yellow

Chemistry 271, Section 22xx
Prof. Jason Kahn
University of Maryland, College Park
General Chemistry and Energetics
Final Exam (200 points total)

Your Name: _____

Your SID #: _____

Your Section # or time: _____

December 16, 2011

VIEWING: Monday, May 19, 9:30-10:30 a.m., Chem 1356-1360

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) If the rate law for a process A + B → C is observed to be Rate = k[A][B]

(1) the reaction must be an elementary reaction.
(2) the reaction cannot be an elementary reaction.
(3) the reaction might be an elementary reaction.
(4) the experiment was done wrong.

(b; 4 pts) If the rate law for a process A + B → C + D is observed to be Rate = $k[A]^2/[C]$

(1) the reaction must be an elementary reaction.
(2) the reaction cannot be an elementary reaction.
(3) the reaction might be an elementary reaction.
(4) the experiment was done wrong.

(c; 4 pts) The melting temperature in DNA hybridization

(1) increases with the number of mismatches between target and probe.
(2) increases with the length of the complementary region.
(3) increases as the concentration of DNA decreases.
(4) None of the above.

(d; 4 pts) Cyclic reactions A → B → C → A

(1) are impossible.
(2) can proceed in a net forward direction as drawn only if we heat the reaction to drive it.
(3) at equilibrium, must also proceed in reverse at the same rate for each step.
(4) None of the above.

(e; 4 pts) Nitrogen fixation describes conversion of

(1) N_2 to NH_3.
(2) NH_3 to NO_3^-.
(3) NO_3^- to N_2.
(4) NH_3 to NO_3^-.

oops

(f; 4 pts) The lead-acid battery used in cars is so large and heavy because

(1) the weight of the battery is needed to adjust the car's suspension.
(2) it needs to store a lot of energy to recharge the alternator while driving.
(3) it needs to have 60 internal cells to provide 120 V to the distributor and the car's electronics.
(4) the starter motor requires high power and therefore current to move the pistons in the engine.

Score for the page 24

2. (48 pts) Kinetics, Rate Laws, and Arrhenius

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

The rate constant k for this reaction, which occurs during combustion as a precursor to NO_2 in smog formation, is 318 (units) at 2000 K and 7396 (units) at 2400 K. (Derived from Gilbert 15.85.)

(a; 6 pts) Write down the rate law for the reaction assuming that it is elementary. What are the units for the rate constant?

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = k[N_2][O_2] \text{ or } k P_{N_2} P_{O_2}$$ (+3)

(+1) for any one of the three is fine

units are $M^{-1} s^{-1}$ (+2)

(b; 12 pts) Calculate the activation energy (Ea) and the pre-exponential factor (A) for the reaction.

$$k_1 = A e^{-Ea/RT_1}$$

$$k_2 = A e^{-Ea/RT_2}$$

$$\frac{k_1}{k_2} = e^{-\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\ln\frac{k_1}{k_2} = -\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ (+2)

$$Ea = \frac{-R \ln(k_1/k_2)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{(8.314\ J/mol\text{-}K)\ln\left(\frac{318}{7396}\right)}{\frac{1}{2000} - \frac{1}{2400}}$$ (+3)

$$= 313934.3\ J/mol \rightsquigarrow 314000\ J/mol$$ (+3)

$$A = \frac{k_1}{e^{-(Ea/RT_1)}} = \frac{318\ M^{-1}s^{-1}}{e^{-(314000/(8.314\times 2000))}}$$ (+2)

for any attempt $= 5.04 \times 10^{10}\ M^{-1} s^{-1}$ (+2)

(c; 6 pts) Calculate the rate constant at 300 K. Given that NO is poisonous, it's a good thing the reaction is slow at anything close to room temperature.

$$k = (5.04 \times 10^{10})\, e^{-(314000/(8.314\times 300))}$$ (+3)

$$= 1.07 \times 10^{-44}\ M^{-1} s^{-1}$$ (+3)

Score for the page 24

(d; 12 pts) The half-life of ^{137}Cs, one of the main radioactive pollutants from the Fukushima and Chernobyl disasters, is 30.2 years. From the integrated rate equation for a first-order reaction, derive an expression for the half-life in terms of the rate constant, and calculate the rate constant for Cs-137 decay.

(+2) $[A] = [A]_0 e^{-kt}$

(+2) at $t = t_{1/2}$, $[A] = \frac{[A]_0}{2}$

$$\frac{[A]_0}{2} = [A]_0 e^{-kt_{1/2}}$$

$$\ln \tfrac{1}{2} = -k t_{1/2}$$

(+3) $$t_{1/2} = -\frac{\ln 1/2}{k} = \frac{\ln 2}{k}$$

(+2) $$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{30.2 \text{ yrs}}$$

$$= 0.0229 \text{ yr}^{-1}$$ (+3)

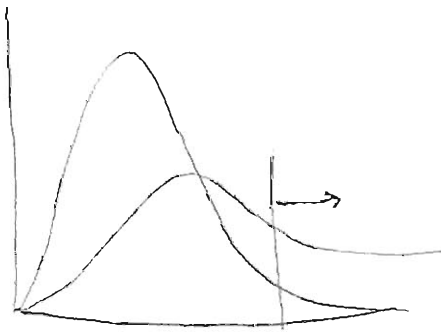
or

$$k = \frac{0.693}{30.2 \times 365.25 \times 24 \times 360}$$

$$= 7.27 \times 10^{-10} \text{ s}^{-1}$$

(e; 12 pts) Explain the functional form of the Maxwell-Boltzmann distribution $P(v)dv = Cv^2 exp(-mv^2/2kT)$. In other words, where do the v^2 and $exp(-mv^2/2kT)$ factors come from? Explain why doubling the temperature typically causes much more than a factor of 2 increase in the rate of elementary processes.

