Chemistry 271
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University of Maryland, College Park
General Chemistry and Energetics
Final Exam (200 points total)

Your Name: ______________________________

Your SID #: ______________________________

Your Section # or time: ______________________________

December 14, 2012

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:

$K_a = [H^+][A^-]/[HA]$ $\quad$ $pH = -\log([H^+])$ $\quad$ $K_b = [HA][HO^-]/[A^-]$

$K_w = [H^+][HO^-]$ $\quad$ $pH = pK_a + \log [A^-]/[HA]$ $\quad$ $\Delta G° = -RT\ln K_{eq}$

$R = 0.08206$ L·atm/mole K $\quad$ $k_B = 1.38 \times 10^{-23}$ J/K $\quad$ $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$\Delta S - q/T \geq 0$ $\quad$ R = 8.314 J/mole K = 1.987 cal/mole K = $N_A k_B$

$S = k_B \ln W$ $\quad$ $\Delta G = \Delta H - T\Delta S$ $\quad$ $E = \Sigma\, n_i\, \varepsilon_i$

$W = N!/(\prod n_i!)$ $\quad$ $n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$ $\quad$ $N = \Sigma\, n_i$

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

°C = °K – 273.15 $\quad$ $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\quad$ $E = E° - 2.303(RT/n\mathcal{F})\log_{10}Q$

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C $\quad$ $\mathcal{F} = 96500$ C(oulomb)/mole

$\Delta G° = -n\mathcal{F}E°_{cell}$ $\quad$ $\ln k = (-E_a/RT) + \ln A$ $\quad$ 1 Volt = 1 Joule/Coulomb

$[A] = [A]_0 - kt$ $\quad$ $\ln[A] = \ln[A]_0 - kt$ $\quad$ $1/[A] = 1/[A]_0 + 2kt$

Standard hydrogen electrode: $2\ H^+ (aq, 1\ M) + 2\ e^- \rightarrow H_2\ (g)$ $\quad$ $E° = 0.000$ 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."

1. Kinetics

Chlorofluorocarbon refrigerants (CFCs) were banned because they destroy UV-protective ozone, O_3, in the atmosphere. UV photolysis of CFCs gives chlorine radicals ($Cl = Cl\cdot$). For complicated reasons, Cl is produced most efficiently in the Antarctic, hence the ozone hole there. One of several ozone-destroying catalytic cycles is described below. There is a significant concentration of both O_3 and O atoms in the upper stratosphere due to photolysis of O_2. We will assume $[O_3] = 2 \times 10^{-9}$ M and $[O] = 3 \times 10^{-12}$ M. Chlorine radicals catalyze the recombination of these "odd-oxygen" species to give two molecules of O_2 according to reactions (1) and (2) below. The same recombination can also happen in an uncatalyzed fashion. We will apply the Steady State Approximation (SSA) to the reactive intermediates ClO and Cl and compare the catalyzed and uncatalyzed rates. [Sources: Davis and Davis, *Fundamentals of Chemical Reaction Engineering*, and www.ccpo.odu.edu/~lizsmith/SEES/ozone/oz_class.htm]

(1) $Cl\ (g) + O_3\ (g) \rightarrow ClO\ (g) + O_2\ (g)$ $k_1 = 3 \times 10^{10}\ M^{-1}s^{-1} \exp(-1200\ (J/mole)/RT)$

(2) $ClO\ (g) + O\ (g) \rightarrow Cl\ (g) + O_2\ (g)$ $k_2 = 6 \times 10^{10}\ M^{-1}s^{-1} \exp(-1800\ (J/mole)/RT)$

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(3) $O_3\ (g) + O\ (g) \rightarrow 2\ O_2\ (g)$ net rxn, uncatalyzed $k_3 = 1 \times 10^{10}\ M^{-1}s^{-1} \exp(-19000\ (J/mole)/RT)$

(a; 3 pts) Write down the differential expression for the rate law for the uncatalyzed loss of O_3 according to reaction (3), assuming that it is an elementary reaction.

(b; 3 pts) Explain how the reactive Cl/ClO species meet the definition of a catalyst.

