Chemistry 271, Section 21xx **Your Name:** KEY
University of Maryland, College Park **Your SID #:**
General Chemistry and Energetics **Prof. Jason Kahn**
Exam II (100 points total) **April 13, 2009**

You have 53 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.

Partial credit will be given, *i.e.*, if you don't know, guess.

Numbers to Live By:

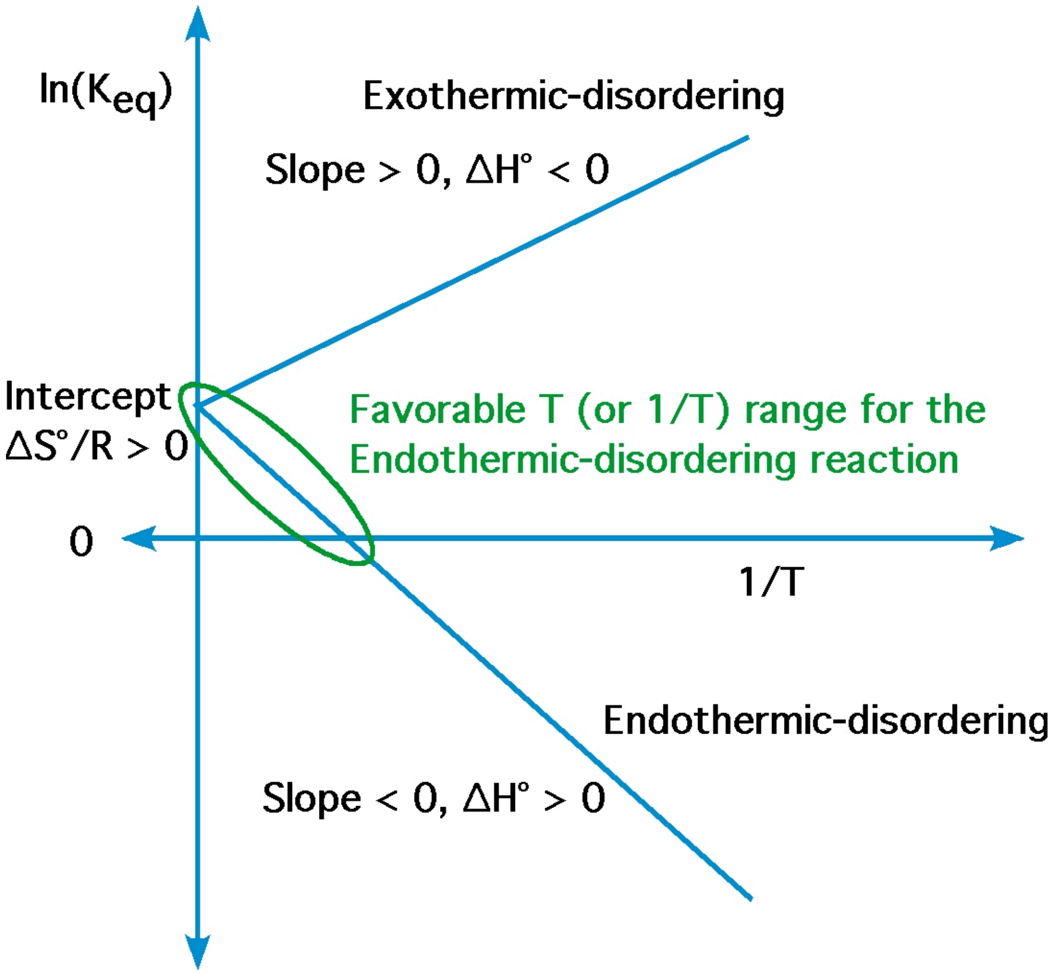
$\Delta S - q/T \geq 0$
$\text{pH} = -\log([\text{H}^+])$
$E = mc^2$
$S = k\ln W$
$\Delta G = \Delta H - T\Delta S$
$PV = nRT$
$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$
$\Delta G° = -RT\ln K_{eq}$
$e^{i\pi} + 1 = 0$
$W = N!/(\prod n_i!)$
$n_i/n_0 = \exp[-(E_i - E_0)/kT]$
$T_M = \Delta H°/[\Delta S° + R\ln(C_T/4)]$
$°C = °K - 273.15$
$R = 8.314$ J/mole K
$E = E° - 2.303(RT/n\mathcal{F})\log_{10}Q$
$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C
$\Delta G = -n\mathcal{F}E$
$\mathcal{F} = 96500$ C(oulomb)/mole
1 V = 1 J/C
$a^2 + b^2 - 2ab\cos C = c^2$
Chemical standard state: 1M solutes, pure liquids, 1 atm gases
Biochemical standard state: pH 7, all species in the ionic form found at pH 7
$\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$
$\forall i, x_i \in S_i, x_i \neq x_i^* : f_i(x_i^*, x_{-i}^*) \geq f_i(x_i, x_{-i}^*).$

