Chemistry 271, Section 22xx University of Maryland, College Park
General Chemistry and Energetics Prof. Jason Kahn
Final Exam (200 points total) December 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 <u>concise</u> and <u>clear</u>. 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.

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

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

Your Name: KEY

Your SID #:

<u>Viewing: Friday, December 17, 11-2 Chemistry 1110-1111</u>

<u>Useful Equations:</u>

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

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

$S = k\ln W$

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

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

$PV = nRT$

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

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

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

$°C = °K - 273.15$

$R = 8.314$ J/mole K

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

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C

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

Standard hydrogen electrode: $2\,H^+(aq, 1\text{ M}) + 2\,e^- \rightarrow H_2(g)$ $E° = 0.000$ V

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

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

1 Volt = 1 Joule/Coulomb

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

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

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

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

$dS = (c_p/T)\,dT$

$c_p = q_p/dT = dH/dT$

1. Multiple Choice (24 pts)

(i; 4 pts) The half life $t_{1/2}$ of a first order reaction $A \rightarrow B$

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

(ii; 4 pts) A first-order rate constant

[✓ (a)] has units of time^{-1}.
(b) changes during the course of the reaction as the reactant is depleted.
(c) cannot be faster than diffusion-controlled.
(d) has units of $M^{-1}s^{-1}$.
(e) none of the above.

(iii, 4 pts) The function of Photosystem II in plants is to

(a) use light energy to reduce NADP$^+$ to NADPH.
(b) collect light energy and deliver it to Photosystem I.
(c) oxidize water to provide light.
[✓ (d)] re-reduce the reaction center of Photosystem I.
(e) reduce water to maintain a basic pH.

(iv, 4 pts) Dissimilation is defined as

[✓ (a)] using a substance as a terminal electron acceptor and making no further use of the product.
(b) reducing a substance in order to incorporate it into biomass.
(c) nitrogen fixation and other processes that split diatomic molecules.
(d) disguising (one's intentions, for example) under a feigned appearance.
(e) none of the above.

(v, 4 pts) The Third Law of Thermodynamics gives us a reference state of zero entropy. What else is necessary for measuring absolute entropies of pure substances at non-zero temperature?

(a) The First Law of Thermodynamics.
[✓ (b)] Measurements of heat capacity as a function of temperature.
(c) Calculation of the free energy of formation from tabulated data.
(d) Enumeration of microstates.
(e) We cannot measure absolute entropy, only changes in entropy.

(vi, 4 pts) The Steady State Approximation

(a) is not useful in enzyme kinetics because substrate concentration is constantly changing.
(b) can be applied only to reactions of the type $A \rightarrow B \rightarrow C$.
(c) holds only at equilibrium, when the state of the system is steady.
[✓ (d)] includes rapid pre-equilibrium as a special case.
(e) is applicable to the product of any rapid reaction.

Score for the page____________

2. Heat Capacity (20 pts)

The graph at the right shows the absolute entropy of benzene as a function of temperature.

(a; 6 pts) Label the boxes in the graph with the physical process that is occurring at the indicated vertical segments.

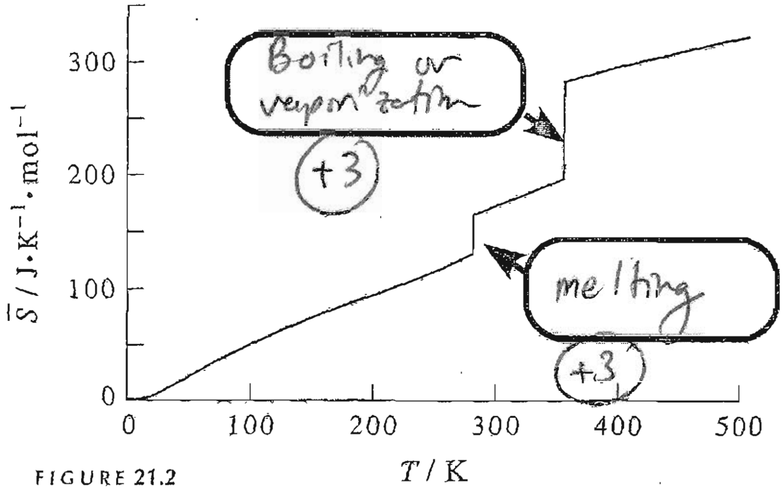

FIGURE 21.2
The molar entropy of benzene plotted against temperature from 0 K to 500 K.

(b; 9 pts) For a given gas and temperature, think about what happens when the gas is heated at constant pressure vs. constant volume. Why is the heat capacity at constant pressure (C_p) greater than the heat capacity at constant volume (C_V)?

