REMOVE THIS PAGE PRIOR TO STARTING EXAM.

ANSWER KEY

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:

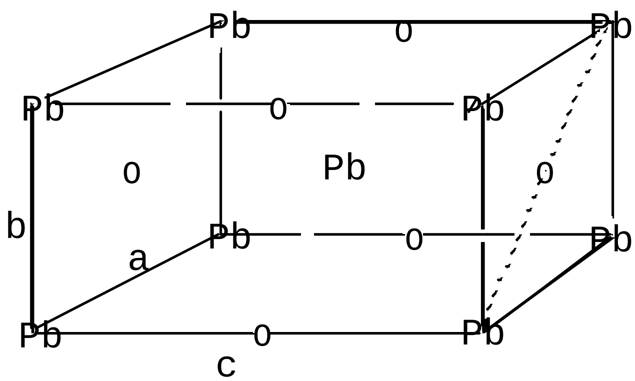
_______(130)	_______(80)	_______(60)

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.

Litharge



a = b = 4.000 Å   ? Åc
Molar mass = 223.2 g/m
density = 9.000 g/c^3

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)

$$\frac{g}{cm^3} = \left(\frac{g}{mol}\right)\left(\frac{mol}{molecule}\right)\left(\frac{molecules}{uc}\right)\left(\frac{uc}{cm^3}\right)$$

$$d = (685.598)\left(\frac{1}{6.022x10^{23}}\right)(4)\left(\frac{1}{(8.806)^2(6.564)x10^{-24}}\right)$$

$$d = 8.95 \frac{g}{cm^3}$$

ANSWER IS: _______

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

$$\frac{cm^3}{uc} = \left(\frac{cm^3}{g}\right)\left(\frac{g}{mol}\right)\left(\frac{mol}{molecule}\right)\left(\frac{molecule}{uc}\right) \text{ WHERE } \frac{molecule}{uc} = 2$$

$$\frac{cm^3}{uc} = axbxcx10^{-24} = (4.000)^2(c)x10^{-24} = \left(\frac{1}{9.000}\right)(223.2)\left(\frac{1}{6.022x10^{23}}\right)(2)$$

$$c = 5.148 \text{ Å}$$

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)

$$\frac{g}{mol} = \left(\frac{g}{cm^3}\right)\left(\frac{atoms}{mol}\right)\left(\frac{cm^3}{uc}\right)\left(\frac{uc}{atom}\right)$$

$$\frac{g}{mol} = (7.470)(6.022x10^{23})(8.914x10^{-8})^3\left(\frac{1}{58}\right)$$

$$\frac{g}{mol} = 54.93$$

ANSWER IS: _______

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

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

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) $3.20x10^{-4}\ \frac{L^2}{mol^2{\cdot}min}$ b) $7.00x10^{-6}\ \frac{mol^2}{L^2{\cdot}sec}$ c) $3.20x10^{-4}\ \frac{mol^2}{L^2{\cdot}min}$

d) $2.52x10^{-4}\ \frac{mol^2}{L^2{\cdot}min}$ e) $5.33x10^{-6}\ \frac{mol^2}{L^2{\cdot}sec}$

$$\frac{1}{2}\left((0.10)^2 - (0.04)^2\right) = k(10.0)$$

` $$k = 4.20x10^{-4}\ \frac{mol^2}{L^2{\cdot}min} = 7.00x10^{-6}\ \frac{mol^2}{L^2{\cdot}sec}$$

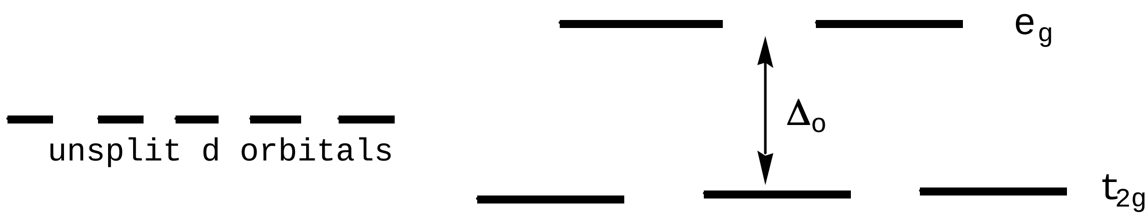
ANSWER IS: _______

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: e

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

$$\varepsilon = \frac{hc}{\lambda} = \Delta_o = 3.501 \text{ eV} \qquad \therefore\ \lambda = \frac{hc}{\Delta_o}$$

