Chemistry 271, Section 21xx **Your Name:** Key
Prof. Jason Kahn
University of Maryland, College Park **Your SID #:**
General Chemistry and Energetics
Final Exam (200 points total) **Your Section # or time:**

May 13, 2011

VIEWING: Monday, May 16, 9:30-10:30 a.m., Chem 1112

N = 169

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:

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

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

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

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

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

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

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

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

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

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

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

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

(+2 pts)

1. (24 pts) Multiple choice: Circle the single best answer for each question

(a; 4 pts) Stratification in sediments or the water column comes about because

[✓ (1)] the best available terminal electron acceptor is used by the local flora and fauna until it's gone.
(2) microorganisms have variable densities so they settle to different levels.
(3) the organisms that can grow in the water vary with temperature.
(4) None of the above.

(b; 4 pts) DNA hybridization (formation of double strand) has

(1) $\Delta H^\circ < 0$ and $\Delta G^\circ < 0$ at any temperature.
(2) $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$.
[✓ (3)] $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$.
(4) $\Delta H^\circ > 0$ and $\Delta G^\circ > 0$ above T_m.

(c; 4 pts) A DNA microarray is used to

(1) measure T_m on small samples.
[✓ (2)] perform multiple simultaneous hybridization experiments.
(3) clone a variety of plasmids in cells that float across the array.
(4) None of the above.

(d; 4 pts) Overpotential is

(1) the reason car batteries can be recharged effectively.
(2) frequently observed for electrode reactions where a state change (i.e. aqueous → gas) occurs.
(3) the requirement that a voltage greater than E_{cell} must actually be applied to convince a redox reaction to proceed.
[✓ (4)] All of the above.

(e; 4 pts) The rate law for a process aA + bB -> cC + dD

(1) is given by Rate = $k[A]^a[B]^b$.
[✓ (2)] can be correctly written down by inspection if and only if the reaction is elementary.
(3) can never depend on [C] and [D] because they are products.
(4) None of the above.

(f; 4 pts) The equilibrium constants for electrochemical reactions

(1) are easily measured by measuring the final concentrations of reactants and products.
(2) are usually independent of pH.
(3) are unmeasurable because we use E instead.
[✓ (4)] None of the above.

2. (55 pts) Kinetics, Rate Laws, and Arrhenius

(a; 12 pts) Ethane, C_2H_6, dissociates into methyl radicals at 700 °C with a rate constant $k = 5.5 \times 10^{-4}\ \text{s}^{-1}$. The activation energy is 384 kJ/mole. Determine the rate constant at 800 °C.

(+3) $k = Ae^{-E_a/RT}$

At 700°C $5.5\times10^{-4}\,s^{-1} = Ae^{-384000/(8.314\cdot 973.15)}$

$$A = \frac{5.5\times10^{-4}\,s^{-1}}{e^{-47.46}} = 2.25\times10^{17}\,s^{-1}$$ (+3)

$$k \text{ at } 800\,°C = 2.25\times10^{17}\,s^{-1}\,e^{-384000/(8.314\times1073.15)}\Big]$$ (+3)

$$k = \underbrace{4.58\times10^{-2}}_{+2}\ \underbrace{s^{-1}}_{+1}$$

If you get the answer w/out the intermediate calculation of A that's fine.

(b; 12 pts) The rate constant for the second-order reaction 2 HI (g) → H_2 (g) + I_2 (g) is $2.4 \times 10^{-6}\ \text{M}^{-1}\text{s}^{-1}$ at 575 K and it is $6.0 \times 10^{-5}\ \text{M}^{-1}\text{s}^{-1}$ at 630 K. Calculate the activation energy.

k at 575 K $= 2.4\times10^{-6}\,M^{-1}s^{-1} = Ae^{-E_a/R\cdot575}$

k at 630 K $= 6.0\times10^{-5}\,M^{-1}s^{-1} = Ae^{-E_a/R\cdot630}$ } (+3)

$$\frac{k\text{ at }630}{k\text{ at }575} = \frac{6.0\times10^{-5}}{2.4\times10^{-6}} = \frac{Ae^{-E_a/R\cdot630}}{Ae^{-E_a/R\cdot575}} = e^{-\frac{E_a}{R}\left(\frac{1}{630}-\frac{1}{575}\right)}$$ (+4) for recognizing division