(c; 6 pts) For the catalyzed reaction, write down the differential rate equation for the rate of change of [ClO], set it to zero according to the SSA, and solve for [ClO] in terms of k_1, k_2, $[O_3]$, [O], and [Cl].

(d; 10 pts) In this scheme, the total concentration of activated chlorine species is equal to a constant we denote $[Cl/ClO]_T = [Cl] + [ClO]$. Use this relationship and your answer to (c) to show that [ClO] in terms of k_1, k_2, $[O_3]$, [O], and $[Cl/ClO]_T$ is given by $[ClO] = (k_1[Cl/ClO]_T[O_3])/(k_2[O] + k_1[O_3])$. Explain in terms of the rates for reactions (1) and (2) why the steady state concentration of [ClO] is decreased when we carry out the experiment at increased [O].

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(e; 8 pts) Write down the differential rate law for the loss of [O_3] in the catalytic cycle, and show that the rate law in terms of k_1, k_2, [O_3], [O], and [Cl/ClO]$_T$, starting from the expression in (d), is

$$-\frac{d[O_3]}{dt}=\frac{k_1k_2[O][Cl/ClO]_T[O_3]}{k_2[O]+k_1[O_3]}\approx k_2[O][Cl/ClO]_T \text{ for } k_2[O]= k_1[O_3]$$

(f; 8 pts) Calculate initial rates for both the catalyzed and the uncatalyzed destruction of O_3 at 200 K (it's cold up there), with [Cl/ClO]$_T$ = 10^{-12} M, [O_3] = 2×10^{-9} M, and [O] = 3×10^{-12} M. At 200 K, $k_1 = 1.5 \times 10^{10}$ M^{-1}s^{-1}, $k_2 = 2 \times 10^{10}$ M^{-1}s^{-1}, and $k_3 = 1 \times 10^{5}$ M^{-1}s^{-1}.

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2. Electrochemistry

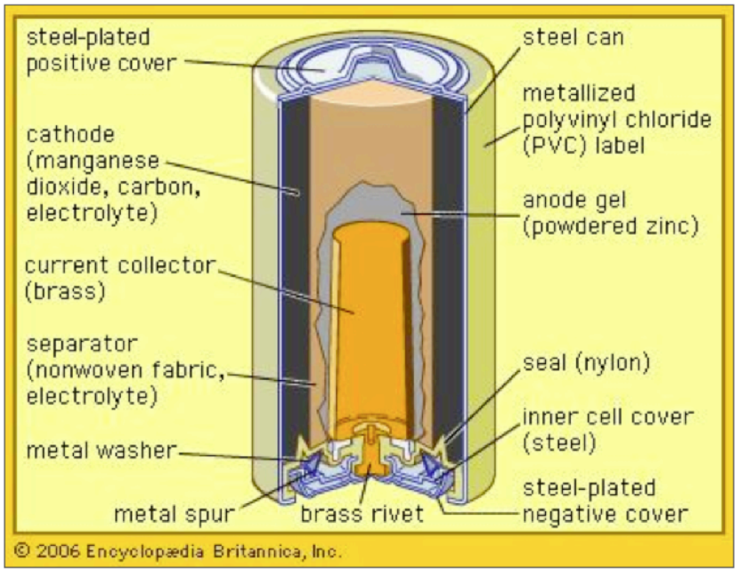
The standard nonrechargeable (“primary”) alkaline cell shown at the right is based on the half reactions below:

$ZnO (s) + H_2O (l) + 2 e^- \rightarrow$
$Zn (s) + 2 OH^- (aq) \qquad E°_{red} = -1.28$ V

$2 MnO_2 (s) + H_2O (l) + 2 e^- \rightarrow$
$Mn_2O_3 (s) + 2 OH^- (aq) \quad E°_{red} = 0.15$ V

The OH^- comes from the potassium hydroxide electrolyte present in both the anode and the cathode (that’s why they call it an alkaline cell). The carbon in the cathode is just for conductivity.

alkaline cell



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Cutaway view of an alkaline–manganese dioxide power cell.

(a; 10 pts) Write down the overall cell reaction and calculate $E°_{cell}$.

(b; 3 pts) Why are finely powdered Zn(s) and MnO_2(s) used instead of just a chunks o’ zinc and manganese dioxide?

