

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

1. (40 points) Circle ALL correct answers, fill-in, or provide a short answer, as appropriate:

a) For a process that can be carried out by either a reversible or an irreversible path, the change in (**H, P, T, V, q, E, w**) can be different for the two paths.

q, w - The others are all state variables and so are path independent

b) For the mixing of benzene (a nonpolar solvent) and water, the overall entropy of the system will (**increase / decrease / remain unchanged**).

Decrease - the hydrophobic effect

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

Less than zero - adiabatic means $q=0$, while the expansion does work on the surroundings, or **negative** work on the system. Energy is removed from the system.

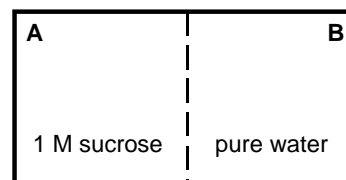
d) According to the 2nd law of thermodynamics, a spontaneous process, such as a balloon filled with a hot gas cooling to the surroundings at constant pressure, will always occur (**adiabatically, reversibly, irreversibly, without work done**).

Irreversibly - a spontaneous expansion against a constant pressure - textbook.

e) To return the system (balloon, in the previous question) to its initial state requires from the surroundings an expenditure of entropy whose magnitude is (**greater than, equal to, less than**) that which is gained during the spontaneous process.

Greater than - if equal to, then the net change in entropy of the universe would be 0, but at least a part of the process was irreversible, so the net change in entropy must be greater than 0.

f) A system is initially 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).



Prior to the establishment of equilibrium, which of the following statements are is/true:

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

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

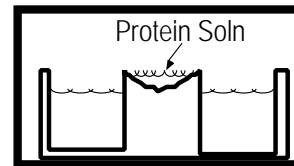
the activity of water on side A is less than the activity of water on side B

(Chapt 5, Prob 28)

g) Consider two aqueous solutions containing different amounts of the same nonvolatile solute. At exactly the same temperature, solution A has a higher vapor pressure than solution B. The concentration of solute in solution A is (**greater than / identical to / less than**) the concentration of solute in solution B.

less than (related to Chapt 5, Prob 16)

h) In protein crystallography, one desires to slowly increase the concentration of protein (and of nonvolatile solutes such as salt or ethylene glycol), to the point that the protein is no longer fully soluble and crystallizes. A typical setup for achieving this is shown at right. The protein sits in a small well, surrounded by a larger volume of solution. The solution in the larger volume contains no protein, but a higher concentration (1 M or so) of the nonvolatile solutes than in the protein well. The entire setup is sealed in a small volume container. With time, the volume of the protein solution will (**increase / stay the same / decrease**).



Decrease. The activity of water is lower in the larger volume, so water will flow (via gas phase) from the protein solution to the larger volume solution.

i) 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 mL water 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. Since the partial molal volume is less than zero, the volume will decrease. (we talked about this as due to electrostriction)

j) Autoclaves are used in biochemistry to sterilize liquid media. Briefly, the samples are brought to temperatures near 120°C and pressures greater than 1 atm. Explain the advantages of high pressure and high temperature.

raising the temperature both shifts the equilibrium for most proteins toward the unfolded state and speeds the process (thereby killing bacteria). Increased pressure is necessary because at 1 atm, the solution would vaporize at 120°C . Increasing the pressure raises the boiling point.

k) Hexachlorobenzene, C_6Cl_6 , is a solid compound that is somewhat volatile, but only slightly soluble in water. It also binds to proteins. A protein is added to the aqueous solution and equilibrium with solid C_6Cl_6 is established. The vapor pressure of C_6Cl_6 for the aqueous solution (**increases / decreases / stays the same**)

stays the same (From Chapter 5, Problem 20)

Gas	Molec weight (g/mol)	Collisional diameter (\AA)
N_2	28.0	140
Xe	131.3	130

l) At 298 K and 1 atm, the root mean square velocity of N_2 is (**greater than / equal to / less than**) that of Xe.

$$\text{greater than } \frac{\sqrt{\langle u_{N_2}^2 \rangle}}{\sqrt{\langle u_{Xe}^2 \rangle}} = \frac{\sqrt{\frac{3RT}{M_{N_2}}}}{\sqrt{\frac{3RT}{M_{Xe}}}} = \frac{\sqrt{\frac{1}{M_{N_2}}}}{\sqrt{\frac{1}{M_{Xe}}}} = \sqrt{\frac{M_{Xe}}{M_{N_2}}} = 2.2$$

m) At 298 K and 1 atm, the number of collisions each N_2 encounters per second is (**greater than / equal to / less than**) that of Xe.

