**Chemistry 271 – 22XX** **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 15, 2017**

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:**

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

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

$R = 0.08206$ L·atm/mole K $k_B = 1.38 \times 10^{-23}$ J/K $\ln K_{eq} = (-\Delta H°/R)(1/T) + \Delta S°/R$

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

$S = k_B \ln W$ $\Delta G = \Delta H - T\Delta S$ $\Delta G = \Delta G° + RT\ln Q$

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

°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 $e^-$

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

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

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

$\Delta H°_{rxn} = \sum \Delta H°_f(\text{products}) - \sum \Delta H°_f(\text{reactants})$

$W = \frac{N!}{\prod_i (m_i!)}$ where the product is over all energy levels, indexed by $i$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surroundings} > 0$$

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**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."

## 1. Fundamental thermodynamics (50 pts)

(a; 3 pts) We showed that the free energy per mole of a substance A is $G_A = G°_A + RT \ln [A]$. If you forgot the sign, how could you logically figure out that it should be "+" and not "–"?

We know that expansion + dilution are spontaneous, so ΔG for compression/concentration should be ⊕, so the sign is ⊕.

(+3)

(b; 5 pts) Similarly, the free energy of *b* moles of substance B is $bG_B = bG°_B + bRT \ln [B]$. Write down the change in free energy $\Delta G_{rxn}$ for the reaction $aA \rightleftharpoons bB$, for *a* moles of A converting to *b* moles of B.

$G \text{ of } A = aG_A = aG_A^\circ + aRT \ln [A]$ (+2)

$\Delta G = bG_B^\circ + bRT \ln [B] - aG_A^\circ - aRT \ln [A]$ (+3)

$\Delta G = G(\text{products}) - G(\text{reactants})$ [+1]

(c; 9 pts) In the expression for $\Delta G_{rxn}$, separate terms that depend on [A] and [B] from those that don't, and derive $\Delta G_{rxn} = \Delta G° + RT \ln Q$, with the appropriate expressions for ΔG° and Q.

see if it is partially answered above.

$$\Delta G = \underbrace{bG_B^\circ - aG_A^\circ}_{} + bRT \ln [B] - aRT \ln [A]$$

$$= \Delta G^\circ_{rxn} \text{ (+3)} + RT \ln [B]^b - RT \ln [A]^a$$

(+3) for getting exponents

$$\Delta G = \Delta G^\circ_{rxn} + RT \ln \frac{[B]^b}{[A]^a} \rightarrow Q \text{ (+3)}$$

Score for the page 17

(d; 3 pts) Under what conditions does the actual measured ΔG equal the standard state ΔG°?

$\Delta G = \Delta G^\circ + RT \ln Q$ so when $Q = 1$ (+3), either b/c

all reactants are @ standard state or product + reactant [ ]'s cancel.

either is OK

(e; 4 pts) Under what conditions does ΔG = 0, and which important equation from the front page comes from this fact?

$\Delta G = 0$ at equilibrium (+2), giving us $\Delta G^\circ = -RT \ln K$ (+2)

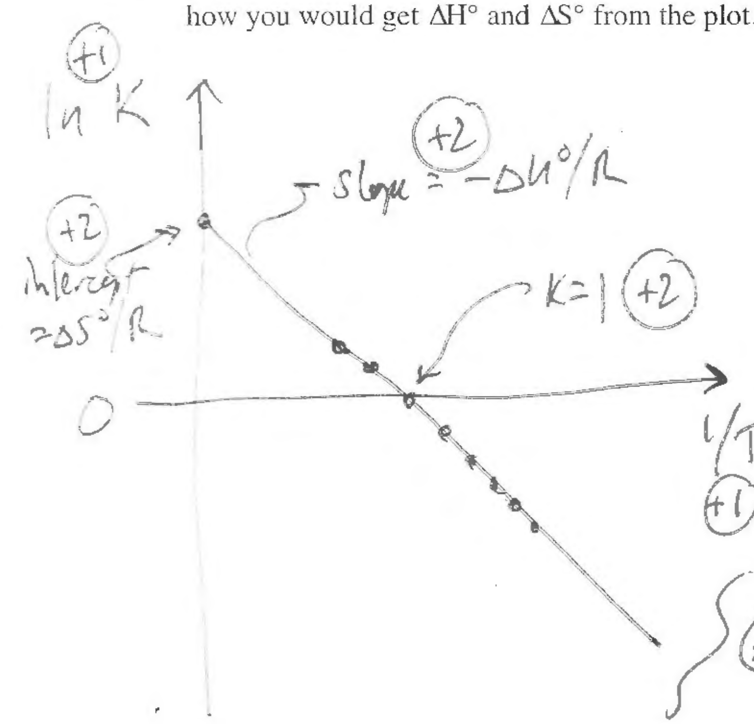
$\left( K = Q\big|_{\text{at equilibrium}} \right)$

