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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 upon request only for clarification.

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Theoretical Problems

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD
Nakhon Pathom, THAILAND

Student Code

General Instructions.

- **Pages:** This theoretical exam booklet contains 55 pages. There are 11 Problems in total.

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

- **Exam Time:** Students will have a total of **5 ADDITIONAL hours** after exam reading to complete the exam.

- **Start/Stop:** Students may begin as soon as the **"Start"** command is given and must stop working immediately when the **"Stop"** command is announced.
  - Failure to stop the task by 1 minute or longer after the **"Stop"** command is given will lead to nullification of your theoretical exam.
  - After the **"Stop"** command is given, place your exam booklet back in your exam envelope and wait at your seat. The exam supervisor will come to collect your exam paper.

- **Answer sheets:** All results/answers must be clearly written in pen, in their respective designated areas for credit.
  - Only use the provided pens.
  - You may use the backside of these exam sheets as scratch paper, however, nothing outside of designated areas will be marked.

- **Calculator:** For any calculation, you may only use the 49th IChO calculator provided.

- **Assistance:** If you need assistance (*e.g.* more snacks, drinks, or you need to use the restroom), wave the orange IChO flag on your desk and wait for the exam supervisor.

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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 in in the world, as well as in Thailand's petrochemical industry. One example of the commercial use of propene is in the production of polypropylene (PP).

Part A.

Propene can be synthesized *via* the direct dehydrogenation of propane in the presence of a heterogeneous catalyst. However, such a reaction is not economically feasible due to its thermodynamic properties. Based on the provided thermodynamic information below:

$H_{bond}(C{=}C) = 1.77H_{bond}(C\text{-}C)$,

$H_{bond}(H\text{-}H) = 1.05H_{bond}(C\text{-}H)$, and

$H_{bond}(C\text{-}H) = 1.19H_{bond}(C\text{-}C)$,

where H_{bond} refers to the average bond enthalpy of the indicated chemical bond, answer the following questions.

1-A1) DETERMINE the enthalpy change of the direct dehydrogenation of propane and **EXPRESS** your answer in terms of $H_{bond}(C\text{-}C)$. **SHOW** all work and calculations.

Calculation:

1-A2) For the dehydrogenation reaction above, raising the external pressure at constant temperature fails to increase the yield of propene.

SELECT the law or principle that best explains this phenomenon. **MARK** "✓" in the open circle for your answer.

◯ Boyle's law
◯ Charles' law
◯ Dalton's law
◯ Raoult's law
◯ Le Chatelier's principle

1-A3) After the dehydrogenation reaction is at equilibrium, changing the temperature will perturb the equilibrium of the system when the partial pressures of the components are held constant.

SELECT the correct set(s) of signs of the thermodynamic variables applicable to the change. **MARK** "✓" in the open circle(s) for **ALL** your choice(s).

	ΔH	ΔS	ΔG	T^*
◯	-	+	+	lower
◯	-	+	-	higher
◯	-	-	+	lower
◯	-	-	-	higher
◯	+	+	+	lower
◯	+	+	-	higher
◯	+	-	+	lower
◯	+	-	-	higher

◯ None of the above is correct

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

Part B.

A more efficient reaction which produces large quantities of propene is *oxidative dehydrogenation (ODH)* using solid catalysts, such as vanadium oxides, in the presence of molecular oxygen gas. It is more promising for the industrial production of propene than direct dehydrogenation.

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

where k_{red} and k_{ox} are rate constants for the reduction of the metal oxide catalyst by propane and the oxidation of the catalyst by molecular oxygen, respectively. Standard pressure of 1 bar is represented by p^o. The rate of oxidation of the catalyst is found to be 100,000 times faster than that of the propane oxidation, and the experimental rate at 600 K is represented by: $r_{C_3H_8} = k_{obs}\dfrac{p_{C_3H_8}}{p^o}$, where k_{obs} is the observed rate constant (0.062 mol s^{-1}).

If the reactor containing the above catalyst is maintained at a total pressure of 1 bar with propane and oxygen, **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. One of the proposed mechanisms for the ODH in the presence of the catalyst can be written as follows (where red* represents a reduced site and O(*s*) represents an oxygen atom on the surface of the catalyst):

$C_3H_8(g) + O(s) \xrightarrow{k_1} C_3H_6(g) + H_2O(g) + red^*$ (1)

$C_3H_6(g) + 9O(s) \xrightarrow{k_2} 3CO_2(g) + 3H_2O(g) + 9red^*$ (2)

$O_2(g) + 2red^* \xrightarrow{k_3} 2O(s)$ (3)

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

$r_1 = k_1 p_{C_3H_8}(1-\beta)$,
$r_2 = k_2 p_{C_3H_6}(1-\beta)$,
and $r_3 = k_3 p_{O_2}\beta$.

1-C) Assuming that the amount of oxygen atoms on the surface remains constant throughout the reaction, **DETERMINE** β in terms of k_1, k_2, k_3, $p_{C_3H_8}$, $p_{C_3H_6}$, and p_{O_2}.

Calculation:

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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 in which the rate constant of the reaction changes when one of the atoms in the reactants is replaced by its isotope. KIE can be used to confirm whether a particular covalent bond to hydrogen is broken in the reaction. To this end, the harmonic oscillator model is used to estimate the difference in the rate between C-H and C-D bond dissociation (D = $^{2}_{1}$H).

The wave number (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 the vibrational quantum number with possible values of 0, 1, 2, ... and ν is the frequency. 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 μ_{CH} = 1.008 and μ_{CD} = 2.016 for subsequent questions. 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 of the C-D stretching (D = deuterium) and the C-H stretching frequency expressed in wave-number units is 2900 cm^{-1}, **DETERMINE** the corresponding C-D stretching frequency **(in cm^{-1})**.

Calculation:

2-A3) Using the C-H and C-D stretching frequencies from 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 kJ mol^{-1} and ZPE_{CD} = 2.15 kJ mol^{-1} for subsequent questions. Note that the given values are not necessarily close to the correct values.]

Kinetic isotope effect (KIE)

Due to their difference in zero-point vibrational energies, a non-deuterated molecule and its corresponding deuterated form are expected to react at different rates in chemical reactions.

For the C-H and C-D bond dissociation reactions, the energies of both transition states and both products are identical. Thus, 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 energies (BDE) between C-D and C-H bonds ($BDE_{CD} - BDE_{CH}$) in kJ mol^{-1}.

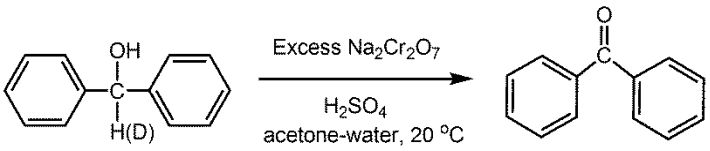
Calculation:

2-A5) Assuming that the activation energy (E_a) for the C-H and C-D bond cleavage is approximately equal to the bond dissociation energy in each case, and the Arrhenius factor is the same for both C-H and C-D bond cleaving reactions, **DETERMINE** the relative rate constant (k_{CH}/k_{CD}) for the C-H/C-D bond cleavage at 25° C.

