Chemistry 425  
Fall 2011  
Practice Final  

Name: ____________________________

Instructions:

Please do not start working on the exam until you are told to begin. Check the exam to make sure that it contains exactly 9 different pages, including this one and a periodic table.

Some useful constants and equations:

\[ R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \quad h = 6.63 \times 10^{-34} \text{ J s} \]

\[ m_e = 9.11 \times 10^{-31} \text{ kg} \quad c = 3.00 \times 10^8 \text{ m s}^{-1} \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \]

\[ H = U + PV \quad \Delta H = C_p \Delta T \quad f = c - p + 2 \quad \text{(degrees of freedom)} \]

\[ \Delta_r G = \Delta_r G^\circ + RT \ln Q \quad Y/\text{[L]} = n/K - Y/K \]

\[ \ln \left( \frac{K_2}{K_1} \right) = \left( \Delta_r H^\circ / R \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{(van't Hoff equation)} \]

\[ [A]/[A]_0 = e^{-kt} \quad \text{(first order)} \quad 1/[A] = 1/[A]_0 + kt \quad \text{(second order)} \]

\[ \ln \left( \frac{k_2}{k_1} \right) = \left( E_a / R \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ln k = \ln A - E_a/RT \]

\[ \lambda \nu = c, \quad \frac{\nu}{\lambda} = 1/\lambda, \quad E = h \nu, \quad \Delta E = h/4\pi\Delta t \quad \text{(Energy uncertainty),} \quad \Delta x = h/4\pi\Delta p \]

\[ \lambda = h/mv, \quad \Delta E = (N+1)h^2/8m_eL^2 \quad \text{(Energy level difference for linear polyenes)} \]

Bond Order = \((1/2)(n(\text{bonding}) - n(\text{antibonding}))\)

\[ N_1/N_2 = e^{-\Delta E/RT} \quad \text{(Boltzmann equation)} \quad \text{CFSE} = n(e_g)(0.6\Delta - n(t_{2g})(0.4\Delta) \]

\[ A = -\log(I/I_0) = \varepsilon bc \quad \text{(Beer-Lambert law)} \quad [\alpha]_T^\lambda = \alpha/lc \quad \text{(Specific Rotation)} \]
Part 1. Write the letter of the answer which best satisfies each statement or question in the blank at the left (4 points each).

_____ 1. The first law of thermodynamics tells us that
   (A) energy is conserved  (B) the entropy of an isolated system increases
   (C) entropy is 0 when temperature is 0 K  (D) PV = nRT

_____ 2. Which of the following is an extensive property?
   (A) temperature (B) molar volume (C) entropy  (D) density

_____ 3. Which of the following can we conclude about the reaction
   \[ \text{2H}_2\text{O}_2(l) \rightarrow \text{2H}_2\text{O}(l) + \text{O}_2(g) \]
   (A) \( \Delta_r H > 0 \)  (B) \( \Delta_r H < 0 \)  (C) \( \Delta_r S < 0 \)  (D) \( \Delta_r S > 0 \)

_____ 4. For the reaction in Problem 3 above, how does the rate of formation of \( \text{H}_2\text{O} \)
   compare with the rate of formation of \( \text{O}_2 \)?
   (A) the same  (B) 2 times faster  (C) 2 times slower  (D) 4 times slower

_____ 5. In a region of the phase diagram where pure \( \text{CO}_2 \) can exist both in the solid
   phase and in the gas phase, how many independent intensive variables can be
   varied while still maintaining these two phases in coexistence?
   (A) 0  (B) 1  (C) 2  (D) 3

_____ 6. The energy of a photon doubles if I reduce by one-half its
   (A) wavelength  (B) frequency  (C) wave number  (D) phase

_____ 7. Which of the following octahedral complexes goes from high-spin to low-spin
   as the crystal field splitting increases?
   (A) complex with \( d^1 \) configuration  (B) complex with \( d^6 \) configuration
   (C) complex with \( d^8 \) configuration  (D) complex with \( d^{10} \) configuration

_____ 8. In solution, 11-cis-retinal absorbs maximally at 380 nm. As part of
   rhodopsin, it absorbs at 500 nm. This shift in wavelength occurs because, by
   analogy to the “particle in a box”, the \( \pi \) electrons in retinal bound to opsin
   (rhodopsin)
   (A) are more delocalized, and therefore absorb light of lower frequency
   (B) are more delocalized, and therefore absorb light of higher frequency
   (C) are more delocalized, and therefore absorb more photons of light
   (D) are more delocalized, and therefore absorb fewer photons of light

_____ 9. For retinal in an excited electronic state, isomerization occurs only if crossing
   the barrier is faster than which of the following processes?
   (A) fluorescence  (B) absorption  (C) phosphorescence  (D) vibration of \text{C=C} bond
10. The bond order of He$_2^+$ is
   (A) 0  (B) 0.5  (C) 1  (D) 1.5

11. Consider the exothermic reaction $2A(g) \rightleftharpoons B(g)$ at equilibrium. To increase the concentration of B, I can increase
   (A) Gibbs Energy  (B) temperature  (C) volume  (D) pressure

12. Which of the following is a diamagnetic compound?
   (A) octahedral complex with metal ion in $3d^3$ configuration  (B) Li$_2$
   (C) octahedral complex with metal ion in $3d^8$ configuration  (D) H$_2^+$

