

**Chemistry 271, Section 22xx
General Chemistry and Energetics
Final Exam (200 points total)**

**University of Maryland, College Park
Prof. Jason Kahn
May 14, 2010**

You have 120 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. 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.

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

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."

Your Name: _____

Your SID #: _____

Viewing: Monday, May 17, 9:30-10:30 a.m., Chemistry 1112 (Wing 1)

Useful Equations:

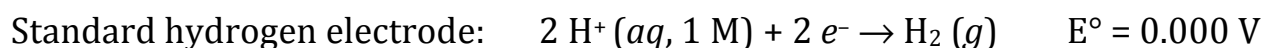
$$\Delta S - q/T \geq 0$$

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

$$K_a = [H^+][A^-]/[HA]$$

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

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



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

$$[A] = [A]_0 - kt$$

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

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

$$n_i/n_0 = \exp[-(E_i - E_0)/kT]$$

$$R = 8.314 \text{ J/mole K}$$

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

$$S = k \ln W$$

$$PV = nRT$$

$$\Delta G = -n\mathcal{F}E$$

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

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

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

$$1/[A] = 1/[A]_0 + 2kt$$

1. Multiple Choice (30 pts)

(i; 5 pts) The half life $t_{1/2}$ of a second order reaction $A + A \rightarrow B$

- (a) $= \ln 2/k$.
- (b) $= \{k([A]_0)^2\}^{-1}$.
- (c) $= [A]_0/k$.
- (d) is shorter than the half life of a first-order reaction.
- (e) none of the above

(ii; 5 pts) A first-order rate constant

- (a) has units of time^{-1} .
- (b) is inversely related to half-life.
- (c) depends on reactant concentration.
- (d) has units of $\text{M}^{-1}\text{s}^{-1}$.
- (e) (a) and (b).

(iii, 5 pts) The function of Photosystem I in plants is to

- (a) use light energy to oxidize carbon dioxide.
- (b) use light energy to reduce NADP^+ to NADPH.
- (c) oxidize water to provide light.
- (d) re-reduce Photosystem II.
- (e) oxidize water and transfer electrons to H^+ .

(iv, 5 pts) Syntrophy is defined as

- (a) consumption of the product of the reduction of one microbe's terminal electron acceptor by another microbe for their mutual benefit.
- (b) any interaction among microorganisms that live in the same environment.
- (c) microorganisms that make synthetic chemicals.
- (d) [deleted bad pun on Sin Trophy]
- (e) pathogens that co-infect target hosts.

(v, 5 pts) Stratification of inorganic NO_3^- , SO_4^{2-} , and other species in the water column or in sediments originates because

- (a) anaerobes are heavier than aerobes so they sink.
- (b) sulfate and nitrate react with metals in the soil so they are present only near the top.
- (c) weathering and currents leach out different ions at different depths.
- (d) at any depth, the organism that is capable of using the best available terminal electron acceptor dominates, so the other terminal electron acceptors are left alone.
- (e) None of the above.

(vi, 5 pts) The fundamental condition for applicability of the Steady State Approximation is

- (a) The product concentration must be zero.
- (b) The concentration of the intermediate cannot change at all during the reaction.
- (c) There must be a rapid pathway for decay of the steady state intermediate.
- (d) The activation energy for the reaction must be smaller than the ΔG° .
- (e) The reaction must be second-order.

2. Short Answer (36 pts)

(a; 6 pts) Give two statements that must be true for a substance to be called a catalyst for a reaction.

(b; 6 pts) Why does www.350.org call “350” the most important number in the world?

(c; 6 pts) The main function of Photosystem II in plants is to provide electrons to re-reduce Photosystem I. What is the oxidation half-reaction used, and why was that choice advantageous during evolution?

(d; 9 pts) What is a “sustainability wedge”? Algal biofuel may provide one: what is an advantage of biofuel in general over wind/solar/nuclear energy?

(e; 9 pts) We considered the temperature dependence of rate constants in light of both the Maxwell-Boltzmann distribution and also Eyring theory. Choose one and briefly explain, qualitatively, how it rationalizes the observed form of the Arrhenius equation.

3. Kinetics and the Steady State Approximation (50 pts)

Consider the reaction $\text{NO}_2 (\text{g}) + \text{CO} (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{CO}_2 (\text{g})$. It is important in understanding atmospheric chemistry of air pollution, and it has been proposed as one step in a potential series of reactions that could be useful in catalytic converters.

