

Exam Reading: Students will have 15 minutes to read this exam booklet before starting the exam. **Do not write or calculate during this period, otherwise YOU will be disqualified.** The official English version of this examination is available on request only for clarification.

Theoretical Problems

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD

Nakhon Pathom, THAILAND



General Instructions.

- **Pages:** This theoretical exam booklet contains 54 pages. There are 11 Problems in total.
- **Exam Reading:** Students will have 15 minutes to read this exam booklet before starting the exam. **Do not write or calculate during this period, otherwise YOU will be disqualified.** The official English version of this examination is available on request only for clarification.
- **Exam Time:** Students will have a total of 5 hours to complete the exam.
- **Start/Stop:** Students may begin as soon as the “**Start**” command is given and must stop your work immediately when the “**Stop**” command is announced.
 - Failure to stop the task by 1 minute or longer after the “**Stop**” command has been announced will lead to nullification of your theoretical exam.
 - After the “**Stop**” command has been given, place your exam booklet back in your exam envelope and wait at your seat. The Exam Supervisor will come pick up your exam paper.
- **Answer sheets:** All results and answers must be clearly written in the appropriate area on the exam papers for grading. Only answers written in pen will be graded.
 - Use only pens provided for you.
 - You may use the backside of the sheets as scratch papers. They will not be marked.
- **Calculator:** For any calculation, use only the 49th IChO calculator provided.
- **Need Assistance:** If you need assistance (*e.g.* more snacks or drinks or go to a restroom), Waive the orange IChO flag provided on your table.

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11	Twist & Chirality	53	2%

Problem 1

6% of the total

Problem 1	A			B	C	Total
	A1	A2	A3			
Total	4	1	2	7	6	20
Score						

Problem 1: Production of propene using heterogeneous catalysts

Propene or propylene is one of the most valuable chemicals for the petrochemical industry in Thailand and around the world. One good example of the commercial use of propene is for the production of polypropylene (PP).

Part A.

Propene can be synthesized via a direct dehydrogenation of propane in the presence of a heterogeneous catalyst. However, such a reaction is not economically feasible due to the nature of the reaction itself. Provide a concise explanation to each of the questions below. Additional information: $H_{\text{bond}}(\text{C}=\text{C}) = 1.77H_{\text{bond}}(\text{C}-\text{C})$, $H_{\text{bond}}(\text{H}-\text{H}) = 1.05H_{\text{bond}}(\text{C}-\text{H})$, and $H_{\text{bond}}(\text{C}-\text{H}) = 1.19H_{\text{bond}}(\text{C}-\text{C})$, where H_{bond} refers to average bond enthalpy of the indicated chemical bond.

1-A1) What is the enthalpy change of the direct dehydrogenation of propane? Show your calculation and express your answer in terms of $H_{\text{bond}}(\text{C}-\text{C})$.

Calculation:

1-A2) It is difficult to increase the amount of propene by increasing pressure at constant temperature. Which law or principle can best explain this phenomenon? Select your answer by marking “✓” in **one** of the open circles.

- Boyle’s law
- Charles’ law
- Dalton’s law
- Raoult’s law
- Le Chatelier’s principle

1-A3) Initially, the system is in equilibrium. Consistent with question **1-A1)**, what is/are correct set(s) of signs for the following thermodynamic variables of the system for the direct dehydrogenation of propane? Select your answer(s) by marking “✓” in any of the open circle(s).

- | | ΔH | ΔS | ΔG | T^* |
|-----------------------|------------------------------|------------|------------|--------|
| <input type="radio"/> | - | + | + | lower |
| <input type="radio"/> | - | + | - | higher |
| <input type="radio"/> | - | - | + | lower |
| <input type="radio"/> | - | - | - | higher |
| <input type="radio"/> | + | + | + | lower |
| <input type="radio"/> | + | + | - | higher |
| <input type="radio"/> | + | - | + | lower |
| <input type="radio"/> | + | - | - | higher |
| <input type="radio"/> | None of the above is correct | | | |

* Relative to the initial temperature at the same partial pressure.

Part B.

A better reaction to produce large quantity of propene is the *oxidative dehydrogenation (ODH)* using solid catalysts, such as vanadium oxides, under molecular oxygen gas. Although this type of reaction is still under intense research development, its promise toward the production of propene at an industrial scale eclipses that of the direct dehydrogenation.

1-B) The overall rate of propane consumption in the reaction is $r_{C_3H_8} = \frac{I}{\left(\frac{p^o}{k_{red} p_{C_3H_8}} + \frac{p^o}{k_{ox} p_{O_2}} \right)}$,

where k_{red} and k_{ox} are the rate constants for the reduction of metal oxide catalyst by propane and for the oxidation of the catalyst by molecular oxygen, respectively, and p^o is the standard pressure of 1 bar. Some experiments found that the rate of oxidation of the catalyst is 100,000

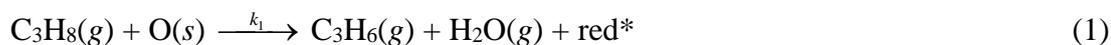
times faster than that of the propane oxidation. The experimental $r_{C_3H_8} = k_{obs} \frac{p_{C_3H_8}}{p^o}$ at 600 K,

where k_{obs} is the observed rate constant (0.062 mol s^{-1}). If the reactor containing the catalyst is continuously passed through with propane and oxygen at a total pressure of 1 bar, determine the value of k_{red} and k_{ox} when the partial pressure of propane is 0.10 bar. Assume that the partial pressure of propene is negligible.

Calculation:

Part C.

The metal oxide catalyst contains oxygen atoms on its surface that serve as active sites for the ODH. Denoting red* as a reduced site and O(s) as an oxygen atom on the surface of the catalyst, one of the proposed mechanisms for the ODH in the presence of the catalyst can be written as follows:



Given $\beta = \frac{\text{number of reduced sites}}{\text{total number of active sites}}$, the rate laws for the above 3 steps are:

$$r_1 = k_1 p_{\text{C}_3\text{H}_8} (1 - \beta),$$

$$r_2 = k_2 p_{\text{C}_3\text{H}_6} (1 - \beta),$$

$$\text{and } r_3 = k_3 p_{\text{O}_2} \beta.$$

1-C) Assuming that the amount of oxygen atoms on the surface stays constant at any time of reaction, calculate β as a function of k_1 , k_2 , k_3 , $p_{\text{C}_3\text{H}_8}$, $p_{\text{C}_3\text{H}_6}$, and p_{O_2} .

Calculation:

Problem 2

6% of the total

Problem 2	A								Total
	A1	A2	A3	A4	A5	A6	A7	A8	
Total	2	2	7	3	3	1	5	1	24
Score									

Problem 2: Kinetic isotope effect (KIE) and zero-point vibrational energy (ZPE)

Calculation of ZPE and KIE

Kinetic isotope effect (KIE) is a phenomenon associated with a change in rate constant of the reaction when one of the atoms is replaced by its isotope. KIE can be used to confirm whether a particular bond to hydrogen is broken in the reaction. Harmonic oscillator model is used to estimate the difference in the rate between C-H and C-D bond activation ($D = {}^2\text{H}$).

The vibrational frequency (ν) represented by harmonic oscillator model is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},$$

where k is the force constant and μ is the reduced mass.

The vibrational energies of the molecule are given by

$$E_n = \left(n + \frac{1}{2} \right) h\nu,$$

where n is vibrational quantum number with possible values of 0, 1, 2, ... The energy of the lowest vibrational energy level (E_n at $n = 0$) is called **zero-point vibrational energy (ZPE)**.

2-A1) Calculate the reduced mass of C-H (μ_{CH}) and C-D (μ_{CD}) in atomic mass unit. Assume that the mass of deuterium is twice that of hydrogen.

Calculation:

[If students are unable to calculate the values for μ_{CH} and μ_{CD} in **2-A1**), use $\mu_{CH} = 1.008$ and $\mu_{CD} = 2.016$ for the subsequent parts of the question. Note that the given values are not necessarily close to the correct values.]

2-A2) Given that the force constant (k) for C-H stretching is the same as that for the C-D stretching and the C-H stretching frequency is 2900 cm^{-1} , find the corresponding C-D stretching frequency (in cm^{-1}).

Calculation:

2-A3) According to the C-H and C-D stretching frequencies in question **2-A2**), calculate the zero-point vibrational energies (ZPE) of C-H and C-D stretching in kJ mol^{-1} .

Calculation:

[If students are unable to calculate the values for *ZPE* in **2-A3**), use $ZPE_{CH} = 7.23 \text{ kJ/mol}$ and $ZPE_{CD} = 2.15 \text{ kJ/mol}$ for the subsequent parts of the question. Note that the given values are not necessarily close to the correct values.]

Kinetic isotope effect (KIE)

Due to the difference in zero-point vibrational energies, a protonated compound and its corresponding deuterated compounds are expected to react at different rates.

For the C-H and C-D bond dissociation reactions, the energies of both transition states and both products are identical. Then, the isotope effect is controlled by the difference in the ZPE's of the C-H and C-D bonds.

2-A4) Calculate the difference in the bond dissociation energy (BDE) between C-D bond and C-H bond ($BDE_{CD} - BDE_{CH}$) in kJ mol^{-1} .

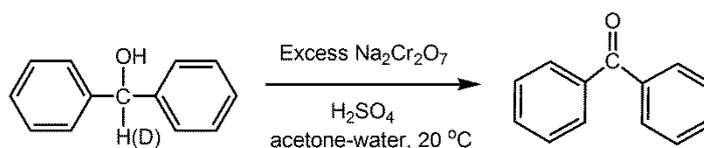
Calculation:

2-A5) Assume that the activation energy (E_a) for the C-H/C-D bond cleavage is approximately equal to the bond dissociation energy and the Arrhenius factor is the same for both C-H and C-D bond cleavage. Find the relative rate constant for the C-H/C-D bond cleavage (k_{CH}/k_{CD}) at $25\text{ }^\circ\text{C}$.

