

**2009 FALL Semester Midterm Examination  
For General Chemistry II (CHEM103)**

**Date: October 21, 2009 (Wed), Time Limit: 7:00 ~ 9:00 p.m.**

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

| Professor Name | Class | Student I.D. | Name |
|----------------|-------|--------------|------|
|                |       |              |      |

| Problem  | points | Problem   | points | TOTAL pts   |
|----------|--------|-----------|--------|-------------|
| <b>1</b> | /10    | <b>6</b>  | /10    | <b>/100</b> |
| <b>2</b> | /5     | <b>7</b>  | /5     |             |
| <b>3</b> | /10    | <b>8</b>  | /10    |             |
| <b>4</b> | /10    | <b>9</b>  | /10    |             |
| <b>5</b> | /10    | <b>10</b> | /20    |             |

**\*\* This paper consists of 11 sheets with 10 problems. Please check all page numbers before taking the exam. Write down your work and answers in the (Answer) space below each question. And take a good use of the reference materials (page 10, 11), which include (a) Fundamental constants, (b) Conversion factors, and (c) Periodic table with atomic weights.**

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.

(채점답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

- 1) Return and Claim Period: **October 26 (Mon), 9: 00 ~ 18:00 p.m.**
- 2) **Location: Lobby (1<sup>st</sup> floor), GoongNi lab Bldg.**
- 3) Procedure: During the period, you can take your mid-term paper scored. If you have any claims on it, you can submit a claim paper with your opinion. After writing your opinions on any paper you can get easily, attach it with a stapler to your mid-term paper scored (Please, write your name, professor, and class.). Put them into a paper box in front of elevator.. The papers with the claims will be re-examined by TA.

***The claim is permitted only on the period. Keep that in mind!***

***(A solution file with answers will be uploaded on 10/24 at the web.)***

2. Final Confirmation

- 1) Period: October 29 (Thu)-30 (Fri)
- 2) Procedure: During this period, you can check final score of the examination *on the website* again.

\*\* For further information, please visit a *General Chemistry website* at [www.gencheminkaist.pe.kr](http://www.gencheminkaist.pe.kr).

1. Suppose that a gas obeys the van der Waals equation of state with the repulsive effects much greater than the attractive effects.

(a) (4 pt) Find an expression for the change in **molar Gibbs energy** when the pressure is changed from  $P_i$  to  $P_f$  ( $P_i < P_f$ ) isothermally.

(Answer)

The van der Waals equation of state is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad [V_m = \text{molar volume}]$$

After neglecting attractive effects, it becomes

$$p(V_m - b) = RT$$

Solving for  $V_m$  we get

$$V_m = \frac{RT + bp}{p} = \frac{RT}{p} + b$$

Then,

$$\Delta G_m = \int_{P_i}^{P_f} V_m dp = \int_{P_i}^{P_f} \frac{RT}{p} dp + \int_{P_i}^{P_f} b dp = RT \ln \frac{P_f}{P_i} + b(p_f - p_i) = \text{ideal value} + b(p_f - p_i)$$

(b) (2 pt) Is the change greater or smaller than for a perfect gas?

(Answer)

For  $p_f > p_i$ , the change is greater for this gas by the amount  $b(p_f - p_i)$ .

(c) (4 pt) Estimate the percentage difference between the van der Waals and perfect gas calculations for carbon dioxide undergoing change from 1.0 atm to 10.0 atm at 298.15 K (van der Waals parameters of carbon dioxide:  $a = 3.610 \text{ atm dm}^6 \text{ mol}^{-2}$ ,  $b = 0.0429 \text{ dm}^3 \text{ mol}^{-1}$ ,  $1.0 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$ ,  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ ).

(Answer)

$$\text{ideal value} = RT \ln \frac{P_f}{P_i} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times \ln \frac{10.0 \text{ atm}}{1.0 \text{ atm}} = 5.71 \times 10^3 \text{ J} = 5.71 \text{ kJ}$$

$$b(p_f - p_i) = 0.0429 \text{ dm}^3 \text{ mol}^{-1} \times \frac{1 \text{ m}^3}{10^3 \text{ dm}^3} \times (10 - 1) \text{ atm} \times \frac{1.013 \times 10^5 \text{ Pa}}{1.0 \text{ atm}} = 39 \text{ J}$$

The van der Waals gas value is then  $5.71 \times 10^3 \text{ J} + 39 \text{ J} = 5.75 \times 10^3 \text{ J} = 5.75 \text{ kJ}$

