

2021 Fall Semester Midterm Examination For General Chemistry II

Date: Oct 20 (Wed), Time Limit: 19:00 ~ 22:00

NOTICE

- If you have a printer, print the papers and write the answers in the space of each question. If not, prepare several A4-size papers to write only question # and the answers on it in the following example. And for clarity, marking your answer is recommended. Please, print your Student ID in the upper right corner of every page for both of them. (**Handwriting only is acceptable** and typing is not.)

Example:

Professor Name	Class	Student I.D. Number	Name

#1. (a).....

(b).....

- If you have any questions during the period, please contact the TA of your class using the Zoom chat channel to “Everyone” (the only possible choice). Proctors will make any announcements relevant to all students *via* audio.
- While still in the video conference, submit your file to [Midterm Examination], an assignment on Turnitin of your class. **Do not leave the video conference** until your TA is confirmed and tells you that it is fine to leave.

**** This paper consists of 12 sheets with 10 problems (page 11 - 12: Equation, constants & periodic table).** Please check all page numbers before taking the exam. Please write down the unit of your answer when **applicable**. You will get 30% deduction for a value that is missing its unit.

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

(채점 답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure

- 1) Return and Claim Period: **Oct 25 (Mon 12:00~24:00)**
- 2) **Location: Each class of Turnitin site (online)**
- 3) Procedure: If you have any claims on it, email them (Question# and reasons) to your TA.
(The claim is permitted only during the designated claim period. Keep that in mind! A solution file with answers for the examination will be uploaded on the web.)

2. Final Confirmation

- 1) Period: **Oct 28-29 (Thu – Fri)**
- 2) Procedure: During this period, you can check final score of the examination *on the website* again.
(No additional corrections. If no change in your score after reasoning, the claims were not accepted.)

**** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr**

1. (total 8 pts)

(a) [2 pts] What is the definition of a 'chirality center (chiral center)'? Explain it.

(Answer)

IUPAC full definition: An atom holding a set of ligands in a spatial arrangement which is not superposable on its mirror image. A chirality centre is thus a generalized extension of the concept of the asymmetric carbon atom to central atoms of any element.

Simpler statement: an atom that has all four different groups attached to it

(b) [6 pts] Do the below molecules have the chirality center (at ambient temperature)? Indicate the chirality center and rationalize your answer. R, R', R'', and R''' indicate the different functional groups.

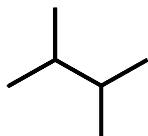
$N+RR'R''R'''$ $CRR'R''R'''$ $PRR'R''$ $NRR'R''$

(Answer)

From the IUPAC definition, $N+RR'R''R'''$, $CRR'R''R'''$, and $PRR'R''$ molecules have the chiral center (N, C, P, each case). However, the N-atom of $NRR'R''$ is not the chiral center as the inversion barriers of amines are typically low (usually 5~10 kcal/mol) and can be overcome at ambient temperatures. In the case of phosphines, the barriers are much higher (> 30 kcal/mol).

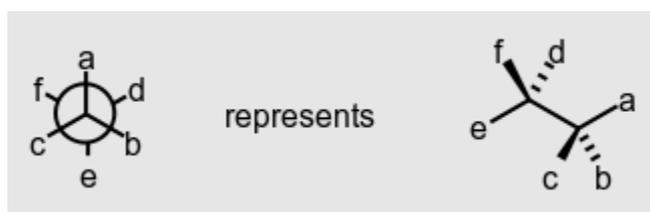
2. (total 12 pts)

(a) [4 pts] Draw two conformational isomers, the gauche form and the anti form of tetramethylethane using the Newman projections as we discussed with ethane and butane in the class.



tetramethylethane

(Newman projection: A projection formula representing the spatial arrangement of bonds on two adjacent atoms in a molecular entity. The structure appears as viewed along the bond between these two atoms, and the bonds from them to other groups are drawn as projections in the plane of the paper. The bonds from the atom nearer to the observer are drawn so as to meet at the centre of a circle representing that atom. Those from the further atom are drawn as if projecting from behind the circle.)

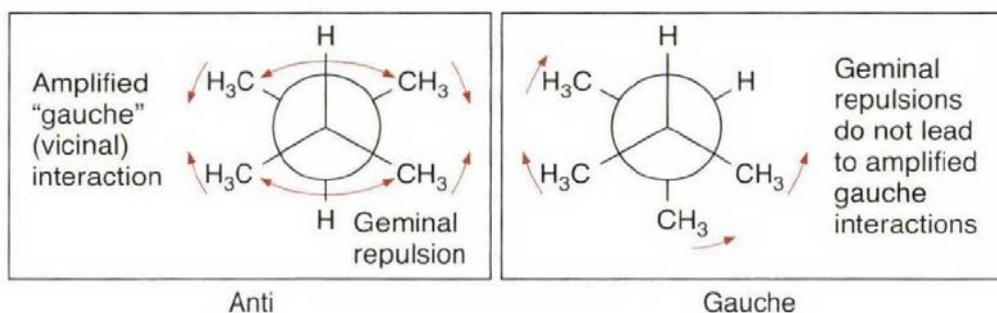


(answer) See the answer of (b).

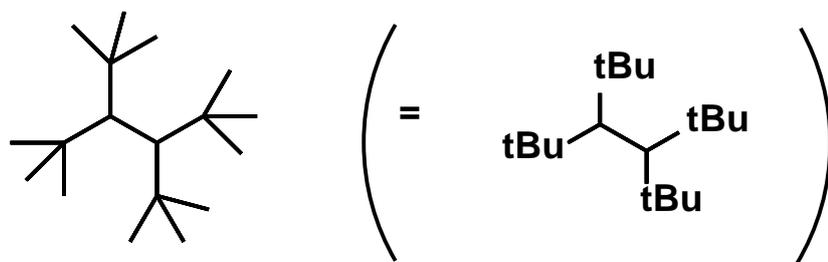
(b) [4 pts] Differently from the butane molecule, it is known that the gauche form is a little more stable than the anti form in the case of tetramethylethane (gauche : anti = 3:2 at 298K). Why do you think it is?

(answer)

From the Newman projection, you can see the $\text{CH}_3\text{-CH}_3$ interaction of the same C (called geminal repulsion) could exist. This geminal repulsion causes expansion of the C-C-C angle, leading to enhanced gauche butane-type interactions in the anti form. In the gauche form, such interaction can be relatively more relieved. (The students do not need to specify the term 'geminal' repulsion. Just conceptual explanation is enough for the credit.)

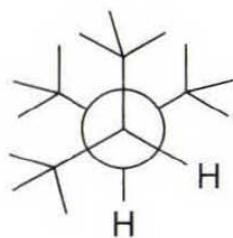


(c) [4 pts] In the case of 1,1,2,2-tetrakis(t-butyl)ethane, the one conformer is dominant at room temperature. Which form do you think is dominant? Rationalize your answer by drawing the Newman projection of the related conformers.



1,1,2,2-tetrakis(*t*-butyl)ethane

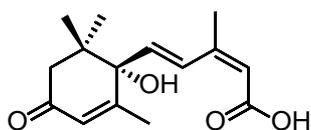
(answer) As discussed in (b), in the case of 1,1,2,2-tetrakis(*t*-butyl)ethane, the increased *t*-butyl maximized the geminal interaction so that the gauche form exists as the dominant form.



1,1,2,2-Tetrakis(*t*-butyl)ethane

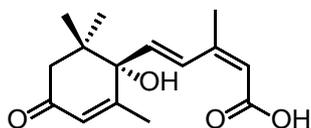
3. (total 10 pts)

Abscisic acid is one kind of plant hormones. The following figure is the structure of abscisic acid.