Calculation:

Using KIE to study reaction mechanism

The oxidation of nondeuterated and deuterated diphenylmethanol using an excess of chromic acid was studied.



2-A6) Let C_0 be the initial concentration of either nondeuterated diphenylmethanol or deuterated diphenylmethanol and C_t its concentration at time t . The experiment led to two plots (Figure 2a and Figure 2b), from which the first-order rate constant can be determined.

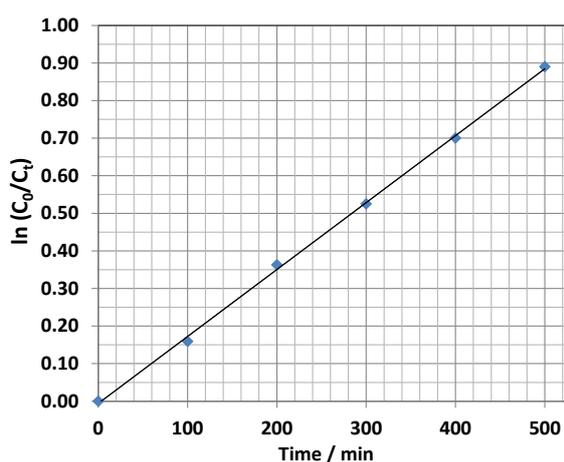


Figure 2a

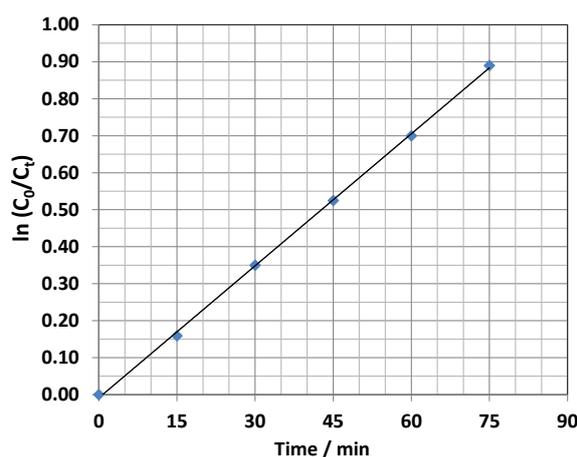


Figure 2b

Which plot should be for the oxidation of nondeuterated diphenylmethanol and which one is for the oxidation of deuterated diphenylmethanol?

For each statement, select your answer by marking “✓” in **one** of the open circles.

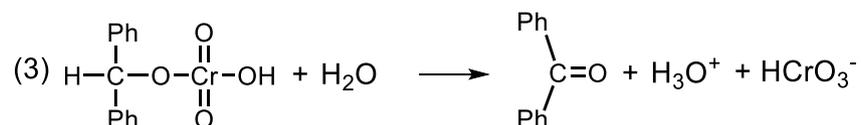
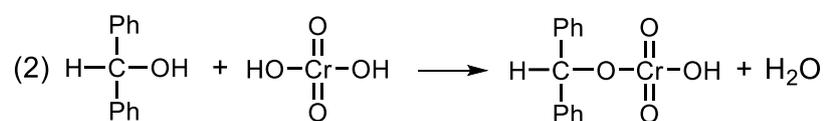
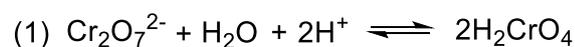
The oxidation of nondeuterated diphenylmethanol: Figure 2a Figure 2b

The oxidation of deuterated diphenylmethanol: Figure 2a Figure 2b

2-A7) Determine k_{CH} , k_{CD} (in min^{-1}), and the k_{CH}/k_{CD} of this reaction from the plots in question 2-A6).

Calculation:

2-A8) The mechanism has been proposed as follows:



According to the information in 2-A6) and 2-A7), which step should be the rate determining step?

Select your answer by marking “✓” in **one** of the open circles.

- Step (1)
 Step (2)
 Step (3)

Problem 3

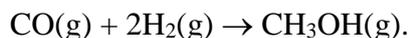
6% of the total

Problem 3	A			B	Total
	A1	A2	A3		
Total	7	3	8	6	24
Score					

Problem 3: Thermodynamics of chemical reactions

Part A.

Methanol is produced commercially by using a mixture of carbon monoxide and hydrogen over zinc oxide/copper oxide catalyst:



The standard enthalpy of formation (ΔH_f°) and the absolute entropy (S°) for each of the three gases at room temperature (298 K) and at a standard pressure of 1 bar are given as follows.

Gas	ΔH_f° (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
CO(g)	-111	198
H ₂ (g)	0	131
CH ₃ OH(g)	-201	240

3-A1) Calculate ΔH° , ΔS° , ΔG° , and K_p for the reaction at 298 K.

Calculation:

$$\Delta H^\circ = \dots\dots\dots \text{ kJ}$$

$$\Delta S^\circ = \dots\dots\dots \text{ J K}^{-1}$$

$$\Delta G^\circ = \dots\dots\dots \text{ kJ}$$

$$K_p = \dots\dots\dots$$

If you are unable to calculate K_p at 298 K in problem **3-A1)**, use $K_p = 9 \times 10^5$ later on.

3-A2) A commercial reactor is operated at a temperature of 600 K. Calculate the value of K_p at this temperature, assuming that ΔH° and ΔS° are independent of temperature.

Calculation:

$$K_p = \dots\dots\dots$$

If you are unable to calculate K_p at 600 K in problem **3-A2)**, use $K_p = 1.0 \times 10^{-2}$ later on.

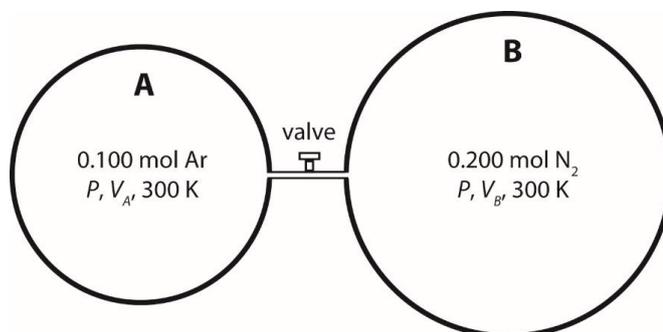
3-A3) Production of methanol in industry is based on flowing of the gas comprising 2.00 moles of H₂ for each mole of CO into the reactor. The mole fraction of methanol in the exhaust gas from the reactor was found to be 0.18. Assuming that equilibrium is established, what is the total pressure in the reactor at a high temperature of 600 K?

Calculation:

Total pressure = bar.

Part B.

3-B) Consider the following closed system at 300 K. The system comprises 2 compartments, separated by a closed valve, which has negligible volume. At the same pressure P , compartment A and compartment B contain 0.100 mol argon gas and 0.200 mol nitrogen gas, respectively. The volumes of the two compartments, V_A and V_B , are selected so that the gases behave as ideal gases.



After opening the valve slowly, the system is allowed to reach equilibrium. It is assumed that the two gases form an ideal gas mixture. Calculate the change in Gibbs free energy at 300 K, ΔG .

Calculation:

$$\Delta G = \dots\dots\dots J$$

Problem 4

5% of the total

Problem 4	A				Total
	A1	A2	A3	A4	
Total	4	1	5	6	16
Score					

Problem 4: Electrochemistry

Part A. Galvanic cell

The experiment is performed at 30.00°C. The electrochemical cell is composed of a hydrogen half-cell [Pt(s) | H₂(g) | H⁺(aq)] containing a metal platinum electrode immersed in a buffer solution under a pressure of hydrogen gas. This hydrogen half-cell is connected to a half-cell of a metal (M) strip dipped in an unknown concentration of M²⁺(aq) solution. The two half-cells are connected *via* a salt bridge as shown in Figure 1.

Note: The standard reduction potentials are given in Table 1.

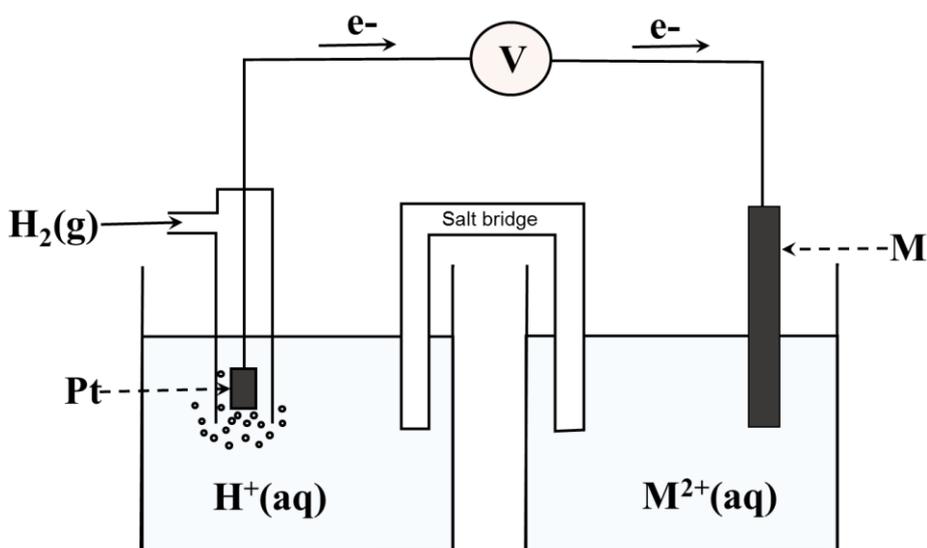


Figure 1 The galvanic cell

Table 1. Standard reduction potential (range 298-308 K)