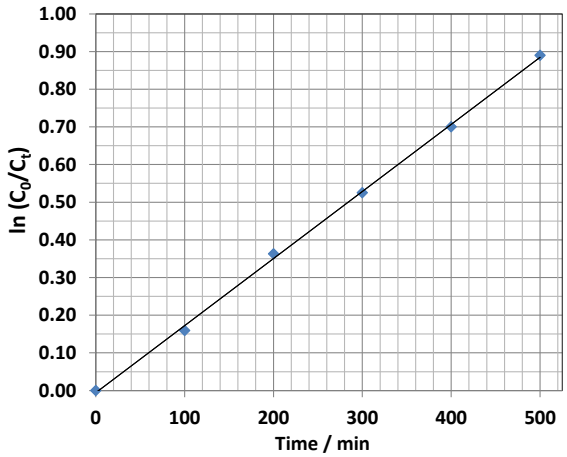
Calculation:

Using KIE to study reaction mechanisms

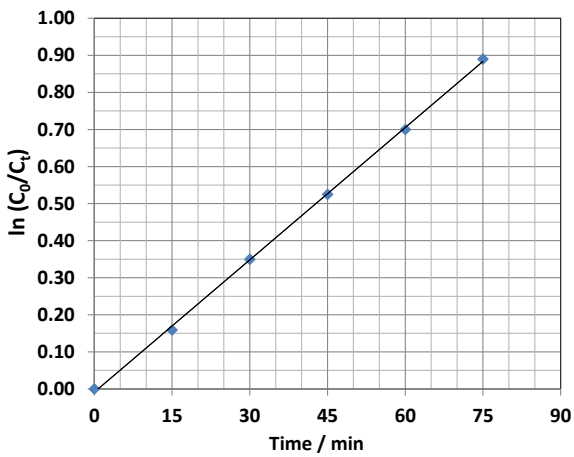
The oxidation of non-deuterated and deuterated diphenylmethanol using an excess of chromic acid was studied.



2-A6) Let C_0 represent 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 (Plot 2a and Plot 2b), from which the first-order rate constant can be determined.



Plot 2a



Plot 2b

DETERNINE which plot represents the oxidation of non-deuterated diphenylmethanol and which represents the oxidation of deuterated diphenylmethanol.

MARK "✓" in the open circles for the CORRECT corresponding plot.

The oxidation of non-deuterated diphenylmethanol:	◯ Plot 2a	◯ Plot 2b
The oxidation of deuterated diphenylmethanol:	◯ Plot 2a	◯ Plot 2b

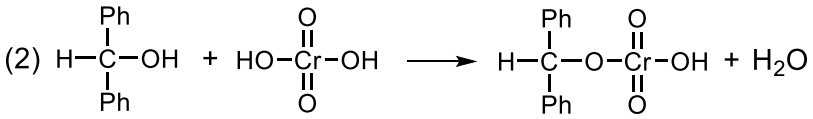
2-A7) Using the plots in question **2-A6), DETERMINE**

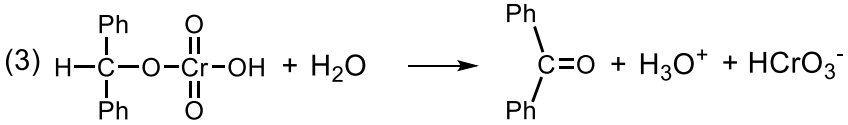
k_{CH} (in min^{-1}),
k_{CD} (in min^{-1}), and
k_{CH}/k_{CD} of this reaction.

Calculation:

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

(1) $Cr_2O_7^{2-} + H_2O + 2H^+ \rightleftharpoons 2H_2CrO_4$

(2) 

(3) 

Based your answers in **2-A6)** and **2-A7)**, **DETERMINE** which step should be the rate determining step.

MARK "✓" in one of the open circles for your choice.

◯ Step (1)
◯ Step (2)
◯ Step (3)

Problem 3	A	B	Total

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Problem 3

6% of the total

	A1	A2	A3		
Total	7	3	8	6	24
Score					

Problem 3: Thermodynamics of chemical reactions

Part A.

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

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g).$$

The standard enthalpy of formation (ΔH_f^o) and the absolute entropy (S^o) 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^o (kJ mol^{-1})	S^o (J K^{-1} mol^{-1})
CO(*g*)	-111	198
H_2(*g*)	0	131
CH_3OH(*g*)	-201	240

3-A1) CALCULATE ΔH^o, ΔS^o, ΔG^o, and K_p for the reaction at 298 K.

Calculation:

ΔH^o = _____ kJ

ΔS^o = _____ J K^{-1}

ΔG^o = _____ kJ

K_p = _____

[If you are unable to calculate K_p at 298 K in problem **3-A1)**, use $K_p = 9 \times 10^5$ for subsequent questions if needed.]

3-A2) A commercial reactor is operated at a temperature of 600 K. **CALCULATE** K_p at this temperature. (Assume that ΔH^o and ΔS^o are independent of temperature.)

Calculation:

K_p = _____

[If you are unable to calculate K_p at 600 K in problem **3-A2)**, use $K_p = 1.0 \times 10^{-2}$ in subsequent questions if needed.]

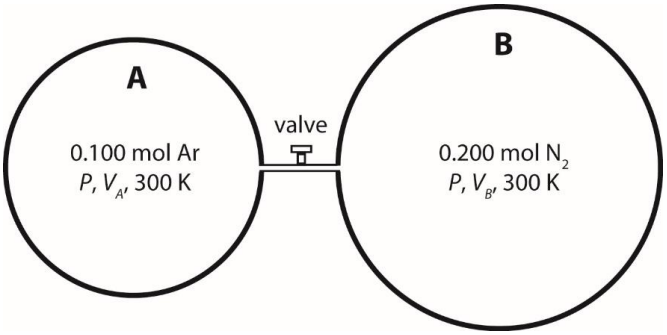
3-A3) Production of methanol in an industrial reactor is carried out with a mixture of H_2 and CO in a 2:1 molar ratio. The mole fraction of methanol in the exhaust gas from the reactor is found to be 0.18. Assuming that equilibrium is established in the exhaust gas, **CALCULATE** the total pressure 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 contains 2 compartments, separated by a closed valve, which has a 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 are V_A and V_B, and the gases behave as ideal gases.



After opening the valve slowly, the system is allowed to reach equilibrium. Assuming that the gas mixture also behaves ideally, **CALCULATE** ΔG (the change in Gibbs free energy) in the mixing process at 300 K.

Calculation:

ΔG = _____ J

Problem 4	A	Total

Student Code

Problem 4

5% of the total

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

Problem 4: Electrochemistry

Part A. Galvanic cells

The following experiment is performed at 30.00ºC. An electrochemical cell is composed of a hydrogen half-cell containing a metal platinum electrode immersed in a buffer solution under a pressure of hydrogen gas, [Pt(*s*) | H_2(*g*) | H^+(*aq*)]. This hydrogen half-cell is connected to a half-cell of a metal (**M**) strip dipped in an unknown concentration of $\mathbf{M}^{2+}$(*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.

