

Chemistry 271 – 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 15, 2016

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:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

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

$$K_b = [\text{HA}][\text{HO}^-]/[\text{A}^-]$$

$$K_w = [\text{H}^+][\text{HO}^-]$$

$$\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}] \quad \Delta G^\circ = -RT \ln K_{eq}$$

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

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

$$\ln K_{eq} = (-\Delta H^\circ/R)(1/T) + \Delta S^\circ/R$$

$$\Delta S = q/T$$

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

$$S = k_B \ln W$$

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

$$\Delta G = \Delta G^\circ + RT \ln Q$$

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

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

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

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

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

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

$$\Delta G^\circ = -n\mathcal{F}E^\circ_{\text{cell}}$$

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

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

$$[\text{A}] = [\text{A}]_0 - kt$$

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

$$1/[\text{A}] = 1/[\text{A}]_0 + kt$$

Standard hydrogen electrode: $2 \text{H}^+(aq, 1 \text{ M}) + 2 e^- \rightarrow \text{H}_2(g)$ $E^\circ_{\text{red}} = 0.000 \text{ V}$

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."

$$89 + 3 + 1 + 1 + 2 = 96$$

1. Fundamental thermodynamics (45 pts)

(a; 15 pts) Fill in the blanks: As a chemical reaction $A(g) \rightleftharpoons B(g)$, starting with pure A, proceeds from left to right (+1) at constant T and P, $Q = \frac{P_B}{P_A}$ or $\frac{[B]}{[A]}$ [enter expression for the reaction quotient] increases until $Q = K_{eq}$ and then remains constant. At this point we have reached the state of equilibrium (+2). The change in the state function Gibbs free energy (+1), denoted ΔG , is zero for converting a small amount of reactants to products or vice versa. This tells us that at these particular partial pressures of A and B, the molar free energy (+1) of A is equal to (+2) the molar free energy of B.

(b; 25 pts) Multiple T/F: Circle ALL correct answers.

Question	Answer 1	Answer 2	Answer 3	
Free energy G...	Is always positive	Is a state function	Is conserved, like E	+3
When G is at a minimum...	The system is at equilibrium	T = 0 K	The enthalpy of the universe is a maximum	+3
ΔG is useful because...	It can easily be calculated from first principles	It lets us focus only on the system and not the surroundings	It gives us the temperature dependence of K_{eq}	+3
An exothermic reaction in system that is in a bath that maintains constant T and P...	Increases the entropy of the surroundings (the bath)	Must take heat in from the bath	Is always spontaneous	+3
The standard state free energy change ΔG° ...	Depends on temperature	Is always = 0 at equilibrium	Is independent of the actual concentrations of reactants and products	+3
The actual measured free energy change ΔG ...	Depends on temperature	Is always = 0 at equilibrium	Is independent of the actual concentrations of reactants and products	+3
The entropy S...	Cannot be measured; only ΔS can be measured	Is = 0 for a perfect crystal at 0 K	Is decreasing for the universe as a whole	+3
Spontaneous protein folding is an example of ...	Endothermic ordering	Exothermic disordering	Endothermic disordering	+3
Time's arrow has a direction because of the ...	Second Law of Thermodynamics			+1