Half-reaction	E° (V)
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.912
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sr}(\text{s})$	-2.899
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.868
$\text{Er}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Er}(\text{s})$	-2.000
$\text{Ti}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ti}(\text{s})$	-1.630
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}(\text{s})$	-1.185
$\text{V}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{V}(\text{s})$	-1.175
$\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cr}(\text{s})$	-0.913
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.447
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.403
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Co}(\text{s})$	-0.280
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.257
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.138
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.126
$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.000
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+0.151
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}^+(\text{aq})$	+0.153
$\text{Ge}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ge}(\text{s})$	+0.240
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.337
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.340
$\text{Tc}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Tc}(\text{s})$	+0.400
$\text{Ru}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ru}(\text{s})$	+0.455
$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	+0.535
$\text{UO}_2^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{U}^{4+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+0.612
$\text{PtCl}_4^{2-}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pt}(\text{s}) + 4\text{Cl}^-(\text{aq})$	+0.755
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.770
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l})$	+0.797
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}(\text{l})$	+0.851
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.920
$\text{Pt}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pt}(\text{s})$	+1.180
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.224
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.360
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Co}^{2+}(\text{aq})$	+1.920
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{SO}_4^{2-}(\text{aq})$	+2.010

4-A1) If the reaction quotient (Q) of the whole galvanic cell is equal to 2.18×10^{-4} at 30.00°C , the electromotive force is $+0.450\text{ V}$. Calculate the value of standard reduction potential (E°) and identify the metal “**M**”.

Note; $\Delta G = \Delta G^\circ + RT \ln Q$

Calculations

The standard reduction potential of **M** isV
(Answer with 3 digits after decimal point)

Therefore, the metal “**M**” strip is

4-A2) Write the balanced equation of the spontaneous redox reaction of the galvanic cell.

4-A3) The unknown concentration of $M^{2+}(aq)$ solution in the cell (Figure 1) can be analyzed by iodometric titration. A 25.00 cm^3 aliquot of $M^{2+}(aq)$ solution is added into a conical flask and an excess of KI added. 25.05 cm^3 of a 0.800 mol dm^{-3} sodium thiosulfate is required to reach the equivalent point. Write all the redox reactions associated with this titration and calculate the concentration of $M^{2+}(aq)$ solution.

Calculations

The concentration of $M^{2+}(aq)$ solution is..... mol dm^{-3}

(answer with 3 digits after decimal point)

If student cannot find the answer, the student can use 0.950 mol dm^{-3} as the concentration of M^{2+} for further calculations.

4-A4) In Figure 1, if the hydrogen half-cell is under 0.360 bar hydrogen gas and the platinum electrode is immersed in a 500 cm³ buffer solution containing 0.050 mol lactic acid (HC₃H₅O₃) and 0.025 mol sodium lactate (C₃H₅O₃Na), the electromotive force of the galvanic cell measured is +0.534 V. Calculate the pH of the buffer solution and the dissociation constant (*K*_a) of lactic acid at 30.00°C.

Calculations of pH of the buffer solution

pH of the buffer solution is
(answer with 2 digits after decimal point)

If student cannot find the answer, the student can use 3.46 as the buffer pH for further calculations.

Calculations of the dissociation constant (K_a) of lactic acid

The dissociation constant of lactic acid is

Problem 5

5% of the total

Problem 5	A		B	C		D	Total
	A1	A2		C1	C2		
Total	1	1	3	1	2	2	10
Score							

Problem 5: Phosphate and silicate in soil

Distribution and mobility of phosphorus in soil are usually studied by sequential extraction. Sequential extraction is performed by the use of acid or alkaline reagents to fractionate inorganic phosphorus in soil. Soil sample was extracted and analyzed as follows:

Part A. Determination of total phosphate (PO_4^{3-}) and silicate (SiO_4^{4-})

A 5.00 gram of soil sample is digested to give a final volume of 50.0 cm^3 digesting solution which dissolves total phosphorus and silicon. The extract is analyzed for the total concentrations of phosphorus and silicon. The concentrations of phosphorus and silicon are found to be 5.16 mg dm^{-3} and 5.35 mg dm^{-3} , respectively.

5-A1) Determine the mass of PO_4^{3-} in mg per 1.00 g of soil.

Calculations

\therefore 1 g of soil contains $\text{PO}_4^{3-} =$ _____ mg (answer with 3 digits after decimal point)

5-A2) Determine the mass of SiO_4^{4-} in mg per 1.00 g of soil.

Calculations

\therefore 1 g of soil contains $\text{SiO}_4^{4-} =$ _____ mg (answer with 3 digits after decimal point)

Part B. Determination of available PO_4^{3-} in acid extract

Phosphate can be analyzed by using molybdenum blue method. One mole of phosphate is converted into one mole of molybdenum blue compound. This method is used for determination of phosphate in the acid extract. Absorbance (A) and transmittance (T) are recorded at 800 nm. The molar absorptivity of the molybdenum blue compound is $6720 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and all measurement is carried out in a 1.00-cm cuvette.

Transmittance and absorbance are given by the following equations:

$$T = I / I_0$$

$$A = \log (I_0 / I)$$

where I is the intensity of the transmitted light and I_0 is the intensity of the incident light.

5-B1) When the sample containing high concentration of phosphate is analyzed, a reference solution of $7.5 \times 10^{-5} \text{ mol dm}^{-3}$ of molybdenum blue compound is used for adjusting zero absorbance. The transmittance of the sample solution is then measured to be 0.55. Calculate the concentration of phosphate (mol dm^{-3}) in the sample solution.

Calculations

\therefore concentration of phosphate in an unknown sample = _____ mol dm^{-3}

Part C. Determination of PO_4^{3-} and SiO_4^{4-} in alkaline extract

Both phosphate and silicate ions can react with molybdate in alkaline solution, producing the yellow molybdophosphate and molybdatosilicate. Further reduction with ascorbic acid produces intense color molybdenum blue compounds. Both complexes exhibit maximum absorption at 800 nm. Addition of tartaric acid helps preventing interference from silicate in the determination of phosphate.

Two series of phosphate standard are treated with and without tartaric acid whereas a series of silicate standard is not treated with tartaric acid. Linear equations obtained from those calibration curves are as follows:

Conditions	Linear equations
Phosphate with and without tartaric acid	$y = 6720x_1$
Silicate without tartaric acid	$y = 868x_2$

y is absorbance at 800 nm,

x_1 is concentration of phosphate as mol dm^{-3} ,

x_2 is concentration of silicate as mol dm^{-3}

Absorbance at 800 nm of the alkaline fraction of the soil extract after treated with and without tartaric acid are 0.267 and 0.510, respectively.

5-C1) Calculate the phosphate concentration in the alkaline soil extract in mol dm^{-3} and calculate the corresponding phosphorous in mg dm^{-3} .

Calculations

\therefore concentration of PO_4^{3-} = _____ mol dm^{-3}

\therefore concentration of P = _____ mg dm^{-3}

(answer with 2 digits after decimal point)

5-C2) Calculate the silicate concentration from the soil sample in the alkaline fraction in mol dm⁻³ and calculate the corresponding silicon in mg dm⁻³.

Calculations

∴ concentration of SiO₄⁴⁻ = _____ mol dm⁻³

(answer with 2 digits after decimal point)

∴ concentration of Si = _____ mg dm⁻³

(answer with 2 digits after decimal point)

Part D. Preconcentration of ammonium phosphomolybdate

A 100 cm^3 of aqueous sample of ammonium phosphomolybdate $((\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40})$ compound is extracted with 5.0 cm^3 of an organic solvent. The organic-water partition coefficient (K_{ow}) is defined as the ratio of the concentration of the compound in the organic phase (c_o) to that in the water phase (c_w). K_{ow} of the ammonium phosphomolybdate is 5.0. The molar absorptivity of ammonium phosphomolybdate in the organic phase is $5000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$.

5-D) If the absorbance in the organic phase is 0.200, calculate the total mass of phosphorus (in mg unit) in the original aqueous sample solution. The optical pathlength of the cuvette is 1.00 cm.

Calculations

\therefore total amount of P in the original aqueous solution = _____ mg

Problem 6

6% of the total

Problem 6	A		B			C		Total
	A1	A2	B1	B2	B3	C1	C2	
Total	3	8	4	3.5	5	2	4	29.5
Score								

Problem 6: Iron

Iron (Fe) is the fourth most abundant element in the Earth's crust and has been used for more than 5,000 years.

Part A.

Pure iron is easily oxidized, which limits its utilization. Element **X** is one of the alloying elements that is added to improve the oxidation resistance property of iron.

6-A1) Below is some information about the element **X**:

- (1) In first ionization, an electron with quantum numbers $n_1 = 4 - l_1$ is removed.
- (2) In second ionization, an electron with quantum numbers $n_2 = 5 - l_2$ is removed.
- (3) The atomic mass of **X** is lower than that of Fe.

What is the element **X**?

(Answer by writing the proper symbol according to the periodic table.)

6-A2) Both Fe and **X** crystallize in the body centered cubic structure. Approximating the Fe atoms as hard-spheres, the volume taken up by the Fe atoms inside the unit cell is $1.59 \times 10^{-23} \text{ cm}^3$. The volume of the unit cell of **X** is 0.0252 nm^3 . A complete substitutional solid solution usually occurs when $\Delta R = \left(\frac{|R_X - R_{Fe}|}{R_{Fe}} \right) \times 100$ is less than or equal to 15, where R_X and R_{Fe} are the atomic radii of **X** and Fe, respectively. Can **X** and Fe form a complete substitutional solid solution? Show your calculation. **No credit is given without calculation presented.** The volume of sphere is $\frac{4}{3}\pi r^3$.

