

**2012 FALL Semester Midterm Examination  
For General Chemistry II (CH103)**

**Date: October 25 (Thu), Time Limit: 14:30 ~ 16:30**

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. Number	Name

Problem	points	Problem	points	TOTAL pts
<b>1</b>	/16	<b>7</b>	/10	<b>/100</b>
<b>2</b>	/6	<b>8</b>	/6	
<b>3</b>	/5	<b>9</b>	/6	
<b>4</b>	/6	<b>10</b>	/14	
<b>5</b>	/8	<b>11</b>	/16	
<b>6</b>	/7			

\*\* This paper consists of 11 sheets with 11 problems (page 9: claim form, page 10: periodic table, page 11: fundamental constants). Please check all page numbers before taking the exam. Write down your work and answers in the sheet.

Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

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 29 (Mon, 7: 00 ~ 8:00 p.m.)**
- 2) **Location: Room for quiz session**
- 3) Procedure:

**Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)**

**Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)**

If you have any claims on it, you can submit the claim paper with your opinion. After writing your opinions on the claim form, attach it to your mid-term paper with a stapler. Give them to TA.

(The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 10/29 on the web.)

2. Final Confirmation

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

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

<The Answers>

Problem	points	Problem	points	TOTAL pts
<b>1</b>	3+3+5+5/16	<b>7</b>	5+5/10	<b>/100</b>
<b>2</b>	2+2+2/6	<b>8</b>	3+3/6	
<b>3</b>	/5	<b>9</b>	3+3/6	
<b>4</b>	3+3/6	<b>10</b>	3+3+2+2+4/14	
<b>5</b>	2+3+3/8	<b>11</b>	4+4+5+3/16	
<b>6</b>	2+5/7			

1.

(a) A 1.00% aqueous solution of NaCl will contain 1.00 g of NaCl for 99.0 g of water. To use the freezing point depression equation, we need the molality of the solution:

$$\text{molality} = \frac{\left( \frac{1.00 \text{ g}}{58.44 \text{ g} \cdot \text{mol}^{-1}} \right)}{0.0990 \text{ kg}} = 0.173 \text{ mol} \cdot \text{kg}^{-1}$$

$$\Delta T_f = i k_f m$$

$$\Delta T_f = i (1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})(0.173 \text{ mol} \cdot \text{kg}^{-1}) = 0.593 \text{ K}$$

$$i = 1.84$$

(b) molality of all solute species (undissociated NaCl(aq) plus Na<sup>+</sup>

$$\text{(aq)} + \text{Cl}^- \text{(aq)}) = 1.84 \times 0.173 \text{ mol} \cdot \text{kg}^{-1} = 0.318 \text{ mol} \cdot \text{kg}^{-1}$$

(c) If all the NaCl had dissociated, the total molality in solution would have been 0.346 mol · kg<sup>-1</sup>, giving an *i* value equal to 2. If no dissociation had taken place, the molality in solution would have equaled 0.173 mol · kg<sup>-1</sup>.



$$(0.173 \text{ mol} \cdot \text{kg}^{-1} - x) \quad x \quad x$$

$$0.173 \text{ mol} \cdot \text{kg}^{-1} - x + x + x = 0.318 \text{ mol} \cdot \text{kg}^{-1}$$

$$0.173 \text{ mol} \cdot \text{kg}^{-1} + x = 0.318 \text{ mol} \cdot \text{kg}^{-1}$$

$$x = 0.145 \text{ mol} \cdot \text{kg}^{-1}$$

$$\% \text{ dissociation} = \left( \frac{0.145 \text{ mol} \cdot \text{kg}^{-1}}{0.173 \text{ mol} \cdot \text{kg}^{-1}} \right) (100) = 83.8\%$$

d)

$$m = \frac{\Delta T_b}{K_b} = \frac{0.029^\circ\text{C}}{0.51^\circ\text{C} m^{-1}} = 0.057 m = 0.057 \text{ mol kg}^{-1}$$

in 100 g solvent 0.0057 mol solute

$$M = \frac{1.0 \text{ g}}{0.0057 \text{ mol}} = 1.8 \times 10^2 \text{ g mol}^{-1}$$

molecular formula is  $\text{C}_6\text{H}_{12}\text{O}_6$  (sugar glucose)

2.

(a) For methanol and ethanol, we expect the types of intermolecular attractions in the mixture to be similar to those in the component liquids, so that an ideal solution is predicted.

(b) For HF and  $\text{H}_2\text{O}$ , the possibility of intermolecular hydrogen bonding between water and HF would suggest that negative deviation would be observed, which is the case.

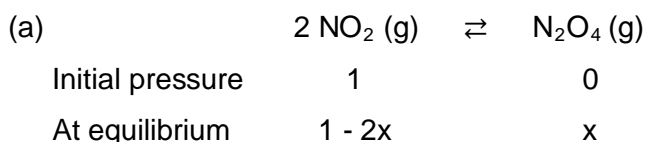
(c) Because hexane is nonpolar and water is polar with hydrogen bonding, we would expect a mixture of these two to exhibit positive deviation (the interactions between the different molecules would be weaker than the intermolecular forces between like molecules).

$$3. K = (K_1)^2 = (3.1 \times 10^4)^2$$

$$\Delta n = 4 - (4 + 2) = -2, T = 400 + 273.15 \text{ K} = 673 \text{ K}$$

$$K_c = (RT)^{-\Delta n} K = (0.083145 \text{ K}^{-1} \times 673 \text{ K})^2 \times (3.1 \times 10^4)^2 = 2.9 \times 10^{12}$$

4.



$$K = x / (1 - 2x)^2 = 6.97 \quad x = 0.383$$

$$P_{\text{NO}_2} = 0.234 \text{ atm}, P_{\text{N}_2\text{O}_4} = 0.383 \text{ atm}$$

$$(b) P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4} = 1 \text{ atm}, \quad K = P_{\text{N}_2\text{O}_4} / P_{\text{NO}_2}^2 = x / (1 - x)^2 = 6.97$$

$$x = 0.686$$

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

5. (a) Lewis acid:  $\text{CO}_2$ , Lewis base:  $\text{H}_2\text{O}$

(b) The  $-\text{CCl}_3$  group that is bonded to the carboxyl group,  $-\text{COOH}$ , in trichloroacetic acid, is more electron withdrawing than the  $\text{CH}_3$  group in acetic acid. Thus, trichloroacetic acid is the stronger acid.

