

**Exam Reading:** You have 15 minutes to read this 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"

49<sup>th</sup> INTERNATIONAL CHEMISTRY OLYMPIAD

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## General Instructions

- **Pages:** This theoretical exam booklet contains 54 pages. There are 11 problems in total.
- **Exam Reading:** You have 15 minutes to read this 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.

**YOU ARE STRONGLY ENCOURAGED TO READ THROUGH ALL OF A QUESTION BEFORE ATTEMPTING IT.**

- **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 and 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 the pens provided for you.
  - You may use the backside of the sheets as scratch papers. They will not be marked.
- **Need Assistance:** If you need assistance (*e.g.* more snacks or drinks or go to a restroom), wave the orange IChO flag provided on your table.

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## Problem 1

6% of the total

Problem 1 (6%)	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 of the commercial uses 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.  $H_{\text{bond}}(\text{C}=\text{C}) = 1.77H_{\text{bond}}(\text{C}-\text{C})$ ,  $H_{\text{bond}}(\text{H}-\text{H}) = 1.05H_{\text{bond}}(\text{C}-\text{H})$ , and  $H_{\text{bond}}(\text{C}-\text{H}) = 1.19H_{\text{bond}}(\text{C}-\text{C})$ , where  $H_{\text{bond}}$  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 the 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).

- |                       | $\Delta H$                   | $\Delta S$ | $\Delta G$ | $T^*$  |
|-----------------------|------------------------------|------------|------------|--------|
| <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 quantities of propene is *oxidative dehydrogenation (ODH)* using solid catalysts, such as vanadium oxides, under molecular oxygen gas.

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

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  $p^\circ$  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 rate expression is then given

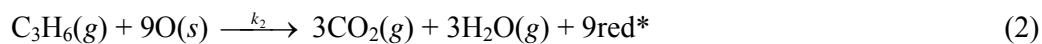
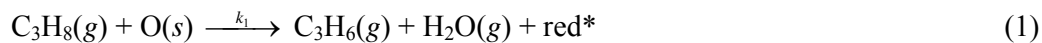
by  $r_{C_3H_8} = k_{obs} \frac{P_{C_3H_8}}{p^\circ}$  at 600 K, where  $k_{obs}$  is the observed rate constant ( $0.062 \text{ mol s}^{-1}$ ). If

oxygen and propane is continuously passed through the reactor containing the catalyst at a total pressure of 1 bar, determine the values 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 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 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 during the reaction, calculate  $\beta$  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  $p_{\text{O}_2}$ .

**Calculation:**



**Problem 2**

6% of the total

Problem 2 (6%)	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**

The kinetic isotope effect (KIE) is a phenomenon associated with a change in the rate constant of a reaction when one of the atoms is replaced by its isotope. Studies on the KIE can be used to confirm whether a particular bond to hydrogen is broken in a reaction. The harmonic oscillator model can be used to estimate the difference in the rate between C-H and C-D bond activation ( $D = \frac{1}{2}H$ ).

The vibrational frequency ( $\nu$ ) from the harmonic oscillator model is given by:

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

where  $k$  is the force constant and  $\mu$  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 the **zero-point vibrational energy (ZPE)**.

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

Calculation:

[If you are unable to calculate the values for  $\mu_{CH}$  and  $\mu_{CD}$  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  $2900\text{ cm}^{-1}$ , find the corresponding C-D stretching frequency (in  $\text{cm}^{-1}$ ).

**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  $\text{kJ mol}^{-1}$ .

**Calculation:**

[If you 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 of the transition states and both of the products are identical. The isotope effect is then 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 a C-D bond and a C-H bond ( $BDE_{CD} - BDE_{CH}$ ) in  $\text{kJ mol}^{-1}$ .

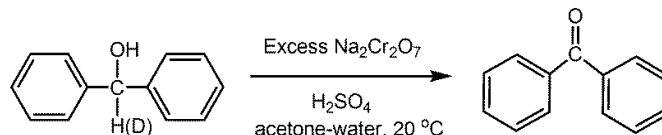
**Calculation:**

**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  $25\text{ }^\circ\text{C}$ .

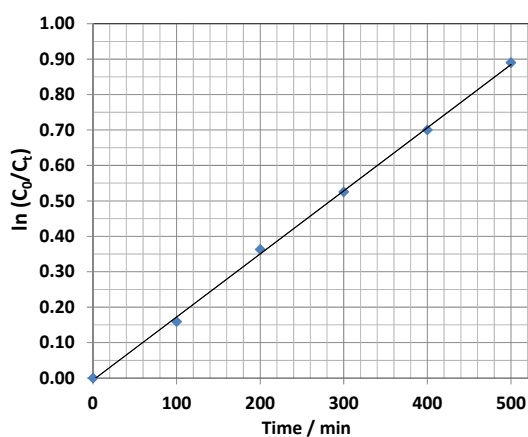
**Calculation:**

### Using KIE to study reaction mechanism

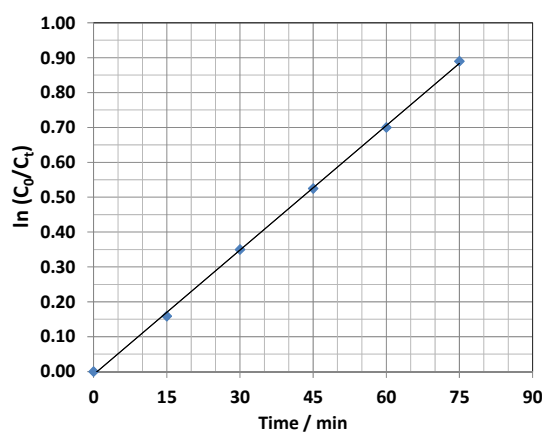
The oxidation of non-deuterated and deuterated diphenylmethanol using an excess of chromic acid was studied. The reaction is shown below.



**2-A6)** Let  $C_0$  be the initial concentration of either non-deuterated 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 constants can be determined.



**Figure 2a**



**Figure 2b**

Which plot should be for the oxidation of non-deuterated 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.

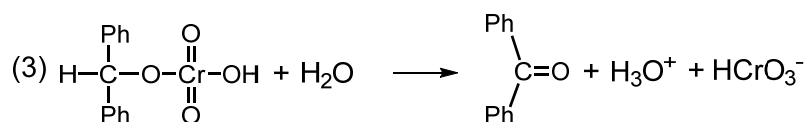
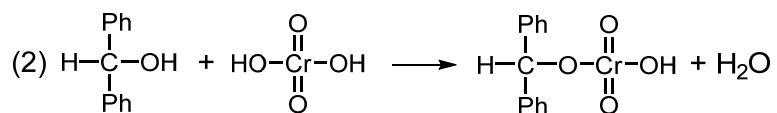
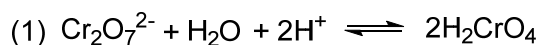
The oxidation of non-deuterated diphenylmethanol:  Figure 2a  Figure 2b

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

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

Calculation:

2-A8) The mechanism for the oxidation 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)

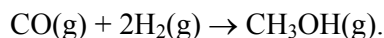
**Problem 3**

6% of the total

Problem 3 (6%)	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 reacting a mixture of carbon monoxide and hydrogen gas over a zinc oxide/copper oxide catalyst:



The standard enthalpy of formation ( $\Delta H_f^\circ$ ) and the absolute entropy ( $S^\circ$ ) for each of the three gases at room temperature (298 K) and at a standard pressure of 1 bar are given as follows.