$$\lambda = \frac{hc}{\Delta_o} = \frac{(6.626\text{x}10^{-34})(3.00\text{x}10^{8})}{(3.501 \text{ eV})(1.6022\text{x}10^{-19}\text{J/eV})} = 3.54\text{x}10^{-7} \text{ m}$$

$$\lambda = 354 \text{ nm}$$

ANSWER IS: _______

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

$$CFSE = 5(\tfrac{2}{5}\Delta_o) - 2(\tfrac{3}{5}\Delta) = \tfrac{4}{5}\Delta_o = \tfrac{4}{5}(2.242\ eV)$$

$$CFSE = 1.794\ eV = (1.794\ \tfrac{eV}{ion})(1.6022x10^{-19}\ \tfrac{J}{eV})(6.022x10^{23}\ \tfrac{ion}{mol})(10^{-3}\ \tfrac{kJ}{J})$$

$$CFSE = (1.794\ \tfrac{eV}{ion})(1.6022x10^{-19}\ \tfrac{J}{eV})(6.022x10^{23}\ \tfrac{ion}{mol})(10^{-3}\ \tfrac{kJ}{J}) = 173.1\ \tfrac{kJ}{mol}$$

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.	9.6×10^{-4}	0.080	0.160	1.00	0.100
3.	1.92×10^{-4}	0.080	0.800	1.00	0.100
4.	9.6×10^{-4}	0.160	0.160	0.50	0.200
5.	6.0×10^{-7}	0.020	1.60	1.00	1.00

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

$$k = 2.4x10^{-3}\ sec^{-1}$$

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

$[Ag^{2+}] = 0.020$ $[Ag^+] = 0.180$ $[N_2H_4] = 0.995$ $[H_3O^+] = 1.020$

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: a

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. The Na^+ ions occupy the corners and the face centers, while the F^- ions occupy the edges. (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: a

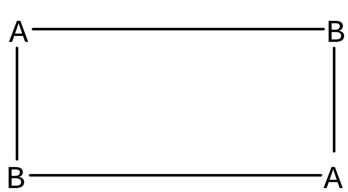
11) Given the following complex ions and their hybridizations:

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: a, g, h

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

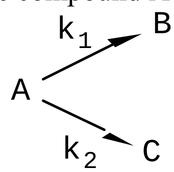


	NUMBER PRESENT
center of symmetry	1
two fold axis of rotation, C_2	1
four fold axis of rotation, C_4	0
planes of symmetry	1

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;



$k_1 = 10^{-2}\ sec^{-1}$ and $[A]_0 = 0.110$ M

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

What is the $\frac{[B]}{[C]}$ ratio after the first half life? (5 pts) ANSWER: $\frac{10}{1}$

What is the [B] after the first half life? (5 pts) [B] = <u>0.050</u> M

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)

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)

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

$0.149 = i(1.86)(0.020)$ ∴ $i = 4$

ANSWER IS: <u>d</u>

16) Which of the following species 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: <u>d</u> and <u>f</u>

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: <u>c</u>

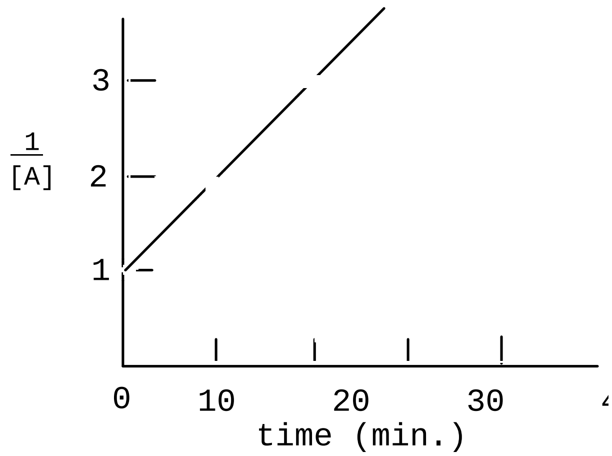
18) This part is not related to the previous parts. If the heat of hydration of Fe^{2+} to form $Fe(H_2O)_6^{2+}$ is -1841 $\frac{kJ}{mol}$ when the Fe^{2+} is in the low spin state, then the heat of hydration for Fe^{2+} in the high spin state would be approximately; (10 pts)

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

ANSWER IS: <u>c</u>

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)

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \qquad \frac{1}{(0.5)} - \frac{1}{(1)} = k(10)$$

$$\therefore\ k = 0.1\ \frac{L}{mol \cdot min}$$

ANSWER IS: $0.1\ \frac{L}{mol \cdot min}$

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

First half life = 10 minutes $\therefore$ second half life is 20 minutes

ANSWER IS: 20 min.