2016 FALL Semester Midterm Examination For General Chemistry II (CH103)

Date: October 26 (Wed), Time Limit: 19:00 ~ 21:00

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
1	/9	6	/11	
2	/11	7	/18	
3	/6	8	/10	
4	/9	9	/4	/100
5	/8	10	/14	

** This paper consists of 13 sheets with 10 problems (pages 11: fundamental constants, page 12: periodic table, page 13: claim form). 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 31 (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.

2. Final Confirmation

- 1) Period: November 2 (Wed) November 4 (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.

1. (total 9 points) A buffer solution with a pH of 12.0 consists of Na_3PO_4 and Na_2HPO_4 . The volume

of solution is 200.0 mL. (H₃PO₄, K_{a1} = 7.5×10⁻³, K_{a2} = 6.2×10⁻⁸, K_{a3} = 4.8×10⁻¹³)

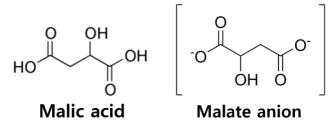
(a) Which component of the buffer is present as a major species?

(Answer)

(b) If the concentration of Na₃PO₄ is 0.400 M, <u>what mass of Na₂HPO₄ is present?</u> (Answer)

(c) <u>Which component of the buffer must be added to change the pH to 12.25?</u> <u>What mass of that component is required?</u>

2. (total 11 points) Living organisms use a huge repertoire of organic acid in their metabolism. Malic acid is an example of them, which contribute to the pleasantly sour taste of fruits and whose anion, malate anion is involved in the citric acid cycle. The acid dissociation constants of malic acid are $pK_{a1} = 3.40$ and $pK_{a2} = 5.20$.

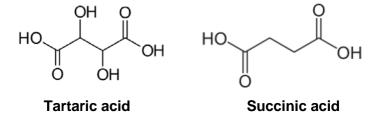


(a) <u>Calculate the pH of a 0.1 M malic acid solution</u>. Assume that the pH is mainly determined by 1st acid dissociation reaction.

(Answer)

(b) Figure out the concentration of malate anion, in (a) solution. (Answer)

(c) There are two closely related dicarboxylic acids; tartaric acid and succinic acid, as below. Predict the order of the acid strength for the malic acid, succinic acid, and tartaric acid, and explain the reason briefly. (It's okay to only consider the pK_{a1} , the 1st acid dissociation constant for the acids.)



3. (6 points) Water containing Ca²⁺ and Mg²⁺ ions is called hard water and is unsuitable for some household and industrial use because these ions react with soap to form insoluble salts. One way to remove the Ca²⁺ ions from hard water is by adding washing soda (Na₂CO₃). The molar solubility of CaCO₃ is 9.3×10^{-5} M. What is its molar solubility in a 0.050 M Na₂CO₃ solution? (Answer)

4. (total 9 points)

(a) <u>Calculate the molar solubility of FeS(s)</u> in a pH 4.5 buffer saturated with H₂S. [H₂S] is fixed at 0.15 M. The acid dissociation constant for H₂S is $K_a(H_2S) = 9.1 \times 10^{-8}$, and equilibrium constant for FeS dissolution is 5×10^{-19} .

 $FeS(s) + H_2O(l)$ \leftarrow $Fe^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq), K = 5 \times 10^{-19}$

(Answer)

(b) <u>Calculate the K_{sp} of CaF₂(s) (The gram solubility for CaF₂ (s) is 0.016 g/L in this case, and the molar mass of CaF₂ is 78.07 g/mol).</u>

5. (total 8 points) The reaction between hydrogen and iodine is a complex reaction

H₂ + I₂ ____ ≥ 2HI

Kinetics experiments show that the reaction is first order with respect to H_2 and first order with respect to I_2 . The following mechanism has been proposed.

(1)
$$l_2 \xrightarrow{k_1} 2l$$
 (2) $H_2 + l \xrightarrow{k_2} H_2l$
(3) $H_2l + l \xrightarrow{k_3} 2Hl$

Where each step is an elementary reaction. Reaction 3 is the rate-determining step and both reactions 1 and 2 form pre-equilibria.

(a) Assuming reaction 1 is at equilibrium, obtain an expression of [I] in terms of [I₂] and the rate constants k_1 and k_{-1} .

(Answer)

(b) <u>Write down the rate equation on the basis of reaction mechanism.</u>

6. (total 11 points)

Br + H₂
$$\xrightarrow{k}$$
 HBr + H

forms a key step in the mechanism for the chain reaction between H_2 and 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.

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

(a) <u>Find the frequency factor (or pre-exponential factor)</u> A for this reaction in cm³ molecule⁻¹ s⁻¹ (Answer)

(b) Determine the activation energy $\underline{E}_{\underline{a}'}$ for the reverse reaction.

(Answer)

(c) Find the amount of decrease in E_a necessary to make the rate constant of the forward reaction 10¹⁵ 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 <u>find a catalyst</u> to achieve this for the above reaction?

7. (total 18 points) The enzyme mechanism might occur is:

$$E+S \xrightarrow{k} E+P \xrightarrow{k} E+P$$

In which E represent the free enzyme, S is the substrate, ES represent the complex formed, and P is the final product.

(a) <u>Write the rate equation governing the formation of product, i.e.</u> $\frac{d[P]}{dt} = ?$.

(Answer)

(b) <u>Write the rate equation for governing the formation ES, i.e.</u> $\frac{d[ES]}{dt} = ?$.

(Answer)

(c) The concentration of [ES] reaches a steady state when the rate of formation equals the rate of decay of ES. Under steady-state condition, $\frac{d[ES]}{dt} = 0$. In this steady-state condition, find the equation for [ES].

<u>kk-1±kk2</u>

(d) KK_{mm} is defined as KK_{mm} = and \mathbf{W}_{mmmmm} is the maximum rate at the saturating concentration of kk₁ [S]. <u>Write</u> $\frac{d[P]}{}$

dt as a function of KK_{mm} , W_{mmmmm} , and [S].