- v^2 comes from the degeneracy (+2), the # of ways a particle can have velocity v, $\propto$ the area of a sphere of radius v (+1)
- $e^{-\frac{1}{2}mv^2/kT} = e^{-\text{Energy}/kT}$ is the Boltzmann factor (+2)
  - this is the energy distributions that maximizes the # of microstates (+1)

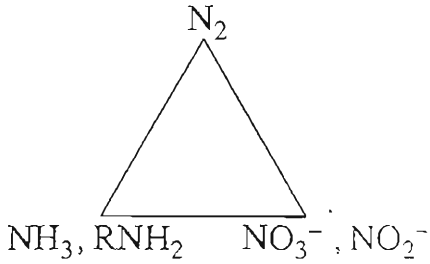


(+3) Doubling the average K.E. causes the # of molecules in the tail of the distribution to ↑ by much more than a factor of 2, so the # of molecules that have $\geq E_a$ is ↑↑ (+3)

Score for the page 12/4

3. (40 pts) Electrochemistry of Life and the Biosphere

The nitrogen triangle describes the interconversions among different oxidation states of nitrogen in the biosphere.



(a; 6 pts) Is conversion of N_2 to NH_3 and amines a reduction or an oxidation? Is it assimilation or dissimilation?

$N_2 \rightarrow NH_3$ is a reduction (+3)

(+3) Assimilation – this is nitrogen fixation

(b; 9 pts) Nitrification refers to the oxidation of ammonia to nitrite or nitrate. Why do prokaryotes do this, assuming that they don't use nitrate for biomass? Why is this generally an aerobic process? What do we call the oxygen in aerobic nitrification?

(+3) They live off the favorable transfer of electrons from NH_3 to an oxidizing agent – NH_3 = food

- Aerobic b/c there has to be an electron (+1) acceptor that is better than NO_3^- (+3)
- The O_2 is the terminal electron acceptor (+2) O_2 e⁻ acceptor

(c; 9 pts) Denitrification is the reduction of nitrate to N_2. What might the reducing agent be, generically? What function is the nitrate serving? Is this assimilation or dissimilation?

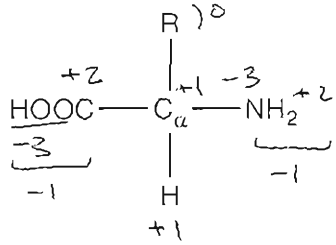
$NO_3^- \rightarrow N_2$

reducing agent is typically organic carbon (+3) – $C_n(H_2O)_n$ etc.

The nitrate is an oxidizing agent (+2) – The terminal electron acceptor (+2)

this is dissimilation (+2)

(d; 6 pts) Eukaryotes like us don't affect the nitrogen triangle very much (at least insofar as our personal metabolisms as opposed to industrial processes are concerned). Why not? What is the oxidation number of nitrogen in an amino acid, as at the right?



- We don't oxidize or reduce nitrogen during metabolism – it's always an amine or similar $R-NH_2$ (+3)

(+3) (-3) oxidation number

Score for the page 30/30

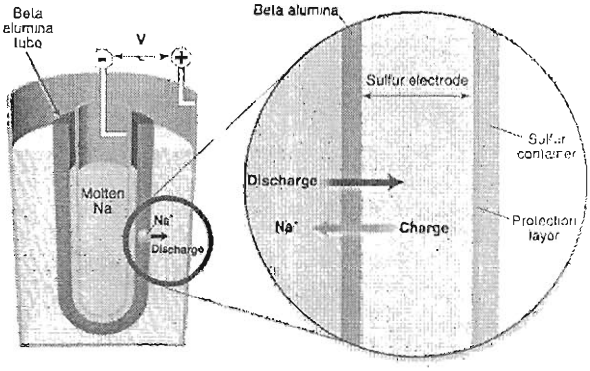
yellow

(e; 10 pts) Why did the emergence of life on land have to wait for all the surface iron to be oxidized to rust?

- Life on land had to wait for an ozone layer (+2) to block UV (+2)
- Ozone comes from dioxygen (O_2) in the upper atmosphere, so life needed an oxygen atmosphere (+3)
- O_2 could not accumulate (+3) in the atmosphere until Fe on the surface was oxidized to Fe_2C_3 $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

4. (40 pts) Electrochemistry and Technology

The sodium-sulfur battery has been proposed as an energy storage component of the "smart grid." Sodium ions migrate through the beta alumina tube, but anions cannot go through it. Molten Na_2S_5 and molten S are immiscible liquids.