Answer (Mark ✓ in an appropriate box.)

Yes ($\Delta R \leq 15$) No ($\Delta R > 15$)

Calculation

$R_{Fe} = \dots\dots\dots \text{nm}$

$R_X = \dots\dots\dots \text{nm}$

$\Delta R =$

$\dots\dots\dots$

Part B.

Iron in natural water is in the form of $\text{Fe}(\text{HCO}_3)_2$, which ionizes to Fe^{2+} and HCO_3^- . To remove iron from water, $\text{Fe}(\text{HCO}_3)_2$ is oxidized to an insoluble complex $\text{Fe}(\text{OH})_3$, which can be filtered out of the water.

6-B1) Fe^{2+} can be oxidized by KMnO_4 in a basic solution to yield $\text{Fe}(\text{OH})_3$ and MnO_2 precipitates. Write the balanced ionic equation for this reaction in a basic solution.

Under this condition, HCO_3^- ions are converted to CO_3^{2-} . Write the balanced ionic equation for this reaction in a basic solution.

6-B2) A covalent compound **A** which contains more than 2 atoms and, a potential oxidizing agent, can be prepared by the reaction between diatomic halogen molecule (Q_2) and NaQO_2 .



where x , y and z are the coefficients for the balanced equation. Among the binary compounds between hydrogen and halogen, HQ has the lowest boiling point. Identify **Q** and if **A** has an unpaired electron, draw a Lewis structure of compound **A** with zero formal charge on all atoms. (Answer by writing the proper symbol according to the periodic table.)

Q =

Lewis structure of compound **A**

What is the molecular geometry of compound **A**? (Mark \checkmark in an appropriate box.)

- linear bent cyclic tetrahedral trigonal planar other

6-B3) Compound **D** is an unstable oxidizing agent that can be used to remove $\text{Fe}(\text{HCO}_3)_2$ from natural water. It consists of elements **G**, **Z** and hydrogen and the oxidation number of **Z** is +1. In this compound, hydrogen is connected to the element having the higher electronegativity among them. Below is some information about the elements **G** and **Z**:

- (1) **G** exists in its normal state as a diatomic molecule, G_2 .
- (2) **Z** has one proton fewer than that of element **E**. **E** exists as a gas under standard conditions. Z_2 is a volatile solid.
- (3) The compound EG_3 has a pyramidal shape.

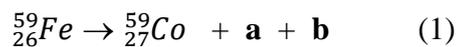
Identify the elements **G** and **Z** and draw a molecular structure of compound **D**.
(Answer by writing the proper symbol according to the periodic table.)

G = **Z** =

Molecular structure of compound **D**

Part C.

^{59}Fe is a radiopharmaceutical isotope which is used in the study of iron metabolism in the spleen. This isotope decays to ^{59}Co as follows:



6-C1) What are **a** and **b** in equation (1)? (Mark ✓ in the appropriate boxes.)

proton	neutron	beta	positron	alpha	gamma

6-C2) Consider equation (1), if the ^{59}Fe isotope is left for 178 days which is n times of its half-life ($t_{1/2}$), the mole ratio of ^{59}Co to ^{59}Fe is 15:1. If n is an integer, what is the half-life of ^{59}Fe in day(s)? Show your calculation.

Calculation:

Half-life of ^{59}Fe =days (1 decimal place)

Problem 7

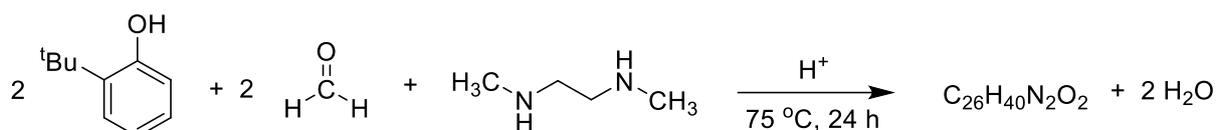
6% of the total

Problem 7	A					Total
	A1	A2	A3	A4	A5	
Total	4.5	1.5	6	6	2	20
Score						

Problem 7: Chemical Structure Puzzles

Titanium complexes have been investigated for their antitumor activity. Many factors including isomerism and sizes have shown to affect the potency of the complexes. This question deals with the synthesis and characterization of some titanium complexes.

7-A1) A reaction of 2 equivalents of 2-*tert*-butylphenol, 2 equivalents of formaldehyde, and *N,N'*-dimethylethylene-1,2-diamine under acidic conditions at 75 °C affords three major products with the same chemical formula of C₂₆H₄₀N₂O₂, as shown in the equation below. Draw the structure of each product.



Product 1:

Product 2:

Product 3:

7-A2) If 2,4-di-*tert*-butylphenol is used as a substrate instead of 2-*tert*-butylphenol using the same stoichiometry as that in **7-A1**), only one product **X** was obtained. Draw the structure of **X**.



A reaction between **X** from 7-A2) and $\text{Ti}(\text{O}^i\text{Pr})_4$ [$i\text{Pr}$ = isopropyl] in diethyl ether under an inert atmosphere resulted in the six-coordinate Ti complex **Y**, as a yellow crystalline solid and isopropanol at room temperature.



UV-Vis spectra of **X**, $\text{Ti}(\text{O}^i\text{Pr})_4$, and **Y** reveal that only the product **Y** has an absorption at $\lambda = 370$ nm. By varying the volumes of **X** and $\text{Ti}(\text{O}^i\text{Pr})_4$, each with the concentration of 0.50 mol dm^{-3} , and using benzene as the solvent, the absorbance data at $\lambda = 370$ nm are given below:

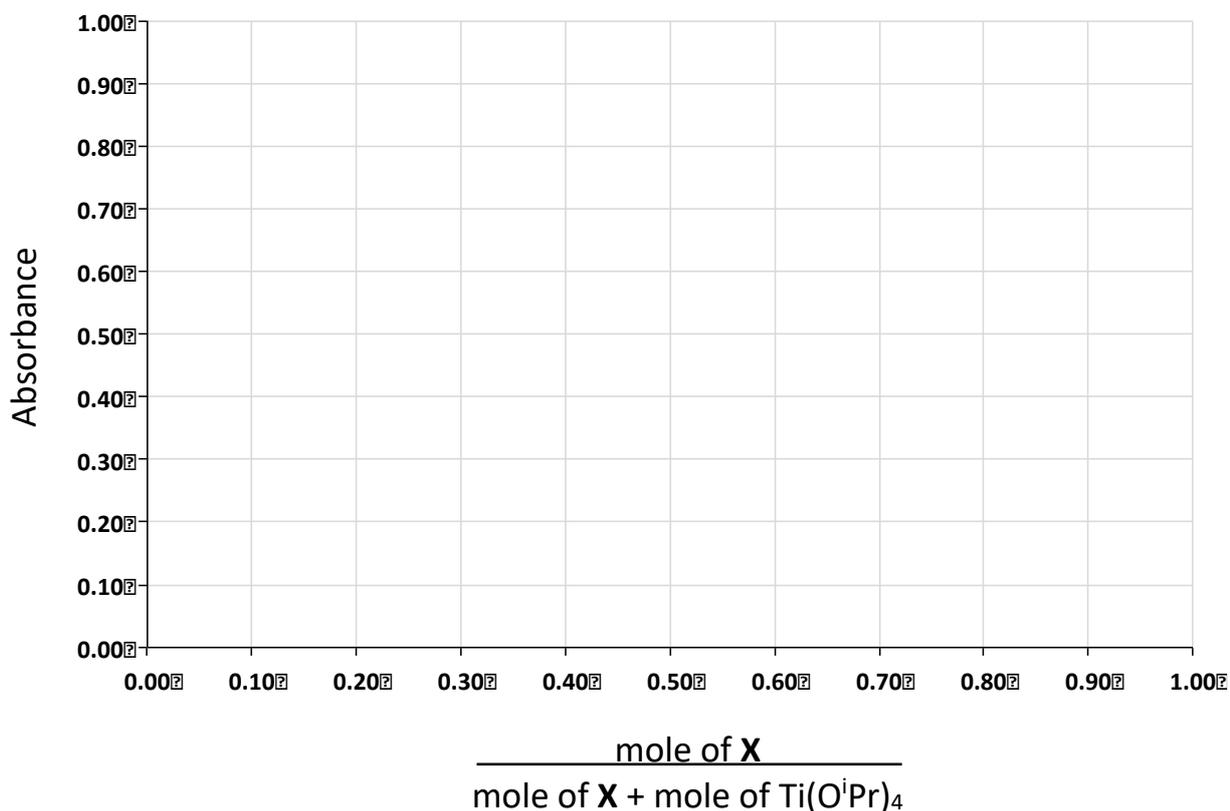
Volume of X (cm^3)	Volume of $\text{Ti}(\text{O}^i\text{Pr})_4$ (cm^3)	Volume of benzene (cm^3)	Absorbance
0	1.20	1.80	0.05
0.20	1.00	1.80	0.25
0.30	0.90	1.80	0.38
0.50	0.70	1.80	0.59
0.78	0.42	1.80	0.48
0.90	0.30	1.80	0.38
1.10	0.10	1.80	0.17
1.20	0	1.80	0.02

7-A3) Fill in appropriate values in the table provided below.