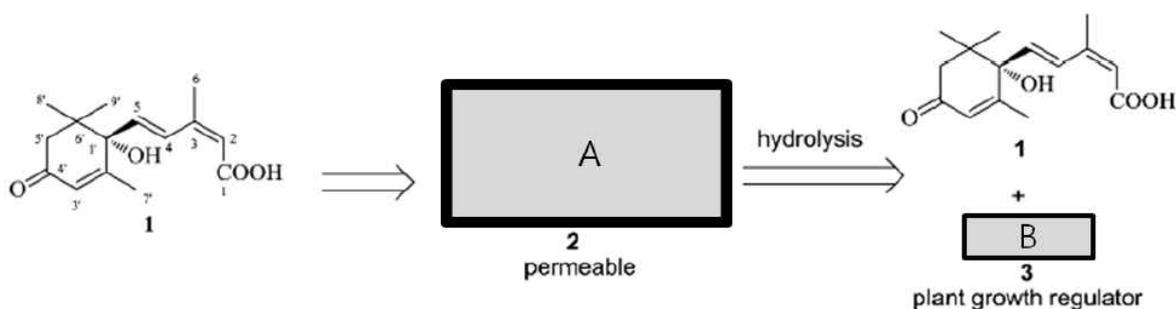
Answer the following questions.

(a) [2 pts] Mark all chiral centers in the following structure.



(b) [2 pts] What is the number of different stereoisomers of abscisic acid?

(c) [4 pts] The given structure above is not permeable for a plant to be used. So, the structure of abscisic acid should be converted into the permeable structure. The process of conversion is described below.

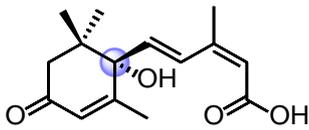


A has an ester group. Let's assume that a net change in the number of atoms is minimum in the reaction to produce **A**. What is the structure of **A** and **B**? **A** and **B** are different compounds. Substitute the unknown structure as R. (Reference: Wan Chaun and others (2015), "Synthesis and biological activity of abscisic acid esters")

(d) [2 pts] In the structure of **A** in problem (c), what is the minimum number of carbon with sp^2 hybridized orbital?

(Answer)

(a) The chiral center includes different four functional groups. So, the chiral center is only one in the abscisic acid like the following figure,



2 pts or 0 pt

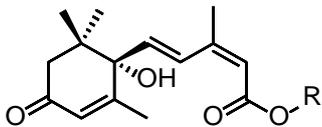
(b) On chiral center: OH and carbon chain can be converted. -> 2 cases

Cis-trans on carbon chain: $2 \times 2 = 4$

The answer is $2 \times 2 \times 2 = 8$

2 pts or 0 pt

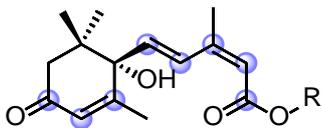
(c) When H is converted to R, the net change of atom's number is minimum. So, the structure of A is same as below.



And when hydrolysis occurs to convert A to original structure, R-OH is emitted. The structure of B is R-OH.

Structure of A: 2 pts, structure of B: 2 pts

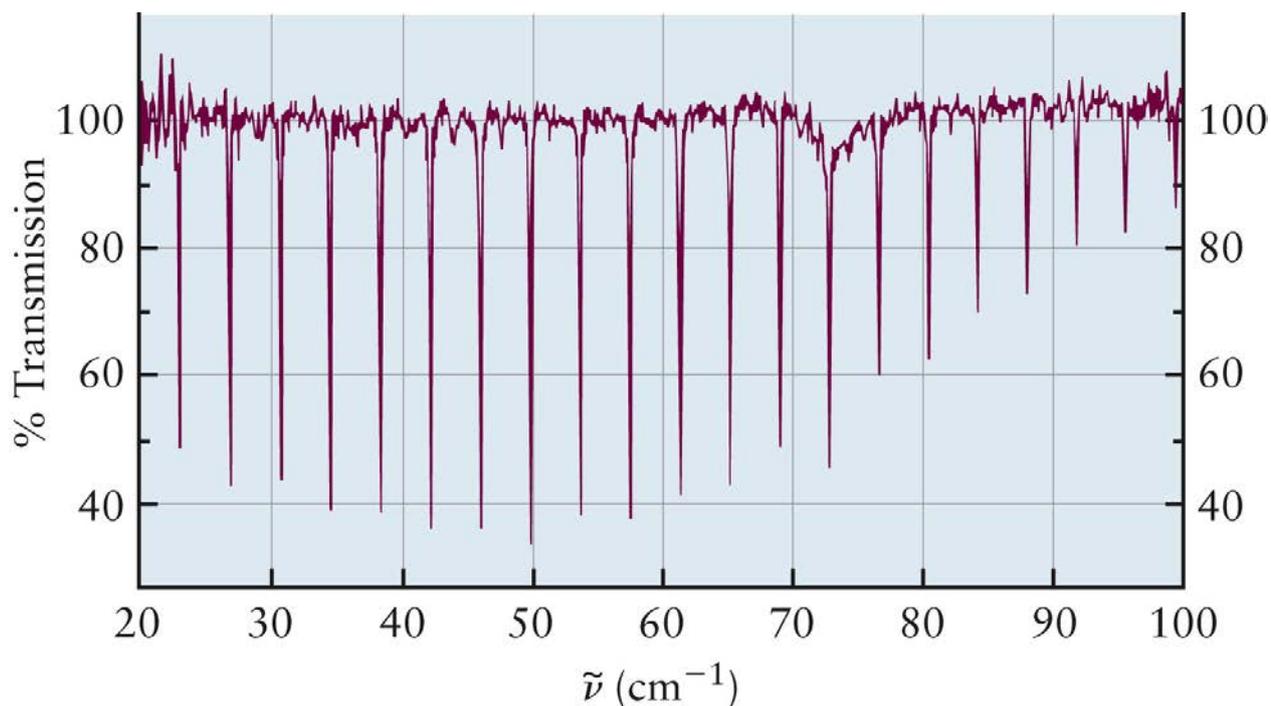
(d) The number of carbon with sp^2 hybridized orbital is same to or more than 8.



2 pts or 0 pt

4. (total 12 pts)

This is a microwave absorption spectrum of gas-phase CO.

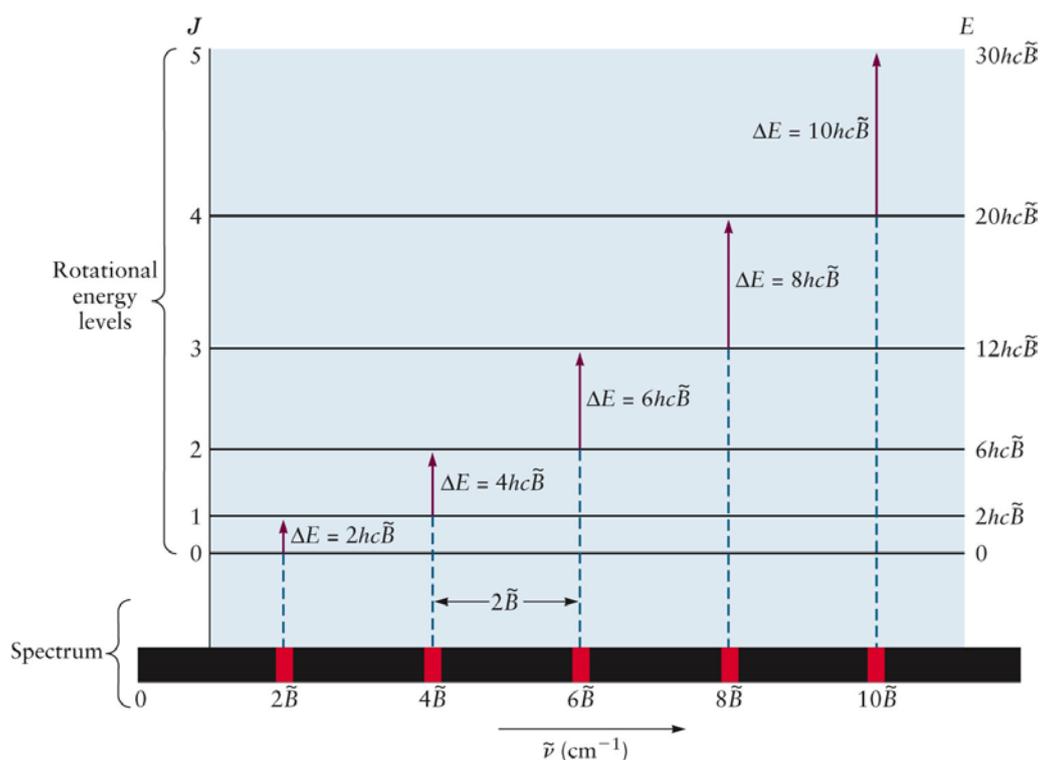


(a) [4 pts] Explain why the peaks are regularly observed in microwave absorption.

