

Third Hour Exam**5.111**

Write your name and your TA's name below. **Do not open the exam until the start of the exam is announced.** The exam is closed notes and closed book.

1. Read all parts of each problem. **MANY OF THE LATTER PARTS OF A PROBLEM CAN BE SOLVED WITHOUT HAVING SOLVED EARLIER PARTS.** However, if you need a numerical result that you were not successful in obtaining for the computation of a latter part, make a physically reasonable approximation for that quantity (and indicate it as such) and use it to solve the latter parts.
2. If asked for a brief explanation, just writing an equation from the equation sheet is not sufficient. You must explain the relevance of the equation to the problem.
3. Significant figure and unit usage must be correct.
4. If you don't understand what the problem is requesting, raise your hand and a proctor will come to your desk.
5. Physical constants, formulas and a periodic table are given on the last page. You may detach this page once the exam has started.

CHEMICAL EQUILIBRIUM

1. (24 points)

THERMODYNAMICS

2. (15 points)

3. (8 points)

SOLUBILITY

4. (6 points)

5. (8 points)

ACID-BASE EQUILIBRIUM

6a,b,c. (20 points)

6d. (13 points)

7. (6 points)

TOTAL

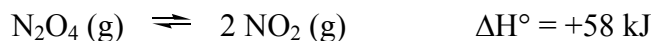
(100 points) _____

Name

TA _____

Chemical Equilibrium

1. (24 points) **Predict** the direction that the equilibrium will shift when each of the following changes occurs. **Briefly explain your answers.**



(a) $\text{NO}_2(\text{g})$ is removed at constant temperature

(i) **Circle** the most likely direction *toward products* *toward reactants* *no change*

(ii) **Briefly explain:**

When a product is removed, the reaction shifts to make more product to minimize stress.

or

When a product is removed, Q falls below K, and the reaction shifts in the forward direction since $\Delta G < 0$.

(b) the total pressure is increased by addition of $\text{N}_2(\text{g})$ at constant temperature

(i) **Circle** the most likely direction *toward products* *toward reactants* *no change*

(ii) **Briefly explain:**

If total pressure is increased, volume didn't change. If volume didn't change, partial pressure didn't change. If partial pressure didn't change, there is no shift.

(c) the volume is increased at constant temperature

(i) **Circle** the most likely direction *toward products* *toward reactants* *no change*

(ii) **Briefly explain:**

An increase in volume causes total pressure to decrease, so reaction shifts to increase pressure with 1 mole of reactant gas and 2 moles of product gas. The reaction shifts to product.

(d) the temperature is decreased

(i) **Circle** the most likely direction *toward products* *toward reactants* *no change*

(ii) **Briefly explain:**

The reaction is endothermic, so decreasing the temperature causes a shift in exothermic (reverse) direction. The stress is minimized by shifting in a direction that produces heat.

Thermodynamics

2. (15 points) **Predict** the sign of ΔH_r° for the following scenarios. **Briefly explain your answers in words. Writing an equation without explanation is not sufficient.**

(a) (5 points) A reaction in which the bonds are stronger in the products than in the reactants.

- (i) **Circle** the most likely sign of ΔH_r° *negative* *positive*
 (ii) **Briefly explain:**

If bonds are stronger in product than reactant, it won't take that much energy to break bonds of reactants and lots of energy will be released when the strong bonds are formed, so net heat released (ΔH_r° is (-))

or

$\Delta H_r = \sum H_B$ (reactants) - $\sum H_B$ (products). If bonds in products are stronger than in reactants, ΔH_r will be negative by the equation above.

(b) (5 points) A reaction that is only spontaneous at high temperatures.

- (i) **Circle** the most likely sign of ΔH_r° *negative* *positive*
 (ii) **Briefly explain:**

$$\Delta G = \Delta H - T\Delta S$$

If ΔG is negative (spontaneous) only when temperature is high, then ΔH must be positive.

(c) (5 points) The equilibrium shifts toward reactants when the temperature increases.

