

Chemistry 271, Section 21xx

Your Name: _____

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University of Maryland, College Park

Your SID #: _____

General Chemistry and Energetics

Final Exam (200 points total)

Your Section # or time: _____

May 13, 2011

VIEWING: Monday, May 16, 9:30-10:30 a.m., Chem 1112

You have 120 minutes for this exam.

Explanations should be concise and clear. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

$$\text{pH} = -\log([\text{H}^+])$$

$$K_b = [\text{HA}][\text{HO}^-]/[\text{A}^-]$$

$$K_w = [\text{H}^+][\text{HO}^-]$$

$$\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}]$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole K}$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$\ln K_{eq} = -\Delta H^\circ/(RT) + \Delta S^\circ/R$$

$$\Delta S - q/T \geq 0$$

$$R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} = N_A k_B$$

$$S = k_B \ln W$$

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

$$E = \sum n_i \varepsilon_i$$

$$W = N!/(\prod n_i!)$$

$$n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$$

$$N = \sum n_i$$

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

Biochemical standard state: pH 7, all species in the ionic form found at pH 7

$$^\circ\text{C} = ^\circ\text{K} - 273.15$$

$$P(v)dv = Cv^2 \exp(-mv^2/2kT)$$

$$E = E^\circ - 2.303(RT/n\mathcal{F})\log_{10}Q$$

$$2.303RT/\mathcal{F} = 0.0592 \text{ Volts at } 25^\circ\text{C}$$

$$\mathcal{F} = 96500 \text{ C (oulomb)/mole}$$

$$\Delta G^\circ = -n\mathcal{F}E^\circ_{\text{cell}}$$

$$\ln k = (-E_a/RT) + \ln A$$

$$1 \text{ Volt} = 1 \text{ Joule/Coulomb}$$

$$[\text{A}] = [\text{A}]_0 - kt$$

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

$$1/[\text{A}] = 1/[\text{A}]_0 + 2kt$$

Standard hydrogen electrode: $2 \text{H}^+(aq, 1 \text{ M}) + 2 e^- \rightarrow \text{H}_2(g)$ $E^\circ = 0.000 \text{ V}$

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

“I pledge on my honor that I have not given or received any unauthorized assistance on this examination.”

(+2 pts)

1. (24 pts) Multiple choice: Circle the single best answer for each question

(a; 4 pts) Stratification in sediments or the water column comes about because

- (1) the best available terminal electron acceptor is used by the local flora and fauna until it's gone.
- (2) microorganisms have variable densities so they settle to different levels.
- (3) the organisms that can grow in the water vary with temperature.
- (4) None of the above.

(b; 4 pts) DNA hybridization (formation of double strand) has

- (1) $\Delta H^\circ < 0$ and $\Delta G^\circ < 0$ at any temperature.
- (2) $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$.
- (3) $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$.
- (4) $\Delta H^\circ > 0$ and $\Delta G^\circ > 0$ above T_m .

(c; 4 pts) A DNA microarray is used to

- (1) measure T_m on small samples.
- (2) perform multiple simultaneous hybridization experiments.
- (3) clone a variety of plasmids in cells that float across the array.
- (4) None of the above.

(d; 4 pts) Overpotential is

- (1) the reason car batteries can be recharged effectively.
- (2) frequently observed for electrode reactions where a state change (i.e. aqueous \rightarrow gas) occurs.
- (3) the requirement that a voltage greater than E_{cell} must actually be applied to convince a redox reaction to proceed.
- (4) All of the above.

(e; 4 pts) The rate law for a process $aA + bB \rightarrow cC + dD$

- (1) is given by $\text{Rate} = k[A]^a[B]^b$.
- (2) can be correctly written down by inspection if and only if the reaction is elementary.
- (3) can never depend on $[C]$ and $[D]$ because they are products.
- (4) None of the above.