The percentage difference is approximately

$$\frac{39 \text{ J}}{5.7 \times 10^3 \text{ J}} \times 100\% = 0.68\%$$

2. (5 pt) The hydrolysis of acetyl phosphate has  $\Delta G = -42 \text{ kJ mol}^{-1}$  under typical biological conditions. If acetyl phosphates were to be synthesized by coupling to the hydrolysis of ATP ( $\Delta G$  for the hydrolysis of ATP to ADP is  $-31 \text{ kJ mol}^{-1}$ ), what is the minimum number of ATP molecules that would need to be involved for the formation of 1 mole of acetyl phosphate molecule?

(Answer)

For the synthesis,  $\Delta G = 42 \text{ kJ mol}^{-1}$ ; hence at least 42 kJ would need to be provided by the ATP in order to make  $\Delta G$  overall negative.

Amount of ATP =  $42 \text{ kJ} / 31 \text{ kJ mol}^{-1} = 1.35 \text{ mol}$

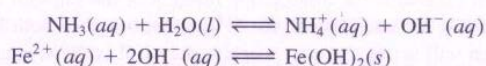
$1.35 \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 8.1 \times 10^{23}$  molecules

3. (10 pt) Calculate the concentration of aqueous ammonia necessary to initiate the precipitation of iron(II) hydroxide from a  $0.0030 \text{ M}$  solution of  $\text{FeCl}_2$  ( $K_{\text{sp}}[\text{Fe}(\text{OH})_2] = 1.6 \times 10^{-14}$ ,  $K_{\text{b}}[\text{NH}_3] = 1.8 \times 10^{-5}$ ).

(Answer)

Text problem 12.15

**Solution** Ammonia reacts with water to produce  $\text{OH}^-$  ions, which then react with  $\text{Fe}^{2+}$  to form  $\text{Fe}(\text{OH})_2$ . The equilibria of interest are



First, we find the  $\text{OH}^-$  concentration above which  $\text{Fe}(\text{OH})_2$  begins to precipitate. We write

$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-14}$$

Because  $\text{FeCl}_2$  is a strong electrolyte,  $[\text{Fe}^{2+}] = 0.0030 \text{ M}$  and

$$[\text{OH}^-]^2 = \frac{1.6 \times 10^{-14}}{0.0030} = 5.3 \times 10^{-12}$$

$$[\text{OH}^-] = 2.3 \times 10^{-6} \text{ M}$$

Next, we calculate the concentration of the weak base  $\text{NH}_3$  that will supply  $2.3 \times 10^{-6} \text{ M}$   $\text{OH}^-$  ions.

Let  $x$  be the initial concentration of  $\text{NH}_3$  in  $\text{mol L}^{-1}$ . We summarize the changes in concentrations resulting from the ionization of  $\text{NH}_3$  as follows:

|                 | $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$ | $\rightleftharpoons$ | $\text{NH}_4^+(\text{aq})$ | + | $\text{OH}^-(\text{aq})$ |
|-----------------|---|----------------------|----------------------------|---|--------------------------|
| Initial (M)     | $x$   |                      | 0.00                       |   | 0.00                     |
| Change (M)      | $-2.3 \times 10^{-6}$                                   |                      | $+2.3 \times 10^{-6}$      |   | $+2.3 \times 10^{-6}$    |
| Equilibrium (M) | $x - 2.3 \times 10^{-6}$                                |                      | $2.3 \times 10^{-6}$       |   | $2.3 \times 10^{-6}$     |

The equilibrium concentrations of  $\text{NH}_3$ ,  $\text{OH}^-$ , and  $\text{NH}_4^+$  are then related by the base ionization constant for  $\text{NH}_3$  (which from Table 11.4 is equal to  $1.8 \times 10^{-5}$ ):

$$K_{\text{b}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{(2.3 \times 10^{-6})(2.3 \times 10^{-6})}{x - 2.3 \times 10^{-6}}$$

Solving for  $x$ , we obtain

$$x = 2.6 \times 10^{-6} \text{ M}$$

Therefore, the concentration of  $\text{NH}_3$  must be slightly greater than  $2.6 \times 10^{-6} \text{ M}$  to initiate the precipitation of  $\text{Fe}(\text{OH})_2$ .

4. (5 pt each) One mole of an ideal gas is first heated at constant pressure from  $T$  to  $3T$  and then it is cooled back to  $T$  at constant volume.