$$\text{greater than } \frac{z_{N_2}}{z_{Xe}} = \frac{4\sqrt{\pi} \frac{N}{V} \sigma_{N_2}^2 \sqrt{\frac{RT}{M_{N_2}}}}{4\sqrt{\pi} \frac{N}{V} \sigma_{Xe}^2 \sqrt{\frac{RT}{M_{Xe}}}} = \frac{\sigma_{H_2}^2 \sqrt{\frac{1}{M_{N_2}}}}{\sigma_{Xe}^2 \sqrt{\frac{1}{M_{Xe}}}} = \frac{\sigma_{N_2}^2}{\sigma_{Xe}^2} \sqrt{\frac{M_{Xe}}{M_{N_2}}}$$

$$\frac{z_{N_2}}{z_{Xe}} = \frac{140}{130} \sqrt{\frac{131.3}{28.0}} = 2.5$$

n) At 298 K and 1 atm, the translational kinetic energy of 1 mol of N_2 is (**greater than / equal to / less than**) that of 1 mol of Xe.

equal to (kinetic energy depends *only* on Temperature and the number of moles)

o) At 298 K, the translational kinetic energy of 1 mol of N_2 at 0.1 atm is (**greater than / equal to / less than**) that of 1 mol of N_2 at 10 atm.

equal to (kinetic energy depends *only* on Temperature and the number of moles)

p) The units for a second order rate constant are ($s^{-1} / M s^{-1} / M^{-1} s^{-1}$).

$M^{-1} s^{-1}$

q) Given the mechanism for a reaction, one (**can / might be able to / cannot**) deduce the rate law.

can

r) The kinetics of a reaction are observed to be first order in A and first order in B. Select the mechanism(s) below which is/are consistent with this observation.

(a)	(b)	(c)	(d)	(e)
$A + B \rightarrow C$	$A \xrightarrow{\text{slow}} A^* \xrightarrow{\text{fast}} A^* + B \rightarrow C$	$B \xrightarrow{\text{slow}} B^* \xrightarrow{\text{fast}} A + B^* \rightarrow C$	$B \xrightarrow{\text{fast}} B^* \xrightarrow{\text{slow}} A + B^* \rightarrow C$	$A \xrightarrow{\text{fast}} A^* \xrightarrow{\text{slow}} A^* + B \rightarrow C$

a, d, and e

s) The following are assumptions necessary in deriving Michaelis-Menten kinetics:

All species at steady state

Intermediate at steady state

Enzyme in excess

Enzyme in fast equilibrium with substrate

Substrate in excess

Product concentration low

Intermediate at steady state, Substrate in excess, Product concentration low

t) Adding a small amount of ethanol to water, leads to:

a lowering of the boiling point of the solution

a lowering of the melting point of the solution

an increase in the activity of water

no change in the activity of water

an increase in the vapor pressure of water

a lowering of the boiling point of the solution (Either answer OK)

a lowering of the melting point of the solution (Yes)

an increase in the activity of water (No, water activity goes down)

no change in the activity of water (No, water activity goes down)

an increase in the vapor pressure of water (No, water activity goes down)

2. (10 points) The solubilities of two amino acids in two solvents at 25°C are given at right. They are the concentrations present in saturated solutions.

	In water	In ethanol
Glycine	3.09 M	0.000404 M
Valine	0.60 M	0.00132 M

Problem 21, Chapter 5

- a) Calculate the standard free energy of transfer, μ° , of 1 mol of glycine from the solid to the aqueous solution at 25°C. The standard state for the solids is the pure solid; the standard state in the solution corresponds to $a=1$ extrapolated from a dilute solution; the molarity scale is used. You may consider the solutions to be ideal.

$$G = G^\circ + RT \ln Q \quad \mu = \mu^\circ + RT \ln Q$$

$$\text{For } \mu = 0 = \mu^\circ + RT \ln Q \text{ then } \mu^\circ = -RT \ln Q$$

$$\mu^\circ = -RT \ln \frac{a_{Gly}^{aqu}}{a_{Gly}^{solid}} = - \frac{8.314 J}{mole K} (298 K) \ln \frac{3.09}{1} = -2.80 \text{ kJ mol}^{-1}$$