(Answer)

Microwave absorption corresponds to rotational transitions. From the selection rule for rotational absorption, the allowed frequencies are indicated as the equations below. By applying this rule to the spectra, the rotational allowed transitions for a heterodiatomic molecule can be predicted to be almost equally spaced ($2\tilde{B}$) wavenumbers.

$$\begin{aligned}\Delta\tilde{\nu} &= \tilde{B}[J_f(J_f + 1) - J_i(J_i + 1)] \\ &= \tilde{B}[(J_i + 1)(J_i + 2) - J_i(J_i + 1)] \\ &= 2\tilde{B}(J + 1)\end{aligned}$$



(b) [8 pts] By analyzing the spectra, please calculate the bond length of CO. (The atomic mass of C and O is 12.01 g/mol and 16.00 g/mol respectively.)

(Answer)

$$2\tilde{B} \approx 30/8 \text{ cm}^{-1} \text{ (from spectra)}$$

$$\tilde{B} \approx \frac{15}{8} \text{ cm}^{-1} \approx 1.875 \times 10^2 \text{ m}^{-1} = \frac{h}{8\pi^2 c I}$$

$$I = \mu R_e^2$$

$$\mu = \frac{m_c m_o}{m_c + m_o} = 1.14 \times 10^{-26} \text{ kg}$$

$$R_e^2 = \frac{h}{8\pi^2 c \mu \tilde{B}} \approx 1.30 \times 10^{-20} \text{ m}^2$$

$$R_e \approx 1.14 \times 10^{-10} \text{ m} \approx 1.14 \text{ \AA}$$

Even if the other value of $2B$ was used, full credits are given as long as the equations and logics are correct

5. (total 8 pts) Answer the following questions.

(a) [2 pts] Describe the vibrational degrees of freedom in linear molecule and nonlinear molecule.

(Answer)

linear molecule: $3N-5$, nonlinear molecule: $3N-6$

(b) [6 pts] Explain the reason why this formula is correct. Explain with the modes of translational, vibrational and rotational mode.

(Answer)

step 1) Find the regularity of the degree of freedom.

In monoatomic molecules, the degrees of freedom is 3. Because it can move to x,y,z axis for three directions.

In diatomic molecules, the degrees of freedom is 6. The diatomic molecule consists of two monoatomic molecules, so we sum up each degrees of freedom together($3+3=6$)

In triatomic molecules, using the same calculation with diatomic molecule, we get 9.

Therefore, we can generalize the degrees of freedom of the molecule which has N atoms as $3N$.

step 2) Calculate the rotational mode and subtract the degrees of freedom in translational mode and rotation mode from total degrees of freedom in all modes.

linear mode:

	linear molecule	nonlinear molecule
translational mode	3	3
vibrational mode	x	y
rotational mode	2	3

$$x=3N-(3+2)=3N-5$$

$$y=3N-(3+3)=3N-6$$

In linear molecule, the degrees of freedom of the rotational mode is 2. Because the rotation centering on the axis doesn't change the energy so it cannot be included in rotation degrees of freedom.

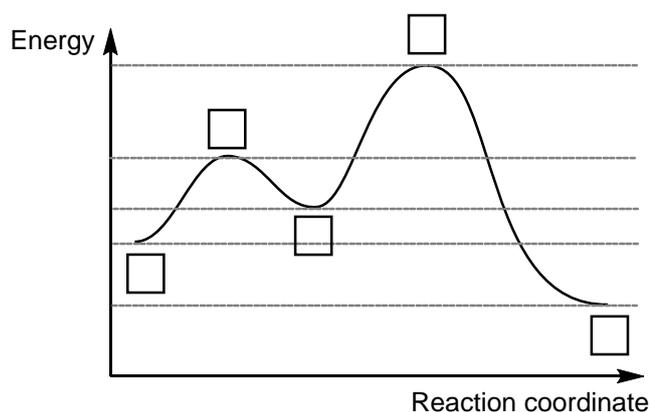
On the contrast, in nonlinear molecule, the axis centered rotation has energy too, so the degrees of freedom should be 3.

What we want to know is the degrees of freedom in vibrational mode, then we have to calculate like below.

(Total degrees of freedom) - (degrees of freedom in translational mode + degrees of freedom in rotational mode)

6. (total 10 pts)

The energy profile for a certain reaction is



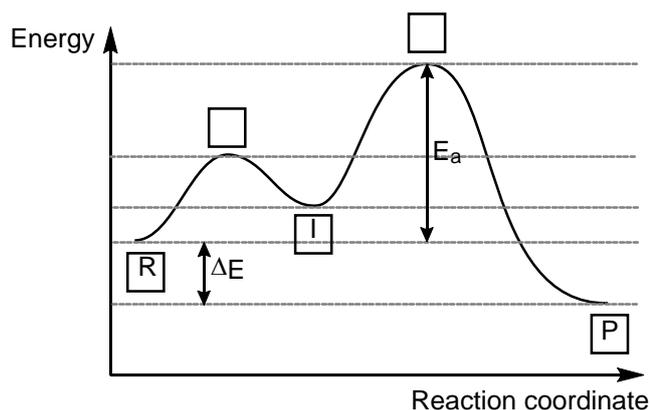
On the energy profile, indicate

(a) [3 pts] The positions of reactant(s) (R), intermediate(s) (I), and product(s) (P).

(b) [2 pts] The activation energy for the overall reaction (E_a).

(c) [2 pts] ΔE for the reaction.

(Answer)



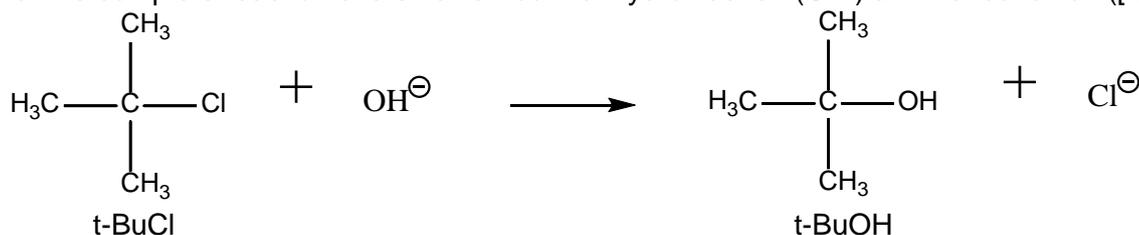
(d) [3 pts] Which step in the mechanism for this reaction is the rate determining step, the first or the second step? Explain the reason including the given keywords.

Keywords: slow, activation energy, rate determining step

(Answer)

In a reaction mechanism, the rate of the slowest step determines the rate of the reaction. The activation energy for the slowest step will be the largest energy barrier that the reaction must overcome. Since the second hump in the diagram is at the highest energy, the second step has the largest activation energy and is the rate determining step (the slow step).

7. (total 12 pts) Conversion of t-butyl chloride (t-BuCl) to t-butyl alcohol (t-BuOH) is a typical example of substitution reaction in organic reactions. The reaction durations were measured at 23°C for the complete reaction of a small amount of hydroxide ion (OH⁻) at initial condition ([M]₀).



Run	[t-BuCl] ₀ (M)	[OH ⁻] ₀ (M)	Time t (sec)	Temp (°C)
1	0.020	0.0040	28	23
2	0.010	0.0040	53	23
3	0.020	0.0020	13	23
4	0.020	0.0040	7	37

a) [4 pts] Use these data to obtain the rate law for this reaction.