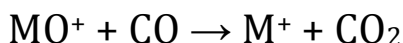
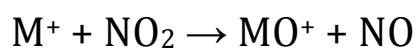
(a; 4 pts) This is a redox reaction: what is the oxidant and what is the reductant?

(b; 4 pts) Assuming the reaction is elementary, write the differential rate law for the production of CO_2 .

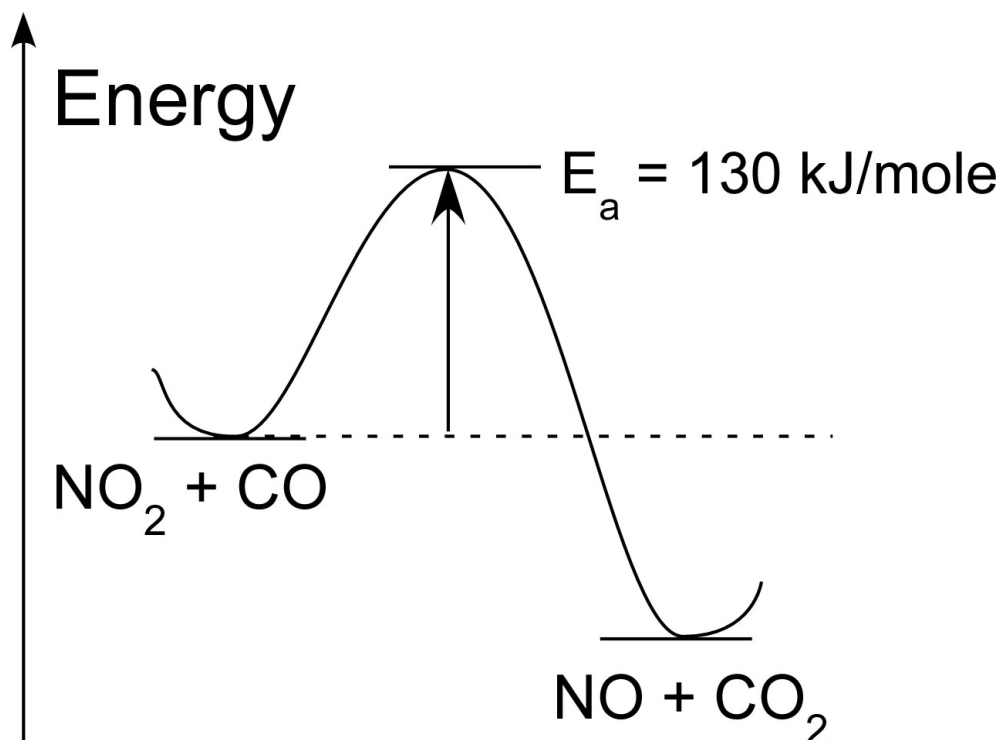
(c; 8 pts) In the 1910s-1970s, the observed activation energy for this reaction was determined to be about 130 kJ/mol. If the second-order rate constant k is $64 \text{ M}^{-1}\text{s}^{-1}$ at 1000 K, what is k at 500K?

(d; 9 pts) At 0.010 M NO_2 and 0.050 M CO , what concentration of CO_2 is produced in 10 minutes for a rate constant $k = 2.4 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$? You can assume that the rate remains constant for this time; based on your answer, why is this assumption justified? [By measuring an initial rate, we avoid the need to use an integrated rate law that we didn't learn.]

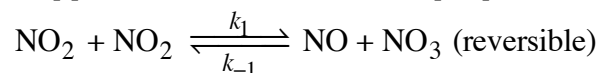
(e; 9 pts) For use in practical systems at reasonable temperatures, catalysis of the above reaction by gas phase metal cations " M^+ " has been proposed, according to this scheme:



On the reaction coordinate diagram below, add in a reasonable curve that could represent the above catalytic scheme.



The perils of textbooks...the reaction $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ can be found in several textbooks (and therefore on hundreds of web pages) as an example of more complicated kinetics, apparently entirely without regard to the fact that as far as I have been able to discover there is no experimental evidence for the more complicated kinetics. (Please correct me if this is wrong, and a shout out to Oxtoby for using original sources.) Be all that as it may, we will still use the reaction as an example for the application of the Steady State Approximation. Consider the proposed mechanism:



(f; 4 pts) Write down the differential rate law for $d[\text{CO}_2]/dt$ by inspection of just the second elementary reaction. It involves $[\text{NO}_3]$ among other things.