(Answer)

(e) At <u>what concentration of S</u> (expressed as a multiple of KK_{mm}) will rate= 0.9 \mathbb{K}_{mmmmmm} ? (Answer)

(f) Calculate KK_{mm} and W_{mmmmm} from the following data.

	[S] (μM)	Rate (mM · s ⁻¹)
	0.1	0.34
	0.2	0.53
	0.4	0.74
(Answer)	0.8	0.91
(Allowel)	1.6	1.04

8. (total 10 points)

(a) The line positions of the fourth, fifth, and sixth lines of the pure rotational microwave spectrum of

HCl are $= 83.03 \text{ ccc}^{-1}$, $= 103.8 \text{ cm}^{-1}$, and $= 124.3 \text{ ccc}^{-1}$. Calculate the equilibrium bond length of the HCl molecule.

(Answer)

(b) The C-H bonds in $CCCC_3$ and $CCCC_2$ groups stretch at frequencies near 2900 $cccc^{-1}$ in the infrared (IR) spectrum. Calculate the vibration frequency if hydrogen atoms were replaced by deuterium.

(Answer)

9. (4 points) Fundamental vibration wavenumbers of ¹H³⁵Cl and ²H³⁷Cl are $V_{1H^{35}Cl}$ and $V_{2H^{37}Cl}$ respectively. <u>Calculate</u> on the assumption that their force constants are same. Note that the atomic masses of ¹H and ³⁵Cl are 1.000 and 35.00 amu respectively.

10. (Total 14 points) Determine whether the following statements are <u>True</u> or <u>False</u>.

(a) Phenol is more acidic than cyclohexanol.

(Answer)

(b) Selection rule for rotational spectroscopy is $\Delta J = \pm 1$, and that for Raman spectroscopy is $\Delta J =$

±2. (Answer)

(c) In a quantized harmonic oscillator, the energy of the ground state is zero.

(Answer)

(d) If an electron in the π orbital of C₂H₄ is excited by a photon to the π^* orbital, the vibrational frequency in the excited state will be higher than in the ground state.

(Answer)

(e) Absorption of ultraviolet lights in 1,3-butadiene occurs at longer wavelength than in ethylene. (Answer)

(f) A strong absorption observed in the ultraviolet region of the spectrum of formaldehyde is attributed to an n to π^* transition.

(Answer)

(g) Phosphorescence generally occurs more slowly than fluorescence.

Physical Constants	
Avogadro's number	$N_{\rm A} = 6.02214179 \times 10^{23} {\rm mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859$ Å = 5. 2917720859 $\times 10^{-11}$ m
Boltzmann's constant	$k_{\rm B} = 1.3806504 \times 10^{-23} { m J} { m K}^{-1}$
Electron charge	$e = 1.602176487 \times 10^{-19} C$
Faraday constant	$F = 96,485.3399 \text{ C mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_{\rm e} = 9.10938215 \times 10^{-31} {\rm kg}$
Proton	$m_{\rm p} = 1.672621637 \times 10^{-27} \rm kg$
Neutron	$m_{\rm p} = 1.674927211 \times 10^{-27} \rm kg$
Permittivity of vacuum	$\epsilon_0 = 8.854187817 \times 10^{-12} \text{ C}^{-2} \text{ J}^{-1} \text{ m}^{-1}$
Planck's constant	$h = 6.62606896 \times 10^{-34} \text{ J s}$
Ratio of proton mass to electron mass	$m_{\rm p}/m_{\rm e} = 1836.15267247$
Speed of light in a vacuum	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$ (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665 \text{ m s}^{-2}$ (exactly)
Universal gas constant	$R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$ = 0.0820574 L atm mol ⁻¹ K ⁻¹

Values are taken from the 2006 CODATA recommended values, as listed by the National Institute of Standards and Technology.

Conversion Factors

Ångström 1	$A = 10^{-10} m$
Atomic mass unit	$1 \text{ u} = 1.660538782 \times 10^{-27} \text{ kg}$
	$1 \text{ u} = 1.492417830 \times 10^{-10} \text{ J} = 931.494028 \text{ MeV}$ (energy equivalent from $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	$1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J}$
	= 96.485335 kJ mol
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U.S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	$1 L = 10^{-3} m^{-3} = 10^3 cm^3$ (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 t = 1000 kg (exactly)
Pound	1 lb = 16 oz 0.4539237 kg (exactly)
Rydberg	$1 \text{ Ry} = 2.17987197 \times 10^{-18} \text{ J}$
	= 1312.7136 kJ mol
	= 13.60569193 eV
Standard atmosphere	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$
	$= 1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$ (exactly)
Torr	1 torr = 133.3224 Pa

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Claim Form for General Chemistry Examination

Page (/)

Class:_____, Professor Name:_____, I.D.# :_____, Name:_____

If you have any claims on the marked paper, please write down them on this form and **submit this with your paper in** the assigned place. (And this form should be attached on the top of the marked paper with a stapler.) Please, copy this sheet if you need more before use.

	By Student		By TA		
	-	Accepted? $Yes(\checkmark) \text{ or } No(\checkmark)$		Yes(√) or No(√)	
Question #	Claims	Yes: 🗆		No: 🗆	
		Pts (+/-)		Reasons	

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	2+3+4/9	6	4+3+4/11	
2	4+4+3/11	7	1+3+3+4+3+4/ 18	
3	/6	8	6+4/10	(100
4	6+3/9	9	/4	/100
5	3+5/8	10	2x7/14	

전체 기준: 전개과정은 맞으나 답이나 unit 이 틀리면 -1

답은 맞으나 전개과정이 약간 틀렸을 때 -1

식을 전혀 쓰지 않고 (혹은 흔적이 전혀 없고) 답만 맞았을 때 -1 (3 pts), -2 (4 pts 이상)

1. (total 9 points)

(a) (2 pts) $pK_{a1} = 2.2$, $pK_{a2} = 7.2$, $pK_{a3} = 12.3$ pH 12 is a bit less than 12.3, so the major component is [HPO₄²⁻] and then [PO₄³⁻] answer: [HPO₄²⁻]

(b) (3 pts) $pH = pKa - \log \frac{[HP04]}{[P04]}$, $12.0 = 12.3 - \log \frac{x}{0.400}$, x = 0.798 M.

