46th International Chemistry Olympiad

July 23, 2014

Hanoi, Vietnam

PRACTICAL EXAMINATION

46th IChO
HANOI, VIETNAM 2014

Country:	
Name as in passport:	
Student Code:	
Language:	

This booklet contains 25523 characters

Chemistry: The flavor of life

GENERAL INTRODUCTION

Safety

- **Safety** is the most important issue in the laboratory. You are expected to follow the safety rules given in the IChO regulations. **Safety glasses** and **lab coats** must be worn in laboratory **ALL TIMES**.
- If you behave in an unsafe manner, you will receive **one warning** before you are asked to leave the laboratory. If required to leave due to a second warning, you will receive a score of zero for the rest practical examination.
- **Eating, drinking, or smoking** in the laboratory or **tasting** a chemical **is strictly forbidden**.
- Pipetting by mouth is strictly forbidden.
- Use the labeled **waste containers** near you for disposal of liquids and solids. A waste container (plastic can) is also available on each bench for organic and inorganic waste. Discard used glass capillaries into a solid trash.
- In case of emergency, follow the instructions given by the lab assistants.

Examination Procedures

- This practical examination has **28 pages** for **3** practical problems. Periodic Table of Elements is at the end of this booklet. Do not attempt to separate the sheets.
- You have **5 hours** to complete **practical problems 1, 2, and 3**. You have **30 min** to read through the problems before the **START command** is given.
- **DO NOT** begin working on the tasks until the **START command** is given.
- When the **STOP command** is given, you must **stop** your work on the tasks **immediately. A delay in doing so may lead to your disqualification from the examination.**
- After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following items should be **left behind**:
  - The practical examination booklet (this booklet),
  - Your chosen TLC plates in Petri dish with your student code (Problem 2).
- **Do not leave the laboratory** until you are instructed to do so by the lab assistants.
- You may need to reuse some glassware during the examination. If this is the case, clean it carefully in the sink closest to you.
- **Replacement of chemicals and laboratory ware** will be provided if necessary. Other than the first, for which you will be pardoned, each such incident will result in the **loss of 1 point** from your 40 practical points. Refilling of wash-bottle water is permitted with no loss of points.
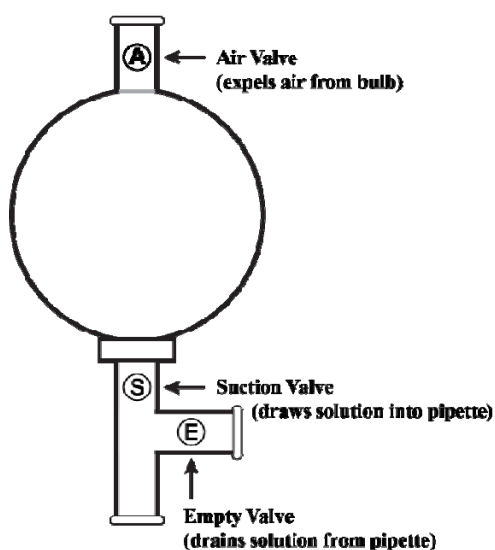
Notes

- Use only the pen provided for **filling in the answer boxes**. You may also use the calculator and the ruler provided. Do not use the mechanical pencil for filling in the **answer boxes**.
- All results must be written in the appropriate areas with the working shown. Results written elsewhere will not be graded. If you need to do **rough calculations, *etc.*,** use the

draft papers or the back of the sheets. All answers on the draft papers or the back of the sheets **will NOT be graded**.

- You should take care to report answers to an appropriate number of significant figures and give the appropriate unit.
- Contact a supervisor near you if you need a refreshment/toilet break.
- **Read the whole description of the problems** before you begin
- An official English version of this examination is available upon request if you require clarification.

Attention: Pipetting by mouth is strictly forbidden. Student was provided a pipette bulb. Make sure that you properly use the pipette bulb shown in Figure below. Description of three-way pipette bulb. An adapter is provided for larger pipettes.	**Instructions for using the thermometer** 1. Press the **[ON/OFF]** button to display the temperature reading in Celsius. 2. Insert the stainless steel probe (at least 5 cm) in the solution to be measured. 3. Wait for display to stabilize (display value is unchanged and stable for 3 seconds) and read the temperature on the display. 4. Press the **[ON/OFF]** button again to turn the thermometer off, then rinse the stainless steel probe with distilled water.

Chemistry: The flavor of life

List of chemicals

The concentration indicated on the label is approximate. The exact values are indicated in the table.

Chemical/Reagent	Quantity	Placed in	Labeled	Safety
Practical Problem 1				
0.100 M KI solution	120 mL	Glass bottle	0.1 M KI	H320
Solution #A1 contains KI, $Na_2S_2O_3$, and starch indicator in distilled water	40 mL	Glass bottle	Solution #**A1**	H314, H302, H315, H319
Solution #B1 contains $Fe(NO_3)_3$, HNO_3 in distilled water	40 mL	Glass bottle	Solution #**B1**	H314, H315, H319, H335
Solution #A2-1 contains 5.883 $\times10^{-4}$ M $Na_2S_2O_3$, KNO_3, and starch indicator in distilled water	360 mL	Glass bottle	Solution #**A2-1**	H314 H272
Solution #B2 contains 0.1020 M $Fe(NO_3)_3$ and HNO_3 in distilled water.	100 mL	Glass bottle	Solution #**B2**	H314, H272, H315, H319
Distilled water	1 L	Glass bottle	H_2O (Practical Problem 1)	
Practical Problem 2				
Artemisinin	1.000 g	Small bottle	Artemisinin	
Sodium borohydride, $NaBH_4$	0.53 g	Small bottle	$NaBH_4$	H301-H311
CH_3OH	20 mL	Glass bottle	Methanol	H225, H301
n-Hexane	30 mL	Bottle	*n*-Hexane	H225
cerium staining reagent for TLC	3-5 mL	Bottle	Ceri reagent	
CH_3COOH	1 mL	1.5 mL vial	Acetic Acid	H226, H314
Ethyl acetate	5 mL	Glass bottle	Ethyl acetate	
Bag of NaCl for salt bath	0.5 kg	Ice bath	NaCl bag	
$CaCl_2$ in drying tube	5-10 g	Tube	$CaCl_2$	H319
Practical Problem 3				
~ 30 wt% H_2SO_4, solution in water	40 mL	Bottle	~30 wt% H_2SO_4	H314
1.00×10^{-2}M $KMnO_4$, aqueous solution	50 mL	Bottle	~0.01 M $KMnO_4$,	H272, H302,
2.00×10^{-3}M EDTA, aqueous solution	40 mL	Bottle	2.00×10^{-3} M EDTA	H319
pH = 9-10 Buffer aqueous Solution, $NH_4Cl + NH_3$	40 mL	Bottle	*pH* = 9-10 Buffer Solution	H302 , H319
~20 wt% NaOH, aqueous solution	20 mL	Plastic bottle	~20 wt% NaOH,	H314
~3 M H_3PO_4, solution in water	15 mL	Bottle	~3 M H_3PO_4	H314
Indicator: ETOO, solid in KCl	*ca.* 0.5 g	Plastic bottle	ETOO	H301

List of Glassware and Equipments

Problem	Item on every working place	Quantity
Practical Problems 1-3	Hotplate stirrer	1
	Magnetic stirring bar **(seek in Kit #1)**	1
	Plastic wash bottle filled with distilled water (refill if necessary from the 1 L glass bottle of distilled water provided)	1
	1-L glass beaker for inorganic waste liquid	1
	250-mL conical flask for organic waste liquid	1

	Pipette rack with:
	    1-mL graduated pipette
	    5-mL graduated pipette (One for Problem 1; another labeled 'MeOH' for Problem 2)
	    10-mL graduated pipette
	    10-mL volumetric pipette
	    25-mL graduated pipette
	    Pasteur pipette and bulb
	    Glass spatula spoon
	    Cleaning brush
	    Large glass stirring rod
	    Glass funnel
		1
		1
		2
		
		1
		1
		1
		2
		2
		1
		1
		1

	Bag of paper towels	1
	Goggles	1
	Digital thermometer	1
	Three-way pipette bulb with a little rubber adapter for bigger pipettes	1
	Ceramic Büchner funnel with fitted rubber bung	1
	Büchner flask	1
	Pair of rubber gloves	1
	One cotton glove	1
KIT # 1	**Practical Problem 1 (KIT # 1)**	
	Digital stop watch	1
	Insulating plate for the hotplate stirrer labeled **I.P.**	1
	100-mL glass beaker	6
KIT # 2	**Practical Problem 2 (KIT # 2)**	
	5-mL graduated measuring cylinder	1
	50-mL graduated measuring cylinder	2
	100-mL two-neck round bottom flask with plastic stopper (in ice bath)	1
	100-mL conical (Erlenmeyer) flask	1
	Hair dryer	1
	Petri dish with cover containing 1 TLC plate, 2 capillaries in paper holder	1
	Plastic pot for ice bath	1
	Stand & clamp	1
	TLC developing chamber with glass lid	1

	Tweezers	2
	Metal spatula	1
	Very small test tubes for TLC in container	2
	Zipper store bag (containing cotton wool, round filter paper, watch glass for Problem 2 labeled with WHITE student code)	1
	Empty Petri dish with cover	1
KIT # 3	**Practical Problem 3 (KIT # 3)**	
	50-mL glass beaker (for transferring EDTA and $KMnO_4$ solutions to burettes)	2
	25-mL burette with BLUE graduation marks	1
	25-mL burette with BROWN graduation marks	1
	250 mL glass beaker	2
	250 mL conical flask (Erlenmeyer flask)	2
	100 mL volumetric flask with stopper	2
	10 mL glass graduated measuring cylinder	1
	100 mL glass graduated measuring cylinder	1
	Burette stand & clamp	1
	Reel of pH paper	1
	Zipper store bag (containing a large round filter paper for the glass funnel)	1
	Items on the tables for the common use:	
	Electronic balance with 0.1-mg resolution (6-8 students/each)	

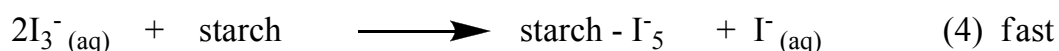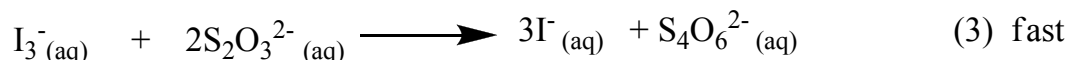| Replacement or extra chemicals	Lab assistant's signature	Student's signature	Penalty
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

**Attention: You MUST do the experiments in the order
Problem 1, 2 and then 3
(this is in order to control
the temperature of the magnetic stirrer properly)**.

PRACTICAL EXAMINATION

Practical Problem 1 14 % of the total	Code:		Question	1	2	3	4	5	6	Total
	Examiner		Mark	2	4	50	2	2	10	**70**
			Grade							

<u>Practical Problem 1</u>. The oxidation of iodide by iron(III) ions – a kinetic study based on the thiosulfate clock reaction

Clock reactions are commonly used as demonstrations by chemical educators owing to their visual appeal. Oxidation of iodide by iron(III) ions in a weakly acidic medium is a reaction that can be transformed into a clock reaction. In the presence of thiosulfate and starch, chemical changes in this clock reaction can be presented by the following equations:

$$Fe^{3+}_{(aq)} + S_2O_3^{2-}_{(aq)} \rightleftharpoons [Fe(S_2O_3)]^+_{(aq)} \qquad (1) \ \text{fast}$$

$$2Fe^{3+}_{(aq)} + 3I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_3^-_{(aq)} \qquad (2) \ \text{slow}$$

$$I_3^-_{(aq)} + 2S_2O_3^{2-}_{(aq)} \longrightarrow 3I^-_{(aq)} + S_4O_6^{2-}_{(aq)} \qquad (3) \ \text{fast}$$

$$2I_3^-_{(aq)} + \text{starch} \longrightarrow \text{starch - } I_5^- + I^-_{(aq)} \qquad (4) \ \text{fast}$$

Reaction **(1)** is a fast reversible equilibrium which occurs in the reaction mixture giving a reservoir of iron(III) and thiosulfate ions. After being produced in reaction **(2)**, iodine in the form of triiodide ion (I_3^-), is immediately consumed by thiosulfate in reaction **(3)**. Therefore, no iodine accumulates in the presence of thiosulfate. When thiosulfate is totally depleted, the triiodide ion accumulates and it may be detected by use of starch indicator according to reaction **(4)**.

The kinetics of reaction **(2)** is easily investigated using the initial rates method. One has to measure the time elapsed between mixing the two solutions and the sudden color change.

For the oxidation of iodide by iron(III) ions (reaction **2**), the reaction rate can be defined as:

$$v = -\frac{d\left[Fe^{3+}\right]}{dt} \qquad (5)$$

The initial reaction rate can then be approximated by:

$$v_0 \approx -\frac{\Delta\left[Fe^{3+}\right]}{\Delta t} \tag{6}$$

with $\Delta[Fe^{3+}]$ being the change in the concentration of iron(III) ions in the initial period of the reaction. If Δt is the time measured, then $\Delta[Fe^{3+}]$ is the change in iron(III) ion concentration from the moment of mixing to the moment of complete thiosulfate consumption (assume that the reaction rate does not depend on thiosulfate concentration). Therefore, from the reactions' stoichiometry it follows:

$$-\Delta\left[Fe^{3+}\right] = \left[S_2O_3^{2-}\right]_0 \tag{7}$$

and consequently:

$$v_0 \approx \frac{\left[S_2O_3^{2-}\right]_0}{\Delta t} \tag{8}$$

The initial thiosulfate concentration is constant and significantly lower than that of iron(III) and iodide ions. The above expression enables us to determine the initial reaction rate by measuring the time required for the sudden color change to take place, Δt.

The rate of reaction is first order with respect to $[Fe^{3+}]$, and you will determine the order with respect to $[I^-]$. This means the initial reaction rate of reaction can be expressed as:

$$v_0 = k[Fe^{3+}]_0[I^-]_0^y \tag{9}$$

where k is the rate constant and y is the order with respect to $[I^-]$.

We assume that the reaction rate does not depend on the thiosulfate concentration, and that the reaction between Fe^{3+} and $S_2O_3^{2-}$ is negligible. You have to observe carefully the color changes during the clock reaction and to determine the reaction order with respect to $[I^-]$, and the rate constant of clock reaction.

Experimental Set-up

Instructions for using the digital timer (stopwatch)

1. Press the **[MODE]** button until the **00:00:00** icon is displayed.
2. To begin timing, press the **[START/STOP]** button.
3. To stop timing, press the **[START/STOP]** button again.
4. To clear the display, press the **[SPLIT/RESET]** button.

PRECAUTIONS

➢   To minimize fluctuations in temperature only use the distilled water on your bench (in the wash bottle and in the glass 1 L bottle).

➢   The heating function of the heating magnetic stirrer must be **TURNED OFF** (as shown in Figure 1 below) and be sure that the stirrer plate is not hot before starting your experiment. Put the insulating plate (labeled I.P.) on top of the stirrer plate for added insulation.

➢   Start the stopwatch as soon as the solutions #A and #B are mixed. Stop the stopwatch as soon as the solution suddenly turns dark blue.

➢   Magnetic stirrer bar (take it with the provided tweezers) and beakers should be washed and rinsed with distilled water and wiped dry with paper towel to reuse.

General Procedure

Solution **# A** (containing $Na_2S_2O_3$, KI, KNO_3 and starch) is first placed in the beaker and is stirred using the magnetic bar. The rate of stirring is set at level 8 as indicated in Figure 1. Solution **#B** (containing $Fe(NO_3)_3$ and HNO_3) is quickly added into solution **#A** and *the stopwatch is simultaneously started. The time is recorded at the moment the solution suddenly turns dark blue*. The temperature of the solution is recorded using the digital thermometer.
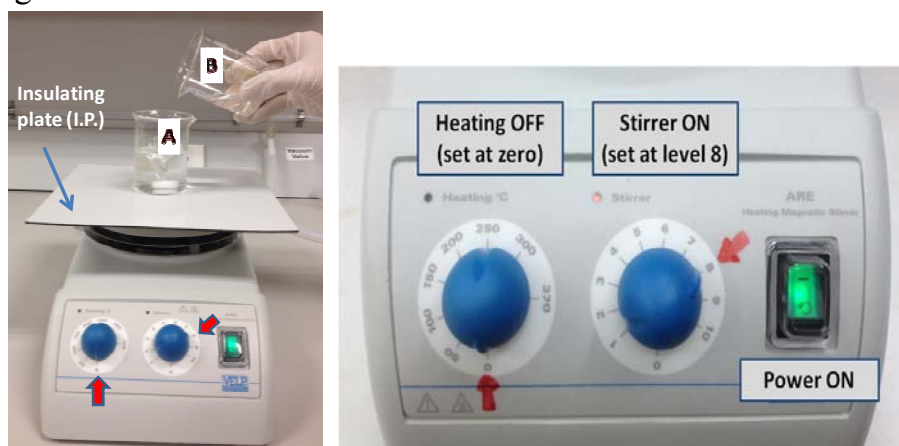

Figure 1. The apparatus employed for kinetic study of the clock reaction.

1. *Practice run to observe the color changes*

- There is no need to accurately measure the volumes used in this part – just use the marks on the beaker as a guide.
- Pour *ca.* 20 mL of solution # **A1** (*containing KI, $Na_2S_2O_3$, and starch in water*) to a 100-mL graduated beaker containing a magnetic stirrer bar. Place the beaker on top of the insulating plate on the magnetic stirrer.
- Pour *ca.* 20 mL of solution # **B1** (*containing $Fe(NO_3)_3$ and HNO_3 in water*) in another 100 mL graduated beaker.
- Quickly pour the solution # **B1** into solution # **A1** and start stopwatch simultaneously. Stop stopwatch when the color of the mixture changes. There is no need to record this time. Answer the following questions.

Task 1.1: **Write down the molecular formula of the limiting reactant for the given clock reaction.**

| |
| |

Task 1.2: **What are the ions or compounds responsible for the colors observed in this experiment? Tick the appropriate box.**

Color	Compound
Purple	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-
Dark blue	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-

2. Determination of the order with respect to [I⁻] (y), and the rate constant (k)

In this section, Δt is determined for different initial concentrations of KI according to the table below. The experiment is repeated as necessary for each concentration of KI.

Hint: Use 25 mL graduated pipette for solution #A2-1, 10 mL graduated pipette for KI, 5 mL graduated pipette for solution #B2, and one of the burettes for water (you will need to refill the burette from the wash bottle for each measurement).

- Prepare 55 mL of solution **# A2** in a 100 mL beaker containing a magnetic stirrer bar and place it on top of the insulating plate on the stirrer. Solution #**A2** contains solution #**A2-1**, KI, and distilled water (see the table below for the volume of each component).

- Add 5 mL of solution **# B2** in another 100 mL beaker.

Quickly pour prepared solution #**B2** into solution #**A2**. Determine the time (Δt) necessary for the color change by a stopwatch. The temperature of the solution is recorded.

***Task 1.3**: Record the time (Δt) for each run in the table below. (You DO NOT need to fill all three columns for the runs.) For each concentration of KI, record your accepted reaction time ($\Delta t_{accepted}$) and temperature. You will be only graded on your values of $\Delta t_{accepted}$ and $T_{accepted}$.*

| No | 55 mL of solution #A2 | | | Run 1 | | Run 2 | | Run 3 | | $\Delta t_{accepted}$ (s) | $T_{accepted}$ (°C) |
	#A2-1 (mL)	H₂O (mL)	0.100M KI (mL)	Δt (s)	T (°C)	Δt (s)	T (°C)	Δt (s)	T (°C)		
1	20.4	31.6	3.0								
2	20.4	30.1	4.5								
3	20.4	28.6	6.0								
4	20.4	27.4	7.2								
5	20.4	25.6	9.0								

> **When you are satisfied you have all the necessary data for Problem 1, before continuing further with the analysis, it is strongly recommended that you start the practical procedure for Problem 2 since there is a reaction time of one hour in that Problem.**

Task 1.4: **Fill in the table below and plot the results in the graph.**

   Hint: Make sure your data is graphed as large as possible in the provided space.