- b) Calculate the standard free energy of transfer, μ° , of 1 mol of glycine from ethanol to the aqueous solution at 25°C.

$$\mu^\circ = -RT \ln \frac{a_{Gly}^{aqu}}{a_{Gly}^{Ethanol}} = - \frac{8.314 J}{mole K} (298 K) \ln \frac{3.09}{4.04 \times 10^{-4}} = -22.2 \text{ kJ mol}^{-1}$$

- c) Assume that the effects of the backbone and side chain are simply additive (glycine essentially has no side chain), and calculate the standard free energy of transfer of 1 mol of the (CH₃)CH– side chain of valine from water to ethanol at 25°C.

First calculate the energy of transfer of valine from water to ethanol

$$\mu^\circ = -RT \ln \frac{a_{Val}^{ethanol}}{a_{Val}^{aqu}} = - \frac{8.314 J}{mole K} (298 K) \ln \frac{1.32 \times 10^{-3}}{0.60} = +15.2 \text{ kJ mol}^{-1}$$

But that's for the whole amino acid. We want the number corresponding to only the side chain. The problem told us that Gly is simply the non-side chain part of amino acids, so we can subtract its contribution. Part (b) gives us what we need here. The energy of transfer from water to ethanol is $-(-22.2 \text{ kJ mol}^{-1}) = +22.2 \text{ kJ mol}^{-1}$.

So μ° for transfer of the Val side chain (only) from water to ethanol is:

$$15.2 - 22.2 = -7.0 \text{ kJ mol}^{-1}.$$

- d) Ethanol is considered by some to mimic the interior of a protein. Will the mutation of a glycine to a valine in the interior of a protein favor the folding of the protein if interaction with the solvent is the dominant effect? Explain.

The answer to part (c) tells us that the transfer of the hydrophobic Val side chain from water to a less polar environment is in fact **favorable**. Therefore mutation of Gly to Val, where the side chain is in the interior of the protein, should favor folding of the protein. Effects like this have in fact been observed.

Chem 471 (1999) Final Exam Name: _____

3. (10 points) Calculate the work of expansion of an ideal gas from 1L to 4 L under the following conditions (a and b):

- (a) The gas expands against a constant $P_{\text{ext}} = 1\text{atm}$ (ie., you suddenly remove blocks holding the piston); the initial temperature is 25°C .

Note that unless otherwise stated, when asked for work, it is the work done ON the system.

$$w = - P_{\text{ext}} dV = -P_{\text{ext}} \Delta V = -P_{\text{ext}}(V_2 - V_1) = -1\text{atm}(4 - 1)\text{l} = -3\text{l} \cdot \text{atm} = -304\text{J}$$

- (b) The expansion is done reversibly, at a constant temperature of 25°C . The final pressure is 1 atm.

$$w = -nRT \ln \frac{V_2}{V_1} = -P_2 V_2 \ln \frac{V_2}{V_1} = -4\text{l} \text{ atm} \ln \frac{4}{1} = -5.55\text{l} \text{ atm} = -562\text{J}$$

4. (5 points) In general, native proteins are in equilibrium with denatured forms

For ribonuclease (a protein), the following concentration data for the two forms were experimentally determined for a total protein concentration of $1 \times 10^{-3}\text{ M}$.

Temperature ($^\circ\text{C}$)	Native	Denatured
50	$9.97 \times 10^{-4}\text{ M}$	$2.57 \times 10^{-6}\text{ M}$
100	$8.60 \times 10^{-4}\text{ M}$	$1.40 \times 10^{-4}\text{ M}$

Determine H° for the denaturation reaction, assuming it to be independent of temperature.

(T,S,&W Ch 4 Pb 16) Native Denatured $K = (\text{D})/(\text{N})$

$$K(T_1 = 50^\circ\text{C}) = \frac{2.57 \times 10^{-6}}{9.97 \times 10^{-4}}, \quad K(T_2 = 100^\circ\text{C}) = \frac{1.4 \times 10^{-4}}{8.6 \times 10^{-4}}$$

$$\ln \frac{K_2}{K_1} = \frac{-H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad H^\circ = -R \ln \frac{K_2}{K_1} \frac{1}{\frac{1}{T_2} - \frac{1}{T_1}}^{-1}$$

$$H^\circ = \frac{-8.314\text{J}}{\text{moleK}} \ln \frac{1.4 \times 10^{-4}}{8.6 \times 10^{-4}} \times \frac{9.97 \times 10^{-4}}{2.57 \times 10^{-6}} \frac{1}{\frac{1}{373\text{K}} - \frac{1}{323\text{K}}}^{-1}$$

$$H^\circ = 83\text{kJ} / \text{mole}$$

Chem 471 (1999) Final Exam

Name: _____

5. (5 points) Consider the kinetic mechanism shown at right.