Mass of $Na_2HPO_4 = 0.798 \text{ mol/L} \times 141.96 \text{ g/mol} \times 0.2 \text{ L} = 22.7 \text{ g}$

(c) (4 pts) To increase the pH, the basic part, $[PO_4^{3-}]$ should be added.

 $12.25 = 12.3 - \log \frac{0.798}{x}$, x = 0.711 M.

Additional mass of $Na_3PO_4 = (0.711-0.400) \text{ mol/L} \times 163.94 \text{ g/mol} \times 0.2 \text{ L} = 10.2 \text{ g}$

2. (total 11 points)

(a) (4 pts) $H_{2}^{A} (aq) + H_{2}O(l) \rightleftharpoons H_{3}O^{+}(aq) + H_{4}^{-} (aq), \qquad K_{a1} = 10^{-3.40} = 3.98 \times 10^{-4}$ $H_{2}^{A} (aq) + H_{2}O(l) \rightleftharpoons H_{3}O^{+}(aq) + A^{-2} (aq), \qquad K_{a2} = 10^{-5.20} = 6.31 \times 10^{-6}$

pH is mainly determined by the first acid dissociation reaction. (assumption)

	$H_{2}^{A} A_{sc}(aq) + H_{2}O(l)$	${\downarrow}$	H ₃ O ⁺	⁺ (<i>aq</i>) + HA (<i>aq</i>)
Starting	0.1		0	0
Change	-x		+x	+x
Equilibrium	0.1 - x		х	х

 $K_{a1} = \frac{[H_3O^+][HA_{malate}]}{[H_2A_{malate}]} = \frac{x^2}{0.1 - x} = 3.98 \times 10^{-4}$ Assuming x to be much smaller than $0.1 \Rightarrow 0.1 - x \approx 0.1$ $\Rightarrow x^2/0.1 = 3.98 \times 10^{-4}$ $\Rightarrow x = 6.31 \times 10^{-3}$ $\Rightarrow pH = -\log[H_3O^+] = -\log[6.31 \times 10^{-3}] = 2.20$

(b) (4 pts)

	HA ⁻ ^{malate} (<i>aq</i>) + H ₂ O (<i>I</i>)	₹	+ H₃O ⁺ (<i>aq</i>) +	A ⁻² (<i>aq</i>)
Starting	6.31×10 ^{-°}		6.31×10 ⁻	0
Change	-у		+y	+y
Equilibrium	6.31×10 ^{⁻³} - y		6.31×10 ⁻³ +y	у

$$K_{a2} = \frac{[H_3O^+][A_{malate}^{2-}]}{[HA_{malate}^{-}]} = \frac{(6.31 \times 10^{-3} + y)y}{6.31 \times 10^{-3} - y} = 6.31 \times 10^{-6}$$

≈ 6.31×10^{-3} y/6.31×10⁻³ = 6.31×10^{-6} (Assume that y is much smaller than 0.0028) ⇒ y = [A⁻²_{malate}] = 6.31×10^{-6}

(c) (3 pts)

Tartaric acid > Malic acid > Succinic acid Due to electronegativity effect from the –OH group.

3. (6 points) Ksp 3 pts, S 3 pts

Molar solubility of $CaCO_3$ is S

$$CaCO_{3} \longrightarrow Ca^{2^{+}} + CO_{3}^{2}$$

$$S \qquad S$$

$$K_{sp} = S^{2} = (9 \ 3 \ \times \ 10^{5})^{2} = 8 \ 65 \ X \ 10^{9}$$

$$CaCO_{3} \longrightarrow Ca^{2^{+}} + CO_{3}^{2}$$

$$S \qquad 0.500 \ +S$$

$$K_{sp} = S(0 \ 0.50 \ +S) = 0 \ 0.50S = 8 \ 65 \ X \ 10^{9}$$

$$S = 1.73 \ \times \ 10^{-7}$$

Answer: molar solubility is 1.73×10^{-7}

4. (total 9 points)

(a) (6 pts) [HS ⁻] 3 pts, [Fe ²⁺] 3 pts pH = 4.5, [H ₃ 0 ⁺] = 1 x 10 ^{-4.5} = 3.2 x10 ⁻⁵
$[OH^{-}] = 3.1 \times 10^{-10}$ (fixed)
$H_{2}S(aq) + H_{2}O(I) \longrightarrow H_{3}O^{+}(aq) + HS^{-}(aq)$ $K_{a} = \frac{[H_{3}O^{+}][[HS^{-}]]}{[H_{2}S]} = \frac{3.2 \times 10^{-5} \times [HS^{-}]}{0.15} = 9.1 \times 10^{-5}$
$\Rightarrow [HS^{-}] = 4.3 \times 10^{-4}$
FeS(s) + H ₂ O(l) Fe ²⁺ (aq) + HS ⁻ (aq) + OH ⁻ (aq), $K = 5 \times 10^{-19}$
$K = [Fe^{2+}][HS^{-}][OH^{-}] = 5 \times 10^{-19}$
$[Fe^{2+}] = \frac{K}{[0H^{-}][HS^{-}]} = \frac{5 \times 10^{-19}}{(3.1 \times 10^{-10})(4.3 \times 10^{-4})} = 3.8 \times 10^{-6} M$
(b) (3 pts)
$CaF_2(s)$ $Ca^{2+}(aq) + 2F^{-}(aq)$
Initial 0 0
Reaction +S +2S
Equilibrium +S +2S
S (Molar solubility) = $\frac{0.016g/L}{78.07g/mol} = 2.0x10^{-4} \text{ mol/L}$
$K_{sp} = [Ca^{2+}] [F^{-}]^2 = S(2S)^2 = 4S^3$
$= 4 \cdot (2.0 \times 10^{-4})^3 = \frac{3.2 \times 10^{-11}}{10^{-11}}$