Gas	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
CO(g)	-111	198
H <sub>2</sub> (g)	0	131
CH <sub>3</sub> OH(g)	-201	240

**3-A1)** Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ , 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  $K_p = 9 \times 10^5$

**3-A2)** A commercial reactor is operated at a temperature of 600 K. Calculate the value of  $K_p$  at this temperature, assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  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.



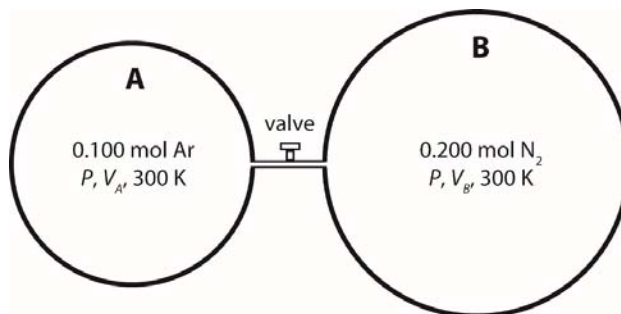
**3-A3)** Production of methanol in industry is based on flowing of the gas (comprised of 2.00 moles of H<sub>2</sub> for each mole of CO) into the reactor. The mole fraction of methanol in the exhaust gas from the reactor was found to be 0.18. Assuming that equilibrium is established, what is the total pressure in the reactor at a temperature of 600 K?

Calculation:

Total pressure = ..... bar.

**Part B.**

**3-B)** Consider the following closed system at 300 K. The system is comprised of 2 compartments. The compartments are 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 ( $\Delta G$ ) at 300 K.

Calculation:

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

**Problem 4**

5% of the total

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

**Problem 4: Electrochemistry****Part A. Galvanic cell**

The experiment in Figure 1 is performed at 30.00°C. The electrochemical cell is composed of a hydrogen half-cell  $[\text{Pt}(s) | \text{H}_2(g) | \text{H}^+(aq)]$  containing a platinum electrode immersed in a buffer solution with hydrogen gas bubbled in. This hydrogen half-cell is connected to a half-cell of a metal (**M**) strip dipped in an unknown concentration of  $\text{M}^{2+}(aq)$  solution. The two half-cells are connected *via* a salt bridge.

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

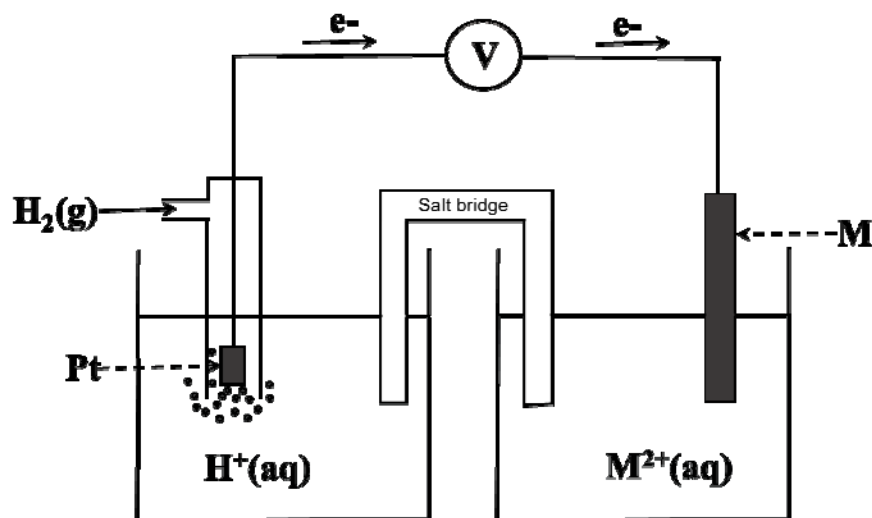


Figure 1 The galvanic cell

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

Half-reaction	$E^\circ$ (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
$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$	<b>0.000</b>
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+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  $2.18 \times 10^{-4}$  at  $30.00^\circ\text{C}$ , the electromotive force is  $+0.450\text{ V}$ . Calculate the value of the standard reduction potential ( $E^\circ$ ) and identify the metal “M”.

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

**Calculations**

The standard reduction potential of **M** is .....V  
(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 mL aliquot of  $M^{2+}(aq)$  solution is added into a conical flask and an excess of KI added. 25.05 mL of a 0.800 M sodium thiosulfate is required to reach the equivalent point. Write all of the balanced redox reactions associated with this titration and calculate the concentration of  $M^{2+}(aq)$  solution.

**Calculations:**

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

(answer with 3 digits after decimal point)

If you cannot find the answer, you can use 0.950 M as the concentration of  $M^{2+}$  for further calculations.

**4-A4)** In Figure 1, if the hydrogen half-cell is under 0.360 bar of hydrogen gas and the platinum electrode is immersed in a 500 mL buffer solution containing 0.050 mol lactic acid ( $\text{C}_3\text{H}_5\text{O}_3\text{H}$ ) and 0.025 mol sodium lactate ( $\text{C}_3\text{H}_5\text{O}_3\text{Na}$ ), 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 you cannot find the answer, you 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 (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**

The 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. A sample of soil was extracted and analyzed as follows:

**Part A. Determination of total phosphate ( $\text{PO}_4^{3-}$ ) and silicate ( $\text{SiO}_4^{4-}$ )**

5.00 g of soil sample is digested to give a final volume of 50.0 mL 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  $5.16 \text{ mg L}^{-1}$  and  $5.35 \text{ mg L}^{-1}$ , respectively.

**5-A1)** Determine the mass of  $\text{PO}_4^{3-}$  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  $\text{SiO}_4^{4-}$  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  $\text{PO}_4^{3-}$  in acid extract**

Phosphate can be analyzed by using the molybdenum blue method. In this method, one mole of phosphate is converted into one mole of a molybdenum blue compound. This method is used for the determination of phosphate concentration in the acid extract.

The absorbance (A) and transmittance (T) were recorded at 800 nm in an experiment. The molar absorptivity of the molybdenum blue compound was found to be  $6720 \text{ M}^{-1} \text{ cm}^{-1}$  and all measurements were 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  $7.5 \times 10^{-5} \text{ M}$  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 (M) in the sample solution.