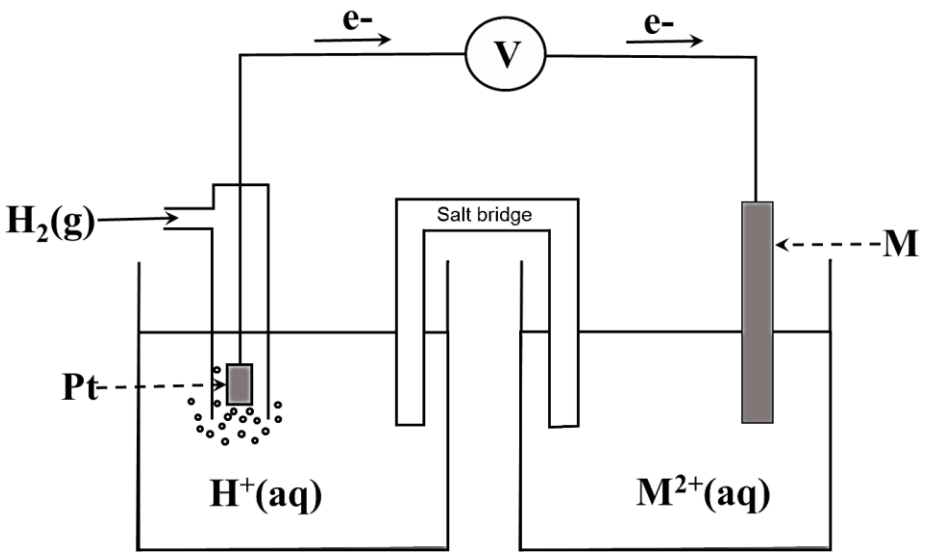


Figure 1: The galvanic cell

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

Half-reaction			**E° (V)**
$Ba^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ba(s)$	-2.912
$Sr^{2+}(aq) + 2e^-$	$\longrightarrow$	$Sr(s)$	-2.899
$Ca^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ca(s)$	-2.868
$Er^{2+}(aq) + 2e^-$	$\longrightarrow$	$Er(s)$	-2.000
$Ti^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ti(s)$	-1.630
$Mn^{2+}(aq) + 2e^-$	$\longrightarrow$	$Mn(s)$	-1.185
$V^{2+}(aq) + 2e^-$	$\longrightarrow$	$V(s)$	-1.175
$Cr^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cr(s)$	-0.913
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow$	$Fe(s)$	-0.447
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cd(s)$	-0.403
$Co^{2+}(aq) + 2e^-$	$\longrightarrow$	$Co(s)$	-0.280
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ni(s)$	-0.257
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow$	$Sn(s)$	-0.138
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow$	$Pb(s)$	-0.126
$2H^+(aq) + 2e^-$	$\longrightarrow$	$H_2(g)$	0.000
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow$	$Sn^{2+}(aq)$	+0.151
$Cu^{2+}(aq) + e^-$	$\longrightarrow$	$Cu^+(aq)$	+0.153
$Ge^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ge(s)$	+0.240
$VO^{2+}(aq) + 2H^+(aq) + e^-$	$\longrightarrow$	$V^{3+}(aq) + H_2O(l)$	+0.337
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cu(s)$	+0.340
$Tc^{2+}(aq) + 2e^-$	$\longrightarrow$	$Tc(s)$	+0.400
$Ru^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ru(s)$	+0.455
$I_2(s) + 2e^-$	$\longrightarrow$	$2I^-(aq)$	+0.535
$UO_2^{2+}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow$	$U^{4+}(aq) + 2H_2O(l)$	+0.612
$PtCl_4^{2-}(aq) + 2e^-$	$\longrightarrow$	$Pt(s) + 4Cl^-(aq)$	+0.755
$Fe^{3+}(aq) + e^-$	$\longrightarrow$	$Fe^{2+}(aq)$	+0.770
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow$	$2Hg(l)$	+0.797
$Hg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Hg(l)$	+0.851
$2Hg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Hg_2^{2+}(aq)$	+0.920
$Pt^{2+}(aq) + 2e^-$	$\longrightarrow$	$Pt(s)$	+1.180
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow$	$Mn^{2+}(aq) + 2H_2O(l)$	+1.224
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow$	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.360
$Co^{3+}(aq) + e^-$	$\longrightarrow$	$Co^{2+}(aq)$	+1.920
$S_2O_8^{2-}(aq) + 2e^-$	$\longrightarrow$	$2SO_4^{2-}(aq)$	+2.010

4-A1) When the reaction quotient (Q) of the galvanic cell is equal to 2.18×10^{-4} at 30.00°C, the electromotive force is +0.450 V.

CALCULATE the value of the standard reduction potential (E°) and identify the metal "**M**".

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

Calculations

$\therefore$ The standard reduction potential of **M** is _____V
(answer with 3 digits after decimal point)

$\therefore$ 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 the $\mathbf{M}^{2+}(aq)$ solution in the cell (Figure 1) can be determined by iodometric titration. A 25.00 mL aliquot of $\mathbf{M}^{2+}(aq)$ solution is added to a flask and an excess of KI is added. To reach the equivalent point, 25.05 mL of 0.800 M sodium thiosulfate is required.

WRITE all redox reactions associated with this titration and **CALCULATE** the concentration of the $\mathbf{M}^{2+}(aq)$ solution.

Calculations

$\therefore$ The concentration of the $\mathbf{M}^{2+}(aq)$ solution is _____ M

(answer with 3 digits after the decimal point)

[If the student cannot find the answer, they can use 0.950 M as the concentration of $\mathbf{M}^{2+}$ in further calculations.]

4-A4) When the hydrogen half-cell in Figure 1 is under 0.360 bar of hydrogen gas and the platinum electrode is immersed in a 500 mL buffer solution containing 0.050 mol of lactic acid ($HC_3H_5O_3$) and 0.025 mol of sodium lactate ($C_3H_5O_3Na$), the measured electromotive force of the cell is +0.534 V.

CALCULATE the pH of the buffer solution **and** the dissociation constant (K_a) of lactic acid at 30.00°C (next page).

Calculations of the pH for the buffer solution

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

[If the student cannot determine the answer, they can use 3.46 as the buffer pH for further calculations.]

Calculations for the dissociation constant (K_a) of lactic acid

$\therefore$ The dissociation constant of lactic acid is _____

(answer with 2 digits after decimal point)

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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 using acid or alkaline reagents to fractionate inorganic phosphorus. A particular soil sample was extracted and analyzed as described below.

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

A 5.00 gram soil sample was digested (*i.e.* dissolving all phosphorus and silicon) to give a final volume of 50.0 mL. The extract was analyzed and was found to contain 5.16 mg L^{-1} and 5.35 mg L^{-1} of phosphorus and silicon, respectively.

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

Calculations

$\therefore$ mass of PO_4^{3-} in 1.00 g soil = _____ mg
(answer with 3 digits after the decimal point)

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

Calculations

$\therefore$ mass of SiO_4^{4-} in 1.00 g soil = _____ mg
(answer with 3 digits after the decimal point)

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

Phosphate in the acid extract can be analyzed using the molybdenum blue method. In this method, one mole of phosphate is converted into one mole of molybdenum blue. Absorbance (A) and transmittance (T) values are recorded at 800 nm. The molar absorptivity of the molybdenum blue compound is 6720 M^{-1} cm^{-1}, and all measurements are carried out in a 1.00 cm cuvette.

Transmittance and absorbance values are determined by the following equations:

$$T = I / I_o$$

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

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

5-B1) When a sample containing high concentrations of phosphate is analyzed, a reference solution of 7.5×10^{-5} M molybdenum blue is used to adjust the spectrophotometer to zero absorbance. Under these conditions, the transmittance of an unknown sample is 0.55.

CALCULATE the concentration of phosphate (M) in the unknown sample solution.

Calculations

$\therefore$ phosphate concentration of the unknown sample = _____ M

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, respectively. Further reduction with ascorbic acid produces an intensely colored molybdenum blue solution. Both complexes exhibit maximum absorbance values at 800 nm. Addition of tartaric acid helps prevent silicate interference in phosphate determinations.

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

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

y is absorbance at 800 nm,
x_1 is concentration of phosphate as M,
x_2 is concentration of silicate as M

Absorbance values at 800 nm of alkaline soil extracts after treatment 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 concentration (in mg L^{-1}).

Calculations

$\therefore$ concentration of PO_4^{3-} = _____ M

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

(answer with 2 digits after decimal point)

5-C2) **CALCULATE** the silicate concentration for the alkaline-treated soil sample (in M) and **CALCULATE** the corresponding silicon concentration (in mg L^{-1}).

Calculations

$\therefore$ concentration of SiO_4^{4-} = _____ M

(answer with 2 digits after the decimal point)

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

(answer with 2 digits after the decimal point)

Part D. Preconcentration of ammonium phosphomolybdate

A 100 mL aqueous sample of ammonium phosphomolybdate ($(NH_4)_3PMo_{12}O_{40}$) 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). K_{ow} of the ammonium phosphomolybdate is 5.0. The molar absorptivity of ammonium phosphomolybdate in the organic phase is 5000 M^{-1} cm^{-1}.