5. (total 8 points)

(a) (3 pts)

At equilibrium, $k_1[I_2] = k_1[I]^2$ $[I] = \sqrt{\frac{k_1[I_2]}{k_{-1}}}$ (b) (5 pts) $[H_2I]$ 2 pts, rate 3 pts similar to (a), from reaction 2, $[H_2I] = \frac{k_2}{2} [H_2][I]$

similar to (a), from reaction 2,
$$[H_2I] = \frac{1}{k_{-2}} [H_2I[I]$$

Thus, rate =
$$k_3[H_2I][I] = \frac{k_1k_2k_3}{k_1k_2} [H_2][I_2]$$

6. (total 11 points)

(a) (4 pts) $k = A \exp(-E_a/RT)$ $ln(k_1/k_2) = E_a/R \times (1/T_2 - 1/T_1)$ $E_a = R(ln k_1 - ln k_2) / (1/T_2 - 1/T_1)$ $= (1.9827 \text{ calK}^{-1}\text{mol}^{-1})(-1.6534)/(-1.7857\times10^{-4} \text{ K}^{-1})$ $= 18.35 \text{ kcalmol}^{-1}$ $A = k \exp(E_a/RT) = (6.74\times10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \times \exp(18.35/(1.9827\times800))$ $= 7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

(b) (3 pts) $\Delta H_R = 104 - 88 = 16 \text{ kcalmol}^{-1}$ $E_a \text{ (reverse)} = 18.35 - 16 = 2.4 \text{ kcalmol}^{-1}$

(c) (4 pts) calculation 3 pts, statement 1 pt $k'/k = A/A \exp[(E_a - E_a') / RT] = 10^{15}$ $E_a - E_a' = (RT) \ln (10^{15}) = (1.9827x100) (15) (2.303) = 6.85 \text{ kcalmol}^{-1}$

No, it is not possible. The reduction of E_a (6.8 kcalmol⁻¹) is larger than the activation energy for the reverse reaction (2.4 kcalmol⁻¹).

7. (total 18 points)

(a) (1 pts) d[P]/dt = *k*₂[ES]

(b) (3 pts) d[ES]/dt = $(k_1[E][S]) - (k_{-1}[ES] + k_2[ES]) = k_1[E][S] - k_{-1}[ES] - k_2[ES]$

(c) (3 pts) Since $k_1[E][S]=k_{-1}[ES] + k_2[ES]$, $k_1[E][S]= (k_{-1}+k_2)[ES]$. Therefore, $[ES] = k_1[E][S]/(k_{-1}+k_2)$

(d) (4 pts)

$$\frac{d[ES]}{dt} = 0 = k_1[E] [S] - k_{-1}[ES] - k_2[ES]$$

$$\frac{[E_T]}{dt} = [E] + [ES]$$

$$\frac{d[ES]}{dt} = 0 = k_1 [E_T] [S] - k_1 [ES] [S] - k_{-1} [ES] - k_2 [ES]$$

$$[ES] = \frac{k_1[E_T][S]}{(k_{-1} + k_2) + k_1[S]}$$

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

$$[ES] = \frac{k_1[E_T][S]}{K_m + [S]}$$

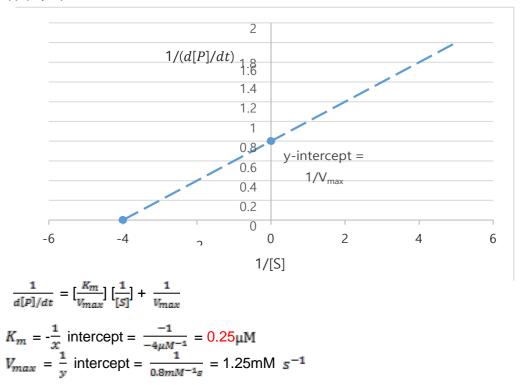
$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E_T][S]}{K_m + [S]}$$
Taking the limit in which [S] > K_m V_{max} = k_2
$$[E_T] \frac{d[P]}{dt} = [ES] = \frac{V_{max}[S]}{K_m + [S]}$$

(e) (3 pts)

Rate =
$$\frac{v_{max}[S]}{\kappa_m + [S]}$$

 $\frac{rats}{v_{max}} = \frac{[S]}{\kappa_m + [S]}$
 $0.9 = \frac{[S]}{K_m + [S]}$
 $[S] = 0.9K_m + 0.9[S]$
 $0.1[S] = 0.9K_m$
∴ $[S] = \frac{0.9}{0.1}K_m = 9K_m$

(f) (4 pts)



8. (total 10 points)

(a) (6 pts)
$$\overline{v_5} - \overline{v_4} = 20.8 \ cm^{-1}$$
 $\overline{v_6} - \overline{v_5} = 20.5 \ cm^{-1}$
 $average \frac{1}{2} (20.8 + 20.5) = 20.65$
 $2\widehat{B} = 20.65$ $\overline{B} = 10.32 \ cm^{-1}$
 $I = \mu r^2 = \frac{h}{8\pi^2 C\overline{B}}$ $r = \sqrt{\frac{h}{8\pi^2 C\overline{B}\mu}}$
 $\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{(1.008)(35.0)}{1.008 + 35.0} \ amu \left(\frac{1g}{6.0221 \times 10^{28} \ amu}\right) \left(\frac{1Kg}{1000g}\right)$
 $= 1.627 \times 10^{-27} \ kg$
 $r = \left[\frac{6.6261 \times 10^{-84} Js}{(8\pi^{2}) (2.997 \times 10^8 \ ms^{-1}) (10.52 \times 10^2 \ m^{-1})(1.624 \times 10^{-27} \ kg)}\right]^{\frac{1}{2}}$
 $= 1.291 \times 10^{-10} \ m = 1.291 \ Angstrom$
(b) (4 pts) $v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$
 $\mu_{C-\mu} = \frac{m_{C}m_{D}}{m_{C}+m_{D}} = \frac{12\times 2}{12+2} = 1.714 \ atomic \ mass \ unit$
 $\mu_{C-\mu} = \frac{m_{C}m_{H}}{m_{C}+m_{H}} = \frac{12\times 1}{12+1} = 0.923 \ atomic \ mass \ unit$
 $v_{C-D} = \sqrt{\frac{\mu H}{\mu_{D}}} \times v_{C-H} = \sqrt{\frac{0.923}{1.714}} \ (2900 \ cm^{-1}) = 2130 \ cm^{-1}$

