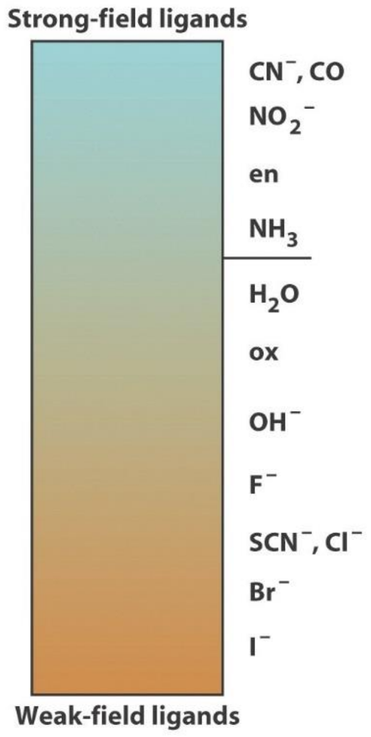
Chemistry II Final Exam (Total 105 points)
June 21, 2013 (3 hours exam)

Periodic Table of Elements

1 H 1.0																	2 He 4.0
3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 40.0
19 K 39.1	20 Ca 40.1	21 鈧	22 鈦	23 釩	24 鉻	25 錳	26 鐵	27 鈷	28 鎳	29 銅	30 鋅	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 釔	40 鋯	41 鈮	42 鉬	43 鎝	44 釕	45 銠	46 鈀	47 銀	48 鎘	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 鑭	72 鉿	73 鉭	74 鎢	75 錸	76 鋨	77 銥	78 鉑	79 金	80 汞	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)



Constants

R = 8.314 J / mol K = 0.08314 Lbar / K mol = 8.314 L kPa / K mol

$h = 6.63\times10^{-34}$ J·s

$k = 1.3806504 \times 10^{-23}$ J / K

1. The rate law for the decomposition of ozone, $2O_3(g) \rightarrow 3O_2(g)$, has been determined as

   Rate of decomposition of $O_3 = k[O_3]^2/[O_2]$

   The following mechanism has been proposed:

   Step 1 $O_3 \rightleftharpoons O_2 + O$ (fast, k_1 and k_1' both large)

   Step 2 $O + O_3 \rightarrow O_2 + O_2$ (slow, k_2 very small and k_2' negligible)

   (a) (6 points) Write the rate law for each step (forward and reverse for step 1 and only forward for step 2) and indicate its molecularity.

   (b) (2 points) What is the reaction intermediate?

   (c) (6 points) Use the steady-state approximation to derive the rate law implied by the proposed mechanism. Does the proposed mechanism agree with the observed rate law?

   (d) (3 points) Chlorine atoms produced from chlorofluorocarbons in the presence of UV light have been considered primary causes of the destruction of stratospheric ozone by various mechanisms such as

   $Cl + O_3 \rightarrow ClO + O_2$

   $ClO + O \rightarrow Cl + O_2$

   Write the net reaction of the above two elementary reactions and explain why a very small amount of chlorine atoms can damage the ozone layer so severely.

2. Sulfuryl chloride, SO_2Cl_2, decomposes by first-order kinetics, and $k = 2.81\times10^{-3}$ min^{-1} at a certain temperature.

   (a) (3 points) Determine the half-life for the reaction.

   (b) (3 points) If 12.0 g of SO_2Cl_2 is sealed in a 2000.0-L reaction vessel and heated to the specified temperature, what mass will remain after half a day?

3. For the reversible, one-step reaction $2A \leftrightarrow B + C$, the forward rate constant is 9.7×10^{10} L mol^{-1} s^{-1} at 800 ℃. The activation energy of the reaction is 315 kJ mol^{-1} for the forward reaction. This reaction follows the Arrhenius behavior.

   (a) (4 points) Calculate the forward rate constant at 600 ℃.

   (b) (3 points) The rate constant of the reverse reaction is 1.3×10^{11} L mol^{-1} s^{-1} at 800 ℃. What is the equilibrium constant at this temperature?

4. (10 points) Quick answer questions

   On the first page, a part of the periodic table for transition metals is written in Chinese character. Each box contains atomic number and name of each element given in Chinese character. Please write the English names and abbreviations of elements for shaded boxes in the periodic table of the first page.

