Chemistry 112 **Final Homework**

Name____________________

####____________________

This homework is due and will only be accepted prior to the final exam. It is, in fact, the final exam from last semester. The best way to prepare for this years final exam will be to work in a thorough way these problems, and also your previous exams from earlier this semester. This is best done by not just learning "tricks" about how to do this or that in some situation, but by understanding the problems from all directions. Many of the questions on this years all new final will be variations on the themes of problems here—so work the problem thoroughly with a view to understanding the process not just getting the answer.

The formulas listed below will be available for you on the front page of the final exam as well. **Do not forget to bring your valid Photo UM-ID to the exam as well as a non-programmable calculator.**

4.184 J = 1 cal

R = 8.3 J/mol K

1 F = 96,500 C

c = speed of light = 3.0×10^{8} m/sec

h = Planck's constant = 6.63×10^{-34} J-sec

m_e =mass of electron = 9.11×10^{-31} Kg

Bohr eqns.

$r_n = (n^2/Z)a_o$

$E_n = -(Z^2/n^2)R_y$

$a_o = 0.529$ A = 5.29×10^{-11} m

$R_y = 2.18 \times 10^{-18}$ J

Nernst eqn.

$\Delta\mathcal{E} = \Delta\mathcal{E}^{\circ} - (.059/n)\log(Q)$

For Grading Use Only—Do not write in this box.

section 1__________________

section 2__________________

section 3__________________

section 4__________________

section 5__________________

section 6__________________

Homework Grade:

/50

1. A Styrofoam cup calorimeter is calibrated by adding heat to the water in it with an electrical heater. When 1,350 J of heat is added the temperature of the calorimeter raises by 3.5 C. When 1.0 g of NaOH is dissolved in this same calorimeter the temperature raises by 1.6 C. Calculate the calorimeter constant and enthalpy of solution for one mole of NaOH.

$$q = C\Delta T$$

$$C = \frac{q}{\Delta t} = \frac{1350}{3.5} = 385.7$$

$$q_{NaOH} + q_c = 0$$

$$q_{NaOH} = -q_c$$

$$q_{NaOH} = -C\Delta T$$

$$= (-385.7)(1.6)$$

$$= -617.12 \frac{J}{1g} \times \frac{40g}{1mole} =$$

1. Include sign, units.

Cal. Const. = $385.7\ J/C°$

$\Delta H_{soln}^{one\ mole}$ =

$24.7\ KJ/mole$

2. Given the following bond strengths and the enthalpy of the reaction below, calculate the N-N bond enthalpy in hydrazine ($H_2N\text{-}NH_2$) (N≡N 915 kJ/mol; H-H 436 kJ/mol, N-H 391 kJ/mol)

$N{\equiv}N + 2\ H\text{-}H \rightarrow H_2N\text{-}NH_2 \quad \Delta H° = +\ 50\ kJ/mol$

$$[(915) + 2(436)] - [4(391) + x] = 50$$

$$[1787] - 1564 - x = 50$$

$$+x = +173$$

2. Include sign, units

$173\ KJ/mole$

3. The enthalpy of the reaction shown below is + 820 kJ/mole:

$8 CO_2 (g) + Si_3N_4(s) \rightarrow 3 SiO_2(s) + 2 N_2O(g) + 8 CO (g)$

The enthalpies of formation of CO_2 (g) = -394 kJ/mol, CO (g) = -111 kJ/mol, SiO_2 (s) = -910 kJ/mol, N_2O (g) = + 82 kJ/mol. Calculate the standard enthalpy of formation of Si_3N_4 (s).

$$[3(-910) + 2(82) + 8(-111)] - [8(-394) + x] = -820$$

$$[-2730 + 164 + -888] - [-3152 + x] = -820$$

$$-3454 + 3152 - x = -820$$

$$x = 518$$

3. Include sign and units

518 KJ/mole

4. a. In the space below write a balanced chemical reaction, which if you measured its enthalpy would give you the standard enthalpy of formation of glucose, $C_6H_{12}O_6$.