5-D) If the absorbance of the organic extract is 0.200, **CALCULATE** the total mass of phosphorus (in mg) in the original aqueous sample. The optical path length of the cuvette is 1.00 cm.

Calculations

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

Student Code

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

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, limiting its use. Element **X** is one of the alloying elements that is added to improve the oxidation resistance of iron.

6-A1) Below is some information about element **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 Fe.

DETERMINE element **X**.
(Answer by writing the proper symbol according to the periodic table.)

6-A2) Both Fe and **X** crystallize in a body centered cubic structure. Treating the Fe atoms as hard-spheres, the volume taken up by the Fe atoms inside the unit cell is 1.59×10^{-23} 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.

DETERMINE if **X** and Fe form a complete substitutional solid solution and **MARK** "✓" in the appropriate box. **SHOW** your calculations. **No credit is given without calculations**. The volume of a 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} = _____nm R_X = _____nm ΔR = _____

Part B.

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

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

Under these conditions, HCO_3^- ions are converted to CO_3^{2-}. **WRITE** the balanced ionic equation for this reaction in basic solution.

6-B2) A covalent compound **A**, which contains more than 2 atoms and is a potential oxidizing agent, can be prepared by the reaction between diatomic halogen molecule ($\mathbf{Q}_2$) and Na**Q**O_2:

$$1\mathbf{Q}_2 + x\text{Na}\mathbf{Q}\text{O}_2 \rightarrow y\mathbf{A} + z\text{Na}\mathbf{Q} \qquad \text{where } x+y+z \leq 7$$

where x, y and z are the coefficients of the balanced equation. It is known that among the binary compounds between hydrogen and halogen, H**Q** has the lowest boiling point. It is also known that compound **A** has an unpaired electron.

IDENTIFY Q and **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:**

DETERMINE the molecular geometry of compound **A**. (**MARK** "✓" 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 $Fe(HCO_3)_2$ 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 the other two. Below is some information about the elements **G** and **Z**:

(1) **G** exists in its normal state as a diatomic molecule, $\mathbf{G}_2$.
(2) **Z** has one proton fewer than of element **E** and **E** exists as a gas under standard conditions. $\mathbf{Z}_2$ is a volatile solid.
(3) The compound $\mathbf{EG}_3$ 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 to study iron metabolism in the spleen. This isotope decays to ^{59}Co as follows:

$$^{59}_{26}Fe \rightarrow {}^{59}_{27}Co + a + b \qquad (1)$$

6-C1) **IDENTIFY 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, **DETERMINE** the half-life of ^{59}Fe in day(s). **SHOW** your calculation.

Calculation:

Half-life of ^{59}Fe = _____days (answer with 1 decimal place)

Student Code

Problem 7

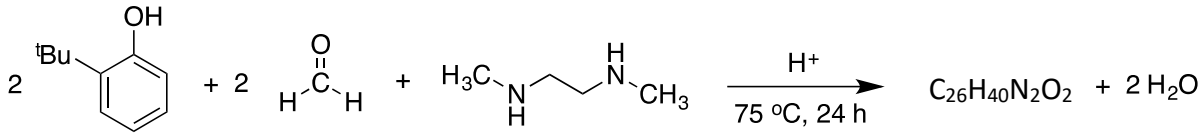
6% of the total

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) A reaction of 2 equivalents of 2-*tert*-butylphenol, 2 equivalents of formaldehyde, and 1 equivalent of *N*,*N'*-dimethylethylene-1,2-diamine under acidic conditions at 75 °C affords three major products with the same chemical formula of $C_{26}H_{40}N_2O_2$, 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 (assuming the same stoichiometry as that in **7-A1)**), only one product **X** is obtained.

DRAW the structure of **X**.

Structure of X

A reaction between **X** from **7-A2)** and $Ti(O^iPr)_4$ [^iPr = 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.

$$a\,\mathbf{X} + b\,Ti(O^iPr)_4 \xrightarrow{Et_2O} d\,\mathbf{Y} + c\,{}^iPrOH \qquad (\textbf{equation 1})$$

UV-Vis spectral analysis of **X**, $Ti(O^iPr)_4$, and **Y** reveal that only product **Y** absorbs at λ = 370 nm. By varying the volumes of **X** and $Ti(O^iPr)_4$ solutions, each with initial concentrations of 0.50 M, and using benzene as the solvent, the absorbance values at λ = 370 nm are given below:

Volume of X (mL)	**Volume of $Ti(O^iPr)_4$ (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

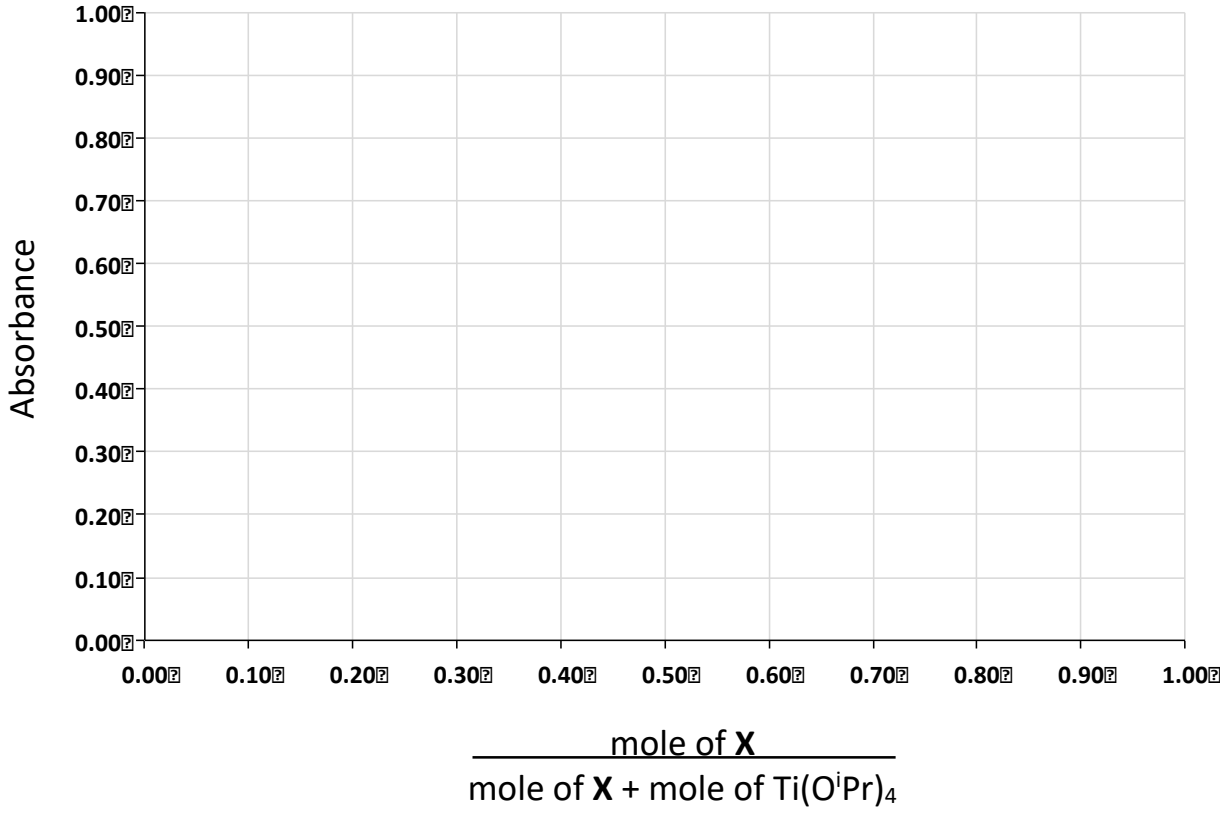
7-A3) FILL IN appropriate values in the table provided below.

