INSTRUCTIONS/SUGGESTIONS.
READ THIS CAREFULLY!

OMIT ANY TWO (2) OF THE SEVEN 20 POINT QUESTIONS.
OMIT ANY THREE (3) OF THE FOURTEEN 10 POINT QUESTIONS.

INDICATE ON THE NEXT PAGE WHICH **5** QUESTIONS ARE NOT TO BE GRADED BY WRITING DNG (DO NOT GRADE) NEXT TO THE PROBLEM NUMBER.

NO PARTIAL CREDIT on any question except where indicated by the statement SHOW WORK. When work is requested, set up equations (with numbers substituted in appropriate units) in space provided, but do the calculations on scrap sheet.

IF QUESTION STATES "SHOW WORK" AND YOU GUESS CORRECTLY WITHOUT SHOWING WORK - YOU GET 1/2 CREDIT.

CHECK FRONT BLACKBOARD FOR CORRECTIONS/CHANGES.

IF ANY QUESTION IS NOT CLEAR - ASK DAVID OR ME ABOUT IT!

CONSTANTS AND CONVERSION FACTORS ARE ON THE PAGE FOLLOWING THE LAST PROBLEM. PLEASE LOOK THERE!
LAST THREE PAGES ARE FOR SCRAP WORK.
FEEL FREE TO TEAR THESE PAGES OFF.

REMOVE THIS PAGE PRIOR TO STARTING EXAM.

CHEMISTRY F14O4 THIRD EXAM 4/26/00
PROFESSOR J. MORROW

PRINT NAME, LAST: ______________________

FIRST: ______________________

I.D.# : ______________________

MAXIMUM POINT VALUE IS IN PARENTHESES

1. ________ (20)	8. ________ (20)	15. ________ (10)
2. ________ (20)	9. ________ (10)	16. ________ (10)
3. ________ (20)	10. ________ (10)	17. ________ (1O)
4. ________ (20)	11. ________ (1O)	18. ________ (1O)
5. ________ (10)	12. ________ (10)	19. ________ (1O)
6. ________ (20)	13. ________ (10)	20. ________ (10)
7. ________ (20)	14. ________ (10)	

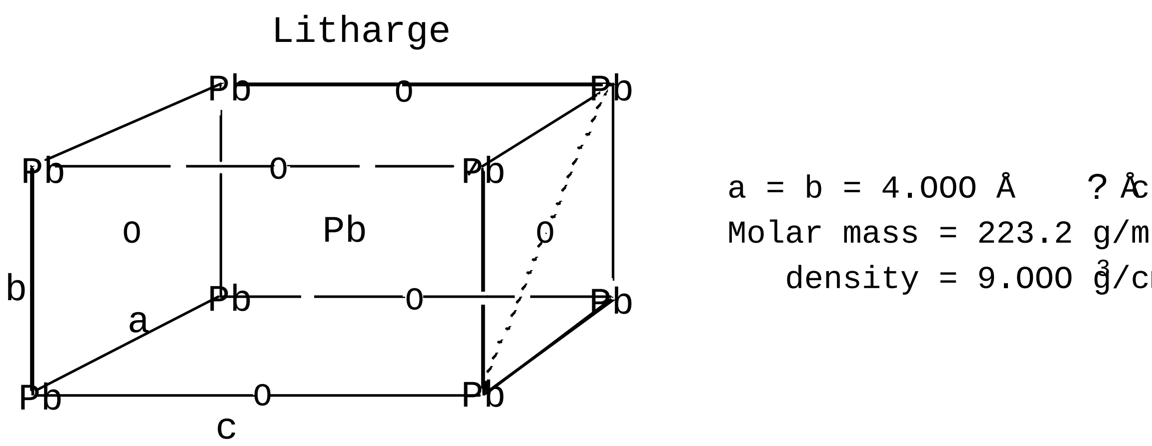
COLUMN TOTALS:

_______(130)	_______(80)	_______(60)

EXAM TOTAL (220 pts) ____________ ____________
OUT OF 100

USE THE FOLLOWING INFORMATION TO ANSWER QUESTIONS 1 AND 2

There are two different compounds containing lead and oxygen; Litharge (PbO) and Orthoplumbate (Pb_3O_4). The crystal structure of Litharge is shown below.



In this crystal, the atoms on a dashed line are linearly arranged.