5. (5 points) Answer the following question related to the properties of transition metals.

   (a) The only transition metal element that is radioactive.

(b) The element that features the most unique and complex structure type compare to other transition metals.

(c) The element used as the filament material in light bulbs.

(d) The element form a metal-organic compound that cause damage of human's neural system named "水俣症".

(e) The metal ion in the center of vitamin B12.

6. (2 points for each answer, total 20 points) Fill the Blanks with line structures and classify the reaction (if asked):

- (a) an alcohol + (b) a carboxylic acid → propyl pentanoate, type of reaction: (c)
- (d) 2-bromo-2,3-dimethylbutane + ethoxide ion → (e) an alkene + (f) an alcohol + Br^-, type of reaction: (g)
- nitrobenzene + HNO_3 + H_2SO_4 → (h) the major product, type of reaction: (i)
- propanone + Ag^+ → (j) an organic compound

7. By controlling the process of producing polyethylene, we can obtain products with different degree of branching.

(a) (2 points) Does low-density or high-density polyethylene product contain more branches?

(b) (3 points) Why?

8. (3 points for each questions, total 15 points) Please select the proper answers (1 or 2 correct answers for each question)

(i) Which of the following interaction (or chemical bond) do not influence the structure of a protein molecule? (A) –N–N– bond ; (B) –S–S– bond ; (C) hydrogen bond ; (D) dipole-dipole interaction ; (E) hydrophobic interaction.

(ii) Which of the following compound has the highest base strength? (A) $(CH_3)_4N^+Cl^-$; (B) CH_3COONa ; (C) CHF_2COONa ; (D) CF_3COONa ; (E) C_6H_5OH

(iii) Which of the following species may function as a nucleophile in a nucleophilic substitution reaction? (A) CH_3Br ; (B) H_2O ; (C) NH_4^+ ; (D) OH^- ; (E) SiH_4.

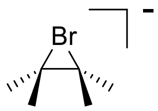
(iv) Predict the number of isomers of the hydrocarbon C_5H_{10}:
(A) 6 ; (B) 9 ; (C) 10 ; (D) 11 ; (E) 12.

(v) Which of the following statements is true?

(A) H_2 is more difficult to be added to an alkene than Br_2.

(B) The hydrochlorination reaction of 2-butene produce no chiral product.

(C) Electrophilic substitution also occurs on the π-bonds of an alkyne.

(D) The intermediate of bromination of an alkene is a cyclic anion 

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(E) The hydrogenation converts liquid vegetable oil into soft solid fats by decreasing the number of double bonds on the long hydrocarbon chain.

9. (20 points) The following questions are related to the molecules of (**A**) $CoCl_4^{2-}$, (**B**) $Fe(H_2O)_6^{3+}$, (**C**) $Mn(CN)_6^{4-}$, (**D**) $CoCl_2(en)_2^{+}$, (**E**) $Fe(NH_3)_4(Cl)_2^{+}$, and theories related to transition metal complexes.

(a) (4 points) Identify the following statements whether they belong to the similarities or differences between the crystal field theory and ligand field theory and compare their.

(i) The ligands are assumed as point charges

(ii) The d orbital splitting is caused by ligands around the metal center.

(iii) The spectrochemical series of ligands demonstrates the relative magnitude of the d orbital splitting.

(iv) The spectrochemical series of ligands is explained by a simplified molecular orbital theory that is made up of metal valence orbitals (eg. 3d, 4s, 4p) and the electron pairs from filled orbitals of ligands.

(b) (4 points) Draw qualitative energy level diagrams of d orbitals for molecule **A**, **B**, and **C**. Whose ligand field splitting shows the largest energy gap?