$\frac{\text{mole of } \mathbf{X}}{\text{mole of } \mathbf{X} + \text{mole of } \text{Ti}(\text{O}^i\text{Pr})_4}$	Absorbance
	0.05
	0.25
	0.38
	0.59
	0.48
	0.38
	0.17
	0.02

(2 digits after the decimal)

Plot a graph showing a relationship between $\frac{\text{mole of X}}{\text{mole of X} + \text{mole of Ti(O}^i\text{Pr)}_4}$ and absorbance in the space provided below.

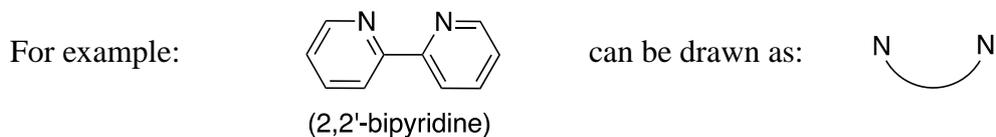


The value of $\frac{\text{mole of X}}{\text{mole of X} + \text{mole of Ti(O}^i\text{Pr)}_4}$ which maximizes the amount of the product **Y** represents the stoichiometry of **X** in the chemical formula of **Y**. Based on the graph above, what is the molar ratio between Ti:**X** in the complex **Y**?

The molar ratio between Ti:**X** in the complex **Y** is

7-A4) The Ti complex **Y** is six-coordinated. The IR spectrum of **Y** does not contain a broad absorption band in the range of 3200–3600 cm^{-1} . **Y** exists as three diastereomers. Ignoring stereochemistry at N atoms, draw clearly the structures of all three diastereomers.

Note that you do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination with titanium and the ligand framework between the donor atoms can be drawn as follows:



If you did not get a structure of **X from 7-A2), use the following ligand symbol to represent **X** (**A** and **Z** are donor atoms):



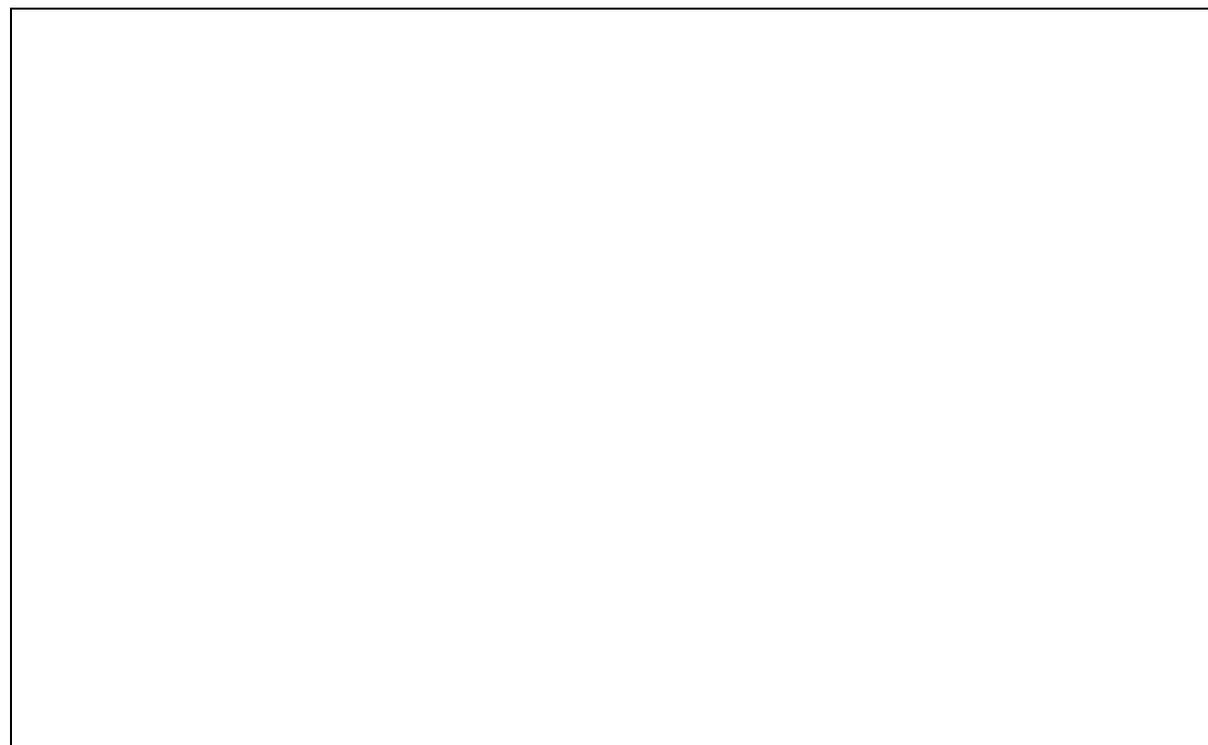
Diastereomer 1:

Diastereomer 2:

Diastereomer 3:

7-A5) Under certain conditions, the reaction shown in **equation 1** affords only one diastereomer of **Y**. Given that structures of **Y** are "fixed" (no intramolecular movement), the ^1H NMR spectrum of **Y** in CDCl_3 shows four singlet resonances at δ 1.25, 1.30, 1.66, and 1.72 corresponding to the *tert*-butyl groups. Draw a structure of the only possible diastereomer of **Y**.

(You do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination and the ligand framework between the donor atoms can be drawn as shown in **7-A4**)



Problem 8

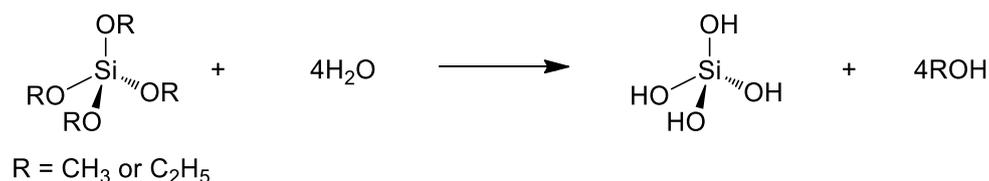
5% of the total

Problem 8	A					Total
	A1	A2	A3	A4	A5	
Total	6	5.5	3	4	1.5	20
Score						

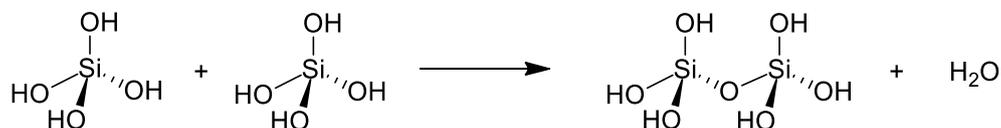
Problem 8: Silica Surface

Silica exists in various forms like amorphous and crystalline. Silica can be synthesized *via* sol-gel process by using silicon alkoxides like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) as the details below:

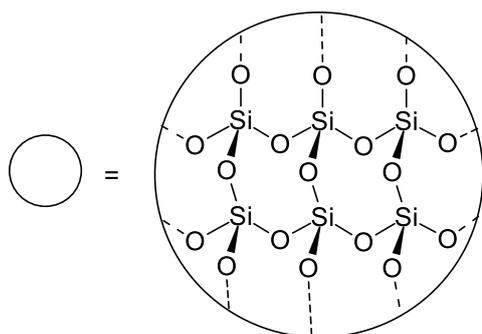
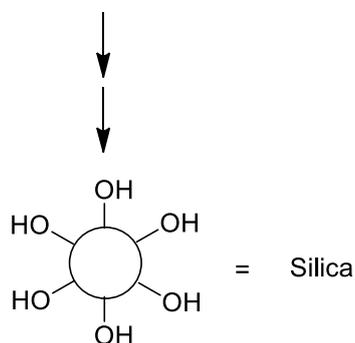
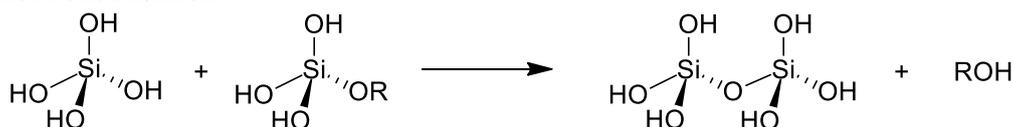
a. Hydrolysis



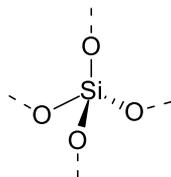
b. Water condensation



c. Alcohol condensation

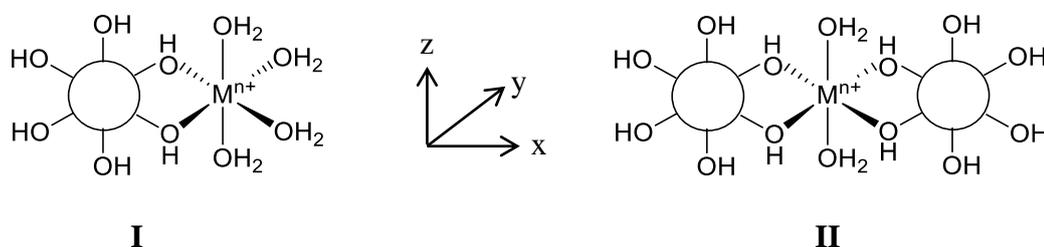


In bulk silica, all silicon atoms are tetrahedrally bonded to four oxygen atoms giving three-dimensional solid network. The silicon environments found inside silica is presented below:



8-A1) Three silicon atom environments (similar to the example above) are commonly observed at the silica **surface**. The three structures of the silicon environments must be **drawn** in the provided boxes.