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

(2 digits after the decimal)

Student Code

PLOT a graph of absorbance *versus* $\frac{\text{mole of } \mathbf{X}}{\text{mole of } \mathbf{X} + \text{mole of Ti}(O^{i}Pr)_4}$ below.



The value of $\frac{\text{mole of } \mathbf{X}}{\text{mole of } \mathbf{X} + \text{mole of Ti}(O^{i}Pr)_4}$ which maximizes the amount of the product **Y** represents the stoichiometry of **X** in the chemical formula of **Y**.

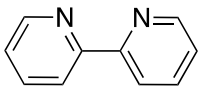
Based on the graph above, **DETERMINE** the molar ratio between Ti:**X** in complex **Y**.

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

7-A4) The Ti complex **Y** is six-coordinate. The IR spectrum of **Y** does not contain a broad absorbance band in the range of 3200–3600 cm^{-1}. **Y** exists as three diastereomers.

DRAW the structures of all three diastereomers, ignoring stereochemistry at N atoms.

Note: You do not need to draw the complete structure of the ligand. Only identify donor atoms that are involved in coordination with titanium. Also, the ligand framework between the donor atoms can be simplified. For example:



(2,2'-bipyridine)

can be drawn as:

If you did not determine 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**. The ^{1}H NMR spectrum of **Y** in $CDCl_3$ shows four singlet resonances at δ = 1.25, 1.30, 1.66, and 1.72 ppm corresponding to the *tert*-butyl groups. These peaks can be interpreted as in conventional organic spectroscopy. Assume that structures of **Y** are "fixed" (no intramolecular movement).

DRAW the 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)**)

Diastereomer of Y:

Student Code

Problem 8

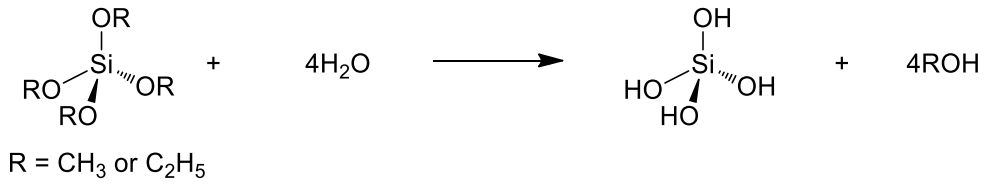
5% of the total

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

Problem 8: Silica Surface

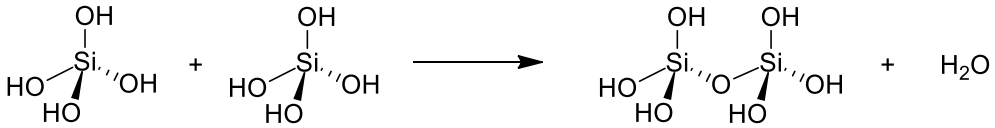
Silica exists in various forms such as amorphous and crystalline. Silica can be synthesized *via* a sol-gel process using silicon alkoxides like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) as the shown in the scheme below:

a. Hydrolysis

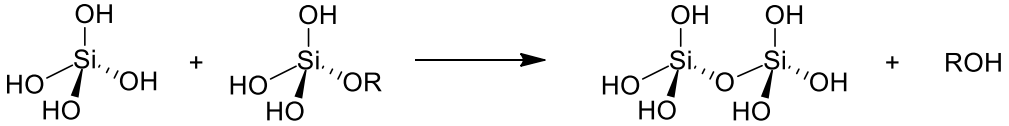


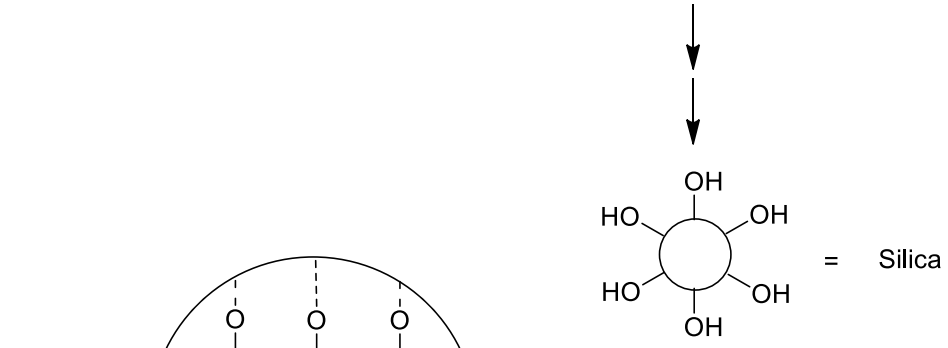
R = CH_3 or C_2H_5

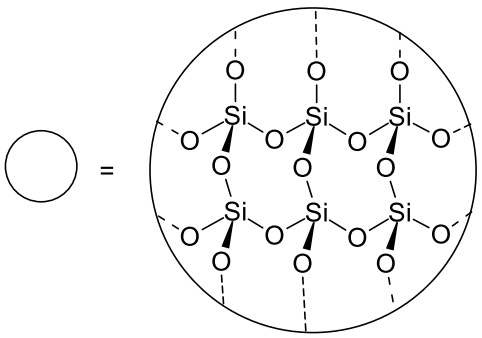
b. Water condensation



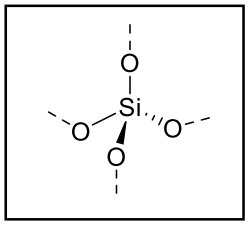
c. Alcohol condensation







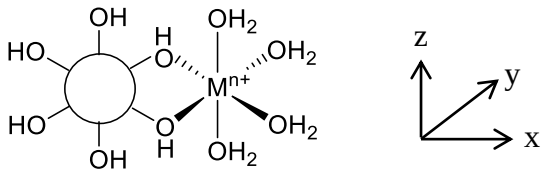
In bulk silica, all silicon atoms are tetrahedrally bonded to four oxygen atoms yielding a three-dimensional solid network. The silicon environments found inside silica are presented below:



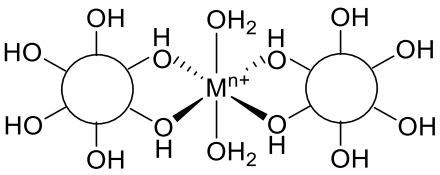
8-A1) There are three silicon atom environments (similar to the example above) commonly observed at the silica **surface**.

DRAW the three structures of the silicon environments 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:



I



II

8-A2) After 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 λ_{max} = 550 nm. Cu^{2+} binds to silica adopting a similar structure to **II**.

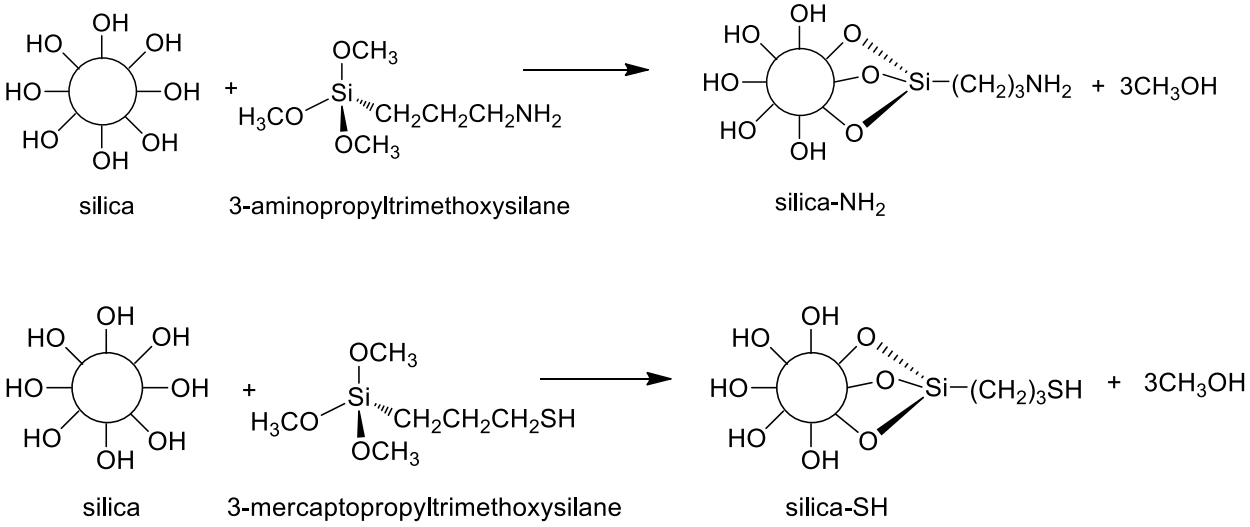
DRAW the splitting diagram for the *d*-orbitals of the Cu^{2+} ion, including the labels for the *d*-orbitals in the complex, and **SPECIFY** the corresponding electronic transition(s) for the visible absorption.

