Name _____

CHM 1046
Spring 2017
April 7

EXAMINATION FOUR

I _____ II _____ III _____ IV _____ V _____ VI _____ VII _____

Total _____

Glance over the entire exam, and then attempt the problems in the order of your choice. Rough point values are given for each problem. The total will be scaled to ***200 points*** after the exams are marked. For questions with multiple parts, you do not necessarily need the answer to part A in order to work part B, etc. For calculations, give your answer to the correct number of ***significant figures***, and be sure to include the ***correct units*** for your answer. ***You must show your work to receive any credit for a calculated answer.*** Additional information is provided in a separate information packet; you can use the back for scratch work. Good luck!

I. (25 points) Dilute solutions of hypochlorous acid, HClO(aq), as low as 20 mg/L will completely inactivate noroviruses on surfaces such as stainless steel and ceramic tile.

https://www.sciencedaily.com/releases/2005/12/051220182057.htm

Hypochlorous acid is formed by dissolving chlorine gas in water, as shown below.

$$Cl_2(g) + H_2O(\ell) \rightleftharpoons HClO(aq) + HCl(aq)$$

A. Assign the oxidation number of chlorine for each of the chlorine-containing molecules in the chemical equation above.

Cl_2 _____ HClO _____ HCl _____

B. You will notice that the above reaction is a redox reaction where Cl_2 is both oxidized and reduced. This reaction can be separated into two half-reactions. Balance the half-reactions under acidic conditions.

1. $Cl_2 \rightleftharpoons HClO$

Is Cl_2 oxidized or reduced? _____

2. $Cl_2 \rightleftharpoons HCl$

Is Cl_2 oxidized or reduced? _____

C. Show that the two half-reactions from Part B can be combined to give the chemical equation at the top of the page.

D. Even though HClO is formed from Cl_2 as shown above, HClO is a stronger oxidant than chlorine under standard conditions.

$$2HClO(aq) + 2H^+(aq) + 2e^- \rightarrow Cl_2(g) + 2\,H_2O(\ell) \qquad E° = +1.63\ V$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^- \qquad E° = +1.36\ V$$

Speculate on why HClO is a better oxidizing agent.

II. (7 points) Balance the following half-reaction, this time under basic conditions.

$ClO^- \rightarrow Cl^-$

Is ClO^- oxidized or reduced? _____

III. (25 points) A small-scale fuel cell that generates energy from urine was recently reported (*Electrochimica Acta*, **2016**, *92*, 89–98). Urea is enzymatically hydrolyzed to give ammonia, NH_3, which is oxidized to give (mainly) nitrite, NO_2^-. Oxygen from the air is reduced at the other electrode, and we'll assume the product is hydroxide. The half-reactions and half-cell potentials are given below.

	E°(V)
$O_2(g) + 2H_2O(\ell) + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$NO_2^-(aq) + 5H_2O(\ell) + 6e^- \rightarrow NH_3(aq) + 7OH^-(aq)$	−0.16

A. Determine the standard cell potential.

B. Write a balance chemical equation for the spontaneous redox reaction that drives this cell.

C. The microbes that facilitate this process are unlikely to survive under very basic conditions, so let's work at pH 9.00, giving $[OH^-] = 1.00 \times 10^{-5}$ M. Assuming $[NO_2^-]$ and $[NH_3]$ are 0.10 M, and $[O_2] = 0.20$ atm (use 0.20, you do not need to convert atmospheres to molarity), calculate the potential delivered by this cell.

1. First, write the mathematical equation you are going to use to find the answer.

2. Next, plug in the numbers you are going to use in your calculation. Write clearly so we can assign partial credit.

3. Now solve for the cell potential under the conditions given above.

IV. (35 points) If you don't want to build fuel cell, how about getting the energy from reacting ammonia and oxygen in a combustion reaction as shown below.

$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(\ell)$

	$\Delta H_f°$ (kJ/mol)	$S°$ (J/K·mol)
$H_2O(\ell)$	−285.8	69.9
$N_2(g)$	0	191.5
$NH_3(g)$	−46.3	193.0
$O_2(g)$	0	205.0

A. Determine the following values for the reaction above at 25°C.

1. ΔH°

2. ΔS°

3. ΔG°

4. K_{eq}

B. So, is the combustion of ammonia as written above spontaneous? _____

Is it enthalpy driven, entropy driven, both, or neither?

C. Will the reaction be more favored or less favored at a higher temperature? _____

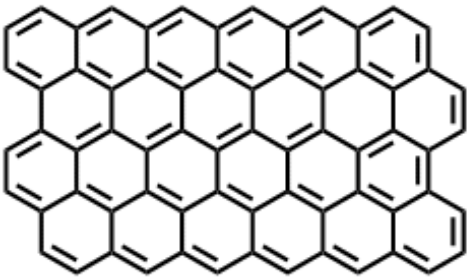
Explain your reasoning.

D. Why is the entropy of H_2O so much lower than the other molecules in the reaction?

V. (10 points)The Science Daily article "***Freshmen-level chemistry solves solubility mystery of graphene oxide films***" practically begs to become a general chemistry exam question.