The relevant half-reactions are

$Na^+ + e^- \rightarrow Na\ (l)$ $\quad E°_{red} = -2.71$ V

$5\ S\ (l) + 2e^- \rightarrow S_5^{2-}$ $\quad E°_{red} = -0.48$ V

(a; 21 pts) Write down the overall reaction for the discharge part of the cycle (getting energy out of the battery), and calculate n. What is the composition of the molten sulfur electrode as the discharge progresses? The beta alumina tube is acting like a component of the simple beaker-based reactions we studied. Which component? How could you tell by just looking at the inside of the battery over time whether it was charging or discharging? Finally, why must water be rigorously excluded from the inside of the battery?

$2\ (Na \rightarrow Na^+ + e^-)$ $\quad E°_{ox} = 2.71$ V

$5S + 2e^- \rightarrow S_5^{-2}$ $\quad E°_{red} = -0.48$ V

(+6) $2Na + 5S \rightarrow 2Na^+ + S_5^{-2}$ (1) $E°_{cell} = 2.23$ V (+3) $n = 2$

(1) S, Na^+, Na_2S_5

this will combine to make $Na_2S_5\ (l)$ — sulfur side will be a mixture of two liquids (+3)

(+3) β-alumina acts like the salt-bridge to complete the circuit

(+3) Over time, the level of Na(l) will drop and the level of the sulfur electrode will rise during discharge

(+3) Water would react violently with the Na(l), especially at 250°C!

Score for the page 131

(b; 9 pts) Calculate $E°_{cell}$, $\Delta G°$, and K_{eq} for the sodium-sulfur battery, all at 300 °C, assuming that the $E°_{cell}$ is the same as it is at 25 °C. (The battery actually operates at about 300 °C to keep everything molten, which is why you are not likely to have one at home.)

(+3) $E°_{cell} = 2.71\,V - 0.48\,V = 2.23\,V$

(+3) $\Delta G° = -nF E° = -2\,mole\,(96500\,C/mole)(2.23\,J/C)$

$= -4.30 \times 10^5\,J/mole = -430\,kJ/mole$

(+3) $K_{eq} = e^{-\Delta G°/RT} = e^{-(-430000\,J/mole)/(8.314 \cdot 573)\,J/mole}$

$= e^{90.3}$

$= 1.59 \times 10^{39}$ (!)

(c; 10 pts) Energy storage in a smarter grid would allow for "load shifting," for example from mid-afternoon to nighttime. What does this mean and why is it a good idea?

(+4) - Load shifting means that power can be produced at one time of day and used at another time of day.

(+3) - It allows power companies to use the cheapest or most environmentally-friendly sources of power like nuclear or hydroelectric to meet peak demand, instead of needing to go to less benign sources like coal-fired plants.

(+3) For any example of good vs. bad power

Score for the page 19

yay! blue/white

5. (20 pts) SSA

The gas phase decomposition of NO_2Cl to give 2 NO_2 + Cl_2 was proposed to occur as follows:

$$NO_2Cl \rightleftharpoons NO_2 + Cl \quad \text{forward rate constant } k_1, \text{ backward } k_{-1}$$

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2 \quad \text{rate constant } k_2$$

(a; 16 pts) Apply the SSA to the reactive chlorine atoms to show that the rate of appearance of Cl_2 should be

$$\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

(+4) $\frac{d[Cl_2]}{dt} = k_2 [NO_2Cl][Cl]$ *

$\frac{d[Cl]}{dt} \overset{SSA}{=} 0 = k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl]$ (+4) (+2)

So $[Cl](k_{-1}[NO_2] + k_2[NO_2Cl]) = k_1[NO_2Cl]$

$[Cl] = \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}$ (+3) *

$\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$ (+3) for any indication that it comes from somewhere

(b; 4 pts) Under what conditions would you expect to observe a rate that is second order with respect to NO_2Cl ? (+3)

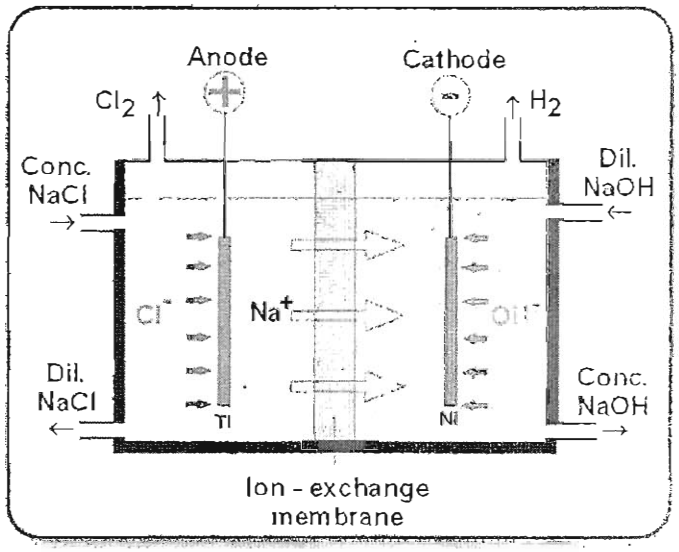
If $k_{-1}[NO_2] \gg k_2[NO_2Cl]$ we have

$\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2]}$ (+1) for any indication as to why rate is 2nd order

Score for the page 20

6. (28 pts) Industrial electrochemistry

The Chloralkali process is the source of most chlorine gas and other oxidized forms of chlorine used for bleach etc. It is also a major player in Neal Stephenson's early science fiction novel *Zodiac*. The electrolysis process occurs under aqueous basic conditions.