(c) The  $-\text{CH}_3$  group in acetic acid has electron-donating properties, which means that it is less electron withdrawing than the  $-\text{H}$  attached to the carboxyl group in formic acid,  $\text{HCOOH}$ . Thus, formic acid is a slightly stronger acid than acetic acid.

$$6. (a) \text{pH} = -\log(6.55 \times 10^{-7}) = 6.184$$

(b)

We can use the relationship derived in the text,

$$[\text{H}_3\text{O}^+]^2 - [\text{HA}]_{\text{initial}}[\text{H}_3\text{O}^+] - K_w = 0, \text{ in which HA is any strong acid.}$$

$$[\text{H}_3\text{O}^+]^2 - (6.55 \times 10^{-7})[\text{H}_3\text{O}^+] - (1.00 \times 10^{-14}) = 0$$

Solving using the quadratic equation gives

$$[\text{H}_3\text{O}^+] = 6.70 \times 10^{-7}, \text{pH} = 6.174.$$

7.

(a) This value is calculated as described in Example 11.12. First, we calculate the molarity of the starting phosphorous acid solution:

$$\frac{0.122 \text{ g}}{81.99 \text{ g} \cdot \text{mol}^{-1}} / 0.0500 \text{ L} = 0.0298 \text{ mol} \cdot \text{L}^{-1}. \text{ We then use the first acid}$$

dissociation of phosphorous acid as the dominant equilibrium. The

$K_{a1}$  is  $1.0 \times 10^{-2}$ . Let  $\text{H}_2\text{P}$  represent the fully-protonated phosphorus acid.

Concentration

(mol · L <sup>-1</sup> )	$\text{H}_2\text{P}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HP}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$			
initial	0.0298	—	0	0
change	-x	—	+x	+x
final	0.0298 - x	—	+x	+x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HP}^-]}{[\text{H}_2\text{P}]} = 1.0 \times 10^{-2}$$

$$1.0 \times 10^{-2} = \frac{x \cdot x}{0.0298 - x} = \frac{x^2}{0.0298 - x}$$

If we assume  $x \ll 0.0298$ , then the equation becomes

$$x^2 = (1.0 \times 10^{-2})(0.0298) = 2.98 \times 10^{-4}$$

$$x = 1.73 \times 10^{-2}.$$

Because this value is more than 10% of 0.0300, the full quadratic solution should be undertaken. The equation is

$$x^2 = (1.0 \times 10^{-2})(0.0298 - x) \text{ or}$$

$$x^2 + (1.0 \times 10^{-2}x) - (2.98 \times 10^{-4}) = 0.$$

Using the quadratic formula, we obtain  $x = 0.013$ .

$$\text{pH} = 1.89$$

The calculation is performed as in part (a):

$$1.0 \times 10^{-2} = \frac{(0.0159 + x)x}{0.0112 - x}$$

$$x = 3.75 \times 10^{-3}$$

$$\text{pH} = 2.42$$

8. At pH = 12, the effective charge of lysine is -1, and that of tyrosine is -2.

9.

$$(a) K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$5.5 \times 10^{-5} = (x)(2x)$$

$$X = 2.4 \times 10^{-2} \text{ mol/L}$$

$$2.4 \times 10^{-2} \text{ mol/L} \times 74 \text{ g/mol} \times 0.5 \text{ L} = 0.89 \text{ g}$$

$$(b) [\text{OH}^-]^2 = 2 \times 2.4 \times 10^{-2} \text{ M}$$

$$\text{pOH} = 1.32$$

$$\text{pH} = 14 - 1.32 = 12.68$$

$$10. (a) \Delta G^\circ = -nFE^\circ_{\text{cell}} = -2.303RT \log K$$

$$-2 \times 9.65 \times 10^4 \text{ C/mol} \times 1.10 \text{ V}$$

$$= -2.303 \times 8.31 \text{ J/(mol}\cdot\text{K)} \times 298 \text{ K} \times \log K$$

$$\log K = 37.2$$

$$K = 1.6 \times 10^{37}$$

(b)

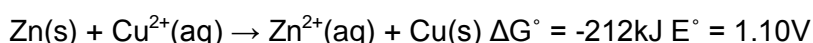
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.001}{10.0} = 1.00 \times 10^{-4}$$

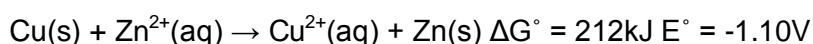
$$n = 2$$

$$\begin{aligned} E_{\text{cell}} &= 1.10 - \frac{0.0592}{2} \log (1.0 \times 10^{-4}) \\ &= 1.10 - (-0.12) \\ &= 1.22 \text{ V} \end{aligned}$$

(c) A spontaneous redox reaction occurs, driven forward by a fall in free energy.



(d) Nothing.



is not spontaneous.  $\text{Zn}^{2+}$  does not oxidize copper.

(e)

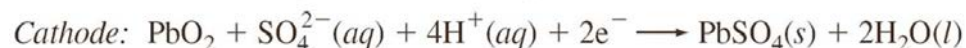
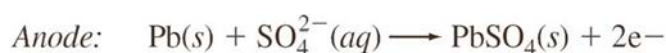
$$1 \text{ mol Cu} = 2 \text{ mol } e^{-}$$

$$0.404 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.6 \text{ g Cu}} \times \frac{2 \text{ mol } e^{-}}{1 \text{ mol Cu}} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol } e^{-}}$$

$$= 1.23 \times 10^3 \text{ C}$$

$$\text{Current} = \frac{\text{charge}}{\text{time}} = \frac{1.23 \times 10^3 \text{ C}}{5 \text{ hr} \times 3600 \text{ s/hr}} = \frac{1.23 \times 10^3 \text{ C}}{1.80 \times 10^4 \text{ s}} = 6.83 \times 10^{-2}$$

11. (a)



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(b) (Volume of the acid solution = 724 ml)

$$\text{Initial mass of H}_2\text{SO}_4 = 724 \times 1.29 \times 0.38 = 355 \text{ g}$$

$$\text{Initial conc of [H}_2\text{SO}_4] = (355 / 98.09) / 0.724 = 5.0 \text{ M}$$

$$[\text{SO}_4^{2-}] = 5 \text{ M}, [\text{H}_3\text{O}^{+}] = 10 \text{ M}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 1.46 - (-0.36) = 1.82 \text{ v}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

$$Q = 1 / ([\text{SO}_4^{2-}]^2 [\text{H}^+]^4) = 1 / (5^2 \times 10^4) = 4 \times 10^{-6}$$

$$E = E^{\circ} - RT/nF \ln Q = E^{\circ} - RT/2F \ln Q$$

$$= 1.82 - (0.05917 / 2) \log 4 \times 10^{-6}$$

$$= 1.82 - 0.02959 \log 4 \times 10^{-6} = 1.98 \text{ v}$$

(c)

The overall reaction is:  $\text{Pb} + \text{PbO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}$