**Calculations**

$\therefore$  concentration of phosphate in an unknown sample = \_\_\_\_\_ M

**Part C. Determination of  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  in alkaline extract**

Both phosphate and silicate ions can react with molybdate in alkaline solution, producing the yellow molybdophosphate and molybdosilicate. Further reduction with ascorbic acid produces intensely coloured 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 the absorbance at 800 nm,

$x_1$  is the concentration of phosphate in M,

$x_2$  is the concentration of silicate in M

The absorbances at 800 nm of the alkaline fraction of the soil extract after being 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 M and calculate the corresponding phosphorous in  $\text{mg L}^{-1}$ .

**Calculations**

$\therefore$  concentration of  $\text{PO}_4^{3-} =$  \_\_\_\_\_ M

$\therefore$  concentration of P = \_\_\_\_\_  $\text{mg L}^{-1}$

(answer with 2 digits after decimal point)

5-C2) Calculate the silicate concentration from the soil sample in the alkaline fraction in M and calculate the corresponding amount of silicon in  $\text{mg L}^{-1}$ .

**Calculations**

$\therefore$  concentration of  $\text{SiO}_4^{4-} =$  \_\_\_\_\_ M

(answer with 2 digits after decimal point)

$\therefore$  concentration of Si = \_\_\_\_\_  $\text{mg L}^{-1}$

(answer with 2 digits after decimal point)

**Part D. Preconcentration of ammonium phosphomolybdate**

A 100 mL of aqueous sample of ammonium phosphomolybdate ( $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ ) compound is extracted with 5.0 mL 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 ( $c_w$ ). The  $K_{ow}$  of the ammonium phosphomolybdate is 5.0. The molar absorptivity of ammonium phosphomolybdate in the organic phase is  $5000 \text{ M}^{-1} \text{ cm}^{-1}$ .

**5-D)** If the absorbance in the organic phase is 0.200, calculate the total mass of phosphorus (in mg) 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 (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 (Fe)**

Iron 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 an alloying element added to improve the oxidation resistance property of iron.

6-A1) Below is some information about X:

- (1) In the first ionization, an electron with quantum numbers  $n_1 = 4 - l_1$  is removed.
- (2) In the 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 iron.

What is the element X?

(Answer by writing the element symbol according to the periodic table)

X:

**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  $1.59 \times 10^{-23}$  mL. The volume of the unit cell of X is  $0.0252 \text{ nm}^3$ . 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? **To earn full credit you need to show your calculation. The volume of a sphere is  $4/3\pi r^3$ .**

**Answer** (Mark ✓ in the appropriate box.)

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

**Calculation**

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

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

$\Delta R =$

$\dots\dots\dots$

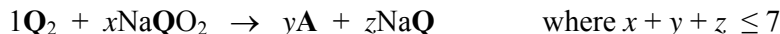
**Part B.**

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

**6-B1)**  $\text{Fe}^{2+}$  is oxidized by  $\text{KMnO}_4$  **under basic conditions** to form  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2$  as precipitates. Write the balanced ionic equation for this reaction:

**Under identical basic conditions**,  $\text{HCO}_3^-$  ions are converted to  $\text{CO}_3^{2-}$  ions. Write the balanced ionic equation for this reaction:

**6-B2)** A covalent compound **A** (which contains more than 2 atoms and is an oxidizing agent) can be prepared by the reaction between a diatomic halogen molecule ( $\text{Q}_2$ ) and  $\text{NaQO}_2$ :



where  $x$ ,  $y$  and  $z$  are the coefficients for the balanced equation. Among the binary compounds between hydrogen and halogen,  $\text{HQ}$  has the lowest boiling point. Identify **Q** and draw a Lewis structure of compound **A** with zero formal charge on all atoms. **Note that A has an unpaired electron.**

**(Answer by writing the element 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. In compound **D**, hydrogen is connected to the element having the highest electronegativity amongst them. Below is some information about the elements **G** and **Z**:

- (1) **G** exists in its normal state as a diatomic molecule,  $\text{G}_2$ .
- (2) **Z** has an oxidation number of +1, and has one proton fewer than that of element **E**. **E** exists as a gas under standard conditions.  $\text{Z}_2$  is a volatile solid.
- (3) The compound  $\text{EG}_3$  has a pyramidal shape.

Identify the elements **G** and **Z** and draw a Lewis structure that indicates the molecular shape of compound **D**.

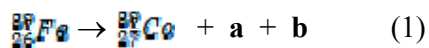
**(Answer by writing the proper elements according to the periodic table)**

**G** = .....      **Z** = .....

Lewis structure of compound **D** indicating molecular shape:

**Part C**

$^{59}\text{Fe}$  is a radiopharmaceutical isotope used in the study of iron metabolism in the spleen. This isotope decays to  $^{59}\text{Co}$  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  $^{59}\text{Fe}$  isotope is left for 178 days (which is  $n$  times of its half-life ( $t_{1/2}$ )), the mole ratio of  $^{59}\text{Co}$  to  $^{59}\text{Fe}$  is 15:1. If  $n$  is an integer, what is the half-life of  $^{59}\text{Fe}$  in day(s)? Show your calculation:

**Calculation:**

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

**Problem 7**

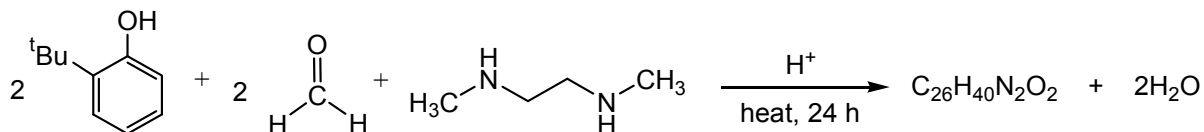
6% of the total

Problem 7 (6%)	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 size have shown to affect the potency of the complexes. This question deals with the synthesis and characterization of some titanium complexes.

**7-A1)** The reaction of 2 equivalents of 2-*tert*-butylphenol, 2 equivalents of formaldehyde, and one equivalent of *N,N'*-dimethylethylene-1,2-diamine under acidic conditions on heating forms **three major products** with the same chemical formula of  $C_{26}H_{40}N_2O_2$  (below). Draw the structure of each product.

**Product 1:****Product 2:****Product 3:**

**7-A2)** If **2,4-di-*tert*-butylphenol** is used as the reactant 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**.

**X:**



7-A3) The 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 two products: (i) a six-coordinate Ti complex **Y** as a yellow crystalline solid; and (ii) isopropanol.