No.	1	2	3	4	5
$\ln([I^-]_0 / M)$	- 5.30	- 4.89	- 4.61	- 4.42	- 4.20
$\Delta t_{accepted}$ (s)					
$\ln(\Delta t_{accepted} / s)$					

$\ln(\Delta t_{accepted} \; / \; s)$

$\ln([I^-]_0 \; / \; M)$
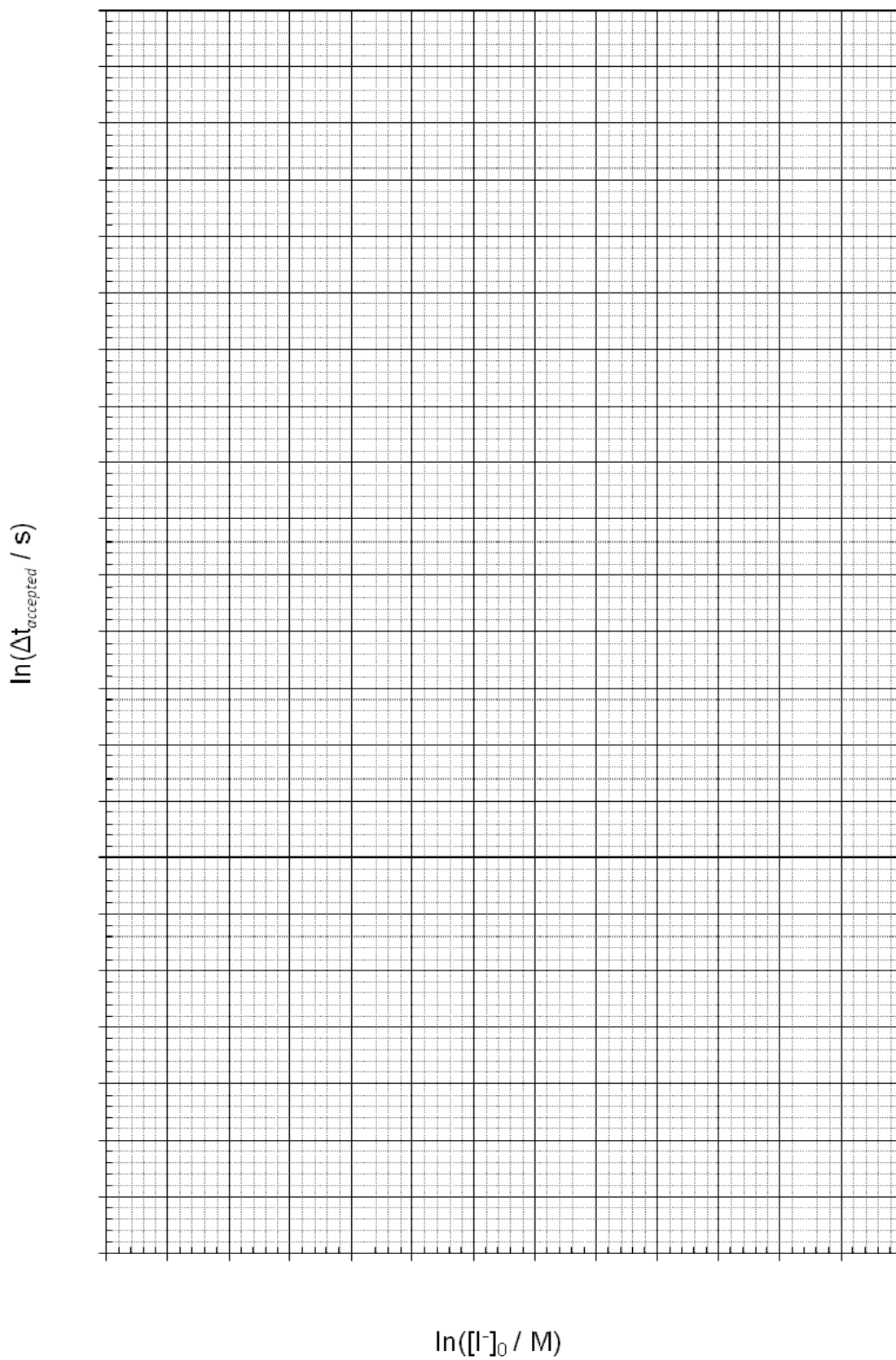
Task 1.5: *Draw the best fit line on your graph and use this to determine the order with respect to [I$^-$] (y).*

y = ...

Task 1.6: *Complete the table below and calculate k for each of the concentrations of iodide. Report your accepted value for the rate constant, giving the appropriate unit. Remember that the order with respect to [Fe^{3+}] is equal to one.*

No	$\Delta t_{accepted}$ (s)	$[Fe^{3+}]_0$ ($\times 10^{-3}$ M)	$[I^-]_0$ ($\times 10^{-3}$ M)	$[S_2O_3^{2-}]_0$ ($\times 10^{-3}$ M)	k
1			5.0		
2			7.5		
3			10.0		
4			12.0		
5			15.0		
$k_{accepted}$ = ...					

Practical Problem 2 13 % of the total	Code:		Task	1	2	3	4	5	Total
	Examiner		Mark	35	15	20	4	2	**76**
			Grade						

Practical Problem 2. Synthesis of a derivative of Artemisinin

Artemisinin (also known as Quinghaosu) is an antimalarial drug isolated from the yellow flower herb *Artemisia annua* L., in Vietnam. This drug is highly efficacious against the chloroquine-resistant *Plasmodium falciparum*. However, artemisinin has a poor solubility in both oil and water so that one needs to prepare its new derivatives to improve the applicability of this drug. The reduction of artemisinin is an attractive method to synthesize new derivatives of artemisinin as shown in Scheme 1.

artemisinin
Molecular Weight: 282.3
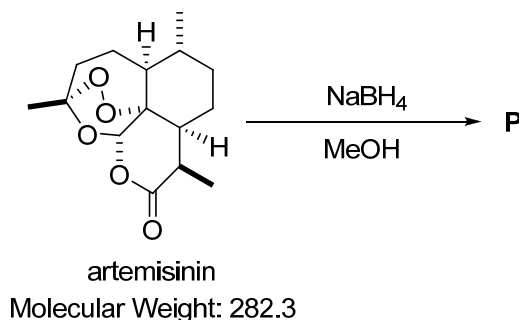
Scheme 1

In this practical exam you are going to reduce artemisinin to product **P** and check its purity using Thin-Layer Chromatography (TLC).

Experimental Set-up

- The experimental set-up is shown in Figure 2.1.

- By moving the finger clamp, you can adjust the position of the two-neck round-bottom flask.
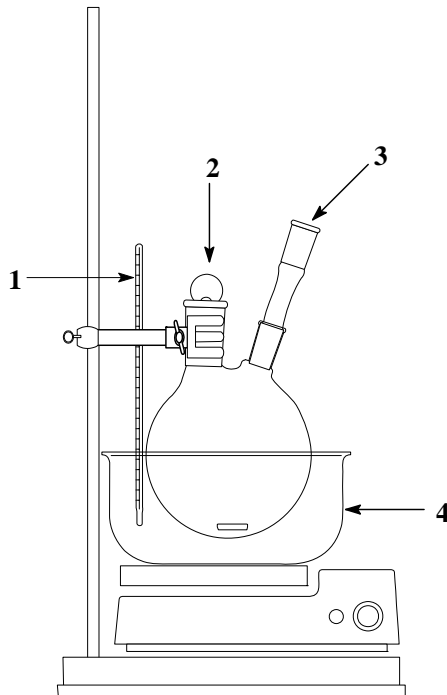
1: Digital thermometer; 2: Plastic Stopper; 3: CaCl₂ drying tube; 4: Ice Bath

Figure 2.1. Reaction system for Problem 2

Procedure

Step 1. Synthesis of a Derivative of Artemisinin

1. Prepare an ice bath with a temperature between –20 and –15 ^{o}C by mixing ice and sodium chloride in the plastic pot (approximate ratio of NaCl : crushed ice = 1 scoop : 3 scoops). Use the digital thermometer to monitor the temperature. Place the bath on the magnetic stirrer. Put a layer of three tissues between the bath and the stirrer.

2. Connect the CaCl₂ drying tube to the small neck of the round-bottom flask and close the other neck with the plastic stopper.

3. Place a magnetic stirring bar into the dry round-bottom flask and set up the reaction system onto the clamp-stand so that the system is immersed in the ice bath. Monitor the temperature using the digital thermometer.

4. *Setting aside a tiny amount (ca. 2 mg) of artemisinin for TLC analysis*, open the stopper and add the 1 gram of artemisinin through the bigger neck.

5. Use the glass funnel to add 15 mL of methanol (measured using the 50-mL graduated cylinder). Close the stopper and turn on the magnetic stirrer. (*Set the magnetic stirrer to <u>level 4</u>*). Start the stopwatch to keep track of the time.

6. After *ca.* 5 min stirring, open the stopper and add carefully 0.53 g of NaBH₄ in small portions over 15 min using a spatula. Close the stopper in between addition. (*Caution: Adding NaBH₄ rapidly causes side-reactions and overflowing*). Keep stirring for 50 min. Maintain the temperature of the ice bath below –5 ^{o}C; remove

some of the liquid and add more NaCl-crushed ice mixture if necessary. Cool the vial containing the 1 mL of acetic acid in the ice bath.

During this waiting time, you are advised to finish calculations from Problem 1, answer the questions below, and prepare further experimental steps.

7. Prepare 50 mL of ice-cold distilled water *(cooled in the ice bath)* in the 100 mL-conical flask. Measure *ca.* 20-22 mL *n*-hexane in the 50 mL measuring cylinder and cool it in the ice bath. After the reaction is complete, keep the reaction flask in the ice bath below 0 $^{\circ}$C. Remove the $CaCl_2$ tube, open the stopper, and add gradually *ca.* 0.5 mL of the cold acetic acid from the vial into the reaction flask until the pH is between 6 and 7. (Use the glass rod to spot the reaction mixture on to the pH paper.) With stirring, slowly add the 50 mL of ice cold water over 2 min. A white solid precipitates in the reaction flask.

8. Assemble the vacuum filtration apparatus. Put a filter paper onto the Büchner funnel, wet the filter paper with distilled water and open the vacuum valve. Transfer the reaction mixture on to the filter, and remove the stirring bar from the reaction flask using the spatula. Wash the product three times with portions of 10 mL ice-cold water *(cooled in the ice bath)*. Wash the product two times with portions of 10 mL ice-cold *n*-hexane *(cooled in the ice bath).* Continue to use the pump to dry the solid on the filter. After *ca.* 5 min, carefully transfer the dried powder on to the watch glass labeled with your code and put into the labeled Petri dish. **Turn off the vacuum valve when you do not use it!** *Note: Your sample will be collected, dried and weighed later by the lab assistant.*

Task 2.1 – the recording of your yield –will be performed after the exam by the lab assistants.

Step 2. TLC Analysis of the product

1. Check your TLC plate before use. Unused damaged plates will be replaced upon request without penalty. Use the pencil to draw the start front line, and the line where the solvent front will be run to **exactly as shown in Figure 2.2**. Write your student code on the top of the TLC plate in pencil.
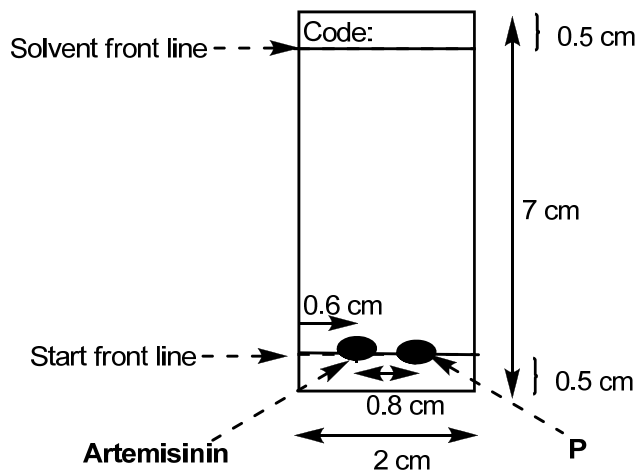
Figure 2.2. Instruction of TLC plate preparation

2. Dissolve *ca.* 1 mg of artemisinin *(a spatula tip)* in *ca.* 0.5 mL of methanol in the labeled very small test tube (use the labeled 5 mL graduated pipette). Dissolve *ca.* 1 mg of the product in *ca.* 1 mL of methanol in the labeled test tube.

3. Spot the artemisinin solution and the product solution on the TLC plate using two different glass capillary spotters so the finished plate is as shown in Figure 2.2.

4. Prepare the TLC developing chamber. Use the 5 mL graduated cylinder to make 5 mL of a mixture of *n*-hexane/ethyl acetate (7/3, v/v) as the solvent system. Pour the mixture of *n*-hexane/ethyl acetate into the chamber *(Note: The solvent level should not reach the spots on the plate if prepared as shown).* Cover and swirl the chamber and allow it to stand for 2 min.

Calculate $R_f (A) = \dfrac{a}{b}$
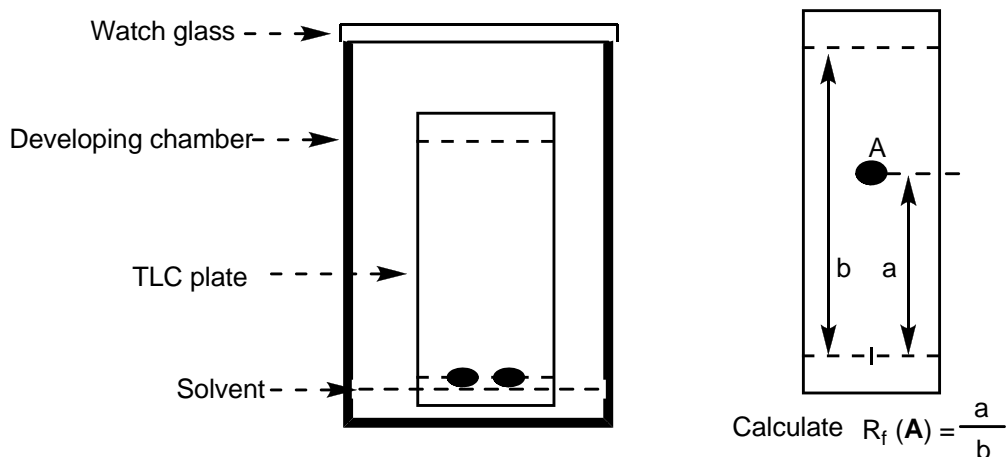
Figure 2.3. A TLC plate placed in the TLC developing chamber and instruction for R_f calculation of compound **A**

5. Insert the TLC plate upright into the TLC developing chamber. Wait until the solvent system reaches the pre-drawn solvent front line. (*Note: You are advised to work on some question below while you wait for the TLC to run.*)

6. When the solvent front reaches the line, remove the TLC plate using the tweezers and then dry the solvent using the hair dryer set at <u>level 1</u>.

7. Dip the piece of cotton wool into the cerium staining reagent, *taking care not to let the tweezers come into contact with the solution since the metal stains the plate*. Carefully apply the stain to the whole TLC plate.

8. Heat the TLC plate using the hair dryer set at <u>level 2</u> (***Attention: Do NOT set the hair dryer to COLD***) until the blue spots of artemisinin and the product appear on the TLC plate.

9. Ask the lab assistant to take a photo of your final TLC plate together with your student code.

10. Circle all the visualized spots and calculate the R_f values of both artemisinin and the product (*See instruction in Fig. 2.3*). Store your TLC plate in the Petri dish.

Task 2.2: Fill the values of R_f in Table below.

$R_{f, Artemisinin}$	$R_{f, Product}$	$R_{f\ Artemisinin}/R_{f\ Product}$
----------------------	-------------------------	-------------------------

Task 2.3: Check the <u>total number</u> of developed spots on the TLC plate:

1 ☐	2 ☐	3 ☐	4 ☐	5 ☐

Step 3. Identifying the reaction product P

The reduction of artemisinin leads to the formation of two stereoisomers (**P**). Comparing the ^{1}H-NMR spectrum (in CDCl$_3$) of one of these isomers with the spectrum of artemisinin shows an extra signal at $\delta_H = 5.29$ ppm as a doublet, and also an extra signal as a broad singlet at $\delta_H = 2.82$ ppm.

artemisinin
C$_{15}$H$_{22}$O$_5$

$\xrightarrow[\text{MeOH}]{\text{NaBH}_4}$

P
C$_{15}$H$_{24}$O$_5$
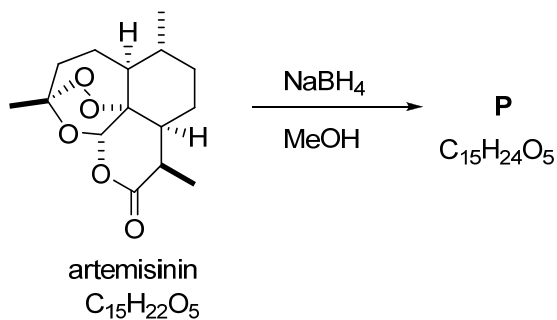
Task 2.4: Suggest structure for P. (*You do not need to draw the stereochemistry of the compounds*).

P
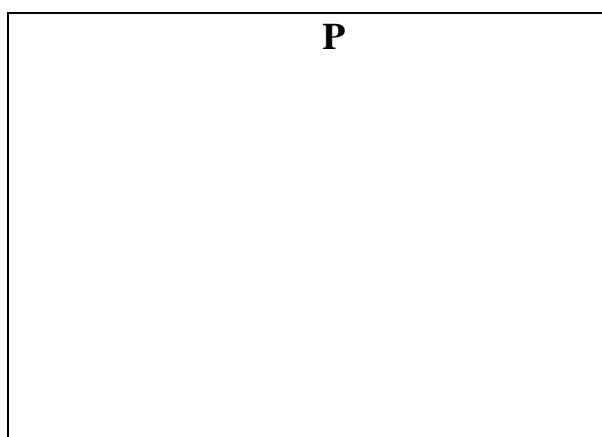
Task 2.5: P is mixture of two stereoisomers. What is their stereochemical relationship? Check the appropriate box below.

Z/E Isomers	Enantiomers	Diastereomers	Constitutional Isomers
☐	☐	☐	☐

Practical Problem 3 13 % of the total	Code:		Task	1	2	3	4	5	6	7	8	9	10	Total
	Examiner		Mark	0	25	2	25	3	4	3	2	5	2	71
			Grade											

Practical Problem 3. Analysis of a hydrated zinc iron(II) oxalate double salt

Zinc iron(II) oxalate double salt is a common precursor in the synthesis of zinc ferrite which is widely used in many types of electronic devices due to its interesting magnetic properties. However, such double salts may exist with different compositions and different amount of water depending on how the sample was synthesized.

You will analyze a pure sample of hydrated zinc iron(II) oxalate double salt (**Z**) in order to determine its empirical formula.

Procedure

The concentration of the standard KMnO₄ is posted on the lab walls.

