

Chemistry 271, Section 22xx

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: \_\_\_\_\_

December 16, 2011

**VIEWING: Monday, May 19, 9:30-10:30 a.m., Chem 1356-1360**

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

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

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

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

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

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

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

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

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

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

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

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

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) If the rate law for a process  $A + B \rightarrow C$  is observed to be  $\text{Rate} = k[A][B]$

- (1) the reaction must be an elementary reaction.
- (2) the reaction cannot be an elementary reaction.
- (3) the reaction might be an elementary reaction.
- (4) the experiment was done wrong.

(b; 4 pts) If the rate law for a process  $A + B \rightarrow C + D$  is observed to be  $\text{Rate} = k[A]^2/[C]$

- (1) the reaction must be an elementary reaction.
- (2) the reaction cannot be an elementary reaction.
- (3) the reaction might be an elementary reaction.
- (4) the experiment was done wrong.

(c; 4 pts) The melting temperature in DNA hybridization

- (1) increases with the number of mismatches between target and probe.
- (2) increases with the length of the complementary region.
- (3) increases as the concentration of DNA decreases.
- (4) None of the above.

(d; 4 pts) Cyclic reactions  $A \rightarrow B \rightarrow C \rightarrow A$

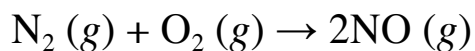
- (1) are impossible.
- (2) can proceed in a net forward direction as drawn only if we heat the reaction to drive it.
- (3) at equilibrium, must also proceed in reverse at the same rate for each step.
- (4) None of the above.

(e; 4 pts) Nitrogen fixation describes conversion of

- (1)  $N_2$  to  $NH_3$ .
- (2)  $NH_3$  to  $NO_3^-$ .
- (3)  $NO_3^-$  to  $N_2$ .
- (4)  $NH_3$  to  $NO_3^-$ .

(f; 4 pts) The lead-acid battery used in cars is so large and heavy because

- (1) the weight of the battery is needed to adjust the car's suspension.
- (2) it needs to store a lot of energy to recharge the alternator while driving.
- (3) it needs to have 60 internal cells to provide 120 V to the distributor and the car's electronics.
- (4) the starter motor requires high power and therefore current to move the pistons in the engine.

**2. (48 pts) Kinetics, Rate Laws, and Arrhenius**

The rate constant  $k$  for this reaction, which occurs during combustion as a precursor to  $\text{NO}_2$  in smog formation, is 318 (units) at 2000 K and 7396 (units) at 2400 K. (Derived from Gilbert 15.85.)

(a; 6 pts) Write down the rate law for the reaction assuming that it is elementary. What are the units for the rate constant?

(b; 12 pts) Calculate the activation energy ( $E_a$ ) and the pre-exponential factor ( $A$ ) for the reaction.

(c; 6 pts) Calculate the rate constant at 300 K. Given that NO is poisonous, it's a good thing the reaction is slow at anything close to room temperature.

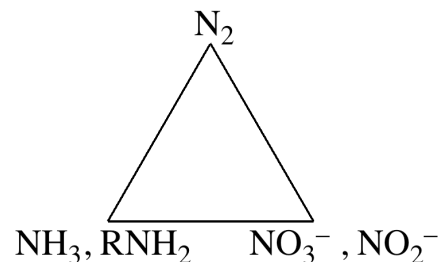
(d; 12 pts) The half-life of  $^{137}\text{Cs}$ , one of the main radioactive pollutants from the Fukushima and Chernobyl disasters, is 30.2 years. From the integrated rate equation for a first-order reaction, derive an expression for the half-life in terms of the rate constant, and calculate the rate constant for Cs-137 decay.

(e; 12 pts) Explain the functional form of the Maxwell-Boltzmann distribution  $P(v)dv = Cv^2 \exp(-mv^2/2kT)$ . In other words, where do the  $v^2$  and  $\exp(-mv^2/2kT)$  factors come from? Explain why doubling the temperature typically causes much more than a factor of 2 increase in the rate of elementary processes.

**3. (40 pts) Electrochemistry of Life and the Biosphere**

The nitrogen triangle describes the interconversions among different oxidation states of nitrogen in the biosphere.

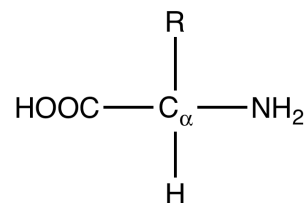
(a; 6 pts) Is conversion of  $N_2$  to  $NH_3$  and amines a reduction or an oxidation? Is it assimilation or dissimilation?



(b; 9 pts) Nitrification refers to the oxidation of ammonia to nitrite or nitrate. Why do prokaryotes do this, assuming that they don't use nitrate for biomass? Why is this generally an aerobic process? What do we call the oxygen in aerobic nitrification?

(c; 9 pts) Denitrification is the reduction of nitrate to  $N_2$ . What might the reducing agent be, generically? What function is the nitrate serving? Is this assimilation or dissimilation?

(d; 6 pts) Eukaryotes like us don't affect the nitrogen triangle very much (at least insofar as our personal metabolisms as opposed to industrial processes are concerned). Why not? What is the oxidation number of nitrogen in an amino acid, as at the right?