9. (4 points)

Ans. Since
$$\nu \propto \sqrt{\frac{1}{\mu}}$$
, $\frac{V_{1}}{V_{2}}^{35}}_{\text{H Cl}} = \sqrt{\frac{\mu_{2}}{\mu_{1}}^{35}}_{\text{H Cl}} = \sqrt{\frac{\frac{2.000 \times 37.00}{2.000 + 37.00}}{\frac{1.000 \times 35.00}{1.000 + 35.00}}} = \sqrt{1.952} = 1.397$

10. (Total 14 points) each 2 pts

(a) T, due to the resonance stabilization of the conjugated base

- (b) F, **∆J** = **±2,0**
- (c) F, $\frac{1}{2}hv$

(d) F, The weaker C-C bond gives the lower vibrational frequency.

(e) T

(f) F, attributed to pi to pi* transition

(g) T

2016 FALL Semester Final Examination For General Chemistry II (CH103)

Date: December 21 (Wed), Time Limit: 19:00 ~ 21:00

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
1	/9	7, 8	/8	
2	/6	9	/9	
3	/10	10	/8	
4	/8	11	/6	
5	/7	12	/12	/100
6	/10	13	/7	

** This paper consists of 14 sheets with 13 problems (page 12: fundamental constants, page 13: periodic table, page 14: claim form). 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.

1. Period, Location and Procedure

- 1) Return and Claim Period: December 23 (Friday, 12:00-14:00 p.m.)
- 2) Location: Creative Learning Bldg.(E11)

Class	Room	Class	Class
Α	205	С	202
В	201	D	203

3) Claim Procedure:

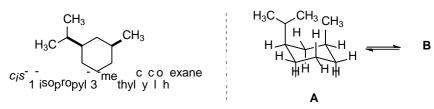
Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)

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. The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 12/23 on the web.)

2. Final Confirmation

1) Period: December 24(Sat) - 25(Sun)

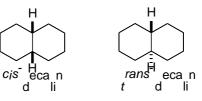
 Procedure: During this period, you can check the final score of the examination *on the website* again. To get more information, visit the website at <u>www.gencheminkaist.pe.kr</u>. 1. (Total 9 pts) Among possible conformational isomers, a chair form of cyclohexane is known to be the most stable. *Cis*-1-isopropyl-3-methylcyclohexane can have two conformational isomers in the chair form, and one of the isomer, **A** is shown below.



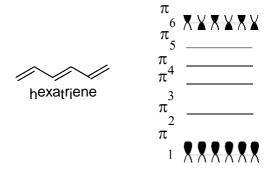
(a) <u>Draw the other chair conformer **B**</u> with all functional groups including hydrogens. **(Answer)**

(b) Which conformer **A** or **B** is <u>more stable</u>? <u>Explain the reason for the energy difference</u>. **(Answer)**

(c) *Cis*- or *trans*-decalin is one of fused bicyclic alkanes. <u>Draw the most stable conformational</u> <u>isomer of *cis*-decalin and *trans*-decalin (hydrogens may be omitted).</u>



2. (Total 6 pts) Molecular orbitals of conjugated alkenes can be drawn by a liner combination of atomic *p* orbitals. For hexatriene, there are six levels of π -orbitals.



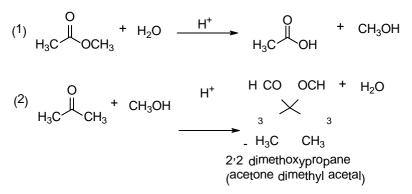
(a) Similar to π_1 and π_6 , <u>draw other π orbitals</u>. (Answer)

(b) Which π orbital(s) are bonding and anti-bonding orbital(s)?

(Answer)

(c) Which π orbital(s) are <u>HOMO or LUMO orbital(s)</u>? (Answer)

3. (Total 10 pts) In the presence of an acid catalyst, (1) esters can be hydrolyzed to carboxylic acids and (2) acetals can be formed from ketones.



(a) <u>Draw the reaction mechanism of the reaction (1)</u> using the arrow notation. In your drawing, specify the role of acid and provide all possible intermediates.

(Answer)

(b) <u>Draw the reaction mechanism of the reaction (2)</u> using the arrow notation. In your drawing, specify the role of acid and provide all possible intermediates.

4. (Total 8 pts) Identify the element with the larger atomic radius in each of the following pairs.

(a) iron and chromium

(Answer)

(b) vanadium and titanium

(Answer)

(c) rhodium and iridium

(Answer)

(d) scandium and yttrium

(Answer)

5. (Total 7 pts) Cobalt(II) forms more tetrahedral complexes than any other ion except Zinc(II).

(a) <u>Draw the structure(s)</u> of the tetrahedral complex [CoCl₂(en)], en = ethylenediamine. Could this complex exhibit <u>geometric or optical isomerism</u>?

(Answer)

(b) If one of the Cl⁻ ligands is replaced by Br⁻, <u>what kinds of isomerism</u>, if any, are possible in the resulting compound?

- 6. (Total 10 pts) The compound $Cs_2[CuF_6]$ is bright orange and paramagnetic.
- (a) <u>Determine the oxidation number of copper in this compound.</u>

(Answer)

(b) <u>Determine</u> the most likely <u>geometry of the coordination</u> around the copper. (Answer)

(c) <u>Determine</u> the possible <u>configurations of the d electrons</u> of the copper.