(g; 9 pts) Apply the steady state approximation to the reactive intermediate NO_3 to obtain its concentration in terms of $[\text{NO}_2]$, $[\text{CO}]$, and $[\text{NO}]$, and substitute into your answer from (f) to obtain the overall rate law for CO_2 production.

(h; 3 pts) The textbook problems state that the observed rate is $d[\text{CO}_2]/dt = k[\text{NO}_2]^2$. How do we know that this can't possibly be true under all conditions? (Hint: what is the order of reaction with respect to CO ?)

4. Ecological Electrochemistry (30 pts)

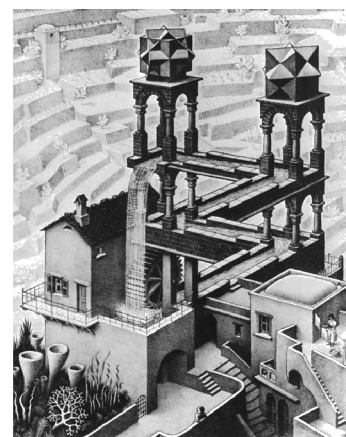
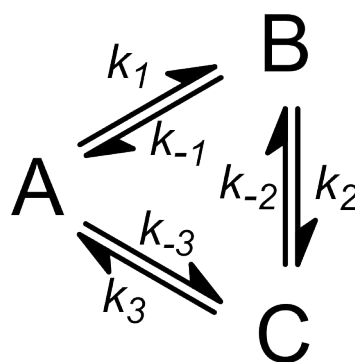
Hydrogenosomes are organelles related to mitochondria. They transfer electrons from NADH to protons to produce hydrogen. Tiny but multicellular crustaceans that use hydrogenosomes instead of mitochondria have recently been discovered in the Mediterranean.

(a; 15 pts) Write the two half-reactions and the balanced chemical reaction for oxidation of NADH by protons and determine " n ." E° for this reaction is -0.106 V. One of the half-reactions is the SHE, but the standard reduction potential we use for it is -0.414 V instead of 0.000 V – why?

(b; 15 pts) Assuming $[\text{NADH}] = 2$ mM, $[\text{NAD}^+] = 1$ mM, and $\text{pH} = 6$, use the Nernst equation to calculate the maximum possible partial pressure of H_2 $[P(\text{H}_2)]$ that a hydrogenosome can produce, i.e. the $P(\text{H}_2)$ at which the reaction grinds to a halt. In light of your answer, why might it be advantageous to make the final destination of one's electrons a volatile gas?

5. Chemistry, Art, and Imagination (34 pts)

Consider the elementary reactions among A, B, and C sketched at the right.



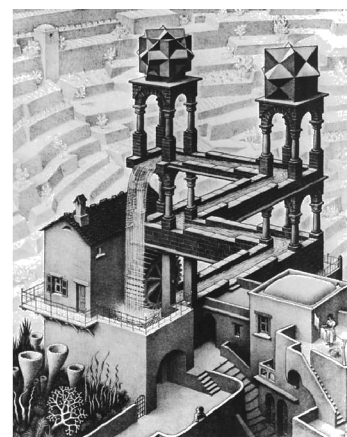
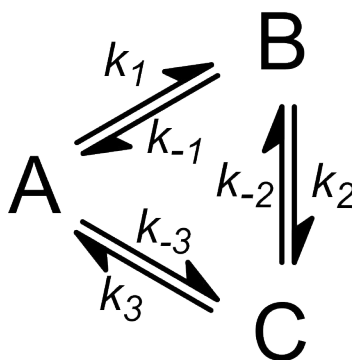
(a; 16 pts) Sketch two free energy reaction coordinate diagrams below that each illustrate the two reactions of reactant A. On the first diagram show B as the thermodynamic product and C as the kinetic product. On the second diagram show B as both the kinetic and the thermodynamic product (they are often the same!). You do not need to show the equilibration of B and C with each other.

(b; 4 pts) Experimentally, how does one attempt to obtain the kinetic product of a reaction as opposed to the thermodynamic product?

(c; 4 pts) If we know the equilibrium constants $K_1 > 1$ and $K_2 > 1$ for the ABC cycle shown, what is the value and magnitude (circle one: >1 or <1) of K_3 ?