Initial mass of  $\text{H}_2\text{SO}_4$ :  $724 \text{ mL} \times 1.29 \text{ g} / 1 \text{ mL} \times 0.380 = 355 \text{ g}$

Final mass of  $\text{H}_2\text{SO}_4$ :  $724 \text{ mL} \times 1.19 \text{ g} / 1 \text{ mL} \times 0.260 = 224 \text{ g}$

Mass of  $\text{H}_2\text{SO}_4$  reacted  $\square 355 \text{ g} - 224 \text{ g} = 131 \text{ g}$

Moles of  $\text{H}_2\text{SO}_4$  reacted  $= 131 \text{ g} \times \frac{1 \text{ mol}}{98.09 \text{ g}} = 1.34 \text{ mol}$

$$Q = 1.34 \text{ mol H}_2\text{SO}_4 \times \frac{2 \text{ mol } e^-}{2 \text{ mol H}_2\text{SO}_4} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = \mathbf{1.29 \times 10^5 \text{ C}}$$

$$(d) \ t = \frac{Q}{I} = \frac{1.29 \times 10^5 \text{ C}}{22.4 \text{ A}} = 5.76 \times 10^3 \text{ s} = \mathbf{1.60 \text{ hr}}$$



1. (Total 16 pts) A 1.00 wt % NaCl(aq) solution has a freezing point of  $-0.593\text{ }^{\circ}\text{C}$ .  $k_f$  of water is  $1.86\text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$ .

(a) (3 pts) Estimate the van't Hoff  $i$  factor from the data.

**(Answer)**

(b) (3 pts) Determine the total molality of all solute species. The molality calculated from the freezing point depression is the sum of the molalities of the undissociated NaCl(aq),  $\text{Na}^+(\text{aq})$ , and  $\text{Cl}^-(\text{aq})$ .

**(Answer)**

(c) (5 pts) Calculate the percentage dissociation of NaCl in this solution.

**(Answer)**

(d) (5 pts) A 1.0 g sample of an unknown molecular compound  $C_nH_{2n}O_n$ , dissolved in 100 g of water, produces a boiling point elevation of  $0.029\text{ }^\circ\text{C}$  ( $k_b = 0.51\text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$ ). Compute the molar mass and molecular formula.

**(Answer)**

2. (total 6 pts) Which of the following mixtures would you expect to show a positive deviation, negative deviation, or no deviation (that is, form an ideal solution) from Raoult's law? Explain your conclusion.

(a) (2 pts) methanol,  $CH_3OH$ , and ethanol,  $CH_3CH_2OH$

**(Answer)**

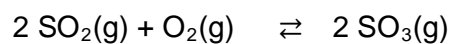
(b) (2 pts) HF and  $H_2O$

**(Answer)**

(c) (2 pts) hexane,  $C_6H_{14}$ , and  $H_2O$

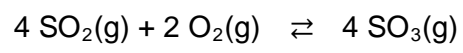
**(Answer)**

3. (total 5 pts) At  $400\text{ }^\circ\text{C}$ , the equilibrium constant of the following reaction,



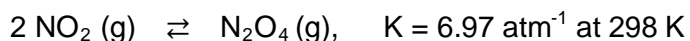
is  $3.1 \times 10^4$ . What is the value of  $K_c$  (equilibrium constant in terms of concentration) for the following

reaction at 400 °C?



**(Answer)**

4. (total 6 pts) Nitrogen dioxide gas ( $\text{NO}_2$ ) undergoes dimerization reaction to  $\text{N}_2\text{O}_4(\text{g})$  at 298 K.



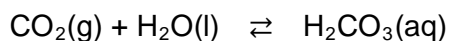
(a) (3 pts) Calculate the partial pressure of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at equilibrium when the initial pressure of  $\text{NO}_2$  was 1 atm, and there was no  $\text{N}_2\text{O}_4$  at the beginning.

**(Answer)**

(b) (3 pts) What are the partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , if the total pressure at the equilibrium is 1 atm?

**(Answer)**

5. (total 8 pts) (a) (2 pts) The hydration of carbon dioxide produces carbonic acid as shown in the following chemical equation. Identify the acid and the base of this reaction based on Lewis definition of acids and bases.



**(Answer)**

(b) (3 pts) Suggest an explanation for the different strength of acetic acid and trichloroacetic acid.

**(Answer)**

(c) (3 pts) Suggest an explanation for the different strength of acetic acid and formic acid.

**(Answer)**

6. (total 7 pts) (a) (2 pts) Calculate the pH of  $6.55 \times 10^{-7}$  M  $\text{HClO}_4(\text{aq})$ , ignoring the effect of the autoprotolysis of water.

**(Answer)**

(b) (5 pts) Repeat the calculations, taking into account the autoprotolysis of water.

**(Answer)**

7. (total 10 pts) Suppose that 0.122 g of phosphorus acid,  $\text{H}_3\text{PO}_3$ , is dissolved in water and that the total volume of the solution is 50.0 mL.  $K_{a1}$  is  $1.0 \times 10^{-2}$ .

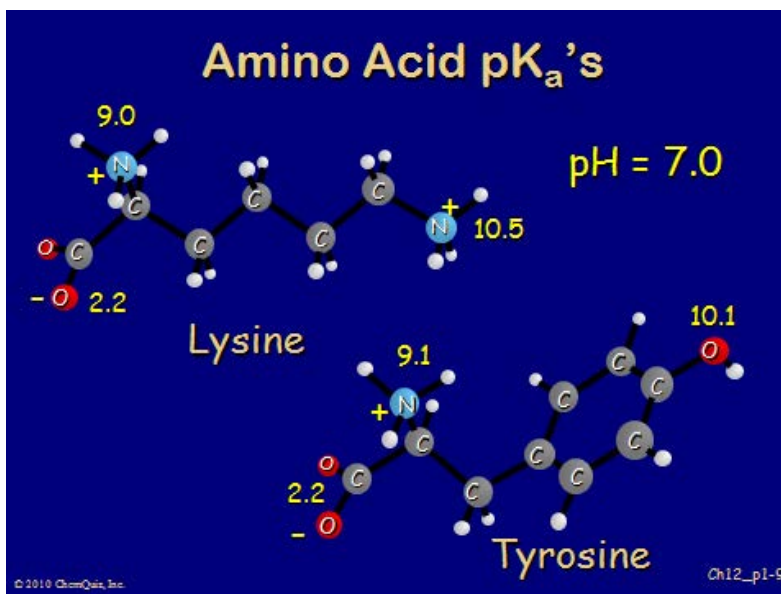
(a) (5 pts) Estimate the pH of this solution.

**(Answer)**

(b) (5 pts) Estimate the pH of the solution that results when 5.00 mL of 0.175 M  $\text{NaOH}(\text{aq})$  is added to the phosphorus acid solution.

