Your Name: _________________________________

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General Chemistry and Energetics
Final Exam (200 points total)

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:

\[ K_w = [H^+][OH^-] \]

\[ K_a = \frac{[H^+][A^-]}{[HA]} \]

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

\[ pH = pK_a + \log[A^-]/[HA] \]

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

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

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

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

\[ \Delta S - q/T \geq 0 \]

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

\[ S = k_B \ln W \]

\[ \Delta G = \Delta H - T \Delta S \]

\[ E = \Sigma n_i \epsilon_i \]

\[ W = N!/(\Pi n_i!) \]

\[ n_i/n_0 = \exp[-(\epsilon_i-\epsilon_0)/kT] \]

\[ N = \Sigma n_i \]

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

\[ ^\circ C = ^\circ K - 273.15 \]

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

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

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

\[ \Delta G^\circ = -nF \epsilon^\circ_{\text{cell}} \]

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

\[ 1 \text{ Volt} = 1 \text{ Joule/Coulomb} \]

\[ [A] = [A]_0 - kt \]

\[ \ln[A] = \ln[A]_0 - kt \quad \frac{\ln[A]}{\ln[A]_0} = 1/[A] = 1/[A]_0 + 2kt \quad \frac{\ln[A]}{\ln[A]_0} = \frac{1}{[A]} \]

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

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.”
1. Kinetics

Chlorofluorocarbon refrigerants (CFCs) were banned because they destroy UV-protective ozone, O₃, in the atmosphere. UV photolysis of CFCs gives chlorine radicals (Cl = Cl⁺). 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 O₃ and O atoms in the upper stratosphere due to photolysis of O₂. We will assume [O₃] = 2 × 10⁻⁹ M and [O] = 3 × 10⁻¹² M.

Chlorine radicals catalyze the recombination of these “odd-oxygen” species to give two molecules of O₂ 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) + O₃ (g) → ClO (g) + O₂ (g) \( k₁ = 3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \exp(-1200 \text{ (J/mole)/RT}) \)

(2) ClO (g) + O (g) → Cl (g) + O₂ (g) \( k₂ = 6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \exp(-1800 \text{ (J/mole)/RT}) \)

(3) O₃ (g) + O (g) → 2 O₂ (g) \( \text{net rxn, uncatalyzed} \quad k₃ = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \exp(-19000 \text{ (J/mole)/RT}) \)

(a; 3 pts) Write down the differential expression for the rate law for the uncatalyzed loss of O₃ according to reaction (3), assuming that it is an elementary reaction.

\[
\text{Rate} = -\frac{d[O_3]}{dt} = k₃ [O_3][O]
\]

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

- The reactive chlorine species participate in the reaction but are neither created nor destroyed.

(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 \( k₁, k₂, [O₃], [O], \) and [Cl].

\[
\frac{d[\text{ClO}]}{dt} = k₁ [\text{Cl}][O₃] - k₂ [\text{ClO}][O] = 0
\]

\[
 k₂[\text{ClO}][O] = k₁[\text{Cl}][O₃]
\]

\[
[\text{ClO}] = \frac{k₁[\text{Cl}][O₃]}{k₂[O]}
\]
(d; 10 pts) In this scheme, the total concentration of activated chlorine species is equal to a constant we denote $[\text{Cl}/\text{ClO}]_t = [\text{Cl}] + [\text{ClO}]$. Use this relationship and your answer to (c) to show that $[\text{ClO}]$ in terms of $k_1, k_2, [O_3], [O],$ and $[\text{Cl}/\text{ClO}]_t$ is given by $[\text{ClO}] = \left( k_1 [\text{Cl}/\text{ClO}]_t [O_3] \right) / \left( k_2 [O] + k_3 [O_3] \right)$. Explain in terms of the rates for reactions (1) and (2) why the steady state concentration of $[\text{ClO}]$ is decreased when we carry out the experiment at increased $[O]$.