Take ln:

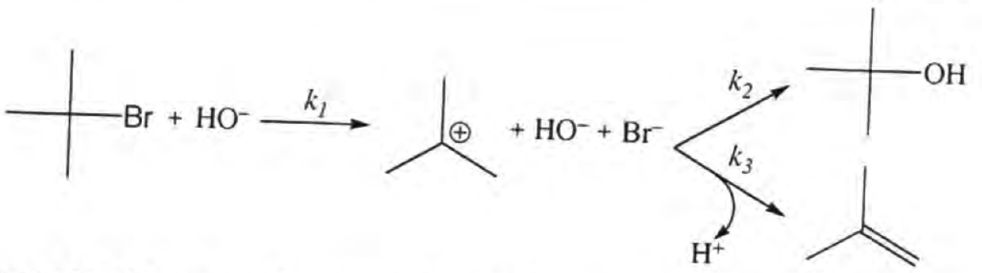
$$\ln(25) = -\frac{E_a}{8.314}\left(\frac{1}{630}-\frac{1}{575}\right) = -E_a\cdot\frac{-1.5183\times10^{-4}\,(1/K)}{8.314\ J/mole\ K}$$

(+3) for doing some math

$$E_a = \frac{3.2189\times8.314\ J/mole}{1.5183\times10^{-4}} = 1.8\times10^{5}\ J/mol = \underline{180\ kJ/mole}$$

(+2) units must be correct

Score for the page____________



The experimental rate law for the reaction $(CH_3)_3CBr + HO^- \rightarrow (CH_3)_3COH + Br^-$ (above, top) in an organic solvent is Rate $\equiv -d[(CH_3)_3CBr]/dt = k[(CH_3)_3CBr]$.

(c; 2 pts) What is the observed order of reaction with respect to HO^-? Zero or 0 (+2)

(d; 6 pts) The S_N1 mechanism below has been proposed for the reaction. Which step must be rate limiting for the mechanism to agree with the experiment? Briefly explain your reasoning.

$$(CH_3)_3CBr \xrightarrow{k_1} (CH_3)_3C^+ + Br^-$$

$$(CH_3)_3C^+ + HO^- \xrightarrow{k_2} (CH_3)_3COH$$

(+2) The first step must be rate-determining

(+4) – If the 2nd step were the r.l.s. then $[HO^-]$ would have to appear in the rate law

↕ for either and/or

carbocation unstable or reacts fast ⇒ 4

(+4) – The rate of the first step is $k_1[(CH_3)_3CBr]$, which matches the experimental rate law.

(e; 9 pts) If the concentration of HO^- is decreased to a small enough value, the rate law changes: why must this be so? Explain why the steady-state approximation does not apply to anything in the reaction under these conditions.

(+3) for either idea

– If there isn't any HO^- then can't be any reaction – there's no such things as a truly zero-order reaction

– At low enough concentration the second step must be slow enough so that it becomes partially rate limiting → therefore there is no rapid decay path for the carbocation. (+3)

– The SSA only applies if there is a fast decay path (+3)

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(f; 14 pts) However, the change in the rate law at low [HO$^-$] might be hard to observe because the E1 (Elimination 1) product can also appear, according to the mechanism below

$$(CH_3)_3CBr \xrightarrow{k_1} (CH_3)_3C^+ + Br^-$$
$$(CH_3)_3C^+ \xrightarrow{k_3} (CH_3)C{=}CH_2 + H^+$$

At low T the substitution is favored, but the E1 reaction is found to dominate more and more over the S$_N$1 reaction as the temperature is increased (assume [HO$^-$] is constant). What does this suggest about the values of the k_2 and k_3 rate constants for the second steps of the S$_N$1 and E1 reactions respectively, and the activation energies for the k_2 and k_3 steps? Sketch an Arrhenius plot to illustrate your answer.