Relevant half reactions are:

$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-$	$E°_{red} = +1.36$ V
$O_2(g) + 2\,H_2O + 4\,e^- \rightarrow 4\,HO^-$	$E°_{red} = +0.40$ V
$Na^+ + 1\,e^- \rightarrow Na(s)$	$E°_{red} = -2.71$ V
$2\,H_2O + 2\,e^- \rightarrow H_2(g) + 2\,HO^-$	$E°_{red} = -0.83$ V

(a; 9 pts) Calculate $E°_{cell}$ for each of the following reactions.

(+1) each for work
(+2) each for answer

$2\,Cl^- + 2\,H_2O \rightarrow H_2(g) + 2\,HO^- + Cl_2(g)$

$2\,H_2O \rightarrow 2\,H_2(g) + O_2(g)$

$2\,Cl^- + 2\,Na^+ \rightarrow 2\,Na(s) + Cl_2(g)$

$E°_{cell} = E°_{ox}(Cl^-) + E°_{red}(H_2O) = (-1.36\text{V}) + (-0.83\text{V}) = -2.19\text{V}$

$E°_{cell} = ?$ $\quad 4HO^- \rightarrow O_2 + 2H_2O + 4e^- \quad E°_{ox} = -0.40\text{V}$

$2H_2O + 4e^- \rightarrow 2H_2 + 4HO^- \quad E°_{red} = -0.83\text{V}$

$2H_2O \rightarrow 2H_2 + O_2 \quad E°_{cell} = -1.23\text{V}$

$E°_{cell} = E°_{ox}(Cl^-) + E°_{red}(Na^+) = -1.36\text{V} - 2.71\text{V} = -4.07\text{V}$

(b; 6 pts) Calculate E_{cell} for $2\,Cl^- + 2\,H_2O \rightarrow H_2(g) + 2\,HO^- + Cl_2(g)$ at 4 M NaCl, pH 10, 0.1 atm each gas.

$[HO^-] = 10^{-4}$ M

$E_{cell} = E°_{cell} - \frac{0.0592}{n}\log_{10} Q$ +1

$= -2.19\text{V} - \frac{0.0592}{2}\log_{10}\left(\frac{[H_2][HO^-]^2[Cl_2]}{[Cl^-]^2[H_2O]^2}\right)$ +1

$= -2.19 - 0.0296\log_{10}\left(\frac{(0.1)\cdot(10^{-4})^2\cdot 0.1}{(1)^2\cdot(4)^2}\right)$ +1 +1 −4 +1 −1.94

$= -2.19 - 0.0296\log_{10}(6.25\times10^{-8}) = -2.19 + 0.33 = -1.85\text{V}$ +1

Score for the page 15

(c; 13 pts) Explain why it is not surprising that solid Na is not produced from the electrolysis of brine, but it is surprising that we actually get any chlorine gas! What must be true of the electrochemistry occurring at the titanium anode? Where have we seen a very similar situation before? Give the balanced total reaction for the chloralkali cell.

- The reduction to give solid Na is highly unfavorable — applying a voltage to the cell will reduce water before it will reduce Na^+ — that's why NaCl electrolysis to give Na(ℓ) must occur in molten salt, not aqueous solution. (+3)
- It is surprising that Cl_2 gas is produced, because according to the $E°_{cell}$ values, water oxidation to give O_2 would be favored instead (+3)
- There must be a large <u>overpotential</u> at the Ti electrode for water oxidation, so Cl^- is oxidized at a lower voltage than H_2O. [This is why we use platinum wire in gel electrophoresis, to make O_2 instead of Cl_2!] (+3)
- The lead-acid battery is similar — H_2 and O_2 production is minimized (+2)
- $2Cl^- + 2H_2O \rightarrow H_2 + 2OH^- + Cl_2$ [(+1) for just this]

So net rxn is:

$$\underbrace{2NaCl + H_2O}_{\text{brine (on the left)}} \rightarrow H_2 + \underbrace{2NaOH}_{\text{caustic soda (on the right)}} + \underbrace{Cl_2}_{\text{bleach}}$$

(+2)

H_2 ↓ energy

Page	Score
1	12
2	24
3	24
4	24
5	30
6	31
7	19
8	20
9	15
10	13
Total	202

Score for the page_____

blue/white

Chemistry 271, Section 23xx
Prof. Jason Kahn
University of Maryland, College Park
General Chemistry and Energetics
Final Exam (200 points total)

Your Name: Key

Your SID #:

Your Section # or time:

December 16, 2011

VIEWING: Monday, May 19, 9:30-10:30 a.m., Chem 1356-1360

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) If the rate law for a process A + B → C is observed to be Rate = k[A][B]

(1) the reaction must be an elementary reaction.
(2) the reaction cannot be an elementary reaction.
(3) the reaction might be an elementary reaction.
(4) the experiment was done wrong.