(Answer)

The rate law is given in the following form.

$$\text{Rate} = -d[\text{OH}^-]/dt = k [\text{t-BuCl}]^m [\text{OH}^-]^n$$

Initial rate of the reaction (-d[OH⁻]/dt) is calculated as follows.

$$\text{Run 1} - \left\{ \frac{[\text{OH}^-] - [\text{OH}^-]_0}{dt} \right\} = - \left\{ \frac{0.0 - 0.0040}{28} \right\} = 1.43 \times 10^{-4} \text{ M/sec.}$$

Run	[t-BuCl] ₀ (M)	[OH ⁻] ₀ (M)	Time t (sec)	Initial rate -d[OH ⁻]/dt (M/sec)
1	0.020	0.0040	28	1.43 × 10 ⁻⁴
2	0.010	0.0040	53	0.75 × 10 ⁻⁴
3	0.020	0.0020	13	1.54 × 10 ⁻⁴
4	0.020	0.0040	7	5.71 × 10 ⁻⁴

Comparing the data of run 1 and run 2, we see that halving [t-BuCl]₀ halves the rate (m = 1), while the data of run 1 and run 3 show that halving [OH⁻]₀ has almost no effect on the rate (n = 0).

$$\text{Rate} = k [\text{t-BuCl}]$$

(b) [2 pts] Calculate the rate constant at 23 °C.

(Answer)

$$\text{average } k = 7.45 \times 10^{-3} \text{ sec}^{-1}$$

$$(\text{Run 1: } k = 7.15 \times 10^{-3} \text{ sec}^{-1}, \text{ Run 2: } k = 7.5 \times 10^{-3} \text{ sec}^{-1}, \text{ Run 3: } k = 7.7 \times 10^{-3} \text{ sec}^{-1})$$

OR

$$\int_{[\text{t-BuCl}]_0}^{[\text{t-BuCl}]} \frac{d[\text{t-BuCl}]}{[\text{t-BuCl}]} = \int_0^t -k dt$$

$$\ln \frac{[\text{t-BuCl}]}{[\text{t-BuCl}]_0} = -kt$$

$$\text{From Run 1, } [\text{t-BuCl}]_0 = 0.02 \text{ M, } [\text{t-BuCl}] = 0.016 \text{ M, } t = 28; k = 7.97 \times 10^{-3} \text{ sec}^{-1}$$

$$\text{From Run 2, } [\text{t-BuCl}]_0 = 0.01 \text{ M, } [\text{t-BuCl}] = 0.006 \text{ M, } t = 53; k = 9.64 \times 10^{-3} \text{ sec}^{-1}$$

$$\text{From Run 3, } [\text{t-BuCl}]_0 = 0.02 \text{ M, } [\text{t-BuCl}] = 0.018 \text{ M, } t = 13; k = 8.10 \times 10^{-3} \text{ sec}^{-1}$$

$$\text{Average } k = 8.57 \times 10^{-3} \text{ sec}^{-1}$$

(c) [6 pts] When the reaction was carried out at 37°C (Run 4), the measured reaction time was 7 sec. Find the rate constant k at 37 °C and estimate the activation energy E_a and preexponential factor A for this reaction.

(Answer)

Considering $k = 7.45 \times 10^{-3} \text{ sec}^{-1}$

The rate constant k at 37°C is $28.5 \times 10^{-3} \text{ sec}^{-1}$, and from the following equation, ($T_1 = 296\text{K}$) and $T_2 = 310\text{K}$), E_a is 18 kcal/mol.

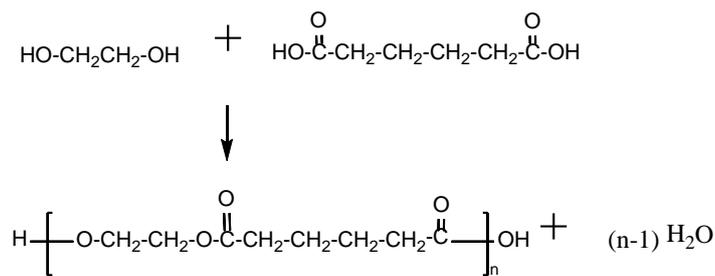
$$\ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

From Arrhenius equation, $k = A \exp(-E_a/RT)$,
 A is $1.4 \times 10^{11} \text{ sec}^{-1}$.

2 pts each

*** Even if the other value of k is used, full credits are still given if all the logics and equations used are correct.

8. (10 pts) In an acid catalyzed polymerization of ethylene glycol ($[\text{HO-CH}_2\text{-CH}_2\text{-OH}]$ ($[\text{A}]_0 = 1.0 \text{ M}$)) and adipic acid ($[\text{HOOC-(CH}_2)_4\text{-COOH}]$ ($[\text{B}]_0 = 1.0 \text{ M}$)) in equimolar amount at 109 °C, the number average degree of polymerization (DP) of poly(ethylene adipate) product was found to increase from 8 at 1 min to 50 at 300 min. All conditions were held constant, and number average degree of polymerization (DP) X_n is given as follow: $X_n = N_0/N = [\text{A}]_0/[\text{A}] = 1/(1-p)$



a) [5 pts] Determine the rate constant k as defined by:

$$-d[\text{A}]/dt = k [\text{A}] [\text{B}],$$

where the concentrations are in [mol/L] and time t is in [sec].

(Answer)

$$-d[\text{A}]/dt = k [\text{A}] [\text{B}] = k [\text{A}]^2 \text{ (ethylene glycol: A, adipic acid: B, } [\text{A}] = [\text{B}] \text{)}$$

It is a second order reaction.

$$1/[\text{A}] - 1/[\text{A}]_0 = k t$$

$$X_n = 1 + [\text{A}]_0 k t \text{ (because } X_n = N_0/N = [\text{A}]_0/[\text{A}] \text{)},$$

$$X_{n, t_2} - X_{n, t_1} = (1 + [\text{A}]_0 k t_2) - (1 + [\text{A}]_0 k t_1) = [\text{A}]_0 k (t_2 - t_1)$$

$$t_1 = 1 \text{ min, and } t_2 = 300 \text{ min, } (t_2 - t_1) = 300 - 1 = 299 \text{ min} = 17,940 \text{ sec}$$

$$X_{n, t_2} = 50 \text{ and } X_{n, t_1} = 8$$

$$42 = [\text{A}]_0 k 17940 = 17940 k \text{ (} [\text{A}]_0 = 1 \text{ M)}$$

$$k = 2.34 \times 10^{-3} \text{ (L mol}^{-1} \text{ sec}^{-1}\text{)}$$

b) [5 pts] The equilibrium constant $K = \frac{[-\text{COO}^-][\text{H}_2\text{O}]}{[-\text{COOH}][-\text{OH}]}$ is 1 at 109 °C. What molar ratio (Y) of water to carboxylic acid end group concentration ($Y = \frac{[\text{H}_2\text{O}]}{[-\text{COOH}]}$) would lead to an equilibrium value of DP (\bar{X}_n) = 50 at 109 °C?

(Answer)

$$\begin{aligned} K &= \frac{[-\text{COO}^-][\text{H}_2\text{O}]}{[-\text{COOH}][-\text{OH}]} \\ &= Y \frac{[-\text{COO}^-]}{[-\text{OH}]} \quad (\text{because } Y = \frac{[\text{H}_2\text{O}]}{[-\text{COOH}]}) \\ &= Y \left\{ \frac{p[A]_0}{(1-p)[A]_0} \right\} \end{aligned}$$

(because $[-\text{OH}]$ is the concentration of remaining $-\text{OH}$ group, and $[-\text{COO}^-]$ is equal to the concentration of reacted $-\text{OH}$ group at time t)

$$Y = K / \left\{ \frac{p[A]_0}{(1-p)[A]_0} \right\} = K / \left\{ \frac{p}{(1-p)} \right\}$$

(because $K = 1$, and $1/(1-p) = \bar{X}_n = 50$, $p = 0.98$)

$$Y = 1 / \left\{ \frac{0.98}{(1-0.98)} \right\} = 0.02 / 0.98 = 2.04 \times 10^{-2}$$

9. (total 6 pts)

Paraffins and polyethylenes consisting of methylene repeating units have very different molecular weights and show very different mechanical properties. Even though both of them are solids at room temperature, polyethylene is tough while paraffin can be deformed easily. Explain these very different mechanical properties with at least two reasons.