(f; 4 pts) Explain why the reaction A → B progresses to some small extent even if the standard state molar free energy of B is much larger than the standard state molar free energy of A.

when [B] is @ very low [ ] (+2) its free energy is large and ⊖. (+2)

(Rare stuff is valuable in terms of entropy)
+4 OK

(g; 12 pts) Unrelated to above. Sketch a van't Hoff plot for an endothermic disordering reaction, including how you would get ΔH° and ΔS° from the plot. Indicate the temperature at which K = 1.

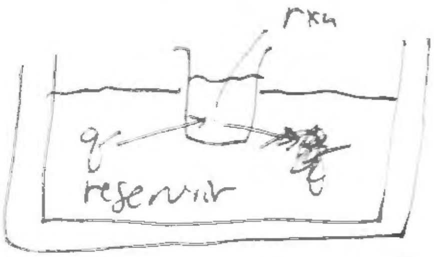


$$\ln K_{eq} = \underbrace{\left(-\frac{\Delta H^\circ}{R}\right)}_{\ominus\text{ slope}}\left(\frac{1}{T}\right) + \underbrace{\frac{\Delta S^\circ}{R}}_{\oplus\text{ intercept}}$$

(+2) for downward slope w/ ⊕ intercept (+2)

Score for the page ______ /23

(h; 10 pts) Consider an endothermic disordering reaction occurring in a beaker in a large thermal reservoir. Sketch the direction of heat flow and give the signs of the entropy changes in the system and the reservoir. In terms of the second law of thermodynamics, explain why the reaction is unfavorable when T is too low.



$\Delta H^\circ > 0$ so q goes ~~out~~ in $(q > 0)$

q goes in (+2)

$\Delta S_{sys} > 0$ (+2)

(+2) $\Delta S_{reservoir} < 0$ b/c it is losing heat

(+2)

So when T is too low, $\Delta S_{reservoir} = -q/T$ is too negative, and the overall $\Delta S_{universe} = \Delta S_{sys} + \Delta S_{reservoir}$ is ⊖, therefore ~~unfavorable~~ non-spontaneous. (+2)

## 2. Chemical equilibrium (30 pts)

Enormous amounts of lime, CaO, are relaased in the process of making cement from limestone and clay (in fact, cement production makes a significant contribution to anthropogenic $CO_2$). The table gives the thermodynamic values for $CaCO_3$, CaO, and $CO_2$.

| | $\Delta H^\circ_f$ (kJ/mol) | S° (J/mol K) |
|---|---|---|
| $CaCO_3$ | –1207 | 93 |
| CaO | –636 | 40 |
| $CO_2$ | –394 | 214 |

(a: 3 pts) Why is the molar entropy of $CO_2$ much larger than the entropy of CaO and $CaCO_3$?

(+3) $CO_2$ is a gas – many more ways for it to move around.

(b; 3 pts) Why is the molar entropy of $CaCO_3$ greater than that of CaO?

more atoms, meaning more possible rotations + vibrations and electronic states – mostly vibrations in the solid.

