

Chemistry 271, Section 22xx

Your Name: _____

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Your SID #: _____

General Chemistry and Energetics

Exam II (100 points total)

Your Section #: _____

November 4, 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.

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

Useful Equations:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

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

$$K_b = [\text{HA}][\text{HO}^-]/[\text{A}^-]$$

$$K_w = [\text{H}^+][\text{HO}^-]$$

$$\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}]$$

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

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole K}$$

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$\ln K_{eq} = -\Delta H^\circ/(RT) + \Delta S^\circ/R$$

$$\Delta S - q/T \geq 0$$

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

$$PV = nRT$$

$$S = k \ln W$$

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

$$R = 8.314 \text{ J}/\text{mole K}$$

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

$$1 \text{ V} = 1 \text{ J/C}$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

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

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

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

$$2.303RT/\mathcal{F} = 0.0592 \text{ Volts at } 25^\circ\text{C}$$

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

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."

(3 pts extra credit for filling out this page accurately and completely)

1. (20 pts) Multiple choice: Circle the single best answer for each question

(a; 4 pts) The Boltzmann distribution refers to the distribution of

- (a) microstates over configurations.
- (b) particles within boxes.
- (c) energy among particles.
- (d) entropy among reactants.
- (e) None of the above.

(b; 4 pts) Free energy is useful because it

- (a) tells us the amount of heat released by a reaction.
- (b) is maximized when reactions come to equilibrium.
- (c) is constant during isothermal expansion of a gas.
- (d) reduces the fundamental spontaneity condition $\Delta S_{\text{universe}} > 0$ to state functions solely of the system.
- (e) All of the above.

(c; 4 pts) Entropy is given as a logarithm of the number of microstates because

- (a) it must be an increasing and extensive function of W . $\ln(W_1 W_2) = \ln W_1 + \ln W_2$
- (b) the number of microstates cannot be calculated.
- (c) the K_a and K_b equilibria add to give the water self-dissociation equilibrium.
- (d) Boltzmann chose the functional form arbitrarily.
- (e) None of the above.

(d; 4 pts) Reduced carbon (like humans) and molecular oxygen can coexist because

- (a) our skin protects our contents.
- (b) the kinetics of human oxidation are slow at room temperature.
- (c) redox reactions require electrodes.
- (d) we breathe out oxygen.
- (e) (b) and (d).

(e; 4 pts) The expansion of an ideal gas into a vacuum occurs with

- (a) no work being done.
- (b) no change in internal energy.
- (c) no heat exchange with the surroundings.
- (d) a positive entropy change.
- (e) All of the above. (The Joule Experiment)

2. (40 pts) Redox chemistry

Ammonium, NH_4^+ (aq), can be converted to nitrate, NO_3^- (aq), by molecular oxygen, O_2 (g), in acidic solution.

(a; 3 pts) What are the oxidation numbers of nitrogen in ammonium, nitrogen gas, and nitrate?

+1 point each: -3, 0, and 5 respectively, so it is progressively more oxidized.

(b; 10 pts) The balanced reduction half-reaction for the conversion above is good old

$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$. What is the balanced oxidation half-reaction? What is the balanced overall reaction? (Hint: $n = 8$).

The other reaction must start from $\text{NH}_4^+ \rightarrow \text{NO}_3^-$

N is balanced. Balance O with water and H with protons: $\text{NH}_4^+ + 3 \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 10 \text{H}^+$

Balance charge with electrons: check that it's an oxidation. $\boxed{\text{NH}_4^+ + 3 \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- \text{ (+4 pts)}}$

To balance the overall reaction we add 2X the oxygen reduction: $2 \text{O}_2 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow 4 \text{H}_2\text{O}$ (+2 pts)

So the total is $\text{NH}_4^+ + 3 \text{H}_2\text{O} + 2 \text{O}_2 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow \text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- + 4 \text{H}_2\text{O}$

Cancelling: $\boxed{\text{NH}_4^+ + 2 \text{O}_2 \rightarrow \text{NO}_3^- + 2 \text{H}^+ + \text{H}_2\text{O} \text{ (+4 pts)}}$

(c; 5 pts) The E°_{red} values for the reduction and oxidation half-reactions are +1.23 V and +0.88 V respectively. Calculate ΔE° and show that $\Delta G^\circ = -270$ (enter units here: $\rightarrow$ kJ/mol).

We need to change the sign of E°_{red} for the ammonia/nitrate half reaction

$$\Delta E^\circ = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = 1.23 - 0.88 = +0.35 \text{ V (+3 pts)}$$

$$\Delta G^\circ = -nF\Delta E^\circ = -8 \text{ moles electrons} * 96500 \text{ C/mole} * 0.35 \text{ J/C} = -270200 \text{ J/mol (+2 pts)}$$

(d; 3 pts) The above is all at the chemical standard state. In general, what does this mean in terms of concentrations and partial pressures of reactants and products?