**(Answer)**

8. (Total 6 pts) Two of amino acids are shown with pK<sub>a</sub>'s for all acid(base) sites and their expected form at pH=7.0. In this case, the effective charge of lysine is +1 and that of tyrosine 0. What will be the effective charges of these two amino acids at pH = 12?



**(Answer)**

9. (total 6 pts) Calcium hydroxide is a slightly soluble base ( $K_{sp} = 5.5 \times 10^{-5}$ ). A 1.0 g sample of solid  $\text{Ca}(\text{OH})_2$  is shaken with 0.5 L of water.

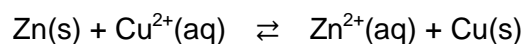
(a) (3 pts) Calculate the mass (grams) of  $\text{Ca}(\text{OH})_2$  that dissolves.

**(Answer)**

(b) (3 pts) What is the pH of the saturated  $\text{Ca}(\text{OH})_2$  solution formed in this process?

**(Answer)**

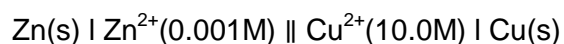
10. (total 14 pts) (a) (3 pts) Calculate the equilibrium constant at 25 °C for the reaction.



The corresponding standard cell potential is 1.10V.

**(Answer)**

(b) (3 pts) Which is the potential at 25 °C of the following cell?



**(Answer)**

(c) (2 pts) What happens when we dip a strip of zinc into a solution of  $\text{CuSO}_4$ ?

**(Answer)**

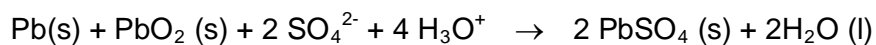
(d) (2 pts) What happens when we dip a strip of copper into a solution of  $\text{ZnSO}_4$ ?

**(Answer)**

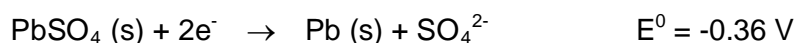
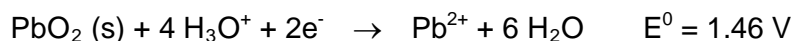
(e) (4 pts) When an aqueous solution of copper(II) sulfate,  $\text{CuSO}_4$ , is electrolyzed, copper metal is deposited. If a constant current was passed for 5 h and 404 mg of copper metal were deposited, what must have been the current?

**(Answer)**

11. (total 16 pts) The concentration of sulfuric acid in the lead storage battery of an automobile over a period of time has decreased from 38.0% by mass (density = 1.29 g mL<sup>-1</sup>) to 26 % (density = 1.19 g mL<sup>-1</sup>) at 25 °C. Assume the volume of the acid remains constant at 724 mL and all the sulfuric acid is dissociated to SO<sub>4</sub><sup>2-</sup> and H<sub>3</sub>O<sup>+</sup>. The overall reaction is as follows.



Standard reduction potential



(a) (4 pts) Write the half cell reactions at anode and cathode.

**(Answer)**

(b) (4 pts) What is the initial cell potential?

**(Answer)**

(c) (5 pts) Calculate the total charge in coulombs supplied by the battery.

**(Answer)**

(d) (3 pts) How long (in hours) will it take to recharge the battery back to the original sulfuric acid concentration using a current of 22.4 A?

**(Answer)**



**2013 FALL Semester Final Examination  
for General Chemistry II (CH103)**

**Date: December 20 (Thu), Time Limit: 2:30 ~ 4:30 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. Number	Name

Problem	points	Problem	points	TOTAL pts
<b>1</b>	/10	<b>6</b>	/11	<b>/100</b>
<b>2</b>	/12	<b>7</b>	/12	
<b>3</b>	/12	<b>8</b>	/15	
<b>4</b>	/8	<b>9</b>	/12	
<b>5</b>	/8			

\*\* This paper consists of 12 sheets with 9 problems (page 10,11: constants & periodic table, page 12: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the space. Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

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

1. Period, Location and Procedure

- 1) Return and Claim Period: **December 21 (Friday, 12:00 ~ 14:00, 2 hours)**
- 2) **Location: Creative Learning Bldg.(E11)**

Class	Room
<b>A</b>	<b>205</b>
<b>B</b>	<b>206</b>
<b>C</b>	<b>207</b>
<b>D</b>	<b>208</b>
<b>E</b>	<b>211</b>

3) Claim Procedure:

**Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)**

**Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)**

(During the period, you can check the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it.)

To get more information, visit the website at [www.gencheminkaist.pe.kr](http://www.gencheminkaist.pe.kr).

2. Final Confirmation

- 1) Period: **December 22 (Sat, 24 hours)**
- 2) Procedure: During this period, you can check final score of the examination *on the website* again.

**2013 FALL Semester Final Examination  
for General Chemistry II (CH103)**

Problem	points	Problem	points	TOTAL pts
<b>1</b>	5+3+2/10	<b>6</b>	3+8/11	<b>/100</b>
<b>2</b>	12/12	<b>7</b>	6+6/12	
<b>3</b>	5+3+4/12	<b>8</b>	3+3+3+3+3/15	
<b>4</b>	4+4/8	<b>9</b>	3+3+3+3/12	
<b>5</b>	4+4/8			

1.

(a) (5 points)

rate =  $-d[\text{OH}^-]/dt = k[\text{OH}^-][\text{NH}_4^+]$  (first order in both  $\text{OH}^-$  and  $\text{NH}_4^+$  concentration)

Throughout the reaction,  $[\text{OH}^-] = [\text{NH}_4^+]$

Let this concentration be represented by  $c$  ( $[\text{OH}^-] = [\text{NH}_4^+] = c$ )

$$-dc/dt = kc^2$$

$$1/c = 1/c_0 + kt$$

$$c_0 = \text{initial concentration} = 1.0 \times 10^{-3} / 2 = 5.0 \times 10^{-4} \text{ M}$$

$$c = \text{final concentration} = 1.0 \times 10^{-5} \text{ M}$$

$$k = 3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 20^\circ \text{C}$$

$$\therefore \mathbf{t = 2.9 \times 10^{-6} \text{ sec}}$$

(b1) (3 points)

$$\ln[A/A_0] = -kt = -(0.693/6.3) \times 15$$

Fraction remaining = 0.19

**Fraction decomp. = 0.81**

(b2) (2 points)

Half of the  $\text{N}_2\text{O}$  has reacted. That is 1.2 moles. Decomp. of 1.2 mole of  $\text{N}_2\text{O}$  forms **0.6 moles of  $\text{O}_2$** .