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. van't Hoff plots and DNA Thermodynamics (35 pts)

(a; 18 pts) Sketch a single van't Hoff plot comparing an exothermic-disordering reaction and an endothermic-disordering reaction, with the two having the same value of ΔS°. Label your axes. Which reaction is thermodynamically spontaneous (favorable) at some but not all temperatures? Indicate on the graph the temperature range over which that reaction is spontaneous. Give an example of each type of reaction.



Examples:

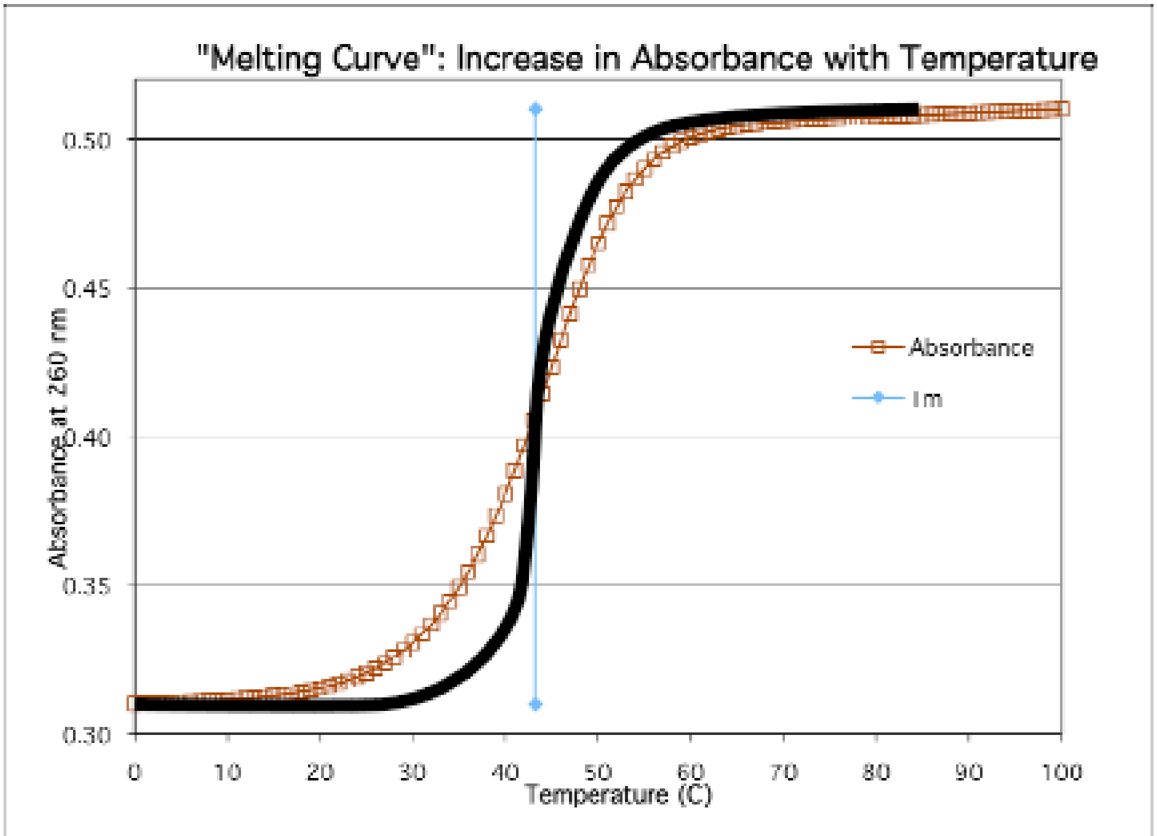
Endothermic-disordering: ice melting, cold-pack cooling, DNA melting. Favorable at some but not all temperatures, specifically high temperature as shown in the graph.