4a.

$$\underset{(s,\ graphite)}{6C} + 6H_2 + 3O_2 \rightarrow C_6H_{12}O_6$$

b. In the space below write a balanced chemical reaction which if you measured its enthalpy would give you the enthalpy of combustion of glucose, $C_6H_{12}O_6$.

4b.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

c. In the space below write a balanced chemical reaction, which if you measured its enthalpy would give you the sum of all the C-H, C-C, C-O and C-H (i.e. all the bonds) of $C_6H_{12}O_6$.

4c.

$$C_6H_{12}O_6 \rightarrow \underset{(s,\ graphite)}{6C} + 6H_2 + 3O_2$$

5. Give brief definitions of the following:

a. First law of thermodynamics.

see text

b. Second law of thermodynamics.

see text

c. Third law of thermodynamics.

see text

6. A liquid has a molar enthalpy of vaporization of 66 kJ/mol and a molar entropy of vaporization of 94 J/mol K.

a. Calculate the normal boiling point of the liquid.

$$\Delta H = 66 \quad \Delta S = 94$$

$$T = \frac{\Delta H}{\Delta S} = \frac{66 \text{ kJ/mol}}{.094 \text{ kJ/mole}}$$

6a.

702 K

b. Calculate the temperature at which the vapor pressure will be 20 atm.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{20}{1} = \frac{66{,}000}{8.31}\left(\frac{1}{702} - \frac{1}{T_2}\right)$$

6b.

955 K

7. Given the thermodynamic data below, calculate the indicated property for the reaction:

$H_2(g) + N_2(g) + 2\,O_2(g) \rightarrow 2\,HNO_2(g)$

	ΔH° kJ/mol	S° J/mol K
H_2	0	130
N_2	0	192
O_2	0	205
HNO_2	-60	244

a. Calculate ΔH°

$$\Delta H = 2(-60) - 0 = -120$$

7a. Include sign, units

-120 KJ/mol

b. Calculate ΔS°

$$\Delta S = 2(244) - [130 + 192 + 2(205)] =$$

$$488 - 732 = -244$$

7b. Include sign, units

-244 J/mol·K

c. Calculate ΔG° at 298 K.

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

$$\Delta G = -120 - 298(-.244)$$

$$\Delta G =$$

7c. Include sign, units

-47.3 KJ/mole

d. Calculate Keq at 298 K.

$$\Delta G = -R \cdot T \cdot \ln K$$

$$\ln K = \frac{\Delta G}{-R \cdot T} = \frac{-47300}{-(8.31)\,298}$$

7d. Include sign.

1.97×10^{8}

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

8. A certain chemical reaction has a value of K_{eq} = 1500 at 800 K and a value of K_{eq} = 15,000 when the temperature is raised to 1200 K. Calculate ΔH° and ΔS° for this reaction.

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{15000}{1500} = \frac{\Delta H}{8.31}\left(\frac{1}{800} - \frac{1}{1200}\right)$$

$$2.3 = \frac{\Delta H}{8.31}(.000417)$$

$$\Delta G = -R \cdot T \cdot \ln K = -8.31(800)\ln 1500$$

$$\Delta G = -48.6 \text{ KJ/mol}$$

8. Include sign, units.

ΔH° = 45.8 KJ/mole

ΔS° = 118 J/mol K

9. Write brief definitions of the following:

$$-48.6 = 45.8 - 800(\Delta S)$$

9a. In a plot of ln (Keq) versus 1/T what is the exact mathematical value of the slope and intercept of this line.

Slope = $\frac{-\Delta H}{R}$

Intercept = $\frac{\Delta S}{R}$

9b. In the formula S = k ln (W) what is the meaning of the term W.

Thermodynamic probability

9c. Endothermic Reaction.

