THE CANADIAN CHEMISTRY CONTEST 2022
for high school and CEGEP students

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2022

(120 minutes)

This segment has five (5) questions. While students are expected to attempt **all** questions for a complete examination in 2 hours, it is recognized that backgrounds will vary and **students will not be eliminated from further competition because they have missed parts of the paper.**

Your answers are to be written in the spaces provided on this paper. All of the paper, is to be returned **immediately** by upload.

— PLEASE READ —

1. BE SURE TO COMPLETE THE INFORMATION REQUESTED AT THE BOTTOM OF THIS PAGE BEFORE BEGINNING PART C OF THE EXAMINATION.
2. STUDENTS ARE EXPECTED TO ATTEMPT ALL QUESTIONS OF **PART A** AND **PART C**. CREDITABLE WORK ON A LIMITED NUMBER OF THE QUESTIONS MAY BE SUFFICIENT TO EARN AN INVITATION TO THE NEXT LEVEL OF THE SELECTION PROCESS.
3. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.
4. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.
5. PART A DATASHEET IS THE ONLY DATASHEET THAT MAY BE USED ON THIS EXAMINATION.

PART A ( ) Correct Answers

25 x 1.6 = ... /040

PART C

1. .... /012
2. .... /012
3. .... /012
4. .... /012
5. .... /012

TOTAL .... /100

Name ________________________________ School ________________________________
(LAST NAME, Given Name; Print Clearly)

City & Province ________________________________ Date of Birth ____________________

E-Mail ________________________________ Home Telephone (   ) - ____________________

Years at a Canadian high school ___ No. of chemistry courses at a Québec CÉGEP ___

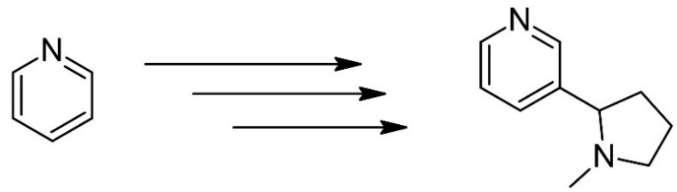
Male ☐ Canadian Citizen ☐ Landed Immigrant ☐ Visa Student ☐

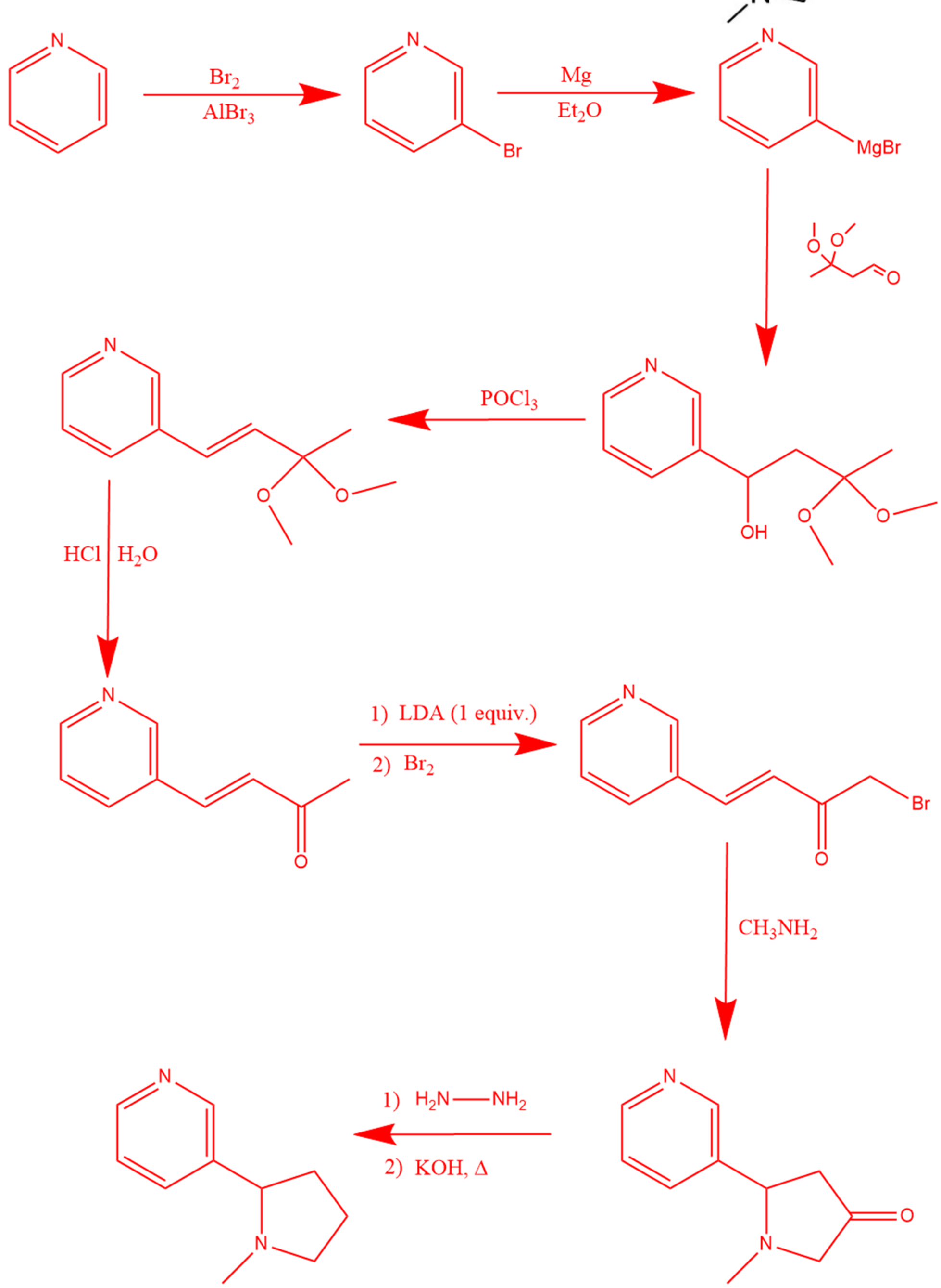
Female ☐ Passport valid until February 2023 ☐ Nationality of Passport ____________