Bring a clean 250 mL beaker to the lab assistant who will be waiting by the balance. You will receive a pure sample of **Z** for analysis. Accurately weigh between 0.7-0.8 g of the pure sample **Z** onto the weighing paper (*m*, grams). This should then be immediately quantitatively transferred into your 250 mL beaker for analysis, and its mass recorded in table below.

Task 3.1: Record the mass of the sample of pure Z taken.

Mass of sample, *m* (gram)	Lab assistant's signature
------------------	---------------------

Analysis of Z

- Using the 100 mL graduated measuring cylinder, measure *ca.* 30 mL of 30 wt% H₂SO₄ solution and add it into the 250-mL beaker containing your accurately weighed pure sample of **Z**. To speed up the dissolving of your sample you may use

the hotplate stirrer to warm up the mixture, **but be careful not to boil** it. *You should not use the digital thermometer as the acid may damage it*. After the solid has dissolved, remove the beaker from the hotplate stirrer and cool it to close to room temperature. After the solution has cooled, quantitatively transfer it into the 100 mL volumetric flask. Add distilled water up to the 100 mL–mark. We will now call this solution **C.**

- Use an appropriately labeled beaker to transfer the standardized **KMnO₄** solution into the burette graduated with **brown** marks.

- Use another appropriately labeled beaker to transfer the standardize **EDTA** solution into the burette graduated with **blue** marks.

Titration with KMnO$_4$

a) Using the 5 mL graduated pipette add 5.00 mL of the solution **C** into a 250 mL conical flask.

b) To this conical flask add about 2 mL of 30 wt% H_2SO_4 solution, about 3 mL of 3.0 M H_3PO_4 solution, and about 10 mL of distilled water. Heat the mixture on the hot plate stirrer until hot, **but be careful not to boil** it.

c) Titrate the hot solution with the standardized $KMnO_4$ solution, recording your burette readings in the table below. At the end point of the titration, the pink color of the solution appears. Repeat the titration as desired and report your accepted volume of $KMnO_4$ solution consumed (V_1 mL) in the table.

Task 3.2: Record volumes of standardized KMnO$_4$ solution consumed

(You DO NOT need to fill in the entire table)

	Titration No			
	1	**2**	**3**	**4**
Initial reading of the burette of $KMnO_4$, mL				
Final reading of the burette of $KMnO_4$, mL				
Consumed volume of $KMnO_4$, mL				

Accepted volume, V_1 = _____ mL

Task 3.3: Can aqueous HCl or HNO$_3$ be used instead of H$_2$SO$_4$ for the dissolving of sample Z and the subsequent analyses?

HCl	**YES** ☐	**NO** ☐
HNO$_3$	**YES** ☐	**NO** ☐

Titration with EDTA

- Clean both the 250 mL beakers ready for the next part of the experiment. Pipette 10.00 mL of solution **C** into a 250 mL beaker. Heat and stir the solution on the hotplate stirrer, **but be careful not to boil** it. Add *ca.* 15 mL of 20 wt% NaOH solution to the beaker and keep it on the hotplate for *ca. 3-5* min in order to complete the precipitation of iron hydroxide, and to convert all Zn^{2+} ions into the ionic complex [Zn(OH)$_4$]$^{2-}$.

- Using a glass funnel and the large quantitative filter paper, filter the hot suspension directly into the 250 mL conical flask. **From this point take care with the volumes as you will be preparing a standard solution of exactly 100 mL from the filtrate**. As it is filtering, prepare some warm distilled water in a 250 mL beaker (*ca.* 50 mL). Wash the precipitate on the filter paper (at least 5 times) with small portions (*ca.* 5 mL) of the warm distilled water. Cool the filtrate down and then quantitatively transfer it into the 100 mL volumetric flask via a glass funnel. Add distilled water to make up to the 100 mL mark. This will now be referred to as solution **D**.

- Pipette 10.00 mL of solution **D** into a 250 mL conical flask. Add *ca.*10 mL ammonia buffer solution (*pH* = 9 – 10) and a small quantity of the ETOO indicator using the glass spatula spoon. Mix well to obtain a purple solution. Titrate the solution with the standardized 2.00 × 10^{-3} M EDTA solution, recording your burette readings in table below. At the end point, the color of the solution turns blue. Repeat the titration as desired and report your accepted volume of EDTA solution consumed (V$_2$ mL) in the table.

Task 3.4: *Record the volumes of EDTA solution consumed*

(You DO NOT need to fill in the entire table)

	Titration No			
	1	**2**	**3**	**4**
Initial reading of the burette of EDTA, mL				
Final reading of the burette of EDTA, mL				
Consumed volume of EDTA, mL				

Accepted volume,V_2 = _____ **mL**

Determination of the empirical formula of Z

Task 3.5: *Calculate the number of moles of Zn^{2+}, $n_{Zn^{2+}}$, present in 100 mL of solution C.*

$n_{Zn^{2+}}$ (mol): ……………

Task 3.6: *Give the ionic equations for the reduction-oxidation reactions taking place in the titration with $KMnO_4$.*

__*Task 3.7:*__ *Calculate the number of moles of Fe^{2+}, $n_{Fe^{2+}}$, present in 100 mL of solution* __*C.*__ **[YOU WILL NEED THE PRECISE CONCENTRATION OF KMnO$_4$ POSTED ON THE WALLS IN YOUR LAB]**

V_1, mL = …………………………………….

$n_{Fe^{2+}}$ (mol): …………………………

__*Task 3.8:*__ *Calculate the number of moles of C$_2$O$_4^{2-}$ anion, $n_{C_2O_4^{2-}}$, in 100 mL of solution* __*C.*__

$n_{C_2O_4^{2-}}$ = ……………………………………..

Task 3.9: *Calculate the number of moles of water,* n_{H_2O} *, in the original sample of Z taken for analysis.*

Task 3.10*: Give the empirical formula of Z:*

46th International Chemistry Olympiad

46th International Chemistry Olympiad

July 25, 2014

Hanoi, Vietnam

THEORETICAL EXAMINATION

WITH ANSWER SHEETS GRADING

46th IChO

HANOI, VIETNAM 2014

Country:	
Name as in passport:	
Student Code:	
Language:	

Chemistry: The flavor of life

GENERAL INTRODUCTION

- You have **additional 15 minutes** to read the whole set.

- This booklet is composed of 9 problems. You have **5 hours to fulfill the problems.** Failure to stop after the STOP command may result in zero points for the current task.

- Write down answers <u>and calculations </u>within the designated boxes. Give your work where required.

- Use only the pen and calculator provided.

- The draft papers are provided. If you need more draft paper, use the back side of the paper. <u>Answers on the back side and the draft papers will NOT be marked.</u>

- There are **<u>52 pages</u>** in the booklet including the answer boxes, Cover Sheet and Periodic Table.

- The official English version is available on demand for clarification only.

- Need to go to the restroom – raise your hand. You will be guided there.

- **After the STOP signal** put your booklet in the envelope (do not seal), leave at your table. Do not leave the room without permission.

Good luck !

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HANOI, VIETNAM 2014

Chemistry: The flavor of life

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2

Physical Constants, Units, Formulas and Equations

Avogadro's constant	$N_A = 6.0221 \times 10^{23}$ mol^{-1}
Universal gas constant	$R = 8.3145$ J·K^{-1}·mol^{-1}
Speed of light	$c = 2.9979 \times 10^8$ m·s^{-1}
Planck's constant	$h = 6.6261 \times 10^{-34}$ J·s
Standard pressure	$p° = 1$ bar $= 10^5$ Pa
Atmospheric pressure	1 atm $= 1.01325 \times 10^5$ Pa $= 760$ mmHg
Zero of the Celsius scale	273.15 K
Mass of electron	$m_e = 9.1094 \times 10^{-31}$ kg

1 nanometer (nm) $= 10^{-9}$ m ; 1 angstrom (Å) $= 10^{-10}$ m

1 electron volt (eV) $= 1.6022 \times 10^{-19}$ J $= 96485$ J·mol^{-1}

Energy of a light quantum with wavelength λ	$E = hc / \lambda$
Energy of one mole of photons	$E_m = hcN_A / \lambda$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\dfrac{\Delta G°}{RT}\right)$
van't Hoff equation in integral form	$\ln\dfrac{K_2}{K_1} = \dfrac{\Delta H^0}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$
Relationship between internal energy, heat and work	$\Delta U = q + w$
Molar heat capacity at constant volume	$C_{v,m} = \left(\dfrac{dU}{dT}\right)_v$
Change in internal energy from T_1 to T_2 assuming constant $C_{v,m}$	$U(T_2)=U(T_1)+nC_{v,m}(T_2-T_1),$
Spin only formula relating number of unpaired electrons to effective magnetic moment	$\mu_{eff} = \sqrt{n(n+2)}$ B.M.

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Theoretical	Code:		Question	1	2	3	4	5	Total
Problem 1	**Examiner**		Mark	3	7	6	4	7	**27**
5.0 % of the total			**Grade**						

Problem 1. Particles in a box: polyenes

In quantum mechanics, the movement of π electrons along a neutral chain of conjugated carbon atoms may be modeled using the 'particle in a box' method. The energy of the π electrons is given by the following equation:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where n is the quantum number ($n = 1, 2, 3, \ldots$), h is Planck's constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2)\times 1.40$ Å (k being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength λ may promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength λ, to the number of double bonds k and constant B is as follows:

$$\lambda \text{ (nm)} = B \times \frac{(k+2)^2}{(2k+1)} \qquad \text{Equation 1}$$

1. Using this semi-empirical formula with $B = 65.01$ nm **calculate** the value of the wavelength λ (nm) for octatetraene ($CH_2 = CH - CH = CH - CH = CH - CH = CH_2$).

1. From the given semi-empirical formula, the wavelength λ (nm) is calculated as follows: $\lambda (nm) = 65.01 \times \dfrac{(k+2)^2}{(2k+1)}$ For octatetraene molecule, with $k = 4$; $\lambda = \textbf{260.0 nm}$	3 points

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2. <u>Derive</u> Equation 1 (an expression for the wavelength λ (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of k and the fundamental constants, and hence **<u>calculate</u>** theoretical value of the constant $B_{calc.}$.

---

2. The formula: $E = \dfrac{n^2 h^2}{8mL^2}$ (1)

ΔE is calculated as: $\Delta E = E_{LUMO} - E_{HOMO} = h\nu = \dfrac{hc}{\lambda}$ (2)

In which, λ and ν are wavelength and frequency for the corresponding photon respectively, k is the quantum number for the HOMO, which is equal to the number of double bonds. So, we have:

$\Delta E = \dfrac{h^2}{8mL^2}[(k+1)^2 - k^2] = \dfrac{hc}{\lambda} = \dfrac{h^2}{8mL^2}[2k+1]$ (3)

Replace $L = (k+2) \times 1.40$ Å into (3):

$\dfrac{hc}{\lambda} = \dfrac{h^2(2k+1)}{8m[(k+2)\times1.40\times10^{-10}]^2} \Rightarrow \lambda = \dfrac{8mc[(k+2)\times1.40\times10^{-10}]^2}{h(2k+1)}$

$\Rightarrow \lambda = \dfrac{8\times9.1094\times10^{-31}\times2.9979\times10^8\times(1.40\times10^{-10})^2}{6.6261\times10^{-34}} \times \dfrac{(k+2)^2}{(2k+1)}$ **5 points**

$\Rightarrow \lambda\,(m) = 6.462\times10^{-8}\times\dfrac{(k+2)^2}{(2k+1)};$ $\Rightarrow \lambda\,(nm) = 64.62\times\dfrac{(k+2)^2}{(2k+1)}$ (4)   **2 points**

$B_{calc.} = 64.6$ nm

---

3. We wish to synthesize a linear polyene for which the excitation of a π electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part 2, **<u>determine</u>** the <u>number of conjugated double bonds</u> (k) in this polyene and **<u>give</u>** its structure. [*If you did not solve Part 2, use the semi-empirical Equation 1 with B = 65.01 nm to complete Part 3.*]

---

3. With λ = 600 nm, we have

$\dfrac{600}{64.62} = \dfrac{(k+2)^2}{(2k+1)} = 9.285 \Rightarrow k^2 - 14.57k - 5.285 = 0$

Solve the equation to obtain: $\boldsymbol{k_1 = 14.92}$, $k_2 = -0.355$ (Eliminated).   **4 points**

Thus, $k = 15$.

So, the formula of polyene is:
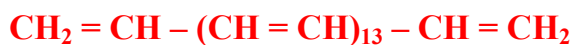
$$CH_2 = CH - (CH = CH)_{13} - CH = CH_2$$ | 2 points

4. For the polyene molecule found in Part 3, **calculate** the difference in energy between the HOMO and the LUMO, ΔE, (kJ·mol^{-1}).

In case Part 3 was not solved, take k = 5 to solve this problem.

$$\Delta E = E_{LUMO} - E_{HOMO} = \frac{h^2}{8mL^2}\left[(k+1)^2 - k^2\right]$$

$$\Delta E = \frac{(6.6261 \times 10^{-34})^2 \times 10^{-3} \times 6.022 \times 10^{23}}{8 \times 9.1094 \times 10^{-31} \times (1.40 \times 10^{-10})^2} \times \left[\frac{2k+1}{(k+2)^2}\right] \quad (\text{kJ·mol}^{-1})$$

$$\Delta E = 1851 \times \left[\frac{2k+1}{(k+2)^2}\right] \quad (\text{kJ/mol})$$

For polyene **with** $k = 15$; $\Delta E = $ **199** kJ·mol^{-1}.

Taking the value of $k = 5$; $\Delta E = $ **415** kJ·mol^{-1} | 4 points

5. The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions L_x, L_y and L_z, yielding the following expression for the allowed energy levels:

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

The three quantum numbers n_x, n_y, and n_z must be integer values and are independent of each other.

5.1 Give the expressions for the three **different** lowest energies, assuming that the box is cubic with a length of L.

$$L_x = L_y = L_z; \quad E_{xyz} = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2}$$ | 1 point

$$E_{111} = \frac{h^2(1^2 + 1^2 + 1^2)}{8mL^2} = \frac{3h^2}{8mL^2}$$ | 1 point

$$E_{112} = \frac{h^2(1^2 + 1^2 + 2^2)}{8mL^2} = \frac{6h^2}{8mL^2} = E_{121} = E_{211}$$

$$E_{122} = \frac{h^2(1^2 + 2^2 + 2^2)}{8mL^2} = \frac{9h^2}{8mL^2} = E_{212} = E_{221}$$

1 point

5.2 Levels with the same energy are said to be degenerate. **<u>Draw</u>** a sketch showing all the energy levels, including any degenerate levels, that correspond to quantum numbers having values of 1 or 2 for a cubic box.

E_{111}: only a single state.

E_{112}: triple degenerate, either n_x, n_y or n_z can equal to 2.

E_{122}: triple degenerate, either n_x, n_y or n_z can equal to 1.

E_{222}: single state.

Energy diagram:

Cubic box

E_{222} ⎯⎯⎯

E_{122} ⎯⎯⎯ ⎯⎯⎯ ⎯⎯⎯

E_{112} ⎯⎯⎯ ⎯⎯⎯ ⎯⎯⎯

E_{111} ⎯⎯⎯

↑ Energy

4 pts

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Theoretical	Code:		Question	1a	1b	2	3	Total
Problem 2	**Examiner**		Mark	12	8	3	10	**33**
5.0 % of the total			Grade					

Problem 2. Dissociating Gas Cycle

Dininitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
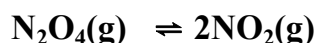
1.00 mole of N_2O_4 was put into an empty vessel with a fixed volume of 24.44 dm^3. The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

1a. <u>Calculate</u> ΔG^0 of the reaction at 298K, assuming the gases are ideal.

1b. <u>Calculate</u> ΔH^0 and ΔS^0 of the reaction, assuming that they do not change significantly with temperature.

1a. N_2O_4 $\rightleftharpoons$ $2 NO_2$

Initial molar number   1   0

At equilibrium   1 - x   2x

$n_{total,equi.}$ = 1 - x + 2x = 1 + x (mol)

$P_{total,equi}$ = P_{ini}(1 + x)

(P_{ini} - initial pressure; $n_{total,equi.}$ – total molar number of gases at equilibrium; $P_{total,equi}$ - total pressure of gases at equilibrium; x – number of moles N_2O_4 dissociated).

$$n_{total,equi} = \frac{PV}{RT} = \frac{(1.190\,\text{bar})\left(\dfrac{10^5\,\text{Pa}}{1\,\text{bar}}\right)(24.44\,\text{dm}^3)\left(\dfrac{1\,\text{m}^3}{1000\,\text{dm}^3}\right)}{(8.3145\,\text{J}\cdot\text{K}^{-1}\cdot mol^{-1})(298\,\text{K})} = 1.174\,(\text{mol})$$

$1.174 = 1 + x$

                                                          4pts

x = 0.174 (mol)

ΔG⁰ at 298 K

At equilibrium:

$$P_{N_2O_4} = \frac{1-x}{1+x} \times P_{total} = \frac{1-0.174}{1+0.174} \times (1.190 \text{ bar}) = 0.837 \text{ bar}$$

$$P_{NO_2} = \frac{2x}{1+x} \times P_{total} = \frac{2 \times 0.174}{1+0.174} \times (1.190 \text{ bar}) = 0.353 \text{ bar}$$

$$K_{298} = \frac{\left(\dfrac{P_{NO_2}}{P^0}\right)^2}{\left(\dfrac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\dfrac{0.353}{1}\right)^2}{\left(\dfrac{0.837}{1}\right)} = 0.1489$$

At 298 K,

$$\Delta G^0 = -RT \ln K_{298} = -8.3145 \times 298 \times \ln(0.1489) = 4719 \,(J \cdot mol^{-1}) = 4.72 \,(\text{kJ} \cdot \text{mol}^{-1})$$

1b. ΔG⁰ at 348 K

$$n_{total,equi} = \frac{PV}{RT} = \frac{(1.886 \text{ bar})\left(\dfrac{10^5 \text{ Pa}}{1 \text{ bar}}\right)(24.44 \text{ dm}^3)\left(\dfrac{1 \text{ m}^3}{1000 \text{ dm}^3}\right)}{(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot mol^{-1})(348 \text{ K})} = 1.593 \,(\text{mol})$$

1.593 = 1 + x

x = 0.593 (mol)

At equilibrium:

$$P_{N_2O_4} = \frac{1-x}{1+x} \times P_{total} = \frac{1-0.593}{1+0.593} \times (1.886 \text{ bar}) = 0.482 \text{ bar}$$

$$P_{NO_2} = \frac{2x}{1+x} \times P_{total} = \frac{2 \times 0.593}{1+0.593} \times (1.886 \text{ bar}) = 1.404 \text{ bar}$$

$$\Rightarrow K_{348} = \frac{\left(\dfrac{P_{NO_2}}{P^0}\right)^2}{\left(\dfrac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\dfrac{1.404}{1}\right)^2}{\left(\dfrac{0.482}{1}\right)} = 4.0897$$

At 348 K,

$$\Delta G^0 = -RT \ln K_{348} = -8.3145 \times 348 \times \ln(4.0897) = -4075 \,(J \cdot mol^{-1}) = -4.07 \,(\text{kJ} \cdot \text{mol}^{-1})$$

4pts

4pts

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ΔS^0	4pts
$\Delta G^0_{348} = -4.07 \text{ kJ} = \Delta H - 348\Delta S$ (1)	
$\Delta G^0_{298} = 4.72 \text{ kJ} = \Delta H - 298\Delta S$ (2)	
$(2) - (1) \rightarrow \Delta S = 0.176 \text{ kJ·mol}^{-1}\text{·K}^{-1}$	
ΔH^0	
$\Delta H^0 = 4.720 + 298 \times 0.176 = 57.2 \text{ (kJ·mol}^{-1})$	4pts

If you cannot calculate ΔH^0, use $\Delta H^0 = 30.0 \text{ kJ·mol}^{-1}$ for further calculations.