4 pts each, no partial credit

(b; 4 pts) If the rate law for a process A + B → C + D is observed to be Rate = k[A]^2/[C]

(1) the reaction must be an elementary reaction.
(2) the reaction cannot be an elementary reaction.
(3) the reaction might be an elementary reaction.
(4) the experiment was done wrong.

(c; 4 pts) Cyclic reactions A → B → C → A

(1) are impossible.
(2) can proceed in a net forward direction as drawn only if we heat the reaction to drive it.
(3) at equilibrium, must also proceed in reverse at the same rate for each step.
(4) None of the above.

(d; 4 pts) The melting temperature in DNA hybridization

(1) increases with the number of mismatches between target and probe.
(2) increases with the length of the complementary region.
(3) increases as the concentration of DNA decreases.
(4) None of the above.

(e; 4 pts) The lead-acid battery used in cars is so large and heavy because

(1) the weight of the battery is needed to adjust the car's suspension.
(2) it needs to store a lot of energy to recharge the alternator while driving.
(3) it needs to have 60 internal cells to provide 120 V to the distributor and the car's electronics.
(4) the starter motor requires high power and therefore current to move the pistons in the engine.

(f; 4 pts) Nitrogen fixation describes conversion of

(1) N_2 to NH_3.
(2) NH_3 to NO_3^-.
(3) NO_3^- to N_2.
(4) NH_3 to NO_3^-.

Score for the page_____

2. (48 pts) Kinetics, Rate Laws, and Arrhenius

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

The rate constant k for this reaction, which occurs during combustion as a precursor to NO_2 in smog formation, is 318 (units) at 2000 K and 7396 (units) at 2400 K. (Derived from Gilbert 15.85.)

(a; 6 pts) Write down the rate law for the reaction assuming that it is elementary. What are the units for the rate constant?

$Rate = -\frac{d[N_2]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = k[N_2][O_2]$ or $k P_{N_2} P_{O_2}$ (+1) / any one of the three is fine. (+3) Rother

units are $M^{-1}s^{-1}$ (+2) units +2 rate +1

(b; 12 pts) Calculate the activation energy (Ea) and the pre-exponential factor (A) for the reaction.

$k_1 = Ae^{-E_a/RT_1}$ $T_1 = 2000K$

$k_2 = Ae^{-E_a/RT_2}$ $T_2 = 2400K$

$\frac{k_1}{k_2} = e^{-\left(\frac{E_a}{RT_1} - \frac{E_a}{RT_2}\right)}$

$-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln\frac{k_1}{k_2}$ (+3) expression +2

$E_a = -\ln\left(\frac{318}{7396}\right) \cdot 8.314\ \frac{J/mol}{K} \cdot \left(\frac{1}{2000K} - \frac{1}{2400K}\right)^{-1}$ (+3) diff +3

$E_a = -(-3147)(8.314)(8.333\times10^{-5})^{-1} = \frac{314000}{}$ J/mol (+3) answer +3

$\frac{A}{e^{-E_a/RT}} = k$ (+2) for any attempt

$A = \frac{318\ M^{-1}s^{-1}}{e^{-314000/(8.314\times2000)}}$ expression +2

$= \frac{318\ M^{-1}s^{-1}}{e^{-15.882}}$

$A = 5.04\times10^{10}\ M^{-1}s^{-1}$ (+2) +2 answer

(c; 6 pts) Calculate the rate constant at 400 K. Given that NO is poisonous, it's a good thing the reaction is slow at anything close to room temperature.

(+3) $k = 5.04\times10^{10} \cdot e^{-314000/(8.314\times400)} = 4.99\times10^{-31}\ M^{-1}s^{-1}$ (+3)

substitution +3

answer +3

Score for the page_____

(d; 12 pts) The half-life of ^{90}Sr, one of the main radioactive pollutants from the Fukushima and Chernobyl disasters, is 28.8 years. From the integrated rate equation for a first-order reaction, derive an expression for the half-life in terms of the rate constant, and calculate the rate constant for Sr-90 decay.