(a) Determine an expression for  $\Delta S$  for the overall process.

(Answer)

$$(a) \Delta S = C_p \ln(3T/T) + C_v \ln(T/3T) = C_p \ln 3 - C_v \ln 3 = R \ln 3$$

where  $C_p$  and  $C_v$  are molar heat capacities.

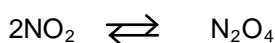
(b) Show that the value of  $\Delta S$  for the process in part (a) is the same as that for an isothermal expansion of the gas at  $T$  from  $V$  to  $3V$ , where  $V$  is the original volume.

(Answer)

$$(b) \Delta S = R \ln(3V/V) = R \ln 3$$

5. (10 pt) Suppose that nitrogen dioxide ( $\text{NO}_2$ ) gas is allowed to dimerize into  $\text{N}_2\text{O}_4$  gas until the reaction reaches equilibrium 1.00 atm at  $25^\circ\text{C}$ . What are the partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ ? The equilibrium constant  $K$  is  $8.06 \times 10^5$  at  $-75^\circ\text{C}$  and the standard enthalpy change for this reaction ( $\Delta H^\circ$ ) is  $-57.2 \text{ kJ mol}^{-1}$ .

(Answer)



$$P_{\text{NO}_2} = 1 - x \text{ and } P_{\text{N}_2\text{O}_4} = x$$

$$K = x/(1 - x)^2 \quad 0 \leq x \leq 1$$

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

$$\ln \frac{K_2}{8.06 \times 10^5} = \frac{-57200}{8.314} \left( \frac{1}{198} - \frac{1}{298} \right)$$

$$K_2 = 6.96$$

$$x^2 - 2.1435x + 1.00 = 0, \quad x = 0.686$$

$$P_{\text{N}_2\text{O}_4} = 0.686 \text{ atm}, \quad P_{\text{NO}_2} = 0.314 \text{ atm}$$

6. (10 pt) Calculate the concentrations of all the species present at equilibrium in a 0.10 M solution of oxalic acid ( $C_2H_2O_4$ ) ( $K_{a1}[C_2H_2O_4] = 6.5 \times 10^{-2}$ ,  $K_{a2}[C_2H_2O_4] = 6.1 \times 10^{-5}$ ).

(Answer)

Text problem 11.15

**Solution** We proceed as follows:  
*First ionization stage:* The first ionization of oxalic acid is given by

$$C_2H_2O_4(aq) \rightleftharpoons H^+(aq) + C_2HO_4^-(aq) \quad K_{a1} = 6.5 \times 10^{-2}$$

Letting  $x$  be the equilibrium concentration of  $H^+$  and  $C_2HO_4^-$ , Equation 11.19 gives

$$K_{a1} = \frac{x^2}{[C_2HO_4^-]_0 - x}$$

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

If we ignore the  $x$  in the denominator (assuming it is small relative to 0.10), we obtain

$$x = 0.081 M$$

—Continued

Continued—  
 This concentration is larger than 5 percent of the initial concentration, so we must recalculate  $x$  using the quadratic equation:

$$x^2 + (6.5 \times 10^{-2})x - 6.5 \times 10^{-3} = 0$$

The result is  $x = 0.054 M$ .  
 The second ionization constant is significantly smaller than the first ( $6.1 \times 10^{-5}$  versus  $6.5 \times 10^{-2}$ ), so the second ionization will make very little additional contribution to the  $H^+$  ion concentration. Therefore, we can calculate the pH of the solution at this point:

$$pH = -\log_{10}(0.054) = 1.27$$

*Second ionization stage:* The second ionization of oxalic acid is given by

$$C_2HO_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq) \quad K_{a2} = 6.1 \times 10^{-5}$$

Letting  $y$  be the equilibrium concentration of  $H^+$  and  $C_2O_4^{2-}$  ions in  $\text{mol L}^{-1}$ , we construct the following table:

|                     | $C_2HO_4^-$ | $H^+$       | $C_2O_4^{2-}$ |
|---------------------|-------------|-------------|---------------|
| Initial ( $M$ )     | 0.054       | 0.054       | 0             |
| Change ( $M$ )      | $-y$        | $+y$        | $+y$          |
| Equilibrium ( $M$ ) | $0.054 - y$ | $0.054 + y$ | $y$           |

Thus, the equilibrium expression for the second ionization stage becomes

$$K_{a2} = \frac{[H^+][C_2O_4^{2-}]}{[C_2HO_4^-]}$$

$$6.1 \times 10^{-5} = \frac{(0.054 + y)(y)}{0.054 - y}$$

Applying the approximation  $0.054 + y \approx 0.054$  and  $0.054 - y \approx 0.054$ , we obtain

$$6.1 \times 10^{-5} = \frac{(0.054)(y)}{0.054}$$

$$y = 6.1 \times 10^{-5} M$$

This value is less than 5 percent of 0.054, so the approximation is justified.