For Orthoplumbate (Pb_3O_4):

a = b = 8.8O6 Å, c = 6.564 Å, F = 685.598 $\frac{g}{mol}$, density = ? $\frac{g}{cm^3}$

1) In Orthoplumbate there are 4 molecules per unit cell (empirical formula units). What is the density of Orthoplumbate. SHOW WORK (20 pts)

ANSWER IS: _______

2) Calculate the unit edge length, C, of Litharge (PbO). SHOW WORK (20 pts)

ANSWER IS: _______

3) An unknown element has a cubic structure with 58 atoms per unit cell. The density of this element is 7.470 $\frac{g}{cm^3}$ and its edge length is 8.914 Å. Calculate

the atomic weight of this element. SHOW WORK (20 pts)

ANSWER IS: _______

4) A reaction is found to be inverse first order in the reactant, A. The rate expression is

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^{-1} = \frac{k}{[A]}$$

The integrated rate expression is

$$\frac{1}{2}\left([A]^2_o - [A]^2 \right) = kt$$

Starting with $[A]_o$ = 0.100 M it takes 10.0 min for 60.0 % of A to be lost. The numerical value of k (with units) is; (20 pts) SHOW WORK

a) $3.20 \times 10^{-4}\ \frac{L^2}{mol^2 \cdot min}$

b) $7.00 \times 10^{-6}\ \frac{mol^2}{L^2 \cdot sec}$

c) $3.20 \times 10^{-4}\ \frac{mol^2}{L^2 \cdot min}$

d) $2.52 \times 10^{-4}\ \frac{mol^2}{L^2 \cdot min}$

e) $5.33 \times 10^{-6}\ \frac{mol^2}{L^2 \cdot sec}$

ANSWER IS: _______

THE FOLLOWING INFORMATION IS FOR USE IN PROBLEMS 5, 6, AND 7

Values of Δ_o (in eV/ion) for some transition metal complexes are:

	Δ_o (eV/ion)	
Co^{3+}	3.501	in $Co(NO_2)_6^{3-}$
Co^{2+}	2.242	in $Co(NO_2)_6^{4-}$

In octahedral symmetry the d orbitals are split as shown:

The t_{2g} orbitals are lowered by $\frac{2}{5}\ \Delta_o$, and the e_g orbitals are raised by $\frac{3}{5}\ \Delta_o$.

You are given the complex ions: $Co(NO_2)_6^{3-}$ and $Co(NO_2)_6^{4-}$. Assume all complexes can be either in the high spin (H.S.) state or the low spin (L.S.) state .

5) The sequence of these complex ions in order of increasing paramagnetism is, (10 pts)

a) $Co(NO_2)_6^{3-}$ (L.S.) < $Co(NO_2)_6^{3-}$ (H.S.) < $Co(NO_2)_6^{4-}$ (H.S.) < $Co(NO_2)_6^{4-}$ (L.S.)

b) $Co(NO_2)_6^{4-}$ (L.S.) < $Co(NO_2)_6^{4-}$ (H.S.) < $Co(NO_2)_6^{3-}$ (H.S.) < $Co(NO_2)_6^{3-}$ (L.S.)

c) $Co(NO_2)_6^{3-}$ (L.S.) < $Co(NO_2)_6^{4-}$ (H.S.) < $Co(NO_2)_6^{3-}$ (H.S.) < $Co(NO_2)_6^{4-}$ (L.S.)

d) $Co(NO_2)_6^{3-}$ (L.S.) < $Co(NO_2)_6^{3-}$ (H.S.) < $Co(NO_2)_6^{4-}$ (H.S.) < $Co(NO_2)_6^{4-}$ (L.S.)

e) $Co(NO_2)_6^{3-}$ (L.S.) < $Co(NO_2)_6^{4-}$ (L.S.) < $Co(NO_2)_6^{4-}$ (H.S.) < $Co(NO_2)_6^{3-}$ (H.S.)

f) $Co(NO_2)_6^{4-}$ (L.S.) < $Co(NO_2)_6^{3-}$ (H.S.) < $Co(NO_2)_6^{4-}$ (H.S.) < $Co(NO_2)_6^{3-}$ (L.S.)

g) $Co(NO_2)_6^{3-}$ (L.S.) < $Co(NO_2)_6^{4-}$ (L.S.) < $Co(NO_2)_6^{3-}$ (H.S.) < $Co(NO_2)_6^{4-}$ (H.S.)