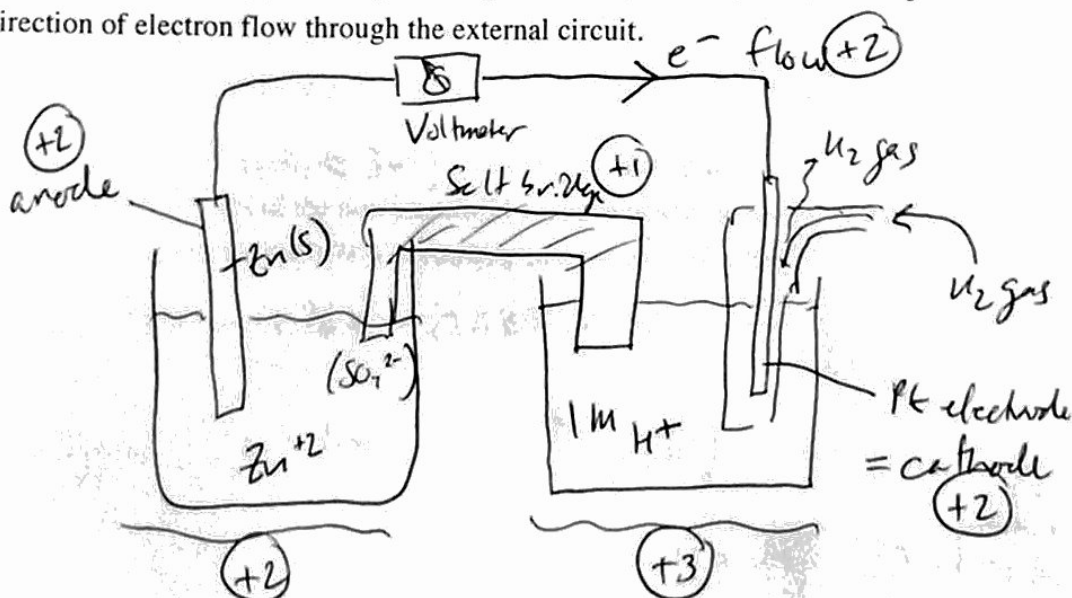
(c; 5 pts) If you memorized the equation $G = G^\circ + RT \ln P$, but forgot the sign, how could you figure out whether $+$ or $-$ is logically correct?

- (+3) We know that expansion and dilution are spontaneous due to entropy.
 (+2) Therefore G must increase with ~~decrease~~ increasing partial pressure, so the sign must be $+$.

2. Electrochemistry (40 pts)

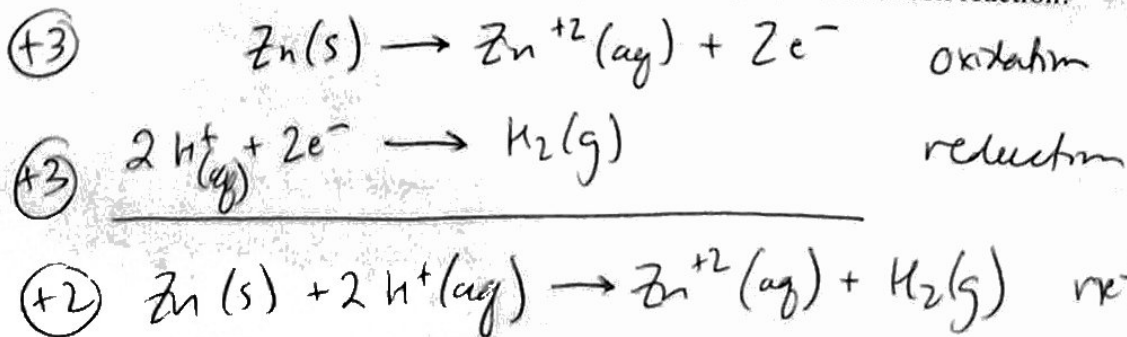
Consider a $Zn(s)/Zn^{2+}(aq)$ half cell set up by one of your lab partners, hooked up to what your other lab partner told you is a Standard Hydrogen Electrode (SHE).

(a; 12 pts) Sketch the setup, including labeling the anode, cathode, and salt bridge and indicating the direction of electron flow through the external circuit.



Based on the standard reduction potential tables, the voltage should be +0.76 V for the oxidation of Zn to reduce H^+ to H_2 .

(b; 8 pts) Write down each half-reaction and the balanced overall redox reaction.



Instead of 0.76V, you measure 0.71 V. You suspect that one, but only one, of the aqueous components was prepared incorrectly, i.e. that either the Zn^{+2} concentration or the H^+ concentration is not at the standard state. [We ignore any possible overpotential or conductivity complications.]