See text

10. A first order reaction A → B has a rate constant at 298 K of 500 s^{-1} and an activation energy of 35 kJ/mol. The equilibrium constant for this reaction K_{eq} = 200 at 298 K and the value of $\Delta H^o = \Delta E^o = +8$ kJ/mol for this reaction. In an experiment at 298 K the initial concentration of A = 2.0 M. Calculate the following quantities for this reaction:

a. The value of $t_{1/2}$ the half life of the reaction.

$$t = \frac{\ln 2}{K}$$

$$t = \frac{\ln 2}{500}$$

a. Include sign, units.

1.4×10^{-3} s

b The exact time for the concentration of A to decrease to 0.001 M.

$$A = A_0 e^{-Kt}$$

$$.001 = (2)\, e^{-500 \cdot t}$$

$$.0005 = e^{-500t}$$

$$-7.6 = -500t$$

b. Include sign, units.

1.5×10^{-2} s

c. The temperature at which the rate constant will equal 30 s^{-1}

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{30}{500} = \frac{35,000}{8.31}\left(\frac{1}{298} - \frac{1}{T_2}\right)$$

$$-2.81 = 4211.79\left(\frac{1}{298} - \frac{1}{T_2}\right)$$

c. Include sign, units.

248.6 K

d. The value of rate constant for the reverse reaction B → A at 298 K.

$$K_{eq} = \frac{K_1}{K_{-1}}$$

$$200 = \frac{500}{K_{-1}}$$

d. Include sign, units.

$2.5\ s^{-1}$

e. The value of activation energy for the reverse reaction B → A.

$$\Delta E = E_{a_f} - E_{a_r}$$

$$8 = 35 - E_{a_r}$$

$$E_{a_r} = 27$$

e. Include sign, units.

27 KJ/mol

11. The following table of initial rate data are collected for the reaction A + B → C

initial [A]	initial [B]	initial [C]	initial rate
0.1	0.1	0.1	25 $M s^{-1}$
0.2	0.1	0.1	12.5 $M s^{-1}$
0.1	0.2	0.1	100 $M s^{-1}$
0.1	0.1	0.2	50 $M s^{-1}$

A: $2^x = \frac{1}{2}$

B: $2^x = 4$

C: $2^x = 2$

rate = $K(A^{-1})(B^2)(C^1)$

Determine the reaction order in each of the reagents A, B, C, and the numerical value of the rate constant k(including units) for this reaction.

$25 = K(.1^{-1})(.1)^2(.1)^1$

11.

order in: [A] -1 [B] 2 [C] 1 k = 2500

12. Give brief definitions of the following:

12a. Transition state in a chemical reaction.

See text

12b. Propagation step in a chain reaction.

See text

12c. Elementary step in a chemical reaction.

See text

13. Balance the redox reactions shown below which occurs in acid solution. Write in the coefficient for each reagent. There are spaces on both sides of the equation for H^+ and H_2O. In your final balanced equation fill in the space on the correct side of the equation and leave the unneeded one blank.

13 a.

4 MnO_4^- + 5 Sn → 4 Mn^{++} + 5 Sn^{++++}

32 H^+ + ____ H_2O ____ H^+ + 16 H_2O

13 b.

5 Nb^{++} → 3 Nb + 2 NbO_3^-

____ H^+ + 6 H_2O 12 H^+ + ____ H_2O

14. Equation 13b. is a special type of redox reaction, what is the name for it?

14.

disproportionation

15. What is the oxidation number of Nb in NbO_3^- ?

$Nb + 3(O) = -1$

$Nb + 3(-2) = -1$

$Nb = +5$

15.

+5

16. Standard half cell reduction potentials are given for the following reactions at 298K:

$\mathcal{E}o$ (Volts) { Nernst eqn. $\Delta\mathcal{E} = \Delta\mathcal{E}o$ - (.059/n)(log(Q)) }
{ 1 Faraday = 96,500 Coulombs }

$F_2 + 2e^- \rightarrow 2F^-$ 2.87

$Au^{+++} + 3e^- \rightarrow Au$ 1.42

a. Write the balanced spontaneous cell reaction that will occur if these two half cells are combined.