(+2) $[A] = [A]_0 e^{-kt}$

(+2) At $t = t_{1/2}$, $[A] = [A]_0/2$

$\frac{[A]_0}{2} = [A]_0 e^{-k t_{1/2}}$

$\ln(\frac{1}{2}) = -k t_{1/2}$

(+3) $t_{1/2} = \frac{-\ln 2}{-k} = \frac{\ln 2}{k}$

$k = \frac{\ln 2}{t_{1/2}}$

$k \overset{(+2)}{=} \frac{0.693}{28.8 \text{ years}} = 0.0241 \text{ years}^{-1}$ (+3)

or

$k = \frac{0.693}{28.8 \cdot 365.25 \times 24 \times 3600 \text{ sec}} = 7.62 \times 10^{-10} \text{ s}^{-1}$

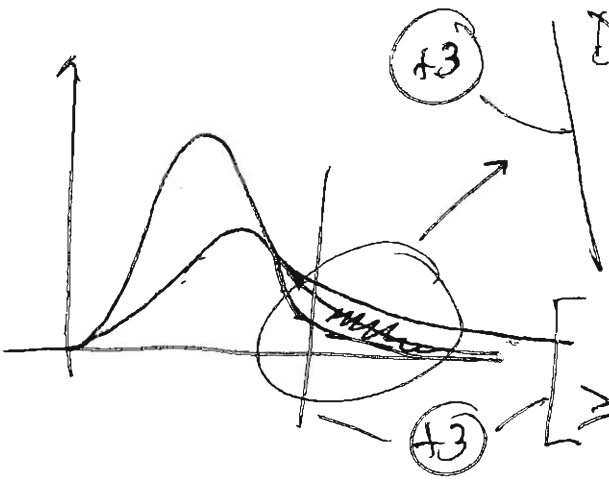
(e; 12 pts) Explain the functional form of the Maxwell-Boltzmann distribution $P(v)dv = Cv^2 exp(-mv^2/2kT)$. In other words, where do the v^2 and $exp(-mv^2/2kT)$ factors come from? Explain why doubling the temperature typically causes much more than a factor of 2 increase in the rate of elementary processes.

(+2)

- v^2 comes from the degeneracy, the # of ways a particle can have velocity v, (+1) the area of a sphere of radius v

- $e^{-\frac{1}{2}mv^2/kT} = e^{-(\text{energy})/kT}$ (+2) is the Boltzmann factor - this is the energy distribution that maximizes the # of microstates (+1)

-

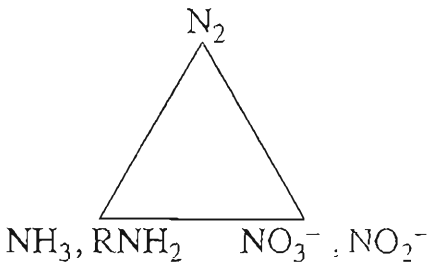


Doubling the average K.E. causes the # of molecules in the tail of the distribution to ↑ by much more than a factor of 2, so the # of molecules that have $\geq E_a$ is ↑.

Score for the page_____

3. (40 pts) Electrochemistry of Life and the Biosphere

The nitrogen triangle describes the interconversions among different oxidation states of nitrogen in the biosphere.



(a; 6 pts) Is conversion of N_2 to NH_3 and amines a reduction or an oxidation? Is it assimilation or dissimilation?

$N_2 \rightarrow NH_3$ is a reduction (+3)

(+3) Assimilation – this is nitrogen fixation

(b; 9 pts) Denitrification is the reduction of nitrate to N_2. What might the reducing agent be, generically? What function is the nitrate serving? Is this assimilation or dissimilation?

$NO_3^- \rightarrow N_2$ (+3)

reducing agent is typically organic carbon – $C_n(H_2O)_n$ etc.

the nitrate is an oxidizing agent – the terminal electron acceptor (+2) (+2)

this is dissimilation (+2)

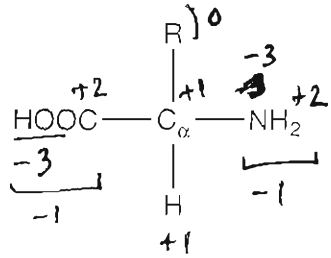
(c; 9 pts) Nitrification refers to the oxidation of ammonia to nitrite or nitrate. Why do prokaryotes do this, assuming that they don't use nitrate for biomass? Why is this generally an aerobic process? What do we call the oxygen in aerobic nitrification?

(+3) They live off the favorable transfer of electrons from NH_3 to an oxidizing agent – NH_3 = food.

– Aerobic b/c there has to be an electron acceptor that is better than NO_3^- (+3) (+1)

– The O_2 is the terminal electron acceptor (+2)

(d; 6 pts) Eukaryotes like us don't affect the nitrogen triangle very much (at least insofar as our personal metabolisms as opposed to industrial processes are concerned). Why not? What is the oxidation number of nitrogen in an amino acid, as at the right?



– we don't oxidize or reduce nitrogen during metabolism – it's always an amine or similar $R-NH_2$

(+3) – (−3)

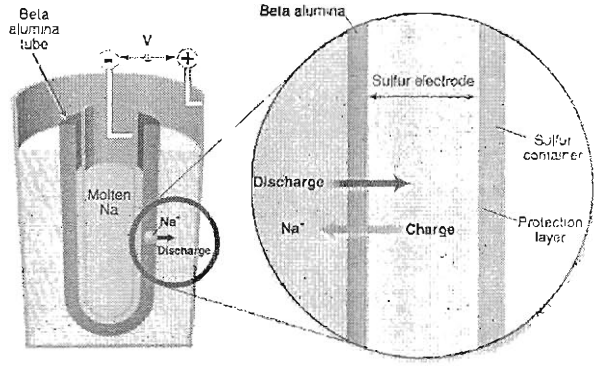
Score for the page_____

(e; 10 pts) Why did the emergence of life on land have to wait for all the surface iron to be oxidized to rust?