The tendency of N_2O_4 to dissociate reversibly into NO_2 enables its potential use in advanced power generation systems. A simplified scheme for one such system is shown below in Figure (a). Initially, "cool" N_2O_4 is compressed (1→2) in a compressor (**X**), and heated (2→3). Some N_2O_4 dissociates into NO_2. The hot mixture is expanded (3→4) through a turbine (**Y**), resulting in a decrease in both temperature and pressure. The mixture is then cooled further (4→1) in a heat sink (**Z**), to promote the reformation of N_2O_4. This recombination reduces the pressure, thus facilitates the compression of N_2O_4 to start a new cycle. All these processes are assumed to take place reversibly.
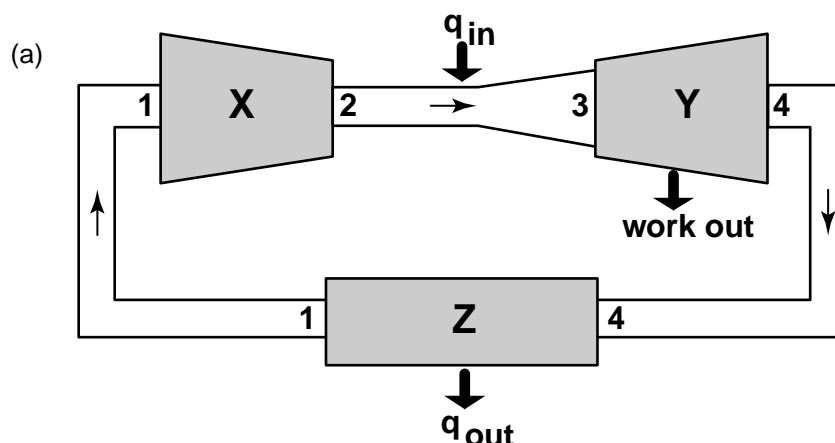
To understand the benefits of using reversible dissociating gases such as N_2O_4, we will focus on step 3 → 4 and consider an ideal gas turbine working with 1 mol of air (which we assume to be an inert, non-dissociating gas). During the reversible adiabatic expansion in the turbine, **no heat is exchanged**.

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2. **Give the equation** to calculate the work done by the system w(air) during the **reversible adiabatic** expansion for 1 mol of air during stage 3 → 4. Assume that $C_{v,m}$(air) (the isochoric molar heat capacity of air) is constant, and the temperature changes from T_3 to T_4.

$\Delta U = q + w$; work done by turbine w(air)=-w	1 pt
$q = 0$, thus $w(\text{air}) = \Delta U = C_{v,m}(\text{air})[T_3\text{-}T_4]$	2 pts

3. **Estimate** the ratio $w_{(N2O4)}/w_{(air)}$, in which $w_{(N2O4)}$ is the work done by the gas during the reversible adiabatic expansion process 3 → 4 with the cycle working with 1 mol of N_2O_4, T_3 and T_4 are the same as in Part 2. Take the conditions at stage 3 to be T_3 = 440 K and P_3 = 12.156 bar and assume that:

   (i) the gas is at its equilibrium composition at stage 3;

   (ii) $C_{v,m}$ for the gas is the same as for air;

   (iii) the adiabatic expansion in the turbine takes place in a way that the composition of the gas mixture (N_2O_4 + NO_2) is unchanged until the expansion is completed.

$\ln\dfrac{K_{440}}{K_{348}} = \dfrac{\Delta H^0}{R}\left(\dfrac{1}{348} - \dfrac{1}{440}\right) = \dfrac{57200}{8.3145}\left(\dfrac{1}{348} - \dfrac{1}{440}\right)$ $\ln K_{440} = \ln K_{348} + \dfrac{57200}{8.3145}\times\left(\dfrac{1}{348} - \dfrac{1}{440}\right) = \ln 4.0897 + \dfrac{57200}{8.314}\times\left(\dfrac{1}{348} - \dfrac{1}{440}\right) = 5.542$ → **K_{440} = 255.2** $\qquad\qquad N_2O_4 \qquad \rightleftharpoons \qquad 2\ NO_2 \qquad (1)$ Initial molar number $\qquad\qquad\quad 1 \qquad\qquad\quad 0$ At equilibrium $\qquad\qquad\qquad 1 - x \qquad\qquad 2x$ n_{total} = 1 - x + 2x = 1 + x (mol);$\qquad$ P_{total} = 12.156 bar At equilibrium: $P_{N_2O_4} = \dfrac{1-x}{1+x}\times 12.156\,(\text{bar})$;$\qquad$ $P_{NO_2} = \dfrac{2x}{1+x}\times 12.156\,(\text{bar})$	3 pts

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$$\Rightarrow K_{440} = \frac{\left(\dfrac{P_{NO_2}}{P^0}\right)^2}{\left(\dfrac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\dfrac{\dfrac{2x}{1+x} \times 12.156}{1}\right)^2}{\left(\dfrac{\dfrac{1-x}{1+x} \times 12.156}{1}\right)} = 255.2$$

$(P^0 = 1 \text{ bar}) \;\rightarrow\; \dfrac{\left(\dfrac{2x}{1+x}\right)^2}{\left(\dfrac{1-x}{1+x}\right)} = 20.99 \Rightarrow \dfrac{4x^2}{1-x^2} = 20.99 \Rightarrow \quad 4x^2 = 20.99 - 20.99\, x^2$

$\rightarrow 24.99\, x^2 = 20.99 \quad \rightarrow \qquad x = 0.92; \qquad\qquad n_{total} = 1 + x = 1.92$

$\rightarrow \qquad w_{N_2O_4} = 1.92 \times C_{v,air} \times (T_3 - T_4); \qquad \rightarrow \qquad \dfrac{w_{N_2O_4}}{w_{air}} = 1.92$

3pt

4 pt

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Theoretical	Code:		Question	1	2	3	4	Total
Problem 3	**Examiner**		Marks	8	14	2	12	**36**
9.0 % of the total			**Grade**					

Problem 3. High-valent Silver Compounds

Silver chemistry is dominated by Ag (I) compounds. Compounds of silver in higher oxidation state (from +2 to +5) are not very abundant due to their instability with respect to reduction. High-valent silver compounds are very reactive and can be synthesized from Ag(I) compounds in electro-chemical oxidations or in chemical oxidations using powerful oxidizing agents.

1. In some peroxydisulfate ($S_2O_8^{2-}$) oxidations catalyzed by Ag^+, black solid (**A**) with the composition AgO can be isolated.

1a. **Choose** the appropriate magnetic behaviour of **A** if it exists as $Ag^{II}O$.

☐	☐
Diamagnetic	Paramagnetic
	x 1 point

Single crystal X - ray studies reveal that the lattice of **A** contains two nonequivalent Ag atom sites (in equal proportions) of which one denoted as Ag1 and the other denoted as Ag2. Ag1 shows a linear O atom coordination (O-Ag-O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, **A** should be assigned as $Ag^IAg^{III}O_2$ rather than $Ag^{II}O$.

1b. **Assign** the oxidation number of Ag1 and Ag2.

Oxidation number of Ag1 : ……….+1
Oxidation number of Ag2 : ……… +3   2 points

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1c. What is the coordination number of O atoms in the lattice of **A**?

The coordination number of O atoms =……… 3   1 point

1d. How many Ag^I and Ag^{III} bond to one O atom in the lattice of **A**?

Number of Ag^I = ……… 1
Number of Ag^{III} = ……. 2   2 points

1e. Predict the magnetic behaviour of **A. Check** the appropriate box below.

☐   ☐
   Diamagnetic   Paramagnetic
         x   1 point

The Ag^I is d^{10} hence diamagnetic; the Ag^{III} is square planar d^8 also diamagnetic

1f. The compound **A** can also be formed on warming a solution of Ag^+ with peroxydisulfate. **Write down** the equation for the formation of **A**.

$S_2O_8^{2-}{}_{(aq)} + 2Ag^+{}_{(aq)} + 2H_2O_{(l)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + Ag^IAg^{III}O_2{}_{(s)} + 4H^+{}_{(aq)}$
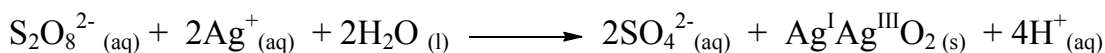
1 point

2. Among the silver oxides which have been crystallographically characterized, the most surprising is probably that compound **A** is not a $Ag^{II}O$. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed:

Atom	Standard enthalpy of formation (kJ·mol⁻¹)	1st ionization (kJ·mol⁻¹)	2nd ionization (kJ·mol⁻¹)	3rd ionization (kJ·mol⁻¹)	1st electron affinity (kJ·mol⁻¹)	2nd electron affinity (kJ·mol⁻¹)
Cu(g)	337.4	751.7	1964.1	3560.2		
Ag(g)	284.9	737.2	2080.2	3367.2		
O(g)	249.0				-141.0	844.0

Compounds	$\Delta H^o{}_f$ (kJ·mol^{-1})
$Ag^IAg^{III}O_{2\,(s)}$	−24.3
$Cu^{II}O_{\,(s)}$	−157.3

The relationship between the **lattice dissociation energy** (U_{lat}) and the **lattice dissociation enthalpy** (ΔH_{lat}) for monoatomic ion lattices is: $\Delta H_{lat} = U_{lat} + nRT$, where n is the number of ions in the formula unit.

2a. <u>Calculate</u> U_{lat} at 298 K of $Ag^IAg^{III}O_2$ and $Cu^{II}O$. Assume that they are ionic compounds.

U_{lat} **of** $Ag^IAg^{III}O_2$

Calculations:

$\Delta H_{lat}(Ag^IAg^{III}O_2)$ = $2\,\Delta H^o{}_f(O^{2-}) + \Delta H^o{}_f(Ag^+) + \Delta H^o{}_f(Ag^{3+}) - \Delta H^o{}_f(Ag^IAg^{III}O_2)$

= (2×249 − 2 × 141 + 2 × 844) + (284.9 + 737.2) + (284.9 + 737.2 + 2080.2 + 3367.2) − (−24.3)

= +9419.9 (kJ·mol^{-1})

$U_{lat}(Ag^IAg^{III}O_2)$ = $\Delta H_{lat}(Ag^IAg^{III}O_2) - 4RT$

= + 9419.9 − 10.0 = + **9409.9** (kJ·mol^{-1})　　　3 points

(no penalty if negative sign)

U_{lat} **of** $Cu^{II}O$

Calculations for: U_{lat} **of** $Cu^{II}O$

$\Delta H_{lat}(Cu^{II}O)$ = $\Delta H^o{}_f(O^{2-}) + \Delta H^o{}_f(Cu^{2+}) - \Delta H^o{}_f(Cu^{II}O)$

= (249 − 141 + 844) + (337.4 + 751.7 + 1964.1) − (−157.3)

= 4162.5 (kJ·mol^{-1})

$U_{lat}(Cu^{II}O)$ = $\Delta H_{lat}(Cu^{II}O) - 2RT$ = 4162.5 − 5.0 = **4157.5** (kJ·mol^{-1})

3 points

(no penalty if negative sign)

*If you can not calculate the U_{lat} of $Ag^IAg^{III}O_2$ and $Cu^{II}O$, use following values for further calculations: U_{lat} of $Ag^IAg^{III}O_2$ = **8310.0** kJ·mol^{-1}; U_{lat} of $Cu^{II}O$ = **3600.0** kJ·mol^{-1}.*

The lattice dissociation energies for a range of compounds may be estimated using this simple formula:

$$U_{lat} = C \times \left(\frac{1}{V_m}\right)^{\frac{1}{3}}$$

Where: V_m (nm^3) is the volume of the formula unit and C (kJ·nm·mol^{-1}) is an empirical constant which has a particular value for each type of lattice with ions of specified charges.

The formula unit volumes of some oxides are calculated from crystallographic data as the ratio between the unit cell volume and the number of formula units in the unit cell and listed as below:

Oxides	V_m (nm^3)
$Cu^{II}O$	0.02030
$Ag^{III}_2O_3$	0.06182
$Ag^{II}Ag^{III}_2O_4$	0.08985

2b. Calculate U_{lat} for the hypothetical compound $Ag^{II}O$. Assume that $Ag^{II}O$ and $Cu^{II}O$ have the same type of lattice, and that $V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}_2O_4) - V_m(Ag^{III}_2O_3)$.

Calculations:

$V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}_2O_4) - V_m(Ag^{III}_2O_3) = 0.08985 - 0.06182 = \textbf{0.02803 nm}^3$

From the relationship $U_{lat} = C \times (V_m)^{-1/3}$ we have

$$\frac{U_{lat}(\text{Ag oxide})}{U_{lat}(\text{Cu oxide})} \approx \left[\frac{V_m(\text{Cu oxide})}{V_m(\text{Ag oxide})}\right]^{1/3}$$

$$U_{lat}(Ag^{II}O) = 4157.5 \times \sqrt[3]{\frac{0.02030}{0.02803}} = \textbf{3733.6} \text{ (kJ·mol}^{-1}) \qquad \text{3 points}$$

Answer: **3733.6** (kJ.mol^{-1}) [or 3232.9 kJ·mol^{-1} if using $U_{lat} Cu^{II}O = 3600$ kJ·mol^{-1}]

2c. By constructing an appropriate thermodynamic cycle or otherwise, **estimate** the enthalpy change for the solid-state transformation from $Ag^{II}O$ to 1 mole of $Ag^IAg^{III}O_2$.

(Use $U_{lat} Ag^{II}O = 3180.0$ kJ·mol^{-1} and $U_{lat} Ag^IAg^{III}O_2 = 8310.0$ kJ·mol^{-1} if you cannot calculate $U_{lat} Ag^{II}O$ in Part 2b).

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$$2Ag^{II}O_{(s)} \xrightarrow{\quad \Delta H_{rxn} \quad} Ag^{I}Ag^{III}O_{2\,(s)}$$

$$\downarrow\; 2U_{lat}(AgO) + 4RT \qquad\qquad \uparrow\; - U_{lat}(Ag^{I}Ag^{III}O) - 4RT$$

$$2Ag^{2+}_{(g)} + 2O^{2-}_{(g)} \xrightarrow{\quad IE_3(Ag) - IE_2(Ag) \quad} Ag^{+}_{(g)} + Ag^{3+}_{(g)} + 2O^{2-}_{(g)}$$

Calculations:

$$\Delta H_{rxn} = 2U_{lat}(Ag^{II}O) + 4RT + IE_3 - IE_2 - U_{lat}(Ag^{I}Ag^{III}O_2) - 4RT$$

$$= 2 \times 3733.6 + 3367.2 - 2080.2 - 9409.9$$

$$= -\textbf{655.7 (kJ/mol)} \text{ or } \textbf{- 663.0 kJ/mol} \text{ using given } U_{lat} \text{ values} \qquad \textbf{4 pts}$$
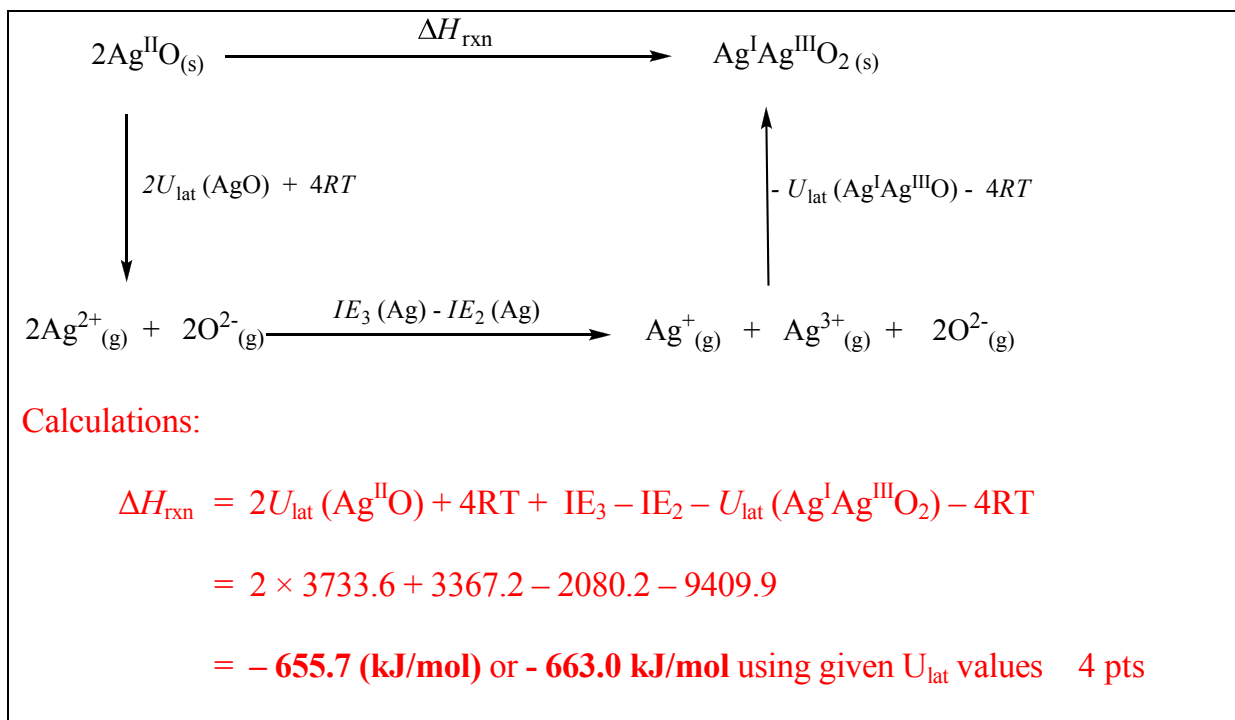
2d. <u>Indicate</u> which compound is thermodynamically more stable by checking the appropriate box below.

$Ag^{II}O$ ☐

$Ag^{I}Ag^{III}O_2$ ☐

x   1 point
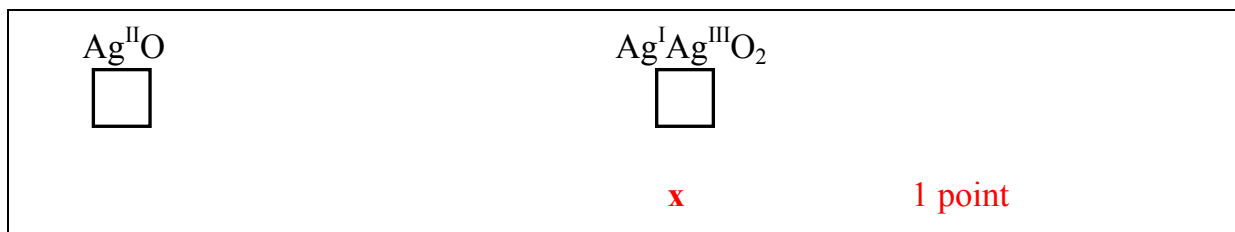
3. When $Ag^{I}Ag^{III}O_2$ is dissolved in aqueous $HClO_4$ solution, a paramagnetic compound (**B**) is first formed then slowly decomposes to form a diamagnetic compound (**C**). Given that **B** and **C** are the only compounds containing silver formed in these reactions, **<u>write down</u>** the equations for the formation of **B** and **C**.

