (**less than zero** / **equal to zero / greater than zero**).

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(Chapt 5, Prob 28) **equal to zero** or **less than zero**, depending on how you answered above

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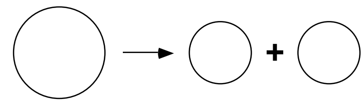
A spherical cell 1 µm in diameter divides into two spherical daughter cells (with no change in total volume). This process (**is spontaneous** / **cannot occur spontaneously** / **is poised at equilibrium**)

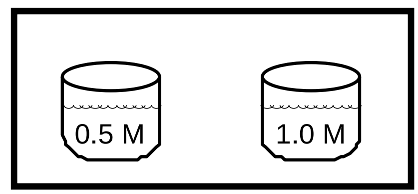


will not occur spontaneously (Chapt 5, Prob 30)

(**ΔH**, **ΔS**, **ΔG**, **ΔE**) implies constant pressure.

ΔH, ΔG

Two solutions of sucrose (in water) are placed in an isolated, closed container, under 1 atm of air. Which of the following will occur with time?



the solution in the left container will decrease in volume relative to the right

the solution in the left container will increase in volume relative to the right

the volume of both solutions will increase

the temperature of the left solution will increase relative to the right

the temperature of the right solution will increase relative to the left

The solution in the left container will decrease in volume relative to the right (Chapt 5, Prob 31)

The volume per mole of solid $MgCl_2$ is about 40 mL mol^{-1}. The partial molal volume of $MgCl_2$ in dilute aqueous solution is less than zero. Adding 1.0 g $MgCl_2$ to 100 mLwater will cause the volume of the resulting solution to be (**equal to 100 mL** / **greater than 100 mL** / **less than 100 mL**)

less than 100 mL - electrostriction

An ideal gas expands adiabatically into a vacuum. ΔE for the system is (**greater than zero / equal to zero / less than zero**).

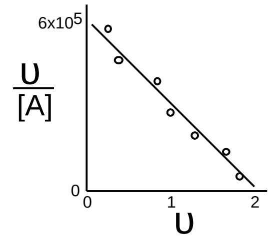
Zero - expansion against Pext = 0 yields w=0. Adiabatic means that q=0.

An ideal gas expands isothermally against an external pressure of 1 atm. ΔE for the system is (**greater than zero / equal to zero / less than zero**).

….

Zero - isothermal means that temperature doesn't change. For ideal gases, E is proportional to T

For the data plotted at right, the ligand has _**2**_ independent, identical binding sites, each with a binding constant of __**$3x10^5$**_.



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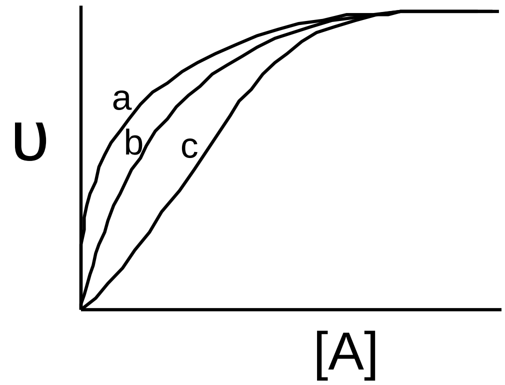
2. (15 points) For the binding of ligand A to three different macromolecules, you get the 3 plots at right. You know that the macromolecules each have 3 identical sites for binding of ligand. Describe each macromolecule-ligand interaction in *5 words or less* (each):



a)

anti-cooperative binding

b)

(identical) independent binding sites

c)

cooperative binding

3. (15 points) Phosphoric acid is multiprotic and dissociates according to the following reactions:

$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ $K_1 = 7.1 \times 10^{-3}$ M

$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$ $K_2 = 6.2 \times 10^{-8}$ M

$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$ $K_3 = 4.5 \times 10^{-13}$ M

If you know that the total concentration of all phosphoric acid species is 0.10 M at equilibrium, you can calculate (exactly) the concentrations of the five unknowns above.

Write the independent equations which you need to solve the above situation exactly (don't actually try to solve the problem, merely write the equations).

At first glance, you will assume that we will need five independent equations. Charge balance means that we need also to know [OH$^-$], so six equations are required.

From the equilibra, 3 equations:

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \qquad K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \qquad K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

From mass balance:

$$0.10M = [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

From charge balance:

$$[H^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-]$$

From water dissociation:

$$K_w = 10^{-14} = [H^+][OH^-]$$

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For the following questions, answer in the space provided. Show your work clearly and completely, but show only the relevant work. Use the back for scratch.