(Answer)

i) Tie molecules (tie polymer chains) in the crystalline region and ii) chain entanglements in the amorphous region of polymers make polymeric materials very strong and tough. (Secondary interaction (van der Waals force) among polyethylene chains is not a major factor).

3 pts for each reason

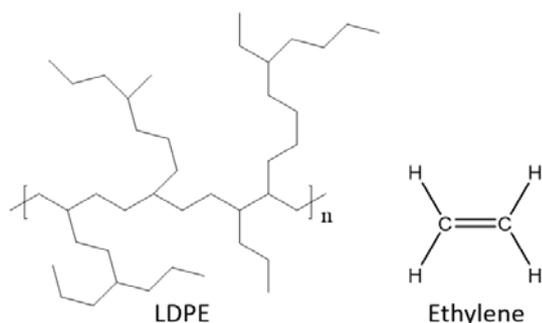
10. (total 12 pts)

a) [8 pts] Draw a representative molecular structure of the following polymers and the corresponding monomer for each polymer.

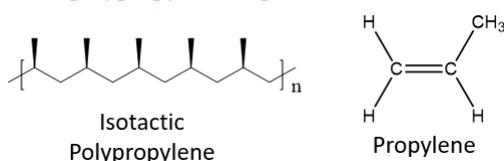
- (1) Low density polyethylene (LDPE)
- (2) Isotactic polypropylene
- (3) Polyethylene terephthalate (PET)
- (4) Poly(hexamethylene adipamide) (nylon 66)

(Answer)

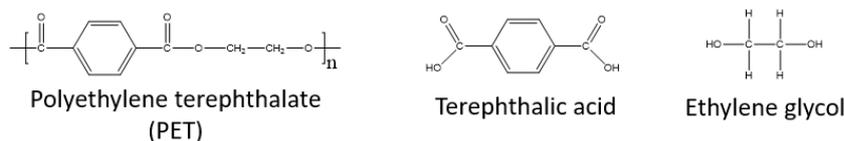
- (1) Low density polyethylene (LDPE) [2 pts]



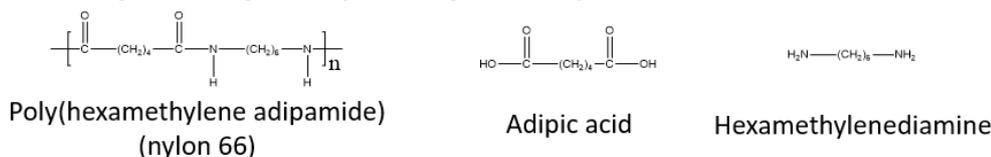
- (2) Isotactic polypropylene [2 pts]



- (3) Polyethylene terephthalate (PET) [2 pts]



- (4) Poly(hexamethylene adipamide) (nylon 66) [2 pts]



b) [4 pts] Describe the difference in the synthesis method of two polymers.

- (1) Low density polyethylene (LDPE) and High density polyethylene (HDPE)
- (2) Polyethylene (PE) and Polyethylene terephthalate (PET)

Answer

(1) Both LDPE and HDPE are synthesized with addition polymerization method. LDPE is synthesized with free-radical-initiated addition polymerization in high temperature and pressure, which introduces heavily branched polyethylene with an imperfect linear chain. In contrast to LDPE,

HDPE is synthesized using a Ziegler catalyst to lower the reaction temperature and pressure. As a result, linear polyethylene with fewer branches is synthesized.

(2) Polyethylene is synthesized with addition polymerization. This polymerization is chain-growth polymerization that proceeds through a free-radical mechanism. The free radical mechanism of addition polymerization is completed by three steps: Initiation, propagation, and termination.

Polyethylene terephthalate is synthesized with condensation polymerization. This polymerization is a step-growth polymerization that proceeds through condensation reaction where monomers join together and lose small molecules as byproducts.

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ \AA} = 5.2917720859 \times 10^{-11} \text{ m}$
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19} \text{ C}$
Faraday constant	$F = 96485.3399 \text{ C mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31} \text{ kg}$
Proton	$m_P = 1.672621637 \times 10^{-27} \text{ kg}$
Neutron	$m_n = 1.674927211 \times 10^{-27} \text{ kg}$
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	$m_P / m_e = 1836.15267247$
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	$R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1}$

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

Conversion factors

Ångström	$1 \text{ \AA} = 10^{-10} \text{ m}$
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 form $E = mc^2$)
Calorie	$1 \text{ cal} = 4.184 \text{ J}$ (exactly)
Electron volt	$1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J} = 96.485335 \text{ kJ mol}^{-1}$
Foot	$1 \text{ ft} = 12 \text{ in} = 0.3048 \text{ m}$ (exactly)
Gallon (U. S.)	$1 \text{ gallon} = 4 \text{ quarts} = 3.785412 \text{ L}$ (exactly)
Liter	$1 \text{ L} = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3$ (exactly)
Liter-atmosphere	$1 \text{ L atm} = 101.325 \text{ J}$ (exactly)
Metric ton	$1 \text{ t} = 1000 \text{ kg}$ (exactly)
Pound	$1 \text{ lb} = 16 \text{ oz} = 0.4539237 \text{ kg}$ (exactly)
Rydberg	$1 \text{ Ry} = 2.17987197 \times 10^{-18} \text{ J} = 1312.7136 \text{ kJ mol}^{-1} = 13.60569193 \text{ eV}$
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	$1 \text{ torr} = 133.3224 \text{ Pa}$

2021 Fall Semester Final Examination
For General Chemistry II

Date: Dec 15 (Wed), **Time Limit:** 19:00 ~ 22:00

NOTICE

- If you have a printer, print the papers and write the answers in the space of each question. If not, prepare several A4-size papers to write only question # and the answers on it in the following example. And for clarity, marking your answer is recommended. Please, print your Student ID in the upper right corner of every page for both of them. (*Handwriting only is acceptable* and typing is not.)

Example:

Professor Name	Class	Student I.D. Number	Name

#1. (a).....

(b).....

- If you have any questions during the period, please contact the TA of your class using the Zoom chat channel to “Everyone” (the only possible choice). Proctors will make any announcements relevant to all students *via* audio.
- While still in the video conference, submit your file to [Final Examination], an assignment on Turnitin of your class. **Do not leave the video conference** until your TA is confirmed and tells you that it is fine to leave.

** This paper consists of 13 sheets with 10 problems (page 12 - 13: Equation, constants & periodic table). Please check all page numbers before taking the exam. Please write down the unit of your answer when applicable. You will get 30% deduction for a value that is missing its unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.
(채점 답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure

- 1) Return and Claim Period: **Dec 18 (Sat 12:00~24:00)**
- 2) **Location: Each class of Turnitin site (online)**
- 3) Procedure: If you have any claims on it, email them (Question# and reasons) to your designated TA.
(The claim is permitted only during the designated claim period. Keep that in mind! A solution file with answers for the examination will be uploaded on the web.)

2. Final Confirmation

- 1) Period: **Dec 20 (Mon 12:00 ~ 24:00)**
- 2) Procedure: During this period, you can check final score of the examination *on the website* again.
(No additional corrections. If no change in your score after reasoning, the claims were not accepted.)

** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr

1. (total 8 pts) For each inorganic compound below, write the formula or name, the coordination number of the metal ion, and the number of individual ions per formula unit:

Formula	Name	Coordination Number
(a) $K_2[Cr(OH_2)_2(C_2O_4)_2]$		
(b) $[Ir(CO)Cl(PPh_3)_2]$		
(c)	pentaamminecarbonatocobalt(III) bromide	
(d)	sodium hexafluoroaluminate	

2 pts each

Formula	Name	Coordination Number
$K_2[Cr(OH_2)_2(C_2O_4)_2]$	potassium diaquabis(oxalato)chromate(II)	6
$[Ir(CO)Cl(PPh_3)_2]$	Carbonylchlorobis(triphenylphosphine)iridium(I)	4
$[Co(NH_3)_5(CO_3)]Br$	pentaamminecarbonatocobalt(III) bromide	6
$Na_3[AlF_6]$.	sodium hexafluoroaluminate	6

2. (Total 12 pts) Complete electron configurations and fill in the blank related to energy level structures and crystal field stabilization energies for high and low spin octahedral complexes.

Example		(a) Mn ²⁺	(b) Ni ³⁺	(c) Ti ²⁺
d-orbital electron configuration				
HIGH SPIN	Energy diagram	e _g _____ t _{2g} _____	e _g _____ t _{2g} _____	e _g _____ t _{2g} _____
	CFSE			
LOW SPIN	Energy diagram	e _g _____ t _{2g} _____	e _g _____ t _{2g} _____	e _g _____ t _{2g} _____
	CFSE			

[Solution] (4pts each)

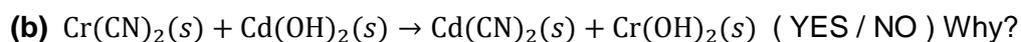
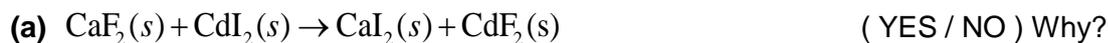
TABLE 8.5

Electron Configurations and Crystal Field Stabilization Energies for High- and Low-Spin Octahedral Complexes

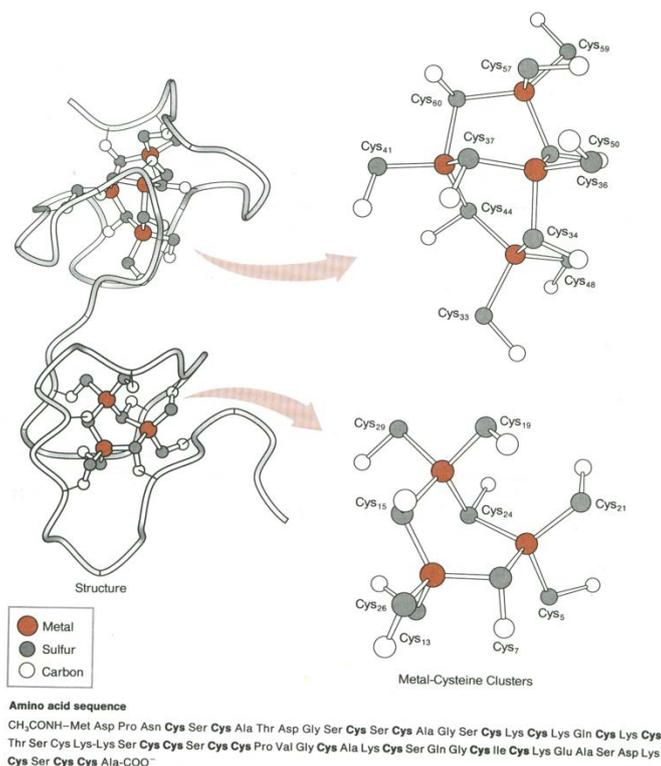
Configuration	d ¹	d ²	d ³	d ⁴	d ⁵	d ⁶	d ⁷	d ⁸	d ⁹	d ¹⁰
Examples	Ti ³⁺	Ti ²⁺ , V ³⁺	V ²⁺ , Cr ³⁺	Cr ²⁺ , Mn ³⁺	Mn ²⁺ , Fe ³⁺	Fe ²⁺ , Co ³⁺	Co ²⁺ , Ni ³⁺	Ni ²⁺ , Pt ²⁺	Cu ²⁺	Zn ²⁺
HIGH SPIN	e _g	_____	_____	_____	↑↑	↑↑	↑↑	↑↑	↑↓↑	↑↓↑↓
	t _{2g}	↑	↑↑	↑↑↑	↑↑↑	↑↑↑	↑↓↑↑	↑↓↑↓	↑↓↑↓	↑↓↑↓
	CFSE	- $\frac{2}{5} \Delta_o$	- $\frac{4}{5} \Delta_o$	- $\frac{6}{5} \Delta_o$	- $\frac{3}{5} \Delta_o$	0	- $\frac{2}{5} \Delta_o$	- $\frac{4}{5} \Delta_o$	- $\frac{6}{5} \Delta_o$	- $\frac{3}{5} \Delta_o$
LOW SPIN	e _g			_____	_____	_____	↑			
	t _{2g}			↑↑↑	↑↓↑↑	↑↓↑↓	↑↓↑↓			
	CFSE	Same as high spin			- $\frac{8}{5} \Delta_o$	- $\frac{10}{5} \Delta_o$	- $\frac{12}{5} \Delta_o$	- $\frac{9}{5} \Delta_o$	Same as high spin	

CFSE, Crystal field stabilization energies.

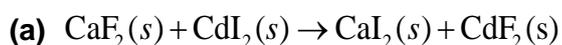
3. (total 6 pts) Use the hard / soft acid / base concept to predict whether the following reactions will occur.



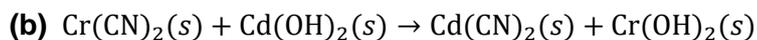
(c) Which metal ion (Hg²⁺ or Fe³⁺) would be favored to bind to metallothionein (MT; structure shown below)? Why?



[Solution] (2 pts each)



(YES / **NO**) Calcium is a hard acid that prefers to bond to the hard base F⁻.



(**YES** / NO) Chromium is a hard acid that prefers to bond to the hard base OH⁻.

(c) **Hg²⁺**

Cysteine (Cys) is a soft base that prefers to bond to the soft acid Hg²⁺.

4. (total 16 pts) The octahedral complex ions $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{Fe}(\text{CN})_6]^{3-}$ are all paramagnetic. But $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{OH}_2)_6]^{3+}$ are high spin and $[\text{Fe}(\text{CN})_6]^{3-}$ is low spin. Answer for each question below.

(a) [10 pts] Draw an orbital energy-level diagram for each octahedral complex ion (show how to get the oxidation numbers for Fe ions in each complex).

(b) [3 pts] Predict the number of unpaired electrons for each complex.

(c) [3 pts] Place which of the complexes has the shorter absorption λ_{max} in order and explain your answer.

[Solution]

(a) * Electron configuration of Fe: $[\text{Ar}] 3d^6 4s^2$

* The oxidation numbers of $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{Fe}(\text{CN})_6]^{3-}$ molecules

$$[\text{FeF}_6]^{3-} : x + 6(-1) = -3, \quad x = +3 \text{ (+1 pt)}$$

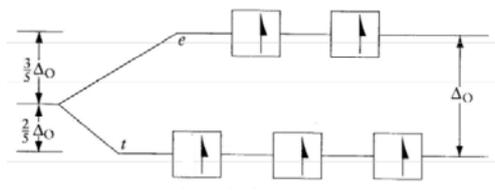
$$[\text{Fe}(\text{OH}_2)_6]^{3+} : x + 6(0) = +3, \quad x = +3 \text{ (+1 pt)}$$

$$[\text{Fe}(\text{CN})_6]^{3-} : x + 6(-1) = -3, \quad x = +3 \text{ (+1 pt)}$$

* Electron configuration of Fe^{3+} : $[\text{Ar}] 3d^5 \rightarrow 5 \text{ d electrons (+1 pt)}$

* The orbital energy-level diagrams of $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{OH}_2)_6]^{3+}$ (high spin)

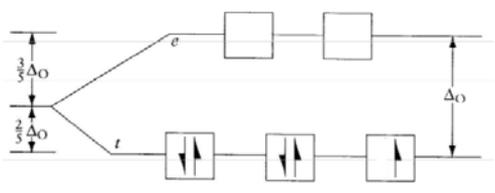
* the configuration of *d*-electrons: $t_{2g}^3 e_g^2$



+2 pts for each correct diagram

* The orbital energy-level diagram of $[\text{Fe}(\text{CN})_6]^{3-}$ (low spin)

* the configuration of *d*-electrons: t_{2g}^5



+2 pts for the correct diagram

(b) The number of unpaired electrons and the magnetic property of $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{Fe}(\text{CN})_6]^{3-}$

$$[\text{FeF}_6]^{3-} : 5 \text{ unpaired electrons} \rightarrow \text{paramagnetic}$$

$[\text{Fe}(\text{OH}_2)_6]^{3+}$: 5 unpaired electrons \rightarrow paramagnetic

$[\text{Fe}(\text{CN})_6]^{3-}$: 1 unpaired electron \rightarrow paramagnetic

(c) $[\text{Fe}(\text{CN})_6]^{3-}$ has the strongest field ligands of the three complexes; thus, its energy levels are split by the greatest amount. The energy of the light absorbed should be greatest, and λ_{max} should be the shortest for this ion.