(f; 4 pts) The equilibrium constants for electrochemical reactions

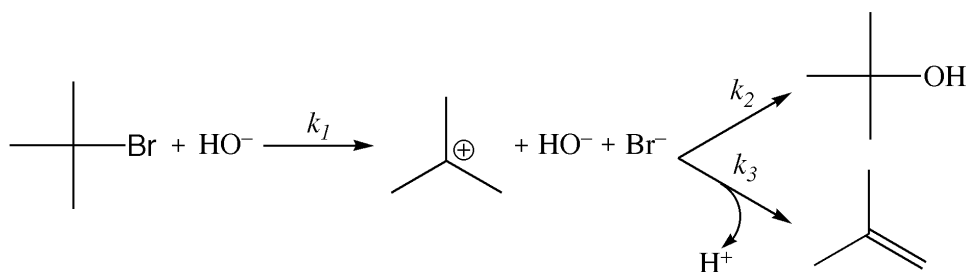
- (1) are easily measured by measuring the final concentrations of reactants and products.
- (2) are usually independent of pH.
- (3) are unmeasurable because we use E instead.
- (4) None of the above.

2. (55 pts) Kinetics, Rate Laws, and Arrhenius

(a; 12 pts) Ethane, C_2H_6 , dissociates into methyl radicals at $700\text{ }^\circ\text{C}$ with a rate constant $k = 5.5 \times 10^{-4}\text{ s}^{-1}$.

The activation energy is 384 kJ/mole . Determine the rate constant at $800\text{ }^\circ\text{C}$.

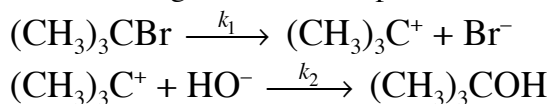
(b; 12 pts) The rate constant for the second-order reaction $2\text{ HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$ is $2.4 \times 10^{-6}\text{ M}^{-1}\text{s}^{-1}$ at 575 K and it is $6.0 \times 10^{-5}\text{ M}^{-1}\text{s}^{-1}$ at 630 K . Calculate the activation energy.



The experimental rate law for the reaction $(\text{CH}_3)_3\text{CBr} + \text{HO}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$ (above, top) in an organic solvent is $\text{Rate} \equiv -d[(\text{CH}_3)_3\text{CBr}]/dt = k[(\text{CH}_3)_3\text{CBr}]$.

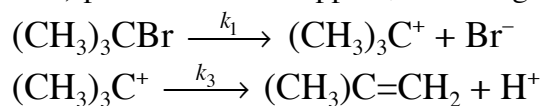
(c; 2 pts) What is the observed order of reaction with respect to HO^- ?

(d; 6 pts) The $\text{S}_{\text{N}}1$ mechanism below has been proposed for the reaction. Which step must be rate limiting for the mechanism to agree with the experiment? Briefly explain your reasoning.



(e; 9 pts) If the concentration of HO^- is decreased to a small enough value, the rate law changes: why must this be so? Explain why the steady-state approximation does not apply to anything in the reaction under these conditions.

(f; 14 pts) However, the change in the rate law at low $[\text{HO}^-]$ might be hard to observe because the E1 (Elimination 1) product can also appear, according to the mechanism below



At low T the substitution is favored, but the E1 reaction is found to dominate more and more over the $\text{S}_{\text{N}}1$ reaction as the temperature is increased (assume $[\text{HO}^-]$ is constant). What does this suggest about the values of the k_2 and k_3 rate constants for the second steps of the $\text{S}_{\text{N}}1$ and E1 reactions respectively, and the activation energies for the k_2 and k_3 steps? Sketch an Arrhenius plot to illustrate your answer.

3. (45 pts) Electrochemistry of Life and the Biosphere

The aerobic nitrification of ammonia is carried out by soil bacteria (unfortunately... excess ammonia applied as fertilizer is converted to nitrate, which is more readily washed into the Chesapeake Bay). The overall reaction at pH 7 is

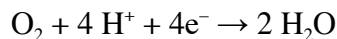


The first step in nitrification is the oxidation of ammonia to give hydroxylamine, NH_2OH , which is then converted to nitrite, NO_2^- , by the enzyme hydroxylamine oxidase (HAO). A different bug then oxidizes nitrite to nitrate.

