Chemistry 271, Section 22xx
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Your Name: ______________________

Your SID #: ______________________

General Chemistry and Energetics
Exam II (100 points total)

Your Section #: ______________________

April 7, 2010

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:

$K_a = [H^+][A^-]/[HA]$

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

$K_b = [HA][HO^-]/[A^-]$

$K_w = [H^+][HO^-]$

$pH = pK_a + \log [A^-]/[HA]$

$\Delta G = -n\mathcal{F}\Delta E$

$R = 0.08206$ 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

$S = k\ln W$

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

$L' = L(1 - v^2/c^2)^{1/2}$

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

$1\ V = 1\ J/C$

$\Delta G° = -RT\ln K_{eq}$

$W = N!/(\prod n_i!)$

$n_i/n_0 = \exp[-(E_i - E_0)/kT]$

$T_M = \Delta H°/[\Delta S° + R\ln(C_T/4)]$

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C

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

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

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

(A; 4 pts) The “predominant configuration” is

a. The microstate that has the most uniform distribution of energy.
b. The microstate that corresponds to a Boltzmann distribution of particles.
c. A set of microstates that is more likely to be observed than any other possible configuration, at equilibrium.
d. Only observed when systems are small enough so molecules can be enumerated.
e. None of the above.

(B; 4 pts) The Joule experiment on the expansion of an ideal gas into a vacuum showed that

a. The entropy change for the isothermal expansion of an ideal gas is negative.
b. The enthalpy change for the isothermal expansion of an ideal gas is zero.
c. The free energy change for any expansion of an ideal gas is negative.
d. The heat transfer q for expansion of an ideal gas into vacuum is positive.
e. None of the above.

(C; 4 pts) State functions are useful in thermodynamics because

a. Crashing them gets us into the news.
b. The value of a state function for a system is independent of the path taken to arrive there.
c. The use of state functions allows us to avoid doing any work.
d. They are independent of temperature.
e. They are independent of concentration.

2. (28 pts) Short-answer questions

(a; 6 pts) Briefly describe what a DNA microarray is and how it is used.

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(b; 5 pts) What is the difference between a voltaic cell and an electrolytic cell? What metal is obtained from its oxide using an industrially important electrolytic cell?

(c; 8 pts) Give an example of an exothermic ordering reaction. Briefly explain why exothermicity *per se* makes a reaction thermodynamically favorable, but on the other hand explain why at high enough temperature an exothermic ordering reaction will become nonspontaneous.

(d; 4 pts) What is required to describe a microstate of a sample of a gas?

(e; 5 pts) Define a “high energy bond” or “high energy molecule” and give an example.

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3. (22 pts) Applied thermodynamics

DNA hybridization is described by the equilibrium $W + C \rightleftharpoons W{\bullet}C$, with equilibrium constant K_{hyb}. We assume that $\Delta H° = -70000$ cal/mole and $\Delta S° = -185$ cal/mole K.

Recall that the T_m for DNA melting is defined as the temperature at which $\alpha = ½$, i.e. half of the total concentration C_T of strands are in double-stranded form. Thus $[WC] = (C_T \times ½)/2 = C_T/4$ (we divide by 2 because y Molar W•C has a strand concentration of $2y$ M), $[W] = (C_T \times ½)/2 = C_T/4$, and $[C] = C_T/4$. Therefore, the equilibrium constant $K_{hyb} = [W{\bullet}C]/[W][C] = 4/C_T$ at $T = T_m$. For $C_T = 2.5$ μM, the thermodynamic values above give $T_m = 55$ °C.

We want to measure the temperature $T_{0.05}$ at which $\alpha = 0.05$.

(a; 4 pts) What is K_{hyb} in terms of C_T when $\alpha = 0.05$, so $[WC] = C_T \times 0.05/2$?

(b; 12 pts) The van't Hoff equation we used in class is $\ln(K_{eq}) = (-\Delta H°/R)(1/T) + (\Delta S°/R)$. First, plug in the expression for K_{hyb} at T_m for K_{eq} and "T_m" for T. Second, write a similar equation by plugging in the expression for K_{hyb} at $T_{0.05}$ for K_{eq} and "$T_{0.05}$" for T. Subtract one equation from the other and solve to obtain an expression for $T_{0.05}$ in terms of T_m and $\Delta H°$. Give a numerical answer for $T_{0.05}$.

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(c; 6 pts) As you know, oligonucleotide T_m tends to increase with length. In detecting SNPs (single-nucleotide polymorphisms or single-base pair differences between people's genome sequences), we use hybridization to oligonucleotides that are as short as possible but no shorter. Based on optimizing hybridization signal and specificity, explain this statement.

4. (22 pts) Thermodynamics

The Second Law of Thermodynamics states that the entropy of the universe increases for any spontaneous process: $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$. We derived the "master relation" $\Delta S_{\text{system}} - q_{\text{system}}/T \geq 0$ to convert the 2nd Law to a form that refers only to the system.

(a; 6 pts) What restriction does the master relation require for the nature of the interaction between the system and the surroundings? Briefly and qualitatively explain the origin of the second term's dependence on "1/T".

(b; 3 pts) For a reversible process carried out at constant T and P we were able to replace the master relation with the equation $\Delta S - \Delta H/T \geq 0$, which motivated us to define the Gibbs free energy $G = H - TS$. How does this give us a simple condition for spontaneity?

We showed that $G_A = G°_A + RT\ln P_A$ describes the molar free energy of substance A.

(c; 9 pts) For the reaction A <-> 2 B, use this equation to calculate the free energy change ΔG for converting a mole of A to 2 moles of B. At equilibrium we know that $\Delta G = 0$ for any infinitesimal change. Use this to demonstrate that a ratio of partial pressures must be a constant, K_p.

(d; 4 pts) We see that even if the standard state molar free energy of substance B is more positive than that of substance A, there will still be some B present at equilibrium. Give a qualitative argument based on microstates that rationalizes this conclusion.

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5. (16 pts) Electrochemistry

Consider the reduction of the iodate anion IO_3^- to iodide, I^-.

(a; 8 pts) Balance the half-reaction in acidic solution. Its standard reduction potential $E°_{red} = 1.085$ V. Why is the iodate anion a relatively good oxidizing agent?

The reduction of ferric iron to ferrous iron is described by $Fe^{+3} + e^- \rightarrow Fe^{+2}$, $E°_{red} = 0.771$ V.

(b; 8 pts) What is the net reaction if IO_3^-/I^- are in one half cell and Fe^{+3}/Fe^{+2} in the other, all at standard conditions? What is $E°_{cell}$?

Page	Score
2	/18
3	/22
4	/16
5	/15
6	/13
7	/16
Total	

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