(c; 8 pts) Calculate the non-standard Zn^{+2} concentration that would be required for you to observe 0.71 V, assuming that the SHE was set up correctly.

Nernst: $E_{cell} = E_{cell}^0 - \frac{0.0592V}{n} \log_{10} Q$ (+2)

$$0.71V = 0.76V - \frac{0.0592V}{2} \log_{10} \frac{P_{H_2} [Zn^{+2}]}{Zn(s) [H^+]^2} \quad \begin{matrix} \text{=} 1 \\ \text{=} 1M \end{matrix} \quad \textcircled{+2} \text{ for plugging in}$$

$$-0.0592 = -0.0296 \log_{10} [Zn^{+2}]$$

(+2) for work

$$\log_{10} ([Zn^{+2}(aq)]) = \frac{5}{2.96} \approx 1.69 \text{ so } [Zn^{+2}(aq)] = 49M \quad \textcircled{+2} \text{ (Impossible)}$$

(solubility of $ZnSO_4 \approx 3M$) since $ZnSO_4$ is $\sim 20M$

(d; 6 pts) Calculate the pH of the non-standard hydrogen electrode (denoted the %\$@#*&%\$-NSHE) that would be required to give 0.71 V, assuming that the $Zn(s)/Zn^{+2}(aq)$ half-cell was set up correctly.

$$0.71V = 0.76V - 0.0296V \log_{10} \frac{1 \cdot 1}{1 \cdot [H^+]^2} \quad \textcircled{+2} \text{ for set up}$$

$$\log_{10} \frac{1}{[H^+]^2} = 1.69 \quad \textcircled{+2}$$

$$-2 \log [H^+] = 1.69$$

$$-\log [H^+] = \frac{1.69}{2} = 0.85 \quad \textcircled{+2}$$

~~$\log_{10} \frac{1}{[H^+]^2} = 1.69$~~

(The SHE at 1M $[H^+]$ is $pH = 0$)

$[H^+] = 0.143M$ - only a factor of 7, easily possible.

(e; 6 pts) Which half-cell is the likely culprit: explain your reasoning?

- (+2) 50M Zn^{+2} is impossible
- (+2) $pH \approx 1$ instead of $pH = 0$ would be an easy mistake to make
- (+2) It's the SHE

3. van't Hoff and DNA (40 pts)

(a; 7 pts) We know that $\Delta G = \Delta H - T\Delta S$ in general, and $\Delta G^\circ = -RT \ln K_{eq}$ for chemical equilibrium. Use these two equations to derive the van't Hoff equation, and indicate the dependent and independent variables.

$$\Delta G = \Delta H - T\Delta S \quad (+2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq} \quad (+1)$$

independent variable

So $\ln K_{eq} = \left(-\frac{\Delta H^\circ}{R} \right) \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (+3)$

total of 5 for leaving out the "6"