Exothermic-disordering: Combustion (NOT DNA hybridization!). Favorable at all temperatures.

+ 2 for idea of van't Hoff plot
+ 2 for axis labels (+1 each)
+ 2 for exothermic sloping up
+ 2 for endothermic sloping down
+ 2 for common intercept on the positive y-axis: ΔS° is the same
+ 2 for identifying endothermic reaction as the one that is positive at high T
+ 6 for examples (+3 each)

Score for the page_____________

(b; 10 pts) The melting curve below shows the absorbance as a function of temperature for a short oligonucleotide. Recall (or believe) that the nearest-neighbor enthalpy change for base pair formation is always negative and that T_M decreases as concentration decreases. Given these facts, we could make a longer oligonucleotide **[and melt it at lower CT to give a curve]** that has exactly the same melting temperature as the one on the curve shown. On the graph, draw the resulting melting curve. Below, briefly give your reasoning for its shape.



Longer oligo -> more negative ΔH° -> free energy depends changes more sharply with T -> Keq changes more with temperature -> sharper curve.

+2 for any curve, +2 for a sharper increase, +2 for unchanged T_M, +2 for anything about greater enthalpy or more stability, +2 for connecting that to a stronger temperature dependence for Keq.

(c; 7 pts) In DNA melting experiments, $\Delta G°_{37}$ can actually be determined with better precision (lower % error) than ΔH° or ΔS°, even though $\Delta G°_{37} = \Delta H° + 310*\Delta S°$. Why is this initially surprising, and how is it possible?

Since ΔH° is one term that is added to give $\Delta G°_{37}$, one would think that the error in $\Delta G°_{37}$ must be larger than the error in ΔH°, and this would be true if ΔH° and ΔS° were uncorrelated.

But in fact, we recall from the problem set that a wide range of ΔH° and ΔS° values give very similar melting curves. Their values are highly correlated, so the acceptable combinations of ΔH° and ΔS° give a much smaller range of $\Delta G°_{37}$ values.

+3 for the idea that errors should add, +2 for combinations of ΔH° and ΔS°, +2 for connection to ΔG.

Score for the page_____________

2. Free Energy and Equilibrium (35 pts)

(a; 22 pts) For the reaction $A \rightleftharpoons B + C$, ΔH° = –75 kJ/mol and ΔS° = –120 J/mol K, and as usual we assume that ΔH° and ΔS° are constant. Calculate the free energy change and the equilibrium constant at 25 °C and at 150 °C. If we add in more A at constant temperature, what happens to the reaction mixture as it equilibrates, and how does the equilibrium constant change?

$\Delta G = \Delta H - T\Delta S$ $\Delta G° = -RT\ln K_{eq}$ +2 (+1 each)

At 25 °C,

ΔG° = ΔH° – TΔS° = -75000 J/mole [NOT 0.075 J/mole !] – **(25 + 273.15) Kelvin** (–120 J/mole K)

+2 for plugging in

= –39222 J/mole or –39.2 kJ/mole +2 for correct answer

Keq = exp(—ΔG°(T)/RT) = exp(39222/(8.314*298.15) +2 for plugging in

= 7.44 x 10^6 +1 for answer

At 150 °C,

ΔG° = ΔH° – TΔS° = -75000 J/mole – (150 + 273.15) K (–120 J/mole K) +2 for plugging in

= –24222 J/mole or –24.2 kJ/mole +2 for correct answer

Keq = exp(—ΔG°(T)/RT) = exp(24222/(8.314*423.15) +2 for plugging in

= 9.77 x 10^2 +1 for answer

Note Keq is much smaller at high T, as it must be for an exothermic reaction.