Silica can be used as an effective metal ion adsorbent in water. The proposed structure for metal-silica complex is as follows:



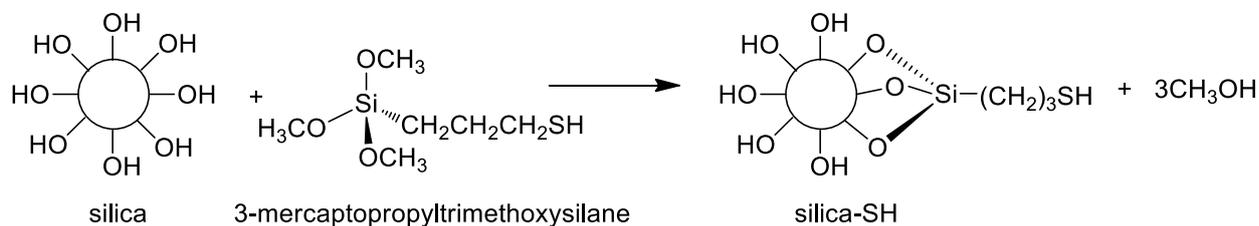
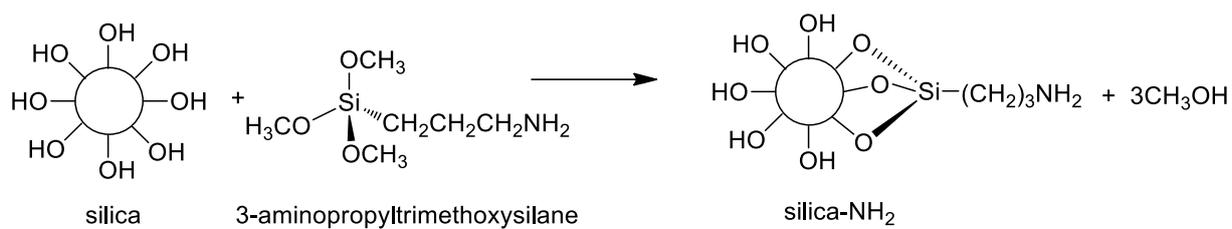
8-A2) After Cu^{2+} is being adsorbed, the color of silica changes from white to pale blue. The visible spectrum shows a broad absorption band (with a shoulder) at $\lambda_{\text{max}} = 550 \text{ nm}$. If Cu^{2+} can bind with silica and adopt the structure similar to **II**, draw the splitting diagram of the d -orbitals of Cu^{2+} ion including the label of the d orbitals in the complex and **specify** the corresponding electronic transition(s) for the visible absorption.

The splitting diagram:

The corresponding electronic transition(s) (indicate the lower energy d -orbital and higher energy d -orbital)

8-A3) If the first row transition metal ions form complexes with silica analogous to Cu^{2+} , which metal ion(s) do(es) have the analogous to electronic transition(s) to Cu^{2+} ? The metal ion(s) must be in +2 or +3 oxidation state. Please note that the silanol groups (Si-OH) and water are weak field ligands.

However, silica is randomly bonded to various types of metal ion. To increase the selectivity, modification of silica surface has been performed by grafting with various organic molecules like 3-aminopropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane.

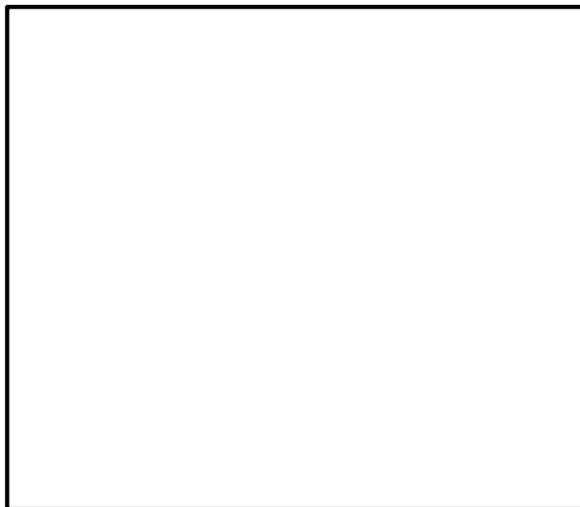


8-A4) If Hg^{2+} is only bonding to sulfur binding sites in silica-SH, the **symmetric** complex of $[\text{Hg}(\text{silica-SH})_2]^{2+}$ is formed. Draw the structure of $[\text{Hg}(\text{silica-SH})_2]^{2+}$, specify the direction of the bond axes, and draw the corresponding d -orbital splitting. (You may use R-SH instead of drawing the whole structure of silica-SH.)

The structure:



d -orbital splitting diagram :



8-A5) Specify true or false for the following statements:

a) $d-d$ transition is found in $[(\text{Hg}(\text{silica-SH})_x)]^{2+}$

True

False

b) The $[\text{Cu}(\text{silica-NH}_2)_x]^{2+}$ in a similar geometry, is expected to have a color similar to other copper(II) amine complexes.

True

False

c) In the visible absorption spectra, λ_{max} of $[\text{Cu}(\text{silica-NH}_2)_x]^{2+}$ is greater than that of $[\text{Cu}(\text{silica-OH})_x]^{2+}$.

True

False

Problem 9

6% of the total

Problem 9	A			Total
	A1	A2	A3	
Total	6	6	11	23
Score				

Problem 9: Into the Unknown

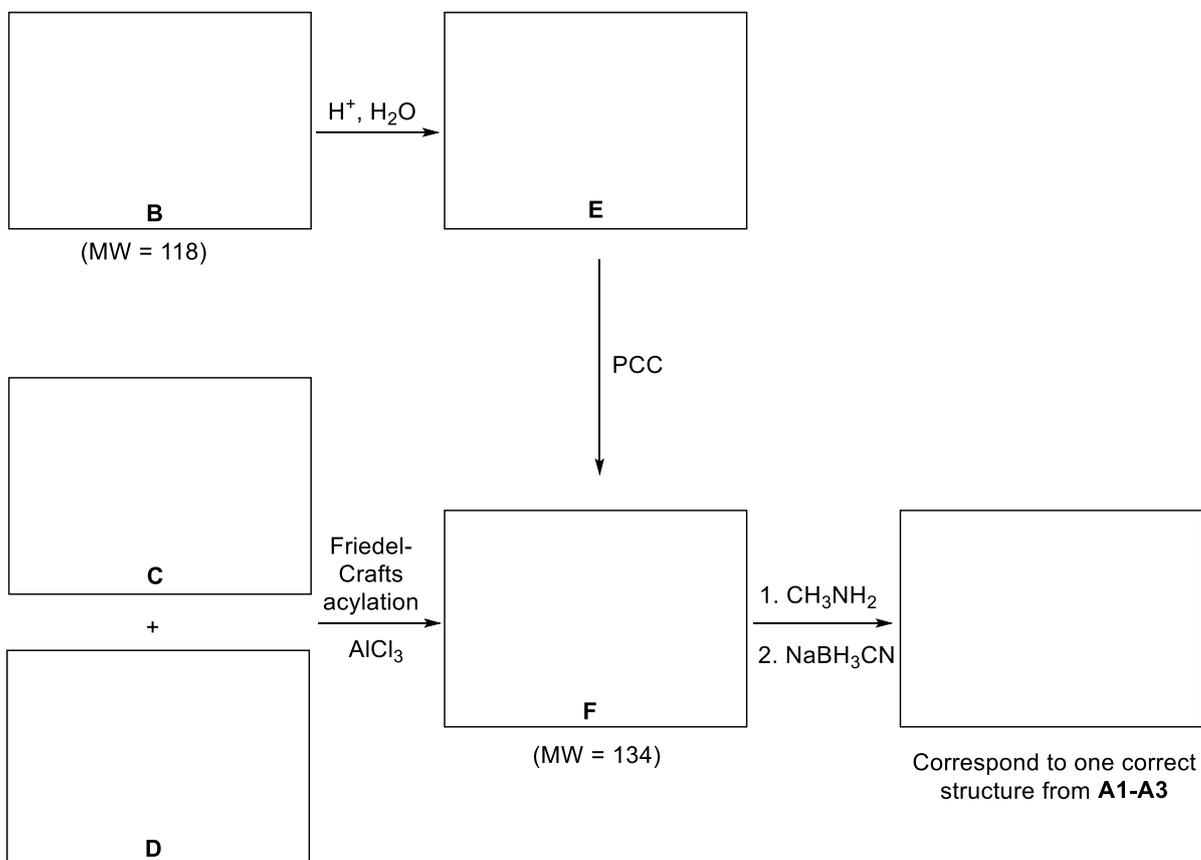
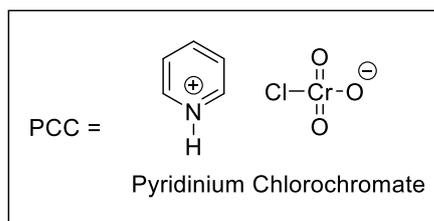
9-A1) Organic compound **A** is **chiral** and contains only three elements with the molecular weight (MW) of 149 (rounded to an integer).

^1H NMR spectrum of compound **A** shows among others, three types of aromatic protons, and its ^{13}C NMR spectrum shows eight signals, of which four signals are in the range of 120-140 ppm.

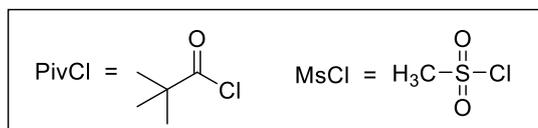
Compound **A** can be prepared by treating a carbonyl compound with methylamine followed by NaBH_3CN . Write all possible structural formulae of compound **A**. No stereochemistry is required, and **do not** include stereoisomers.