$$y = m x + b$$

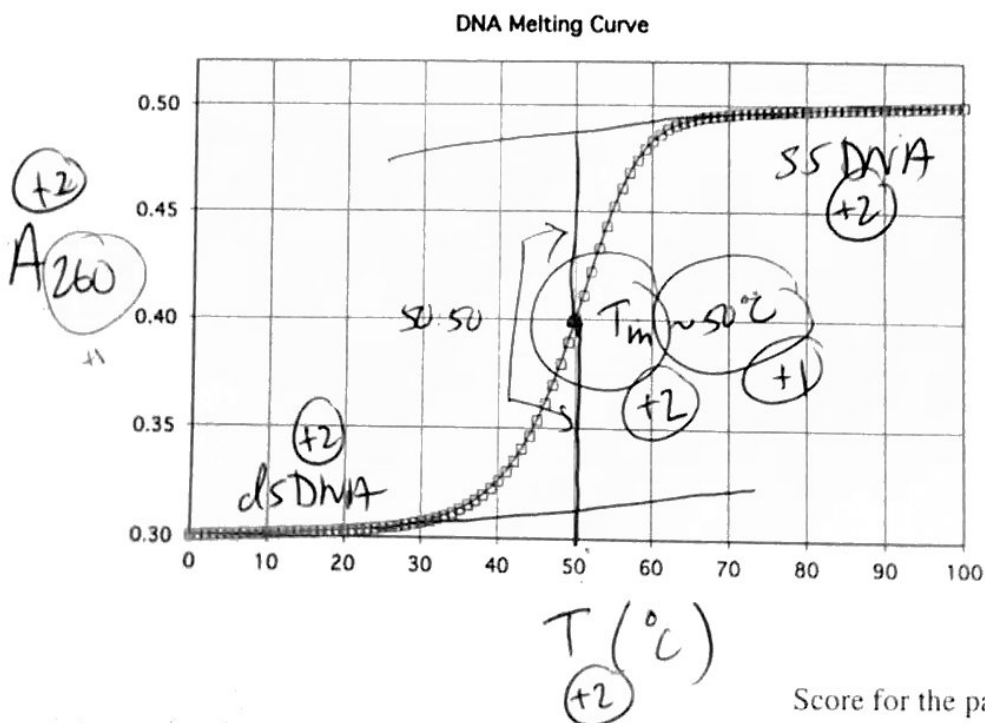
(+1) dependent variable y
 (+1) independent variable x

(b; 6 pts) For DNA hybridization $W + C \rightleftharpoons W \cdot C$, ΔH° and ΔS° are both negative: explain why, physically.

$\Delta H^\circ < 0$ because bonds are being formed - stacking and H-bonds } +3 for both what stacking
 (+2) (+1 for either)

$\Delta S^\circ < 0$ because translational entropy \downarrow and conformational entropy \downarrow in ds. }
 (+1) (+2)

(c; 11 pts) The sketch below shows the primary data for a melting curve for a DNA oligonucleotide. Label the axes, indicate the part of the curve where the DNA is almost all double stranded (ds), indicate the part where it is single-stranded (ss), and estimate the "melting temperature" T_m , the temperature at which half the DNA is in single-stranded form and half is double stranded.



The value of T_m is given by the following equation:
$$T_m = \frac{\Delta H^\circ}{\Delta S^\circ + R \ln\left(\frac{CT}{4}\right)} = \frac{\ominus}{\ominus + \ominus} = \oplus$$

where CT is the total input strand concentration of the two input single-stranded DNAs (W and C), and $R = 1.987 \text{ cal/mole K}$ in the traditional non-SI units used in this field. In this example, $\Delta H^\circ = -71.3 \text{ kcal/mole}$, $\Delta S^\circ = -194 \text{ cal/mol K}$, and $CT = 6 \mu\text{M}$.

(d; 8 pts) Without doing a numerical calculation, use the equation to say whether T_m increases or decreases as CT increases, and give a rationale for this trend based on LeChatelier or kinetic arguments.

- As $T_m \uparrow$ the denominator becomes less negative so the quotient increases (+2) (+2)

LeC - As $[W]$ and $[C] \uparrow$, the equilibrium is driven to the right and $f_{ds} \uparrow$ at any T either (+3)

Kinetics - Rate of dsDNA dissociation stays the same, rate of hybridization goes up - at any T , equilibrium shifts to the right. (+3) (+1)

So - what was a $T > T_m$ now has $f_{ds} = 0.5$ so it's the new $T_m >$ the old T_m .

