## **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.

 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.
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	
ТΔ	

# **Chemical Equilibrium**

**1.** (20 points) **Predict** the direction that the equilibrium will shift when each of the following changes occurs. **Briefly explain your answers**.

 $N_2O_4(g) \rightleftharpoons 2 NO_2(g) \Delta H^\circ = +58 kJ$ 

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

(i) <u>Circle</u> the most likely direction	toward products	toward reactants	no change
(ii) <u>Briefly explain</u> :			

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

(i) <u>Circle</u> the most likely direction	toward products	toward reactants	no change
(ii) <u>Briefly explain</u> :			

(c) the volume is increased at constant temperature

(i) <u>Circle</u> the most likely direction	toward products	toward reactants	no change
(ii) <u>Briefly explain</u> :			

(d) the temperature is decreased

(i) <u>Circle</u> the most likely direction	toward products	toward reactants	no change
(ii) <u>Briefly explain</u> :			

## Thermodynamics

# 2. (15 points) Predict the sign of $\Delta H_r^{\circ}$ 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) <u>Circle</u> the most likely sign of $\Delta H_r^{\circ}$	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 $\Delta H_r^{\circ}$	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 $\Delta H_r^{\circ}$	negative	positive
(ii) <u>Briefly explain</u> :		

### Thermodynamics

**3.** (8 points)

(a) (4 points) Calculate the standard reaction enthalpy for the formation of CO<sub>2</sub> (g) from CO (g) and O<sub>2</sub> (g): CO (g) +  $\frac{1}{2}$  O<sub>2</sub> (g)  $\rightarrow$  CO<sub>2</sub> (g), given that:

 $\begin{array}{ll} C(\text{graphite}) + \frac{1}{2} O_2(g) \rightarrow CO(g) & \Delta H^\circ = -110.54 \text{ kJ} \\ C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ = -393.51 \text{ kJ} \end{array}$ 

(b) (4 points) Consider CO (g). Given that its  $\Delta H_f^\circ$  is -110.54 kJ/mol and its  $\Delta G_f^\circ$  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) <u>Briefly explain your answer.</u>

### 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	$k_{\rm H}$ (mol • L <sup>-1</sup> • atm <sup>-1</sup> )
Oxygen	$1.3 \times 10^{-3}$
Nitrogen	7.0 x 10 <sup>-4</sup>
Hydrogen	8.5 x 10 <sup>-4</sup>

(a) (8 points) **Draw** a single plot with Molar Solubility (mol $\bullet$ L<sup>-1</sup>) on the y-axis and Partial Pressure in atm on the x-axis for <u>each of the three</u> 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<sub>3</sub>COOH (aq) is titrated with a 0.1000 M solution of NaOH (aq) at 25°C. The  $K_a$  for CH<sub>3</sub>COOH is 1.8 x 10<sup>-5</sup> at 25°C.

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

(b) (5 points) Calculate the <u>pH</u> at the half-equivalence (half-stoichiometric) point.

(c) (3 points) Calculate the <u>volume</u> of NaOH titrant needed to reach the equivalence (stoichiometric) point.

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

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).