(Answer)

(d) <u>Calculate the crystal field stabilization energy</u> of this compound in the unit of Δ . (Answer)

7. (Total 4 pts) For each question, choose the correct answer.

(a) In an **electrolytic cell** the electrode at which the electrons enter the solution is called the _____; the chemical change that occurs at this electrode is called _____.

(Answer)

- A. anode, oxidation
- B. anode, reduction
- C. cathode, oxidation
- D. cathode, reduction
- E. cannot tell unless we know the species being oxidized and reduced

(b) Choose the correct statement.

(Answer)

- A. $E_{\text{cell}} = E_{\text{cathode}} E_{\text{anode}}$ for both galvanic cells and electrolytic cells
- B. $E_{\text{cell}} = E_{\text{cathode}} E_{\text{anode}}$ for galvanic cells and $E_{\text{cell}} = E_{\text{anode}} E_{\text{cathode}}$ for electrolytic cells
- C. $E_{\text{cell}} = E_{\text{anode}} E_{\text{cathode}}$ for galvanic cells and $E_{\text{cell}} = E_{\text{cathode}} E_{\text{anode}}$ for electrolytic cells
- D. $E_{\text{cell}} = E_{\text{cathode}} E_{\text{anode}} \ge 0$ is always true.
- 8. (Total 4 pts) Followings are units for physical and chemical quantities.
 - A. J (joule)
 - B. V (volt)
 - C. W (watt)
 - D. Whr (watt-hour)
 - E. C (coulomb)
 - F.mAh (milliamp hour)

(a) Choose **two** units for the **energy** among the above six units.

(Answer)

(b) Choose **two** units for the **electric charge** among the above six units.

(Answer)	
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9. (Total 9 pts) A **galvanic cell** is constructed as Cd | 1.0 M Cd²⁺ || x M Fe²⁺, 1.0 M Fe³⁺ | Pt where x = 1.0 or 0.10. The standard potential for Fe³⁺ + $e^- \rightarrow$ Fe²⁺ is +0.752 V and Cd²⁺ + 2 $e^- \rightarrow$ Cd is -0.410 V at 25 °C and $\frac{RT}{F} \ln 10 = \frac{RT}{F} 2.303 = 0.0592$ V at 25 °C.

(a) Write the overall cell reaction without phase notation.

(Answer)

(b) <u>Calculate the cell potential (E_{cell}^{o}) when x = 1.0.</u>

(Answer)

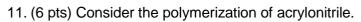
(c) <u>Calculate the cell potential (E_{cell}) when x = 0.10.</u>

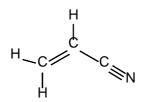
10. (Total 8 pts)

(a) In an alkaline dry cell, Zn(s) is oxidized to $Zn(OH)_2(s)$ at anode, and $MnO_2(s)$ is reduced to $Mn_2O_3(s)$ at cathode. Write the cathode and anode reactions with phase notations (*s*, *l*, *g*, or *aq*). (Answer)

(b) Estimate the standard potential for $Cu^+(aq) + e^- \rightarrow Cu(s)$ where the standard potential for $Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$ is 0.340 V and the standard potential for $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ is 0.159 V.

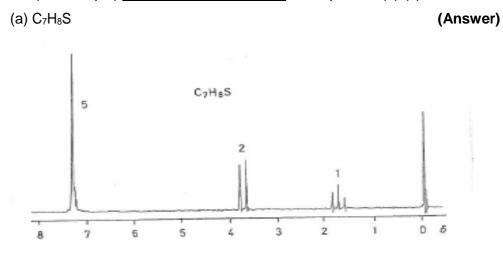
(Answer)





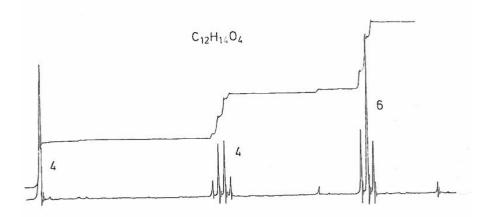
Describe 3 steps of addition polymerization that involves butyl lithium ion (Bu⁻Li⁺) as an initiator.

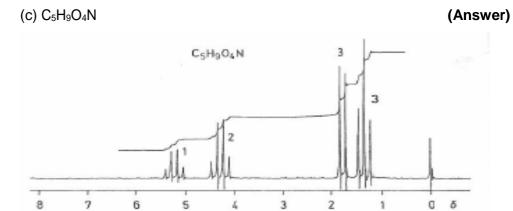
12. (Total 12 pts) Determine the structures of compounds (a)-(c)



(b) C₁₂H₁₄O₄

(Answer)





10

13. (Total 7 pts)

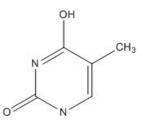
(a) Straight-chain form of D- ribose is shown below. <u>Draw the structure of the ring form of D-ribose</u> and indicate <u>how many chiral carbon</u> exists.

$$\begin{array}{c} H \\ C \\ \end{array} O \qquad (Answer) \\ H - C - OH \\ CH_2OH \end{array}$$

(b) 40-residue protein is folded into two-stranded antiparallel β -structure by 4-residue hairpin turn. <u>Estimate the length of this protein.</u>

(Answer)

(c) The tautomer of thymine has the following structure and can make a base pair with guanine. <u>Show the structure of this G.T base pair</u>.