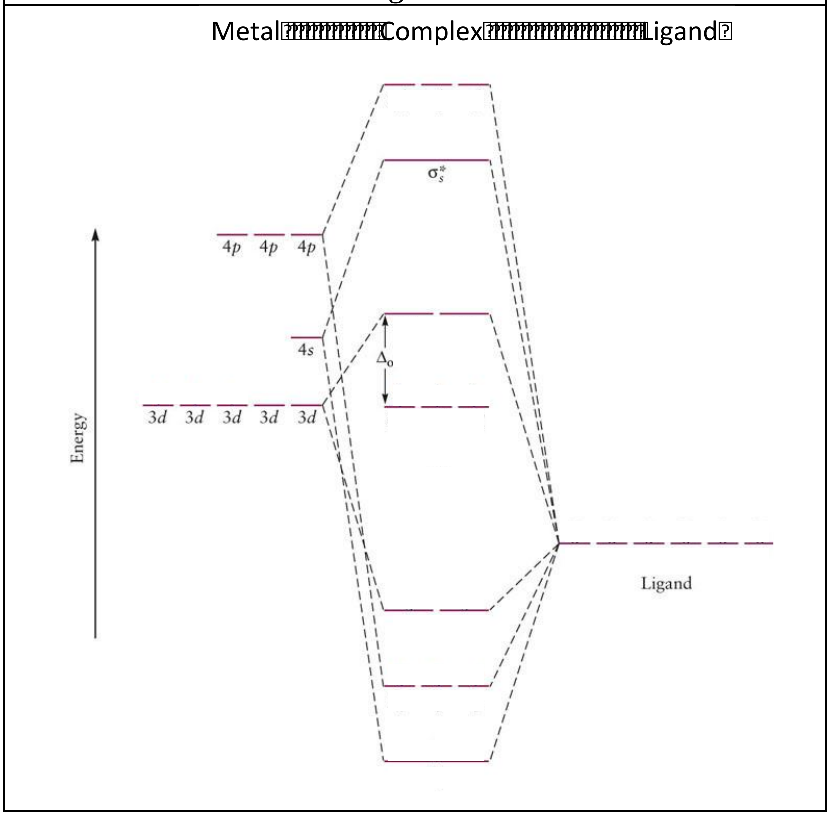
(c) (3 points) Base on the results in b), please write the electronic configuration of d electrons for metal ions in molecules **A**, **B**, and **C**.

(d) (4 points) By using Figure 1, please draw an MO diagram and fill electrons in the energy levels for molecue **B**. What is the main type of the molecular orbital bonding between the ligand and the central metal?

(e) (3 points) Draw the structures of all possible isomers for the molecule **E**. Indicate which isomers are enantiomer pairs.

(f) (2 points) From the molecules A~E, please identify which ones own optical isomers.

Figure 1



Solutions

1. Example 14.7 & Box 14.3

(a) Step 1 forward: rate of decomposition of O_3 = $k_1[O_3]$ (molecularity = 1)

Or Step 1 forward: rate of formation of O_2 = $k_1[O_3]$ (molecularity = 1)

Step 1 reverse: rate of formation of O_3 = $k_1'[O_2][O]$ (molecularity = 2)

Or Step 1 reverse: rate of decomposition of O_2 = $k_1'[O_2][O]$ (molecularity = 2)

Step 2 forward: rate of consumption of O_3 = $k_2[O][O_3]$ (molecularity = 2)

Or Step 2 forward: rate of formation of O_2 = $2k_2[O][O_3]$ (molecularity = 2)

(Each rate law 1 point; each molecularity 1 point)

(b) O atom

(c) The net rate of decomposition of O_3 is given by

$$\text{Rate} = k_1[O_3] - k_1'[O_2][O] + k_2[O][O_3] \quad \text{... (1)}$$ **(1 point)**

Apply the steady-state approximation to the intermediate (O atom).

$$k_1[O_3] - k_1'[O_2][O] - k_2[O][O_3] = 0$$

$$\therefore\ [O] = \frac{k_1[O_3]}{k_1'[O_2] + k_2[O_3]} \quad \text{... (2)}$$ **(2 points)**

From (1) and (2), we have

$$\text{Rate} = k_1[O_3] - \frac{k_1 k_1'[O_2][O_3]}{k_1'[O_2] + k_2[O_3]} + \frac{k_1 k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]}$$

$$= \frac{2k_1 k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]}$$ **(1 point)**

Because step2 is slow relative to step 1, we can make the approximation $k_2[O][O_3] << k_1'[O_2][O]$, i.e., $k_2[O_3] << k_1'[O_2]$. Then we get

$$\text{Rate} = \frac{2k_1 k_2[O_3]^2}{k_1'[O_2]} = k[O_3]^2 / [O_2]$$ **(1 point)**

with $k = 2k_1k_2/k_1'$.

