Chemistry 271, Section 21xx Your Name: KEY

Prof. Jason Kahn

University of Maryland, College Park Your SID #:

General Chemistry and Energetics Your Section # or time:

Exam II (100 points total) **April 6, 2011**

N = 178 + 4 + 1
= 183

You have 52 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. 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.

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	0 °C = 273.15 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	
$S = k_B \ln W$	$\Delta G = \Delta H - T\Delta S$	$E = \Sigma\, n_i\, \varepsilon_i$
$W = N!/(\prod n_i!)$	$n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$	$N = \Sigma\, n_i$
$R = N_A k_B$	$k_B = 1.38 \times 10^{-23}$ J/K	$t' = t - vx/c^2$

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

nano: 10^{-9} pico: 10^{-12} zepto: 10^{-21}

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 pt) Extra credit!

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

(a; 4 pts) An ensemble in statistical thermodynamics is:

(1) A description of the position and velocity of each particle in a system. → microstate
(2) A set of microstates that all share the same set of observables P, T, n, etc. → configuration
[✓ (3)] The set of all of the possible microstates that have a given value of total E.
(4) A set of imaginary replicates of the system.

(b; 4 pts) The idea of the Predominant Configuration is that:

(1) The configuration with the lowest energy is the one we observe. – all have same E
[✓ (2)] The vast majority of microstates correspond to the same set of macroscopic observables.
(3) The individual microstates with the largest entropy are most likely to be observed. – a microstate has no entropy
(4) All of the above.

(c; 4 pts) When a gas in a thermally insulated piston expands against a non-zero external pressure that is less than the internal pressure ↳ so $q = 0$ ↳ $w < 0$

(1) $q = 0, w = 0$, and $\Delta E = 0$
(2) $q < 0, w > 0$, and $\Delta E = 0$
[✓ (3)] $q = 0, w < 0$, and $\Delta E < 0$ $= q + w$
(4) None of the above.

(d; 4 pts) Endothermicity *per se* makes reactions tend to be unfavorable (non-spontaneous) because

(1) It accompanies bond formation, and the universe prefers bond breaking.
(2) It always decreases the total entropy of the universe.
(3) It requires heat to flow uphill.
[✓ (4)] It decreases the entropy of the surroundings.

(e; 4 pts) $\Delta S = q_{rev}/T$ for the entropy change of a reservoir

(1) Means that exothermicity buys less entropy when heat is rejected to a hot reservoir.
(2) Lets us convert the second law of thermodynamics into a statement that concerns only the system.
(3) Is incorrect.
[✓ (4)] (1) and (2)

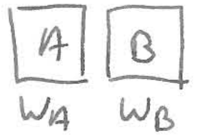
(f; 4 pts) The entropy of a pure substance is

(1) always positive
(2) always an increasing function of temperature
(3) always more when it is a liquid than a solid
[✓ (4)] All of the above

Score for the page____________

2. (21 pts) Microstates

(a; 9 pts) In terms of combinations of sets of microstates, explain why S is defined as a logarithm of W (times a constant k_B). Why not just define S = k_B W, or W^2, or some other function of W?

(+3) 

Total $W_{A+B} = W_A \times W_B \rightarrow$ prod of individual microstates

(+3) ~~th~~ we want S to be an extensive state function

So $S_{(A+B)} = S_A + S_B$

(+3) The log function converts products to sums.

or W is a huge number $\rightarrow$ (+3) if missing points above

(b; 12 pts) Consider a solution of sodium chloride in liquid water. To completely describe a microstate of the system, what would one have to specify? Give an example of a configuration of the solution that has the same total energy as the predominant configuration but includes many fewer microstates.

(+2) for each of 4 items

- Position, velocity, vibrational + rotational state, bonding among all molecules of H_2O, Na^+, Cl^-, H^+, HO^- electronic, all [ ]'s
- A set of microstates would $\rightarrow$ P, T, $[Na^+]$, $[Cl^-]$, pH, $[H^+]$, $[HO^-]$, density. In the PC they will all be uniform.

