$\qquad$

## 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 (might be different / are identical ) .

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

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

A system is set up with a solution (in water) of 1 M sucrose separated from pure water by a membrane permeable only to water (see diagram at right). The entire system is sealed under 1 atm pressure and has just been set up (equilibrium has not yet been established).


Which of the following statements are/is true:
the activity of water on side $A$ is greater than the activity of water on side $B$ the activity of water on side $A$ equals 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 $A$

For the transfer of a small amount of water through the membrane from side A to side B (at constant T and P ), $\Delta \mathrm{G}$ is (less than zero / equal to zero / greater than zero).

For the transfer of a small amount of water through the membrane from side A to side B (at constant T and P ), $\Delta \mathrm{H}$ is (less than zero / equal to zero / greater than zero).

For the transfer of a small amount of water through the membrane from side A to side B (at constant T and P ), $\Delta \mathrm{S}$ is (less than zero / equal to zero / greater than zero).

A spherical cell $1 \mu \mathrm{~m}$ 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)
$\qquad$
$(\Delta \mathbf{H}, \Delta \mathbf{S}, \Delta \mathbf{G}, \Delta \mathbf{E})$ implies constant pressure.

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 volume per mole of solid $\mathrm{MgCl}_{2}$ is about $40 \mathrm{~mL} \mathrm{~mol}{ }^{-1}$. The partial molal volume of $\mathrm{MgCl}_{2}$ in dilute aqueous solution is less than zero. Adding $0.5 \mathrm{~g} \mathrm{MgCl}_{2}$ to 50 mL water will cause the volume of the resulting solution to be (equal to $\mathbf{5 0} \mathbf{~ m L}$ / greater than $\mathbf{5 0} \mathbf{~ m L}$ / less than 50 mL )

An ideal gas expands adiabatically into a vacuum. $\Delta \mathrm{E}$ for the system is (less than zero / equal to zero / greater than zero).

An ideal gas expands isothermally against an external pressure of $1 \mathrm{~atm} . \Delta \mathrm{E}$ for the system is (greater than zero / equal to zero / less than zero).

For the data plotted at right, the ligand has $\qquad$ independent, identical binding sites, each with a binding constant of $\qquad$ .

$\qquad$
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)

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

$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{PO}_{4} \rightarrow \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} & \mathrm{K}_{1}=7.1 \times 10^{-3} \mathrm{M} \\
\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightarrow \mathrm{H}^{+}+\mathrm{HPO}_{4}^{2-} & \mathrm{K}_{2}=6.2 \times 10^{-8} \mathrm{M} \\
\mathrm{HPO}_{4}^{2-} \rightarrow \mathrm{H}^{+}+\mathrm{PO}_{4}^{3-} & \mathrm{K}_{3}=4.5 \times 10^{-13} \mathrm{M}
\end{array}
$$

If you know that the total concentration of all phosphoric acid species is 0.05 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).
$\qquad$
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.
a) Consider the following process at $37^{\circ} \mathrm{C}$ and 1 atm

$$
1 \mathrm{~mol} \mathrm{NaCl}(0.05 \mathrm{M} \text { inside }) \rightarrow 1 \mathrm{~mol} \mathrm{NaCl}(0.25 \mathrm{M} \text { outside })
$$

Write an expression for the free energy change for this process in terms of activities. Define all symbols used.
b) Calculate $\Delta \mathrm{G}$ for the process. You may approximate the activities by the concentrations. Will the process proceed spontaneously?
c) Calculate $\Delta \mathrm{G}$ for the process in a very leaky cell (equal activities of NaCl inside and outside the cell).
d) Calculate $\Delta \mathrm{G}$ for the process at equilibrium
e) For the hydrolysis of ATP to ADP in solution at $37^{\circ} \mathrm{C}, 1 \mathrm{~atm}$

$$
\text { ATP }+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{ADP}+\text { phosphate }
$$

The standard free energy is $\Delta \mathrm{G}^{\circ}=-31.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (assume that this is the same at $25^{\circ} \mathrm{C}$ and at $37^{\circ} \mathrm{C}$ ). The free energy of this reaction can be used to power the sodium-ion pump. For a ratio of ATP to ADP of 5, what must be the concentration of phosphate to obtain $-40 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for the hydrolysis? Assume all activity coefficients are 1.
5. (20 points) We just saw that for the hydrolysis of ATP to ADP in solution at $25^{\circ} \mathrm{C}, 1 \mathrm{~atm}$

$$
\mathrm{ATP}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{ADP}+\text { phosphate }
$$

the standard free energy is $\Delta \mathrm{G}^{\circ}=-31.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$.
a) Calculate $\Delta \mathrm{G}$ for the reaction when $[\mathrm{ATP}]=10^{-1} \mathrm{M},[\mathrm{ADP}]=10^{-4} \mathrm{M}$, and [phosphate] $=10^{-1} \mathrm{M}$.
b) Calculate the maximum available work under these conditions when 1 mole of ATP is hydrolyzed (for example, by muscle contractions).
c) Over what maximal vertical distance could a weight of 5 g be moved (against gravity)?