ANSWER IS: _______

6) Calculate the wavelength, λ (in nm), at which the complex $Co(NO_2)_6^{3-}$ absorbs light. SHOW WORK (20 pts)

ANSWER IS: _______

7) Calculate the crystal field splitting, Δ_o (kJ/mole), for the high spin $Co(NO_2)_6^{4-}$ complex ion. (20 pts) SHOW WORK

ANSWER IS: _______

8) Given the following balanced reaction at 25°C;

$$4\ Ag^{2+} + N_2H_4 + 4\ H_2O \longrightarrow 4\ Ag^{+} + N_2 + 4\ H_3O^{+}$$

The observed rate expression was found to be,

$$\frac{\Delta[Ag^{+}]}{\Delta t} = k\frac{[Ag^{2+}]^2[N_2H_4]}{[Ag^{+}][H_3O^{+}]}$$

a) Complete the following table using the data given. Initial rate units are $\frac{mol}{L \cdot sec}$. (8 pts)

Experiment	Initial rate ($\frac{\Delta[Ag^{+}]}{\Delta t}$)	$[Ag^{2+}]$	$[Ag^{+}]$	$[N_2H_4]$	$[H_3O^{+}]$
1.	2.4×10^{-4}	0.040	0.160	1.000	0.100
2.	_________	0.080	0.160	1.00	0.100
3.	_________	0.080	0.800	1.00	0.100
4.	_________	0.160	0.160	0.50	0.200
5.	_________	0.020	1.60	1.00	1.00

b) Calculate the numerical value of k, and, give its units. (4 pts)

c) Starting with the concentrations given in experiment 1 (part a) what would be the following concentrations at the <u>end</u> of the first half life? (8 pts)

$[Ag^{2+}]$ = $[Ag^{+}]$ = $[N_2H_4]$ = $[H_3O^{+}]$=

9) An ionic crystalline solid, MX_3 , has a cubic unit cell. Which of the following arrangements is consistent with the stoichiometry of this compound? (10 pts)

a) M^{3+} ions at the corners, X^{-} ions at the face centers.
b) M^{3+} ions at the corners, X^{-} ions at the body centers.
c) X^{-} ions at the corners, M^{3+} ions at the face centers.

d) X^- ions at the corners, M^{3+} ions at the body centers.

e) M^{3+} ions at the corners and the body centers, X^- ions at the face centers.

ANSWER IS: _______

10) The unit cell length of a NaF crystal is 4.634 Å. If the ionic radius of Na^+ is 0.95 Å what is the ionic radius of F^-, assuming anion-cation contact and a face centered cubic lattice? (10 pts)

a) 1.37 Å   b) 3.06 Å   c) 2.03 Å   d) 2.97 Å   e) 3.33 Å   f) 2.33 Å

ANSWER IS: _______

11) Given the following complex ions and their hybridizations:

a) $[Ni(Cl)_2(NH_3)_2]$ (dsp^2)   b) $[Ni(Cl)_3(NH_3)]^-$ (dsp^2)

c) $[Ni(Cl)_2(NH_3)_2]$ (sp^3)   d) $[Ni(en)(NH_3)_2]$ (dsp^2)

e) $[Ni(en)_2]$ (dsp^2)   f) $[Ni(en)_2]$ (sp^3)

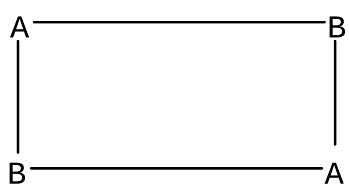
g) $[Cr(en)_3]^{3+}$ (d^2sp^3)   h) $[Cr(en)_2(Cl)_2]^+$ (d^2sp^3)

Which of these complex ions can have more than one (1) isomeric form?
(10 pts)

ANSWER(S) is/are: ________

12) Give the number of symmetry elements of the type requested for the following rectangular structure containing atoms A and B. (10 pts)

NUMBER PRESENT



center of symmetry _____

two fold axis of rotation, C_2 _____

four fold axis of rotation, C_4 _____

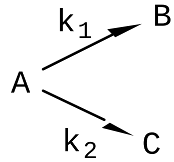
planes of symmetry _____

13) Given the following divalent ions, Cr^{2+}, Mn^{2+}, Fe^{2+}, and Co^{2+} with octahedral symmetry. Assuming they are all in the high spin state, show how the ionic radius varies between adjacent ions in the periodic table by inserting $<$ or $>$ between these ions. (10 pts)

Atomic numbers: Cr (24), Mn (25), Fe (26), Co (27).

ANSWER: Cr^{2+} Mn^{2+} Fe^{2+} Co^{2+} .