a) Place A, B, C, D, E, and F into the following categories:

Reactants:

B, C

Intermediates:

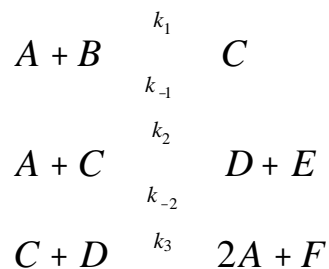
D, (C accepted, but not really)

Products:

E, F

Catalysts:

A

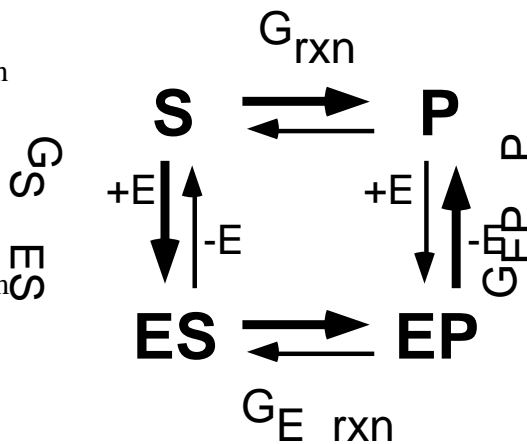


b) Complete the following

$$\frac{dC}{dt} = k_1AB - k_{-1}C - k_2AC + k_{-2}DE - k_3CD$$

$$\frac{dA}{dt} = -k_1AB + k_{-1}C - k_2AC + k_{-2}DE + 2k_3CD$$

6. (10 points) Consider the set of reactions shown at right. The top reaction shows the uncatalyzed reaction of S being converted to P, with equilibrium mildly favoring P. In the other reactions, S first binds to enzyme (E) and then S is converted (more *rapidly* than without E) to P. Finally, the product (P) is released from the enzyme. The G 's for each step are shown in the plot, written in the direction of the thicker arrow, in each case.



Note that this is a thermodynamic cycle. It tells you a lot. However, it does not say anything directly about RATES, only about EQUILIBRIA. Your answers should reflect that!

- a) Assuming (and this *is* an assumption) that the energetics of S \rightleftharpoons P do not change while both are bound to the enzyme (in other words, $G_{rxn} = G_{E_rxn}$), if substrate binds *extremely* tightly to the enzyme ($G_{S_ES} \ll 0$), what can you say about product release from the enzyme? Is this desirable in an enzyme?

Product must also bind extremely tightly to the enzyme. We know that:

$$G_{rxn} = G_{S_ES} + G_{E_rxn} + G_{EP_EP}$$

$$0 = G_{S_ES} + G_{EP_EP}$$

$$G_{EP_EP} = -G_{S_ES}$$

In other words, $G_{EP_P} \gg 0$

This is NOT good. If product binds too tightly, the reaction will not turn over. Each enzyme will only be able to catalyze one round of the reaction.

- b) This time, assuming only that substrate binds *extremely* tightly to the enzyme ($G_{S_ES} \ll 0$), but also that product is not bound tightly by the enzyme, what can you say about another step in the process? Is this desirable in an enzyme?

"product is not bound tightly by the enzyme" means $G_{EP_P} < 0$

Remembering:

$$G_{rxn} = G_{S_ES} (\ll 0) + G_{E_rxn} + G_{EP_EP} (< 0)$$

$$G_{E_rxn} = G_{rxn} - G_{S_ES} (\ll 0) - G_{EP_EP} (< 0)$$

$$G_{E_rxn} = G_{rxn} + [\text{some reasonably big positive number}]$$

In other words, the reaction of S \rightleftharpoons P is much less favorable while bound to the enzyme. Probably not good. Unlikely to proceed very fast.

Both of these situations illustrate that the enzyme does not want to bind its substrate too tightly. A conclusion we might not have reached without careful consideration of thermodynamic cycles. This is, indeed, true.