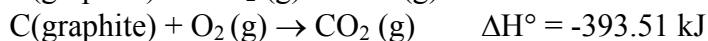
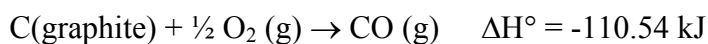
- (i) **Circle** the most likely sign of ΔH_r° *negative* *positive*
 (ii) **Briefly explain:**

Reactions shift in the endothermic direction when temperature is increased such that the added heat is used up. In this case, the reverse direction must be endothermic if an increase in temperature causes a shift in that direction, so the forward direction must be negative.

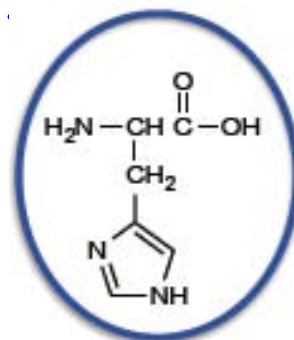
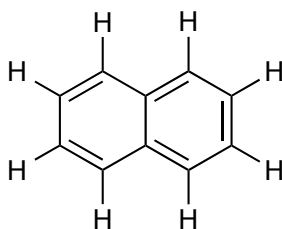
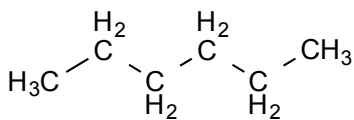
or

The equation $[\ln(K_2/K_1) = -(\Delta H/R)(1/T_2 - 1/T_1)]$ shows us that only when ΔH is negative will an increase in temperature result in $K_1 > K_2$, i.e. more reactants at higher temperatures.

Thermodynamics**3.** (8 points)**(a)** (4 points) **Calculate** the standard reaction enthalpy for the formation of CO_2 (g) from CO (g) and O_2 (g):

$$\text{CO (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)}, \text{ given that:}$$
**(b)** (4 points) Consider CO (g). Given that its ΔH_f° is -110.54 kJ/mol and its ΔG_f° is -137.16 kJ/mol , **(i)** **predict** whether CO (g) is stable or unstable with respect to decomposition into its elements under standard conditions. **(ii)** **Briefly explain your answer.****Stable**If ΔG_f° is negative, then reverse direction (decomposition) is not favored (not spontaneous) so CO is stable compared to its elements.**SOLUBILITY****4.** (6 points) **Circle** the molecule(s) that are likely to be polar and therefore water soluble.

Electronegativity values: C 2.55; H 2.20; N 3.04; O 3.44.

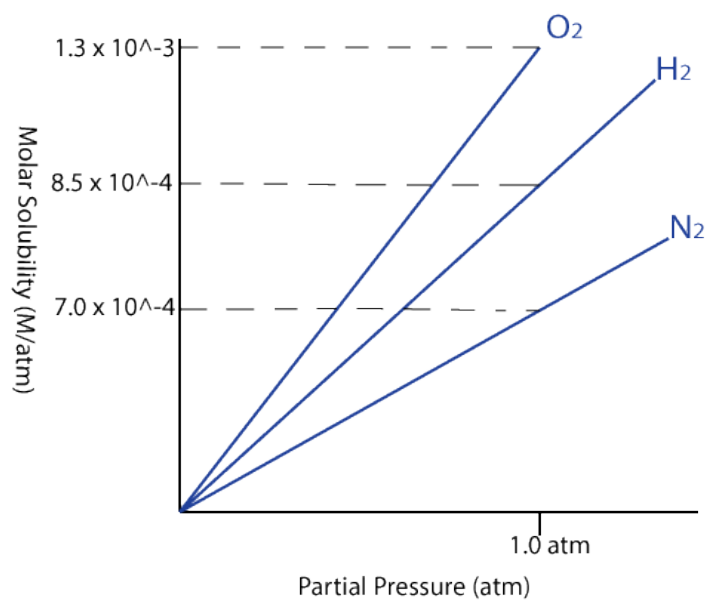


Solubility

5. (8 points) Consider the following Henry's constants for gases in water at 20°C

Gas	k_H (mol • L ⁻¹ • atm ⁻¹)
Oxygen	1.3×10^{-3}
Nitrogen	7.0×10^{-4}
Hydrogen	8.5×10^{-4}

(8 points) **Draw** a single plot with Molar Solubility (mol•L⁻¹) on the y-axis and Partial Pressure in atm on the x-axis for each of the three gases in the table above. **(i)** label the y-axis with the numbers that correspond to Molar Solubility of each gas at 1.0 atm; and **(ii)** label the curve for each gas.