Teacher ____________________________ Teacher E-Mail ____________________________

1. ORGANIC CHEMISTRY

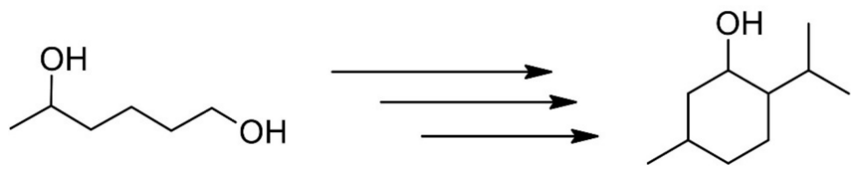
a) Starting with pyridine and any non-cyclic organic reagents with 6 or less carbon atoms, devise a synthesis of nicotine without stereochemistry. You may use any inorganic reagents you wish. Clearly draw the entire scheme containing reagents and intermediates. ***6 marks***



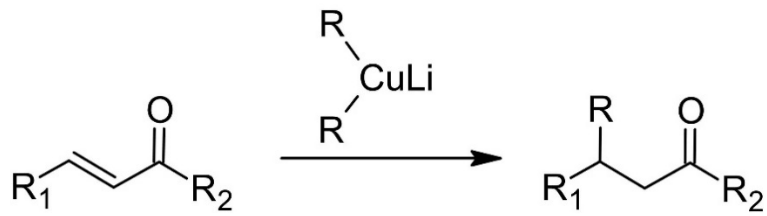


Official answer (other correct answers may also be accepted)

