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

$$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g) \qquad \Delta H° = +58\ kJ$$

(a) NO_2 (g) is removed at constant temperature

(i) Circle the most likely direction *toward products* *toward reactants* *no change*
(ii) Briefly explain:

(b) the total pressure is increased by addition of N_2(g) at constant temperature

(i) Circle the most likely direction *toward products* *toward reactants* *no change*
(ii) Briefly explain:

(c) the volume is increased at constant temperature

(i) Circle the most likely direction *toward products* *toward reactants* *no change*
(ii) Briefly explain:

(d) the temperature is decreased

(i) Circle the most likely direction *toward products* *toward reactants* *no change*
(ii) Briefly explain:

Thermodynamics

2. (15 points) **Predict** the sign of $\Delta H_r°$ for the following scenarios. **<u>Briefly explain your answers in words. Writing an equation without explanation is not sufficient</u>.**

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

(i) <u>Circle</u> the most likely sign of $\mathbf{\Delta H_r°}$ ***negative*** ***positive***

(ii) <u>Briefly explain</u>:

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

(i) <u>Circle</u> the most likely sign of $\mathbf{\Delta H_r°}$ ***negative*** ***positive***

(ii) <u>Briefly explain</u>:

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

(i) <u>Circle</u> the most likely sign of $\mathbf{\Delta H_r°}$ ***negative*** ***positive***

(ii) <u>Briefly explain</u>:

Thermodynamics

3. (8 points)

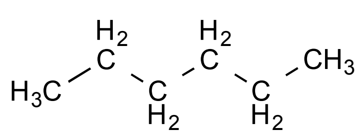
(a) (4 points) **Calculate** the standard reaction enthalpy for the formation of CO_2 (g) from CO (g) and O_2 (g): $CO\ (g) + \frac{1}{2} O_2\ (g) \rightarrow CO_2\ (g)$, given that:

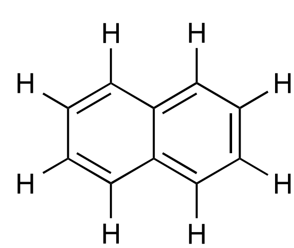
$$C(\text{graphite}) + \tfrac{1}{2} O_2\ (g) \rightarrow CO\ (g) \qquad \Delta H° = -110.54\ \text{kJ}$$
$$C(\text{graphite}) + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H° = -393.51\ \text{kJ}$$

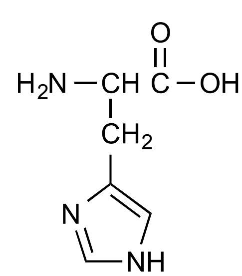
(b) (4 points) Consider CO (g). Given that its $\Delta H_f°$ is -110.54 kJ/mol and its $\Delta G_f°$ is -137.16 kJ/mol, **(i) predict** whether CO (g) is stable or unstable with respect to decomposition into its elements under standard conditions. **(ii) Briefly explain your answer.**

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 x 10^{-3}
Nitrogen	7.0 x 10^{-4}
Hydrogen	8.5 x 10^{-4}

(a) (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. (32 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.

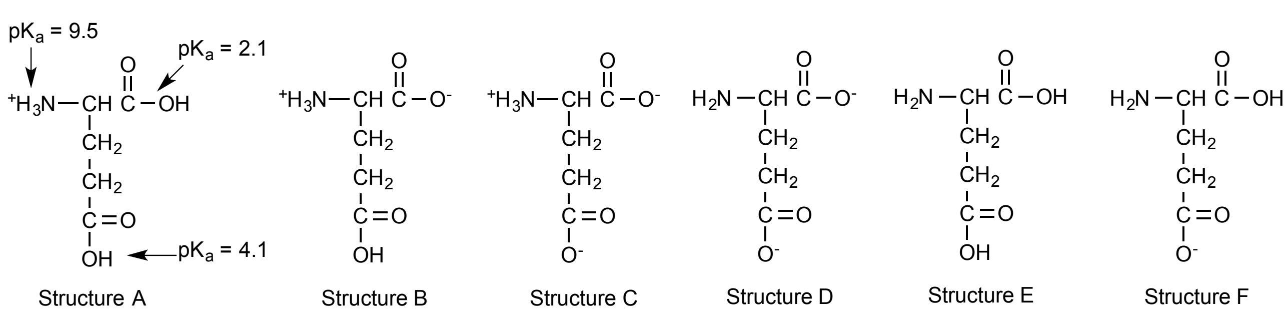
(a) (12 points) **Calculate** the pH of the solution after addition of 20.00 mL of NaOH titrant. You can assume that $[H_3O^+]$ at equilibrium satisfies the 5% rule without checking. Show your work.