16a.

$$3F_2 + 2Au \rightarrow 2Au^{+3} + 6F^-$$

b. What are the values of n, $\Delta\mathcal{E}o$, and $\Delta G°$ for this reaction?

$$(F_2 + 2e^- \longrightarrow 2F^-)3 \quad 2.87$$

$$(Au \longrightarrow Au^{+3} + 3e)2 \quad -1.42$$

$$1.45$$

$$\Delta G = -n \cdot F \cdot E$$

$$\Delta G = -6 \cdot 96500\,(1.45)$$

16b.

n = 6

$\Delta\mathcal{E}o$ = 1.45

$\Delta G°$ = 839.6 KJ/mol.

c. If a cell is set up based on these two half reactions and it is found that the value of $\Delta\mathcal{E}$ for the cell is equal to 1.52 Volt when the F_2= 1 atm and F^- = 1M what is [Au^{+++}] ?

$$\Delta E = \Delta E^\circ - \frac{.059}{n} \log Q$$

$$1.52 = 1.45 - \frac{.059}{6} \log Q$$

$$Q = 7.6\times10^{-8}$$

$$Q = \frac{(Au^{+3})^2 \cdot (F^-)^6}{F_2}$$

$$7.6\times10^{-8} = \frac{x^2 \cdot (1)}{(1)}$$

16c. Include sign, units.

2.76×10^{-4} M

17. Gold is being plated out according to the half reaction: $Au^{+++} + 3e^- \rightarrow Au$. If 2 grams of Au is deposited in 50 seconds what electric current is used to achieve this ?

$$I = \frac{C}{s}$$

$$2.0\text{g Au} \times \frac{1\text{ mole}}{196.97\text{g}} \times \frac{3e^-}{1\text{ Au}} \times \frac{96{,}500\text{C}}{1\text{ mole } e^-} = 2939.5\text{C}$$

$$I = \frac{2939.5}{50}$$

17. Include units.

$I = 58.8A$

18. Give brief definitions of the following:

18a. Anode

See text

18b. Write a balanced chemical electrochemical half cell equation for the half cell that is **defined** as having a potential of exactly 0 volts.

$$2H^+ + 2e^- \rightarrow H_2$$

18c. Electrical potential is measured in volts, define a volt in terms of the fundamental units it is made up of.

$$1V = 1\,J/C$$

18d. What unit is used to measure electrical power, what is its name and what is it equal to in terms of fundamental units.

$$1\text{ Watt} = 1\,J/s$$

19. Write **complete** ground state atomic orbital configurations (starting with 1s orbitals) for the following atoms or ions and indicate the number of unpaired electrons present in the atom or ion:

a. Fe^{++++} (a plus four cation)

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

number unpaired e⁻ 4

b. Se (neutral atom)

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

number unpaired e⁻ 2

20. A C^{+5} ion in the n = 5 state moves to the n = 7 state. Calculate the energy (E) change associated with this transition. Also calculate the frequency (ν), and wavelength (λ) of light which have this same energy and indicate whether light is emitted or absorbed in the process.

$$\Delta E = Z^2 Ry\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\Delta E = \frac{6^2}{1}(2.18\times10^{-18} J)\left(\frac{1}{5^2} - \frac{1}{7^2}\right)$$