*Summary:*

$$[H^+] = [C_2HO_4^-] = 0.054 M$$

$$[C_2H_2O_4] = 0.10 M - 0.054 M = 0.046 M$$

$$[C_2O_4^{2-}] = 6.1 \times 10^{-5}$$

$$[OH^-] = K_w/[H^+] = 1.0 \times 10^{-14}/0.054 = 1.9 \times 10^{-13} M$$

7. (1 pt each) Which one is stronger acid?

(a) HF and HCl  
(Answer) HCl

(b)  $\text{HClO}_4$  and  $\text{HClO}_3$   
(Answer)  $\text{HClO}_4$

(c)  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$   
(Answer)  $\text{HCOOH}$

(d)  $\text{C}_6\text{H}_5\text{COOH}$  and  $\text{C}_6\text{H}_5\text{OH}$   
(Answer)  $\text{C}_6\text{H}_5\text{COOH}$

(e)  $\text{HClO}_3$  and  $\text{HBrO}_3$   
(Answer)  $\text{HClO}_3$



8. (10 pt) What is the pH of a buffer system containing 1.0 M acetic acid and 1.0 M sodium acetate after the addition of 0.10 mole of gaseous HCl to 1.0 L of the solution ( $K_a[\text{CH}_3\text{COOH}] = 1.8 \times 10^{-5}$ ).

(Answer)

Text problem 12.3(b)

(b) When HCl (a strong acid) is added to the solution, it completely dissociates into  $\text{H}^+$  ions and  $\text{Cl}^-$  ions. The initial changes are

|             | $\text{HCl}(aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$ |      |      |
|-------------|---|------|------|
| Initial (M) | 0.10  | 0.0  | 0.0  |
| Change (M)  | -0.10   | 0.10 | 0.10 |
| Final (M)   | 0.00  | 0.10 | 0.10 |

The  $\text{H}^+$  ions are neutralized by the conjugate base ( $\text{CH}_3\text{COO}^-$ ), and  $\text{Cl}^-$  is a spectator ion in solution because it is the conjugate base of a strong acid and will have no tendency to neutralize the weak acid present. At this point, it is more convenient to work with moles rather than molarity. The reason is that in some cases the volume of the solution may change when a substance is added. A change in volume will change the molarity, but not the number of moles. The neutralization reaction is summarized next:

|               | $\text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \longrightarrow \text{CH}_3\text{COOH}(aq)$ |       |       |
|---------------|---|-------|-------|
| Initial (mol) | 1.0   | 0.10  | 1.0   |
| Change (mol)  | -0.10   | -0.10 | +0.10 |
| Final (mol)   | 0.90  | 0.00  | 1.10  |

Finally, to calculate the pH of the buffer after neutralization of the acid, we convert back to molarity by dividing moles by 1.0 L of solution. Thus, the weak acid concentration,  $[\text{CH}_3\text{COOH}]$  after addition of HCl is 1.10 M and the conjugate base concentration  $[\text{CH}_3\text{COO}^-] = 0.90$  M. Reapplying the Henderson-Hasselbalch equation gives

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log_{10} \frac{0.90}{1.10} \\ &= 4.65 \end{aligned}$$

9. (10 pt) Compare the solubility of  $\text{Zn(OH)}_2$  (g/L) in pure water with that in a buffer solution containing 0.60 M  $\text{Na}_2\text{HPO}_4$  and 0.40 M  $\text{NaH}_2\text{PO}_4$  ( $\text{MW}[\text{Zn(OH)}_2] = 99.40$ ,  $K_{\text{sp}}[\text{Zn(OH)}_2] = 4.5 \times 10^{-17}$ ,  $K_{\text{a}1}[\text{H}_3\text{PO}_4] = 7.5 \times 10^{-3}$ ,  $K_{\text{a}2}[\text{H}_3\text{PO}_4] = 6.2 \times 10^{-8}$ ,  $K_{\text{a}3}[\text{H}_3\text{PO}_4] = 4.8 \times 10^{-13}$ ).