2. (12 points)

Equilibrium

$$k_1[\text{I}_2] = k_{-1}[\text{I}]^2 \rightarrow [\text{I}] = \sqrt{(k_1/k_{-1}) [\text{I}_2]^{1/2}} \quad (1)$$

$$-d[\text{I}_2]/dt = k_{\text{obs}}[\text{C}_2\text{O}_4^{2-}][\text{I}_2]^{1/2} = k_1[\text{I}_2] - k_{-1}[\text{I}]^2 \quad (2)$$

$$d[\text{I}]/dt = 2k_1[\text{I}_2] - 2k_{-1}[\text{I}]^2 - k_2[\text{I}][\text{C}_2\text{O}_4^{2-}] - k_3[\text{I}][\text{C}_2\text{O}_4^-] = 0 \text{ (SSA)} \quad (3)$$

$$d[\text{C}_2\text{O}_4^-]/dt = k_2[\text{I}][\text{C}_2\text{O}_4^{2-}] - k_3[\text{I}][\text{C}_2\text{O}_4^-] = 0 \text{ (SSA)} \quad (4)$$

$$(3) - (4) \quad 2k_1[I_2] - 2k_{-1}[I]^2 - 2k_2[I][C_2O_4^{2-}] = 0 \quad (5)$$

$$(2) - 1/2(5) \quad -d[I_2]/dt = k_2[I][C_2O_4^{2-}] = k_2 \sqrt{(k_1/k_{-1})} [I_2]^{1/2} [C_2O_4^{2-}]$$

$$\underline{k_{obs} = k_2 \sqrt{\frac{k_1}{k_{-1}}}}$$

3.

(a) (5 points)

$$k = A \exp(-E_a/RT)$$

$$\ln(k_1/k_2) = E_a/R \times (1/T_2 - 1/T_1)$$

$$E_a = R(\ln k_1 - \ln k_2) / (1/T_2 - 1/T_1)$$

$$= (1.9827 \text{ calK}^{-1}\text{mol}^{-1})(-1.6534)/(-1.7857 \times 10^{-4} \text{ K}^{-1})$$

$$= 18.35 \text{ kcalmol}^{-1}$$

$$A = k \exp(E_a/RT) = (6.74 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \times \exp(18.35/(1.9827 \times 800))$$

$$= \underline{7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}}$$

(b) (3 points)

$$\Delta H_R = 104 - 88 = 16 \text{ kcalmol}^{-1}$$

$$E_a (\text{reverse}) = 18.35 - 16 = 2.4 \text{ kcalmol}^{-1}$$

(c) (4 points)

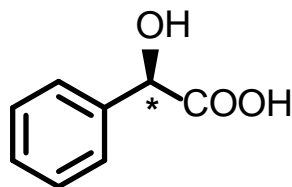
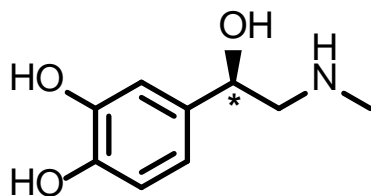
$$k'/k = A/A \exp[(E_a - E_a') / RT] = 10^{15}$$

$$E_a - E_a' = (RT) \ln(10^{15}) = (1.9827 \times 100) (15) (2.303) = \underline{6.85 \text{ kcalmol}^{-1}}$$

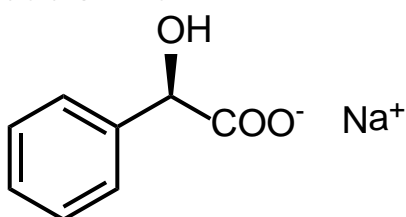
**No, it is not possible. The reduction of  $E_a$  (6.8 kcalmol<sup>-1</sup>) is larger than the activation energy for the reverse reaction (2.4 kcalmol<sup>-1</sup>).**

4.

(a) (4 points)

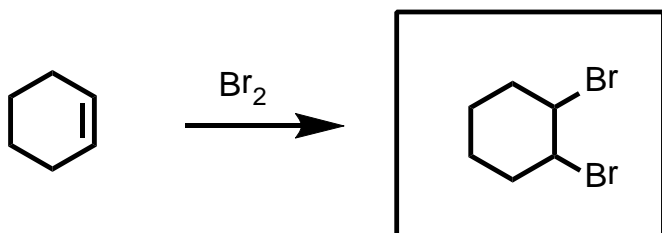


(b) (4 points)

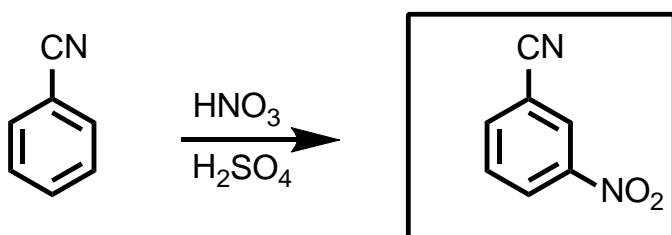


5.

(a) (4 points)



(b) (4 points)



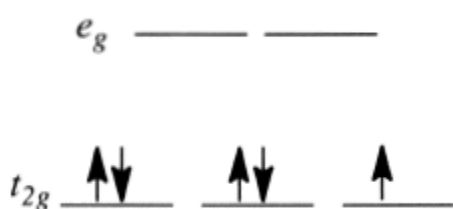
6.

(a) (3 points)

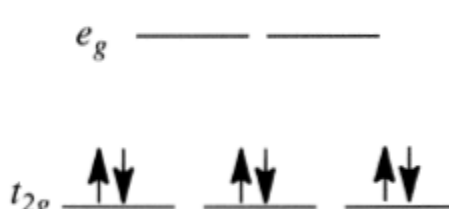
P (Group 15) atoms are replaced by Te (Group 16), and then this is **n-type doping**.

(b) (8 points)

$\text{CN}^-$  is a strong field ligand which leads to form low spin complexes.

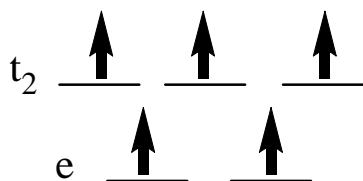


$[\text{Fe}(\text{CN})_6]^{3-}$  ion, **low spin complex**,  
 **$t_{2g}^5$  configuration**, paramagnetic

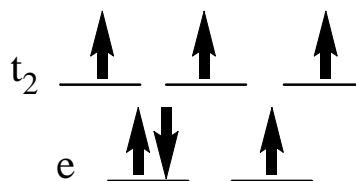


$[\text{Fe}(\text{CN})_6]^{4-}$  ion, **low spin complex**,  
 **$t_{2g}^6$  configuration**, diamagnetic

$\text{Cl}^-$  is a weak field ligand which leads to form tetrahedral high spin complexes.