(+4) for any one

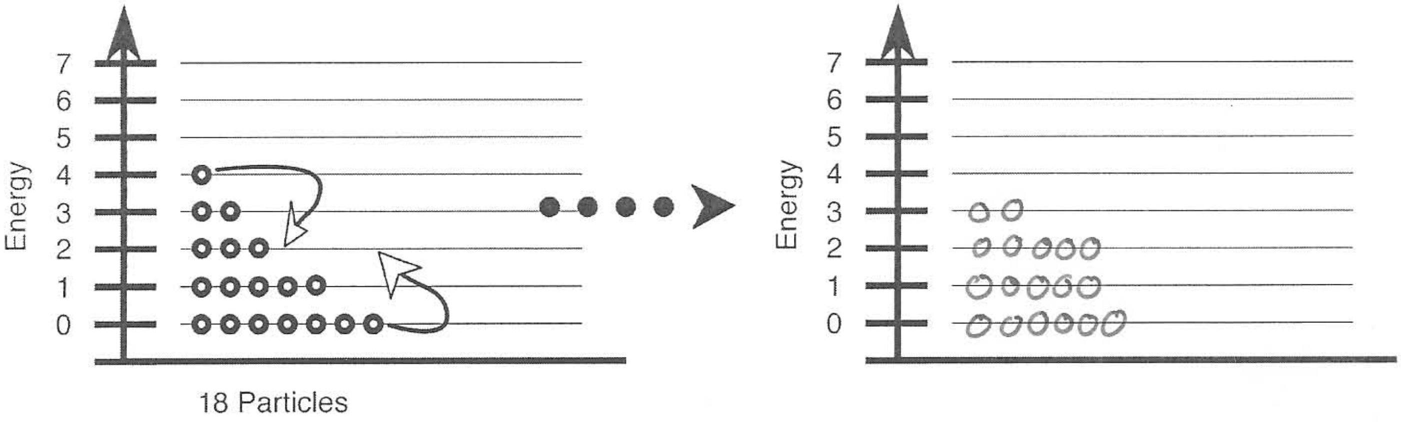
- A rare configuration could have...
  - Much more concentrated salt solution on one side than the other
  - Regions of higher or lower T or P within solution.
  - Density variations
  - Precipitation of NaCl
  - Non-equilibrium distribution of energy, as in excess population of rotational states – non-Boltzmann energies

if 
have to have same energies

Score for the page____________

3. (28 pts) Thermodynamics and Statistical Mechanics

The chart on the left below shows one possible distribution of 21 quanta of energy among ~~17~~ 18 molecules, similar to our discussion of microstates in class and to a past exam, sigh. oops



(a; 6 pts) Write down and evaluate a numerical expression for the number of microstates *W* for the configuration shown on the left above.

Table of factorials:	
3	6
4	24
5	120
6	720
7	5040
8	40320
9	362880
17	3.55687E+14
18	6.40237E+15
21	5.10909E+19
39	2.03979E+46

$$W = \frac{17! \cdot 18}{7!\,5!\,3!\,2!\,1!}$$ (+3) (+2 for idea)

$$= \frac{3.557 \times 10^{14} \cdot 18}{5040 \cdot 120 \cdot 6 \cdot 2 \cdot 1}$$

(+3)

$$= 4.90 \times 10^{7} \cdot 18 \text{ or } 49008960 \cdot 18$$

$$= 8.82 \times 10^{8} \text{ or } 882161280$$ (full credit for consistent)

(b; 6 pts) Now, we transfer two quanta of energy from the highest-energy molecule to the lowest, as indicated by the arrows in the chart. Draw the new configuration in the chart on the right. Write down and evaluate the expression for *W* for this new configuration.

(+2) for drawing

(+2) $$W = \frac{18 \cdot 17!}{6!\,5!\,5!\,2!}$$

$$= \frac{18 \cdot 3.557 \times 10^{14}}{720 \cdot 120 \cdot 120 \cdot 2} = 17153136 \cdot 18 \text{ or } 1.72 \times 10^{7} \cdot 18$$

(+2)

$$= 308756448 \text{ or } 3.08 \times 10^{8}$$

Score for the page____________

(c; 6 pts) Let's do a real example. The molar entropy of liquid water at 298 K is 69.9 J/mol K. Write a numerical expression for W for a mole of water. (This is one reason to use logs!) How many microstates can a mole of water sample in a year (31 million seconds) if it goes through one microstate per picosecond? How many can it sample in the age of the universe (15 billion years)?

$S \underset{(+1)}{=} k_B \ln W = 1.38\times10^{-23}\ \mathrm{J/K}\ \ln W = 69.9\ \mathrm{J/mol\ K}\cdot 1\ \mathrm{mole}$

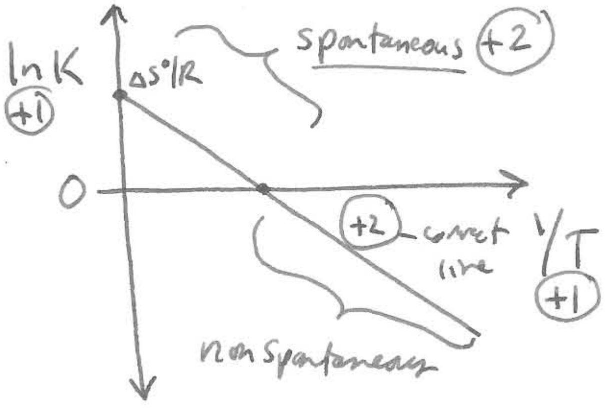
(+1) $\left[\ \ln W = \dfrac{69.9\ \mathrm{J/K}}{1.38\times10^{-23}\ \mathrm{J/K}} = 5.06\times10^{24}\right.$

$\boxed{W = e^{5\times10^{24}}\ (+1)} = 10^{2\times10^{24}}$ .. a 1 followed by 2×10^{24} zeroes -