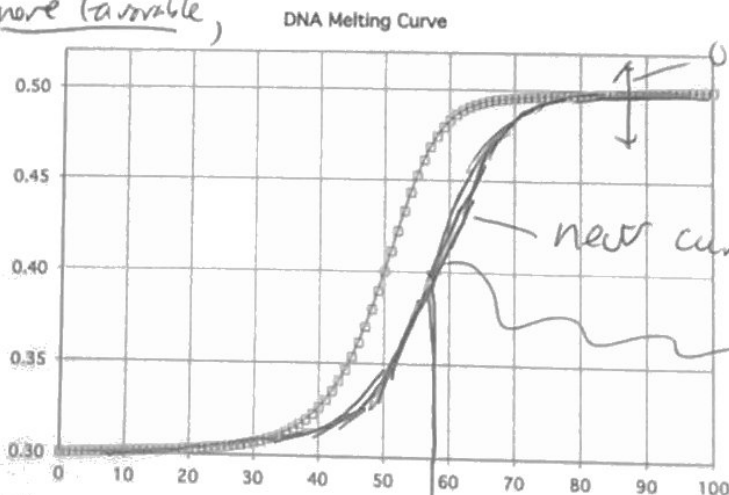
(e; 8 pts) Finally, calculate the T_m and sketch the melting curve you would get if you melted a different oligonucleotide, with $\Delta H^\circ = -73.0 \text{ kcal/mole}$ and $\Delta S^\circ = -194 \text{ cal/mol K}$, at $6 \mu\text{M}$ CT as above.

$$T_m = \frac{-73000 \text{ cal/mole}}{\left(-194 \frac{\text{cal}}{\text{mole K}} + 1.987 \frac{\text{cal}}{\text{mole K}} \ln\left(\frac{6 \times 10^{-6} \text{ M}}{4}\right)\right)} \quad (+3)$$

$$= \frac{-73000 \text{ K}}{-194 + 1.987 \cdot (-13.41)} = 331 \text{ K} = 57.7^\circ\text{C} \quad (+2)$$

$-73.0 \rightarrow \Delta H^\circ$ more favorable,

$T_m \uparrow$



DNA Melting Curve

OK if lines do not match for any curve shifted to the right (+3)

Should be incrementally steeper slope

58°C

4. Environmental thermodynamics, e-chem II (45 pts)

(a; 5 pts) What does the "350" in www.350.org mean?

350 is 350 ppm (parts per million) CO₂, which is the~~amount~~ level needed to ensure not too much global warming. We are above that now. (3) (2)

(b; 8 pts) Where does the energy released in combustion come from? In terms of redox, explain why burning natural gas provides about twice as more free energy per carbon atom released than burning coal or wood. (2)

- The energy comes from making new bonds to oxygen, i.e. the reduction of molecular oxygen. (3)- CH₄ has an oxidation # of -4, vs. 0 for coal or wood - CO₂ is at +4, so CH₄ provides twice as many electrons per carbon given to O₂. (3)(c; 6 pts) List one lifestyle decision (not necessarily your own) and one society-level choice that could lead to a moderation of the rate of increase in atmospheric CO₂.

(3) for - flying less, LED bulbs, solar panels, vegetarianism, driving a hybrid, biking, taking the bus, living near work, etc.

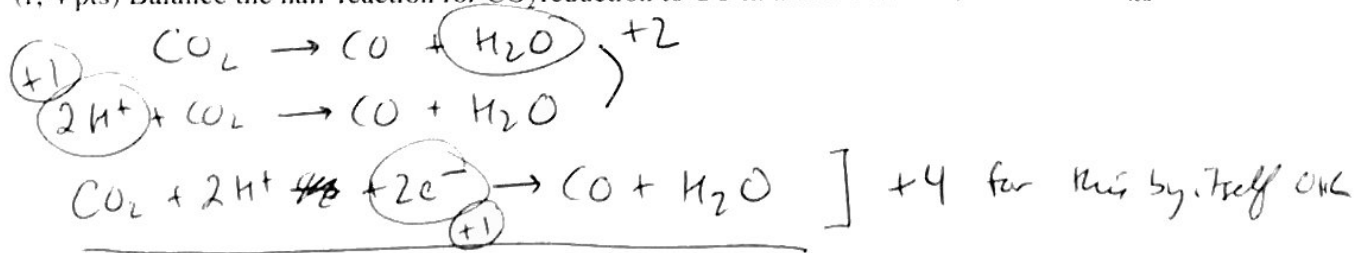
(3) for - ↑ nuclear, wind, solar, tidal, geothermal, or hydroelectric power
Smarter grid, better batteries, widespread biofuel use, carbon taxes (though not true), more planting forests(d; 3 pts) List one greenhouse gas besides CO₂.(3) H₂O, CH₄, N₂O, O₃, CFC'snot N₂, O₂, Ar