13. Which forces account for the fact that benzene has higher melting and boiling points than methane?
   (A) dipole-induced dipole forces  (B) dispersion forces
   (C) dipole-dipole forces  (D) hydrogen bonds

14. Which of the following is not classified as a van der Waals interaction?
   (A) dispersion  (B) ion-dipole  (C) dipole-induced dipole  (D) dipole-dipole

15. The presence of Cl in the stratosphere leads to ozone depletion, where the net reaction is $O_3 + O \rightarrow 2O_2$. For this reaction, Cl is a
   (A) reactant  (B) product  (C) intermediate  (D) catalyst
Part II. Short answer: Answer the following in the space provided. (10 points each)

1. Consider the reaction \( \text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \), where \( \Delta_r H^\circ = 180.8 \text{ kJ mol}^{-1} \). If at 298 K the equilibrium constant is \( 4.0 \times 10^{-31} \), what is the value of the equilibrium constant at 1000 °C?

2. Calculate the time after absorption of light at which 70% of photoexcited naphthalene has fluoresced if the rate constant for fluorescence is \( k = 1.23 \text{ ns}^{-1} \).

3. The concentration of free ligand, bound protein, and total protein were found by equilibrium dialysis to be \( 1.1 \times 10^{-4} \text{ M} \), \( 7.0 \times 10^{-5} \text{ M} \), and \( 1.3 \times 10^{-4} \text{ M} \), respectively. Assuming that there is only one binding site per protein, calculate the association constant, \( K_a \), for the reaction \( \text{P} + \text{L} \rightleftharpoons \text{PL} \).
4. The red color of oxyhemoglobin is in part a consequence of the strong absorption by this protein of blue light around 420 nm. What is the energy in kJ mol$^{-1}$ of a quantum of blue light absorbed by oxyhemoglobin at 420 nm?

5. Suppose that the percent transmittance of lysozyme is 8.3% for incident light of 1645 cm$^{-1}$. The molecular weight of lysozyme is 14,600 g mol$^{-1}$. If the concentration of lysozyme is 80 g L$^{-1}$, and the pathlength of the cell is 0.1 mm, what is the molar absorptivity, $\varepsilon$, of lysozyme?

6. The enthalpy of fusion of ice at 0 °C (1 atm pressure) is 5.98 kJ mol$^{-1}$, and

$$\Delta V_{fus} = -1.621 \times 10^{-3} \text{ L mol}^{-1}.$$  Calculate $\Delta U_{fus}$ at 1 atm pressure.
7. Suppose 0.9 einsteins of photons are needed to melt 5.0 x 10^2 g of ice. On average, how many H_2O molecules (molecular weight 18.0 g mol\(^{-1}\)) does one photon convert from ice to water?

8. Alveoli are sacs of air in the lungs of diameter 5.0 x 10^{-5} m. Calculate the uncertainty in the velocity of an oxygen molecule (5.3 x 10^{-26} kg) trapped within an alveolus, where we can assume that the maximum uncertainty in position of the molecule is the diameter of the sac.

9. The frequency of molecular collisions in the liquid phase is about 1.0 x 10^{13} s\(^{-1}\). Ignoring all other mechanisms contributing to the line width in an absorption spectrum, calculate the width in Hz of vibrational transitions if every collision is effective in deactivating the molecule vibrationally.
10. Calculate the standard Gibbs energy of the fermentation of α-D-glucose (Gibbs energy of formation, \( \Delta_f G^\circ = -914.5 \text{ kJ mol}^{-1} \)) to ethanol (\( \Delta_f G^\circ = -174.2 \text{ kJ mol}^{-1} \)) and \( \text{CO}_2 \) (\( \Delta_f G^\circ = -394.4 \text{ kJ mol}^{-1} \)), where the reaction is, 
\[
\alpha\text{-D-glucose (aq) } \rightarrow 2\text{C}_2\text{H}_5\text{OH (liq)} + \text{2CO}_2 \text{ (g)}.
\]

11. Compute the de Broglie wavelength associated with a tennis ball of mass 50 g at 90 km per hour.

12. There are numerous triple points in the \( \text{H}_2\text{O} \) phase diagram (due to the many different phases of ice), but no quadruple points, at which four phases meet. Why?
13. Consider the conversion of the amino acid glutamate to the amino acid glutamine by the addition of ammonia,

\[
\text{Glutamate} + \text{NH}_3 \leftrightarrow \text{Glutamine} + \text{H}_2\text{O}, \quad \Delta G^\circ = 14 \text{ kJ mol}^{-1}
\]
Suppose that \([\text{NH}_3] = 1 \times 10^{-2} \text{ M}, as is physiologically reasonable. What is the ratio of glutamate to glutamine necessary for the reaction to proceed spontaneously at 300K? (Recall that by convention, we do not include \([\text{H}_2\text{O}]\) in the reaction quotient.)

14. *Cis*-stilbene can undergo photoisomerization to the *trans* isomer. Suppose we find that, following absorption of a 300 nm photon of light, the lifetime of the *cis* isomer in the excited electronic state is 12 ps (1 ps = 10^{-12} \text{ s}) at 300K. What is the activation energy in the excited electronic state? Assume that the pre-exponential factor is \(A = 1 \times 10^{13} \text{ s}^{-1}\).

I_____________  II_____________  Total ____________  (out of 200)