1 M concentration of all solutes (+2 pts), 1 atm partial pressure of all gases (+1 pt)

(e; 12 pts) Calculate ΔE at pH 7, $pO_2 = 0.21$ atm, 1 M each $[NH_4^+]$ and $[NO_3^-]$, and 25 °C. Separately, use the fact that $\Delta E = 0$ at equilibrium or use the ΔG° from (c) above to calculate the ratio of $[NH_4^+]/[NO_3^-]$ at equilibrium at pH 7, $pO_2 = 0.21$ atm, 25 °C. There is no need to worry about K_p vs. K_c .

$$\begin{aligned}\text{Nernst: } \Delta E &= \Delta E^\circ - (0.0592/n)\log Q = 0.35 - 0.00740 \log([NO_3^-][H^+]^2/[NH_4^+]pO_2^2) \text{ Volts} \\ &= 0.35 - 0.00740 \log(1 \times 10^{-14}/1 \times 0.21^2) = 0.44 \text{ V}\end{aligned}$$

(as usual, we see that even large differences between the actual concentration and the reference concentration do not lead to large differences in ΔE_{cell})

(+2 for recognizing that the Nernst eqn is needed, +2 for plugging in correct values, +2 for answer)

2nd calculation:

$$\Delta E = \Delta E^\circ - (0.0592/n)\log Q$$

$$\text{At equilibrium } \Delta E = 0 \text{ so } 0 = 0.35 - 0.00740 \log([NO_3^-] \times 10^{-14}/[NH_4^+] \times 0.21^2)$$

$$\log([NO_3^-]/[NH_4^+]) + \log(10^{-14}/0.21^2) = \log([NO_3^-]/[NH_4^+]) - 12.64 = (-0.35)/(-0.00740) = 47.30$$

$$\log([NO_3^-]/[NH_4^+]) = 47.30 + 12.6444 = 59.94 \text{ so } [NO_3^-]/[NH_4^+] = 8.74 \times 10^{59}$$

(This is why we need the Haber process – ammonia is thermodynamically unstable in air!)

(+3 for plugging in to Nernst, +3 for the answer)

OR

$$\Delta G^\circ = -270 \text{ kJ/mol} = -270000 \text{ J/mol} = -RT \ln K_{\text{eq}} = -8.314 \times 298 \ln ([NO_3^-][H^+]^2/[NH_4^+]pO_2^2) \text{ (J/mol)}$$

$$\ln ([NO_3^-][H^+]^2/[NH_4^+]pO_2^2) = 270000/(8.314 \times 298) = 108.98$$

$$[NO_3^-]/[NH_4^+] = \exp(108.98) \times 0.0441/10^{-14} = 9.42 \times 10^{59}$$

(+3 for plugging in to $\Delta G^\circ = -RT \ln K_{\text{eq}}$, +3 for answer)

(The differences are due to slight errors in truncating numbers or rounding F differently: any answer that is $8.5\text{--}9.8 \times 10^{59}$ gets full credit)

(f; 3 pts) What industrial process is used to make ammonia?

Haber process (+3), or $N_2 + 3 H_2 \leftrightarrow 2 NH_3$ (+2 if the name is not given)

(g; 4 pts) Thinking about the oxidation states of N, and recognizing that NO_3^- is nearly as good an oxidant as O_2 , why do you think NH_4NO_3 is extremely dangerous? Extra credit: name a city that had a very bad experience with it.

Ammonium nitrate has a strong reductant and a strong oxidant packed next to each other (+3), and it can react to generate, in part, very stable N_2 gas (+1). That's a recipe for explosion.

Extra credit (2 pts): Texas City, TX or Galveston, TX or Oklahoma city

3. (40 pts) Thermodynamics, DNA, and van't Hoff.

(a; 4 pts) What does $\Delta S = q/T$ mean in terms of the effect of adding energy to hot and cold systems?

Energy (heat) added to a cold system increases entropy much more than adding the same amount of energy (heat) to a hot system

Or: adding energy to a system that is already substantially disordered makes a much smaller difference to the entropy than adding energy to a highly ordered system.