UV-visible 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 a concentration of 0.50 M), and using benzene as the solvent, the absorbance data at  $\lambda = 370$  nm are given below:

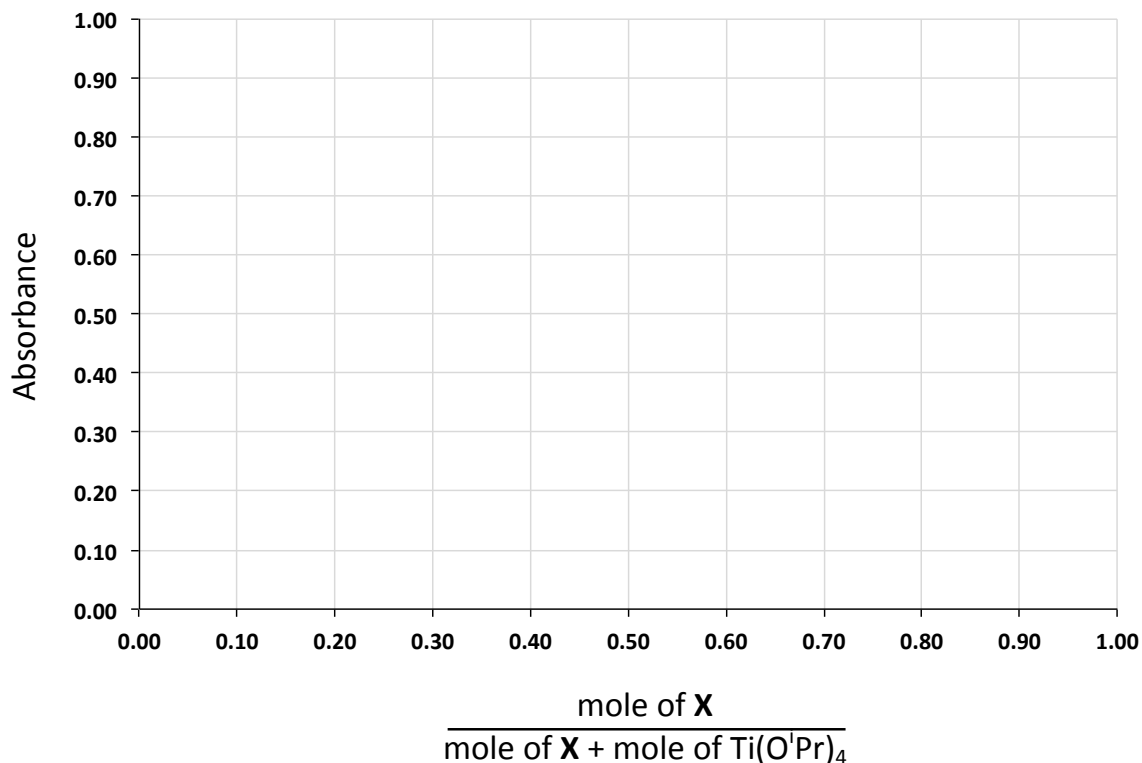
Volume of <b>X</b> (mL)	Volume of $\text{Ti}(\text{O}^i\text{Pr})_4$ (mL)	Volume of benzene (mL)	Absorbance
0	1.20	1.80	0.05
0.20	1.00	1.80	0.25
0.30	0.90	1.80	0.38
0.50	0.70	1.80	0.59
0.78	0.42	1.80	0.48
0.90	0.30	1.80	0.38
1.10	0.10	1.80	0.17
1.20	0	1.80	0.02

Fill in the 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:

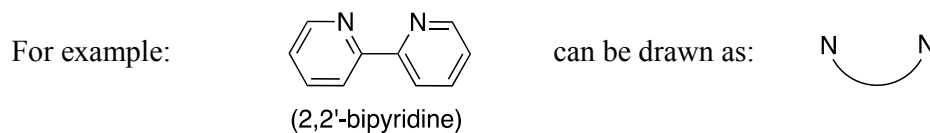


The value of  $\frac{\text{mole of X}}{\text{mole of X} + \text{mole of Ti(O}^i\text{Pr)}_4}$  which maximizes the amount of the product **Y** represents the stoichiometry of **X** in the chemical formula of **Y**. Based on the graph above, what is the molar ratio between Ti:**X** in the complex **Y**?

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

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

**NOTE: you do not need to draw the complete structure of the ligand.** Only include donor atoms that are coordinated to titanium. The ligand framework between the donor atoms should 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):



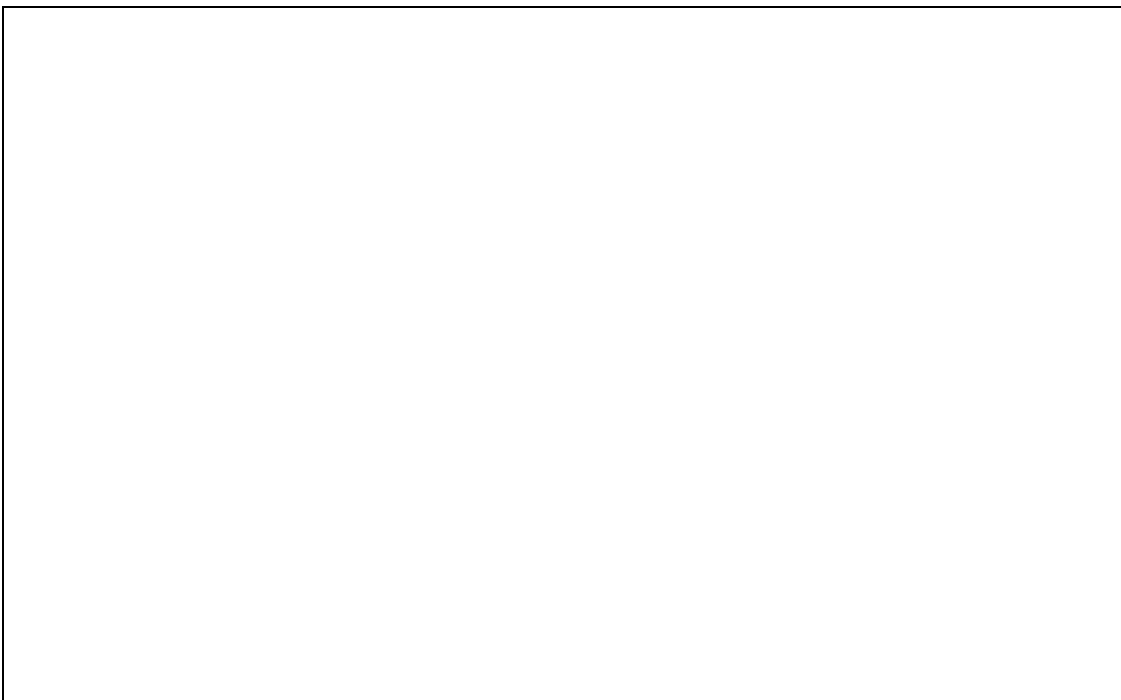
**Diastereomer 1:**

**Diastereomer 2:**

**Diastereomer 3:**

**7-A5)** Under certain conditions, the reaction shown in **equation 1** forms only one diastereomer of **Y**. Given that structures of **Y** are "fixed" (there is no intramolecular movement), the  $^1\text{H}$  NMR spectrum of **Y** in  $\text{CDCl}_3$  shows four singlet resonances at  $\delta$  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**.

