

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 _____

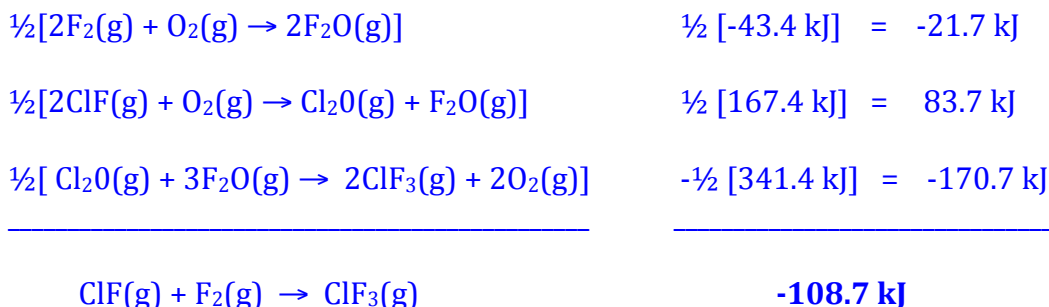
1. (30 points) **Thermodynamics**

(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 ΔH° for the reaction (ΔH_r°) above. Report your answer in units of kJ per mol of ClF_3 formed.

	ΔH_r° (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

We can apply Hess' Law to calculate ΔH° .



$\Delta H = -108.7 \text{ kJ}$ per mol of $\text{ClF}_3(\text{g})$ formed

(ii) (4 points) Would you expect ΔS° for the reaction in part (a) to be positive, negative, or zero. Briefly justify your choice.

ΔS° would be negative. The disorder is decreasing (from 2 mol to 1 mol of gas).

(b) (6 points) Fill in the signs as (-) or (+) for ΔH° and ΔS° to correctly complete the table below.

ΔH	ΔS	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 ΔH_f° of $\text{Fe}_2\text{O}_3 (\text{s})$ is -824.2 kJ/mol and the ΔH_f° for of CO_2 is -393.5 kJ/mol

$$\begin{aligned} \Delta H_r^\circ &= \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants}) \\ &= [4 \text{ mol}(0 \text{ kJ/mol}) + 3 \text{ mol}(-393.5 \text{ kJ/mol})] - [2 \text{ mol}(-824.2 \text{ kJ/mol}) + 3 \text{ mol}(0 \text{ kJ/mol})] \\ &= 467.9 \text{ kJ} \end{aligned}$$

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ = 0 \text{ (at equilibrium)}$$

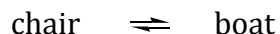
$$\begin{aligned} T\Delta S_r^\circ &= \Delta H_r^\circ \\ T &= \Delta H_r^\circ / \Delta S_r^\circ \\ &= 467,900 \text{ J} / 558.4 \text{ J} \\ &= \mathbf{837.9 \text{ K}} \end{aligned}$$

(d) (4 points) Given that CO_2 has a ΔG_f° of -394.4 kJ . Predict whether CO_2 is more stable or less stable relative to its elements. Briefly explain your answer.

CO_2 is more stable with respect to its elements. Since the ΔG_f° is negative, the formation of CO_2 is stable, therefore the decomposition in to its elements is disfavored.

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:

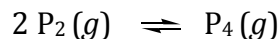


At 580 K, 6.42% of the molecules are in the chair form. Calculate the equilibrium constant for the preceding reaction as written at 580 K.

If 6.42% of the compound is in the chair conformation, then 93.58% of the compound is in the boat conformation. The percentages are proportional to the concentrations of the specific conformation.

$$\begin{aligned} K &= [\text{boat}] / [\text{chair}] \\ &= 93.58 / 6.42 = \mathbf{14.6 \text{ at } 580 \text{ K}} \end{aligned}$$

(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

Toward products.

When excess reactant is added, $Q < K$, and forward direction will be spontaneous (or)
When excess reactant is added, the system will shift toward products until the excess reactant is consumed.

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

Toward products.

When product is removed, $Q < K$, and forward direction will be spontaneous (or)
When product is removed, the system will shift toward products until equilibrium is reached again.

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

No Change.

If the total pressure is increased by addition of an inert gas, then the volume didn't change.
If volume doesn't change, then the partial pressures of gases didn't change.

(iv) (5 points) the volume is increased

Toward Reactant.

When the volume increases, the pressure decreases, so the system responds in such a way to increase the total pressure. Thus the equilibrium shifts from fewer moles (1) to more moles (2) (toward reactant) to increase the total pressure.

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.

If the hydrocarbon is soluble, ΔG must be negative. For ΔG to be negative, the **sign of ΔH_{sol} must be negative and the magnitude must be larger than $T\Delta S$** ($\Delta G = \Delta H - T\Delta S$).

(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.**

Increasing temperature is likely to **decrease spontaneity (or) decrease dissolution (or) decrease solubility**. Since ΔS is negative, increasing temperature will increase the magnitude of the $T\Delta S$ term, which will make ΔG a smaller negative number or even a positive number.

4. (32 points) Acid/Base

20.00 mL of a 0.1000 M solution of the weak base ammonia (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 NH_3 is 1.8×10^{-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.

