Chemistry 271, Section 21xx **Your Name:** ____________________________________
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 $\Delta S°$. 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.

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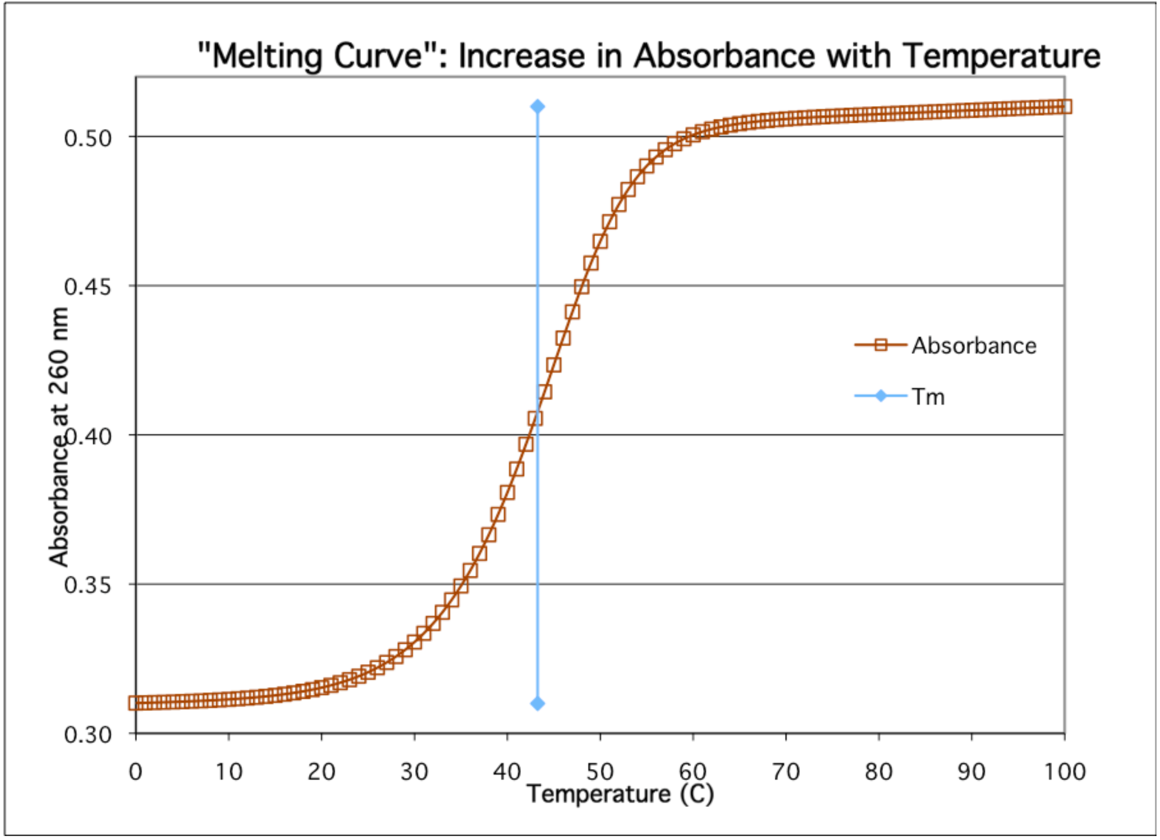
(b; 10 pts) The melting curve below shows the absorbance as a function of temperature for a short oligonucleotide. Recall (or believe) that the nearest-neighbor enthalpy change for base pair formation is always negative and that T_M decreases as concentration decreases. Given these facts, we could make a longer oligonucleotide 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.



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

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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?

ΔG° at 25 °C:	K_{eq} at 25 °C:
ΔG° at 150 °C:	K_{eq} at 150 °C:

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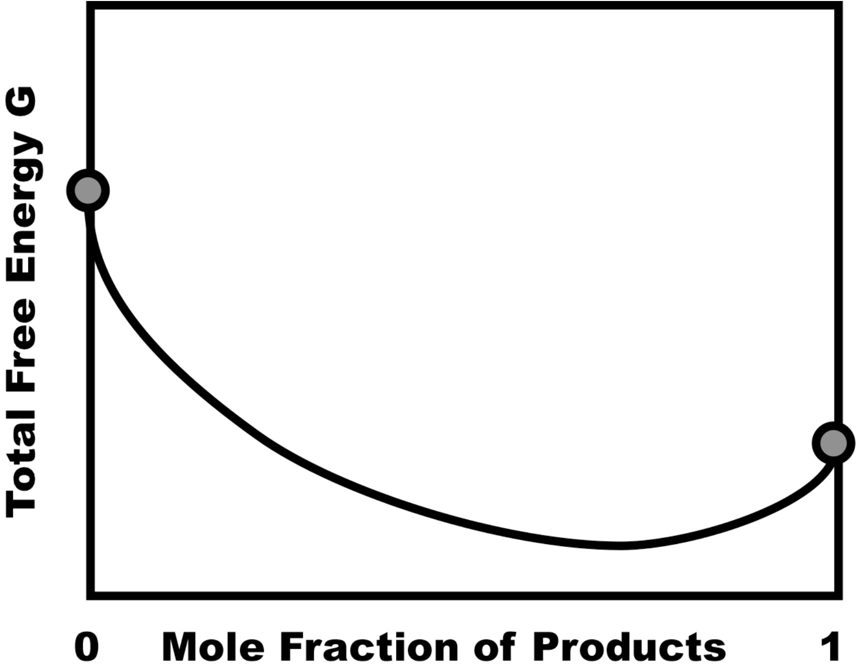
(b; 5 pts) The equation ΔG = ΔG° + RTlnQ was derived from the idea that the molar free energy $\overline{G}$ of a substance is given by $\overline{G} = G^0 + RT \ln P$, where G° is the standard state free energy (at 1 atm) and *P* is the partial pressure of the gas. We will not reproduce the details of the derivation here, but we emphasized that the increase in $\overline{G}$ 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 $\overline{G}$ increase with partial pressure)?

(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.



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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

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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:

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.	Voltaic	Electrolytic

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

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

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