(Answer)

$$[\text{Zn}^{2+}] = s, [\text{OH}^-] = 2s$$

$$K_{\text{sp}} = 4s^3 = 4.5 \times 10^{-17}$$

$$s = 2.2 \times 10^{-6} \text{ M} = [\text{Zn}^{2+}]$$

$$\text{Solubility in pure water} = 2.2 \times 10^{-4} \text{ g/L}$$

Using Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(6.2 \times 10^{-8}) + \log(0.6\text{M} / 0.4\text{M}) = 7.4$$

$$\text{pOH} = 14.0 - 7.4 = 6.6, [\text{OH}^-] = 2.51 \times 10^{-7}$$

$$[\text{Zn}^{2+}] = K_{\text{sp}} / [\text{OH}^-]^2 = 4.5 \times 10^{-17} / (2.51 \times 10^{-7})^2 = 7.14 \times 10^{-4} \text{ M}$$

$$\text{Solubility in the buffer solution} = 0.0709 \text{ g/L}$$



10. (2 pt each) Determine whether the following statements are true or false.

(a) Diethyl ether is volatile.

(Answer) T

(b) The entropy of a pure substance in its thermodynamically most stable form is zero at the absolute zero of temperature, independent of pressure.

(Answer) T

(c) Exothermic reactions are spontaneous.

(Answer) F

(d) CuS is more soluble in acid solution than in water.

(Answer) T

(e) When silver nitrate is slowly added to a solution that contains  $\text{Cl}^-$  and  $\text{Br}^-$ , AgCl precipitates first.

(Answer) F

(f) The pH value of neutral water increases, as temperature increases.

(Answer) F

(g) In the formation of complex ions, metals usually act as a Lewis base.

(Answer) F

(h) The pH value of an aqueous  $\text{AlCl}_3$  solution is less than 7.

(Answer) T

(i)  $\Delta G^\circ_{\text{rxn}}$  determines the direction of reaction spontaneity.

(Answer) F,

(j) If A molecules attract B molecules more strongly than they do their own kind, the vapor pressure of the solution will be less than the sum of the vapor pressures as predicted by Raoult's law.

(Answer) T

# Scoring Guidelines

Wrong works and answers: 0 point

FOR partial correct works with wrong answers, 20 % points

FOR Correct works with wrong answer, 50% deduction  
(Unit: If missing, 30% deduction)

FOR Correct works and answers, 100% points

FOR Correct works and answers( $\pm \square\%$ ), 100% points

**2009 FALL Semester Final Examination  
For General Chemistry II (CHEM103)**

*Date: December 16, 2009 (Wed), Time Limit: 7:00 ~ 9:00 p.m.*

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

| Professor Name | Class | Student I.D. | Name |
|----------------|-------|--------------|------|
|                |       |              |      |

| Problem  | points | Problem   | points | TOTAL pts   |
|----------|--------|-----------|--------|-------------|
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(채점답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

- 1) Return and Claim Period: **December 21 (Mon, 9: 00 a.m.) ~ 22 (Tue, 9: 00 a.m.)**
- 2) **Location: Lobby (1<sup>st</sup> floor), GoongNi lab Bldg.**
- 3) Procedure: During the period, you can take your mid-term paper scored. If you have any claims on it, you can submit a claim paper with your opinion. After writing your opinions on any paper you can get easily, attach it with a stapler to your mid-term paper scored (Please, write your name, professor, and class.). Put them into a paper box in front of elevator.. The papers with the claims will be re-examined by TA.

***The claim is permitted only on the period. Keep that in mind!***

***(A solution file with answers will be uploaded on 12/20 at the web.)***

2. Final Confirmation

- 1) Period: **December 22 (Tue, 18:00)- 23 (Wed)**
- 2) Procedure: During this period, you can check final score of the final examination *on the website* again.