$[\text{FeCl}_4]^-$  ion, **high spin complex**,  
 **$e^2 t_2^3$  configuration**, paramagnetic

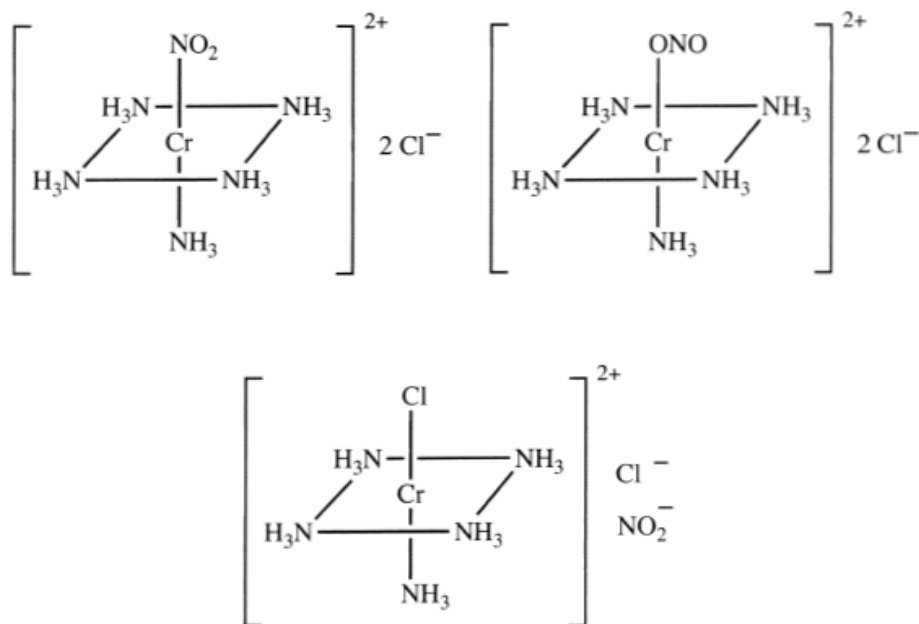


$[\text{FeCl}_4]^{2-}$  ion, **high spin complex**,  
 **$e^3 t_2^3$  configuration**, paramagnetic

7.

(a) (6 points)

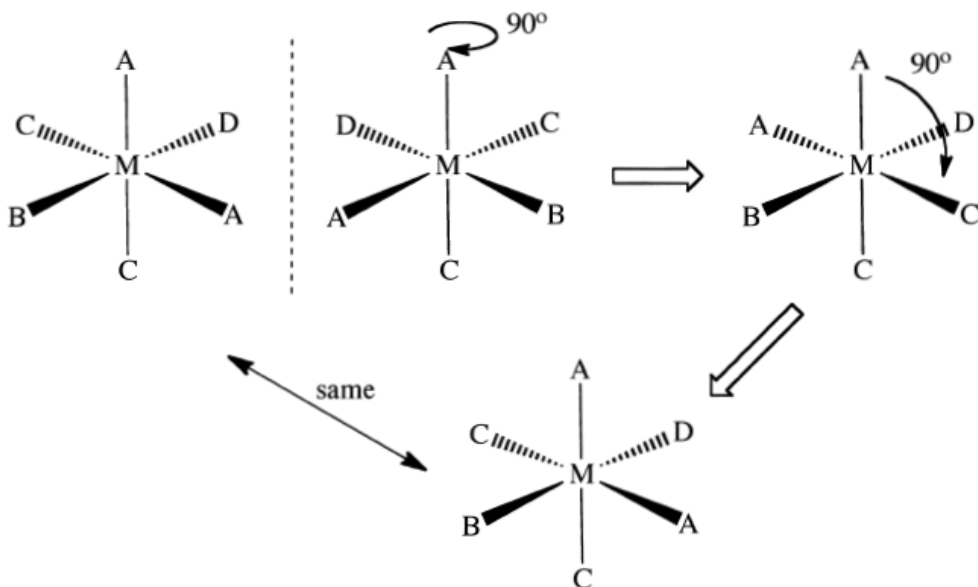
Since nitro can bind as  $\text{NO}_2$  or  $\text{ONO}$ , two linkage isomers are possible, as well as one ionization isomer:



(b) (6 points)

(b1) chiral, form an enantiomeric pair

(b2) not chiral; superimposable with its mirror image



8.

(a) (3 points)

The molecular weight of one  $\alpha$ -helical coiled coil structure is 35,000 dalton.

$$35,000/110 = 318 \text{ amino acids}$$

one rise per residue in  $\alpha$ -helical structure is 1.5 Å

$$318 \times 1.5 \text{ Å} = \underline{477 \text{ Å}}$$

(b) (3 points)

$$40 - 4 = 36$$

$$36/2 = 18$$

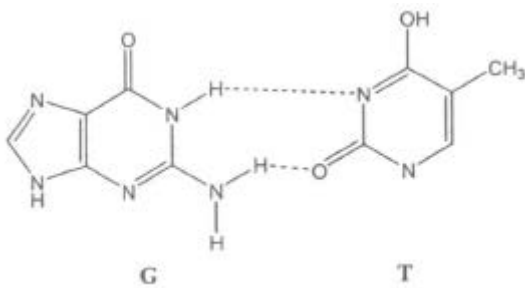
Each  $\beta$  strand has 18 amino acids.

The distance between 2 successive amino acids in  $\beta$  structure is 3.5 Å

$$3.5 \text{ Å} \times 18 = \underline{63 \text{ Å}}$$

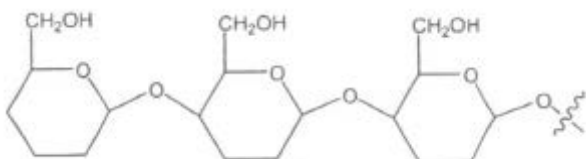
(c) (3 points)

Hydrogen bonded to guanine(G) instead of adenine(A).



(d) (3 points)

Cellulose is a linear polymer of  $\beta$ -glycoside unit. Therefore, human who has an  $\alpha$ -glycosidase cannot digest  $\beta$ -glycoside unit.



(e) (3 points)

5'-UAACGGUACGAU-3'

9.