$$\Delta E = 1.54\times10^{-18}$$

$E = h\nu$

$$\nu = \frac{E}{h} = \frac{1.54\times10^{-18}}{6.626\times10^{-34}}$$

$c = \lambda\nu$

$$\lambda = \frac{c}{\nu} = \frac{3.0\times10^{8}}{2.3\times10^{15}}$$

20. include signs,units

ΔE = 1.54×10^{-18} J

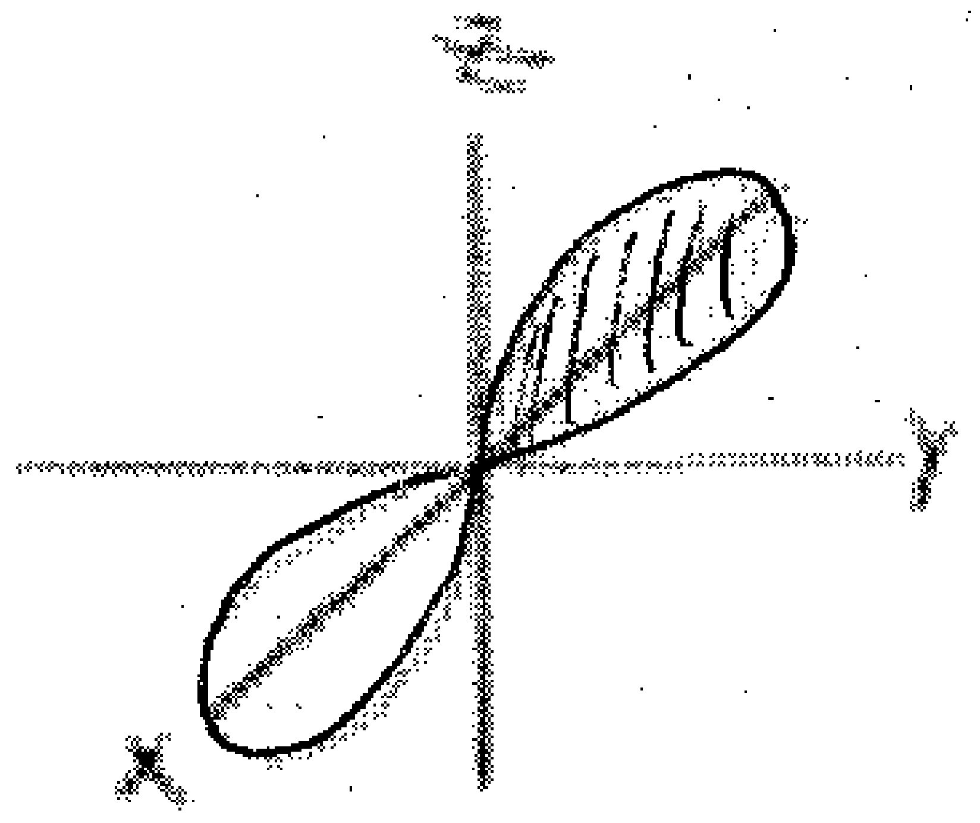
ν = 2.3×10^{15} Hz

λ = 1.3×10^{-7} m

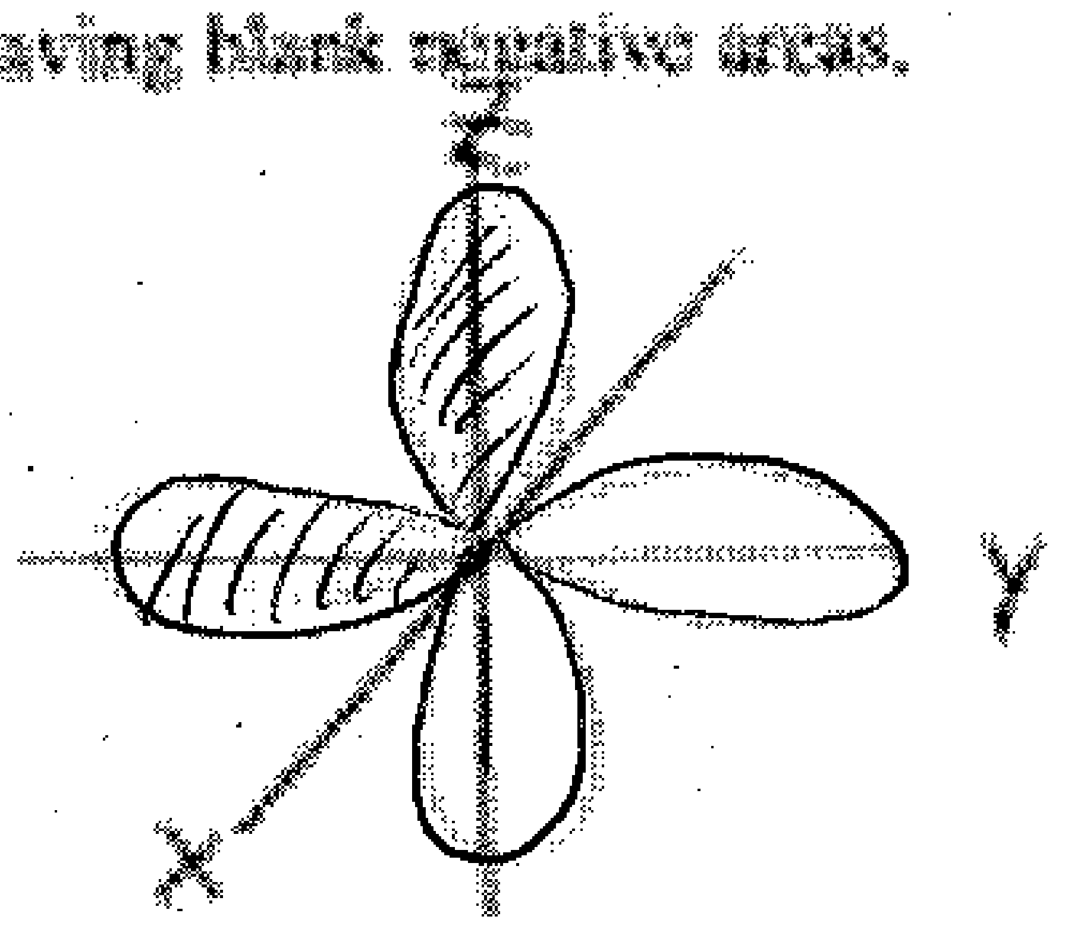
light is (circle one only)

emitted [✓ **absorbed**]

21. On the axis below draw the **shape** of the indicated **atomic** orbitals showing the **signs** of each lobe [area] of the orbital by shading positive and leaving blank negative areas.



[draw a p_x atomic orbital]



[draw a d_{yz} atomic orbital]

22. In going across the periodic table in the second row from Li to F which behavior best describes the variation in atomic radii. Pick an answer and give a brief explanation.

22. Circle and **explain** your choice. **Increase,** [✓ **Decrease,**] **Stay about the Same**

As the nuclear charge increases steadily, electrons successively join the same shell, in which they have about the same distance from the nucleus and are ineffective in shielding each other from its attraction

23. What is the most electronegative element and what is its approximate electronegativity?

23.
Element F , EN 3.98

24. What is the approximate numerical value for the electronegativity of C

24.
EN 2.55

25. Give brief definitions or short answers to the following:

25a. What is the approximate length in meters of a single C-H bond.

1.10 Å

25b. What atomic orbital is filled just before starting to fill the 5f orbitals.

7s

25c. What is the physical meaning of the value of the square of the wave function Ψ^2 ?

The probability that an electron will be found in a small volume.

26. Write **complete** molecular orbital configurations showing how many electrons are in each molecular orbital for the indicated molecule. Indicate how many unpaired electrons there are in the molecule, and what the bond order is

a. C_2 molecular orbital configuration:

$(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$

number unpaired electrons 0

bond order 2

b. O_2 molecular orbital configuration:

$(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_y)^2 (\pi p_x)^2 (\pi^* 2p_y)^1 (\pi 2p_x)^1$

number unpaired electrons 2

bond order 2

c. Briefly describe what you would expect to happen to the C-C and O-O bonds if you removed an electron from each to make $C\text{-}C^{+1}$ and $O\text{-}O^{+1}$. Would the bonds get longer, shorter, or stay the same and why? Circle one answer for each molecule

for $C\text{-}C^{+1}$

[✓ longer], shorter, same

reason

The Bond Order changes from 2 to 1.5.

for $O\text{-}O^{+1}$

longer, [✓ shorter], same

reason

The Bond Order changes from 2 to 2.5

↑ Bond Order ⟺ shorter the bond

↓ Bond Order ⟺ longer the bond