The splitting diagram:

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

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

Interestingly, silica is nonspecific in bonding with metal ions. To increase the selectivity, the silica surface can be modified by grafting various organic molecules like 3-aminopropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane, as depicted in the following scheme:



8-A4) When Hg^{2+} binds exclusively to the sulfur sites in silica-SH, a **symmetric** complex of $[Hg(silica\text{-}SH)_2]^{2+}$ is formed.

DRAW the structure of $[Hg(silica\text{-}SH)_2]^{2+}$ and **SPECIFY** the direction of the bond axes, and **DRAW** the corresponding *d*-orbital splitting diagram. (You may use R-SH instead of drawing the whole structure of silica-SH.)

The structure:

_d_-orbital splitting diagram:

8-A5) **MARK** "✓" true or false for the following statements:

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

☐ True ☐ False

b) The $[(Cu(silica\text{-}NH_2)_x]^{2+}$, having a similar geometry to other copper(II) amine complexes, is expected to have a similar color.

☐ True ☐ False

c) In the visible absorption spectra, λ_{max} of $[(Cu(silica\text{-}NH_2)_x]^{2+}$ is greater than that of $[(Cu(silica\text{-}OH)_x]^{2+}$.

☐ True ☐ False

Student Code

Problem 9

6% of the total

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

Problem 9: Into the Unknown

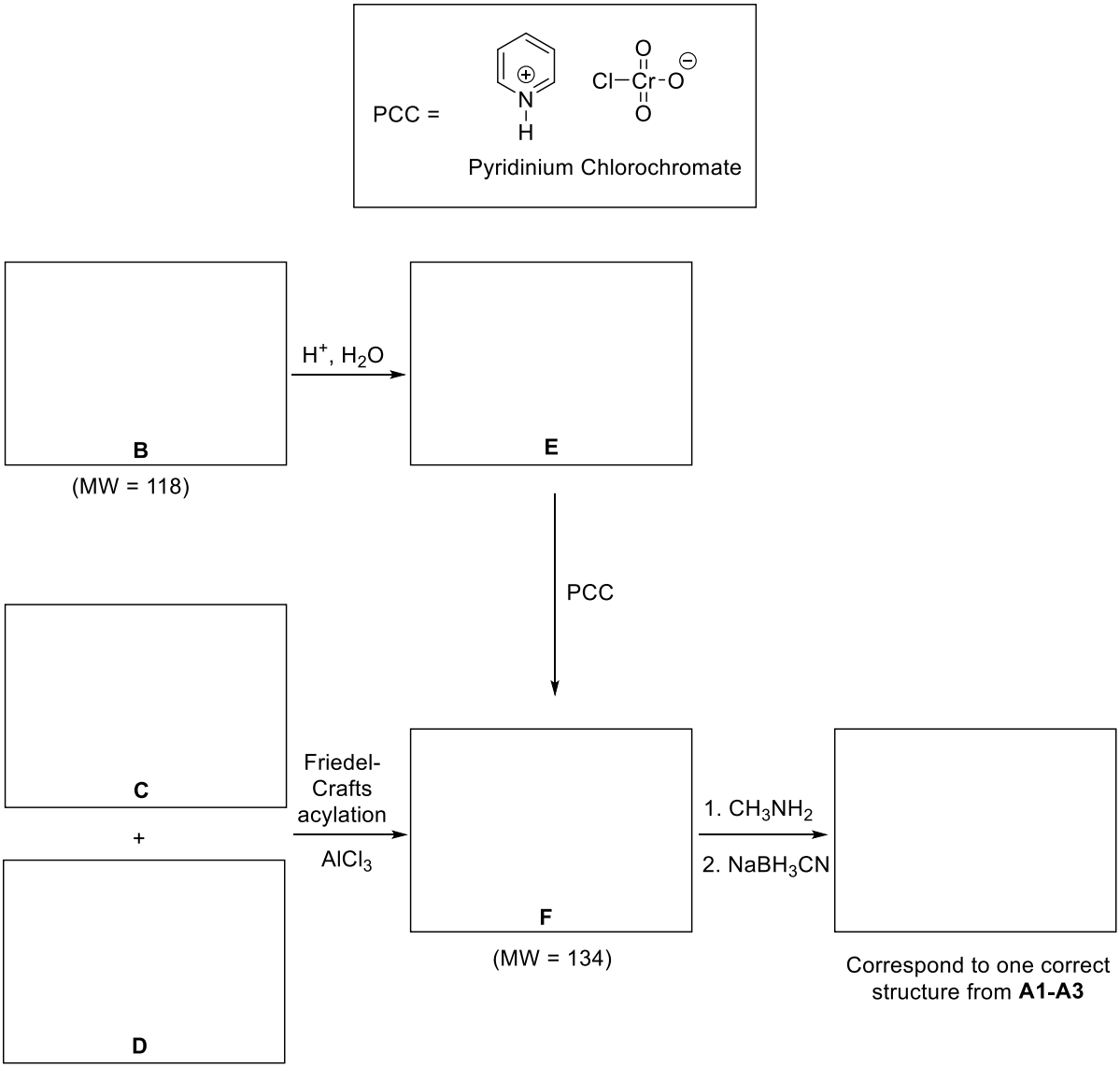
9-A1) Organic compound **A** is **chiral** and contains only three elements with the molecular weight (MW) of 149 (rounded to the nearest integer).

The ^{1}H 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 $NaBH_3CN$. **DRAW** all possible structures for compound **A**. No stereochemistry is required (**do not** include stereoisomers).