For **B**:

$$Ag^{I}Ag^{III}O_{2\,(s)} + 4\,HClO_{4\,(aq)} \longrightarrow 2Ag(ClO_4)_{2\,(aq)} + 2\,H_2O_{(l)} \qquad \text{1 point}$$

For **C**: $4Ag(ClO_4)_{2\,(aq)} + 2\,H_2O_{(l)} \longrightarrow 4\,AgClO_{4\,(aq)} + 4\,HClO_{4\,(aq)} + O_{2\,(g)}$

1 point
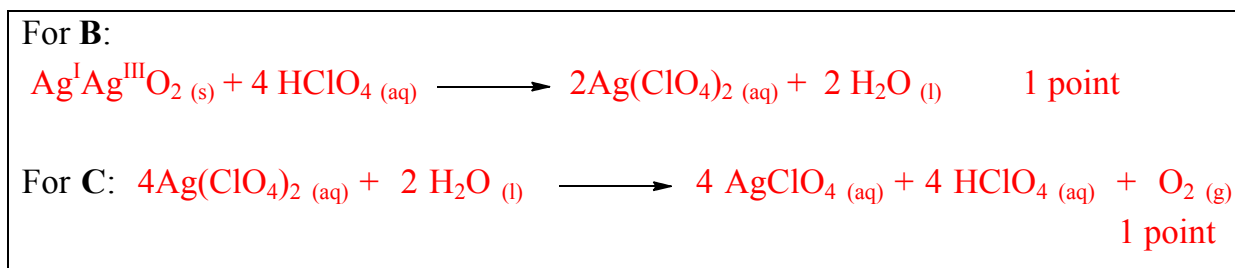
4. Oxidation of Ag^+ with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex **Z** is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of $AgNO_3$ and 2 mL of pyridine (d = 0.982 g/mL) is added to a stirred, ice-cold aqueous solution of 5.000 g of $K_2S_2O_8$. The reaction mixture becomes yellow, then an orange solid (**Z**) is formed which has a mass of 1.719 g when dried.

Elemental analysis of **Z** shows the mass percentages of C, H, N elements are 38.96%, 3.28%, 9.09%, respectively.

A 0.6164 g **Z** is added to aqueous NH_3. The suspension is boiled to form a clear solution during which stage the complex is destroyed completely. The solution is acidified with excess aqueous HCl and the resulting suspension is filtered, washed and dried (in darkness) to obtain 0.1433 g of white solid (**D**). The filtrate is collected and treated with excess $BaCl_2$ solution to obtain 0.4668 g (when dry) of white precipitate (**E**).

4a. <u>Determine</u> the empirical formula of **Z** and calculate the percentage yield in the preparation.

Calculations:

- Mole Ag in 0.6164 g of **Z** = mole of AgCl = 0.001 mole

- Mole SO_4^{2-} from 0.6160 g of **Z** = mole $BaSO_4$ = 0.002 mol

- Mass percentage of Ag = 0.001×107.87/0.6164 = 17.50 %

- Mass percentage of SO_4^{2-} = 0.002×96.06/0.6164 = 31.17 %

- From EA:

Ratio $Ag^{2+} : SO_4^{2-} : C : H : N = \dfrac{17.50}{107.87} : \dfrac{31.17}{192.12} : \dfrac{38.96}{12.01} : \dfrac{3.28}{1.01} : \dfrac{9.09}{14.01} = 1 : 2 : 20 : 20 : 4$

The empirical formula of **Z** is: $C_{20}H_{20}AgN_4O_8S_2$ **2 points**

$\text{Yield} = \dfrac{1.719}{\dfrac{0.500}{169.87} \times 616.4} \times 100\% = \mathbf{94.7\ \%}$ **1 point**

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4b. Ag (IV) and Ag (V) compounds are extremely unstable and found only in few fluorides. Thus, the formation of their complexes with organic ligands in water can be discounted. To confirm the oxidation number of silver in **Z**, the effective magnetic moment (μ_{eff}) of **Z** was determined and found to be 1.78 BM. Use the spin only formula to **determine** the number of unpaired electrons in Z and the molecular formula of **Z**. (**Z** contains a mononuclear complex with only one species of Ag and only one type of ligand in the ligand sphere.)

- $\quad\quad \sqrt{n(n+2)} = 1.78$ (n is number of unpaired electron of Ag)

- $\quad n = 1$, corresponds to Ag^{II} (d^9)

- $\quad$ Most rational molecular formula of **Z** is **[Ag^{II}(Py)$_4$](S$_2$O$_8$)** $\quad\quad$ **3 point**

4c. <u>Write down</u> all chemical equations for the preparation of **Z**, and its analysis.

Formation of **Z**:

$2Ag^+_{(aq)} + 8Py_{(l)} + 3S_2O_8^{2-}_{(aq)} \longrightarrow 2[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 2SO_4^{2-}_{(aq)}$ $\quad\quad$ 2 pts

Destruction of **Z** with NH$_3$:

$[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 6NH_3_{(l)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + \frac{1}{2} N_2_{(g)} + 2SO_4^{2-}_{(aq)} + 3NH_4^+_{(aq)} + 4Py_{(l)}$ $\quad\quad$ 2 pts
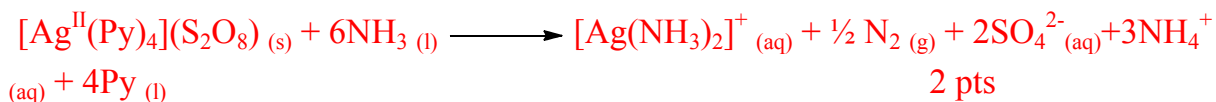
(All reasonable N –containing products and O$_2$ are acceptable)

Formation of **D**:

$[Ag(NH_3)_2]^+_{(aq)} + 2H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)} + 2NH_4^+_{(aq)}$ $\quad\quad$ 1 pt

Formation of **E**:

$Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow BaSO_4_{(s)}$ $\quad\quad$ 1pt

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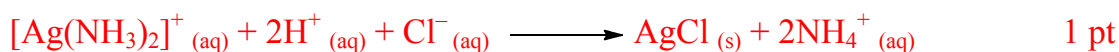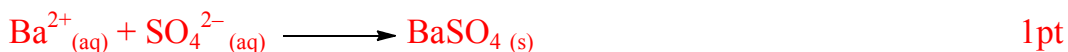
Theoretical	Code:		Question	1a	1b	2a	3a	3b	3c	Total
Problem 4	**Examiner**		Mark	4	1	10	2	**6**	**4**	**27**
4.0 % of the total			Grade							

Problem 4. Zeise's Salt

1. Zeise's salt, K[PtCl₃C₂H₄], was one of the first organometallic compounds to be reported. W. C. Zeise, a professor at the University of Copenhagen, prepared this compound in 1827 by reacting PtCl₄ with boiling ethanol and then adding potassium chloride (Method 1). This compound may also be prepared by refluxing a mixture of K₂[PtCl₆] and ethanol (Method 2). The commercially available Zeise's salt is commonly prepared from K₂[PtCl₄] and ethylene (Method 3).

1a. <u>**Write**</u> balanced equations for <u>each of the above mentioned preparations</u> of Zeise's salt, given that in methods 1 and 2 the formation of 1 mole of Zeise's salt consumes 2 moles of ethanol.

<div style="color:red; border:1px solid black; padding:10px">

$PtCl_4 + 2\ C_2H_5OH \rightarrow H[PtCl_3C_2H_4] + CH_3CH=O + HCl + H_2O$

$H[PtCl_3C_2H_4] + KCl \rightarrow K[PtCl_3C_2H_4] + HCl$

$K_2[PtCl_6] + 2\ C_2H_5OH \rightarrow K[PtCl_3C_2H_4] + CH_3CH=O + KCl + 2\ HCl + H_2O$

$K_2[PtCl_4] + C_2H_4 \rightarrow K[PtCl_3C_2H_4] + KCl$

<div align="right">1pt for each (2 pts if the first two reactions combined), total of 4 pts</div>

</div>

1b. Mass spectrometry of the anion $[PtCl_3C_2H_4]^-$ shows one set of peaks with mass numbers 325-337 *au* and various intensities.

   <u>Calculate the mass number</u> of the anion which consists of the largest natural abundance isotopes (using given below data).

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Isotope	$^{192}_{78}Pt$	$^{194}_{78}Pt$	$^{195}_{78}Pt$	$^{196}_{78}Pt$	$^{198}_{78}Pt$	$^{35}_{17}Cl$	$^{37}_{17}Cl$	$^{12}_{6}C$	$^{13}_{6}C$	$^{1}_{1}H$
Natural abundance, %	0.8	32.9	33.8	25.3	7.2	75.8	24.2	98.9	1.1	99.99

Calculations:

$195 + 3\times35 + 2\times12 + 4\times1 = 328$ 1 pt

2. Some early structures proposed for Zeise's salt anion were:

(Z1)   (Z2)   (Z3)   (Z4)   (Z5)
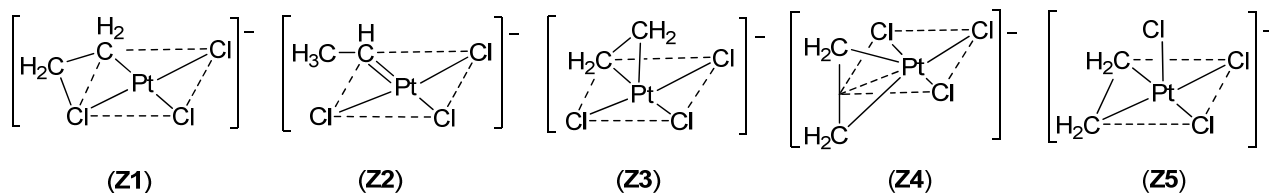
In structure **Z1**, **Z2**, and **Z5** both carbons are in the same plane as dashed square. [You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.]

2a. NMR spectroscopy allowed the structure for Zeise's salt to be determined as structure **Z4**. For each structure **Z1-Z5**, **indicate** in the table below how many hydrogen atoms are in different environments, and how many different environments of hydrogen atoms there are, and how many different environments of carbon atoms there are?

Structure	Number of different environments of hydrogen	Number of different environments of carbon
Z1	2 1pt	2 1 pt
Z2	2 1pt	2 1 pt
Z3	2 1pt	2 1 pt
Z4	1 1pt	1 1 pt
Z5	2 1pt	1 1 pt

3. For substitution reactions of square platinum(II) complexes, ligands may be arranged in order of their tendency to facilitate substitution in the position *trans* to themselves (*the trans effect*). The ordering of ligands is:

$$CO , CN^- , C_2H_4 > PR_3 , H^- > CH_3^- , C_6H_5^- , I^- , SCN^- > Br^- > Cl^- > Py > NH_3 > OH^- , H_2O$$
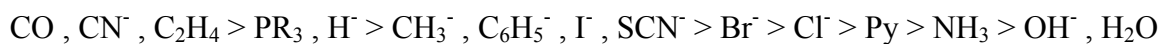
In above series a left ligand has stronger *trans effect* than a right ligand.
Some reactions of Zeise's salt and the complex $[Pt_2Cl_4(C_2H_4)_2]$ are given below.

K[PtCl₃(C₆H₅C₂H₃)]
(D)
C₆H₅CH=CH₂

[PtCl₂(C₂H₄)(CH₃NH₂)]
(B)
CH₃NH₂   CH₃NH₂

[PtCl₂(C₂H₄)₂]
(G)
C₂H₄

(Py)

K[PtCl₃(C₂H₄)]   HCl   [Pt₂Cl₄(C₂H₄)₂]
(A)

H₂NCH₂CH₂NH₂

C₆H₅NH₂   C₆H₅NH₂

[PtCl₂(C₆H₅C₂H₃)(Py)]
(E)

[PtCl₂(C₂H₄)(C₆H₅NH₂)]
(C)

[PtClC₂H₄(H₂NC₂H₄NH₂)]Cl
(F)
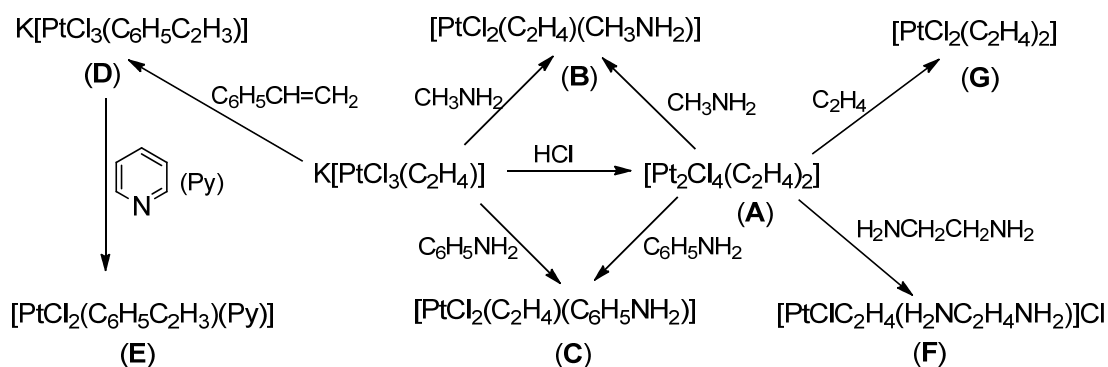
3a. <u>Draw the structure of A</u>, given that the molecule of this complex has a centre of symmetry, no Pt-Pt bond, and no bridging alkene.

Structure of **A**		2 pt

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3b. <u>Draw</u> the structures of **B**, **C**, **D**, **E**, **F** and **G**.

B	C	D
Cl, NH$_2$Me / Pt / Cl (with ethylene) **1 pt**	Cl, NH$_2$C$_6$H$_5$ / Pt / Cl (with ethylene) **1 pt**	K[C$_6$H$_5$ (with ethylene)—Pt with Cl, Cl, Cl] **1 pt**
E	**F**	**G**
[C$_6$H$_5$ (ethylene), Cl, Py, Pt, Cl] **1 pt**	[Cl, H$_2$N~N H$_2$ ethylenediamine, Pt, Cl (with ethylene)] **1 pt**	Cl, Pt, Cl (with two ethylene) **1 pt**

3c. <u>Suggest</u> the <u>driving force(s)</u> for the formation of **D** and **F** by choosing one or more of the following statements (for example, i and ii):

i) Formation of gas
ii) Formation of liquid
iii) Trans effect
iv) Chelate effect

Structure	D	F
Driving force(s)	i	iii and iv
	2 pts	2 pts

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Theoretical	Code:		Question	1	2	3	4	Total
Problem 5	Examiner		Mark	6	4	4	6	**20**
6.5 % of the total			Grade					

Problem 5. Acid-base Equilibria in Water

A solution (**X**) contains two weak monoprotic acids (those having *one* acidic proton); HA with the acid dissociation constant of $K_{HA} = 1.74 \times 10^{-7}$, and HB with the acid dissociation constant of $K_{HB} = 1.34 \times 10^{-7}$. The solution **X** has a pH of 3.75.

1. Titration of 100 mL solution **X** requires 100 mL of 0.220 M NaOH solution for completion.

Calculate the initial (total) concentration (mol·L^{-1}) of each acid in the solution **X**. Use reasonable approximations where appropriate. [$K_W = 1.00 \times 10^{-14}$ at 298 K.]

Solution: In solution **X**, H$^+$ was produced from the reactions :

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad \text{and} \quad \text{HB} \rightleftharpoons \text{H}^+ + \text{B}^- \quad \text{and} \quad \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

The positive and negative charges in an aqueous solution must balance. Thus the charge balance expression is:

$$[\text{OH}^-] + [\text{A}^-] + [\text{B}^-] = [\text{H}^+] \qquad \text{(Eq.1)}$$

In the acidic solution (pH = 3.75), [OH$^-$] can be neglected, so:

$$[\text{A}^-] + [\text{B}^-] = [\text{H}^+] \qquad \text{(Eq. 2)}$$

From equilibrium expression: $\dfrac{[H^+] \times [A^-]}{[HA]} = K_{HA}$

and $[HA] = [HA]_i - [A^-]$ (*where [HA]$_i$ is the initial concentration*)

So: $[H^+] \times [A^-] = K_{HA} \times [HA] = K_{HA}([HA]_i - [A^-])$

Thus, the equilibrium concentration of [A$^-$] can be presented as:

$$[A^-] = \frac{K_{HA} \times [HA]_i}{K_{HA} + [H^+]}$$

Similarly, the equilibrium concentration of [B$^-$] can be presented as:

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$$\left[B^-\right] = \frac{K_{HB} \times [HB]_i}{K_{HB} + [H^+]}$$

Substitute equilibrium concentrations of [A⁻] and [B⁻] into Eq.2:

$$\frac{K_{HA} \times [HA]_i}{K_{HA} + [H^+]} + \frac{K_{HB} \times [HB]_i}{K_{HB} + [H^+]} = \left[H^+\right]$$
2 pts

Since K_{HA}, K_{HB} are much smaller than [H⁺], thus:

$$\frac{K_{HA} \times [HA]_i}{[H^+]} + \frac{K_{HB} \times [HB]_i}{[H^+]} = \left[H^+\right]$$

or $1.74 \times 10^{-7} \times [HA]_i + 1.34 \times 10^{-7} \times [HB]_i = [H^+]^2 = (10^{-3.75})^2$

$1.74 \times [HA]_i + 1.34 \times [HB]_i = 0.316$ (Eq. 3)

Neutralization reactions show:

$$HA \ + \ NaOH \ \longrightarrow \ NaA \ + \ H_2O$$

$$HB \ + \ NaOH \ \longrightarrow \ NaB \ + \ H_2O$$
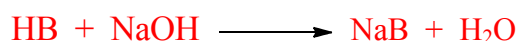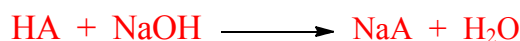
$n_{HA} + n_{HB} = n_{NaOH}$

or $([HA]_i + [HB]_i) \times 0.1 \ L = 0.220 \ M \times 0.1 \ L$ 2 pts

$[HA]_i + [HB]_i = 0.220 \ M$ (Eq. 4)

Solving Eq.3 and Eq.4 gives: $[HA]_i = 0.053 \ M$ and $[HB]_i = 0.167 \ M$

Concentration of HA =   0.053 M

Concentration of HB =   0.167 M **2 pts**

2. **Calculate** the pH of the solution **Y** which initially contains 6.00×10^{-2} M of NaA and 4.00×10^{-2} M of NaB.

Solution:

Solution **Y** contains NaA 0.06 M and NaB 0.04 M. The solution is basic, OH⁻ was produced from the reactions:

$NaA + H_2O \rightleftharpoons HA + OH^-$ $K_{b,A} = K_w/K_{HA} = 5.75 \times 10^{-8}$

$NaB + H_2O \rightleftharpoons HB + OH^-$ $K_{b,B} = K_w/K_{HB} = 7.46 \times 10^{-8}$

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.00 \ 10^{-14}$

and we have:

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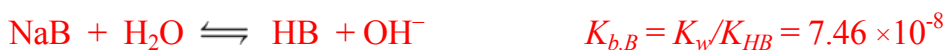
$[H^+] + [HA] + [HB] = [OH^-]$ (Eq. 5)

In the basic solution, $[H^+]$ can be neglected, so:

$[HA] + [HB] = [OH^-]$ (Eq. 6)

From equilibrium expression: $\dfrac{[OH^-] \times [HA]}{[A^-]} = K_{b,A}$

and $[A^-] = 0.06 - [HA]$ 1 pt

Thus, the equilibrium concentration of HA can be presented as: $[HA] = \dfrac{K_{b,A} \times 0.06}{K_{b.A} + [OH^-]}$

Similarly, the equilibrium concentration of HB can be presented as: $[HB] = \dfrac{K_{b,B} \times 0.04}{K_{b.B} + [OH^-]}$

Substitute equilibrium concentrations of HA and HB into Eq. 6:

$\dfrac{K_{b,A} \times 0.06}{K_{b.A} + [OH^-]} + \dfrac{K_{b,B} \times 0.04}{K_{b.B} + [OH^-]} = [OH^-]$ 2 points

Assume that $K_{b,A}$ and $K_{b,B}$ are much smaller than $[OH^-]$ (*), thus:

$[OH^-]^2 = 5.75 \times 10^{-8} \times 0.06 + 7.46 \times 10^{-8} \times 0.04$

$[OH^-] = 8.02 \times 10^{-5}$ (the assumption (*) is justified)

So   pOH = 4.10 and **pH = 9.90**   **1 point**

3. Adding large amounts of distilled water to solution **X** gives a very (infinitely) dilute solution where the total concentrations of the acids are close to zero. **Calculate** the percentage of dissociation of each acid in this dilute solution.