(e; 9 pts) The job of PSII is to make a great oxidizing agent (the P680⁺ cation). What does it oxidize? The job of PSI is to make a strong reducing agent. Where do the electrons from this reducing agent go in the end? Why is it necessary to use two photons in the overall process instead of just one?

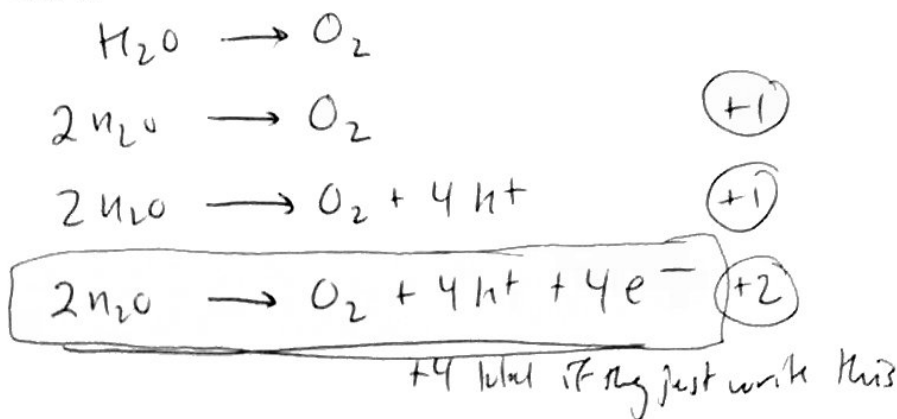
- (+3) - P680⁺ oxidizes water, giving molecular oxygen as a waste product
- PSI electrons end up in NADPH and then Carbohydrates (+3 breaker)
- One visible light photon ~~can~~ does not provide enough energy to take an electron all the way from water to NADPH, at least at achievable efficiency. $2 \text{NADP}^+ + 2 \text{H}_2\text{O} \rightarrow 2 \text{NADPH} + \text{O}_2 + 2 \text{H}^+$

The movie "The Martian" depends on a machine, based on an actual proposed NASA device code-named "MOXIE," that somehow converts CO₂ collected from the Martian atmosphere to O₂ for Matt Damon to breathe. MOXIE expels carbon expelled as CO. We will oversimplify the chemistry by imagining that it occurs in aqueous solution. (In the real future MOXIE will operate without H; if Mars had unlimited water, we would get oxygen simply by electrolysis of water. And if wishes were horses, beggars would ride.)

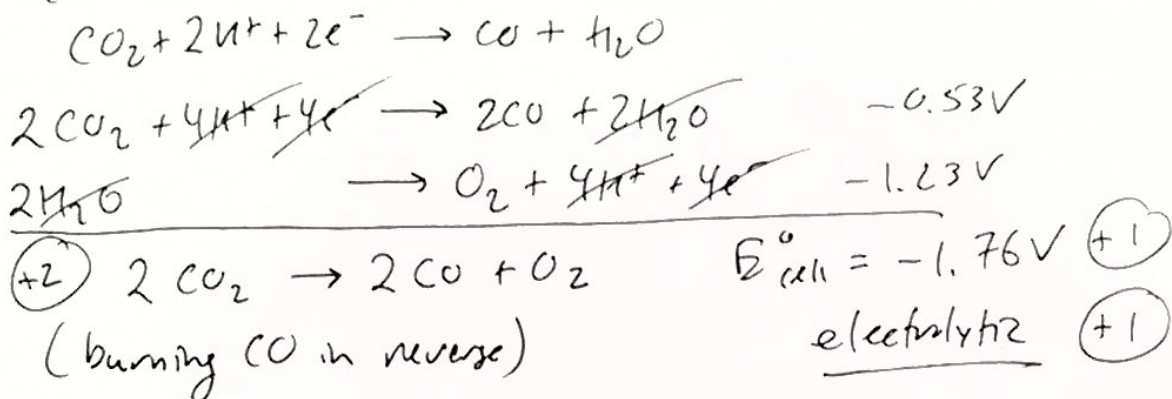
(f; 4 pts) Balance the half-reaction for CO₂ reduction to CO in acidic solution, for which E°_{red} = -0.53 V.