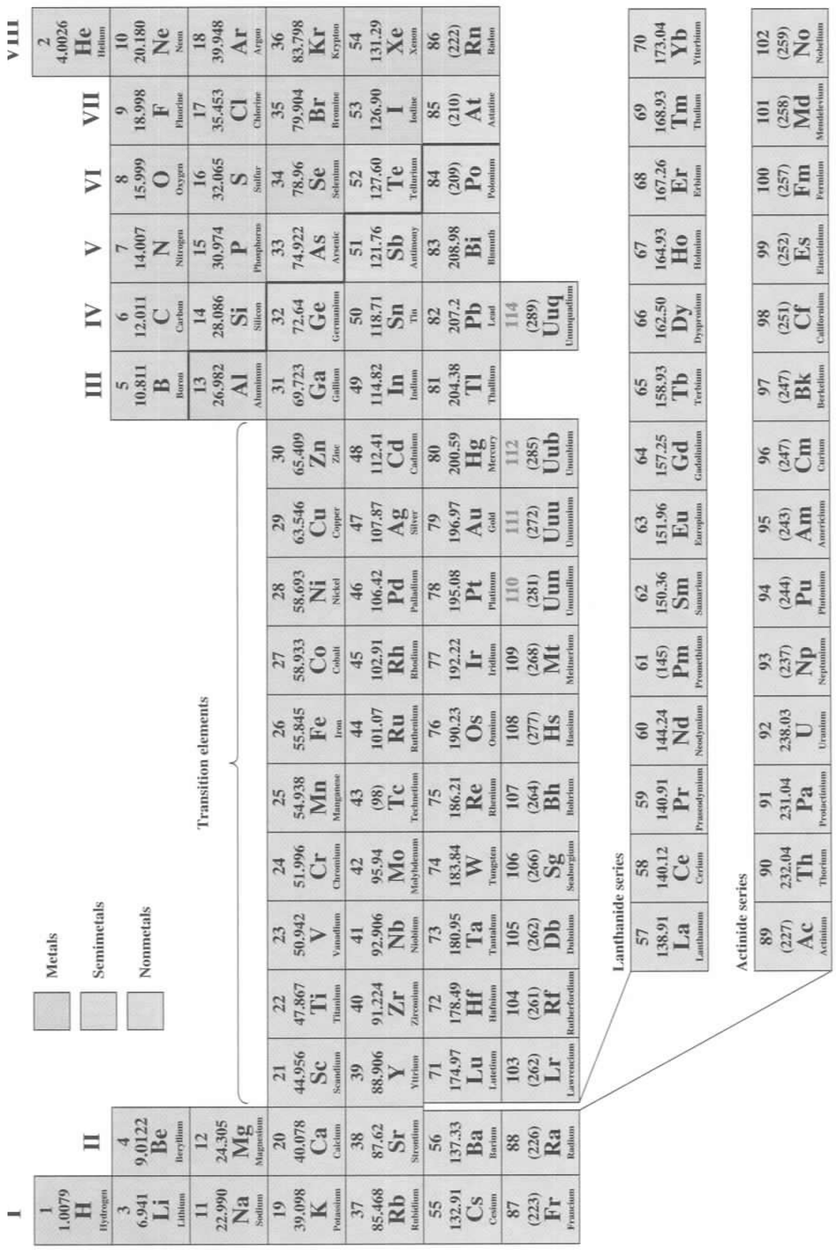
(b) (5 points) **Calculate** the pH at the half-equivalence (half-stoichiometric) point.

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

(d) (12 points) **Calculate** the pH to **2 decimal places** at the equivalence (stoichiometric) point. Check any assumption. Show your work.

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).





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

$\Delta H_r^\circ = \Sigma\Delta H_f^\circ{}_{(products)} - \Sigma\Delta H_f^\circ{}_{(reactants)}$

$\Delta S_r^\circ = \Sigma S^\circ{}_{(products)} - \Sigma S^\circ{}_{(reactants)}$

$\Delta G_r^\circ = \Sigma\Delta G_f^\circ{}_{(products)} - \Sigma\Delta G_f^\circ{}_{(reactants)}$

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

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

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

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

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

$PV = nRT$

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

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

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

$s = k_H P$

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

$pOH = -\log [OH^-]$

$pH = -\log [H_3O^+]$

$K_w = K_a K_b$

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

$pK_a = -\log [K_a]$

$pK_b = -\log [K_b]$

$pH \approx pK_a - \log([HA]/[A^-])$