(+3)

Score for the page /16

(c; 12 pts) Calculate ΔH°, ΔS°, and ΔG° at 800 K for the formation of lime: $CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$

$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$= (-636) + (-394) - (-1207) = \underline{+177\ \text{kJ/mol}} \quad (+4)$$

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}) = (40 + 214) - (93) = \underline{161\ \text{J/mol K}} \quad (+4)$$

$$\Delta G^\circ(800\text{K}) = \Delta H^\circ - T\Delta S^\circ = +177000\ \text{J/mol} - 800 \cdot 161\ \text{J/mol}$$

$$= \underline{48200\ \text{J/mol}} \quad (+4)$$

(d; 12 pts) Calculate the equilibrium partial pressure of $CO_2$ over $CaCO_3$ at 300 K, and calculate the temperature at which the equilibrium partial pressure is 1 atm.

$$\Delta G^\circ(300\text{K}) = 177000 - 300 \cdot 161 = 128700\ \text{J/mol}$$

$$= -RT \ln K = \boxed{-RT \ln P_{CO_2}} \quad (+3)$$

$$\ln P_{CO_2} = \frac{-128700\ \text{J/mol}}{8.314\ \text{J/mol K} \cdot 300\ \text{K}} = -51.6$$

(+3)

$\underline{P_{CO_2} = 3.89 \times 10^{-23}\ \text{atm}}$ [marble does not outgas by itself]

For $P_{CO_2} = 1$ atm, we have $\underline{\Delta G^\circ = 0}$ (+3)

So $\Delta H - T\Delta S^\circ = 0$

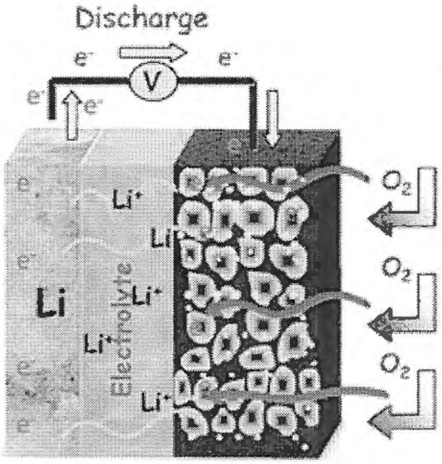
(+3)

$$T = +\frac{\Delta H^\circ}{\Delta S^\circ} = +\frac{177000}{161} = \underline{1099\ \text{K}}$$

(1100 K)

Score for the page /24

## 3. Electrochemistry (40 pts)



Consider the Li-air battery, which is the subject of active research. For simplicity, we imagine that it operates in aqueous medium. Li metal is oxidized at the left, Li⁺ cations migrate through the electrolyte (= separator), and $O_2$ is reduced at the right and the product neutralizes the charge of the Li⁺ cations.

(a; 3 pts) Write down the anodic half-reaction, which is the one-electron oxidation of solid lithium metal Li(s) The corresponding oxidation potential is $E°_{ox} = + 3.04$ V.

(+3) $Li_{(s)} \rightarrow Li^+ + e^-$

(b; 5 pts) Write down the balanced cathodic half-reaction, which we assume is the reduction of $O_2$ gas to give hydroxide as a product. (Real batteries give lithium peroxide $Li_2O_2$, which is too complicated for us.). The reduction potential is +0.40 V.

$O_{2(g)} + 4e^- + \overset{2H_2O}{\cancel{[illegible]}} \rightarrow 4OH^-$

(+1) $O_2$
+1 $OH^-$ ✓
+3 balanced.
↳ +1 if ~~[illegible]~~ $H^+$ is used.

$O_2 \longrightarrow 2H_2O$
$+4H^+$
$+4e^-$ $+4HO^-$ $+4HO^-$

(c; 14 pts) Write down the overall electrochemical reaction for the Li-air battery. Calculate $E°_{cell}$, ΔG° and $K_{eq}$ for the reaction at 298 K.

+4 $4Li_{(s)} + O_{2(g)} + 2H_2O \rightarrow 4Li^+ + 4OH^-$ +2 if good but not balanced.