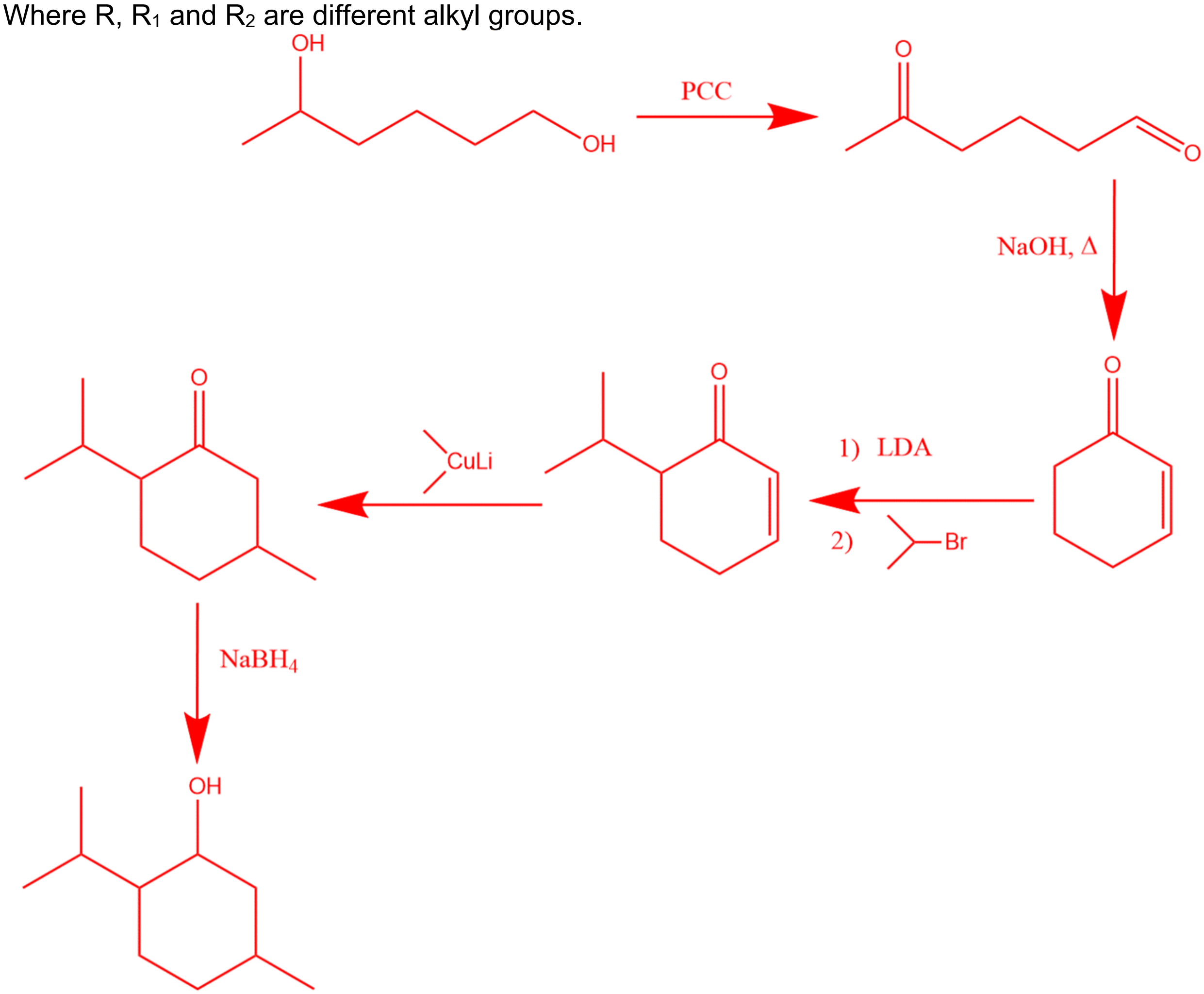
b) Starting with hexan-1,5-diol and any organic and inorganic reagents you wish, devise a synthesis of menthol without stereochemistry. Clearly draw the entire scheme containing reagents and intermediates. ***4 marks***



Hint: here's a reaction that may be useful; a **gilman** reagent is a lithium dialkyl cuprate salt that can perform conjugate addition reactions like so:

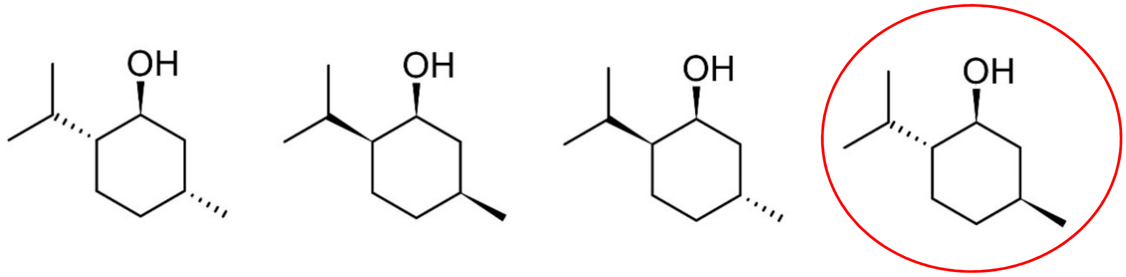


Where R, R_1 and R_2 are different alkyl groups.



Official answer (other correct answers may also be accepted)

c) The following structures are all stereoisomers of menthol. Assuming that all these structures are in their most stable conformations, circle the most stable stereoisomer. ***2 marks***



2. ANALYTICAL CHEMISTRY

Colorless crystal **A** undergoes a thermal decomposition reaction to produce two gases **B** and **C**. When gas **B** is further heated to a higher temperature and then cooled down to the original temperature, the volume the gases increase by 50%. Although **A** is commonly used in agriculture as a fertilizer, it nevertheless is an oxidizing agent. **A** dissolve easily in water and causes the temperature of the solution to decrease noticeably and the resulting solution is slightly acidic (pH between 4.5 and 5.0). Heating equal moles of **A** and solid NaOH produces a gas **D** with unpleasant odor and a white solid **E**. When gas **D** is introduced into a AgNO3 solution, a dark brown solid **F** is formed. However, when gas **D** is continuously introduced, a colorless solution is obtained. Heating solid **E** produces colorless gas **G** which is essential for combustion reaction and a white solid **H**. When **H** is treated with concentrated nitric acid, a brown color gas is evolved.