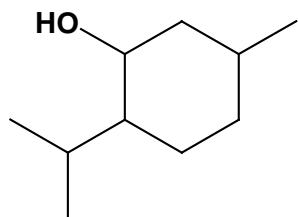
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1. (2 pt each) The atomic number of Fe is 26. The  $\text{Fe}^{3+}$  cation can form a complex ion with six  $\text{F}^-$  or  $\text{CN}^-$  anions. The resultant  $[\text{FeF}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are found to have different magnetic properties.
- A. How many *d*-orbital electrons are there in  $\text{Fe}^{3+}$ ?
  - B. Draw the energy-level diagrams for the free  $\text{Fe}^{3+}$  ion, and the  $[\text{FeF}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  complex ions, by using the crystal field theory.
  - C. How many unpaired electrons does each of the three ions in B have?
  - D. Which is more paramagnetic between  $[\text{FeF}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ ?
  - E. Which complex ion is more stable?
1. A. five  
B. Figure 15.18 in the textbook.  
C. 5 in free  $\text{Fe}^{3+}$ , 5 in  $[\text{FeF}_6]^{3-}$ , 1 in  $[\text{Fe}(\text{CN})_6]^{3-}$   
D.  $[\text{FeF}_6]^{3-}$   
E.  $[\text{Fe}(\text{CN})_6]^{3-}$

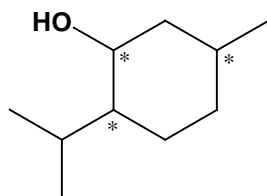
2. (5 pt each) Menthol ( $C_{10}H_{19}O$ ), shown below, is a crystalline organic compound having local anesthetic and counterirritant properties.

A. How many chiral centers does menthol have? Indicate them on the structure.

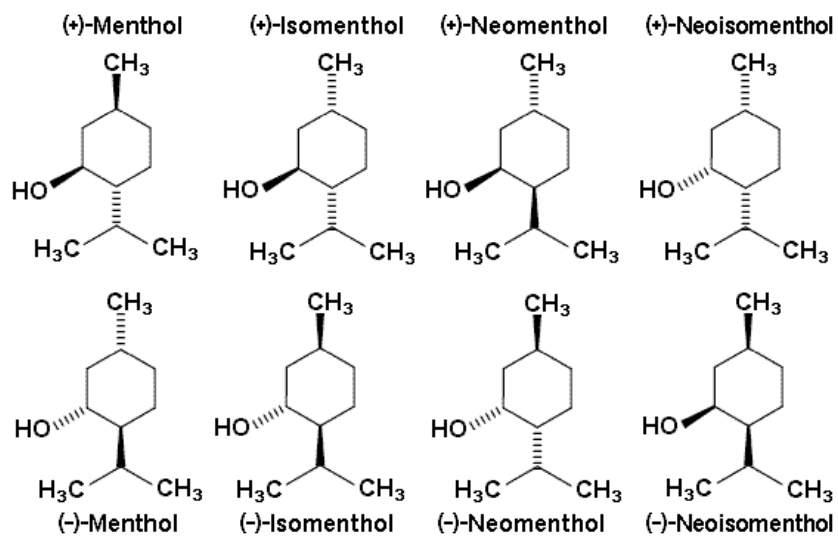
B. Draw all the possible isomers.



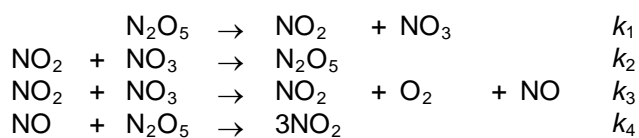
2. A. 3



B. 8 isomers are to be drawn.



3. (10 pt) Derive the rate law for the decomposition reaction of  $\text{N}_2\text{O}_5$ ,  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ , on the basis of the following reaction mechanism.



3. The intermediates are NO and  $\text{NO}_3$ ; by using the steady-state approximation the net rates of change of their concentrations are

$$\begin{aligned}
 d[\text{NO}]/dt &= k_3 [\text{NO}_2][\text{NO}_3] - k_4 [\text{NO}][\text{N}_2\text{O}_5] = 0 \\
 d[\text{NO}_3]/dt &= k_1 [\text{N}_2\text{O}_5] - k_2 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}_2][\text{NO}_3] = 0
 \end{aligned}$$

The net rate of change of concentration of  $\text{N}_2\text{O}_5$  is

$$d[\text{N}_2\text{O}_5]/dt = -k_1 [\text{N}_2\text{O}_5] + k_2 [\text{NO}_2][\text{NO}_3] - k_4 [\text{NO}][\text{N}_2\text{O}_5]$$

and replacing the concentrations of the intermediates by using the equation above gives

$$d[\text{N}_2\text{O}_5]/dt = -2 k_1 k_3 [\text{N}_2\text{O}_5] / (k_2 + k_3)$$

Therefore the rate law is

$$\text{Rate} = 2 k_1 k_3 [\text{N}_2\text{O}_5] / (k_2 + k_3)$$

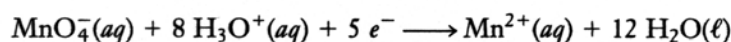
4. (10 pt) The low-resolution proton ( $^1\text{H}$ ) NMR spectrum of ethyl acetate shows three broad peaks, but the high-resolution one shows the splitting of the peaks. How many peaks do you expect to observe in the high-resolution  $^1\text{H}$  NMR spectrum of ethyl acetate (6pts)? Explain why.(4 pts)