(g; 4 pts) Balance the half-reaction for the oxidation of water to produce O₂ in acidic solution, for which E°_{ox} = -1.23 V.



(h; 6 pts) Write down the overall balanced electrochemical reaction for MOXIE and calculate the standard state cell voltage. Is this voltage pH-dependent? Why or why not? Circle one: this is an electrolytic cell or a galvanic cell?

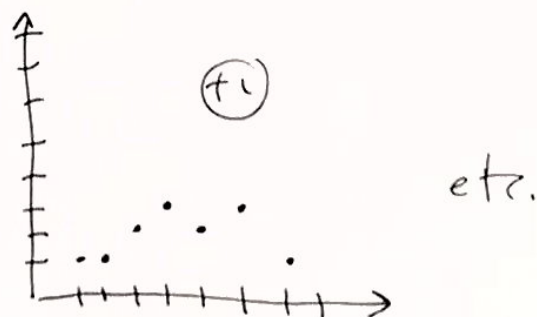
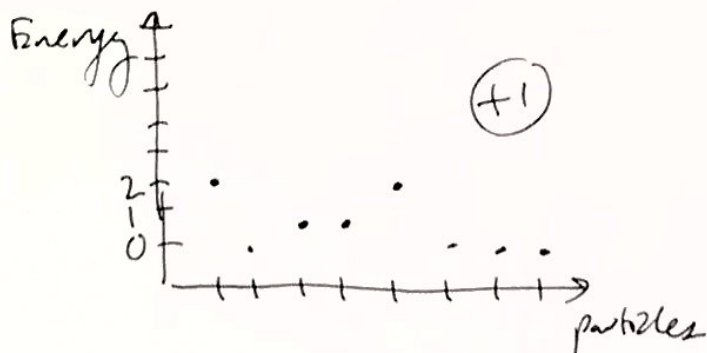


It is not pH dependent - $[\text{H}^+]$ and $[\text{H}_2\text{O}]$ do not appear in Q (+1)

5. Statistical thermodynamics (30 pts)

Consider distributing 6 quanta of energy among 8 particles. The two configurations comprising the largest numbers of microstates in the ensemble comprise about half of the total number of microstates.

(a; 7 pts) One of two dominant configurations has two particles with two quanta each and two particles with one quantum each. Draw two microstates that belong to this configuration, and calculate how many microstates are in it.



$$\# \text{ of microstates} = \frac{(8 \cdot 7)(6 \cdot 5)}{2 \cdot 2} = 28 \cdot 15 = \underline{420}$$

$$\text{or} = \frac{8!}{2! 2! 4!} = \underline{420}$$

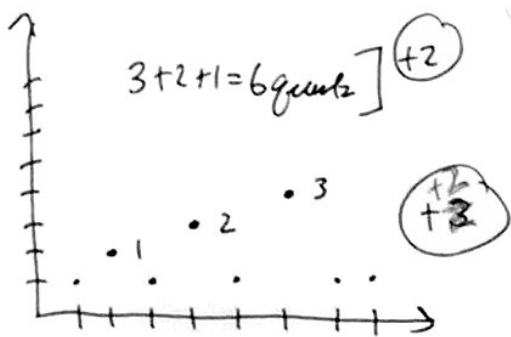
(+2)

(+3) for idea of microstates

+1 for each correct

(b; 7 pts) The other configuration in this ensemble has particles occupying as many different energy levels as possible (i.e. particles that have as many different numbers of quanta as possible). Draw a microstate in that configuration and calculate how many microstates there are in it.