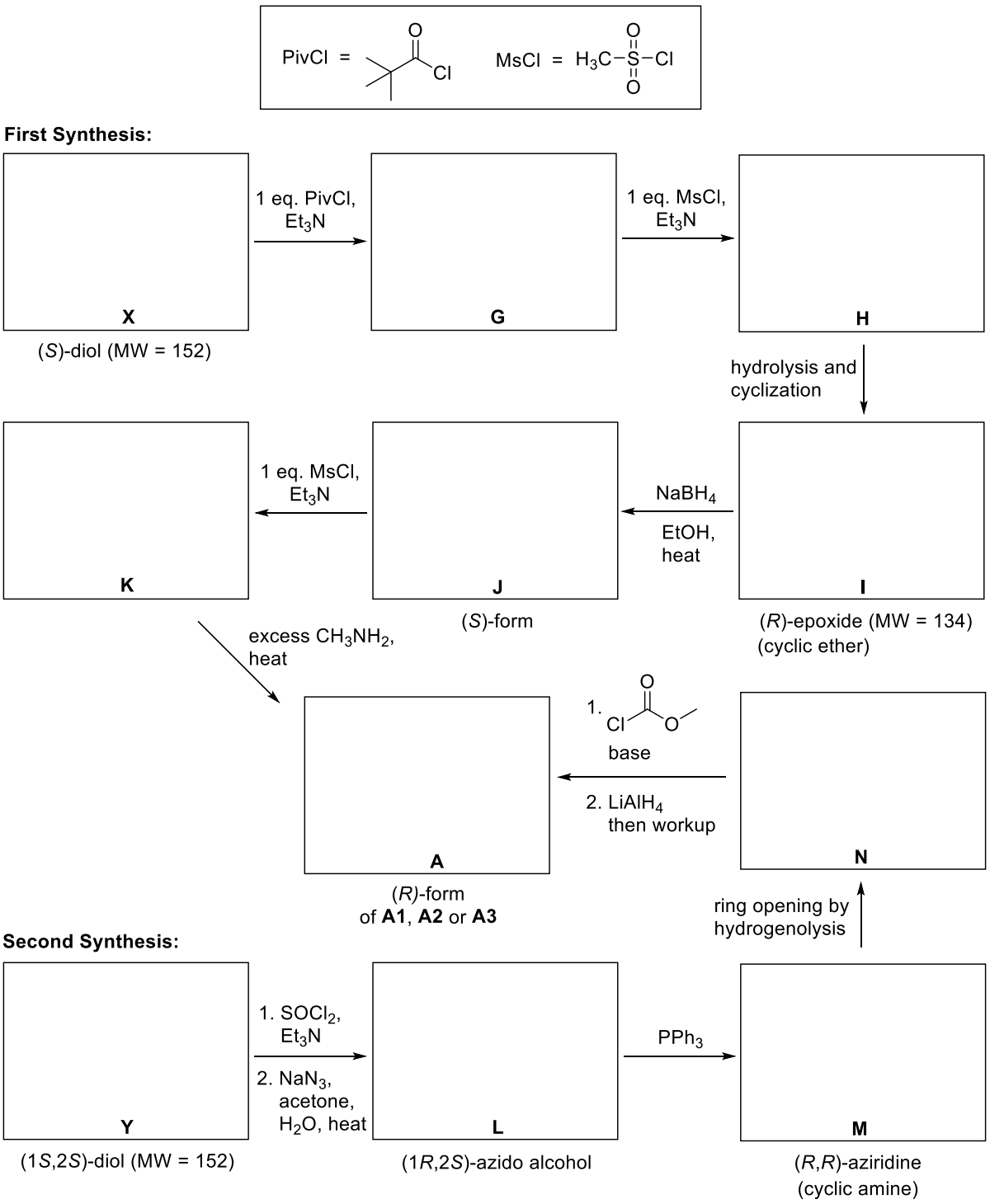
A1	A2	A3

9-A2) One of the structural 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. **DRAW** the structures of compounds **B-F** including the correct structural isomer of **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**.

DRAW the structures of compounds **G**-**N**, **X**, **Y** and the (*R*)-form of compound **A**. You must **show correct stereochemistry** of all compounds for full credit.



Student Code

Problem 10

7% of the total

Problem 10 (6%)	A	B		Total
	A1	B1	B2	
Total	20.5	4	5.5	30
Score				

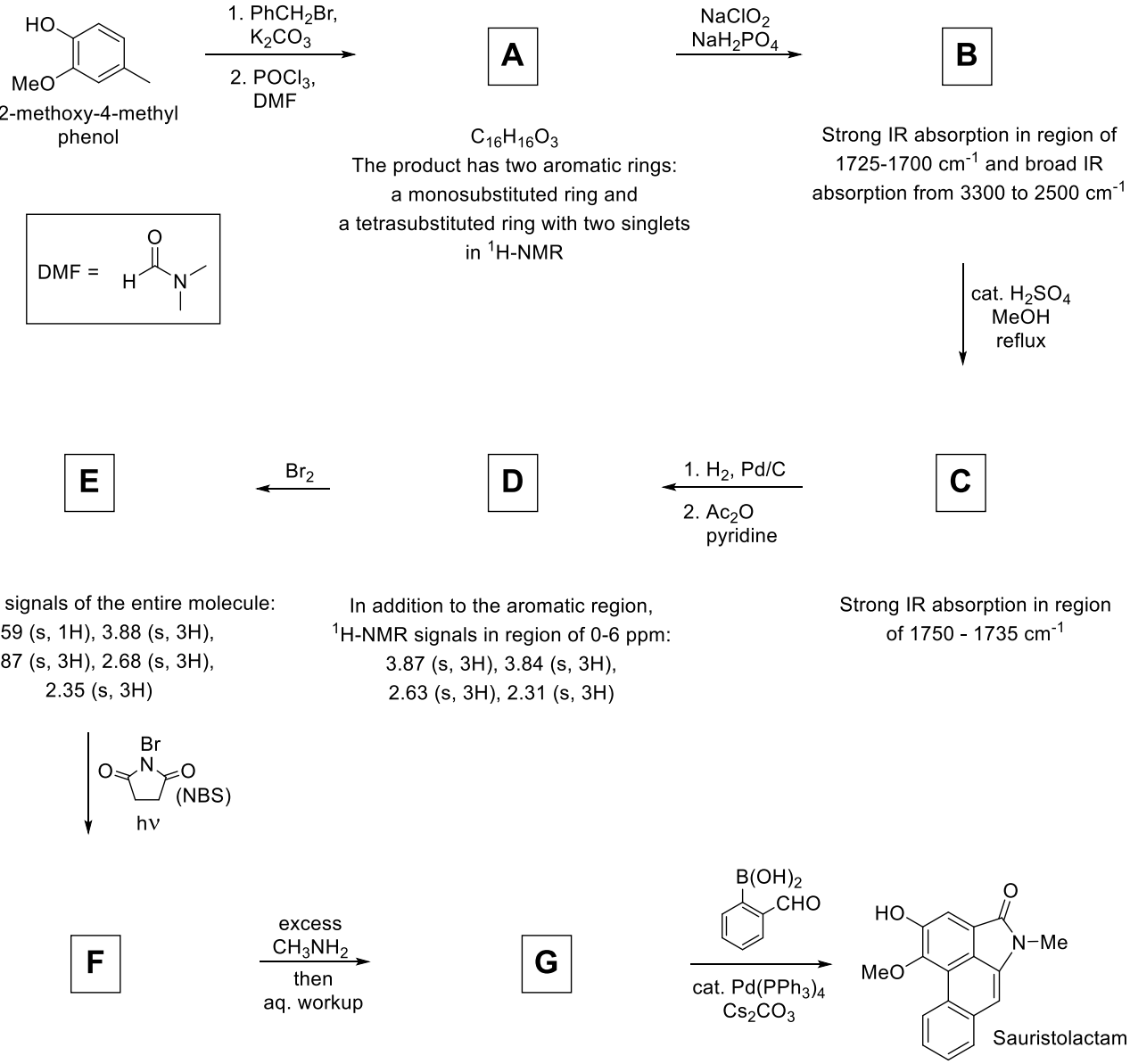
Problem10: Total Synthesis of Alkaloids

Alkaloids are a class of nitrogen-containing natural products. Their structural complexity and potent biological activities have drawn much attention. 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 shown. (^{1}H-NMR spectra were recorded in $CDCl_3$ at 300 MHz.)

10-A1) DRAW the structures of compounds **A-G** depicted in the following reaction sequence on the answer sheet on the next page.

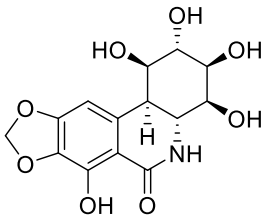


Structures of compounds **A**-**G**.