(a) (3 points)

$A-A + B-B + B_4$  : **Crosslinked polymers** (가교된 고분자)

(b) (3 points)

$A-B + B_4$  : **Branched polymer** (more accurately, polymers with 2 branches, 두 개의 곁가지를 (branch)를 갖는 고분자)

(c) (3 points)

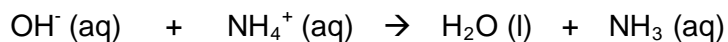
$AB_2 + AB$  : **Highly branched polymers** (or Hyperbranched polymers, 많은 곁가지를 (branch)를 갖는 고분자, 하이퍼브랜치 고분자)

(d) (3 points)

$AB_2 + A_3$  : **Crosslinked polymers** (가교된 고분자)

1. (10 points)

(a) The rate for the reaction



is first order in both  $[\text{OH}^-]$  and  $[\text{NH}_4^+]$ , and the rate constant  $k$  at  $20^\circ\text{C}$  is  $3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . Suppose 1.00 L of a 0.0010 M NaOH solution is rapidly mixed with the same volume of 0.0010 M  $\text{NH}_4\text{Cl}$  solution. Calculate **the time (in seconds)** required for the  $\text{OH}^-$  concentration to decrease to a value of  $1.0 \times 10^{-5} \text{ M}$ .

**(Answer)**

(b1) The thermal decomposition of nitrous oxide,  $2 \text{N}_2\text{O} (\text{g}) \rightarrow 2 \text{N}_2 (\text{g}) + \text{O}_2 (\text{g})$

is first order in  $[\text{N}_2\text{O}]$ . At 967K,  $t_{1/2} = 6.3 \text{ min}$ . Assume that you start, initially, with 2.4 moles of  $\text{N}_2\text{O}$  in a 1.2 L vessel.

After 15 min, **what fraction of  $\text{N}_2\text{O}$**  will have decomposed?

**(Answer)**

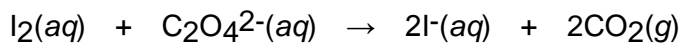
(b2) After 6.3 min, **how many moles of  $\text{O}_2$**  have been formed?

**(Answer)**



2. (12 points)

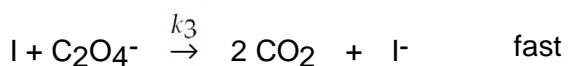
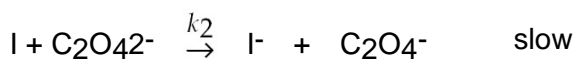
The oxidation of oxalate ion by iodine in aqueous solution,



is an example of a comparatively slow redox reaction. This reaction was found to obey the rate law

$$-\frac{d[\text{I}_2]}{dt} = k_{\text{obs}} [\text{C}_2\text{O}_4^{2-}][\text{I}_2]^{1/2}$$

The proposed reaction mechanism is a free radical mechanism with three steps, as shown below:



Use the pre-equilibrium condition and the Steady State Approximation (SSA) on the above mechanism to determine what  $k_{\text{obs}}$  is in the SSA rate law. It will be a collection of the constants appearing at various points in the above mechanism.

**(Answer)**

3. (12 points)



forms a key step in the mechanism for the chain reaction between  $\text{H}_2$  and  $\text{Br}_2$ . Given the following information:

$$k(700 \text{ K}) = 1.29 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(800 \text{ K}) = 6.74 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$D(\text{H-H}) = 104 \text{ kcal}, \quad D(\text{H-Br}) = 88 \text{ kcal}$$

(Take these values as the temperature independent enthalpies of the diatomic molecule.

$$R = 1.9827 \text{ cal K}^{-1} \text{ mol}^{-1}; \quad 1 \text{ cal} = 4.184 \text{ J}$$

(a) Find **the frequency factor (or pre-exponential factor)  $A$**  for this reaction in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
**(Answer)**

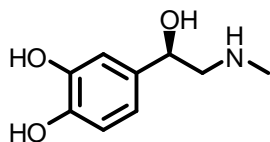
(b) Determine **the activation energy  $E_a'$**  for the reverse reaction.  
**(Answer)**

(c) Find **the amount of decrease in  $E_a$**  necessary to make the rate constant of the forward reaction  $10^{15}$  times faster at 100 K. Assume that pre-exponential factors and activation energies are temperature independent and the reaction is always in gas phase. Can one hope to **find a catalyst** to achieve this for the above reaction?  
**(Answer)**

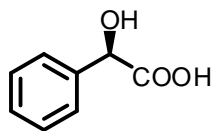
4. (8 points)

Adrenaline is a hormone and neurotransmitter that regulates the supply of oxygen and glucose to the brain and muscles, and one of important regulator of central nervous system (CNS). Mandelic acid, on the other hand, is a main ingredient of almond and believed to be derived from adrenaline as a metabolite by monoamine oxidase. Structures of adrenaline and mandelic acid are shown as follows.

(a) Identify and **mark the chiral carbon atoms** as chiral (\*) of each molecules.



adrenaline



mandelic acid

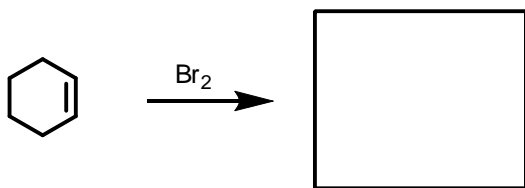
**(Answer)**

(b) When mandelic acid was treated with 1 equivalent of NaOH, draw **the resulting product**.

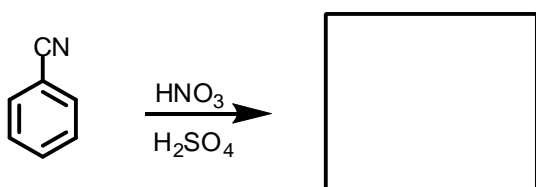
**(Answer)**

5. (8 points)

(a) The double bond induces a dipole in an approaching halogen molecule, making one halogen atom electron deficient and the other electron rich. Predict the **major product** of the following reactions.



(b) The electron withdrawing group deactivates the benzene ring to electrophilic attack. Please draw the **major product** of the reaction.



6. (11 points)

(a) Indium(III) phosphide is a semiconducting material that has been frequently used in lasers, light-emitting diodes (LED), and fiber-optic devices. The semiconducting properties of InP can be altered by doping. If a small number of phosphorus atoms are replaced by atoms with an electron configuration of  $[\text{Kr}]5s^24d^{10}5p^4$ , is this n-type (electron) or p-type (hole) doping?

**(Answer)**

(b) When the paramagnetic  $[\text{Fe}(\text{CN})_6]^{3-}$  ion is reduced to  $[\text{Fe}(\text{CN})_6]^{4-}$ , the ion becomes diamagnetic. However, when the paramagnetic  $[\text{FeCl}_4]^-$  ion is reduced to  $[\text{FeCl}_4]^{2-}$ , the ion remains paramagnetic. Explain these observations.