Solution: HA in the dilute solution:

$[A^-] = \alpha \times [HA]_i$

$[HA] = (1 - \alpha) \times [HA]_i$

$[H^+] = 10^{-7}$

Substitute these equilibrium concentrations into K_{HA} expression:

$\dfrac{10^{-7} \times \alpha \times [HA]_i}{(1-\alpha) \times [HA]_i} = K_{HA}$ or $\dfrac{10^{-7} \times \alpha}{(1-\alpha)} = 1.74 \times 10^{-7}$ 2 pts

Solving the equation gives: $\alpha = 0.635$

Similarly, for HB: $\dfrac{10^{-7} \times \alpha}{(1-\alpha)} = 1.34 \times 10^{-7}$

Solving the equation gives: $\alpha = 0.573$

- The percentage of dissociation of HA = **65.5 %**

- The percentage of dissociation of HB = **57.3 %**   **2 points**

---

4. A buffer solution is added to solution **Y** to maintain a pH of 10.0. Assume no change in volume of the resulting solution **Z**.

<u>Calculate</u> the solubility (in $mol \cdot L^{-1}$) of a subtancce $M(OH)_2$ in **Z**, given that the anions A^- and B^- can form complexes with M^{2+}:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.1 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.0 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^+$ $K'_1 = 6.2 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.3 \times 10^2$

Solution:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.00 \times 10^{-14}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.10 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.00 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^+$ $K'_1 = 6.20 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.30 \times 10^2$

Solubility of $M(OH)_2 = s = [M^{2+}] + [MA^+] + [MA_2] + [MB^+] + [MB_2]$

pH of **Z** = 10.0

$$[M^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{3.10 \times 10^{-12}}{(10^{-4})^2} = 3.10 \times 10^{-4} \text{ M} \qquad \text{Eq.1}$$

At pH = 10.0

$$[A^-]_{total} = \frac{K_{HA} \times 0.06}{(K_{HA} + 10^{-10})} = 0.06$$

$[MA^+] = K_1[M^{2+}][A^-] = 2.1 \times 10^3 \times 3.10 \times 10^{-4} \times [A^-] = 0.651 \times [A^-]$ Eq. 3

$[MA_2] = K_1K_2[M^{2+}][A^-]^2 = 325.5 \times [A^-]^2$ Eq. 4

$[A^-]_{total} = [A^-] + [MA^+] + 2 \times [MA_2] = 0.06$ M   Eq. 5

Substitute Eq. 3 and Eq. 4 into Eq. 5:

$[A^-] + 0.651 \times [A^-] + 2 \times 325.5 \times [A^-]^2 = 0.06$ **2 pts**

Solve this equation: $[A^-] = \mathbf{8.42\times 10^{-3}\ M}$

Substitute this value into Eq. 3 and Eq. 4:

$[MA^+] = 0.651 \times [A^-] = \mathbf{5.48 \times 10^{-3}\ M}$

$[MA_2] = 325.5 \times [A^-]^2 = \mathbf{2.31 \times 10^{-2}\ M}$

Similarly,

$[B^-]_{total} = 0.04\ M$

$[MB^+] = K_1^{'}[M^{2+}][B^-] = 6.2\times10^3 \times 3.10\times10^{-4} \times [B^-] = 1.92\times[B^-]$ Eq. 6

$[MB_2] = K_1^{'}K_2^{'}[M^{2+}][B^-]^2 = 634.3\times[B^-]^2$ Eq.7

$[B^-]_{total} = [B^-] + [MB^+] + 2 \times [MB_2] = 0.04\ M$ Eq. **8**   **2pts**

Substitute Eq. 6 and Eq. 7 into Eq. 8:

$[B^-] + 1.92 \times [B^-] + 2 \times 634.3 \times [B^-]^2 = 0.04$

Solve this equation: $\mathbf{[B^-] = 4.58 \times 10^{-3}\ M}$

Substitute this value into Eq. 6 and Eq. 7:

$[MB^+] = 1.92 \times[B^-] = \mathbf{8.79 \times 10^{-3}\ M}$

$[MB_2] = 634.3 \times[B^-]^2 = \mathbf{1.33 \times 10^{-2}\ M}$

Thus, solubility of $M(OH)_2$ in **Z** is **s'**

s' $= 3.10\times10^{-4} + 5.48\times10^{-3} + 2.31\times10^{-2} + 8.79 \times 10^{-3} + 1.33 \times10^{-2} = \mathbf{5.10\times10^{-2}\ M}$

Answer: Solubility of $M(OH)_2$ in Z = 5.10×10^{-2} M.   **2 points**

Theoretical	Code:		Question	6a	6b	6c	6d	6e	Total
Problem 6	**Examiner**		Marks	6	8	4	12	2	**32**
7.0 % of the total			**Grade**						

Problem 6. Chemical Kinetics
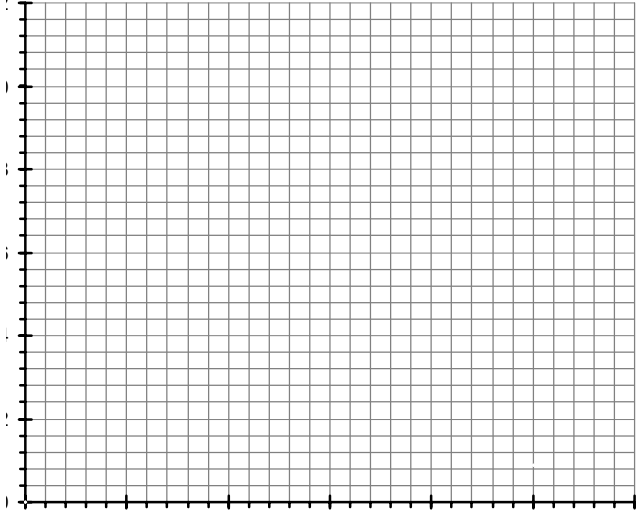
The transition-metal-catalyzed amination of aryl halides has become one of the most powerful methods to synthesize arylamines. The overall reaction for the nickel-catalyzed amination of aryl chloride in basic conditions is:

$$\text{ArCl} + \text{RNH}_2 \xrightarrow[\text{NaO}^t\text{Bu, } Solvent]{\text{NiLL'}} \text{Ar-NHR} + \text{HCl}$$
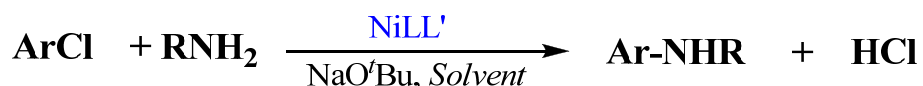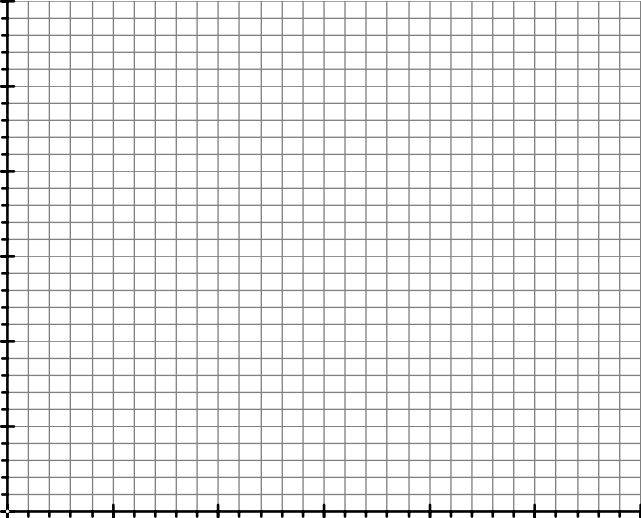
in which NiLL' is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

6a. To determine the reaction order with respect to each reactant, the dependence of the initial rate of the reaction on the concentrations of each reagent was carried out with all other reagents present in large excess. Some kinetic data at 298 K are shown in the tables below. **(Use the grids if you like)**

[ArCl] (M)	Initial rate (M s^{-1})
0.1	1.88×10^{-5}
0.2	4.13×10^{-5}
0.4	9.42×10^{-5}
0.6	1.50×10^{-4}

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[**NiLL'**] (M)	Initial rate (M s^{-1})	
6×10^{-3}	4.12×10^{-5}	
9×10^{-3}	6.01×10^{-5}	
1.2×10^{-2}	7.80×10^{-5}	
1.5×10^{-2}	1.10×10^{-4}	

[**L'**] (M)	Initial rate (M s^{-1})	
0.06	5.8×10^{-5}	
0.09	4.3×10^{-5}	
0.12	3.4×10^{-5}	
0.15	2.8×10^{-5}	

Determine the order with respect to the reagents assuming they are integers.

- Order with respect to [**ArCl**] = = 1
- Order with respect to [**NiLL'**] = = 1
- Order with respect to [**L'**] = = **-1**   6 pts

6b. To study the mechanism for this reaction, ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopy have been used to identify the major transition metal complexes in solution, and the initial rates were measured using reaction calorimetry. An intermediate, NiL(Ar)Cl, may be isolated at room temperature. The first two steps of the overall reaction involve the dissociation of a ligand from NiLL' (step 1) at 50 °C, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

$$\text{NiLL'} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NiL} + \text{L'} \qquad (1)$$

$$\text{NiL} + \text{ArCl} \xrightarrow{k_2} \text{NiL(Ar)Cl} \qquad (2)$$

Using the steady state approximation, **derive** an expression for the rate equation for the formation of [NiL(Ar)Cl].

The rate law expression for the formation of NiLAr(Cl)

$$\text{rate} = \frac{k_1 k_2 [NiLL'] \, [ArCl]}{k_{-1}[L'] + k_2[ArCl]} = \frac{k_1 (k_2 / k_{-1})[NiLL'] \, [ArCl]}{[L'] + (k_2 / k_{-1})[ArCl]} \qquad \textbf{8 pts}$$
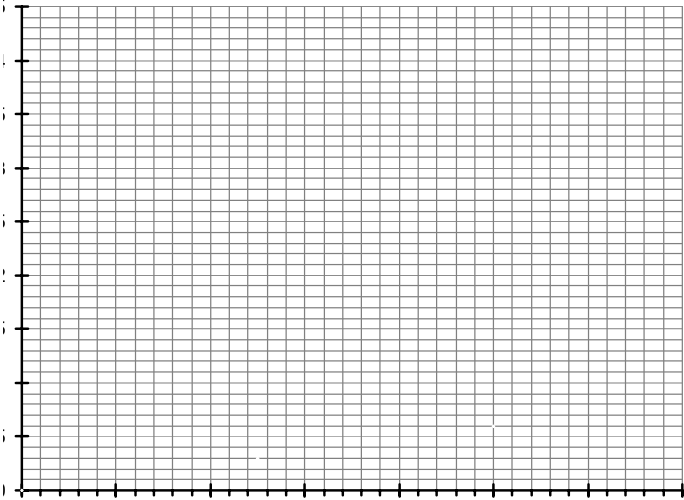
(4pts for [NiL] calculation)
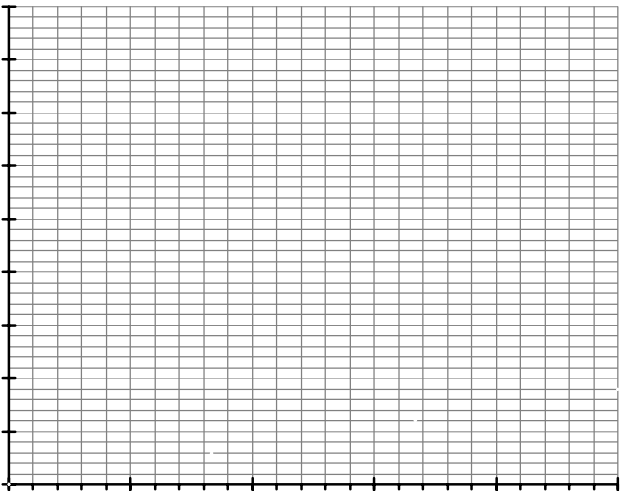
(4 pts for rate calculation)

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The next steps in the overall reaction involve the amine (RNH$_2$) and ^{t}BuONa. To determine the order with respect to RNH$_2$ and ^{t}BuONa, the dependence of the initial rates of the reaction on the concentrations of these two reagents was carried with the other reagents present in large excess. Some results are shown in the tables below.

[NaO^{t}Bu], (M)	Initial rate (M·s^{-1})
0.2	4.16×10^{-5}
0.6	4.12×10^{-5}
0.9	4.24×10^{-5}
1.2	4.20×10^{-5}

[RNH$_2$] (M)	Initial rate (M s^{-1})
0.3	4.12×10^{-5}
0.6	4.26×10^{-5}
0.9	4.21×10^{-5}
1.2	4.23×10^{-5}

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6c. **Determine** the order with each of these reagents, assuming each is an integer. **(Use the grids if you like)**

- Order with respect to $[NaO^tBu]$ =	0	2 pts
- Order with respect to $[RNH_2]$ =	0	2 pts

During a catalytic cycle, a number of different structures may be involved which include the catalyst. One step in the cycle will be rate-determining.
A proposed cycle for the nickel-catalyzed coupling of aryl halides with amines is as follows:

$$NiLL' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad NiL \ + \ L' \tag{1}$$

$$NiL \ + ArCl \xrightarrow{k_2} NiL{<}^{Ar}_{Cl} \tag{2}$$

$$NiL{<}^{Ar}_{Cl} \ + NH_2R \ + NaO^tBu \xrightarrow{k_3} NiL(Ar)NHR + {}^tBuOH \ + NaCl \tag{3}$$

$$NiL(Ar)NHR \xrightarrow{k_4} ArNHR + NiL \tag{4}$$
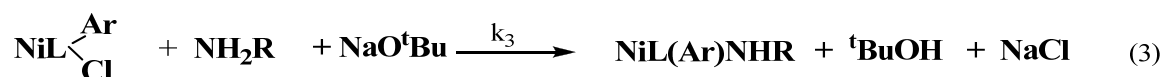
6d. Use the steady-state approximation and material balance equation to **derive** the rate law for d[ArNHR]/dt for the above mechanism in terms of the initial concentration of the catalyst $[NiLL']_0$ and concentrations of [ArCl], $[NH_2R]$, $[NaO^tBu]$, and [L'].

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Using the mechanism depicted by Reaction (1) through (4), the rate equation:

$$\frac{d[NiLL']}{dt} = -k_1[NiLL'] + k_{-1}[NiL][L']$$

$$\frac{d[NiL]}{dt} = k_1[NiLL'] - k_{-1}[NiL][L'] - k_2[NiL][ArCl] + k_4[NiL(Ar)NHR]$$

Apply the steady-state approximation to the concentrations for the intermediates:

$$\frac{d[NiL]}{dt} = 0$$

$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4[NiL(Ar)HNR]$ (Equation 1)   1pt

$$\frac{d[NiL(Ar)Cl]}{dt} = k_2[NiL][ArCl] - k_3[RNH_2][NaOBu][NiL(Ar)Cl] = 0$$

$$[NiL(Ar)Cl] = \frac{k_2}{k_3} \frac{[ArCl][NiL]}{[NH_2R][NaOBu]} \qquad \text{(Equation 2)} \qquad \text{1pt}$$

</div>

$$\frac{d[NiL(Ar)NHR]}{dt} = k_3[NiL(Ar)Cl][NH_2R][NaOBu] - k_4[NiL(Ar)NHR] = 0$$

$$[NiL(Ar)NHR] = \frac{k_3}{k_4}\frac{[NiL(Ar)Cl][NH_2R][NaOBu]}{} \qquad \text{(Equation 3)}$$

Substitute Equation 2 into Equation 3:

$$[NiL(Ar)NHR] = \frac{k_3}{k_4}\frac{[NH_2R][NaOBu]}{} \times \frac{k_2}{k_3}\frac{[ArCl][NiL]}{[NH_2R][NaOBu]} = \frac{k_2}{k_4}[ArCl][NiL] \quad \text{(Eq. 4) 1pt}$$

Substitute Equation 4 into Equation 1:

$$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4[NiL(Ar)NHR]$$

$$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4 \times \frac{k_2}{k_4}[ArCl][NiL] = k_{-1}[NiL][L'] \quad \text{(Eq.5)}$$

The material balance equation with respect to the catalyst is

$$[NiLL']_0 = [NiLL'] + [NiL] + [NiLAr(Cl)] + [NiLAr(Cl)NHR] \qquad \text{2 pts}$$

$$[NiLL']_0 = \frac{k_{-1}}{k_1}[NiL][L'] + [NiL] + \frac{k_2}{k_3}\frac{[NiL][ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[NiL][ArCl]$$

$$[NiLL']_0 = [NiL]\left[\frac{k_{-1}}{k_1}[L'] + 1 + \frac{k_2}{k_3}\frac{[ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[ArCl]\right] \qquad \text{3 pts}$$

$$[NiL] = [NiLL']_0 \times \frac{k_1k_3k_4[NH_2R][NaOBu]}{k_{-1}k_3k_4[L'][NH_2R][NaOBu] + k_1k_3k_4[NH_2R][NaOBu] + k_1k_2k_4[ArCl] + k_1k_2k_3[ArCl][NH_2R][NaOBu]}$$

Equation 6

Substituting Equation 6 into the differential rate for [ArCl]:

$$-\frac{d[ArCl]}{dt} = k_2[ArCl][NiL] \text{, results in the following predicted rate law expression for}$$

the reaction mechanism:

d[ArNHR]/dt = - d[ArCl]/dt =

$k_2[ArCl] [NiL] = k_1k_2k_3k_4 [ArCl][NiLL']_0[NaO^tBu][NH_2R]$

$/\{k_{-1}k_3k_4[NH_2R][NaOBu][L'] + k_1k_3k_4[NaOBu][NH_2R] + k_1k_2k_4[ArCl] + k_1k_2k_3$

$[ArCl][NH_2R][NaOBu]\}$ 4 pts

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6e. <u>Give</u> the simplified form of the rate equation in 6d assuming that k_1 is very small.

d[ArNHR]/dt = - d[ArCl]/dt = $k_2[ArCl]$ $[NiL]$ $= k_1 k_2$ $[ArCl][NiLL']_0 / k_{-1}[L']$
(i.e. consistent with all the orders of reaction as found in the beginning)   2 pts

Problem 7. Synthesis of Artemisinin

(+)-Artemisinin, isolated from *Artemisia annua* L. (Qinghao, *Compositae*) is a potent antimalarial effective against resistant strains of *Plasmodium*. A simple route for the synthesis of Artemisinin is outlined below.
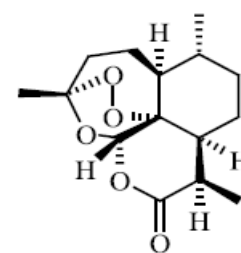
(+)-Artemisinin

First, pyrolysis of (+)-2-Carene broke the cyclopropane ring forming, among other products, (1*R*)-(+)-*trans*-isolimonene **A** (C$_{10}$H$_{16}$), which then was subjected to regioselective hydroboration using dicyclohexylborane to give the required alcohol **B** in 82% yield as a mixture of diastereoisomers. In the next step, **B** was converted to the corresponding γ,δ-unsaturated acid **C** in 80% yield by Jones' oxidation.
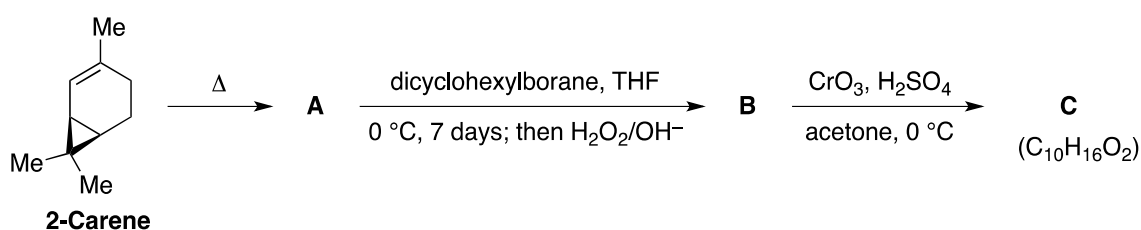
7a. <u>Draw</u> the structures (with stereochemistry) of the compounds **A-C**.