~~+3~~ (+2)

If a gas is heated at constant pressure it will expand and do work on the surroundings. $\Delta E = q + w$

~~+3~~ (+4)

Therefore it takes more heat to raise the temperature at constant pressure, and $C_p > C_V$. Energy to do work comes from q.

(+3)

(Also OK to explain in terms of cooling upon expansion at constant p requiring re-heating)

(b; 5 pts) The enthalpy change for a reaction is usually obtained from the slope of a van't Hoff plot. How can we tell from a van't Hoff plot if a reaction has a non-zero ΔC_p?

(+3)

The van't Hoff plot is curved, showing that ΔH changes with temperature.

(+2)

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3. Photosynthesis and atmospheric chemistry (40 pts)

(a; 15 pts) Why have plants as well as our eyes evolved to be sensitive to the wavelengths that we have so egocentrically named "visible" light? Before the advent of photosynthesis, what was different about the spectrum of light reaching the earth, and why? Why was there no life on land at the time?

(+3) – "Visible light" is the part of the spectrum emitted by the sun most intensely – it's the available light

– Before photosynthesis, there was more UV hitting the (+3) earth, because there was no oxygen atmosphere (+3) and hence no O_3. (+3)

– There was ~~not~~ no life on land because the UV damages DNA. (+3)

(b; 16 pts) Fill in the blanks

Two possible failure pathways for photosynthesis are fluorescence (+2), if the electron is not transferred away from the excited state fast enough, or Charge (+2) recombination, if the electron is not removed from the immediate vicinity fast enough. For an artificial solar cell to be useful, after charge separation the electrons must re-reduce the reductant only after traveling through the external circuit (+2). The excited state chromophore of Photosystem I is a very strong reductant (+2), whereas Photosystem II generates a(n) oxidant (+2) that is strong enough to remove electrons (+2) from water (+2) and generate oxygen (+2) (or reduced quinone).

Score for the page__________

(c; 9 pts) How does increased atmospheric CO_2 cause global warming?

- Visible light passes through the atmosphere and warms the earth, ~~so~~ and the earth radiates in the infra-red or IR region of the spectrum. (+3)
- CO_2 absorbs some of the IR and re-radiates it randomly — so of it will head back to earth. (+2) (+2)
- The net effect is that less IR leaves earth, so by the First Law the earth warms up. (+2)

4. Kinetics and Thermodynamics (45 pts)

(a; 7 pts) The Maxwell-Boltzmann distribution and Arrhenius equation state that the rate of an elementary reaction always increases with increasing temperature. So how is it possible for the equilibrium constant of a ~~reaction~~ $A \rightleftharpoons B$ to decrease as temperature increases? Would the reaction be (circle one) [✓ exothermic] or endothermic?

(+2) (+3 for just this)

$A \rightarrow B$ gets faster

$B \rightarrow A$ gets faster faster, so $K_{eq} = \frac{k_f}{k_r}$ decreases (+5)

Exothermic by Le Chatelier

(+3) each

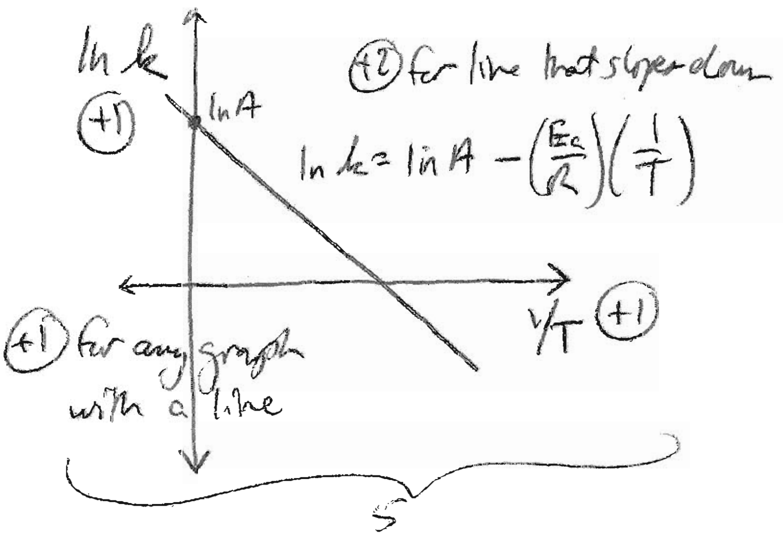
(b; 24 pts) Fill in the blanks. A catalyst can change the rate or rate constant and/or the mechanism of a reaction but not its equilibrium constant.