+3 13 $E^0_{cell} = 3{,}04 + 0{,}4 = 3{,}44\,V$ math error +2

+3 $\Delta G° = -nFE°_{cell} = -(4)(96500)(3{,}44) = -1327840\,J$ math error +2 → missing sign +2 wrong n with right answer +1 (+2)

+4 $\Delta G° = -RT\ln K_{eq} \Rightarrow \ln K_{eq} = \frac{-\Delta G°}{RT} \Rightarrow K_{eq} = e^{-\frac{\Delta G}{RT}} = e^{\frac{+1327840\,J}{(8{,}314)(298)}} = e^{536}$

$= 10^{232}$ !

$\ln K = 536$ OK (+2)

Score for the page_____________

(d; 10 pts) Calculate $E_{cell}$ at $P_{O2} = 0.00001$ atm. [Assume all products are formed at 1 M, and from above we know that n = 4 per $O_2$ reactant molecule.] Clearly the cell still has plenty of voltage, but it would not be very useful under these conditions – why not?

$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log\frac{[Li^+][\text{[illegible]}][OH^-]^4}{[O_2][H^+]^2} \Rightarrow E^\circ_{cell} - \frac{0.0592}{4}\log\frac{1}{P_{O_2}}$

~~(+2) meth~~ (+4) (−2) math error

(+2)
↳ (+1) if 0.592 ln

$3.44 - \frac{0.0592}{4}\log\frac{1}{0.00001} = \cancel{3.2} \Rightarrow \cancel{3.27\,V}$

$3.366\,V$

$P_{O_2}$ is very small = almost fully discharged ⇒ fast voltage drop. (+4)

(cannot provide any current b/c no $O_2$ to react)

(e; 3 pts) Making the approximation that the chemistries of alkali metals Li/Na/K/Rb/Cs are all the same, why is the Li-air battery of more interest than, for example, K-air, especially for phones, smart watches, etc.? ~~higher cell voltage, higher energy density ⇒ smaller battery but same energy~~

(+3) $Li^+$ is lighter or smaller than all the others.

(f; 5 pts) The familiar $Li^+$-ion battery is fundamentally different from the Li-air battery in terms of what the Li is doing. How so?

(+3) Li ion battery → Li ions are shuffled ~~[illegible]~~ between the cathode & the anode

(+2) Li-Air ⇒ Li ~~is ox.~~ metal is oxidized and Li ion is reduced c

Score for the page____________

## 4. $CO_2$, Linkage and connections (45 pts)

(a; 15 pts) When blood arrives in the lungs, hemoglobin is in the T state and $CO_2$ is bound to it. Recall that the ① T state binds $CO_2$ much better than the R state. Draw a linkage square that demonstrates that the R ② state is more stable relative to T in the absence of $CO_2$ than it is when $CO_2$ is bound. Write down the relationship between the four equilibrium constants.

(+3) for any square (+3) for correct

$$\begin{tikzcd}
T + CO_2 \arrow[r, shift left, "K_1"] \arrow[d, shift right, "\cancel{K_3}"'] & T \cdot CO_2 \arrow[l, shift left] \arrow[d, shift right] \\
R + CO_2 \arrow[u, shift right, "K_4"'] \arrow[r, shift left, "K_3"] & R \cdot CO_2 \arrow[l, shift left] \arrow[u, shift right, "K_2"']
\end{tikzcd}$$

(actually 2 $CO_2$'s)

$\underline{K_1 K_2 = K_3 K_4}$ (+3)

Statement ①: $\underline{K_1 > K_3}$ (+3)

The linkage shows that ~~$K_3$~~ $\underline{K_4 > K_2}$ (+3), ~~meaning that~~ which is statement ②.

(b; 15 pts) $CO_2$ is also carried in the blood as bicarbonate, $HCO_3^-$. The R state is a stronger acid than the T state, so linkages lead to the conversion of $T \cdot H^+ \cdot CO_2 \rightarrow R \cdot (O2)_4 + H^+ + CO_2$. Including discussion of the role of carbonic anhydrase, describe how bicarbonate is efficiently converted to $CO_2$ in the lungs.