4. 8 (4+3+1)

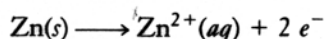


5. (10 pt) An aqueous solution of potassium permanganate ( $\text{KMnO}_4$ ) appears deep purple. In the aqueous acidic solution, the permanganate ion can be reduced to the pale-pink manganese(II) ion ( $\text{Mn}^{2+}$ ). Under the standard conditions, the reduction potential of the  $[\text{MnO}_4^-|\text{Mn}^{2+}]$  half cell is  $\mathcal{E}^\circ = 1.49$  V. Suppose this half-cell is combined with a  $[\text{Zn}^{2+}|\text{Zn}]$  half cell ( $\mathcal{E}^\circ = -0.76$  V) in a galvanic cell, with  $[\text{Zn}^{2+}] = [\text{MnO}_4^-] = [\text{Mn}^{2+}] = [\text{H}_3\text{O}^+] = 1$  M.
- A. (1 pt each) Write the equations for the reactions at the anode and the cathode.  
 B. (2 pt) Write a balanced equation for the overall cell reaction.  
 C. (2 pt) Calculate the standard cell potential difference,  $\mathcal{E}^\circ$ .  
 D. (4 pt) Suppose the cell is operated at pH 2.00 with  $[\text{MnO}_4^-] = 0.12$  M,  $[\text{Mn}^{2+}] = 0.0010$  M, and  $[\text{Zn}^{2+}] = 0.0015$  M. Calculate the cell voltage  $\mathcal{E}$  at 25 °C.

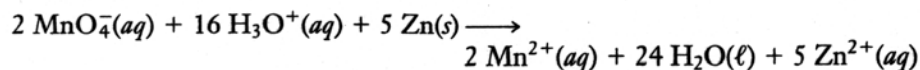
- (a) Because  $\mathcal{E}^\circ(\text{MnO}_4^-|\text{Mn}^{2+}) = 1.49$  V is algebraically greater than  $\mathcal{E}^\circ(\text{Zn}^{2+}|\text{Zn}) = -0.76$  V, permanganate ions will be reduced at the cathode. The balanced half-cell reaction requires the presence of  $\text{H}_3\text{O}^+$  ions and water, giving



The half-equation for the oxidation of Zn at the anode is



- (b) In the overall reaction, the number of electrons taken up at the cathode must equal the number released at the anode, so the first equation must be multiplied by 2 and the second by 5. Adding the two gives the overall reaction:



- (c) The galvanic cell potential is the difference between the standard reduction potential for permanganate (at the cathode) and that for zinc (at the anode):

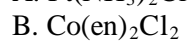
$$\Delta\mathcal{E}^\circ = \mathcal{E}^\circ(\text{MnO}_4^-|\text{Mn}^{2+}) - \mathcal{E}^\circ(\text{Zn}^{2+}|\text{Zn}) = 1.49 - (-0.76) = 2.25 \text{ V}$$

Note that the half-cell potentials are not multiplied by their coefficients (2 and 5) before subtraction. Half-cell potentials are *intensive* properties of a galvanic cell and are therefore independent of the amount of the reacting species.

D. At pH = 2, the concentration of hydronium ion is 0.010 M, and  $n = 10$ .

$$\begin{aligned} \mathcal{E} &= 2.25 - 0.0592/10 \times \log([\text{Mn}^{2+}]^2 [\text{Zn}^{2+}]^5)/([\text{MnO}_4^-]^2 [\text{H}_3\text{O}^+]^{16}) \\ &= 2.25 - 0.0592/10 \times \log(5.3 \times 10^{18}) = 2.14 \text{ (V)} \end{aligned}$$

6. (5 pt each) Draw all the isomers of the following coordination compounds.