If we add A, the reaction will respond by converting some of it to B + C. +3

The equilibrium constant will not change! +3

No points given or deducted for significant figures. Full credit for wrong Keq if it is consistent with ΔG°.

ΔG° at 25 °C:	–39200 J/mole	K_{eq} at 25 °C:	7.44 x 10^6
ΔG° at 150 °C:	–24200 J/mole	K_{eq} at 150 °C:	9.77 x 10^2

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(b; 5 pts) The equation ΔG = ΔG° + RTlnQ was derived from the idea that the molar free energy $\bar{G}$ of a substance is given by $\bar{G} = G^0 + RT \ln P$, where G° is the standard state free energy (at 1 atm) and *P* is the partial pressure of the gas. We will not reproduce the details of the derivation here, but we emphasized that the increase in $\bar{G}$ with partial pressure **makes intuitive sense even if the functional form is not obvious.** **What reasoning did we give** for the dependence (i.e., **why** does $\bar{G}$ increase with partial pressure)?

We know that dilution or expansion of a substance is thermodynamically favorable due to increasing entropy, so it must have ΔG < 0.

Therefore compression or concentration is unfavorable, so increasing partial pressure should have a positive free energy, and $\bar{G}$ is an increasing function of P.

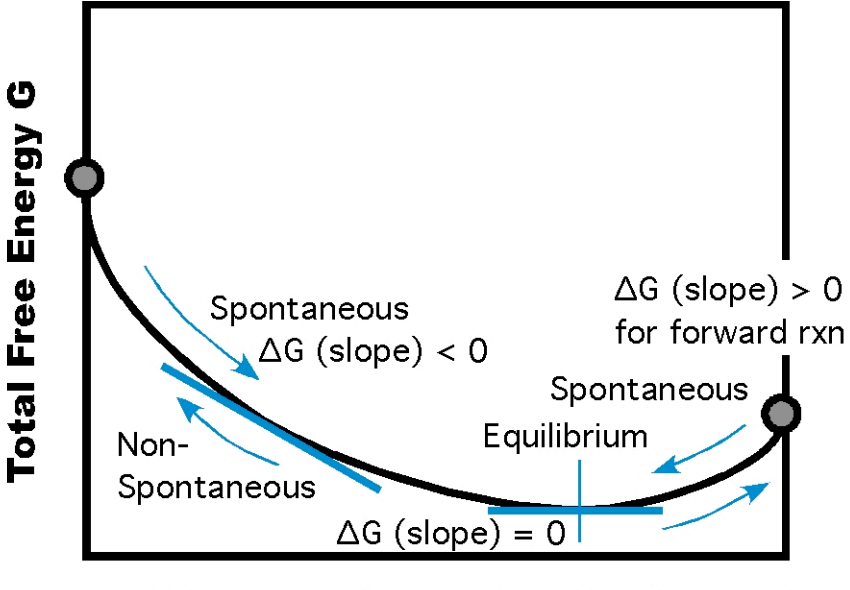
OR: Compression means we are doing work, and creating a system that is capable of doing work if we let it expand again. Therefore the free energy change is positive for compression.

+3 for favorable expansion

+2 for connecting it to ΔG

0 for saying that the equation shows that if P increases, ln P increases, and $\bar{G}$ increases!!

(c; 8 pts) The graph below shows the total free energy of a reaction mixture as a function of the mole fraction X of products. Indicate the point at which equilibrium is reached. Sketch in the aspects of the graph that express the ideas that ΔG is negative for spontaneous changes in reactant and product concentrations and that ΔG = 0 for small changes at equilibrium.