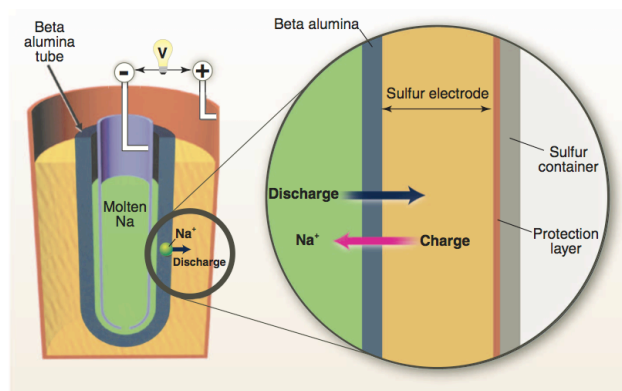


(e; 10 pts) Why did the emergence of life on land have to wait for all the surface iron to be oxidized to rust?

#### 4. (40 pts) Electrochemistry and Technology

The sodium-sulfur battery has been proposed as an energy storage component of the “smart grid.” Sodium ions migrate through the beta alumina tube, but anions cannot go through it. Molten  $\text{Na}_2\text{S}_5$  and molten S are immiscible liquids.

The relevant half-reactions are



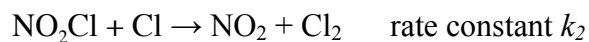
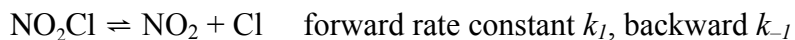
(a; 21 pts) Write down the overall reaction for the discharge part of the cycle (getting energy out of the battery), and calculate  $n$ . What is the composition of the molten sulfur electrode as the discharge progresses? The beta alumina tube is acting like a component of the simple beaker-based reactions we studied. Which component? How could you tell by just looking at the inside of the battery over time whether it was charging or discharging? Finally, why must water be rigorously excluded from the inside of the battery?

(b; 9 pts) Calculate  $E^\circ_{\text{cell}}$ ,  $\Delta G^\circ$ , and  $K_{eq}$  for the sodium-sulfur battery, all at 300 °C, assuming that the  $E^\circ_{\text{cell}}$  is the same as it is at 25 °C. (The battery actually operates at about 300 °C to keep everything molten, which is why you are not likely to have one at home.)

(c; 10 pts) Energy storage in a smarter grid would allow for “load shifting,” for example from mid-afternoon to nighttime. What does this mean and why is it a good idea?

**5. (20 pts) SSA**

The gas phase decomposition of  $\text{NO}_2\text{Cl}$  to give  $2 \text{NO}_2 + \text{Cl}_2$  was proposed to occur as follows:



(a; 16 pts) Apply the SSA to the reactive chlorine atoms to show that the rate of appearance of  $\text{Cl}_2$  should be

$$\frac{d[\text{Cl}_2]}{dt} = \frac{k_1 k_2 [\text{NO}_2\text{Cl}]^2}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2\text{Cl}]}$$

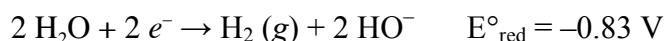
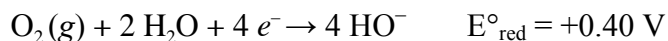
(b; 4 pts) Under what conditions would you expect to observe a rate that is second order with respect to  $\text{NO}_2\text{Cl}$  ?



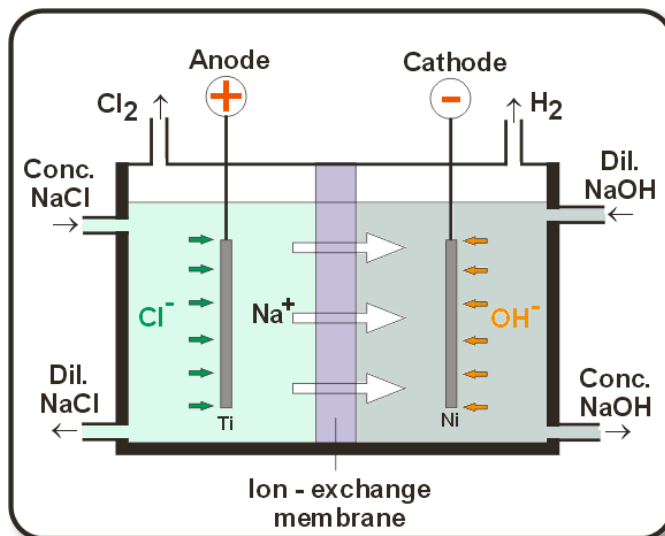
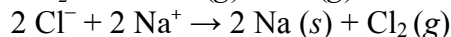
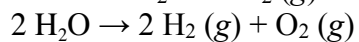
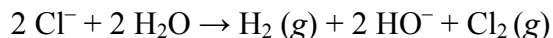
**6. (28 pts) Industrial electrochemistry**

The Chloralkali process is the source of most chlorine gas and other oxidized forms of chlorine used for bleach etc. It is also a major player in Neal Stephenson's early science fiction novel *Zodiac*. The electrolysis process occurs under aqueous basic conditions.

Relevant half reactions are:



(a; 9 pts) Calculate  $E^\circ_{\text{cell}}$  for each of the following reactions.



(b; 6 pts) Calculate  $E_{\text{cell}}$  for  $2 \text{Cl}^- + 2 \text{H}_2\text{O} \rightarrow \text{H}_2(g) + 2 \text{HO}^- + \text{Cl}_2(g)$  at 4 M NaCl, pH 10, 0.1 atm each gas.

(c; 13 pts) Explain why it is not surprising that solid Na is not produced from the electrolysis of brine, but it is surprising that we actually get any chlorine gas! What must be true of the electrochemistry occurring at the titanium anode? Where have we seen a very similar situation before? Give the balanced total reaction for the chloralkali cell.

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