In the lungs, ↑ $P_{O_2}$ gives $R(O_2)_4 + H^+ + CO_2$. (+2)

Then bicarbonate in the RBC is protonated, giving $H_2CO_3$, which (+2) CA equilibrates to give $CO_2$ that diffuses out.
(+3) (+2)

CA in RBC +3

- The carbonic anhydrase is necessary because the blood spends very little time in the lungs, so $CO_2$ must be generated rapidly upon oxygenation. (+3)
- ~~A~~ Mentioning $Cl^- / HCO_3^-$ antiporter —

extra credit (+3) for no more than 12.

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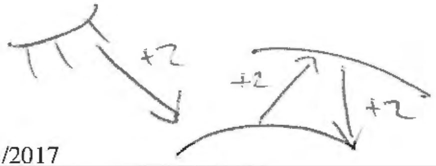
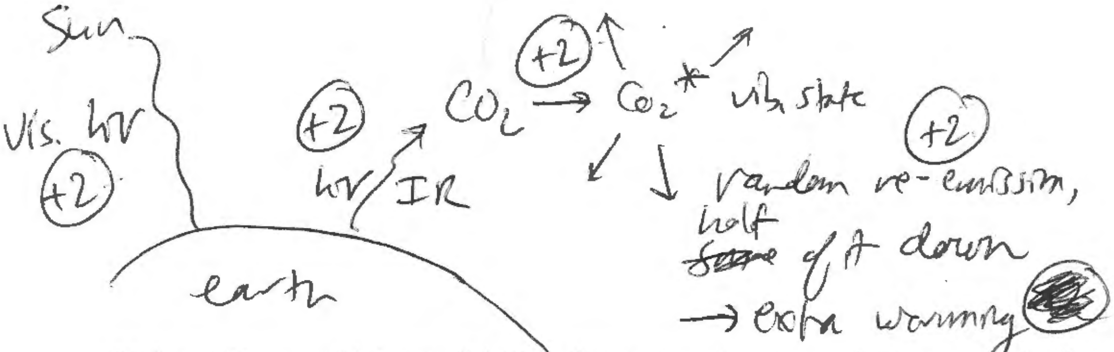


(c; 10 pts) Sketch the fundamental mechanism of net global warming caused by increased $CO_2$ in the atmosphere.



(+2) for $CO_2$ fills holes in the IR absorption spectrum of $H_2O$

(d; 5 pts) How could the availability of high-capacity storage batteries and the "smart electrical grid" help us to moderate the rate of increase in atmospheric $CO_2$?

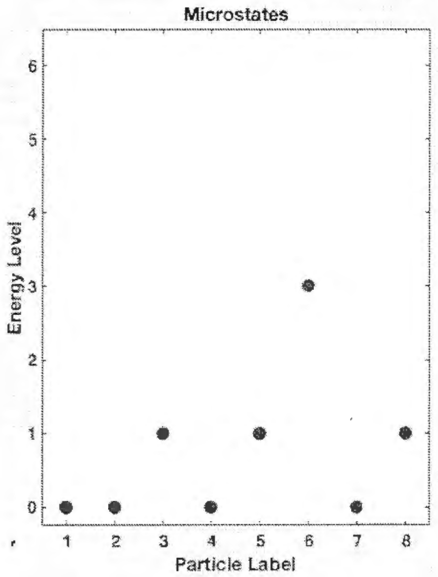
(+3) 5 [illegible]

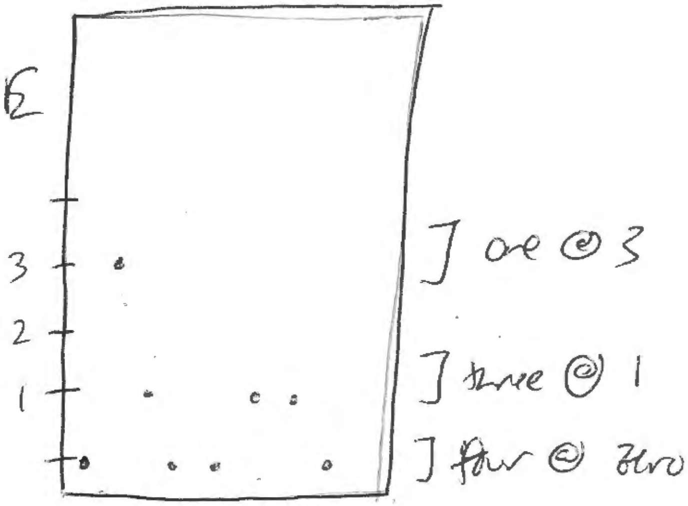
— We could use carbon-neutral sources like wind/solar/nuclear/geothermal/hydroelectric much more efficiently if we could store the energy (+3) to meet peak demand