(c; 7 pts) The “separator” is analogous to the salt bridge in our standard two-beaker setup. What is its function? How is the electrical circuit completed in the alkaline battery?

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(d; 12 pts) Based only on the Nernst equation for the overall cell reaction, how should the voltage change as this battery is depleted? In fact, the cell voltage does drop off gradually as the battery is discharged. Speculate about how/why this occurs, considering that some concentrations may differ in different compartments. In general, why does E_{cell} change only gradually until a battery is nearly completely drained?

(e; 4 pts) Recharging primary cells is not recommended. Considering the half-reaction for the reduction of ZnO, what undesirable competing reaction could cause problems upon recharging? [Hint: is there something else present that could be reduced?]

(f; 10 pts) (Unrelated) Briefly describe the Standard Hydrogen Electrode and why we need an electrode with an arbitrary reference voltage.

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3. Metakinetics

(a; 12 pts) Describe the principle of microscopic reversibility. Sketch the connection between microscopic reversibility and the idea that a cyclic reaction cannot proceed unidirectionally without external inputs. If we could violate the principle, what sort of thermodynamically forbidden machine could we build?

(b; 10 pts) Sketch the linear Arrhenius plot and label how one would use it to calculate A and Ea.

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(c; 4 pts) We have described the Eyring vs. Collision theories for chemical kinetics and shown that they both predict a temperature dependence for the rate constant that agrees with the empirical Arrhenius law, but with different predicted temperature dependences of the preexponential factor, T^1 vs. $T^{1/2}$ vs. T^0 respectively. Why don't the three treatments give us measurably different predictions for the temperature dependence of k?

(d; 15 pts) Explain why the measured half-life for a second order reaction is not quantitatively useful without more information. Explain why the half-life for a first-order reaction is independent of concentration. Explain why there is no such thing as a truly zero order reaction A → B.

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4. DNA hybridization

(a; 8 pts) Give two reasons that DNA hybridization has a negative ΔS°.

(b; 20 pts) The equation for DNA melting temperature is $T_m = \Delta H°/(\Delta S° + R \ln(C_T/4))$, where the total strand concentration C_T is taken to be 10^{-6} M. Calculate T_m for Oligonucleotide #1 with $\Delta H°_1 = -38$ kcal/mole and $\Delta S°_1 = -85$ cal/mole K. Calculate T_m for Oligonucleotide #2 with $\Delta H°_2 = -52$ kcal/mole and $\Delta S°_2 = -130$ cal/mole K. At what temperature would the melting curves cross, assuming we have normalized out any differences among extinction coefficients and changes in extinction coefficient with temperature? [Hint: What is the relationship between the K_{eq}s when the curves cross?] Sketch the melting curves for oligonucleotides 1 and 2.

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(c; 8 pts) Why don't we carry out hybridization reactions either far below or far above the T_m of the desired hybridization?

(d; 9 pts) Sketch the hybridization of a PCR primer to a specific target and sketch two alternative products that could screw up the reaction.

5. Climate change

(a; 6 pts) How does burning fossil fuel to produce CO_2 cause global climate change?

(b; 4 pts) Given that CO_2 emission is bad, the motivation for carbon (= CO_2) capture and sequestration is clear. We already have the technology to liquefy CO_2 under pressure (as in fire extinguishers) and pump it to the bottom of the ocean where it will sit around indefinitely. In terms of thermodynamics, why aren't we already doing this?

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(c; 4 pts) Why does fat have more calories per gram than carbohydrate?

(d; 8 pts) The fracking boom, whereby natural gas = methane is extracted in copious amounts from previously inaccessible deposits, has caused some degree of schizophrenia among environmentalists. One the one hand, fracking may or may not pollute groundwater and cause earthquakes, which is bad. On the other hand, people say that burning natural gas obtained by fracking buys us time in the race against global warming. How is fracking perhaps buying us time? [Hint: What else do we burn to make electricity?]

(e; 8 pts) Current hydrogen-fueled vehicles may improve air quality in cities, but they don't help with global warming. Why not? What further advance would be needed for them to help reduce CO_2 emission?

Page	Score
2	/12
3	/10
4	/16
5	/20
6	/26
7	/22
8	/19
9	/28
10	/27
11	/20
Total	**/200**

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