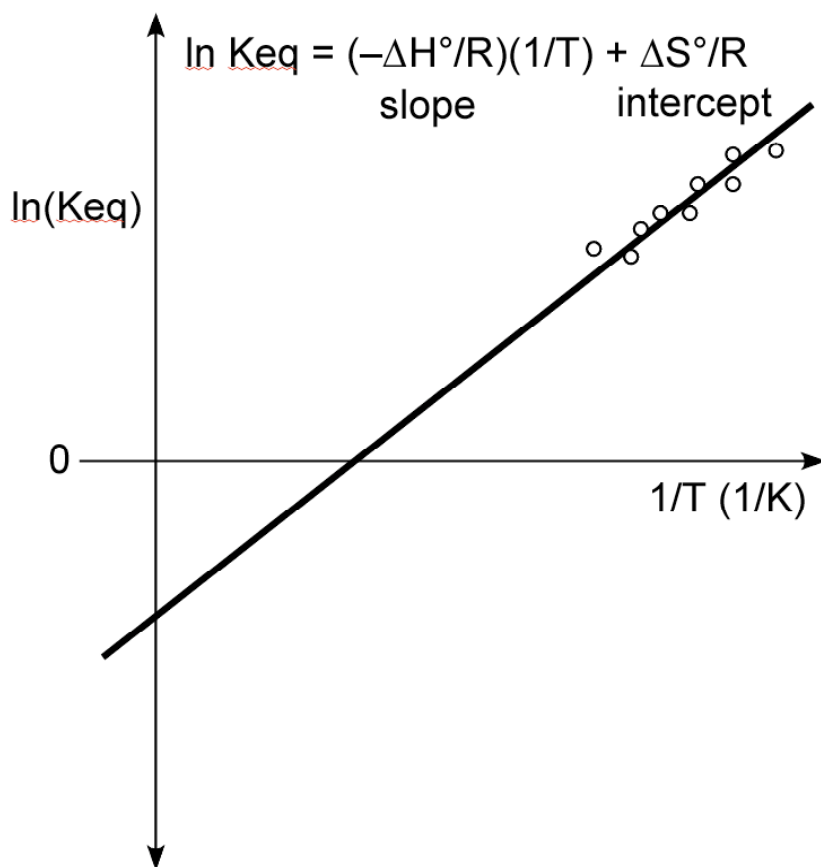
(b; 8 pts) Sketch a van't Hoff plot for an exothermic ordering reaction like DNA hybridization.

+2 for the general idea

+2 for labeling axes

+2 for positive slope

+2 for negative intercept



(c; 6 pts) Rationalize the signs of ΔH° and ΔS° for the hybridization process.

ΔH° is negative because bonds are being formed (+2) – H bonds and stacking/van der Waals interactions (+1 for either)

ΔS° is negative because the double helix has lower entropy than the single strand -- a lot less conformational flexibility than the ssDNA and we are also bringing two molecules together to make one. (+3 for either explanation)

(d; 6 pts) In terms of LeChatelier's principle, why does the reaction become less favorable as temperature increases? In terms of the statistical nature of the universe, why does the reaction become less favorable as temperature increases?

(+3) Heat is a product of an exothermic reaction, so as more heat is available the reaction is driven to the left,

(+3) As temperature increases, rejecting heat to the surroundings gives a smaller entropy increase in the surroundings, so the total entropy change of the universe is less positive as T increases. (This is why we use free energy)

(e; 8 pts) Given $\Delta H^\circ = -20 \text{ kJ/mol}$ and $\Delta S^\circ = -53 \text{ J/mol K}$ for a hybridization reaction, calculate ΔG° and K_{eq} at 20 °C and 60 °C.

20 C = 293.15 K

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-20000 \text{ J/mol}) - 293.15 \text{ K} * (-53 \text{ J/mol K}) = -4463 \text{ J/mol}$, or -4.5 kJ/mol (+2)
 $K_{eq} = \exp(-\Delta G^\circ/RT) = \exp(4463 \text{ J/mol} / (8.314 \text{ J/mol K} * 293.15 \text{ K})) = 6.24$ (+2 for consistent)

60 C = 333.15 K

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-20000 \text{ J/mol}) - 333.15 \text{ K} * (-53 \text{ J/mol K}) = -2343 \text{ J/mol}$, or -2.3 kJ/mol (+2)
 $K_{eq} = \exp(-\Delta G^\circ/RT) = \exp(2343 \text{ J/mol} / (8.314 \text{ J/mol K} * 333.15 \text{ K})) = 2.33$ (+2 for consistent)

(f; 8 pts) $K_{eq} = 2\alpha/[(1-\alpha)^2C_t]$, where α is the fraction of double-stranded DNA and C_t is the total strand concentration. Given that $\alpha = 0.5$ at the melting temperature T_m , use the two main expressions for ΔG° to show that $T_m = \Delta H^\circ/[\Delta S^\circ + R \ln (C_t/4)]$.

$$\alpha = 0.5 \text{ at } T_m, \text{ so } K_{eq} = 2\alpha/[(1-\alpha)^2C_t] = 1/(0.25 \cdot C_t) = 4/C_t \text{ at } T_m \quad +2 \text{ for solving for } K_{eq}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq} \quad +2 \text{ for recognizing you need these}$$

So at T_m we have

$$\Delta H^\circ - T_m\Delta S^\circ = -RT_m \ln 4/C_t \quad +2 \text{ for plugging in } T_m \text{ and } K_{eq}$$

Solve for T_m :

$$T_m = -\Delta H^\circ$$

$$T_m = -\Delta H^\circ/[(R \ln 4/C_t - \Delta S^\circ)] = \Delta H^\circ/[-R \ln 4/C_t + \Delta S^\circ] = \Delta H^\circ/[(R \ln C_t/4 + \Delta S^\circ)]$$

+2 for solving for T_m

Page	Score
1	/3
2	/20
3	/21
4	/19
5	/12
6	/20
7	/8
Total	

Score for the page _____