**(NOTE: you do not need to draw the complete structure of the ligand.** Only include donor atoms that are coordinated to titanium. The ligand framework between the donor atoms should be drawn as shown in **7-A4**):





**Problem 8**

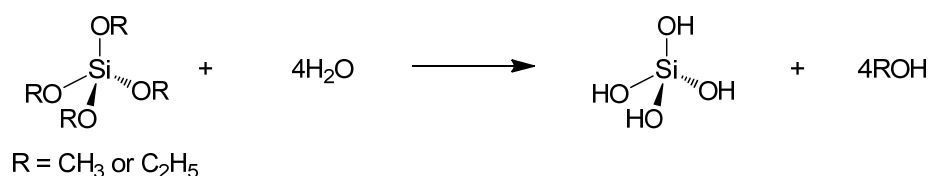
5% of the total

Problem 8 (5%)	A					Total
	A1	A2	A3	A4	A5	
Total	6	5.5	3	4	1.5	20
Score						

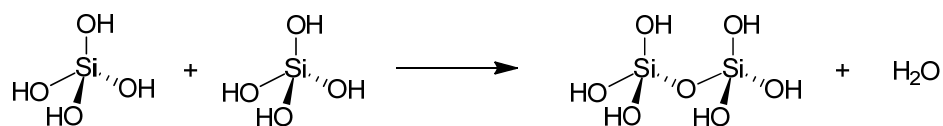
**Problem 8: Silica Surface**

Silica exists in various forms such as amorphous and crystalline. It can be synthesized by using silicon alkoxides like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) as shown by the reactions below:

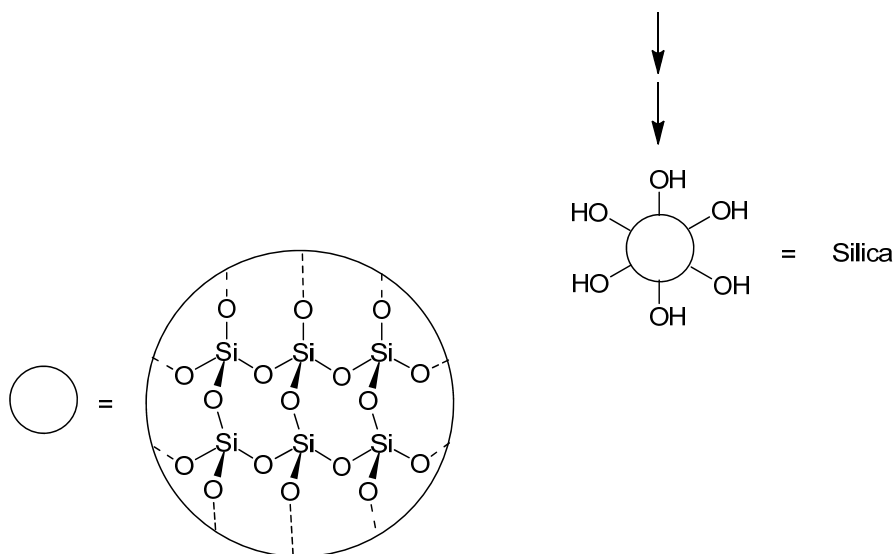
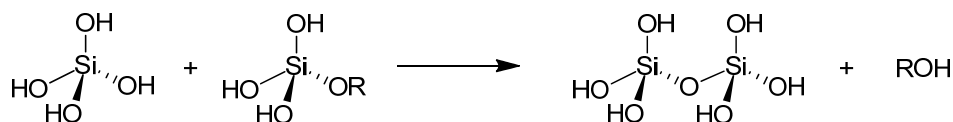
a. Hydrolysis:



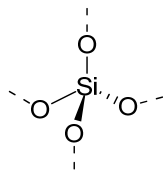
b. Water condensation:



c. Alcohol condensation:

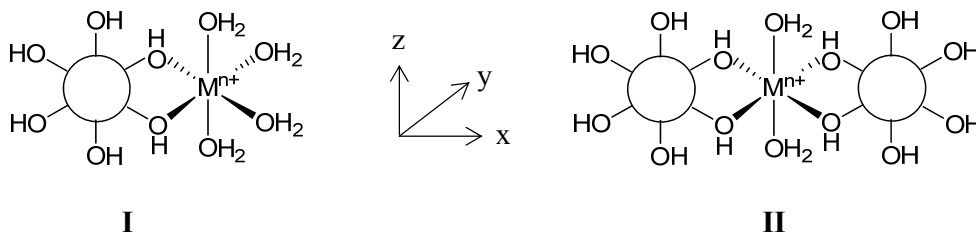


In bulk silica, all silicon atoms are tetrahedrally bonded to four oxygen atoms giving a 3D solid network. The silicon environments found inside silica are as follows:



**8-A1)** Three silicon atom environments (similar to the example above) are commonly observed at the silica **surface**. Draw the three structures of the silicon environments in the following boxes:

Silica can be used as an effective metal ion adsorbent in water. Possible structures for the metal-silica complex are as follows:



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

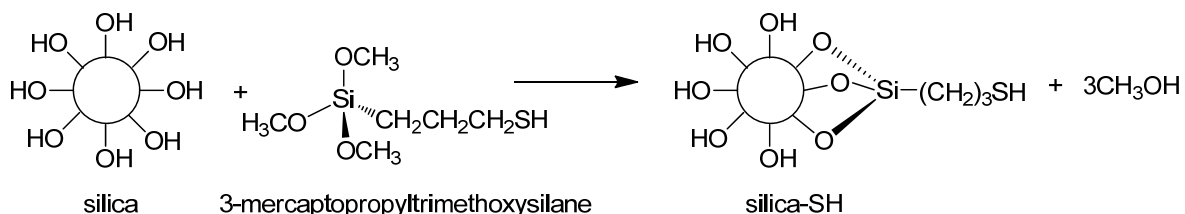
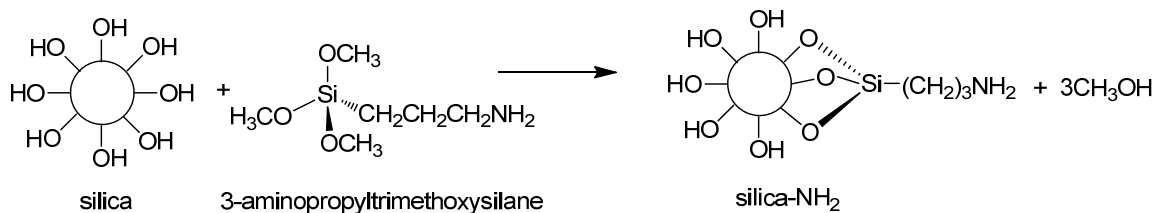
The splitting diagram:

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 in a similar way to  $\text{Cu}^{2+}$ , which metal ion (or ions) have analogous electronic transition(s) to  $\text{Cu}^{2+}$ ?