Physical Constants

Avogadro's number	$N_{\rm A} = 6.02214179 \times 10^{23} {\rm mol}^{-1}$			
Bohr radius	$a_0 = 0.52917720859 \text{ Å} = 5.2917720859 \times 10^{-11} \text{ m}$			
Boltzmann's constant	$k_{\rm B} = 1.3806504 \times 10^{-23} { m J} { m K}^{-1}$			
Electron charge	e = 1.602176487 × 10 ⁻¹⁹ C			
Faraday constant	$F = 96,485.3399 \text{ C mol}^{-1}$			
Masses of fundamental particles:	the second se			
Electron	$m_e = 9.10938215 \times 10^{-31} \text{ kg}$			
Proton	$m_{\rm p} = 1.672621637 \times 10^{-27} \rm kg$			
Neutron	$m_{\rm n} = 1.674927211 \times 10^{-27} \rm kg$			
Permittivity of vacuum	$\epsilon_0 = 8.854187817 \times 10^{-12} \text{ C}^{-2} \text{ J}^{-1} \text{ m}^{-1}$			
Planck's constant	$h = 6.62606896 \times 10^{-34} \mathrm{J s}$			
Ratio of proton mass to electron mass	$m_{\rm p}/m_{\rm e} = 1836.15267247$			
Speed of light in a vacuum	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$ (exactly)			
Standard acceleration of terrestrial gravity	$g = 9.80665 \text{ m s}^{-2}$ (exactly)			
Universal gas constant	$R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$			
	= 0.0820574 L atm mol ⁻¹ K ⁻¹			

Values are taken from the 2006 CODATA recommended values, as listed by the National Institute of Standards and Technology.

Conversion Factors

Ångström 1	$\hat{A} = 10^{-10} m$		
Atomic mass unit	$1 \text{ u} = 1.660538782 \times 10^{-27} \text{ kg}$		
	$1 \text{ u} = 1.492417830 \times 10^{-10} \text{ J} = 931.494028 \text{ MeV}$ (energy equivalent from $E = mc^2$)		
Calorie	1 cal = 4.184 J (exactly)		
Electron volt $1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J}$			
	= 96.485335 kJ mol		
Foot	1 ft = 12 in = 0.3048 m (exactly)		
Gallon (U.S.)	1 gallon = 4 quarts = 3.785412 L (exactly)		
Liter	$1 L = 10^{-3} m^{-3} = 10^3 cm^3$ (exactly)		
Liter-atmosphere	1 L atm = 101.325 J (exactly)		
Metric ton	1 t = 1000 kg (exactly)		
Pound	1 lb = 16 oz 0.4539237 kg (exactly)		
Rydberg	$1 \text{ Ry} = 2.17987197 \times 10^{-18} \text{ J}$		
	= 1312.7136 kJ mol		
	= 13.60569193 eV		
Standard atmosphere	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$		
	$= 1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$ (exactly)		
Torr	1 torr = 133.3224 Pa		

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Соругдит © 198 69 168.93 Тта тницим 101 (258) М[d] МЕИДЕЕ ИИМ	Bi PO BisMJTH POLONIUM	72.64 33 74.922 34 78.96 Je As Se Se Je Assenic selenium selenium Inn 51 121.76 52 127.60 N Sb Te	N O NITROGEN OXYGEN 115 30.974 16 32.065 PHOSPHORUS SULPHUR	dni/en/
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70 173.04 Yb YTTERBIUM 102 (259) NOBELIUM		35 79.904 Br BROMINE 53 126.90 I	9 18.998 F FLUORINE 17 35.453 CHLORINE	
Copyright © 1996-2002 EnG. (en@kf-spit.hy 65 158.93 66 162.20 67 164.93 68 167.26 69 168.93 70 173.04 71 174.97 Tb Dy HO Er Tm Yb Lu TERBIUM DYSPROSIUM HOLMIUM ERBIUM THULIUM YTTERBIUM UTTERBIUM Lu 97 (247) 98 (251) 99 (252) 100 (257) 101 (258) 102 (262) BBRK CCIF IES IFIDDD MIdd N/D IL/I° BERKELUM CALFORNIUM EINSTEINIUM FERMUM MENDELEVIUM NOBELIUM LAWRENCIUM	(210) 86 (222) ATINE RADON	35 79.904 36 83.80 Br Kr ввомие кятуртом 53 128.90 54 131.29 I Xe	9 18.998 10 20.180 F Ne FLUORINE NEON 17 35.453 18 39.948 CI Ar CHLORINE ARGON	18 VIIIA 2 4.0026 He
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Claim Form for General Chemistry Examination

Page (/)

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Question #	Claims	Yes: 🗆	No: 🗆	
		Pts (+/-)	Reasons	

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	3+2+4/9	7, 8	2+2+2+2/8	
2	4+1+1/6	9	3+3+3/9	
3	5+5/10	10	4+4/8	
4	2x4/8	11	2+2+2/6	
5	4+3/7	12	4+4+4/12	/100
6	2+2+3+3/10	13	2+2+3/7	

전체 기준: 전개과정은 맞으나 답이나 unit 이 틀리면 -1

답은 맞으나 전개과정이 약간 틀렸을 때 -1

1. (Total 9 pts)

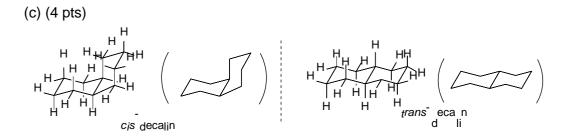
(a) (3 pts)

Conformer B: Chair conformation with iPr and Me groups are all equatorial positions

All C-C and C-H bonds should be parallel with other existing bonds: (-1) point for the wrong structure.

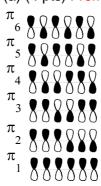
(b) (2 pts)

Conformer B. Conformer **A** is unstable due to the existence of 1,3-diaxial interactions between iPr and CH_3 groups (or steric repulsion between iPr, CH_3 , and H).