λ_{max} : $[\text{FeF}_6]^{3-} > [\text{Fe}(\text{H}_2\text{O})_6]^{3+} > [\text{Fe}(\text{CN})_6]^{3-}$

5. (total 8 pts) The coordination compound which has the molecular formula of $\text{KCo}(\text{CrO}_4)\text{Cl}_2(\text{NH}_3)_4$ possesses following properties.

1. There are two geometric isomers: A (red) and B (blue).
2. 1 mol of A or 1 mol of B can completely react with 2 mol of AgNO_3 and give 1 mol of red precipitate.
3. 1 mol of $\text{Ag}_2\text{C}_2\text{O}_4$ can react with complex ion of A and give 2 mol of white precipitation, but complex ion of B cannot react with $\text{Ag}_2\text{C}_2\text{O}_4$.

Hint: AgNO_3 can react with either CrO_4^{2-} or Cl^- to yield the precipitate.

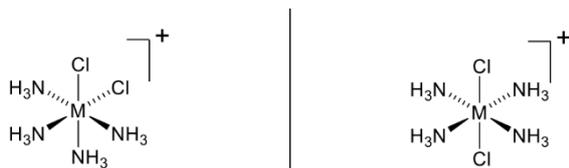
- (a) Draw the structures of complex ions of A and B.
- (b) Do A and B have any optical isomers?
- (c) Determine the oxidation state of the metal center.

Answer

From 2, we will know that the red precipitation is Ag_2CrO_4 . Therefore, the counter ions of this coordination compounds are K^+ and CrO_4^{2-} . The ligands are 2 Cl^- and 4 NH_3 .

From 3, we will know that A should be *cis*-isomer since $\text{C}_2\text{O}_4^{2-}$ is chelating ligand that can substitute 2 Cl^- in the *cis* position. Those 2 Cl^- will react with 2 Ag^+ to give the white precipitate of silver chloride.

(a) (6 pts)



If the overall charge is not correctly indicated, -1 pt

If which is A and which is B is not clearly indicated, -1 pt

If identity of A or B is only vaguely described (e.g. B is either a *cis* or *trans* isomer, etc.), no pts

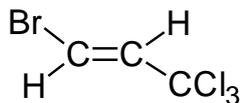
(b) No (1 pts)

(c) oxidation state of cobalt = +3 (1 pts)

(the oxidation state of Cr (VI) was not considered in grading)

6. (total 10 pts) How many lines appear in the proton NMR spectrum? Include signals arising from both the chemical shift and J couplings.

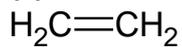
(a)



(b)



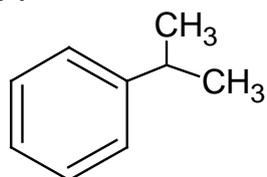
(c)



(d)



(e)



(Note: Consider the signal from the protons on benzene rings to have one line.)

(Sol) (2 pts each)

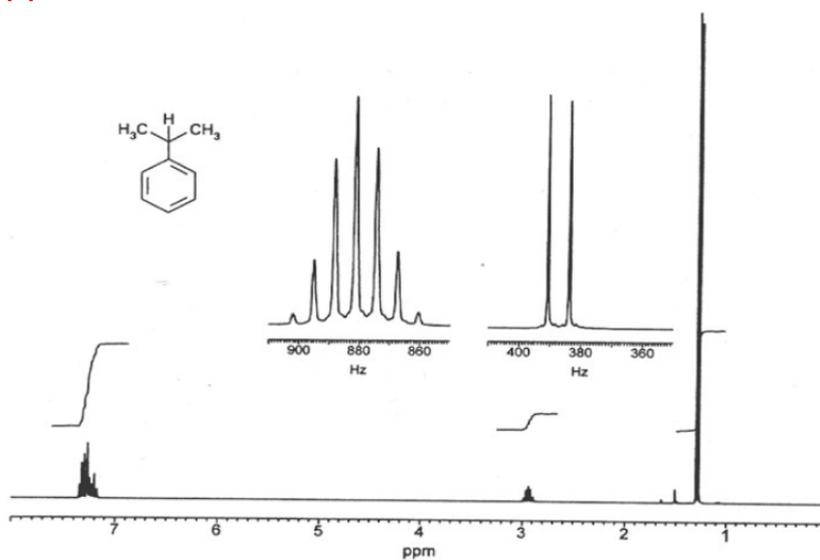
(a) 4

(b) 1

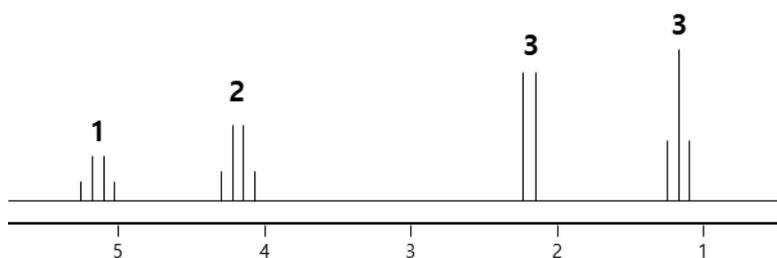
(c) 1

(d) 8

(e) 10



7. (total 8 pts) Determine the structure of compound A with molecular formula $C_5H_9O_4N$ using proton NMR spectrum shown below.



(Sol)

4 groups of hydrogen

Quadruplet on ~5 ppm: 1 hydrogen adjacent to 3 hydrogens

Quadruplet on ~4 ppm: 2 hydrogens adjacent to 3 hydrogens

Doublet on ~2 ppm: 3 hydrogens adjacent to 1 hydrogen -> methyl group

Triplet on ~1 ppm: 3 hydrogens adjacent to 2 hydrogens -> methyl group

Two methyl groups must be separate to each other

No singlet: there are no -OH protons or -NH protons

Quadruplet on ~4 ppm is highly deshielded -> $R_1COOCH_2R_2$

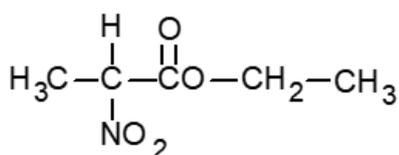
Since the methyl group must be adjacent to 2 hydrogens, $R_2 = -CH_3$

For R_1 , 2 carbons, 4 hydrogens, 2 oxygens, and 1 nitrogen remain

1 carbon belongs to a main backbone of a carbon chain

One methyl group must be attached to this carbon

Naturally, 1 hydrogen and -NO₂ must be attached to the same carbon



8. (total 8 pts)

Consider the following amino acid and its pK_a values:

N

($pK_{a1}=2.18$, $pK_{a2}=8.95$, $pK_{aR}=10.79$)

Draw the structure of the amino acid as the pH of the solution changes from highly acidic to strongly basic.