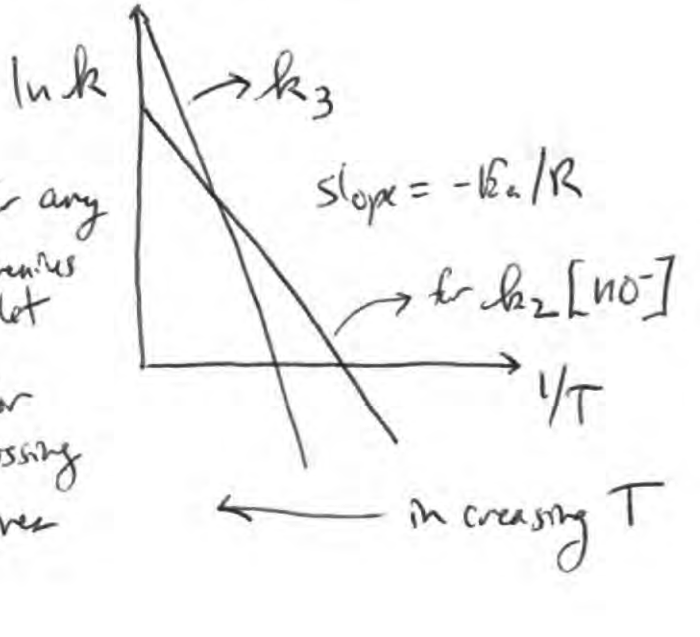
The fact that the E1 reaction takes over tells us that

(+4) (+3) $k_2[HO^-]$ starts out ~~less~~ more than k_3 and then becomes less than k_3 – the rate of the second step of the S_N1 rxn is $k_2[HO^-][(CH_3)C^+]$, vs. $k_3[((CH_3)C^+]$ for the E1.

Arrehenius Plot:

(+3) for any Arrhenius plot

(+3) for crossing lines



→ this tells us that the activation energy for the E1 process is greater than the activation energy for the S_N1. (+4)

3. (45 pts) Electrochemistry of Life and the Biosphere

The aerobic nitrification of ammonia is carried out by soil bacteria (unfortunately… excess ammonia applied as fertilizer is converted to nitrate, which is more readily washed into the Chesapeake Bay). The overall reaction at pH 7 is

$$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + H_2O + 2\,H^+$$

The first step in nitrification is the oxidation of ammonia to give hydroxylamine, NH_2OH, which is then converted to nitrite, NO_2^-, by the enzyme hydroxylamine oxidase (HAO). A different bug then oxidizes nitrite to nitrate.

(a; 6 pts) Balance the half-reaction for hydroxylamine oxidation to nitrite in acidic solution:

Start with: $NH_2OH \rightarrow NO_2^-$

(+1) Balance N ✓ Balance O: $+H_2O$

(+1) Balance H: $+5H^+$

$$NH_2OH + H_2O \rightarrow NO_2^- + 5H^+$$

(+1) Balance charge: $+4e^-$ [Check N ox st goes from -1 to $+3$ ✓]

+6 no work is OK (+3) [$NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^-$

(b; 4 pts) Add the appropriate multiple of the molecular oxygen reduction half-reaction below

↳ × 1 $O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$

to your answer from (a) to give the balanced equation for this oxidation of hydroxylamine by oxygen.

$$NH_2OH + \cancel{H_2O} \rightarrow NO_2^- + \cancel{5}H^+ + \cancel{4e^-}$$
$$O_2 + \cancel{4H^+} + \cancel{4e^-} \rightarrow \cancel{2}H_2O$$

) (+2) for idea

$$NH_2OH + O_2 \rightarrow \underbrace{NO_2^- + H^+}_{HNO_2\ \text{OK}} + H_2O$$ (+2)

(c; 4 pts) The net free energy change for the HAO reaction at the biochemical standard state is $\Delta G^{\circ\prime} = -251$ kJ/mol for $n = 4$. Calculate $E^{\circ\prime}_{cell}$.