2. (Total 6 pts)

(a) (4 pts) From π_2 to π_5 , 1 pt for each MO



(b) (1 pt)

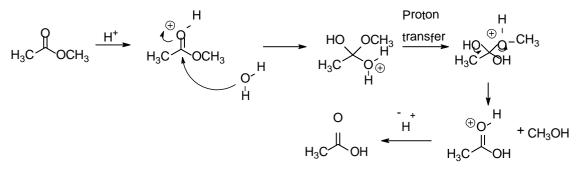
bonding: π_1 , π_2 , and π_3 Anti-bonding: π_4 , π_5 , and π_6

(c) (1 pt)

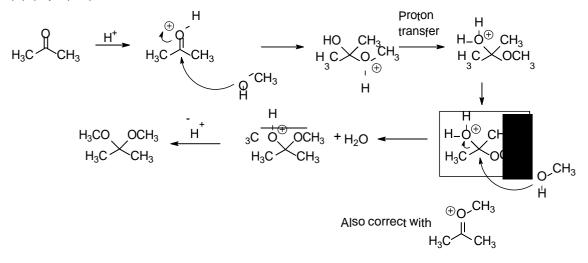
HOMO: π₃ LUMO: π₄

3. (Total 10 pts)

(a) (5 pts) 1 pt for each intermediate, +1 pt for complete rxn



(b) (5 pts) 1 pt for each intermediate



4. (Total 8 pts) each 2 pts

- (a) chromium
- (b) titanium
- (c) iridium (another answer: rhodium and iridium have similar radii.)
- (d) yttrium

5. (Total 7 pts)

(a) (4 pts) 2 pts for drawing (tetrahedral), 2 pts for "no isomer"

In $[CoCl_2(en)]$ the two ends of the ethylenediamine (en) ligand are equivalent and the two Cl ligands are also equivalent, as suggested in the following



Tetrahedral structures do not exhibit *cis-trans* isomerism (geometrical isomerism) because the four corner of a tetrahedron are equidistant from each other. Tetrahedral structure *can* exhibit mirror-image isomerism if they have four different atoms attached to the central atom. The complex $[CoBrCl(NH_3)(NH_2CH_3)]$ would in principle exhibit mirror-image isomerism. But $[CoCl_2(en)]$ does not have four different ligands. Consequently $[CoCl_2(en)]$ cannot exhibit geometrical isomerism and

cannot exhibit optical isomerism.

(b) (3 pts)

No isomers exist, because the ethylenediamine ligand still occupies two out of four sites on the tetrahedral structure, which can be regarded as two identical ligands. Therefore, the tetrahedral coordination cannot exhibit either geometrical nor optical isomerism.

6. (Total 10 pts)

(a) (2 pts) Copper is in the +4 oxidation state.

(b) (2 pts) octahedral

(c) (3 pts) In a weak octahedral field, the d electron configuration would become $(t_{2g})^5(e_g)^2$.

(d) (3 pts) $-2/5\Delta \times 5 + 3/5\Delta \times 2 = -4/5\Delta$ (or $-4/5\Delta_{o}$)

7. (Total 4 pts)

- (a) (2 pts) D
- (b) (2 pts) A

8. (Total 4 pts)

- (a) (2 pts) A, D (A. J (joule), D. Whr (watt-hour)
- (b) (2 pts) E, F (E. C (coulomb), F. mAh (milliamp hour))

9. (Total 9 pts)

(a) (3 pts) The reduction $Fe^{3+} + e^- \rightarrow Fe^{2+}$ takes place at the cathode, and the oxidation $Cd(s) \rightarrow Cd^{2+} + 2 e^-$ takes place at the anode. Only in this way is $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$ of the cell positive.

Cathode: 2 Fe³⁺ + 2 $e^- \rightarrow$ 2 Fe²⁺ Anode: Cd \rightarrow Cd²⁺ + 2 e^- Overall: Cd + 2 Fe³⁺ \rightarrow Cd²⁺ + 2 Fe²⁺

(b) (3 pts)
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = +0.752 - (-0.410) = 1.162 \text{ V}.$$

(c) (3 pts) $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}^{\circ} = \left(0.752 - 0.0592 \log_{10} \frac{0.1}{1.0}\right) - 0.410$

= 0.752 + 0.0592 - 0.410 = **1.221 V**

10. (Total 8 pts)

(a) (4 pts) For this problem, without phase notations, only 2 pts are given.

Cathode: $2 \text{ MnO}_2(s) + H_2O(l) + 2 e^- \rightarrow \text{Mn}_2O_3(s) + 2 \text{ OH}^-(aq)$ Anode: $\text{Zn}(s) + 2 \text{ OH}^-(aq) \rightarrow \text{Zn}(\text{OH})_2(s) + 2 e^-$

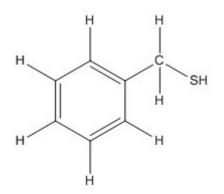
(b) (4 pts)

$$\Delta G_{3}^{\circ} = n_{3}FE_{3}^{\circ} = n_{2}FE_{2}^{\circ} - n_{1}FE_{1}^{\circ}, \quad E_{3}^{\circ} = \frac{n_{2}FE_{2}^{\circ} - n_{1}FE_{1}^{\circ}}{n_{3}F} = \frac{2 \times 0.340 - 1 \times 0.159}{1} = 0.521 \text{ V}$$

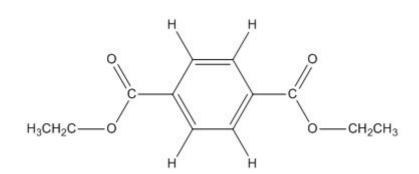
11. (6 pts) 2 pts for each elementary reaction

(termination)

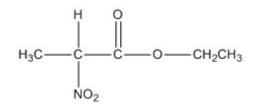
12. (Total 12 pts) All pts can be given when -COO- group is changed by -OCO-.(a) (4 pts)



(b) (4 pts)

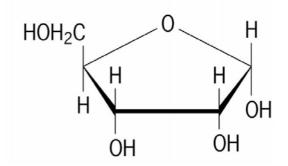


(c) (4 pts)



13. (Total 7 pts)

(a) (2 pts)



D-ribose has 3 asymmetric carbon atom.

(b) (2 pts)

40-4=36

36÷2=18

Each ^β-strand has 18 amino acids.

The distance between 2 successive amino acids in ₿-structure is 3.5 A°.

3.5 A° ≭ 18= **63 A**°

(c) (3 pts)