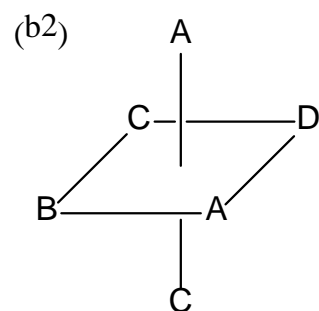
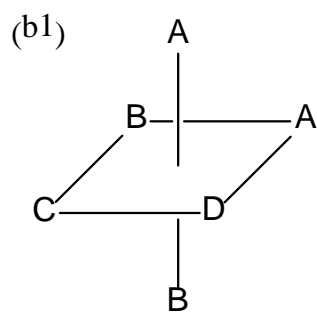
**(Answer)**

7. (12 points)

(a) How many isomers are possible for  $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ ? Consider all types of isomerism and draw each isomer.

**(Answer)**

(b) Is either of the following complexes chiral? If both complexes are chiral, do they form an enantiomeric pair?



**(Answer)**

8. (15 points)

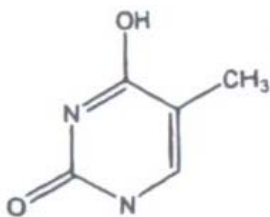
(a) Tropomyosin is 70-kd muscle protein (i.e molecular weight=70,000 dalton). The three dimensional structure of this protein has two-stranded  $\alpha$ -helical coiled coil form. Estimate the length of the tropomyosin. Assume the molecular weight of one amino acid is 110 dalton.

**(Answer)**

(b) 40-residue protein is folded into two-stranded antiparallel  $\beta$ -structure by 4-residue hairpin turn. Estimate the length of this protein.

**(Answer)**

(c) Tautomer form of thymine(T) nucleotide is shown below.



How this tautomer is base paired during the replication of DNA?

**(Answer)**

(d) Explain why human cannot eat cellulose in terms of structural unit.

**(Answer)**

(e) Write the nucleotide sequence of mRNA produced from the DNA template below.

5'-ATCGTACCGTTA-3'

**(Answer)**

9. (12 points)

Identify what kind of polymer is obtained by condensation polymerization of the following monomers (A functional group can react only with B and vice versa).

(a)  $A-A + B-B + B_4$

**(Answer)**

(b)  $A-B + B_4$

**(Answer)**

(c)  $AB_2 + AB$

**(Answer)**

(d)  $AB_2 + A_3$

**(Answer)**

## FUNDAMENTAL CONSTANTS

Name	Symbol	Value
Atomic mass constant	$m_u$	$1.660\ 54 \times 10^{-27}$ kg
Avogadro's constant	$N_A$	$6.022\ 14 \times 10^{23}$ mol <sup>-1</sup>
Boltzmann's constant	$k$	$1.380\ 65 \times 10^{-23}$ J·K <sup>-1</sup>
Fundamental charge	$e$	$1.602\ 18 \times 10^{-19}$ C
Faraday's constant	$F = N_A e$	$9.648\ 53 \times 10^4$ C·mol <sup>-1</sup>
Gas constant	$R = N_A k$	$8.314\ 47$ J·K <sup>-1</sup> ·mol <sup>-1</sup> $8.314\ 47$ L·kPa·K <sup>-1</sup> ·mol <sup>-1</sup> $8.205\ 74 \times 10^{-2}$ L·atm·K <sup>-1</sup> ·mol <sup>-1</sup> $62.36\ 37$ L·Torr·K <sup>-1</sup> ·mol <sup>-1</sup> $8.314\ 47 \times 10^{-2}$ L·bar·K <sup>-1</sup> ·mol <sup>-1</sup>
Mass of electron	$m_e$	$9.109\ 38 \times 10^{-31}$ kg
Mass of neutron	$m_n$	$1.674\ 93 \times 10^{-27}$ kg
Mass of proton	$m_p$	$1.672\ 62 \times 10^{-27}$ kg
Planck's constant	$h$	$6.626\ 08 \times 10^{-34}$ J·s
	$\hbar = h/2\pi$	$1.054\ 57 \times 10^{-34}$ J·s
Rydberg constant	$\mathcal{R}$	$3.289\ 84 \times 10^{15}$ Hz
Speed of light	$c$	$2.997\ 92 \times 10^8$ m·s <sup>-1</sup>
Standard acceleration of free fall	$g$	$9.806\ 65$ m·s <sup>-2</sup>
Vacuum permittivity	$\epsilon_0$	$8.854\ 19 \times 10^{-12}$ J <sup>-1</sup> ·C <sup>2</sup> ·m <sup>-1</sup>

## RELATIONS BETWEEN UNITS\*

Property	Common unit	SI unit
Mass	2.205 lb (lb = pound)	1.000 kg
	1.000 lb	453.6 g
	1.000 oz (oz = ounce)	28.35 g
	1.000 ton (= 2000 lb)	907.2 kg
	1 t (t = tonne, metric ton)	10 <sup>3</sup> kg
Length	1.094 yd (yd = yard)	1.000 m
	0.3937 in. (in. = inch)	1.000 cm
	0.6214 mi (mi = mile)	1.000 km
	1 in.	2.54 cm
	1 ft (ft = foot)	30.48 cm
	1.000 yd	0.9144 m
	1 Å (Å = ångström)	10 <sup>-10</sup> m
Volume	1 L (L = liter)	10 <sup>3</sup> cm <sup>3</sup> , 1 dm <sup>3</sup>
	1.000 gal (gal = gallon) <sup>†</sup>	3.785 dm <sup>3</sup> (3.785 L)
	1.00 ft <sup>3</sup> (ft <sup>3</sup> = cubic foot)	$2.83 \times 10^{-2}$ m <sup>3</sup> (28.3 L)
	1.00 qt (qt = quart) <sup>†</sup>	$9.46 \times 10^2$ cm <sup>3</sup> (0.946 L)
Time	1 min (min = minute)	60 s
	1 h (h = hour)	3600 s
	1 day	86 400 s
Pressure	1 atm (atm = atmosphere)	$1.013\ 25 \times 10^5$ Pa
	1.000 Torr or 1.000 mmHg	133.3 Pa
	1.000 psi (psi = pounds per square inch)	6.895 kPa
	1 bar	10 <sup>5</sup> Pa
Energy	1 cal	4.184 J
	1 eV	$1.60218 \times 10^{-19}$ J; 96.485 kJ·mol <sup>-1</sup>
	1 C·V	1 J
	1 kWh (kWh = kilowatt hour)	$3.600 \times 10^3$ kJ
	1 L·atm	101.325 J
Temperature conversions	(Fahrenheit temperature)/°F = $\frac{9}{5} \times$ (Celsius temperature)/°C + 32 (Celsius temperature)/°C = $\frac{5}{9} + \{$ (Fahrenheit temperature)/°F - 32} (Kelvin temperature)/K = (Celsius temperature)/°C + 273.15	

\*Entries in boldface type are exact.

<sup>†</sup>The European and Canadian Imperial quart and gallon are 1.201 times as large.