$$\Delta G^{\circ\prime} = -nFE^{\circ\prime}_{cell}$$

$$\underbrace{E^{\circ\prime}_{cell} = \frac{-\Delta G^{\circ\prime}}{nF}}_{(+2)} = \frac{251000\ \text{J/mole}}{4 \cdot 96500\ \text{C/mole}} = 0.650\ \text{V}$$ (+2)

sig figs don't matter

must be in volts

$1\ \text{J/C} = 1\ \text{V}$

Score for the page____________

(d; 10 pts) Calculate E_{cell} for the HAO reaction at 0.1 mM NH_2OH, 10 mM NO_2^-, pH 5, pO_2 = 0.1 atm, and 25 °C.

$$E_{cell} = E^{o\prime} - \frac{0.0592}{n} \log Q \quad (+2)$$

$$= 0.650V - \frac{0.0592}{4} \log \frac{[NO_2^-]\overbrace{([H^+]/10^{-7})}^{(+2)}\overset{1}{\cancel{[H_2O]}}}{[NH_2OH]\,(pO_2/1atm)}$$

$$= 0.650V - 0.0148V \log\left(\frac{10^{-2}\cdot(10^{-5}/10^{-7})}{10^{-4}\cdot 10^{-1}}\right)$$

(+3) for plugging in consistent w/ p.6

$$= 0.650V - \underset{0.0740}{0.0148V}\ \underbrace{\log\left(\frac{1}{10^{-5}}\right)}_{5} = 0.576V \quad (+3)$$

or 0.58V (+1 w/out "V")

(e; 9 pts) What are the oxidation numbers of N in NH_2OH and NO_2^-? To get from one to the other we clearly have to pass through zero, which is the oxygen number of N in good old N_2 gas. However, N_2 is not an intermediate in the reaction. In view of what you know about catalysis, why not? [The zero-valent state is believed to be the transition state in dehydrogenation of heme-bound NH_2OH to form bound HNO.]

H: +1, O: -2 so $N = 0-(3-2) = -1$ in NH_2OH (+2)

O: -2 so $N = -1-(-4) = +3$ in NO_2^- (+2)

N_2 is too stable (+3) - the reaction would get stuck (+2) at the N_2 intermediate

(f; 3 pts) A second bug oxidizes nitrite to nitrate. This is an example of what kind of relationship between two bugs? One word answer: Syntrophy (+3).

(g; 9 pts) What do the AOB's (ammonia oxidizing bacteria) gain from this nitrification process? Other bugs carry out the opposite process, reductive denitrification of NO_3^- to convert N back into amine forms—what general type of process is that?

(+3)

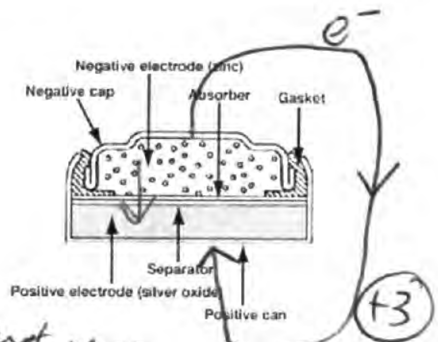
- The AOB's use the redox energy to power their metabolism -

(+3) for either example (they pump protons to make ATP, or they may use the electrons for biosynthesis.

- The denitrification process is assimilation (+3)

4. (40 pts) Electrochemistry and Technology

The silver oxide battery is found in hearing aids and such. It is based on reactions of Zn and Ag metals and their oxides in a basic electrolyte. (http://www.maxell.com.sg/industrial/batteries/sr_button/images/diagram.gif)



The relevant half-reactions are

$ZnO(s) + H_2O(l) + 2e^- \rightarrow Zn(s) + 2HO^-(aq)$ $E^\circ_{red} = -1.26$ V must reverse

$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2HO^-(aq)$ $E^\circ_{red} = +0.34$ V

(a; ~~32~~ 30 pts) Write down the overall cell reaction and calculate E°_{cell}, ΔG°, and K_{eq} at 25°C. Which reaction occurs at the anode and which at the cathode? Which way do electrons flow in the external circuit (sketch it on the diagram)? One advantage of this cell is that its voltage is exceptionally stable during use. Why is this the case?