## 5. Statistical thermodynamics (35 pts)

Consider the ensemble that represents distributing 6 quanta of energy among 8 particles.

(a; 6 pts) A microstate included in the ensemble is shown below. At the right, draw another microstate that is a member of the same configuration.





(+2) for any microstate
(+4) for same energy levels

Score for the page____________

(b; 6 pts) How many microstates are included in this configuration?

$$W = \frac{8!}{\underbrace{1!\,3!\,4!}_{}} = \frac{8\cdot7\cdot6\cdot5}{6} = \underline{280}$$

(+3)

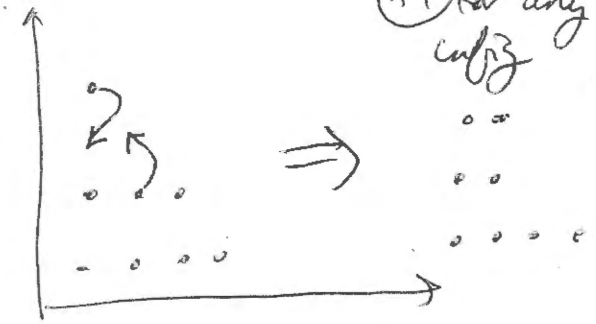
(+3) for idea

+2 for idea of any factorial

(+2)

(c; 9 pts) Circle whether this is or [✓ is not] the predominant configuration, and state how you know.
Large hint: Consider possible similar configurations, recalling what you know about 1!, 2!, and 3!.

(+4) for any new config



$$W = \frac{8!}{\underbrace{2!\,2!}_{=4 \text{ vs. } 6 \text{ above}}\,4!} = \frac{8\cdot7\cdot6\cdot5}{4} = \underline{420}$$

(and here could be more abundant configs)

(+3) for any calculation justifying a larger W

(d; 5 pts) How many microstates would there be for the same configuration in (a) and (b), but with two added particles at zero energy, i.e. how many microstates are in the configuration for 6 quanta distributed amoug 10 particles, with one particle having 3 quanta and three particles having one quantum each?

$$W = \frac{10!}{\underbrace{1!\,3!\,6!}_{}} = \frac{10\cdot9\cdot8\cdot7}{6} = \underline{840}$$

(+2)

(+3) for idea

+2 for any factorial.

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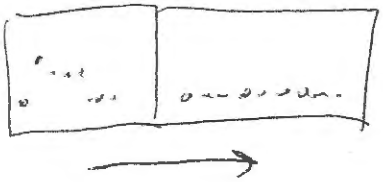
(e; 9 pts) Based on the above, clearly entropy increases as the size of the system increases, at constant energy: we would get many more microstates putting 6 quanta into 10 particles than into 8 particles. How can we square this with the fact that $\Delta S = q/T$, and $q$ is the same for the two cases? Imagine joining the 6 quanta/8 particle system with a system of 10 particles all at zero energy. How does this toy model lead us to the "zeroth law of thermodynamics," that heat flows from hot places to cold places?

- $\Delta S = q/T$ - If $\Delta S$ is larger and $q$ is the same, T must be lower - we are adding heat to a larger cold system so the average energy per particle (T) is smaller at the end, and recall that $\Delta S$ is larger for a given $q$ when T is small.

(+3)

(+3) for either



(+3)

Spreading the energy among more particles will give a larger S. So heat flow is spontaneous.

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| 8 | /30 |
| 9 | /21 |
| 10 | /~~21~~ 20 |
| 11 | /9 |
| **Total** | **/200** |

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