$$[\text{Cl}/\text{ClO}]_t = [\text{Cl}] + [\text{ClO}] \quad \text{so} \quad [\text{Cl}] = [\text{Cl}/\text{ClO}]_t - [\text{ClO}]$$

$$[\text{ClO}] = \frac{k_1 [O_3]}{k_2 [O]} \cdot [\text{Cl}/\text{ClO}]_t$$

need to substitute for $\text{Cl}$ to solve for $[\text{ClO}]$ in terms of total reactive chlorine.

$$[\text{ClO}] \left( 1 + \frac{k_1 [O_3]}{k_2 [O]} \right) = \frac{k_1 [O_3]}{k_2 [O]} \cdot [\text{Cl}/\text{ClO}]_t$$

$$[\text{ClO}] \left( k_2 [O] + k_1 [O_3] \right) = k_1 [O_3] [\text{Cl}/\text{ClO}]_t$$

$$[\text{ClO}] = \frac{k_1 [O_3] [\text{Cl}/\text{ClO}]_t}{k_2 [O] + k_1 [O_3]}$$

- If $[O]$ is increased, we see from the equation that $[\text{ClO}]$ is decreased. Physically this is because the $O$ atoms react with $\text{ClO}$ to form $\text{Cl}_2$, so the higher the $[O]$ the more reactive Cl particles into $\text{Cl}_2$ rather than $\text{ClO}$. (2 points)

Score for the page 10
(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 \([Cl/ClO]_r\), starting from the expression in (d), is

\[
-\frac{d[O_3]}{dt} = k_1[C_1][O_3] = k_1 \left( [Cl/ClO]_r - [ClO] \right) [O_3]
\]

\[
= k_1 \left( [Cl/ClO]_r - \frac{d_1[C_1/ClO]_r + [ClO]}{d_1[C_1/ClO]_r + k_1[O_3]} \right) [O_3]
\]

\[
= k_1 [Cl/ClO]_r [O_3] \left( \frac{d_2[O] + d_1[ClO]}{d_1[C_1/ClO]_r + k_1[O_3]} - \frac{d_2[ClO] + d_1[Cl]}{d_1[C_1/ClO]_r + k_1[O_3]} \right)
\]

If \(d_2[O] < d_1[O_3], \) \(d_2[ClO] \) cancels to give

\[
-k_1 \left( [Cl/ClO]_r - \frac{d_1[C_1/ClO]_r + [ClO]}{d_1[C_1/ClO]_r + k_1[O_3]} \right) [O_3]
\]

(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 \([Cl/ClO]_r = 10^{-12} \text{ M}, [O_3] = 2 \times 10^{-9} \text{ M}, \) and \([O] = 3 \times 10^{-12} \text{ M}. \) At 200 K, \(k_1 = 1.5 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}, \) \(k_2 = 2 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}, \) and \(k_3 = 1 \times 10^{5} \text{ M}^{-1} \text{s}^{-1}.\)

uncatalyzed: \(\frac{-d[O_3]}{dt} = k_3 [O_3] [O]\)

\[
= 1 \times 10^5 \text{ M}^{-1} \text{s}^{-1} \cdot 2 \times 10^{-9} \text{ M} \cdot 3 \times 10^{-12} \text{ M} = 6 \times 10^{-16} \text{ M}^2 \text{s}^{-1}
\]

\(\text{+2 for plugging in}\)

catalyzed: \(k_2[O] = 2 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}, 3 \times 10^{-12} \text{ M} = 6 \times 10^{-2} \text{ s}^{-1}\)

\(k_1[O_3] = 1.5 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}, 2 \times 10^{-9} \text{ M} = 3 \times 10^{-1} \text{ s}^{-1} \Rightarrow k_2[O]\)

\(\text{so } \frac{-d[O_3]}{dt} = k_2[O][Cl/ClO]_r = 6 \times 10^{-2} \text{ s}^{-1} \cdot 10^{-12} \text{ M} = 6 \times 10^{-14} \text{ M}^2 \text{s}^{-1} \Rightarrow 100 \text{ fold faster than uncatalyzed}\)