6. A. Two isomers: *cis* and *trans* isomers with the planar structure. See Figure 15.10.

B. Three isomers: two optical isomers in *cis*, and one isomer in *trans*. See Figure 15.12.

7. (2 pt each) Which reaction is used for the synthesis of the following polymers, addition or condensation reactions?
- A. PVC
  - B. Nylon-66
  - C. Proteins
  - D. Teflon
  - E. Polystyrene (PS)

7. A. addition; B. condensation; C. condensation; D. addition; E. addition

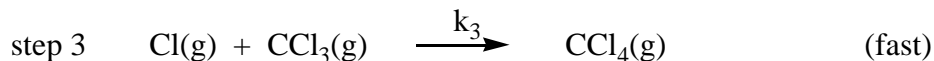
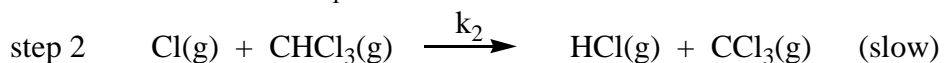
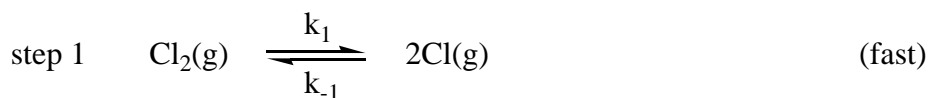
8. (2 pt each) Choose a capital letter for each statement.

A: amide      B: amine      C: alcohol      D: ester  
E: ether      F: carboxylic acid      G: none of the above

- a) \_\_\_\_\_ This functional group is present in the monomer of polyethylene.
- b) \_\_\_\_\_ This functional group contains no oxygen.
- c) \_\_\_\_\_ This functional group holds the monomers of silk and nylon.
- d) \_\_\_\_\_ The odor of fruits is mainly due to the molecules containing this functional group.
- e) \_\_\_\_\_ This functional group is needed to make polyester with a carboxylic acid.

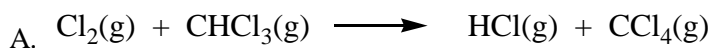
8. G, B, A, D, C

9. (2 pt each) The following mechanism was proposed for the gas phase reaction of chloroform and chlorine.



- What is the overall reaction?
- What are the intermediates in the mechanism?
- What is the molecularity of each of the elementary steps?
- What is the rate determining step?
- What is the rate law and overall order of the reaction predicted by this mechanism?

9.



B.  $\text{Cl}(\text{g}), \text{CCl}_3(\text{g})$

C. step 1: unimolecular, step 2: bimolecular, step 3: bimolecular

D. step 2

E.  $\text{Rate} = k_2[\text{CHCl}_3][\text{Cl}]$

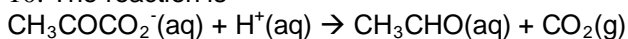
$$k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2, [\text{Cl}] = \left\{ \frac{k_1}{k_{-1}} [\text{Cl}_2] \right\}^{1/2}$$

$$\text{Rate} = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{CHCl}_3][\text{Cl}_2]^{1/2}$$

Overall order is **1.5**

10.(10 pt) The elimination of carbon dioxide from the pyruvate ion ( $\text{CH}_3\text{COCO}_2^-$ ) by a decarboxylase enzyme in the acidic medium was monitored by measuring the partial pressure of the gas, as it was formed in a  $250 \text{ cm}^3$  flask at  $20^\circ\text{C}$ . In one experiment, the partial pressure increased from zero to 100 Pa in 522 seconds in a first-order reaction when the initial concentration of pyruvate in  $100 \text{ cm}^3$  of solution was 3.23 mM. What is the rate constant of the reaction? ( $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ )

10. The reaction is



We can assume that the concentration of pyruvate (P) decreases in proportion to the increase in  $p_{\text{CO}_2}$ . For the  $\text{CO}_2(\text{g})$  formed, we may write

$$pV = nRT$$

$$n_{\text{CO}_2} = pV/RT = V p_{\text{CO}_2}/RT = (250 \times 10^{-6} \text{ m}^3 \times 100 \text{ Pa}) / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}) = 0.0103 \text{ mmol} = \Delta n_P.$$

$$[\text{P}] = [\text{P}]_0 - \Delta n_P / 0.100 \text{ L} = 3.23 \text{ mM} - 0.103 \text{ mM} = 3.13 \text{ mM}$$

For a first-order reaction,

$$[\text{P}] = [\text{P}]_0 e^{-kt}$$

$$k = -\ln([\text{P}]/[\text{P}]_0)/t = \ln(3.13 \text{ mM}/3.23 \text{ mM})/522 \text{ s} = 6.02 \times 10^{-5} \text{ s}^{-1}.$$