**NOTE:** (i) the metal ion(s) must be in the +2 or +3 oxidation state; and (ii) the silanol groups (Si-OH) and water are weak field ligands.

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



**8-A4)** If  $\text{Hg}^{2+}$  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. **Use R-SH instead of drawing the whole structure of silica-SH.**

<p>The structure:</p> <div style="border: 1px solid black; height: 120px; margin-top: 10px;"></div>	<p><math>d</math>-orbital splitting diagram :</p> <div style="border: 1px solid black; height: 120px; margin-top: 10px;"></div>
---	---

**8-A5)** Specify “true” or “false” for the following three statements:

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

True

False

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

True

False

c) in its visible absorption spectra,  $\lambda_{\text{max}}$  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!**

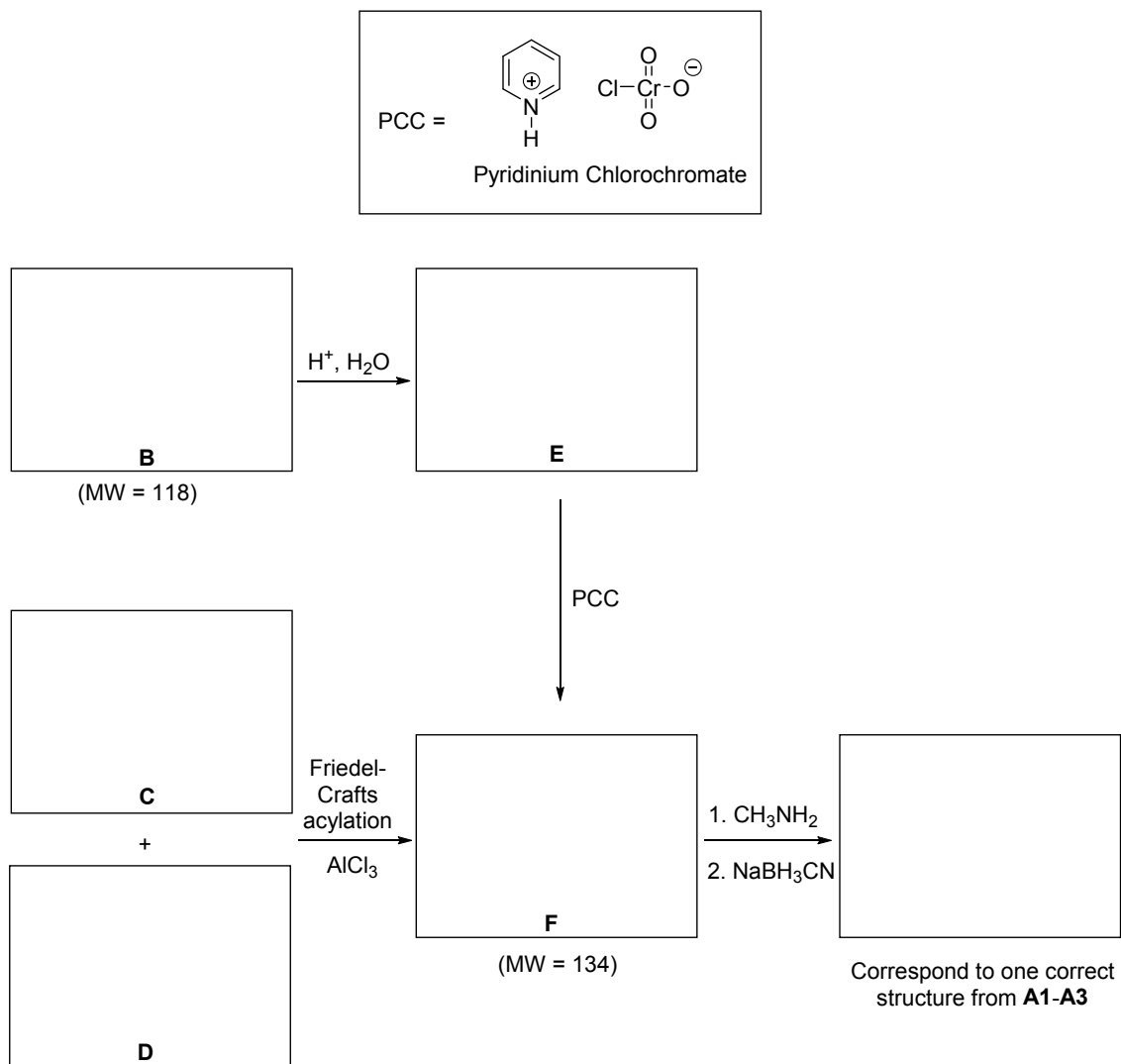
**9-A1)** Organic compound **A** is **CHIRAL** and contains only three elements with a molecular weight (MW) of 149 (rounded to an integer).

The  $^1\text{H}$  NMR spectrum of compound **A** shows three types of aromatic protons (among other types), and its  $^{13}\text{C}$  NMR spectrum shows exactly eight signals, of which four signals are in the range of 120-140 ppm.