A	B	C
4 pts (2 pts if wrong stereochemistry)	4 pts	4 pts

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The acid **C** was subjected to iodolactonization using KI, I_2 in aqueous. $NaHCO_3$ solution to afford diastereomeric iodolactones **D** and **E** (which differ in stereochemistry only at C_3) in 70% yield.

$$\textbf{C} \xrightarrow[\text{48 h, dark}]{\text{I}_2,\ \text{KI, NaHCO}_3\ (\text{aq.})} \textbf{D} \quad + \quad \textbf{E}$$
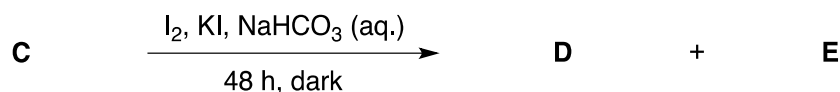
7b. <u>**Draw**</u> the structures (with stereochemistry) of the compounds **D** and **E**.

The acid **C** was converted to diastereomeric iodolactones **D** and **E** (epimeric at the chiral center C_3). Look at the number-indicated in the structure **F** in the next step.
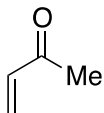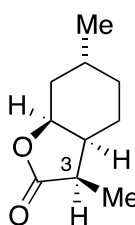
D	E
4 pts	4pts

The iodolactone **D** was subjected to an intermolecular radical reaction with ketone **X** using tris(trimethylsilyl)silane (TTMSS) and AIBN (azobisisobutyronitrile) in a catalytic amount, refluxing in toluene to yield the corresponding alkylated lactone **F** in 72% yield as a mixture of diastereoisomers which differ only in stereochemistry at C_7 along with compound **G** (~10%) and the reduced product **H**, $C_{10}H_{16}O_2$ (<5%).

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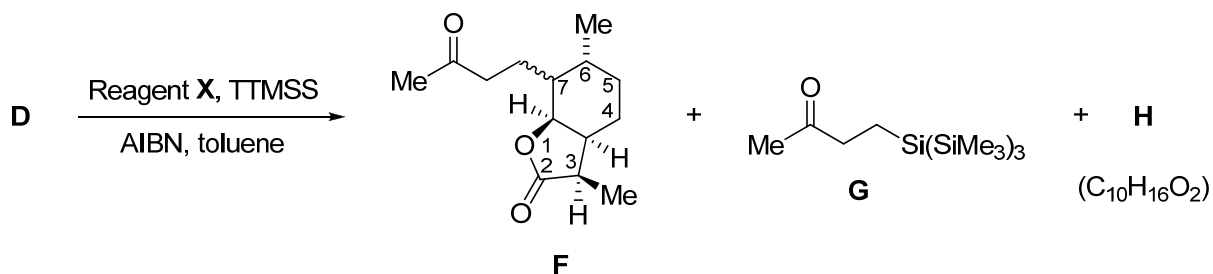
7c. Draw the structures (with stereochemistry) of compound **H** and the reagent **X**.

Because alkylated lactone **F** is known, we can deduce the reagent **X** as methyl vinyl ketone. **H** is the reduced product of **D**.

X	H
methyl vinyl ketone	
2 pts	6 pts

The keto group of **F** reacted with ethanedithiol and $BF_3 \cdot Et_2O$ in dichloromethane (DCM) at 0 °C to afford two diastereomers: thioketal lactones **I** and **J** in nearly quantitative yield (98%). The thioketalization facilitated the separation of the major isomer **J** in which the thioketal group is on the opposite face of the ring to the adjacent methyl group.

$$\mathbf{F} \xrightarrow[\text{BF}_3 \cdot \text{Et}_2\text{O, DCM, 0 °C}]{\text{HSCH}_2\text{CH}_2\text{SH}} \mathbf{I} \quad + \quad \mathbf{J}$$

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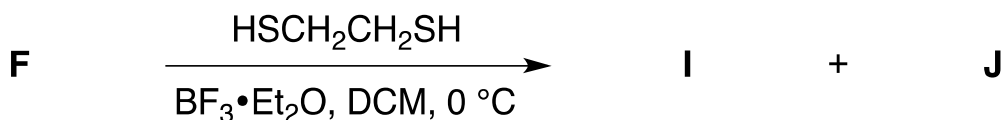
7d. Draw the structures (with stereochemistry) of the compounds **I** and **J**.

The keto group of lactone **F** reacted with ethanedithiol and BF$_3$·Et$_2$O in dichloromethane to afford thioketal lactones, **I** and the major isomer **J**.

I	J
6 pts (3 pts if **I** and **J** are swapped)	6 pts (3 pts if **I** and **J** are swapped)

The isomer **J** was further subjected to alkaline hydrolysis followed by esterification with diazomethane providing hydroxy methyl ester **K** in 50% yield. The hydroxy methyl ester **K** was transformed into the keto ester **L** using **PCC** (**P**yridium **C**hloro**C**hromate) as the oxidizing agent in dichloromethane (DCM).

A two-dimensional NMR study of the compound **L** revealed that the two protons adjacent to the newly-formed carbonyl group are *cis* to each other and confirmed the structure of **L**.

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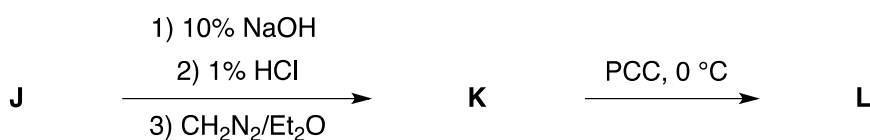
7e. Draw the structures (with stereochemistry) of the compounds **K** and **L**.

Hydrolysis followed by esterification of **J** provided hydroxy ester **K**.	
Oxidation of the hydroxy group in **K** by PCC resulted in the keto ester **L** in which two protons adjacent to the carbonyl group are cis-oriented.	

K	L
6 pts	6 pts
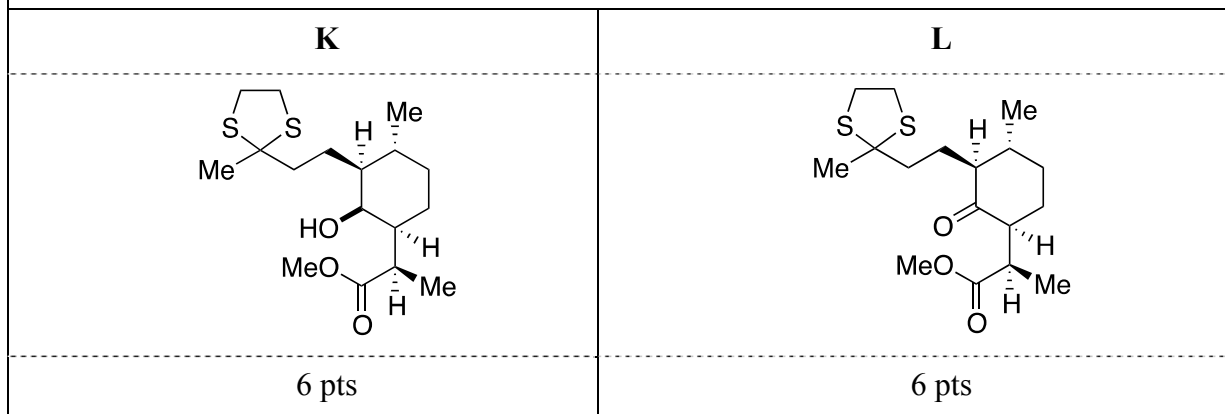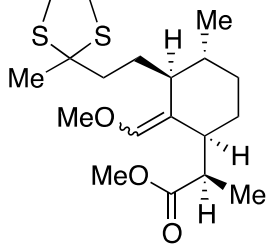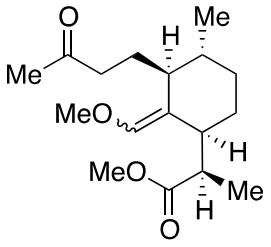
The ketone **L** was subjected to a Wittig reaction with methoxymethyl triphenylphosphonium chloride and KHMDS (**P**otassium **H**exa**M**ethyl**D**i**S**ilazid - a strong, non-nucleophilic base) to furnish the required methyl vinyl ether **M** in 45% yield. Deprotection of thioketal using $HgCl_2$, $CaCO_3$ resulted in the key intermediate **N** (80%). Finally, the compound **N** was transformed into the target molecule Artemisinin by photo-oxidation followed by acid hydrolysis with 70% $HClO_4$.

(+)-Artemisinin

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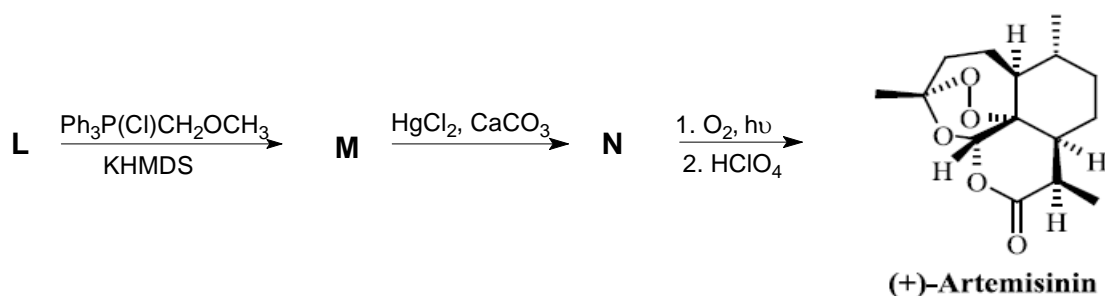
7f. <u>Draw</u> the structures (with stereochemistry) of the compounds **M** and **N**.

The Wittig reaction of the ketone **L** resulted in the formation of methyl vinyl ether **M**.

Deprotection of the thioketal group forms the intermediate **N**.

M	N
6 pts	6 pts

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Theoretical	Code:		Question	8a	8b	8c	8d	Total
Problem 8	**Examiner**		Marks	15	2	12	10	**39**
8.0% of the total			**Grade**					

Problem 8. Star Anise

Illicium verum, commonly called *Star anise*, is a small native evergreen tree grown in northeast Vietnam. *Star anise* fruit is used in traditional Vietnamese medicine. It is also a major ingredient in the making the flavour of *'phở'*, a Vietnamese favourite soup.
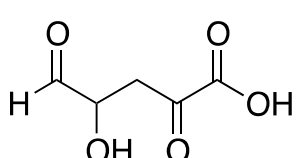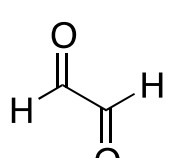
Acid **A** is isolated from the *star anise* fruit. The constitutional formula of **A** has been deduced from the following sequence of reactions:

$$A\ (C_7H_{10}O_5) \quad \xrightarrow[\text{ii) Me}_2\text{S}]{\text{i) O}_3} \quad B\ (C_7H_{10}O_7) \quad \xrightarrow[25\ °C]{CH_3OH,\ H^+} \quad C\ (C_8H_{12}O_7)$$

(I)

$$\Big\downarrow \begin{array}{c} HIO_4 \cdot 2H_2O \\ (\text{or } H_5IO_6) \end{array} \text{(II)}$$

$$Y_3 \ + \ OHCCHO \ + \ OHCCH(OH)CH_2COCOOH \xleftarrow{\ H_2O,\ H^+\ } D$$

$$Y_2 \qquad\qquad\qquad Y_1$$
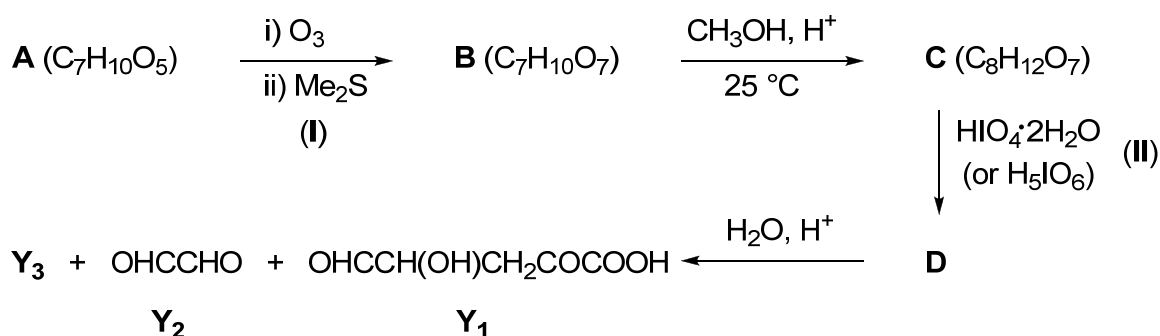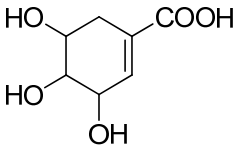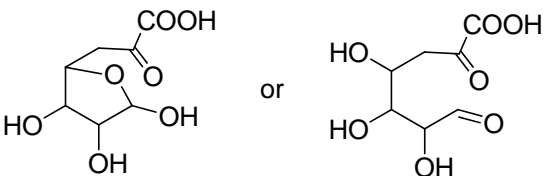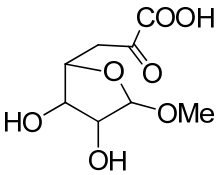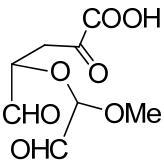
(**I**): this overall process results in alkene cleavage at the C=C bond, with each carbon of this becoming doubly bonded to an oxygen atom.

(**II**): this oxidative cleavage process of 1,2-diols breaks C(OH)–C(OH) bond and produces corresponding carbonyl compounds.

8a. Draw the structures for the compounds Y_1 and Y_2 and hence **deduce** the structure of Y_3 and **A, B, C, D**, given that in **A** there is only one ethylenic hydrogen atom.

Y_1	Y_2	Y_3
		CH$_3$OH
1pt	1 pt	2 pts

A	B
2 pts	2 pts

C	D
3 pts	4 pts

Anethole, a main component of star anise oil, is an inexpensive chemical precursor for the production of many pharmaceutical drugs.
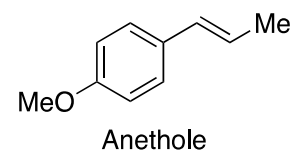
Anethole

Treating anethole with sodium nitrite in acetic acid gives a crystalline solid **E** ($C_{10}H_{10}N_2O_3$). The IR spectrum of **E** shows there is no non-aromatic C=C double bond. The ^1H NMR spectrum of **E** is given below.
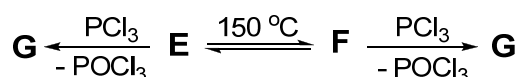
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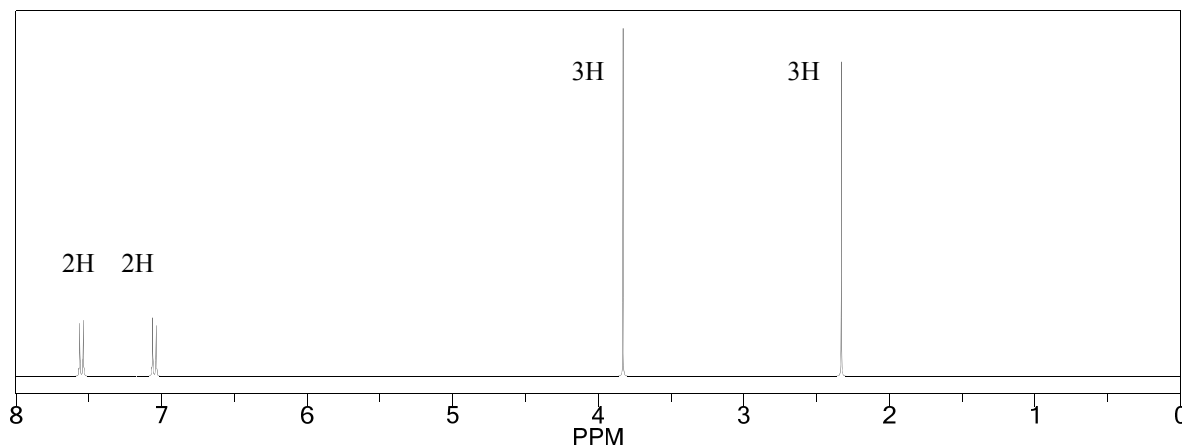
8b. <u>**What differences**</u> in the <u>structure</u> between **E** and anethole can be obtained from the ^{1}H NMR data?

    i) **E** contains a *cis*-C=C ethylenic bond while that of anethole is *trans*.

    ii) **E** cannot contain a non-aromatic C=C bond.

    iii) **E** is the adduct of anethole and N_2O_2.

    iv) **E** is the adduct of anethole and N_2O_3.

    v) **E** does not contain two *trans* ethylenic protons as anethole.

	<u>**Pick one**</u> of the above statements	
From ^{1}H NMR data	*v* [only]	2 pts
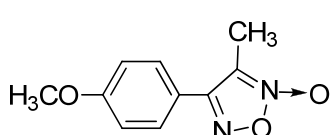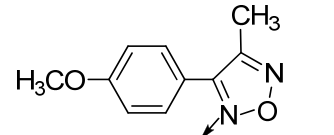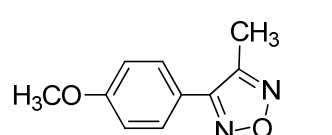
       On heating at 150 °C for several hours, **E** is partially isomerized into **F**. Under the same conditions, **F** gives the identical equilibrium mixture to that obtained from **E**. On heating with phosphorus trichloride, both **E** and **F** lose one oxygen atom giving compound **G**. Compounds **E** and **F** have the same functional groups.

$$\mathbf{G} \xleftarrow[\text{- POCl}_3]{\text{PCl}_3} \mathbf{E} \xrightleftharpoons{150\,°C} \mathbf{F} \xrightarrow[\text{- POCl}_3]{\text{PCl}_3} \mathbf{G}$$

The chemical shifts of methyl protons in **E**, **F** and **G** are given below.

