Chemistry 425
Fall 2007
Practice Exam 1 Solutions

Name: ________________________

Instructions:

Please do not start working on the exam until you are told to begin. Check the exam to make sure that it contains exactly 6 different pages, including this one and a periodic table on the last page.

Some useful constants and equations:

\[ R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \quad 101.3 \text{ J} = 1 \text{ L atm} \]

\[ \Delta U = q + w \quad \Delta H = C_p \Delta T \quad \Delta S = \frac{q_{rev}}{T} \]

\[ H = U + PV \]

\[ \Delta_r G = \Delta_r G^\circ + RT \ln Q \]

\[ \ln \left( \frac{K_2}{K_1} \right) = \left( \frac{\Delta_r H^\circ}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{(van’t Hoff equation)} \]

\[ \ln \left( \frac{P_2}{P_1} \right) = \left( \frac{\Delta_{vap} H}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{(Clausius-Clapeyron equation)} \]

\[ \frac{Y}{[L]} = \frac{n}{K} - \frac{Y}{K} \quad \text{(Scatchard equation)} \]

\[ \log \left( \frac{f}{1-f} \right) = N \log [L] - \log K \quad \text{(Hill equation)} \]

\[ f = c - p + 2 \quad \text{(phase rule)} \]

A periodic table is provided on the last page of the exam.
Part 1. Write the letter of the answer which best satisfies each statement or question in the blank at the left (3 points each).

B 1. \( \Delta G = (A) \Delta H + T \Delta S (B) \Delta H - T \Delta S (C) -\Delta H + T \Delta S (D) -\Delta H - T \Delta S \)

C 2. Which of the following is an intensive property?
   (A) mass (B) volume (C) chemical potential (D) enthalpy

B 3. The first law of thermodynamics tells us that
   (A) the entropy of the universe is increasing (B) energy is conserved (C) enthalpy decreases (D) work is path independent

D 4. For a one-component ideal gas, how many independent intensive properties can be varied while maintaining an ideal gas at equilibrium?
   (A) –1 (B) 0 (C) 1 (D) 2

B 5. In an equilibrium dialysis experiment,
   (A) ligand molecules cannot pass through the membrane
   (B) protein molecules cannot pass through the membrane
   (C) both protein and ligand pass through the membrane
   (D) the membrane separates protein from ligand at equilibrium

A 6. To measure the change in internal energy of a reaction, \( \Delta U \), I could use a
   (A) constant volume calorimeter (B) constant pressure calorimeter (C) equilibrium dialysis (D) mass spectrometer

A 7. Which of the following is not true about the reaction \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \)
   (A) \( \Delta S > 0 \) (B) \( \Delta H^\circ(\text{H}_2(g)) = 0 \) (C) \( \Delta H^\circ = 2\Delta H^\circ(\text{NH}_3(g)) \) (D) \( \Delta G^\circ = 2\Delta G^\circ(\text{NH}_3(g)) \)

D 8. An exothermic reaction comes to equilibrium. If I want to increase the concentration of product molecules, which of the following would I try?
   (A) raise pressure (B) raise temperature (C) lower pressure (D) lower temperature

C 9. For which of the following phase transitions would I expect \( \Delta H \) to be most different from \( \Delta U \)?
   (A) solid -> liquid (B) liquid -> solid (C) solid -> gas (D) diamond -> graphite

D 10. Consider a two-component ideal gas. If we want to increase the partial pressure of each component, we should, while keeping other variables constant,
   (A) increase \( V \) (B) decrease total \( P \) (C) decrease \( T \) (D) increase \( n \)
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. Consider $6O_2(g) + C_6H_{12}O_6(s) \rightarrow 6CO_2(g) + 6H_2O(l)$ at $T = 273$ K and $p = 1.00$ atm. Assuming $O_2$ to be an ideal gas, what is the volume of $O_2(g)$ required to react with 0.010 kg glucose ($C_6H_{12}O_6(s)$)?

$$V_{\text{oxygen}} = n_{\text{oxygen}} \frac{RT}{p} \quad \text{and} \quad n_{\text{oxygen}} = 6n_{\text{glucose}}$$

$$n_{\text{glucose}} = 1.0 \times 10^1 \text{ g/(Mol. Wt. glucose)} = 1.0 \times 10^1 \text{ g/(180.0 g/mol)} = 5.6 \times 10^{-2} \text{ mol}$$

$$V_{\text{oxygen}} = (3.3 \times 10^{-1} \text{ mol})(0.08206 \text{ L atm/mol K})(273 \text{ K})/1.00 \text{ atm} = 7.5 \text{ L}$$

$$V_{\text{oxygen}} = 7.5 \text{ L}$$

2. The molar heat of vaporization of ethanol is 39.3 kJ mol$^{-1}$ and its boiling point is 78.3 °C. Calculate the entropy of vaporization, $\Delta_{\text{vap}} S$, of 1.4 moles of ethanol.