4. (20 points) In living biological cells, the concentration of sodium ions inside the cell is kept at a lower concentration than the concentration outside the cell, because sodium ions are actively transported from the cell.

See Chapter 5, Problem 6.

a) Consider the following process at 37°C and 1 atm

1 mol NaCl (0.05 M inside) → 1 mol NaCl (0.20 M outside)

Write an expression for the free energy change for this process in terms of activities. Define all symbols used.

Note that ΔG°=0, so $\Delta G = RT\ln\left(\frac{a_{Na^+}^{out}\, a_{Cl^-}^{out}}{a_{Na^+}^{in}\, a_{Cl^-}^{in}}\right)$

The activities are of the specified ions, on the inside or on the outside, as indicated.
For transport in the presence of a membrane potential, you could add +ZFV

b) Calculate ΔG for the process. You may approximate the activities by the concentrations. Will the process proceed spontaneously?

$$\Delta G = RT\ln\left(\frac{(0.20M)(0.20M)}{(0.05M)(0.05M)}\right) = (8.314\,JK^{-1}mol^{-1})(310K)\ln(16) = 7.15\ kJ\,mol^{-1}$$

c) Calculate ΔG for the process in a very leaky cell (equal activities of NaCl inside and outside the cell).

Activities are all the same (x) $\Delta G = RT\ln\left(\frac{x\,x}{x\,x}\right) = 0$

d) Calculate ΔG for the process at equilibrium

$$\Delta G_{equilib} = 0$$

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e) For the hydrolysis of ATP to ADP in solution at 37°C, 1 atm

$$ATP + H_2O \rightarrow ADP + \text{phosphate}$$

The standard free energy is $\Delta G° = -31.0$ kJ mol^{-1} (assume that this is the same at 25°C and at 37°C). The free energy of this reaction can be used to power the sodium-ion pump. For a ratio of ATP to ADP of 10, what must be the concentration of phosphate to obtain –40 kJ mol^{-1} for the hydrolysis ? Assume all activity coefficients are 1.

$$\Delta G = \Delta G° + RT\ln\frac{[ADP][Pi]}{[ATP]}$$

$$e^{\frac{\Delta G - \Delta G°}{RT}} = \frac{[ADP][Pi]}{[ATP]}$$

$$[Pi] = \frac{[ATP]}{[ADP]}e^{\frac{\Delta G - \Delta G°}{RT}} = 10e^{\frac{(-40\ kJ\ mol^{-1})-(-31\ kJ\ mol^{-1})}{(0.008314\ kJ\ K^{-1}\ mol^{-1})310\,K}} = 10e^{-3.49} = 0.304\,M$$

5. (20 points) We just saw that for the hydrolysis of ATP to ADP in solution at 25°C, 1 atm

$$ATP + H_2O \rightarrow ADP + \text{phosphate}$$

the standard free energy is $\Delta G° = -31.0$ kJ mol^{-1}.

a) Calculate ΔG for the reaction when [ATP] = 10^{-2} M, [ADP] = 10^{-4} M, and [phosphate] = 10^{-1} M.

$$\Delta G = \Delta G° + RT\ln\frac{[ADP][Pi]}{[ATP]}$$

$$\Delta G = (-31.0\ kJ\ mol^{-1}) + (0.008314\ kJ\ K^{-1}\ mol^{-1})(298K)\ln\frac{(10^{-4}\,M)(10^{-1}\,M)}{(10^{-2}\,M)}$$

$$\Delta G = (-31.0\ kJ\ mol^{-1}) + (-17.1\ kJ\ mol^{-1}) = -48.1\ kJ\,mol^{-1}$$

b) Calculate the maximum available work under these conditions when 1 mole of ATP is hydrolyzed (for example, by muscle contractions).

48.1 kJ mol^{-1}

c) Over what maximal vertical distance could a weight of 10 g be moved (against gravity)?

$$w = mg\Delta h$$

$$\Delta h = \frac{w}{mg} = \frac{48.1\ kJ}{(10\ g)(9.807\ m\,s^{-2})}\ \frac{kg\ m^2\ s^{-2}}{J}\ \frac{10^3 J}{kJ}\ \frac{10^3 g}{kg} = 4.90x10^5\,m$$

Does this answer look like a lot? Remember that a mole is a lot! A typical cell has MUCH less than a mole of ATP in it…

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