	E	**F**	**G**
CH_3-O	3.8 ppm	3.8 ppm	3.8 ppm
CH_3-C	2.3 ppm	2.6 ppm	2.6 ppm

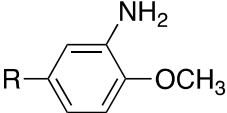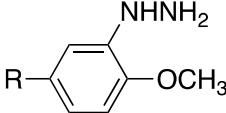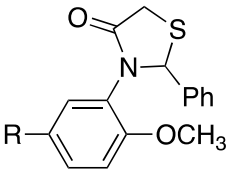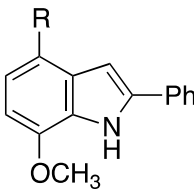**8c.** <u>**Suggest**</u> structures for **E**, **F** and **G**, assuming that they do NOT contain three-membered rings.

E	**F**	**G**
4 pts	4 pts	4 pts

A simplified structure for compound **E** is shown below; the R group does not change throughout the rest of this question. Compound **E** is nitrated and subsequently reduced with sodium dithionite to **H**. Treatment of **H** with sodium nitrite and hydrochloric acid at 0–5 °C and subsequently reduced with stannous chloride to provide **I** (R–$C_7H_9N_2O$). One-pot reaction (three component reaction) of **H**, benzaldehyde and thioglycolic acid ($HSCH_2CO_2H$) leads to the formation of **J**. Reaction of **I** and methyl phenyl ketone in the presence of $ZnCl_2$ affords **K**.


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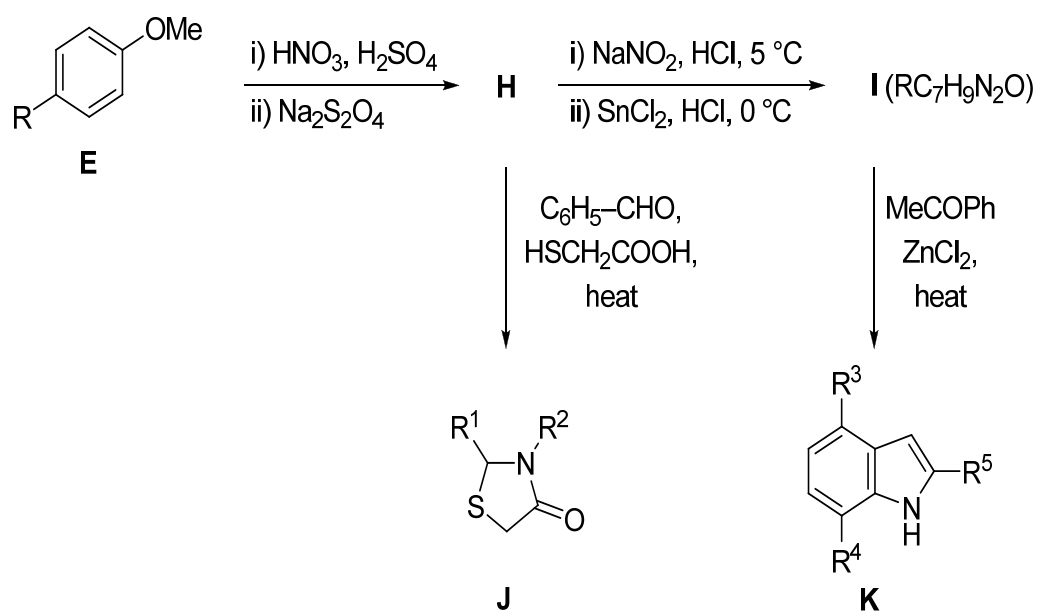
8d. <u>Give</u> the structures for **H**, **I**, **J** and **K**.

H	I
2 pts	2 pts
J	**K**
3 pts	3 pts

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| Theoretical	Code:		Question	9a	9b	9c	9d	9e	9f	Total
Problem 9	**Examiner**		Marks	8	4	6	4	2	9	33
7.5 % of the total			**Grade**							

Problem 9. Heterocycle Preparation

Tetramethylthiurame disulfide (**TMTD**) is emerging as a useful reagent to prepare many sulfur-nitrogen functional groups and heterocycles in organic chemistry. The reactions of **TMTD** with primary amines, as well some corresponding post-transformations of the resulting product(s) are presented in the following schemes:
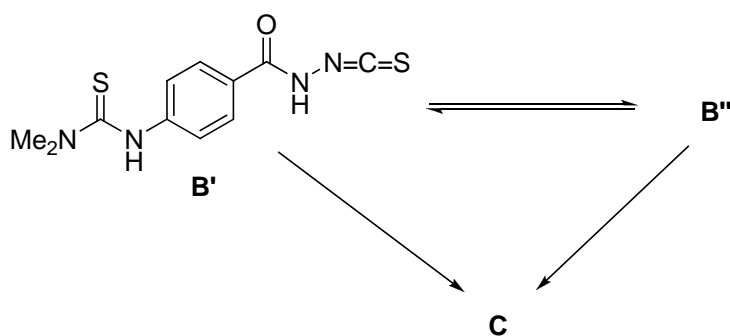

(1)

(2)

(3)

(4)

(5)
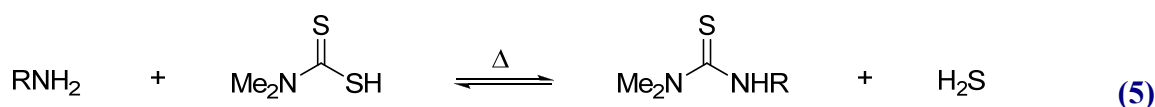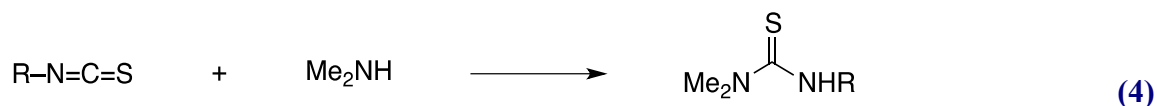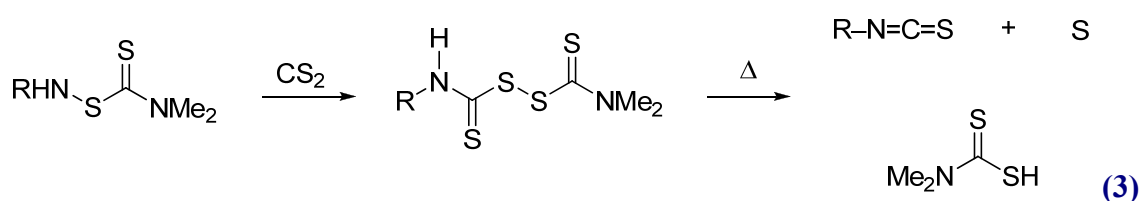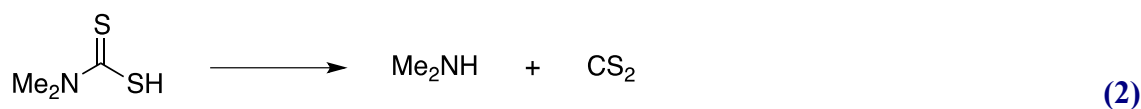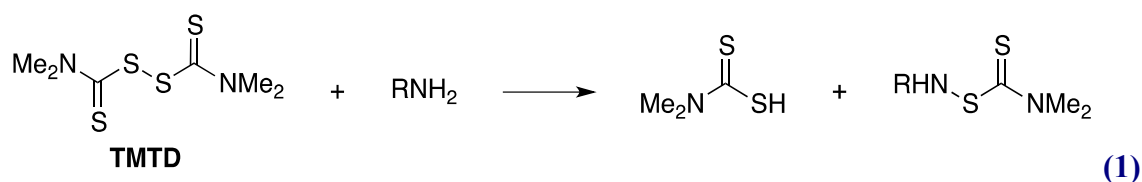
Similar transformations of benzohydrazides (containing nucleophilic NH_2 group) and **TMTD** have been observed.

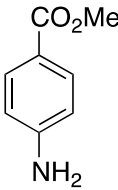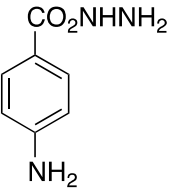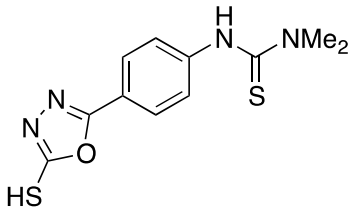The 46th IChO – Theoretical Examination. Official English Version

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In the synthetic scheme below, the thiocarbamoylation reaction of an aroyl hydrazine with **TMTD** produces compound **C** containing a heterocyclic moiety from *p*-aminobenzoic acid.
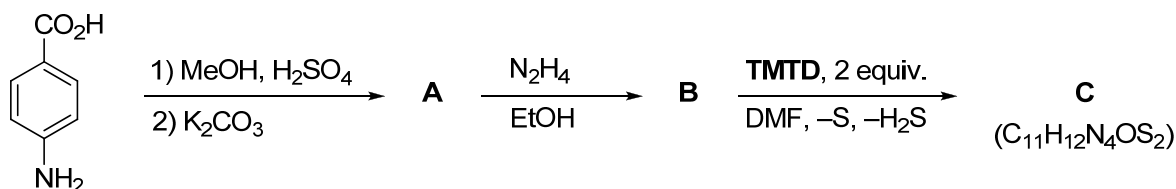
During the formation of **C** from **B**, an intermediate **B'** was observed. This intermediate tautomerizes to **B''**. **C** can be formed from **B'** or **B''**.

9a. **Give** the structures of **A**, **B**, and **C**.

A	B	C
CO₂Me structure with NH₂	CO₂NHNH₂ structure with NH₂	heterocyclic structure, **C**: $C_{11}H_{12}N_4OS_2$
2 pts	2 pts	4 pts

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9b. <u>Suggest</u> a structure for the tautomer **B''** and **give a curly-arrow mechanism** for the formation of **C**.

4 pts
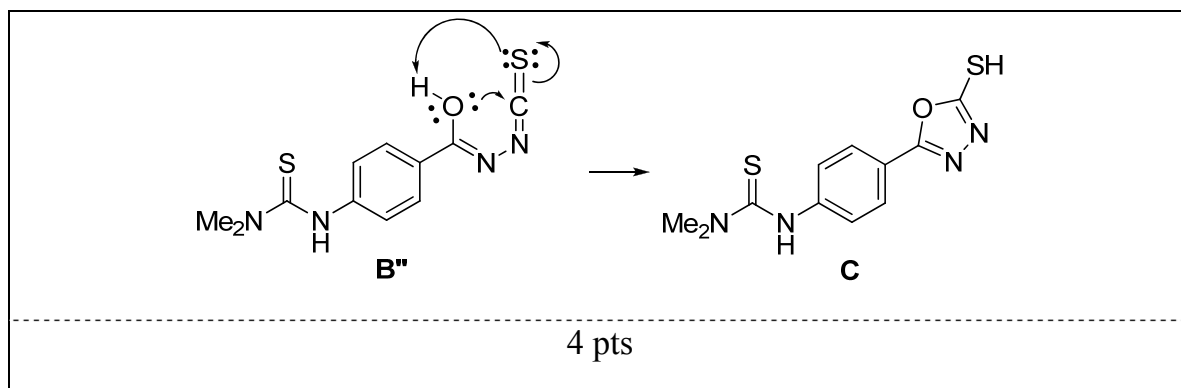
Compound **C** was then converted to **F** by the following pathway:
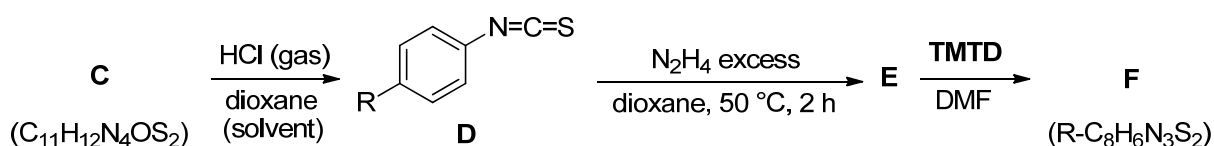
[The group R remains exactly the same throughout the rest of the question.]

9c. <u>Draw</u> the structures of **E**, and **F**. (You do not need to draw the structure for the R group from this point)

E	F
2 pts	4 pts
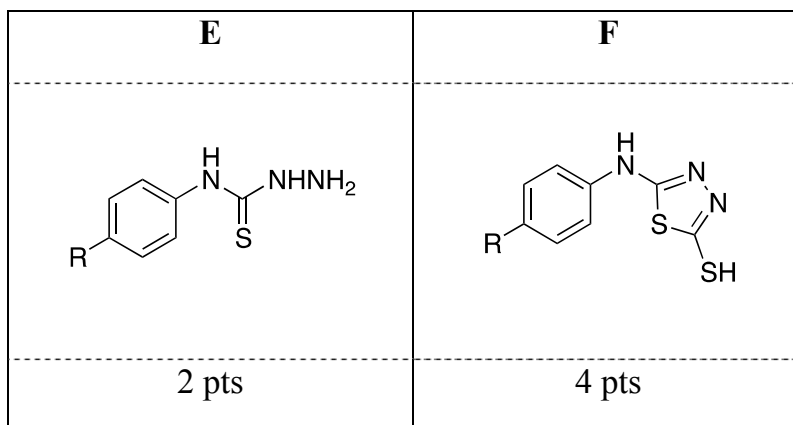
E was only obtained when **D** was slowly added to the solution of excess N_2H_4 in dioxane. If N_2H_4 was added to the solution of **D** in dioxane instead, a major side product **D'** ($R_2C_{14}H_{12}N_4S_2$) was formed.

9d. <u>Give</u> the structure of **D'**.

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D': $R_2C_{14}H_{12}N_4S_2$
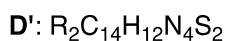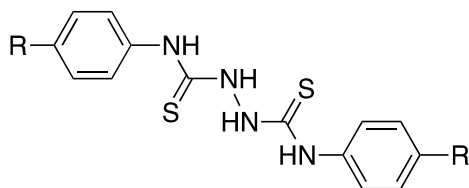
4 pts

Slightly heating **D** with ethanolamine ($HOCH_2CH_2NH_2$) in dioxane for 2 hours yielded **G** ($R–C_9H_{11}N_2OS$).

9e. Draw the structural formula of **G**.

G
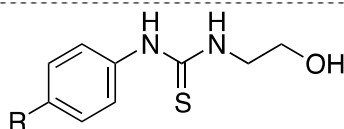
2 pts

9f. Heating **G** in the presence of *p*-toluenesulfonic acid as the catalyst could form a number of different five-membered heterocyclic products.

i) **Draw** 2 structures that have different molecular formulae.
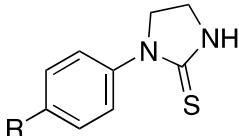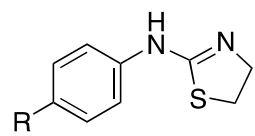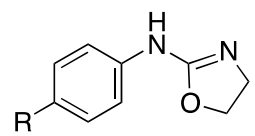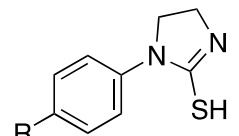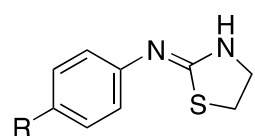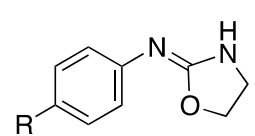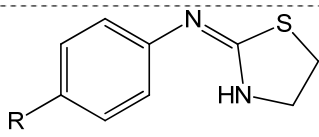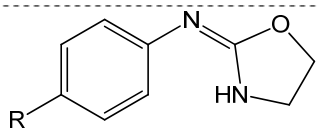
Eg H1	H3
(3 pts)	

ii) **Draw** 2 structures that are constitutional isomers. (3 pts)

E.g H1	H5
(3 pts)	

iii) <u>**Draw**</u> 2 structures that are stereoisomers. (3 pts)

E.g H5	H7
(3 pts)	

H_1	H_2	H_3
2 pts	2 pts	2 pts
H_4	H_5	H_6
2 pts	2 pts	2 pts
	H_7	H_8
	2 pts	2 pts

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Periodic Table of the Elements

1																	18
1 **H** 1.008	**2**											**13**	**14**	**15**	**16**	**17**	**2** **He** 4.003
3 **Li** 6.941	**4** **Be** 9.012	Transition Elements										**5** **B** 10.81	**6** **C** 12.01	**7** **N** 14.01	**8** **O** 16.00	**9** **F** 19.00	**10** **Ne** 20.18
11 **Na** 22.99	**12** **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13** **Al** 26.98	**14** **Si** 28.09	**15** **P** 30.98	**16** **S** 32.07	**17** **Cl** 35.45	**18** **Ar** 39.95
19 **K** 39.10	**20** **Ca** 40.08	**21** **Sc** 44.96	**22** **Ti** 47.87	**23** **V** 50.94	**24** **Cr** 52.00	**25** **Mn** 54.94	**26** **Fe** 55.85	**27** **Co** 58.93	**28** **Ni** 58.69	**29** **Cu** 63.55	**30** **Zn** 65.41	**31** **Ga** 69.72	**32** **Ge** 72.61	**33** **As** 74.92	**34** **Se** 78.96	**35** **Br** 79.90	**36** **Kr** 83.80
37 **Rb** 85.47	**38** **Sr** 87.62	**39** **Y** 88.91	**40** **Zr** 91.22	**41** **Nb** 92.91	**42** **Mo** 95.94	**43** **Tc** (97.9)	**44** **Ru** 101.1	**45** **Rh** 102.9	**46** **Pd** 106.4	**47** **Ag** 107.9	**48** **Cd** 112.4	**49** **In** 114.8	**50** **Sn** 118.7	**51** **Sb** 121.8	**52** **Te** 127.6	**53** **I** 126.9	**54** **Xe** 131.3
55 **Cs** 132.9	**56** **Ba** 137.3	**57** **La** 138.9	**72** **Hf** 178.5	**73** **Ta** 180.9	**74** **W** 183.8	**75** **Re** 186.2	**76** **Os** 190.2	**77** **Ir** 192.2	**78** **Pt** 195.1	**79** **Au** 197.0	**80** **Hg** 200.6	**81** **Tl** 204.4	**82** **Pb** 207.2	**83** **Bi** 209.0	**84** **Po** (209.0)	**85** **At** (210.0)	**86** **Rn** (222.0)
87 **Fr** (223.0)	**88** **Ra** (226.0)	**89** **Ac** (227.0)	**104** **Rf** (261.1)	**105** **Db** (262.1)	**106** **Sg** (263.1)	**107** **Bh** (262.1)	**108** **Hs** (265)	**109** **Mt** (266)	**110** **Ds** (271)	**111** **Rg** (272)	**112** **Cn** (285)	**113** **Uut** (284)	**114** **Fl** (289)	**115** **Uup** (288)	**116** **Lv** (292)	**117** **Uus** (294)	**118** **Uuo** (294)

6 Lanthanides

58 **Ce** 140.1	**59** **Pr** 140.9	**60** **Nd** 144.2	**61** **Pm** (144.9)	**62** **Sm** 150.4	**63** **Eu** 152.0	**64** **Gd** 157.3	**65** **Tb** 158.9	**66** **Dy** 162.5	**67** **Ho** 164.9	**68** **Er** 167.3	**69** **Tm** 168.9	**70** **Yb** 173.0	**71** **Lu** 174.0

7 Actinides

90 **Th** 232.0	**91** **Pa** 231.0	**92** **U** 238.0	**93** **Np** (237.1)	**94** **Pu** (244.1)	**95** **Am** (243.1)	**96** **Cm** (247.1)	**97** **Bk** (247.1)	**98** **Cf** (251.1)	**99** **Es** (252.1)	**100** **Fm** (257.1)	**101** **Md** (258.1)	**102** **No** (259.1)	**103** **Lr** (260.1)

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