Therefore the proposed mechanism is consistent with the observed rate law. **(1 point)**

Or The net rate of formation of O_2 is given by Rate = $2k_2[O][O_3]$ ... (1) **(1 point)** Apply the steady-state approximation to the intermediate (O atom). $k_1[O_3] - k_1'[O_2][O] - k_2[O][O_3] = 0$

$$\therefore\ [O] = \frac{k_1[O_3]}{k_1'[O_2] + k_2[O_3]} \quad \text{... (2)}$$ **(2 points)**

From (1) and (2), we have

$$\text{Rate} = \frac{2k_1k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]}$$ **(1 point)**

Because step2 is slow relative to step 1, we can make the approximation $k_2[O][O_3] << k_1'[O_2][O]$, i.e., $k_2[O_3] << k_1'[O_2]$. Then we get

$$\text{Rate} = \frac{2k_1k_2[O_3]^2}{k_1'[O_2]} = k[O_3]^2 / [O_2]$$ **(1 point)**

with $k = 2k_1k_2/k_1'$.

Therefore the proposed mechanism is consistent with the observed rate law. **(1 point)**

(d) Net reaction: $O_3 + O \rightarrow O_2 + O_2$ **(1 point)**

The net reaction does not involve chlorine atoms. Therefore they act as continuously regenerated catalysts **(2 points)**, and so even a very small amount of chlorine atoms can do a lot of damage on the ozone layer.

2. Exercise 14.35

(a) $t_{1/2} = \ln 2/k = 247$ min

(b) $[A]_0 = (12.0/134.97)/2000.0 = 4.445 \times 10^{-5}$ mol L^{-1}. **(1 point)**

$[A]_{t=12h} = 4.445\times10^{-5}\times \exp(-2.81\times10^{-3}\times12\times60) = 5.878\times10^{-6}$ mol L^{-1}.

Therefore the remaining mass is $5.878\times10^{-6}\times2000.0\times135 = 1.59$ g **(2 points)**

3. Exercise 14.61 & 14.65

(a) From the Arrhenius equations at T_1 and T_2,

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{and} \quad \ln k_2 = \ln A - \frac{E_a}{RT_2}$$

By subtracting the second equation from the first, we get

$$\ln k_1 - \ln k_2 = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ **(2 points)**

Substitution of $k_1 = 9.7\times10^{10}$ L mol^{-1} s^{-1}, $E_a = 315$ kJ mol^{-1}, $T_1 = 800 + 273 = 1073$ K, and $T_2 = 600 + 273 = 873$ K into this equation gives

$k_2 = 3.0\times10^{7}$ L mol^{-1} s^{-1} **(2 points)**

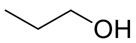
(b) $K = k_1/k'_1 = 9.7\times10^{10}/1.3\times10^{11} = 0.75$

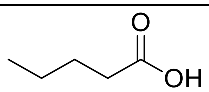
4. **(1 point for each answer, total 10 points)**

22. Ti, Titanium
23. V, Vanadium
24. Cr, Chromium
27. Co, Cobalt
43. Tc, Technetium
44. Ru, Ruthenium
46. Pd, Palladium
72. Hf, Hafnium
77. Ir, Iridium

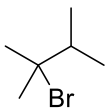
5. **(1 point for each answer, total 5 points)**
   - (a) Tc
   - (b) Mn
   - (c) W or Ta
   - (d) Hg
   - (e) Co

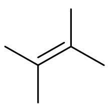
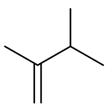
6. (2 points for each answer, total 20 points)

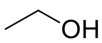
(a) 

(b) 

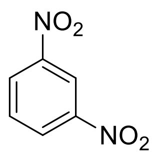
(c) condensation (or esterification)

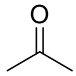
(d) 

(e)  (our text book only gives the major product on p.746, but the minor product  is also acceptable in our exam)

(f) 

(g) elimination

(h) 

(i)	electrophilic substitution	(j)	

7. (Total 5 points)
   (a) (2 points) low-density polyethylene
   (b) (3 points) The branches makes polymer chains pack loosely.