										$\Delta H_{\rm r}^{\rm \circ} = \Sigma \Delta H_{\rm f}^{\rm \circ}_{\rm (products)} - \Sigma \Delta H_{\rm f}^{\rm \circ}_{\rm (reactants)}$
										$\Delta S_{\rm r}^{\rm o} = \Sigma S^{\rm o}_{\rm (products)} - \Sigma S^{\rm o}_{\rm (reactants)}$
V III 2 4.0026 He	10 20.180 Ne	18 39.948 Ar	36 83.798 Kr Kr	54 131.29 Xe	86 (222) <b>Rn</b> Ratue		70 173.04	YIterbium	102 (259) NO Notetium	$\Delta G_{\rm r}^{\circ} = \Sigma \Delta G_{\rm f\ (products)}^{\circ} - \Sigma \Delta G_{\rm f\ (reactants)}^{\circ}$
	9 18.998 F	17 35.453 CI CI	35 79.904 Br	53 126.90 I I	85 (210) At		69 168.93	Tm	101 (258) Md Mendelevium	$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$
	8 15.999 0 0 0 0 0	16 32.065 S	34 78.96 Se	52 127.60 Te returium	84 (209) PO		68 167.26	Er	100 (257) Fm	$\Delta G^{\circ} = - RT \ln K$
	7 14.007 N	15 30.974 Phoenherm	33 74.922 AS Arrente	51 121.76 Sb	83 208.98 Bi		67 164.93	Ho	99 (252) ES	$\Delta G = \Delta G^{\circ} + RT \ln O$
	1 6 C C C C C	14 28.086 Si	32 72.64 Ge	50 118.71 Sn	82 207.2 Pb	114 (289) Uuq	66 162.50	Dy	98 Cf Cattornium	$\Delta G = \Delta G + KT \ln Q$
	5 10.811 B	13 26.982 Al	31 69.723 Ga	49 114.82 In	81 204.38 TT Theffinn		65 158.93	Tb	97 (247) Bk Bertelium	$\Delta G = KI III (Q/K)$
			30 65.409 Zn	48 112.41 Cd	80 200.59 Hg	112 (285) Uub	64 157.25	Gd	96 Cm Carter	$\ln (K_2/K_1) = - (\Delta H^o/R)(1/T_2 - 1/T_1)$
			29 63.546 Cu Cunter	47 107.87 Ag	79 196.97 Au	111 (272) Uuu	63 151.96	Eu	95 (243) Am	PV = nRT
			28 58.693 Ni	46 106.42 Pd Painatium	78 195.08 Pt	110 (281) Uun	62 150.36	Sm	94 (244) <b>Pu</b>	$R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$
			27 58.933 C0 C0	45 102.91 Rh Rhotim	77 192.22 Ir	109 (268) Mt Mainarium	61 (145)	Pm	93 (237) Np Neptuminn	$R = 0.08206 L atm K^{-1} mol^{-1}$
		elements	26 55.845 Fe	44 101.07 Ru Rufentun	76 190.23 OS	108 (277) HS <sup>Hastum</sup>	60 144.24	Nd	92 0 0 0 0	$x = [-b \pm (b^2 - 4ac)^{1/2}] / 2a$
		fransition 人	25 54.938 Mn	43 (98) Tc	75 186.21 Re Rhenium	107 (264) Bh	59 140.91	Pr	91 231.04 Pa	$s = k_H P$
			24 51.996 Cr Cr	42 95.94 Mo	74 183.84 W Tungton	106 (266) Sg	series 58 140.12	Ce	71cs 232.04 Thorism	$14.00 = pH + pOH \text{ at } 25^{\circ}C$
etals	mimetals		23 50.942 V	41 92.906 Nb	73 180.95 Ta	105 (262) Db	57 138.91	La	Actinide se 89 AC Actinium	$pOH = -log [OH^-]$
Σ	x z		22 47.867 Ti	40 91.224 Zr	72 178.49 Hf	104 (261) Rf Rutherfordium				$pH = -log [H_3O^+]$
			21 44.956 Sc	39 88.906 Y	71 174.97 Lu Lu	103 (262) Lr tawrenetum				$K_w = K_a K_b$
;	9.0122 Be	12 24.305 Mg	20 20 Ca	38 87.62 Sr Sr	56 137.33 Ba	88 (226) Ra				$K_w = 1.00 \text{ x } 10^{-14} \text{ at } 25^{\circ}C$
I 1.0079 H	Itydrogen 3 6.941 Li Lithium	11 22.990 Na	19 39.098 K	37 85.468 <b>Rb</b> kubitium	55 132.91 CS Cs	87 (223) Fr Francian				$pK_a = -\log [K_a]$
										$pK_b = -\log [K_b]$

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

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

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