The underlined "v^2" factor in the Maxwell-Boltzmann distribution $C\underline{v^2}(\exp(-mv^2/2kT))$ arises because of the $\omega(\varepsilon)$ factor in the Boltzmann distribution, the degeneracy, which is the number of ways in which a particle can have energy ε. The v^2 comes from the surface area of a sphere of radius v.

A rate law can be determined by inspection only for a(n) elementary reaction.

The "2" in S_N2 comes from the fact that it's a second order reaction.

(c; 8 pts) Sketch the Arrhenius plot used to measure activation energy E_a and the preexponential factor A. Label the axes. What is the molecular meaning of Ea according to collision theory for gas phase reactions?



(+3) – Ea is the energy needed to reach the transition state, or the energy needed for the reaction to occur, which comes from the kinetic energy of the gas.

(d; 6 pts) In discussing gas-phase reactions we frequently discussed the need for a collision gas M to catalyze either dissociation or recombination reactions. It is easy to understand that the collision gas can deliver energy to break apart molecules (think of any parking lot). Why is the collision gas needed to allow atoms/molecules to recombine?

(+3)

Bond formation is exothermic. If the energy is not removed somehow, the bond will simply re-break. "M" removes (+3) the energy liberated by bond formation, leaving the reaction moving faster than when it arrived.

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5. Kinetics and the Steady State Approximation (35 pts)

Leucine zipper proteins (Z) are monomeric in solution by themselves but they bind to DNA (D) as dimers, with the overall reaction being

$$Z + Z + D \underset{}{\overset{K_{bind}}{\rightleftharpoons}} Z_2D$$

There has been debate about the reaction mechanism. One possibility is that a monomer Z binds to DNA to form an unstable intermediate that either rapidly falls apart or else binds another monomer to form the dimer. The proposed mechanism is as follows, where we ignore the reverse of the second step (this is reasonable if the complex is very stable):

$$Z + D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ZD$$

$$ZD + Z \xrightarrow{k_2} Z_2D$$

(a; 5 pts) Write down the differential rate law for the appearance of Z_2D. It includes the unknown [ZD].

$$\underbrace{\frac{d[Z_2D]}{dt}}_{+1} = \underbrace{k_2 [ZD][Z]}_{+4}$$

(b; 12 pts) Apply the Steady State Approximation to the unstable ZD intermediate to determine its steady state concentration during the binding reaction.

$$\underbrace{\frac{d[ZD]}{dt}}_{(+1)} = \underbrace{k_1 [Z][D] - k_{-1}[ZD] - k_2[ZD][Z]}_{(+2) \text{ for each term}} \underbrace{= 0}_{\substack{\uparrow \\ \text{SSA} \\ (\cancel{+2})\ +3}}$$

$$\text{So} \quad [ZD] = \frac{k_1 [Z][D]}{k_{-1} + k_2 [Z]} \quad (\cancel{+3})\ +2$$

Score for the page____________

(c; 4 pts) Substitute your answer for (b) into your answer for (a) to get the rate of production of Z_2D.

$$\underbrace{\frac{d[Z_2D]}{dt}}_{+1} = \underbrace{\frac{k_1 k_2 [Z]^2[D]}{k_{-1} + k_2[Z]}}_{+4}$$

(give credit if consistent w/ a reasonable answer on page 7)

(d; 9 pts) Show that if the ZD intermediate is so unstable that it almost always falls apart rather than binding another molecule of Z, then the differential rate equation you obtained in (c) reduces to the expression below, which is what we expect for (enter a type of kinetic mechanism) rapid pre-equilibrium (+3). If you do not trust your answer to (c), receive partial credit for rationalizing the rate law below based on the idea that the ZD intermediate becomes kinetically irrelevant if it never goes on to product: what form would you expect for a reaction with no intermediates?

$$\frac{d[Z_2D]}{dt} = k_2(k_1/k_{-1})[Z]^2[D]$$

"it almost always falls apart" means that the reverse rxn is fast. (+2)

$$\frac{d[Z_2D]}{dt} \approx \frac{k_1 k_2 [Z]^2[D]}{k_{-1}}$$

[illegible] (+2)

because $\underbrace{k_{-1} \gg k_2[\overset{Z}{\cancel{D}}]}$ [illegible] (+2)

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or no intermediates ⟷ elementary reaction (+3)

therefore $\frac{d[Z_2D]}{dt} = k_3[Z][Z][D]$ (+3)

(e; 5 pts) Assume you can measure the initial rate of formation of Z_2D. Qualitatively, how would you determine the order of reaction with respect to Z by doing two rate measurements ?