8. (3 points for each questions, total 12 points)

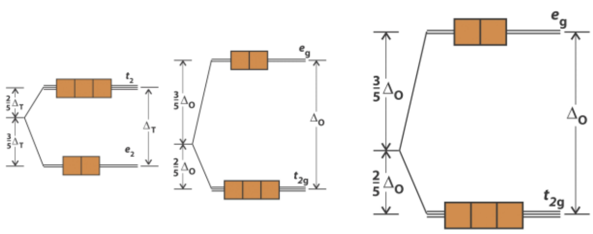
Questions	Answers
(i)	A
(ii)	B
(iii)	B, D
(iv)	D
(v)	A, E

9. **(Total 20 points)**
   (a) (1% for each answer, total 4 points)

Similarity	Differences
(ii) and (iii)	(i) and (iv)

   (b) (4 points)

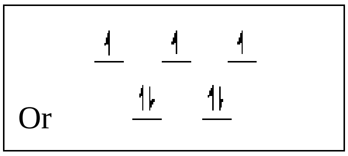
A [illegible] B [illegible] C [illegible]



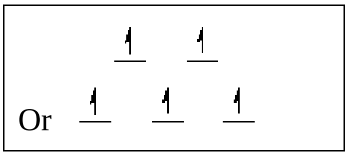
$\Delta_t(A) < \Delta_o(B) < \Delta_o(C)$

(c) (3 points)

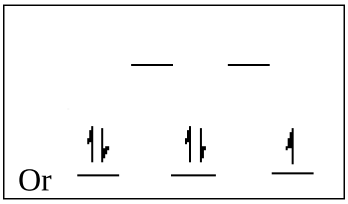
A: Co^{2+}, d^7, e^4t^3



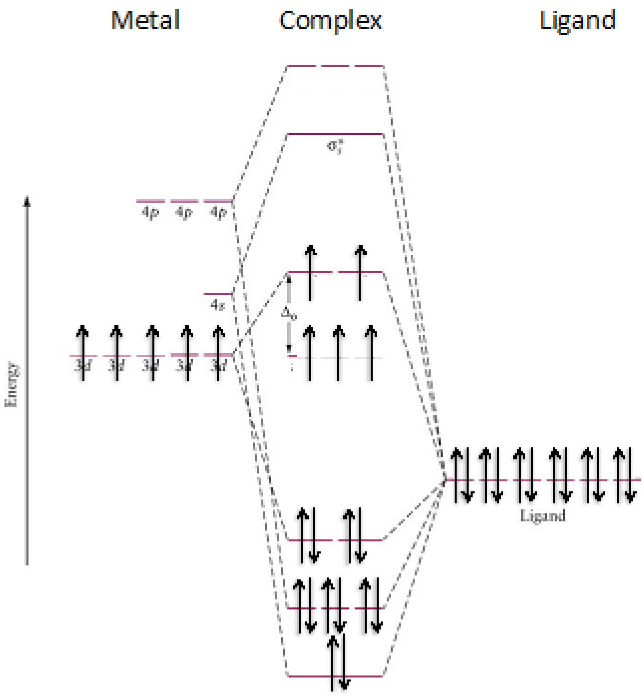
B: Fe^{3+}, d^5, $t_{2g}^3e_g^2$



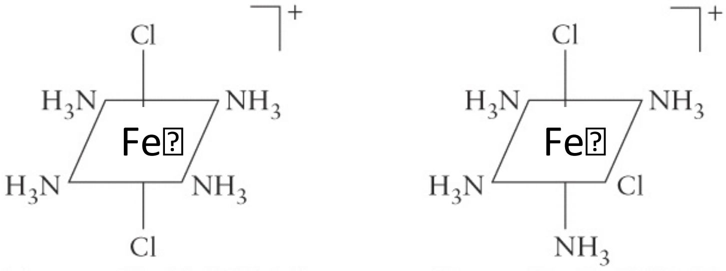
C: Mn^{2+}, d^5, $t_{2g}^5e_g^0$



(d) (4 points) assume **σ-type** orbital interaction between metal d orbital and ligand lone pair electrons



(e) (3 points) $Fe(NH_3)_4(Cl)_2^+$ (**E**), two isomers, no enantiomer



(f) (2 points) Molecule (D) only