\(\text{Score for the page } \frac{11}{16} \)
2. Electrochemistry

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

\[ \text{ZnO (s) + H}_2\text{O (l) + 2 e}^- \rightarrow \text{Zn (s) + 2 OH}^- (\text{aq}) \quad E^\circ_{\text{red}} = -1.28 \text{ V} \]

\[ 2 \text{MnO}_2 (\text{s}) + \text{H}_2\text{O (l) + 2 e}^- \rightarrow \text{Mn}_2\text{O}_3 (\text{s}) + 2 \text{OH}^- (\text{aq}) \quad E^\circ_{\text{red}} = 0.15 \text{ V} \]

The \( \text{OH}^- \) 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.

(a; 10 pts) Write down the overall cell reaction and calculate \( E^\circ_{\text{cell}} \).

\[ \text{Zn(s) + 2MnO}_2 (\text{s}) \rightarrow \text{ZnO(s) + Mn}_2\text{O}_3 (\text{s}) \quad E^\circ_{\text{cell}} = \text{?} \]

(b; 3 pts) Why are finely powdered Zn(s) and MnO\(_2\)(s) used instead of just chunks of zinc and manganese dioxide?

- Greater surface area means that more electrons can be transferred, so the cell can provide higher current.

(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?

\[ \text{MnO}_2 \quad \text{ZnO} \quad \text{Mn}_2\text{O}_3 \quad \text{K}^+ \quad \text{H}_2\text{O} \]

Score for the page____________
(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 $E_{\text{cell}}$ change only gradually until a battery is nearly completely drained?

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

But $Q = 1$ for all solids $\rightarrow$ no change in voltage

But in fact $[\text{NO}]$ is being consumed at the anode and produced at the cathode. If there is any movement of $K^+ \text{ ions}$ instead of NO, the concentration of [NO] will decrease at the anode and $\text{NO}_2$ at cathode, and $E < 0$. Reactions are strongly driven, so $Q$ must be more than 1 for $E$ to change.

(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?]

$$\text{ZnO} \rightarrow \text{Zn} + \text{O}_2 \text{ gas, } E^\circ_{\text{red}} = -1.28 \text{ V}$$

$$2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{O}_2 \text{ gas, } E^\circ_{\text{red}} = 1.23 \text{ V}$$

Water will be reduced to give $\text{H}_2$! needed

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

$$E^\circ_{\text{H}_2 \text{gas}} = 0.000 \text{ V}, \text{ thus } E^\circ_{\text{red}} = 0.000 \text{ V} as well}$$

The reduction $\text{H}_2$ $\text{gas}$ is

$$+3 \cdot 2 \text{H}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$$

But the reaction can go either way without consuming the electrode.

- We need a standard half cell because
  - redox reactions require an oxidation and a reduction so we can only measure
  - voltage differences.

We reference all the differences to an arbitrary set point.

Score for the page
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 $E_a$. 

Score for the page
(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 $k$?

- The temperature dependence of the pre-exponential is much weaker than that of the exponential, so we can distinguish it from noise.

\[
\text{Example: } k = 10^{10} e^{-\frac{10,000}{T}}
\]

For $T = 298 K$,

\[
K = \frac{4 \times 10^{-13}}{250^{-1/2}} \approx 1.1 \times 10^{-11}
\]

For $T = 298 K$,

\[
K = \frac{4 \times 10^{-13}}{300^{-1/2}} \approx 1.4 \times 10^{-11}
\]

- 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 $A \rightarrow B$.

\[
\ell_{1/2} = \frac{1}{2 \ln [A]_0} \quad \text{sec}
\]

For 1st order the half-life depends on the initial concentration - it actually changes during the measurement. We need to know the [A]_0 to get the rate constant which is what's fundamental.

\[
\ell_{1/2} = \ln 2 \quad \text{sec}
\]

For 2nd order reaction -

\[
\ell_{1/2} = \frac{1}{4 \ln [A]_0} \quad \text{sec}
\]

For 3rd order reaction -

\[
\ell_{1/2} = \frac{1}{6 \ln [A]_0} \quad \text{sec}
\]

The rate law must be $0$ if there is no $A$, so at low [A] the rate law must become 1st order or higher in $A$ - it looks zero order only when there is a large $K_S$ of $A$.