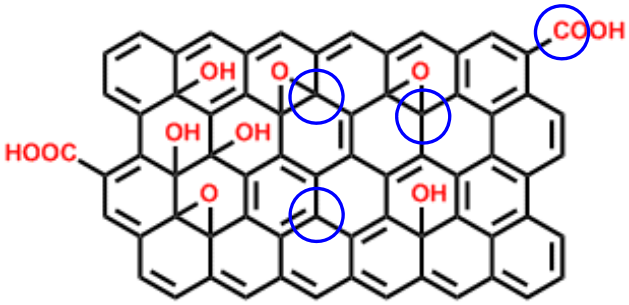
https://www.sciencedaily.com/releases/2015/01/150105125910.htm

Assign the oxidation number for the circled carbon atoms.



Graphene

[G0438, G0441, G0442]



Graphene oxide

[G0443, G0444]

Is the conversion of graphene to graphene a redox reaction? How do you know?

VI. (15 points) Remember hypochlorous acid from Problem I?

Dilute solutions of hypochlorous acid, HClO(aq), as low as 20 mg/L will completely inactivate noroviruses on surfaces such as stainless steel and ceramic tile.

Maybe it's acid/base chemistry instead of redox chemistry that is inactivating the noroviruses.

A. Assume a HClO(aq) concentration of 20 mg/L. What would be the concentration in mol/L?

B. Determine the pH of the solution in Part A. The K_a value for hypochlorous acid is 3.0×10^{-8}.

C. Does your answer to Part B make sense? If so, explain why that is a reasonable pH. If not, what makes it unreasonable and why didn't your approach work.

VII. (6 points) I enjoyed all of the articles about anthropomorphic applications of entropy. The article describing Shannon entropy, "an information theory model that looks at areas of entropy, or disorder, in a complex system like the brain" was especially interesting and let me to a whole new field (or new to me) relating brain entropy to consciousness and how we perceive time, which we talked about briefly in class.

Consider the full quote, part of which was given above.

Shannon entropy, an information theory model that looks at areas of entropy, or disorder, in a complex system like the brain, has advantages over mean FA in the analysis of brain histograms, according to Dr. Alhilali. "A healthy brain has high entropy, but people with injuries to the white matter from trauma may lose some of that complexity and have less entropy," she explained.

https://www.sciencedaily.com/releases/2016/02/160201141911.htm

Does the discussion of brain complexity and disorder make sense to you? Why or why not?

VIII. A little this, a little that...

A. For each of the following pairs of compounds, identify the dominant intermolecular force, and answer the associated question.

1. NF_3 CF_4

_____ _____

Which of the above compounds is expected to have the highest boiling point? _____

2. $CH_3CH_2CH_3$ CH_3CH_2OH

_____ _____

Which of the above compounds is expected to have the highest vapor pressure? _____

3. $SeCl_2$ $SrCl_2$

_____ _____

Which of the above compounds is expected to have the highest enthalpy of vaporization? _____

B. Consider the following aqueous solutions listed below in alphabetical order according to the anion.

0.10 m $NaClO_4$ 0.10 m Na_3PO_4 0.10 m Na_2SO_4

If all of the solutions are initially at 10°C and the temperature is gradually lowered, which solution will freeze first (i.e. at the highest temperature)? Explain your reasoning.

Will that solution freeze above or below 0°C? _____

Which of these solutions will have the highest....

1. boiling point? _____
2. vapor pressure of water? _____
3. osmotic pressure? _____

C. For each of the following groups of compounds, circle the weakest acid (or stronger base).

1. H_3As H_4Ge H_2Se
2. H_2S H_2Se H_2Te
3. As_2O_5 Br_2O_7 CaO

D. Which solution is expected to be more acidic: 0.1 M $HBrO_2(aq)$, 0.1 M $HClO_2(aq)$, or 0.1 M $HClO_3(aq)$?

Explain your reasoning. (Because these weak acids differ in more than one way, you will need more than one trend to justify your answer.)

IX. For the reaction $A + 3B + C \rightarrow AB_2 + BC$ the following rate data was obtained.

exp	[A] (M)	[B] (M)	[C] (M)	rate (M/s)
1	0.14	0.25	0.034	0.40×10^{-1}
2	0.42	0.25	0.034	3.6×10^{-1}
3	0.42	0.75	0.034	3.6×10^{-1}
4	0.42	0.25	0.017	1.8×10^{-1}

A. Determine the rate law for this reaction.

B. In experiment 4, the rate of disappearance of A is 1.8×10^{-1} M/s. What is the rate of disappearance of B?

C. The following mechanism can be proposed for this reaction.

$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2$ rapid equilibrium

$A_2 + C \xrightarrow{k_2} AC + A$ slow

$AC + B \xrightarrow{k_3} AB + C$ fast

$AB + B \xrightarrow{k_4} AB_2$ fast

$B + C \xrightarrow{k_5} BC$ fast

What is the rate determining step in this mechanism?

What is(are) the intermediate(s) in this mechanism?

Determine the theoretical rate law for this mechanism.

Does your theoretical rate law agree with your experimental rate law?