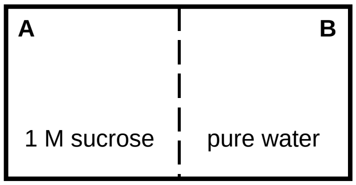
Chem 471 (1999) Exam #2 *Extra* **Name**:____________________________

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

1. (40 points) Circle ALL correct answers, or fill in the blank, as appropriate.

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). Assume ideal solutions.



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 greater than 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 water on side A equals the activity of sucrose on side A

(Chapt 5, Prob 28) **activity of water on side A is less than 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) **greater than zero**

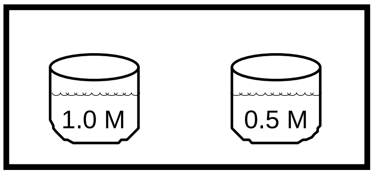
For the transfer of a small amount of water through the membrane from side A to side B (at constant T and P), ΔH is (**less than zero** / **equal to zero / greater than zero**).

(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**).

(Chapt 5, Prob 28) **less than zero**

Two ideal 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?



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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 increase in volume relative to the right
(Chapt 5, Prob 31)

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

Less than **one**

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 5.0 g $MgCl_2$ to 500 mLwater will cause the volume of the resulting solution to be (**equal to 500 mL** / **greater than 500 mL** / **less than 500 mL**)

less than 500 mL - electrostriction

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

Less than zero. The system does work on the surroundings

An ideal gas expands adiabatically against an external pressure of 1 atm. The temperature of the gas will (**decrease / remain constant / increase**).

Decrease. The system does work on the surroundings, so E_{system} decreases, therefore T decreases.

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**).

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

2. (20 points) Phosphoric acid is multiprotic and dissociates according to the following reactions:

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

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

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

If you know that the total concentration of all phosphoric acid species is 0.01 M at equilibrium, you can calculate (exactly) the concentrations of the unknown species, including hydroxide ion.

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a) What are the unknowns here?
$[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$, $[PO_4^{3-}]$, $[H^+]$, $[OH^-]$

b) Write the independent equations which you need to solve for the unknowns exactly, including consideration of hydroxide ion (don't actually try to solve the problem, merely write the equations).
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:

$$0.05M = [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

From charge balance:

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

From water dissociation:

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

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.

3. (40 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 (0.25 M outside)

with a membrane potential of 150 mV (positive inside).

Write an expression for the free energy change for this process in terms of activities and the membrane potential. 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, one would add +ZFV, but in this case, one positive and one negative ion are being transported, so that the net Z=0.

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

$$\Delta G = RT \ln\left(\frac{(0.25M)(0.25M)}{(0.05M)(0.05M)}\right) = (8.314\, JK^{-1}mol^{-1})(310K)\ln(25) = 8.30 kJ\ mol^{-1}$$

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c) Assume that the activity coefficients more accurately reflect reality. Explain what effect this will have on the value for ΔG you just calculated.

To a first approximation, the activity coefficients inside and outside might be expected to be the same, and so should cancel out of the ratio. However, the activity coefficients for Na+ and Cl– will vary with concentration.

d) 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 $\Delta G° = -31.0\ \text{kJ mol}^{-1}$. The free energy of this reaction can be used to power the sodium-ion pump. For a ratio of ATP to ADP of 20, what must be the concentration of phosphate to obtain $-20\ \text{kJ mol}^{-1}$ for the hydrolysis ? Assume all activity coefficients are 1.

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

$$[Pi] = \frac{[ATP]}{[ADP]} e^{\frac{\Delta G - \Delta G°}{RT}} = (20) e^{\frac{(-20\ kJ\ mol^{-1}) - (-31\ kJ\ mol^{-1})}{(0.008314\ kJ\ K^{-1}\ mol^{-1})(310\ K)}} = (20) e^{4.268} = 1428\,M$$

Yikes. Not very realistic question…

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