(d; 4 pts) If we know k_1 , k_2 , and k_3 but not the K_{eq} 's, what do we know about k_{-1} , k_{-2} , and k_{-3} ?

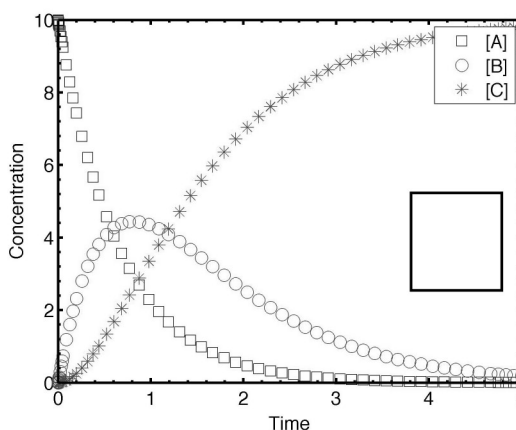
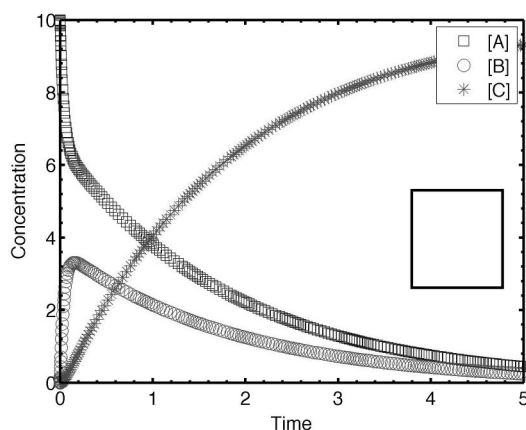
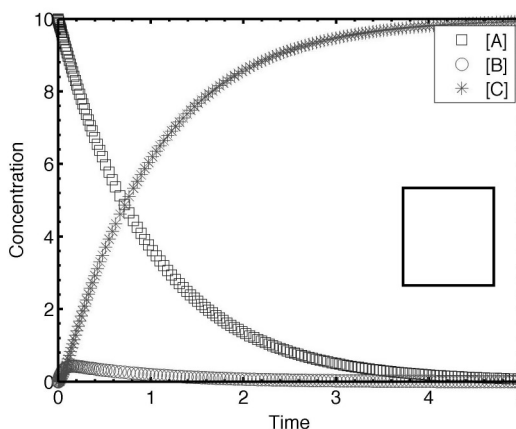
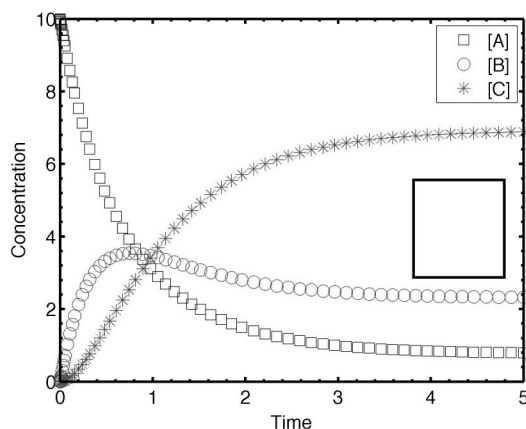
(e; 6 pts) If K_3 also had a value >1 (hopefully an answer different than the one you just derived), what law of nature would be violated? (Hint: consider the analogous M.C. Escher waterfall print shown.) What sort of forbidden machine could we make if the corresponding reaction cycle or waterfall could exist?



6. Kinetic patterns (20 pts)

The progress curves below represent three different $A \rightleftharpoons B \rightarrow C$ reactions and one $A \rightleftharpoons B \rightleftharpoons C$ reaction.

Identify with a (①) in the box on the appropriate graph the one that shows a rate-determining first step, (②) the one with two steps of comparable speed, (③) a rapid pre-equilibrium, and (④) the one with the $A \rightleftharpoons B \rightleftharpoons C$ reaction. Give the number of one $A \rightleftharpoons B \rightarrow C$ graph which is clearly not well-described by the steady-state approximation_____.



Page	Score
2	/30
3	/18
4	/18
5	/16
6	/18
7	/16
8	/30
9	/20
10	/14
11	/20
Total	

Score for the page_____