

### Practice Third Hour Exam for 5.111 FALL 2014

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 each part of each problem carefully and thoroughly.
2. 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.
3. A problem that requests you to "calculate" implies that several steps may be necessary for the problem's solution. You must show these steps clearly and indicate all values, including physical constants used to obtain your quantitative result. 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.**

Thermodynamics	1a, 1b	(18 points) page 2 _____
Thermodynamics and Chemical Equilibrium	1c, 1d, 2a	(18 points) page 3 _____
Chemical Equilibrium	2b	(20 points) page 4 _____
Solubility	3a, 3b	(12 points) page 5 _____
Acid/Base	4a	(12 points) page 6 _____
	4b, 4c	(8 points) page 7 _____
	4d	(12 points) page 8 _____

**Total (100 points)** \_\_\_\_\_

Name \_\_\_\_\_

TA \_\_\_\_\_

1. (30 points) **Thermodynamics**

(a) Consider the following reaction:  $\text{ClF}(\text{g}) + \text{F}_2(\text{g}) \rightarrow \text{ClF}_3(\text{g})$

(i) (8 points) Given the following data, calculate the  $\Delta H^\circ$  for the reaction ( $\Delta H_r^\circ$ ) above. Report your answer in units of kJ per mol of  $\text{ClF}_3$  formed.

	$\Delta H_r^\circ$ (in kJ for each reaction as written)
$2\text{ClF}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}(\text{g}) + \text{F}_2\text{O}(\text{g})$	167.4
$2\text{ClF}_3(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}(\text{g}) + 3\text{F}_2\text{O}(\text{g})$	341.4
$2\text{F}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{F}_2\text{O}(\text{g})$	-43.4

(ii) (4 points) Would you expect  $\Delta S^\circ$  for the reaction in part (a) to be positive, negative, or zero. Briefly justify your choice.

(b) (6 points) Fill in the signs as (-) or (+) for  $\Delta H^\circ$  and  $\Delta S^\circ$  to correctly complete the table below.

$\Delta H$	$\Delta S$	Spontaneity of reaction
		never spontaneous
		spontaneous only at low temperatures
		spontaneous only at high temperatures

**(c)** (8 points) Calculate the temperature at which it is thermodynamically possible for carbon to reduce iron (III) oxide to iron under standard conditions by the following reaction:

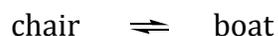


Note that the  $\Delta H_{\text{f}}^{\circ}$  of  $\text{Fe}_2\text{O}_3 (\text{s})$  is  $-824.2 \text{ kJ/mol}$  and the  $\Delta H_{\text{f}}^{\circ}$  for of  $\text{CO}_2$  is  $-393.5 \text{ kJ/mol}$

**(d)** (4 points) Given that  $\text{CO}_2$  has a  $\Delta G_{\text{f}}^{\circ}$  of  $-394.4 \text{ kJ}$ . Predict whether  $\text{CO}_2$  is more stable or less stable relative to its elements. Briefly explain your answer.

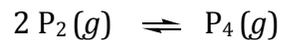
## 2. (26 points) **Chemical Equilibrium**

**(a)** (6 points) The compound 1,3-di-*t*-butylcyclohexane exists in two conformations that are known as the chair and the boat conformations, because their structures resemble those objects. An equilibrium exists between these two forms, represented by the equation:



At 580 K, 6.42% of the molecules are in the chair form. Calculate the equilibrium constant for the preceding reaction as written at 580 K.

**(b)** Consider the equilibrium



State the direction (toward product, toward reactant, no change) that the equilibrium will shift when each of the following changes occurs at constant temperature. **Briefly explain your answers.**

**(i)** (5 points)  $\text{P}_2(g)$  is added

**(ii)** (5 points)  $\text{P}_4(g)$  is removed

**(iii)** (5 points) the total pressure is increased by addition of  $\text{N}_2(g)$

**(iv)** (5 points) the volume is increased

**3. (12 points) Solubility**

Hydrocarbons can have limited solubility in water partially due to entropic effects. Thus researchers were surprised when a particular hydrocarbon was found to be soluble in water, especially since solvent cage formation was known to accompany the dissolving process, decreasing the entropy of the system.

**(a)** (6 points) Given that this hydrocarbon is soluble in water, **explain** what must be true about the sign and magnitude of the enthalpy of solution for this hydrocarbon.

**(b)** (6 points) **Predict** the effect, if any, that increasing temperature will play in the spontaneity of the dissolving process for this hydrocarbon. **Briefly explain your answer.**

**4. (32 points) Acid/Base**

20.00 mL of a 0.1000 M solution of the weak base ammonia ( $\text{NH}_3$ ) is titrated with a 0.1000 M solution of the strong acid HCl at 25°C.

The base ionization constant ( $K_b$ ) for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$  at 25°C.

**(a)** (12 points) **Calculate** the pH of the solution after addition of 5.00 mL of HCl titrant. You can assume that  $[\text{OH}^-]$  at equilibrium satisfies the 5% rule without checking.

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

**(c)** (3 points) **Calculate** the volume of strong acid (HCl) 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.

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