Double (or otherwise change) the concentration of Z and (+3) measure the ratio of rates. (+2)

Rate ∝ $[Z]^x$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{(a)^x[Z]^x}{[Z]^x} = a^x$$ where a = the change in [Z]

so $x = \log\left(\frac{\text{Rate}_2}{\text{Rate}_1}\right) / \log(a)$

Score for the page____________

6. Miscellaneous Electrochemistry (36 pts)

A couple of years ago "Blood Falls" in Antarctica had its 15 minutes of fame. Organisms in an anoxic (no O_2) lake under a glacier live by transferring electrons from organic carbon that was buried with them to Fe^{+3} mobilized when the glacier scrapes rust (Fe_2O_3/$Fe(OH)_3$) from rocks, reducing the ferric iron to Fe^{+2}. The "blood" in Blood Falls comes about because every once in a while the glacier moves and squozes out some of the contents of the under-ice lake, and when the dissolved Fe^{+2} hits the air and re-oxidizes.

We will take acetaldehyde (the metabolite that we make from ethanol) as a model for reduced organic carbon food, although presumably after being buried in the dark for two million years these microbes no longer feel hung over.

Some E°' values:
Acetaldehyde reduction: $E^{\circ\prime} = -0.197$ V
Acetate reduction to acetaldehyde: $E^{\circ\prime} = -0.581$ V
Reduction of ferric iron: $E^{\circ} = +0.770$ V
Reduction of O_2: $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ $E^{\circ\prime} = +0.815$ V (pH 7)

(a; 12 pts) Write the two half-reactions and the overall balanced chemical reaction for the oxidation of CH3CHO (acetaldehyde) to acetate CH_3COO^- and the reduction of Fe^{+3} to Fe^{+2} and determine "*n*." Calculate E°' for this reaction.

$CH_3CHO \longrightarrow CH_3COO^-$ ([illegible] −1
balance (+3) (+2)

$CH_2CHO + H_2O \rightarrow CH_3COO^- + 3H^+ + 2e^-$ $E^{\circ\prime}_{ox} = \oplus 0.581\ V$

$2(\ Fe^{+3} + e^- \rightarrow Fe^{+2}$ (+1) $)$ $E^{\circ}_{red} = 0.770V$ (+1)

$CH_3CHO + H_2O + 2Fe^{+3} \rightarrow CH_3COO^{\ominus} + 3H^+ + 2Fe^{+2}$ $E^{\circ\prime}_{cell} = 1.351\ V$ (+2)

(+2)

$n = 2$ (+1)

(b; 5 pts) When we are balancing electrochemical reactions, if we double a reaction we do not double the voltage. Explain why not.

(+3)

The voltage is an intensive property. We take account of the stoichiometry by changing $\underline{n}$, which shows up in the free energy as $\Delta G = -nFE^{\circ}_{cell}$.

(+2) for any explanation of how we account for doubling

Score for the page________

(c; 8 pts) When the lead-acid storage battery is recharged by the alternator of the car, the reduction half- reaction is $PbSO_4(s) + H^+(aq) + 2\ e^- \rightarrow Pb(s) + HSO_4^-(aq)$ $E°_{red} = -0.356$ V

We usually just accept this, but on second thought it is surprising that it works given that protons are present in the reaction. What redox reaction, which occurs in the standard hydrogen electrode, might be expected to occur instead of the reduction of $PbSO_4$, and why? (The overpotential (+3) explains why the other redox reactions do not occur readily: for complicated reasons, it requires a much higher voltage to actually get them to go. This is one reason that platinum, the metal used for the SHE electrode, is not used in car batteries. Another reason is that a pound of platinum would cost about as much as the rest of the car.)

(+3) $2H^+ + 2e^- \longrightarrow H_2$ $E°_{red} = 0.000$ V

the SHE reaction is more thermodynamically ~~the~~ favorable than the $PbSO_4$ reduction. (+3)

(d; 11 pts) Fill in the blanks. The terminal electron acceptor for our metabolism is O_2 (+3).

Strong oxidants are found at the top left (+2) of the typical table of standard (+2) reduction potentials

need top (+2)

The pH of the biochemical standard state is 7 whereas the pH of the chemical standard state can be either 0 (+1) or 14 (+1) depending on the reaction in question.

Page	Score
2	/24
3	/20
4	/31
5	/16
6	/38
7	/17
8	/18
9	/17
10	/19
Total	**/200**

Score for the page____________