(+2) anode $Zn(s) + \cancel{2HO^-(aq)} \rightarrow ZnO(s) + \cancel{H_2O(l)} + 2e^-$ $E^\circ_{ox} = 1.26V$) (+2)

cathode $Ag_2O(s) + \cancel{H_2O(l)} + 2e^- \rightarrow 2Ag(s) + \cancel{2HO^-(aq)}$ $E^\circ_{red} = 0.34V$

(+2)

(+3) $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$ $E^\circ_{cell} = 1.60V$ (+3)

(+4)

$\Delta G^\circ = \overset{(+2)}{-}nFE^\circ_{cell} = -2 \cdot 96500 \cdot 1.60 = -309$ kJ/mol (+3)

$K_{eq} = \overset{(+2)}{e}^{-\Delta G^\circ/RT} = e^{(309000/(8.314 \cdot 298))} = 1.35 \times 10^{54}$ (+3)

- Voltage is ~~ex~~ stable because Q = 1 is constant - all solid reactants + products (+4)

(b; ~~8~~ 10 pts) Zinc is often used as a sacrificial anode, for example to prevent rusting of structural steel or ship hulls. Briefly describe what a sacrificial anode does and why zinc is a good choice.

-2 for no mention of another specific metal

- When oxidation occurs elsewhere, we form ~~Fe~~ e.g. Fe_2O_3 when Fe is in Fe^{+3} state - ~~this is re-~~reduced by Zn (+2) oxidation to give $Zn \rightarrow Zn^{+2}$ (+2) and ~~Fe_2O_3~~ $Fe^{+2} \rightarrow Fe$ therefore iron is not dissolved away (+2)
- Zn is a good choice b/c it is a good reducing agent (+2) (large ⊕ E°_{ox}) (+2) up to 4

5. (36 pts) Miscellaneous

(a; 16 pts) Describe the two ways you could set up kinetics experiments to determine whether a reaction is first order or second order, and how you would interpret the data.

(+4)

- The first way is to measure concentration as a function of time and then ask whether the time dependence fits $[A]$ vs t, $\ln[A]$ vs. t, or $1/[A]$ vs. time. You look for the ~~correct the~~ expression that gives the appropriate linear dependence. (+4)
- The second way is ~~the~~ to vary the initial [ ]'s of reactants and then measure initial rates or $1/2$ lives to see ~~whether~~ how they vary - For example - is the initial rate $\propto [A]^{0, 1, \text{or } 2}$ or is $t_{1/2}$ independent of A, $\propto 1/[A]$, or $\propto [A]$ (+4) (+4)

(b; 6 pts) Explain how bacteria that live in niches with abundant H_2S can use Photosystem I alone (i.e. they don't have a PS II) to provide reducing power for carbohydrate production.

(+2) (+1)

- The PSI $P680^{\oplus}$ cation must be re-reduced somehow. Plants do this with PSII, but if H_2S ~~(+2)~~ is available in the environment it can serve as an external source of electrons. (+2)
- The H_2S is oxidized ~~(+2)~~ (+1) in the process to S.

$$H_2S \rightarrow S + 2e^- + 2H^+$$] don't need again

for idea on what PSII is used for

Score for the page____________

(c; 5 pts) How many photons must be absorbed per molecule of O_2 produced by photosynthesis in plants? Explain very briefly.

total +3 for $4e^-$ + explanation
+2 total for 2 photons to move each e^-

8 (+2) O_2 each

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (+2)
= need $4e^-$ per O_2

But these electrons are fed into PSI, so PSI has to absorb $4h\nu$ to get the electrons over to NADPH. (+1)

(d; 9 pts) Why did the emergence of life on land have to wait for all the surface iron to be oxidized to rust?

(+3) - The oxygen atmosphere could not develop when there was still a lot of metallic Fe around. Plants had to make enough O_2 to oxidize it. (Bacteria + photosynthesis) (+2)

- Thus the ozone layer could not arise from UV irradiation of O_2 (+3)

- And the UV blasted down destroying DNA above the surface. (+2) (+3) [or +3 for needing O_2 for animal metabolism]

total of 11 pts - max is 9

Page	Score
1	/2
2	/24
3	/24
4	/17
5	/14
6	/14
7	/31
8	/40
9	/22
10	/14
Total	

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