A	**B**
C	**D**
E	**F**
G	

Part B

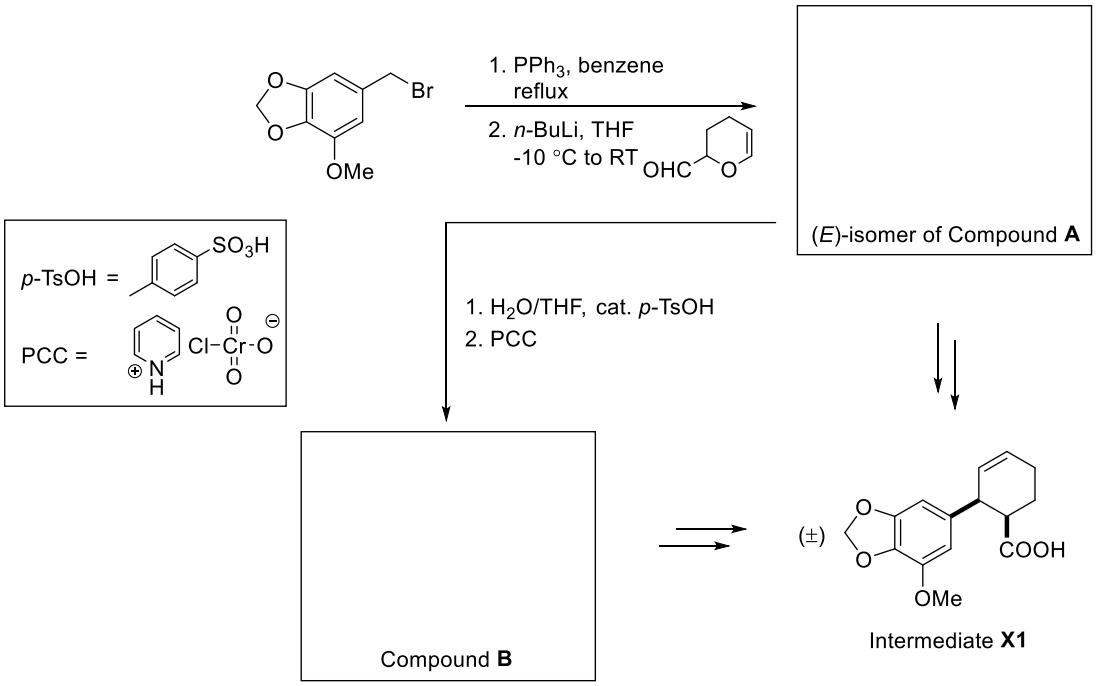
Pancratistatin, isolated from a native Hawaiian plant, spider lily, exhibits potent *in vitro* and *in vivo* inhibitory activity of cancer cell growth in addition to its excellent antiviral activity.



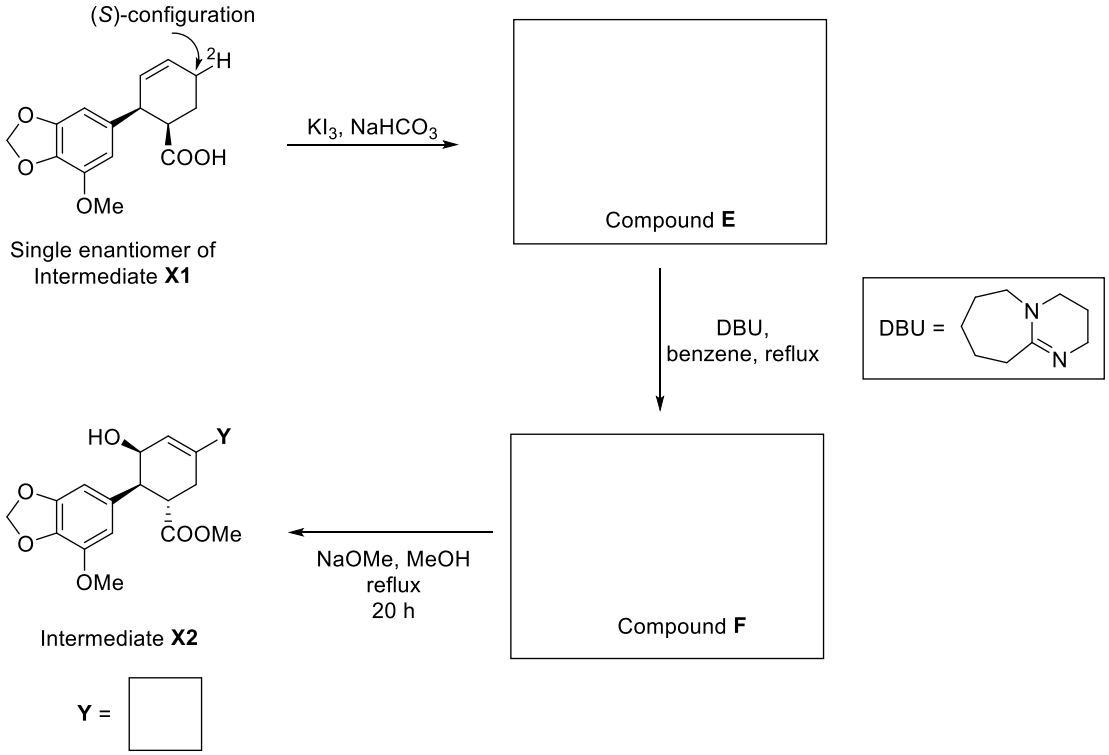
Pancratistatin

Pancratistatin can be synthesized via intermediates **X1** and **X2**. The synthesis of these intermediates are shown in the following reaction 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 the configuration as indicated below, **PROPOSE** the three-dimensional chair structure of compound **E** and the structure of compound **F** with stereochemistry. **ANSWER** whether or not **Y** is a proton (^{1}H) or a deuterium (^{2}H) in intermediate **X2**.



Student Code

Problem 11

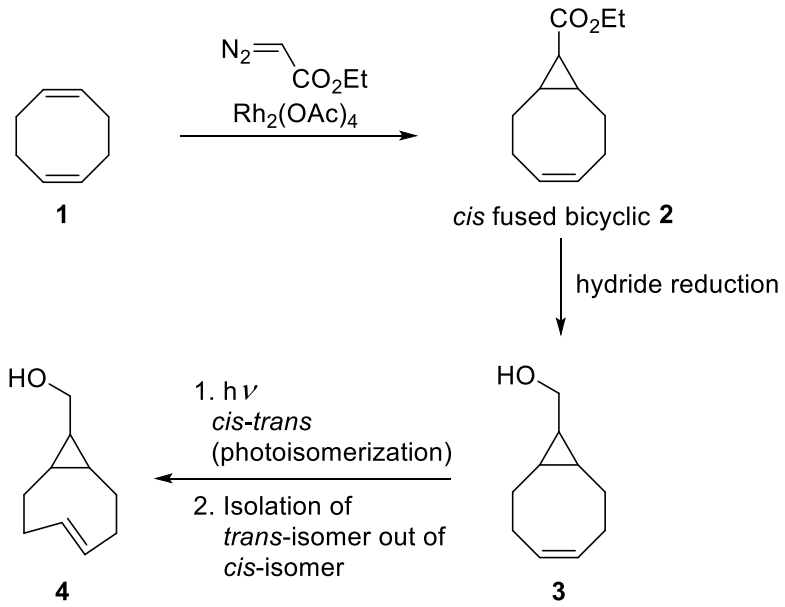
2% of the total

Problem 11	A		Total
	A1	A2	
Total	10	2	12
Score			

Problem 11: Twist & Chirality

trans-Cyclooctene is a chiral molecule with a high barrier for racemization. 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. This process is non-stereospecific and the synthetic scheme is shown below:



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 absolute configurations.

Possible stereoisomers of compound 3:

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

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

Now, assuming there is more than one stereoisomer, is it possible to separate the obtained stereoisomers of compound **4** by achiral chromatography? **MARK** "✓" yes or no.

○ Yes ○ No