At boiling point, liquid and vapor coexist in equilibrium and $\Delta_{\text{vap}} G = 0$

Then $\Delta_{\text{vap}} S = \Delta_{\text{vap}} H/T_b = (1.4 \text{ mol})(39.3 \text{ kJ mol}^{-1})(273+78.3)\text{K} = 156.6 \text{ J K}^{-1}$

$$\Delta_{\text{vap}} S = 156.6 \text{ J K}^{-1}$$

3. In an equilibrium dialysis experiment, the concentration of free ligand and bound ligand at equilibrium is $1.0 \times 10^{-5} \text{ M}$ and $6.0 \times 10^{-6} \text{ M}$, respectively, and the initial concentration of protein is $1.2 \times 10^{-5} \text{ M}$.

Assuming that there is only one binding site per protein, calculate the dissociation constant, $K_d$, for the reaction $P\text{L} \leftrightarrow P + L$.

$$[PL] = [L]_{\text{bound}} = 6.0 \times 10^{-6} \text{ M}$$

$$[P] = [P]_{\text{initial}} - [PL] = 6.0 \times 10^{-6} \text{ M}$$

$$K_d = [P][L]/[PL] \quad \text{(Note: } K_d \text{ is dimensionless, since all concentrations are divided by standard concentration of 1M.)}$$

$$K_d = 1.0 \times 10^{-5}$$
Part III. Write your answer to the problems below in the space provided. Please show all work. Partial credit will be given based on work shown. (17 points each)

1. Consider the gas phase reaction \( \text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \) at \( T = 298 \text{ K} \).
   The molar enthalpy of formation of NO is 90.35 kJ mol\(^{-1}\) and the molar Gibbs energy of formation of NO is 86.70 kJ mol\(^{-1}\).

   (a) Given that at equilibrium the partial pressure of \( \text{N}_2 \) and \( \text{O}_2 \) are 0.8 and 0.2 bar, respectively, what is the partial pressure of NO? (12 points)

   \[ K = \frac{P_{\text{NO}}^2}{P_{\text{N}_2}P_{\text{O}_2}} = \exp(-\Delta_r G^\circ /RT) \]

   \[ \Delta_r G^\circ = 2 \Delta_f G^\circ (\text{NO}) = 173.4 \text{ kJ mol}^{-1} = 1.734 \times 10^5 \text{ J mol}^{-1} \]

   \[ K = e^{-173400/(8.31451)(298)} = 4.05 \times 10^{-31} \]

   \[ P_{\text{NO}} = (K P_{\text{N}_2} P_{\text{O}_2})^{1/2} = ((4.05 \times 10^{-31})(0.2)(0.8))^{1/2} = 2.5 \times 10^{-16} \text{ bar} \]

   Very little formed at \( T = 298 \text{K} \)

   

   (b) Suppose initially the partial pressures of \( \text{N}_2 \) and \( \text{O}_2 \) are 0.6 and 0.1 bar, respectively. Calculate the reaction quotient, \( Q \), assuming that the total pressure is the same as it is at equilibrium. Will products or reactants form as the mixture approaches equilibrium? (5 points)

   \[ Q = \frac{P_{\text{NO}}^2}{P_{\text{N}_2}P_{\text{O}_2}} \]

   At equilibrium, \( P = P_{\text{NO}} + P_{\text{N}_2} + P_{\text{O}_2} = 2.5 \times 10^{-16} \text{ bar} + 0.8 \text{ bar} + 0.2 \text{ bar} = 1.0 \text{ bar} \)

   Initially, \( P_{\text{NO}} = P - (P_{\text{N}_2} + P_{\text{O}_2}) = 1.0 \text{ bar} - 0.6 \text{ bar} - 0.1 \text{ bar} = 0.3 \text{ bar} \)

   Then for the initial conditions, \( Q = (0.3)^2/(0.6)(0.1) = 1.5 \)

   Since \( Q > K \), this favors formation of reactants as the mixture approaches equilibrium.
A polypeptide can exist in either a helical structure or the “random coil” structure. The equilibrium constant for the equilibrium reaction of the helix to the random coil is $3.50 \times 10^{-4}$ at $40 \, ^oC$ and $6.60 \times 10^{-4}$ at $60 \, ^oC$.

(a) Calculate the standard enthalpy of this reaction. (12 points)

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^o}{R}(1/T_1 - 1/T_2)$$

$$\ln \left( \frac{3.50 \times 10^{-4}}{6.60 \times 10^{-4}} \right) = \frac{\Delta_r H^o}{8.31451 \text{ J mol}^{-1} \text{K}^{-1}} \left( \frac{1}{333 \text{ K}} - \frac{1}{313 \text{ K}} \right)$$

$$\Delta_r H^o = 2.75 \times 10^4 \text{ J mol}^{-1}$$

(b) Calculate the standard entropy of this reaction. (5 points)

Using value of $K$ at either temperature gives same $\Delta_r S^o$. Let’s choose $K$ at $40 \, ^oC$.

$$\Delta_r G^o = -RT \ln K = -(8.31451 \text{ J mol}^{-1} \text{K}^{-1})(313 \text{ K}) \ln(3.50 \times 10^{-4}) = 2.07 \times 10^4 \text{ J mol}^{-1}$$

$$\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o$$

$$\Delta_r S^o = \frac{(\Delta_r H^o - \Delta_r G^o)}{T} = 21.7 \text{ J K}^{-1} \text{ mol}^{-1}$$
Periodic Table of the Elements