(a; 6 pts) Balance the half-reaction for hydroxylamine oxidation to nitrite in acidic solution:



(b; 4 pts) Add the appropriate multiple of the molecular oxygen reduction half-reaction below



to your answer from (a) to give the balanced equation for this oxidation of hydroxylamine by oxygen.

(c; 4 pts) The net free energy change for the HAO reaction at the biochemical standard state is

$$\Delta G^{\circ'} = -251 \text{ kJ/mol for } n = 4. \text{ Calculate } E^{\circ'}_{\text{cell}}.$$

(d; 10 pts) Calculate E_{cell} for the HAO reaction at 0.1 mM NH_2OH , 10 mM NO_2^- , pH 5, $p\text{O}_2 = 0.1$ atm, and 25 °C.

(e; 9 pts) What are the oxidation numbers of N in NH_2OH and NO_2^- ? To get from one to the other we clearly have to pass through zero, which is the oxygen number of N in good old N_2 gas. However, N_2 is not an intermediate in the reaction. In view of what you know about catalysis, why not? [The zero-valent state is believed to be the transition state in dehydrogenation of heme-bound NH_2OH to form bound HNO .]

(f; 3 pts) A second bug oxidizes nitrite to nitrate. This is an example of what kind of relationship between two bugs? One word answer:_____.

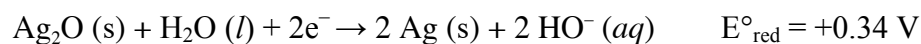
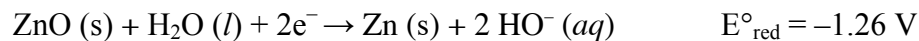
(g; 9 pts) What do the AOB's (ammonia oxidizing bacteria) gain from this nitrification process? Other bugs carry out the opposite process, reductive denitrification of NO_3^- to convert N back into amine forms— what general type of process is that?

4. (40 pts) Electrochemistry and Technology

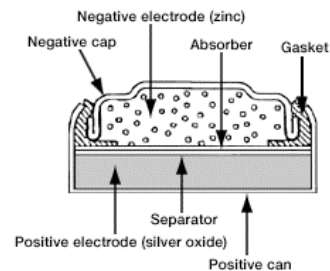
The silver oxide battery is found in hearing aids and such. It is based on reactions of Zn and Ag metals and their oxides in a basic electrolyte.

(http://www.maxell.com.sg/industrial/batteries/sr_button/images/diagram.gif)

The relevant half-reactions are



(a; 30 pts) Write down the overall cell reaction and calculate E°_{cell} , ΔG° , and K_{eq} all at 25 °C. Which reaction occurs at the anode and which at the cathode? Which way do electrons flow in the external circuit? (Sketch it on the diagram.) One advantage of this cell is that its voltage is exceptionally stable during use. Why is this the case?



(b; 10 pts) Zinc is often used as a sacrificial anode, for example to prevent rusting of structural steel or ship hulls. Briefly describe what a sacrificial anode does and why zinc is a good choice.

5. (36 pts) Miscellaneous

(a; 16 pts) Describe the two ways you could set up kinetics experiments to determine whether a reaction is first order or second order, and how you would interpret the data.

(b; 6 pts) Explain how bacteria that live in niches with abundant H_2S can use Photosystem I alone (i.e. they don't have a PS II) to provide reducing power for carbohydrate production.

(c; 5 pts) How many photons must be absorbed per molecule of O_2 produced by photosynthesis in plants?
Explain very briefly.

(d; 9 pts) Why did the emergence of life on land have to wait for all the surface iron to be oxidized to rust?

Page	Score
1	/2
2	/24
3	/24
4	/17
5	/14
6	/14
7	/31
8	/40
9	/22
10	/14
Total	

Score for the page _____