14) The compound A reacts as shown (first order) to give products B and C;



$k_1 = 10^{-2}\ sec^{-1}$

$k_2 = 10^{-3}\ sec^{-1}$

and $[A]_0 = 0.110$ M

What is the $\frac{[B]}{[C]}$ ratio after the first half life? (5 pts) ANSWER: ____

What is the [B] after the first half life? (5 pts) [B] = ____

15) A 0.020 m solution of each of the following compounds is prepared. Which solution would you expect to freeze at -0.149°C? (10 pts)
solution would you expect to freeze at -0.149°C? (10 pts)

a) $[Co(en)_2Cl_2]Cl$ b) $Na[Co(EDTA)]$ c) $[Cr(py)_5Cl]Cl_2$
d) $[Cr(NH_3)_6]Cl_3$ e) $[Co(py)_3Cl_3]$

where py = pyridine (unidentate), en = ethylenediamine (bidentate) , and EDTA = ethylenediaminetetraacetic acid (hexadentate)

ANSWER IS: ___

16) Which of the following specie(s) will not form a coordination complex (complex ion) with Fe^{2+}? (10 pts)

a) CN^- b) NH_2^- c) CO d) CH_3^+ e) CH_3^- f) BF_3

ANSWER IS/ARE: ________

17) If excess $AgNO_3$ solution is added to 100.0 mL of a 0.0240 M solution of dichlorobis(ethylenediamine)cobalt(III) chloride, how many moles of AgCl should be precipitated? (10 pts)

a) 0.00120 b) 0.00160 c) 0.00240 d)0.00480 e) 0.00720

ANSWER IS: ________

18) This part is not related to the previous parts. If the heat of hydration of Fe^{2+} to form $Fe(H_2O)_6^{2+}$ is -1841 $\frac{kJ}{mol}$ when the Fe^{2+} is in the low spin state, then the heat of hydration for Fe^{2+} in the high spin state would be approximately; (10 pts)

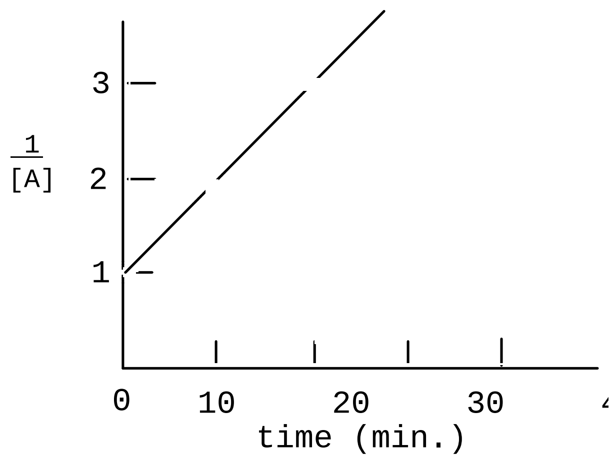
a) -1841 $\frac{kJ}{mol}$ b) -2000 $\frac{kJ}{mol}$ c) -1600 $\frac{kJ}{mol}$

ANSWER IS: ________

THE FOLLOWING INFORMATION IS FOR QUESTIONS 19 AND 20

Consider the second order reaction, A ____> products.

The concentration of A as a function of time is shown below.



19) What is the numerical value of the rate constant? (give units) (10 pts)

20) What is the <u>second</u> half life (in min)?
CREDIT FOR THIS PART IS BASED UPON YOUR ANSWER FROM QUESTION 19.

ANSWER IS: ________

CONVERSION FACTORS and POTENTIALLY USEFUL EQUATIONS

$C = 3.OO \times 1O^{8}$ m/sec $= 3.OO \times 1O^{1O}$ cm/sec

$h = 6.626 \times 10^{-34}$ J·sec $= 6.626 \times 1O^{-27}$ erg·sec

$m_e = 9.1O8 \times 1O^{-28}$ g $= 9.1O8 \times 1O^{-31}$ kg

$\varepsilon = h\nu$

$N_A = 6.O22 \times 1O^{23}$

$$R = O.O821 \frac{L\cdot atm}{mol\cdot degK} = 82.1 \frac{cm^3\cdot atm}{mol\cdot degK}$$

$\Delta T = iK_f m$ where $K_f = 1.86$ deg·m^{-1}

$\lambda\nu = c$

1 Å = O.1 nm = 1O^{-8} cm = 1O^{-1O} m

$\lambda = \frac{h}{p}$ (de Broglie equation) where p = mv

Heisenberg Uncertainty principle: $\Delta P \Delta X = \frac{h}{4\pi}$ where p = mv

kinetic energy: $\varepsilon = \frac{1}{2}\ mv^2 = \frac{p^2}{2m}$ where p = mv

q = e =1.6O22 x 1O^{-19} coulombs = 4.8O6 x 1O^{-1O} esu

1 eV = 1.6O22 x 1O^{-19} J

$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$ (integrated second order equation)

$\ln \frac{[A]_0}{[A]} = kt$ (integrated first order equation)

SCRAP WORK SHEET

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