- Life on land had to wait for an ozone layer (+2) to block UV (+2)
- Ozone comes from dioxygen O_2 in the upper atmosphere, so life needed an oxygen atmosphere (+3)
- O_2 could not accumulate (+3) in the atmosphere until Fe^0 on the surface was oxidized to Fe_2O_3

4. (40 pts) Electrochemistry and Technology

The sodium-sulfur battery has been proposed as an energy storage component of the "smart grid." Sodium ions migrate through the beta alumina tube, but anions cannot go through it. Molten Na_2S_5 and molten S are immiscible liquids.



The relevant half-reactions are

$Na^+ + e^- \rightarrow Na\ (l)$ $\quad E°_{red} = -2.71$ V

$5\ S\ (l) + 2e^- \rightarrow S_5^{2-}$ $\quad E°_{red} = -0.48$ V

(a; 21 pts) Write down the overall reaction for the discharge part of the cycle (getting energy out of the battery), and calculate n. What is the composition of the molten sulfur electrode as the discharge progresses? The beta alumina tube is acting like a component of the simple beaker-based reactions we studied. Which component? How could you tell by just looking at the inside of the battery over time whether it was charging or discharging? Finally, why must water be rigorously excluded from the inside of the battery?

$2(\ Na \rightarrow Na^+ + e^- \quad E°_{ox} = +2.71V\ )$

$5S + 2e^- \rightarrow S_5^{2-} \quad E°_{red} = -0.48V$

(+6) $2\,Na(l) + 5\,S(l) \rightarrow 2\,Na^+ + S_5^{2-} \quad E°_{cell} = 2.23\,V$ (+3) $n = 2$

This will continue to make $Na_2S_5(l)$ - sulfur side will be a mixture of two liquids (+3)

(+3) β-alumina acts like the salt bridge to complete the circuit.

(+3) Over time the level of Na(l) will drop and the level of the sulfur electrode will rise during discharge

(+3) Water would react violently with the Na(l), especially at 250 °C!

Score for the page 131

(b; 9 pts) Calculate $E°_{cell}$, $\Delta G°$, and K_{eq} for the sodium-sulfur battery, all at 250 °C, assuming that the $E°_{cell}$ is the same as it is at 25 °C. (The battery actually operates at about 250 °C to keep everything molten, which is why you are not likely to have one at home.)

(+3) $E°_{cell} = 2.71 - 0.48 = 2.23\ V$

(+3) $\Delta G°_{cell} = -nFE°_{cell} = -2(96500\ C/mol)(2.23\ J/C) = -430390\ J/mol$

(+3) $K_{eq} = e^{-\Delta G°/RT} = e^{+430390/8.314 \times 523\ K} = e^{98.98} = 9.70 \times 10^{42}$

(c; 10 pts) Energy storage in a smarter grid would allow for "load shifting," for example from mid-afternoon to nighttime. What does this mean and why is it a good idea?

- Load shifting means that power can be produced at one time of
(+4) day and used at another time of day.
- It allows power companies to use the cheapest or most
(+3) environmentally-friendly sources of power like nuclear or hydroelectric to meet peak demand, instead of needing to go to less benign sources like coal-fired plants

(+3) for any example of good vs. bad power

Score for the page_____ - ___

Blue

5. (20 pts) SSA

The gas phase decomposition of NO_2Cl to give 2 NO_2 + Cl_2 was proposed to occur as follows:

$$NO_2Cl \rightleftharpoons NO_2 + Cl \quad \text{forward rate constant } k_1, \text{ backward } k_{-1}$$

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2 \quad \text{rate constant } k_2$$

(a; 16 pts) Apply the SSA to the reactive chlorine atoms to show that the rate of appearance of Cl_2 should be

$$\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

(+4) SSA (+2)

$$\frac{d[Cl]}{dt} = k_1[NO_2Cl] + k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl] = 0$$

$$k_1[NO_2Cl] = (k_{-1}[NO_2] + k_2[NO_2Cl])[Cl]$$

$$[Cl] = \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]} \quad (+3)$$

Just this alone +3

$$\frac{d[Cl_2]}{dt} = k_2[NO_2Cl][Cl] = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]} \quad (+3)$$

(+4)

for any indication that it comes from somewhere

(b; 4 pts) Under what conditions would you observe a rate that is first order with respect to NO_2Cl ?