31×10^{6} seconds/year · 1 μstate/10^{-12} sec · ~~15×10^{9} years~~ = $\underline{31\times10^{18}}$ μstates/sec (+2)

$31\times10^{18}\times15\times10^{9} = 450\times10^{27} = 4.5\times10^{29}$ μstates/eternity (+1)

(d; 10 pts) Sketch a van't Hoff plot for the temperature dependence of the equilibrium constant for an endothermic disordering reaction. Indicate the region of the graph that represents a spontaneous reaction. In this context, quantitatively what do we mean by "spontaneous?"



endothermic $\Delta H > 0$

disordering $\Delta S > 0$

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

(+2) "Spontaneous" means $K > 1$, $\ln K > 0$, $\Delta G^\circ < 0$

$\overset{4}{(+2)}$ for idea of the plot and/or the equation

~~for correct line~~

4. (27 pts) Calculation of Free Energy and K_{eq}

(Adapted from Atkins) The reaction of boron oxide with HF is encountered in the etching/removal of borosilicate glass and the synthesis of the useful but corrosive Lewis acid BF_3.

$$B_2O_3\ (s) + 6\ HF\ (g) \rightleftharpoons 2\ BF_3\ (g) + 3\ H_2O\ (g)$$

Compound	ΔH°_f (kJ/mole)	S° (J/mole K)
B_2O_3 (s)	–1272.8	54.0
HF (g)	–271.1	173.8
BF_3 (g)	–1137.0	254.1
H_2O (g)	–241.8	188.8

(a; 10 pts) Use the data in the table to calculate ΔH°(rxn) and ΔS°(rxn) at 25°C for the reaction.

$$\Delta h^\circ(\text{rxn}) = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$$

(+1)

(+2) $$= [2(-1137.0) + 3(-241.8)] - [(-1272.8) + 6(-271.1)] \text{ kJ/mol}$$

$$= -2274 - 725.4 + 1272.8 + 1626.6 = \boxed{-100.6 \text{ kJ/mole}}$$ (+2)

$$\Delta S^\circ(\text{rxn}) = S^\circ(\text{products}) - S^\circ(\text{reactants}) =$$ (+1)

(+2) $$[2(254.1) + 3(188.8)] - [54.0 + 6(173.8)] = \begin{pmatrix} 508.2 + \overset{5}{\cancel{4}}66.4 \\ -54 - 1042.8 \end{pmatrix}$$

$$= 1074.6 - 1096.8 = \boxed{\begin{matrix} -22.2 \\ \cancel{-21.8} \text{ J/mol K} \end{matrix}}$$ (+2)

(b; 5 pts) Calculate the free energy change ΔG°(rxn) and the equilibrium constant for this reaction at 150 °C, assuming that ΔH°(rxn) and ΔS°(rxn) are constant with temperature.

$$\Delta G^\circ = \Delta h^\circ - T\Delta S^\circ = -100.6 \text{ kJ/mole} - (273.15 + 150)(-22.2 \text{ J/mole})$$

$$= (-100600 + 9394) = -91206 \text{ J/mol} \rightarrow \boxed{-91.2 \text{ kJ/mol}}$$ +2

$$\boxed{K_{eq} = e^{-\Delta G^\circ/RT}} = e^{91200/(8.314 \times 473)} = e^{23.2} = \boxed{1.17 \times 10^{10}}$$

(+1) (+2)

Oops -- T = 423.15, not 473, so Keq = e^25.9 = 1.81e11 (c; 2 pts) Write down the expression for the equilibrium constant K_p.

$$K_p = \frac{P_{BF_3}^{\,2} \cdot P_{H_2O}^{\,3}}{P_{HF}^{\,6}}$$ (+2)

(d; 5 pts) What is the actual free energy change for the reaction at $P(\text{HF}) = 2.1$ atm, $P(\text{BF}_3) = 1.2$ atm, and $P(\text{H}_2\text{O}) = 3.6$ atm?

(+2)

$$\Delta G = \Delta G^\circ + RT \ln Q = -91.2\ \text{kJ/mol} + (8.314)(473) \ln \frac{(1.2)^2(3.6)^3}{(2.1)^6}$$

$$= -91200 + 3934 \times (-0.2442) = -92161\ \text{J/mol} = \boxed{-92.[illegible]\ \text{kJ/mol}}$$

(+3)

(e; 5 pts) Since this reaction is an exothermic ordering reaction, in principle at some temperature it will no longer be spontaneous at 1 atm everything. What is that temperature? (Reversing the reaction does not seem practical…)

(+2) $\Delta H^\circ - T\Delta S^\circ = 0$

(+1) $-100600 - T(-22.2) = 0$ (J/mol)

$$T = \frac{100600}{22.2} = 4531\ \text{K}\ (!)$$ (+2)

~~This~~ The melting temperature of tungsten is 3683K. According to Wikipedia, Ta_4HfC_5 melts at 4488K, the highest known melting pt.

Page	Score
1	/1
2	/24
3	/~~24~~ 21
4	/12
5	/16
6	/~~16~~ 15
7	/12
Total	/101

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