(Sol) (2 pts each)

N

N

N

N

9. (total 10 pts)

(a) Given an enzyme with K_M of 0.3 mM, at what substrate concentration will the velocity of the enzyme reach half of the V_{max} ? ($V_{max} = 215 \text{ mmol s}^{-1}$)

(5 pts)

$K_M = 0.3 \text{ mM}$, $V_{max} = 215 \text{ mmol s}^{-1}$, $V_0 = 1/2(V_{max}) = 107.5 \text{ mmol s}^{-1}$ +1pt

$$V_0 = \frac{V_{max}[S]}{K_m + [S]}$$

$$107.5 = (215[S])/(0.3+[S])$$

$$1/2 = [S]/(0.3+[S])$$

$$2[S] = 0.3 + [S] \text{correct calculations +1pt}$$

$$[S] = 0.3 \text{ mM+3 pt}$$

(b) The conversion of dissolved carbon dioxide in blood to HCO_3^- and H_3O^+ is catalyzed by the enzyme carbonic anhydrase. The Michaelis–Menten constants for this enzyme and substrate are $K_m = 4.5 \times 10^{-5} \text{ mol L}^{-1}$ and $k_2 = 3.3 \times 10^5 \text{ s}^{-1}$. What is the maximum rate of reaction of carbon dioxide if the enzyme concentration is $2.7 \times 10^{-6} \text{ M}$?

(5 pts)

$$d[\text{CO}_2]/dt = k_2[E]_0 \text{ (where E = carbonic anhydrase)}$$

$$= (3.3 \times 10^5 \text{ s}^{-1})(2.7 \times 10^{-6} \text{ M})$$

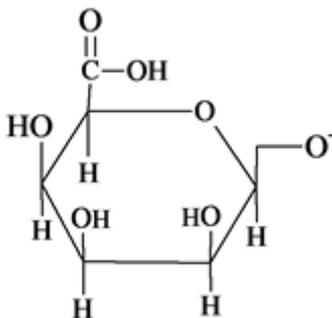
$$= 8.91 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}$$

3 pt for correct substitution to equation

2pts for correct answer

10. (total 14 pts)

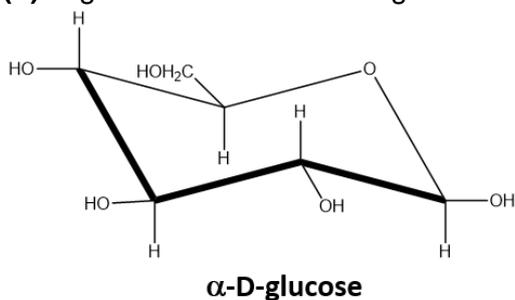
(a) Alginate, isolated from seaweed and used as a thickening agent for ice cream and other foods, is a polymer of D-mannuronic acid with β (1,4) glycosidic linkages.



D-mannuronic acid

- (1) Draw the structure of alginate.
- (2) Why does this substance act as a thickening agent?

(b) D-glucose exists in two ring forms in solution, which interconvert via an open chain form.



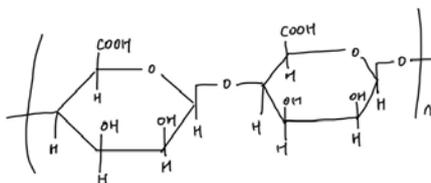
Draw the molecular structure of the open chain form of D-glucose, and indicate the chiral centers in the open-chain D-glucose. Estimate how many enantiomers can be possible from this molecule?

(Sol)

(a)

(1) (4 pts)

○



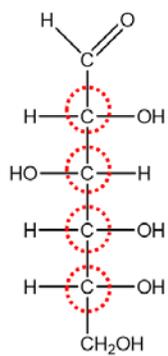
Two are the only accepted answers, no partial points

(2) The polymer acts to **immobilize water** through extensive **hydrogen bonding**. **(2 pts)**

(b) (8 pts)

Indicate chiral center and molecular structure \rightarrow 6 points

Number of enantiomers → 2 point



There are 4 chiral centers, therefore, $2^4 = 16$ conformers can be possible.

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ \AA} = 5.2917720859 \times 10^{-11} \text{ m}$
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19} \text{ C}$
Faraday constant	$F = 96485.3399 \text{ C mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31} \text{ kg}$
Proton	$m_p = 1.672621637 \times 10^{-27} \text{ kg}$
Neutron	$m_n = 1.674927211 \times 10^{-27} \text{ kg}$
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	$m_p / m_e = 1836.15267247$
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	$R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1}$

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

Conversion factors

Ångström	$1 \text{ \AA} = 10^{-10} \text{ m}$
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 form $E = mc^2$)
Calorie	$1 \text{ cal} = 4.184 \text{ J}$ (exactly)
Electron volt	$1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J} = 96.485335 \text{ kJ mol}^{-1}$
Foot	$1 \text{ ft} = 12 \text{ in} = 0.3048 \text{ m}$ (exactly)
Gallon (U. S.)	$1 \text{ gallon} = 4 \text{ quarts} = 3.785412 \text{ L}$ (exactly)
Liter	$1 \text{ L} = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3$ (exactly)
Liter-atmosphere	$1 \text{ L atm} = 101.325 \text{ J}$ (exactly)
Metric ton	$1 \text{ t} = 1000 \text{ kg}$ (exactly)
Pound	$1 \text{ lb} = 16 \text{ oz} = 0.4539237 \text{ kg}$ (exactly)
Rydberg	$1 \text{ Ry} = 2.17987197 \times 10^{-18} \text{ J} = 1312.7136 \text{ kJ mol}^{-1} = 13.60569193 \text{ eV}$
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	$1 \text{ torr} = 133.3224 \text{ Pa}$

PERIODIC TABLE OF THE ELEMENTS

<http://www.kj-soft.com/periodic/>

GROUP	PERIOD																																		
1	IIA												VIIIA																						
1	H															2																			
2	Li	Be											10	11	12	13	14	15	16	17	18														
3	Na	Mg	IIIB		IVB		VB		VIB		VIIB		VIIIB		IIIB		IVA	VA	VA	VIA	VIA	VIA	2												
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				4													
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				5													
6	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				6													
7	Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Uu	Uu	Uu	Uub	Uuq						7															
	Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Uu	Uu	Uu	Uub	Uuq						7															
19	39.098	20	40.078	21	44.956	22	47.867	23	50.942	24	51.996	25	54.938	26	55.845	27	58.933	28	58.693	29	63.546	30	65.39	31	69.723	32	72.64	33	74.922	34	78.96	35	79.904	36	83.80
37	85.468	38	87.62	39	88.906	40	91.224	41	92.906	42	95.94	43	(99)	44	101.07	45	102.91	46	106.42	47	107.87	48	112.41	49	114.82	50	118.71	51	121.76	52	127.60	53	126.90	54	131.29
55	132.91	56	137.33	57-71	72	178.49	73	180.95	74	183.84	75	186.21	76	190.23	77	192.22	78	195.08	79	196.97	80	200.59	81	204.38	82	207.2	83	208.98	84	(209)	85	(210)	86	(222)	
87	(223)	88	(226)	89-103	104	(261)	105	(262)	106	(266)	107	(264)	108	(277)	109	(268)	110	(281)	111	(272)	112	(285)	113	(284)	114	(289)	115	(288)	116	(291)	117	(292)	118	(293)	
101	(258)	102	(259)	103	(262)	104	(261)	105	(262)	106	(266)	107	(264)	108	(277)	109	(268)	110	(281)	111	(272)	112	(285)	113	(284)	114	(289)	115	(288)	116	(291)	117	(292)	118	(293)

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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with the significant figures. For elements with no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However, three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

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LANTHANIDE															
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
LANTHANUM	CERUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLIUM	ERBIUM	THULIUM	YTERBIUM	LUTETIUM	
138.91	140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97	
89	(227)	90	232.04	91	231.04	92	238.03	93	(237)	94	(244)	95	(243)	96	(247)
ACTINIDE	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	EINSTEINIUM	FERMIUM	Mendelevium	NOBELIUM	LAWRENCIUM	