If $k_{-1}[NO_2] \gg k_2[NO_2Cl]$ (+3) we have

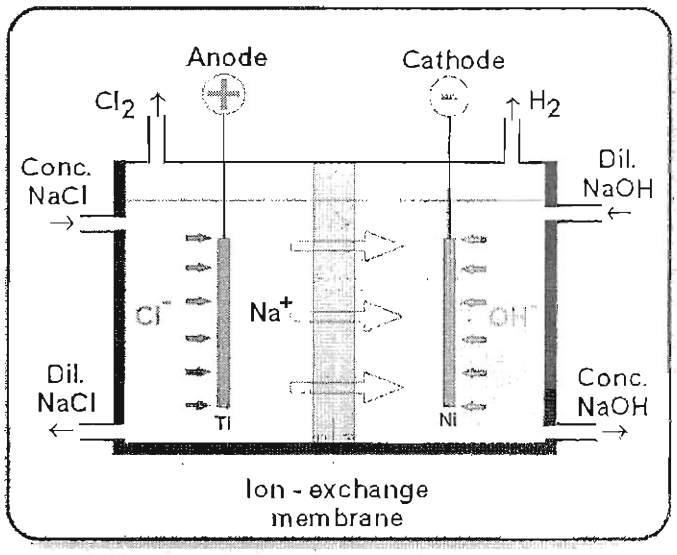
$$\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2]} = \frac{k_1 k_2 [NO_2Cl]^2}{k_2[NO_2Cl]}$$

(+1) for any indication as to why rate is 2nd order

Score for the page_____

6. (28 pts) Industrial electrochemistry

The Chloralkali process is the source of most chlorine gas and other oxidized forms of chlorine used for bleach etc. It is also a major player in Neal Stephenson's early science fiction novel *Zodiac*. The electrolysis process occurs under aqueous basic conditions.



Relevant half reactions are:

$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-$	$E°_{red} = +1.36$ V
$O_2(g) + 2\ H_2O + 4\ e^- \rightarrow 4\ HO^-$	$E°_{red} = +0.40$ V
$Na^+ + 1\ e^- \rightarrow Na\ (s)$	$E°_{red} = -2.71$ V
$2\ H_2O + 2\ e^- \rightarrow H_2\ (g) + 2\ HO^-$	$E°_{red} = -0.83$ V

(a; 9 pts) Calculate $E°_{cell}$ for each of the following reactions.

$2\ Cl^- + 2\ H_2O \rightarrow H_2\ (g) + 2\ HO^- + Cl_2\ (g)$ $\quad E°_{cell} = E°_{ox}(Cl^-) + E°_{red}(H_2O) = -1.36V - 0.83V = -2.19V$

$2\ Cl^- + 2\ Na^+ \rightarrow 2\ Na\ (s) + Cl_2\ (g)$ $\quad E°_{cell} = E°_{ox}(Cl^-) + E°_{red}(Na^+) = -1.36V - 2.71V = -4.07V$

$2\ H_2O \rightarrow 2\ H_2\ (g) + O_2\ (g)$ $\quad E°_{cell} = E°_{ox}(OH^-) + E°_{red}(H_2O) = -0.40V - 0.83V = -1.23V$

(b; 6 pts) Calculate E_{cell} for $2\ Cl^- + 2\ H_2O \rightarrow H_2\ (g) + 2\ HO^- + Cl_2\ (g)$ at 3 M NaCl, pH 11, 0.2 atm each gas.

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$$

$$= -2.19 - \frac{0.0592}{2} \log \frac{[H_2][OH^-]^2[Cl_2]}{[Cl^-]^2[H_2O]^2} = -2.19 - 0.0296 \log \frac{(0.2)(10^{-3})}{}$$

$$= -2.19 - 0.0296 \log \frac{(0.2\ atm)(10^{-3}\ M)^2(0.2\ atm)}{(3\ M)^2}$$

$$= -1.94\ \checkmark$$

Score for the page_____

(c; 13 pts) Explain why it is not surprising that solid Na is not produced from the electrolysis of brine, but it is surprising that we actually get any chlorine gas! What must be true of the electrochemistry occurring at the titanium anode? Where have we seen a very similar situation before? Give the balanced total reaction for the chloralkali cell.

- The reduction to give solid Na is highly unfavorable — applying a voltage to the cell will reduce water before it will reduce Na^+ — that's why NaCl electrolysis to give Na(l) must occur in molten salt, not aqueous solution. (+3)

- It is surprising that Cl_2 gas is produced, because according to the $E°$ cell values, water oxidation to give O_2 would be favored instead. (+3)

- There must be a large overpotential at the Ti electrode for water oxidation, so Cl^- is oxidized at a lower voltage than H_2O. [This is why we use platinum wire in gel electrolysis, to make O_2 instead of Cl_2!] (+3)

- The lead-acid battery is similar — H_2 and O_2 production is minimized (+2)

- $2Cl^- + 2H_2O \rightarrow H_2 + 2HO^- + Cl_2$ ↳ [+1 for just this]

so net rxn is

(+2) $2\,NaCl_{(aq)} + 2\,H_2O_{(l)} \rightarrow H_{2(g)} + 2\,NaOH_{(aq)} + Cl_{2(g)}$

brine (left) → energy; NaOH (right) → caustic soda; Cl_2 → bleach

Page	Score
1	/
2	/
3	/
4	/
5	/
6	/
7	/
8	/
9	/
10	/
Total	

Score for the page_____