→ ~~6 quanta~~ 6 quanta among 8 particles - can have particles of 3, 2, and 1 units of energy

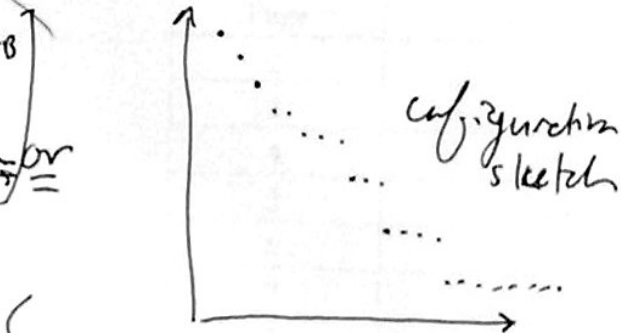
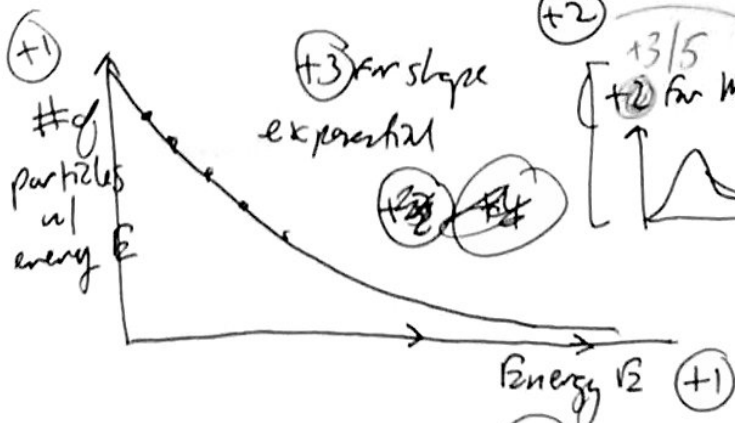


of microstates = $8 \cdot 7 \cdot 6 = 336$ (or +2 for any consistent calculation)



(c; 12 pts) Whose distribution comes from adding up the overall number of particles with each energy? Sketch the distribution. What is the relationship between entropy and microstates? Why do we use the logarithm?

- The Boltzmann Distribution

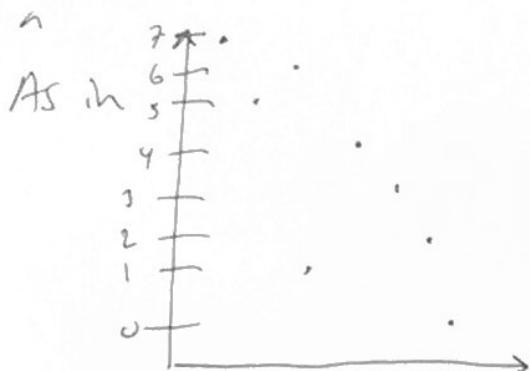


$S = k \ln W$

ok to flip axes

$\ln \rightarrow$ makes giant numbers manageable and makes S an extensive state function

(d; 4 pts) We know that the number of microstates in a configuration is maximized if every particle in has a different energy - why didn't a configuration with every particle at a different level show up as the winner?



every particle at its own energy -

$$W = N! = 8! = 40320$$

[calculation not needed]

- I ~~can~~ can't be out of money - I still have checks left!

~~7~~ +2 [The configuration has to obey conservation of energy -
 this we would have at least $7+6+5+...+1 = 28$ gacenta, not 6
 Entropy increases as heat is added

Anything saying that
+2 6 gacenta is not enough

Page	Score
2	/40
3	/25
4	/20
5	/24
6	/16
7	/22
8	/17
9	/13
10	/19
11	/4
Total	/200