A1	A2	A3
-----------	-----------	-----------

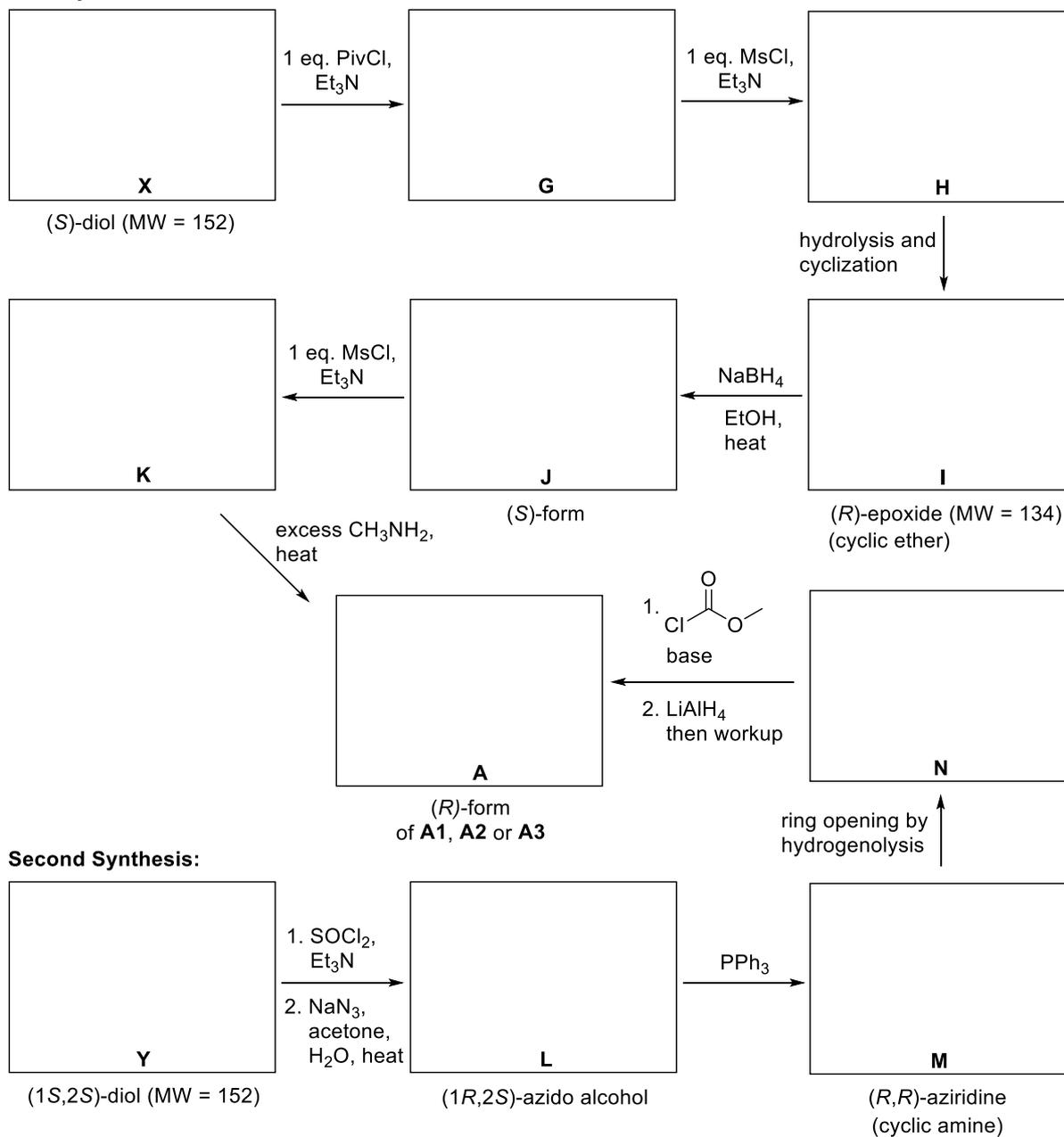
9-A2) One of the position isomers of compound **A** (structure **A1**, **A2** or **A3**) can be synthesized from compound **B** or **C** and **D** as shown in the diagram below. Write down the structural formulae of compounds **B-F**, and the position isomer of compound **A**.



9-A3) Compound **A** is the (*R*)-form of one of structures **A1-A3**. It can be prepared from vicinal diols **X** and **Y** as shown in the diagram below. Both diols are structural isomers, and each structure contains one carbon less than that of compound **A**. Write down the structural formulae of compounds **G-N**, **X**, **Y** and the (*R*)-form of compound **A**. You must show stereochemistry of all compounds.



First Synthesis:



(S)-diol (MW = 152)

(S)-form

(R)-epoxide (MW = 134)
(cyclic ether)

(1S,2S)-diol (MW = 152)

(1R,2S)-azido alcohol

(R,R)-aziridine
(cyclic amine)

(R)-form
of **A1**, **A2** or **A3**

Problem 10

7% of the total

Problem 10	A	B		Total
	A1	B1	B2	
Total	20.5	4	5.5	30
Score				

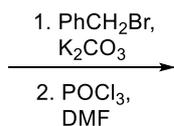
Problem10: Total Synthesis of Alkaloids

Alkaloids are a class of nitrogen-containing natural products. Their structural complexity and potent biological activities has drawn attentions. Two representative examples of alkaloids –sauristolactam and pancratistatin are highlighted in following questions.

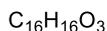
Part A

Sauristolactam possesses excellent cytotoxicity against various cancer cell lines. It could be prepared by following synthetic sequence below. ($^1\text{H-NMR}$ spectra were recorded in CDCl_3 at 300 MHz.)

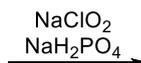
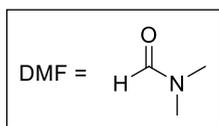
10-A1) Draw the structures of **A-G** in the sequence. Provide your answers on the following blank sheet.



A

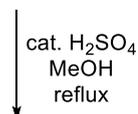


The product has two aromatic rings:
 a monosubstituted ring and
 a tetrasubstituted ring with two singlets
 in ¹H-NMR



B

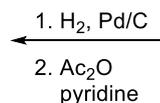
Strong IR absorption in region of
 1725-1700 cm⁻¹ and broad IR
 absorption from 3300 to 2500 cm⁻¹



E



D



C

¹H-NMR signals of the entire molecule:

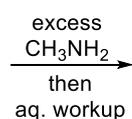
7.59 (s, 1H), 3.88 (s, 3H),
 3.87 (s, 3H), 2.68 (s, 3H),
 2.35 (s, 3H)

In addition to the aromatic region,
¹H-NMR signals in region of 0-6 ppm:
 3.87 (s, 3H), 3.84 (s, 3H),
 2.63 (s, 3H), 2.31 (s, 3H)

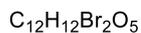
Strong IR absorption in region
 of 1750 - 1735 cm⁻¹



F

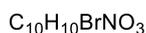


G



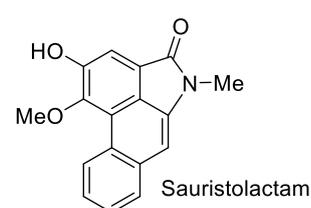
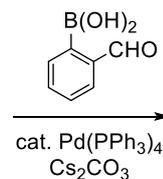
¹H-NMR signals of the entire molecule:

7.74 (s, 1H), 5.19 (s, 2H),
 3.93 (s, 3H), 3.91 (s, 3H),
 2.36 (s, 3H)



¹H-NMR signals of the entire molecule:

7.40 (s, 1H), 4.22 (s, 2H),
 3.98 (s, 3H), 3.19 (s, 3H)
 and a proton exchangeable with D₂O

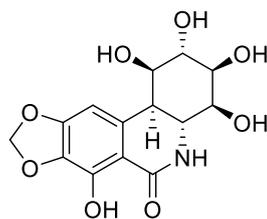


The structures of **A-G**.

A	B
C	D
E	F
G	

Part B

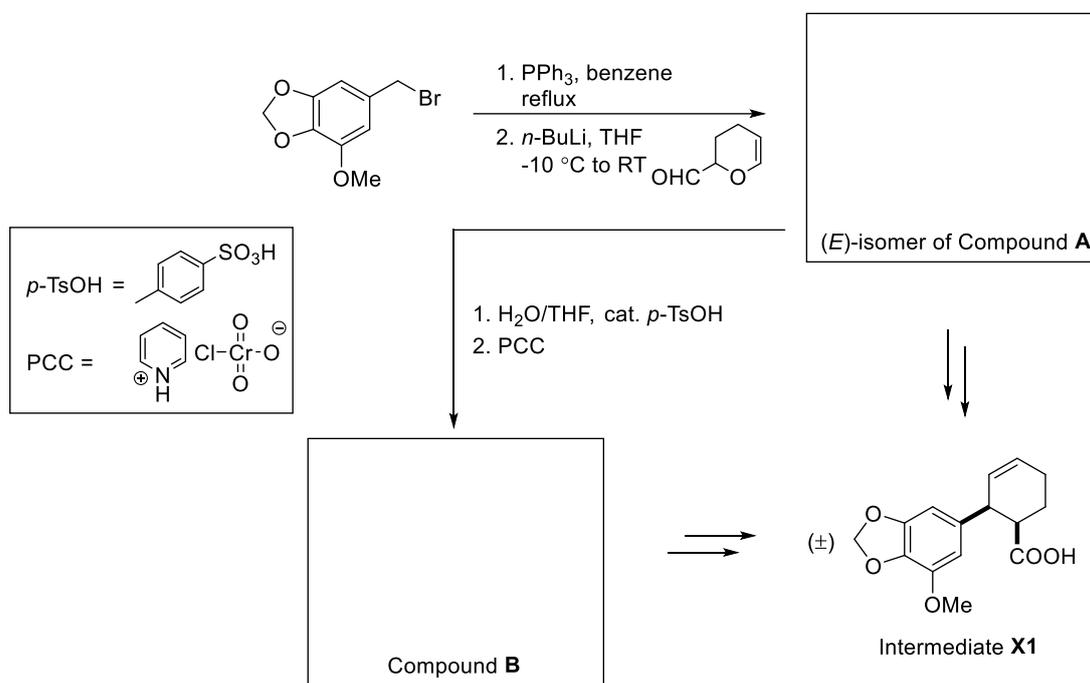
Pancreatistatin, isolated from a Hawaiian native plant, spider lily, exhibits potent in vitro and in vivo inhibitory activity of cancer cell growth in addition to its excellent antiviral activity.