ACID-BASE EQUILIBRIUM

6. (33 points) 50.00 mL of a 0.1000 M solution of weak acid CH_3COOH (aq) is titrated with a 0.1000 M solution of NaOH (aq) at 25°C . The K_a for CH_3COOH is 1.8×10^{-5} at 25°C .

(a) (12 points) **Calculate** the pH of the solution after addition of 20.00 mL of NaOH titrant. You can assume that $[\text{H}_3\text{O}^+]$ at equilibrium satisfies the 5% rule without checking. Show your work.

$$\text{pH} = 4.57$$

(b) (5 points) **Calculate** the pH at the half-equivalence (half-stoichiometric) point.

$$\text{p}K_a = 4.74$$

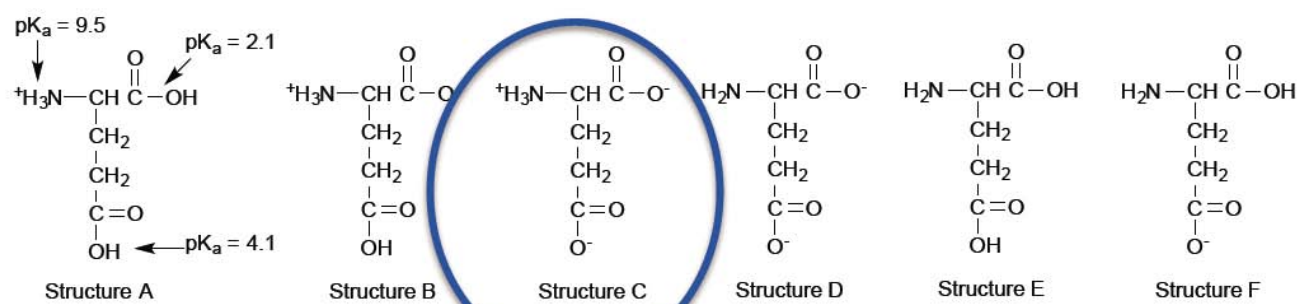
(c) (3 points) **Calculate** the volume of NaOH titrant needed to reach the equivalence (stoichiometric) point.

$$\text{VOL} = 50.00 \text{ mL}$$

(d) (13 points) Calculate the pH to **2 decimal places** at the equivalence (stoichiometric) point. Check any assumption. Show your work.

pH = 8.72

7. (6 points) **Circle** the structure that best represents the ionization state of the amino acid glutamate at pH = 5.0 (the pH of the lysosome).



VIII																	
VII																	
VI																	
V																	
IV																	
III																	
II																	
I																	
Transition elements																	
Lanthanide series																	
Actinide series																	

$$\Delta H_r^\circ = \sum \Delta H_{B(\text{reactants})} - \sum \Delta H_{B(\text{products})}$$

$$\Delta H_r^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

$$\Delta S_r^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$$

$$\Delta G_r^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = RT \ln (Q/K)$$

$$\ln (K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$$

$$PV = nRT$$

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

$$R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$x = [-b \pm (b^2 - 4ac)^{1/2}] / 2a$$

$$s = k_H P$$

$$14.00 = \text{pH} + \text{pOH} \text{ at } 25^\circ\text{C}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$K_w = K_a K_b$$

$$K_w = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$\text{pK}_a = -\log [K_a]$$

$$\text{pK}_b = -\log [K_b]$$

$$\text{pH} \approx \text{pK}_a - \log([\text{HA}]/[\text{A}^-])$$

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5.111 Principles of Chemical Science
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