Score for the page: 119
4. DNA hybridization

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

- Two separate molecules move together → translational entropy
- Each single strand is locked into a more ordered conformation in the double -→ conformational entropy

(b; 20 pts) The equation for DNA melting temperature is \( T_m = \frac{\Delta H^o}{\Delta S^o + R \ln(C_T/4)} \), where the total strand concentration \( C_T \) is taken to be 10⁻⁶ M. Calculate \( T_m \) for Oligonucleotide #1 with \( \Delta H^o_1 = -38 \text{ kcal/mole} \) and \( \Delta S^o_1 = -85 \text{ cal/mole K} \). Calculate \( T_m \) for Oligonucleotide #2 with \( \Delta H^o_2 = -52 \text{ kcal/mole} \) and \( \Delta S^o_2 = -130 \text{ cal/mole K} \). 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 \( K_o \)s when the curves cross?] Sketch the melting curves for oligonucleotides 1 and 2.

\[
T_m = \frac{\Delta H^o}{\Delta S^o + R \ln(C_T/4)}
\]

1. \( T_m = \frac{-38000 \text{ cal/mole}}{-85 + \ln(10^{-6})} = 330K = 56.7 \degree C \)

2. \( T_m = \frac{-52000}{-130 + \ln(10^{-6})} = 324K = 59.4 \degree C \)

For curves to cross, \( K_o's \) are equal, so \( \Delta G's \) are equal.

\[
\Delta G^o = \Delta H^o - T \Delta S^o = \Delta G^o_2 = \Delta H^o_1 - T \Delta S^o_2
\]

\[
T = \frac{\Delta H^o_1 - \Delta H^o_2}{\Delta S^o_1 - \Delta S^o_2} = \frac{-38000 - 52000}{-85 - (-130)} = \frac{14000}{45} \text{ cal/mole} \cdot K = 311K = 38 \degree C
\]

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

- For below $T_m$ there is no specificity - mismatches are stable
- For above $T_m$ there is no signal - nothing is stable.

(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?

- CO$_2$ absorbs IR radiated from the earth and re-emits it randomly. +3 Some of it goes back to earth. +3 for identifying the greenhouse effect.
- There is less IR is emitted to space and the earth warms up. +1 This is the greenhouse effect.

(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?

- If it costs more energy to sequestrate a ton of CO$_2$ than the energy that we get from producing the CO$_2$, it’s a net waste - more CO$_2$ is emitted. +4 So the technology is not yet efficient enough.

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

\[ +4 \]
- more electron per carbon atom
- more efficient packaging of C because H2O vs. H2O with it

\[ -4 \] Per only this answer

(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?]

\[ +4 \]
- If we were not burning CH4, we would still be burning coal to make electricity, so about 2x as much CO2 would be emitted per kWh.

\[ +4 \]
- Fracking means that CO2 emissions are not as large as they would be, so we have more time to create solutions like biomass/smart grid/and/nuclear/solar/H2 that will be sustainable.

(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 CO2 emission?

\[ +4 \]
Right now we make H2 from steam reforming of natural gas or coal + the WASR, so we are emitting CO2.

\[
\begin{align*}
C + H_2O & \rightarrow CO_2 + H_2 \\
CH_4 + O_2 & \rightarrow CO_2 + 2H_2
\end{align*}
\]

So we would need some way to make H2 without generating CO2, like electrolysis of H2O using nuclear power for electricity.

\[ +4 \]

\[
\begin{array}{|c|c|}
\hline
\text{Page} & \text{Score} \\
\hline
2 & /12 \\
3 & /10 \\
4 & /16 \\
5 & /20 \\
6 & /26 \\
7 & /22 \\
8 & /19 \\
9 & /28 \\
10 & /27 \\
11 & /20 \\
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Score for the page__________