THIS IS LIKE A BUFFER PROBLEM

Option 1:

$$20.00 \times 10^{-3} \text{ L} \times 0.1000 \text{ M} = 0.002000 \text{ mol } \text{NH}_3 \text{ (Initial)}$$

$$5.00 \times 10^{-3} \text{ L} \times 0.1000 \text{ M} = 0.000500 \text{ mol HCl added}$$

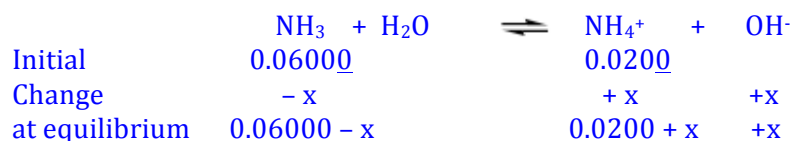
$$0.002000 \text{ mol } \text{NH}_3 - 0.000500 \text{ mol HCl added} = 0.001500 \text{ mol } \text{NH}_3 \text{ left}$$

$$0.000500 \text{ mol } \text{NH}_4^+ \text{ formed}$$

$$\text{Volume} = 25.00 \times 10^{-3} \text{ L}$$

$$[\text{NH}_3] = 0.001500 \text{ mol} / 25.00 \times 10^{-3} \text{ L} = 0.06000 \text{ M}$$

$$[\text{NH}_4^+] = 0.000500 \text{ mol} / 25.00 \times 10^{-3} \text{ L} = 0.0200 \text{ M}$$



$$K_b = 1.8 \times 10^{-5} = \frac{(0.0200 + x)(+x)}{(0.06000 - x)} \approx \frac{(0.0200)(+x)}{0.06000} \quad x = 5.4 \times 10^{-5}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (5.4 \times 10^{-5}) = 4.267$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.267 = 9.73$$

Option 2:

$$20.00 \times 10^{-3} \text{ L} \times 0.1000 \text{ M} = 0.002000 \text{ mol } \text{NH}_3 \text{ (Initial)}$$

$$5.00 \times 10^{-3} \text{ L} \times 0.1000 \text{ M} = 0.000500 \text{ mol HCl added}$$

$$0.002000 \text{ mol } \text{NH}_3 - 0.000500 \text{ mol HCl added} = 0.001500 \text{ mol } \text{NH}_3 \text{ left}$$

$$0.000500 \text{ mol } \text{NH}_4^+ \text{ formed}$$

$$\text{Volume} = 20.00 \times 10^{-3} \text{ L} + 5.00 \times 10^{-3} \text{ L} = 25.00 \times 10^{-3} \text{ L}$$

$$[\text{NH}_3] = 0.001500 \text{ mol} / 25.00 \times 10^{-3} \text{ L} = 0.06000 \text{ M}$$

$$[\text{NH}_4^+] = 0.000500 \text{ mol} / 25.00 \times 10^{-3} \text{ L} = 0.0200 \text{ M}$$

$$\text{pH} \approx \text{p}K_a - \log \left(\frac{[\text{HA}]}{[\text{A}^-]} \right)$$

$$K_a = K_w / K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

$$\text{p}K_a = -\log K_a = -\log 5.56 \times 10^{-10} = 9.255$$

$$\text{pH} = 9.255 - \log (0.0200 / 0.06000)$$

$$\text{pH} = 9.255 - \log (0.3333)$$

$$\text{pH} = 9.255 - (-0.4771) = 9.732 = 9.73$$

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

$\text{pH} \approx \text{pK}_a$ at half-equivalence point

$$K_a = K_w/K_b = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

$$\text{pK}_a = -\log K_a = -\log 5.56 \times 10^{-10} = 9.255$$

$\text{pH} = \mathbf{9.26}$ or $\mathbf{9.25}$

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

$$20.00 \text{ mL} \times 0.1000 \text{ M} = (\text{VOL})(0.1000 \text{ M})$$

$$\text{VOL} = \mathbf{20.00 \text{ mL}}$$

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

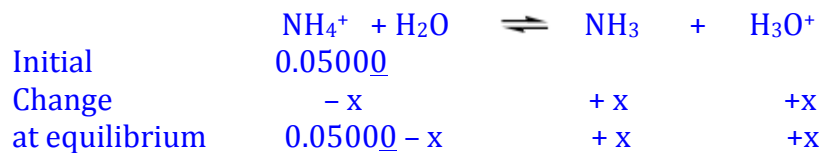
THIS IS LIKE A WEAK ACID IN WATER PROBLEM.

$$20.00 \times 10^{-3} \text{ L} \times 0.1000 \text{ M} = 0.002000 \text{ mol NH}_3 \text{ (Initial)}$$

At equivalence point, all NH_3 has been converted to NH_4^+

$$\text{Volume} = 20.00 \times 10^{-3} \text{ L} + 20.00 \times 10^{-3} \text{ L} = 40.00 \times 10^{-3} \text{ L}$$

$$[\text{NH}_4^+] = 0.002000 \text{ mol} / 40.00 \times 10^{-3} \text{ L} = 0.05000 \text{ M}$$



$$K_a = K_w / K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

$$K_a = 5.56 \times 10^{-10} = \frac{(x^2)}{(0.05000 - x)} \approx \frac{(x^2)}{0.05000} \quad x = 5.27 \times 10^{-6}$$

Assumption is valid: $5.27 \times 10^{-6} / 0.05000 \times 100 \% = 0.0105\% (<5\%)$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.27 \times 10^{-6}) = \mathbf{5.28}$$

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5.111 Principles of Chemical Science
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