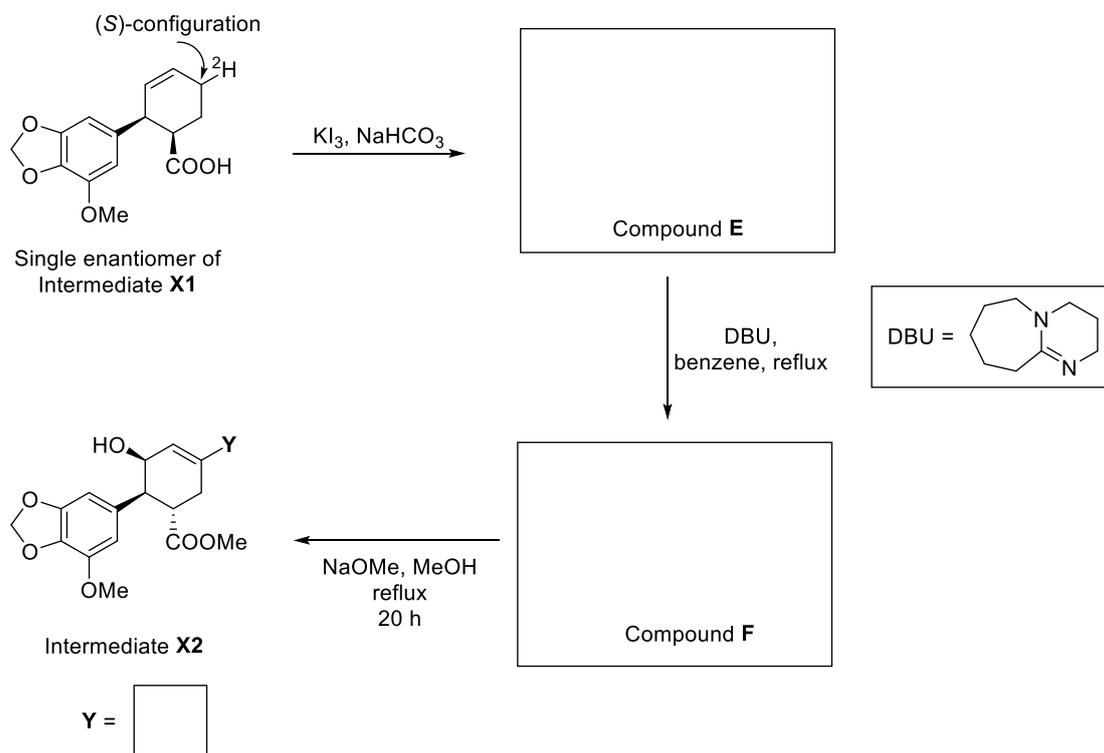
Pancreatistatin

Pancreatistatin could be successfully synthesized via intermediates **X1** and **X2**. The synthesis of these intermediates are shown in the following schemes.

10-B1) Draw the structures of **A** and **B**.



10-B2) Intermediate **X1** (a single enantiomer with the stereochemistry shown) is labeled with deuterium with configuration as indicated below, propose the 3-D chair structure of compound **E** and the structure of compound **F**, with stereochemistry. Is **Y** a proton (^1H) or a deuterium (^2H)?



Problem 11

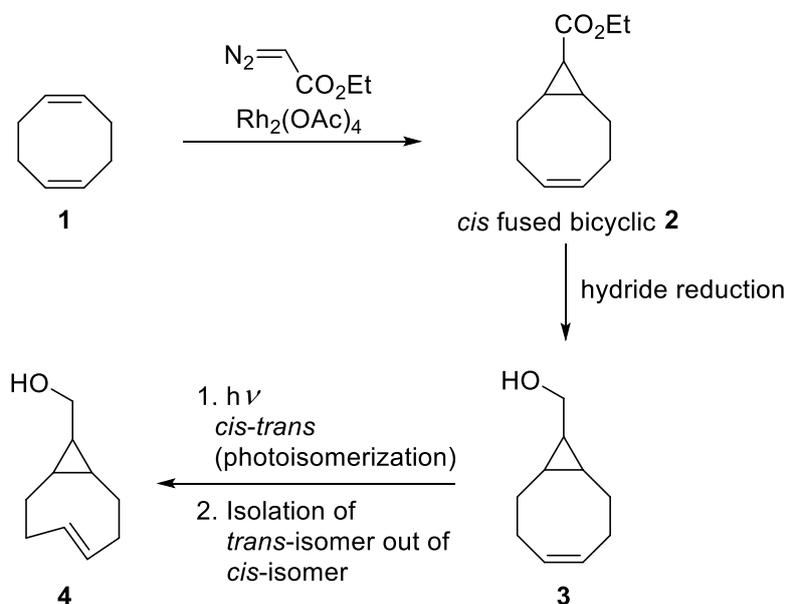
2% of the total

Problem 11	A		Total
	A1	A2	
Total	10	2	12
Score			

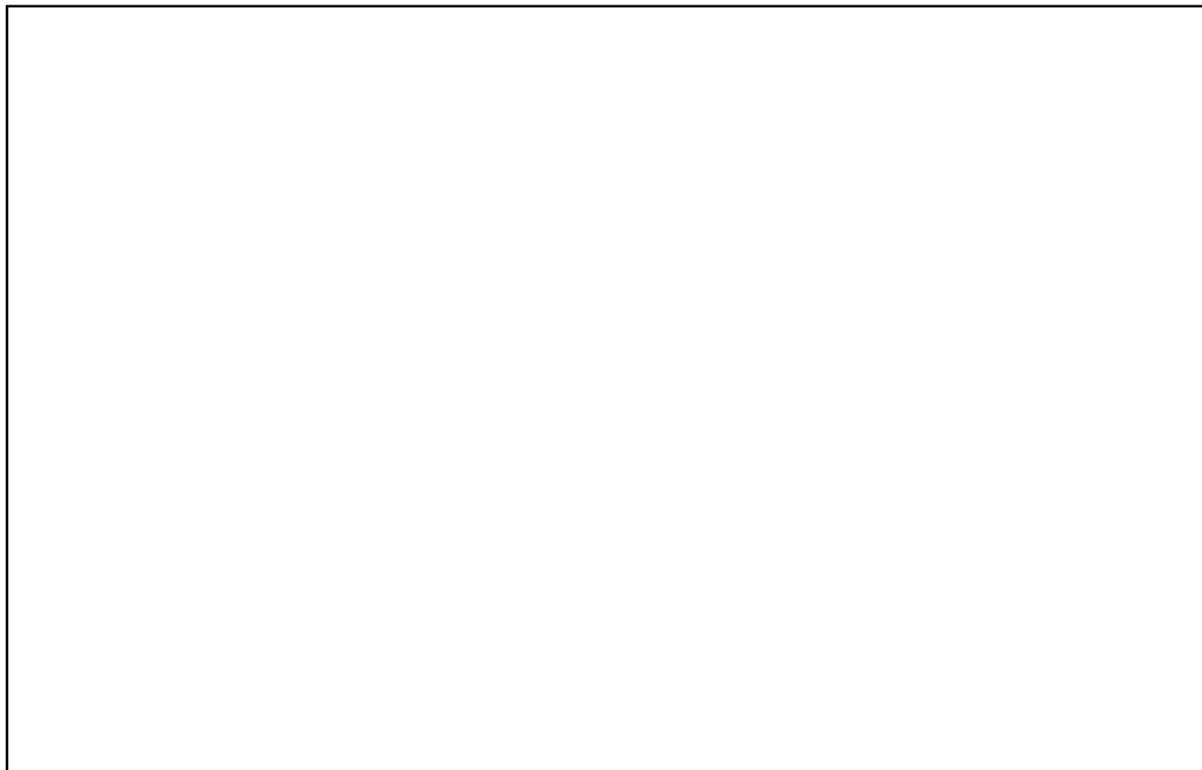
Problem 11: Twist & Chirality

trans-Cyclooctene has a chiral plane and a high barrier for racemization. The double bond of *trans*-cyclooctene is twisted, as a result, the molecule displays unusual reactivity in cycloaddition reactions.

In 2011, Fox and coworkers developed a photochemical synthesis towards a variety of *trans*-cyclooctene derivatives. The process is non-stereocontrolled and the synthetic scheme is as follow.



11-A1) Draw all possible stereoisomers of compound **3** that could be obtained from the reduction of compound **2**. Not necessary to assign *R,S* configuration.



11-A2) If one of the stereoisomers of compound **3** is converted to compound **4**, how many stereoisomeric form(s) of compound **4** will be obtained?

Number of possible stereoisomeric form(s) of compound **4** =

If there are more than one stereoisomer, is it possible to separate the obtained stereoisomers of compound **4** by achiral chromatography?

Yes

No