+3 for equilibrium position

+3 for idea that ΔG is a slope for G changing with mole fraction, or for the arrows indicating direction

+2 for the idea that at equilibrium ΔG = 0 for small changes – i.e. it is a minimum.

3. Redox Reactions (30 pts)

(a; 16 pts) Consider the reduction half-reactions below, combined to make a voltaic cell, operating in basic solution. Give a balanced equation for the overall spontaneous reaction and calculate its voltage under standard conditions (1 M everything). Which is the anode reaction and which is the cathode reaction?

$ZnO(s) + H_2O(\ell) + 2\ e^- \rightarrow Zn(s) + 2\ HO^-(aq)$ E° = –1.25 V

$Ag_2O(s) \rightarrow Ag(s)$ [You balance this one] E° = 0.34 V

Balance Ag and O by adding water: $Ag_2O(s) \rightarrow 2\ Ag(s) + H_2O$
Balance H by adding protons: $Ag_2O(s) + 2\ H^+ \rightarrow 2\ Ag(s) + H_2O$
Balance charge by adding e;ectrons: $Ag_2O(s) + 2\ H^+ + 2\ e^- \rightarrow 2\ Ag(s) + H_2O$
Convert to basic solution by adding HO^-: $Ag_2O(s) + 2\ H^+ + 2\ e^- + 2\ HO^- \rightarrow 2\ Ag(s) + H_2O + 2\ HO^-$

So the half-reaction is $Ag_2O(s) + 2\ H_2O + 2\ e^- \rightarrow 2\ Ag(s) + 2\ HO^-$ E° = 0.34 V
(+5 for balance reduction, if the final answer is incorrect)

For this to be a voltaic cell, ΔE° must be positive, so we use the reverse of the ZnO reduction shown.
(+2 for recognizing this reversal, if the final answer is incorrect)
$Zn(s) + 2\ HO^-(aq) \rightarrow ZnO(s) + H_2O(\ell) + 2\ e^-$ E° = +1.25 V

Adding reactions we have
$Ag_2O(s) + Zn(s) \rightarrow ZnO(s) + 2\ Ag(s)$ E° = +1.59 V
(+9 altogether for the balanced equation, +3 for the correct voltage)

Zinc (Zn) oxidation to give ZnO is the anode reaction.
Silver oxide (Ag_2O) reduction to give solid silver is the cathode reaction.
(+2 each)

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(b; 11 pts) Practical Electrochemistry. Circle whether a car battery is acting as a voltaic cell or an electrolytic cell under the following four conditions: +2 each for correct, everyone got +2 for 4).

1) You are starting the car as usual.	[✓ Voltaic]	Electrolytic
2) You are driving normally and the alternator is working.	Voltaic	[✓ Electrolytic]
3) The engine is off and the battery is powering your monster car stereo and portable refrigerator at the beach, much to everyone's delight.	[✓ Voltaic]	Electrolytic
4) The friendly AAA mechanic is jump-starting your car later that evening after the music has wound down and the soda has warmed up. [Meant to have the neighbor use a plug-in recharger here – jump-starting simply bypasses the bad battery by hooking up the good battery in parallel.]	Voltaic	[✓ Electrolytic] (as the question was intended)

Give one reason that we can't just put eight AA batteries in series to provide the same 12V that a car battery provides:

AA batteries cannot provide enough current to run the starter motor – the motor has to be powerful enough to turn the cam shaft and get the engine started, and AA batteries do not have enough stored energy to provide the needed power. +3 points for measuring power or current, but not "Oomph" – that is voltage.

Also – the internal resistance of the AA battery is high enough, and the resistance of a starter motor is low enough, so that essentially the AA battery is being shorted across the motor, and all the power would be dissipated inside the battery, causing rapid depletion and possible explosion.

(c; 3 pts) Why does oxidation happen at the anode of an electrochemical cell?

Oxidation and Anode both start with a vowel.

Page	Score
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Total	

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