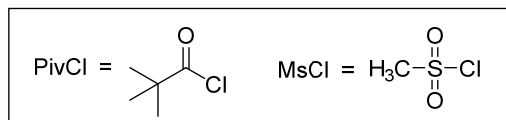
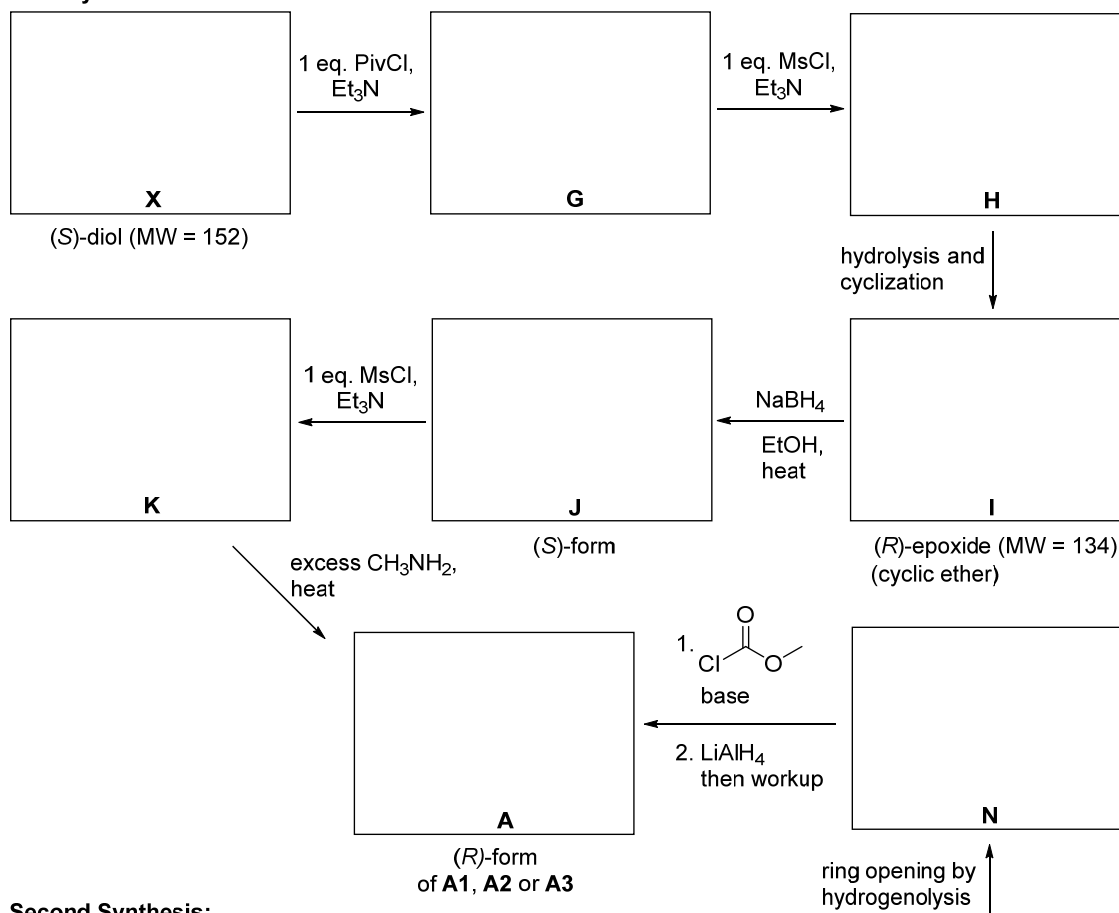
Compound **A** can be prepared by treating a carbonyl compound with methylamine ( $\text{CH}_3\text{NH}_2$ ) followed by  $\text{NaBH}_3\text{CN}$ . Draw all three possible structures of compound **A**. No stereochemistry is required, and **do not** include stereoisomers.

<b>A1</b>	<b>A2</b>	<b>A3</b>
-----------	-----------	-----------

9-A2) One of the constitutional isomers of compound **A** (structure **A1**, **A2** or **A3**) can be synthesized from **EITHER** compound **B** OR compounds **C** and **D** as shown in the diagram below. Draw the structures of compounds **B-F**, and the constitutional isomer of **A** (one of **A1**, **A2** or **A3**).



**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. Diols **X** and **Y** are constitutional isomers, and each compound contains one carbon less than that of compound **A**. Draw the structures of compounds **G-N**, **X**, **Y** and the (*R*)-form of compound **A**. **You must show the important stereochemistry of ALL compounds.**

**First Synthesis:****Second Synthesis:**

**Problem 10**

7% of the total

Problem 10 (7%)	A	B		Total
	A1	B1	B2	
Total	20.5	4	5.5	30
Score				

**Problem 10: Total Synthesis of Alkaloids**

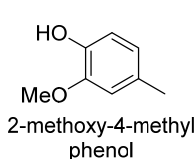
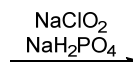
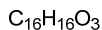
Alkaloids are a class of nitrogen-containing natural products. Their structural complexity and potent biological activities has drawn attention. Two representative examples of alkaloids (sauristolactam and pancratistatin) are highlighted in this question.

**Part A**

Sauristolactam possesses excellent cytotoxicity against various cancer cell lines. It can be prepared by the synthetic sequence on the next page.

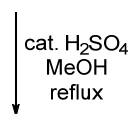
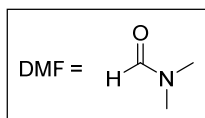
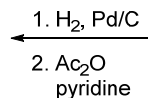


**10-A1)** Draw the structures of **A-G** in the reaction sequence below (write your answers on the following page). All  $^1\text{H-NMR}$  spectra were recorded in  $\text{CDCl}_3$  at 300 MHz.

**A****B**

The product has two aromatic rings:  
 a monosubstituted ring and  
 a tetrasubstituted ring with two singlets  
 in  $^1\text{H-NMR}$

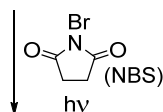
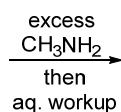
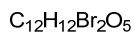
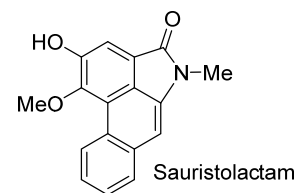
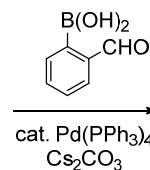
Strong IR absorption in region of  
 $1725\text{-}1700\text{ cm}^{-1}$  and broad IR  
 absorption from  $3300\text{ to }2500\text{ cm}^{-1}$

**E****D****C**

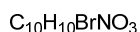
$^1\text{H-NMR}$  signals of the entire molecule:  
 7.59 (s, 1H), 3.88 (s, 3H),  
 3.87 (s, 3H), 2.68 (s, 3H),  
 2.35 (s, 3H)

In addition to the aromatic region,  
 $^1\text{H-NMR}$  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  $1750\text{ - }1735\text{ cm}^{-1}$

**F****G**

$^1\text{H-NMR}$  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)



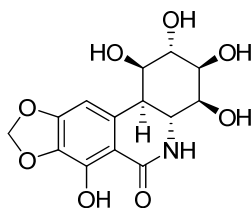
$^1\text{H-NMR}$  signals of the entire molecule:  
 7.40 (s, 1H), 4.22 (s, 2H),  
 3.98 (s, 3H), 3.19 (s, 3H)  
 and a proton exchangeable with  $\text{D}_2\text{O}$

Structures of A-G:

<b>A</b>	<b>B</b>
<b>C</b>	<b>D</b>
<b>E</b>	<b>F</b>
<b>G</b>	

**Part B**

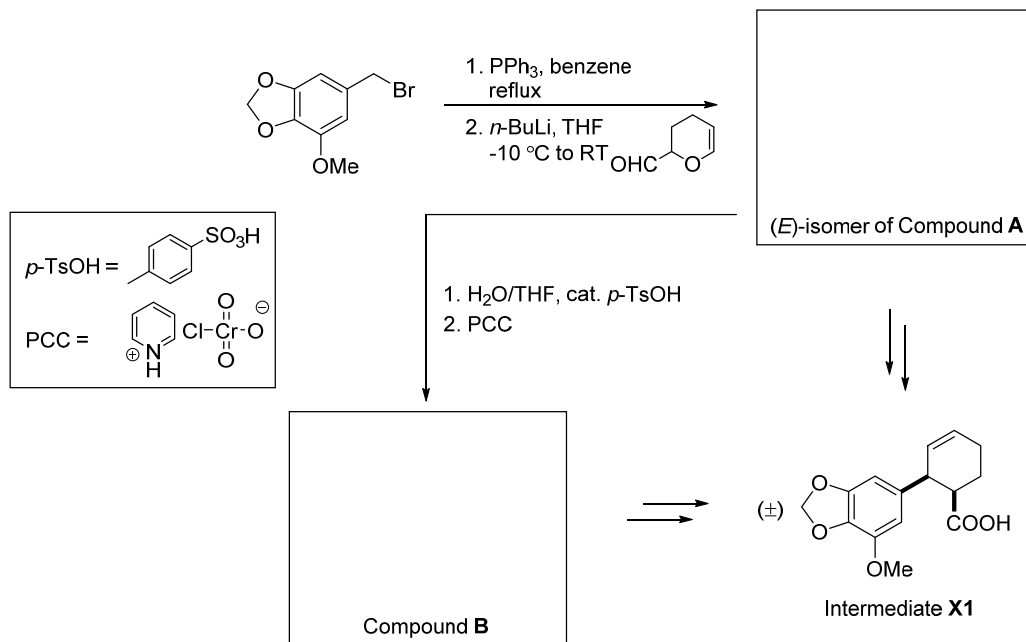
Pancreatistatin (isolated from the Hawaiian spider lily) exhibits potent *in vitro* and *in vivo* inhibitory activity of cancer cell growth, in addition to its excellent antiviral activity.



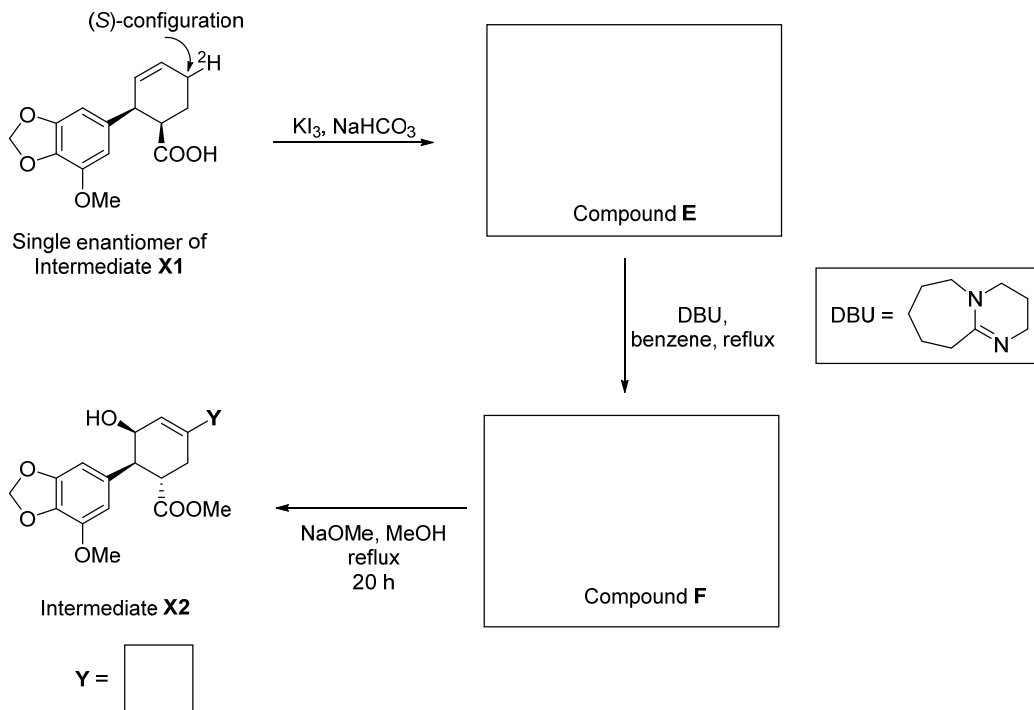
Pancreatistatin

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

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



**10-B2)** Intermediate **X1** (a single enantiomer with the stereochemistry shown) is labeled with deuterium ( $^2\text{H}$ ) with the configuration as indicated below. Propose the 3D chair structure of compound **E** and the structure of compound **F** with appropriate stereochemistry. Is **Y** a proton ( $^1\text{H}$ ) or a deuterium ( $^2\text{H}$ )? (**complete the three boxes**).



## Problem 11

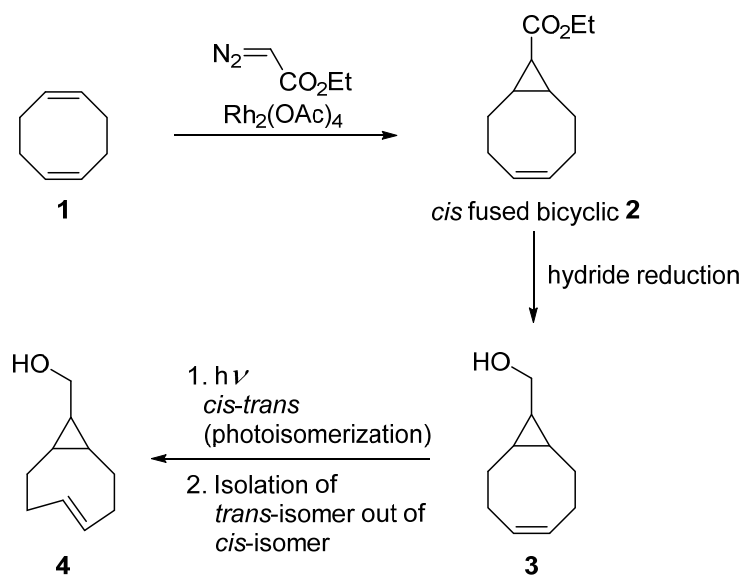
2% of the total

Problem 11	A		Total
	A1	A2	
Total	10	2	12
Score			

### Problem 11: Twist & Chirality

*trans*-Cyclooctene has a chiral plane and a high racemization barrier. The double bond of *trans*-cyclooctene is twisted and 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 follows:



**11-A1)** Draw all possible stereoisomers of compound **3** that could be obtained from the reduction of compound **2**. It is not necessary to assign *R* or *S* configurations.



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

Yes

No