a) Based on information given, please identify **A, B, C, D, E, F, G** and **H**.
4 marks **(0.5 each)**

A: NH_4NO_3 **B:** N_2O **C:** H_2O

D: NH_3 **E:** $NaNO_3$ **F:** Ag_2O

G: O_2 **H:** $NaNO_2$

b) Write the chemical reaction equations for the following
4 marks **(0.6 each, 0.4 last question)**

Reaction to produce **B** & **C**

$NH_4NO_3(s) \rightarrow N_2O(g) + H_2O(g)$

Reaction for heating **B** to increase the volume by 50%

$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

Reaction to produce **D** & **E**

$NH_4NO_3(s) + NaOH(s) \rightarrow NH_3(g) + NaNO_3(s) + H_2O(g)$

Reaction to produce **F**

$2Ag^+(aq) + 2NH_3(g) + H_2O(l) \rightarrow Ag_2O(s) + 2NH_4^+(aq)$

Reaction of **F** to produce the colorless solution

$2Ag_2O(s) + 4NH_3(aq) + H_2O(l) \rightarrow 2[Ag(NH_3)_2]^+ + 2OH^-(aq)$

Reaction of **E** to produce **G** and **H**

$2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$

Reaction of **H** to produce the brown color gas

$NaNO_2(s) + 2HNO_3(aq, concentrated) \rightarrow NO_2(g) + 2NaNO_3(aq) + NO(g) + H_2O(l)$

Leucine $(CH_3)_2CHCH_2CH(NH_2)COOH$ is on the top list of essential amino acids for human body. Leucine contains a carboxylic acid functional group and an amine functional group and has a pK_a = 2.36 and pK_b = 4.40. Leucine has been used in the food industry and as healthy supplement.

c) Using your knowledge of Charge Balance and/or Mass Balance, calculate the pH of a 0.100M aqueous Leucine solution. Show your detailed work to earn full marks.
2.5 marks

Leucine will dissolve and form Zwitterion $(CH_3)_2CHCH_2CH(NH_3^+)COO^-$

Charge balance

$[A^-] + [OH^-] = [A^+] + [H^+]$ (**1.0** point)

$Ka = [A^-][H^+] / [A]$

$[A^-] = Ka[A] / [H^+]$

$Kb = [A^+][OH^-] / [A]$

$[A^+] = Kb[A] / [OH^-]$

Approximation

Since $[A^+] >> [H^+]$ and $[A^-] >> [OH^-]$

$\mathbf{[A^+] \approx [A^-]}$ (**0.5** points)

$Kb[A] / [OH^-] = Ka[A] / [H^+]$

$Kb[A][H+] / kw = Ka[A] / [H^+]$

$[H^+]^2 = Ka[A] * Kw / Kb[A]$

$\mathbf{[H^+] = (Ka * Kw / Kb)^{1/2}}$ (**0.5** points)

pH = 5.98 (**0.5** points)

Any correct final pH value within an error of ±0.02 will get **0.5** points.

In a lab, there are 0.100M NaOH, 0,120M HCl, oxalic acid primary standard ($H_2C_2O_4 \cdot 2H_2O$, 126.07g/mol), Potassium Hydrogenphthalate primary standard ($KHC_8H_4O_4$, 204.22 g/mol), Tris(hydroxymethyl)-aminomethane primary standard (**Tris.** $(HOCH_2)_3CNH_2$, kb = 1.15×10^{-6}, 121.14g/mol), Sodium Carbonate primary standard (Na_2CO_3, 155.99g/mol), and three indictors, Phenolphthalein ($pK_a = 9.4$), methyl orange ($pK_a = 3.4$) and methyl red ($pK_a = 4.95$).

d) The purity of Leucine, which is going to be used in making dietary supplement, is to be determined by titration. A 2.000g of Leucine is taken to make a 250.00mL aqueous solution. Which of the afore listed chemicals would you use as the titrant? Which would you use as the indicator?
0.5 mark

Since the solution is acidic, so **NaOH** would be chosen as the titrant and **Phenolphthalein** would be chosen as the indicator.

(0.25 points for each correct answer)

e) Which of the primary standards would you use to standardize your titrant?
0.5 mark

To standardize NaOH, either **Oxalic Acid** primary standard or **Potassium Hydrogenphthalate** primary standard will be chosen.

(either one gets full points)

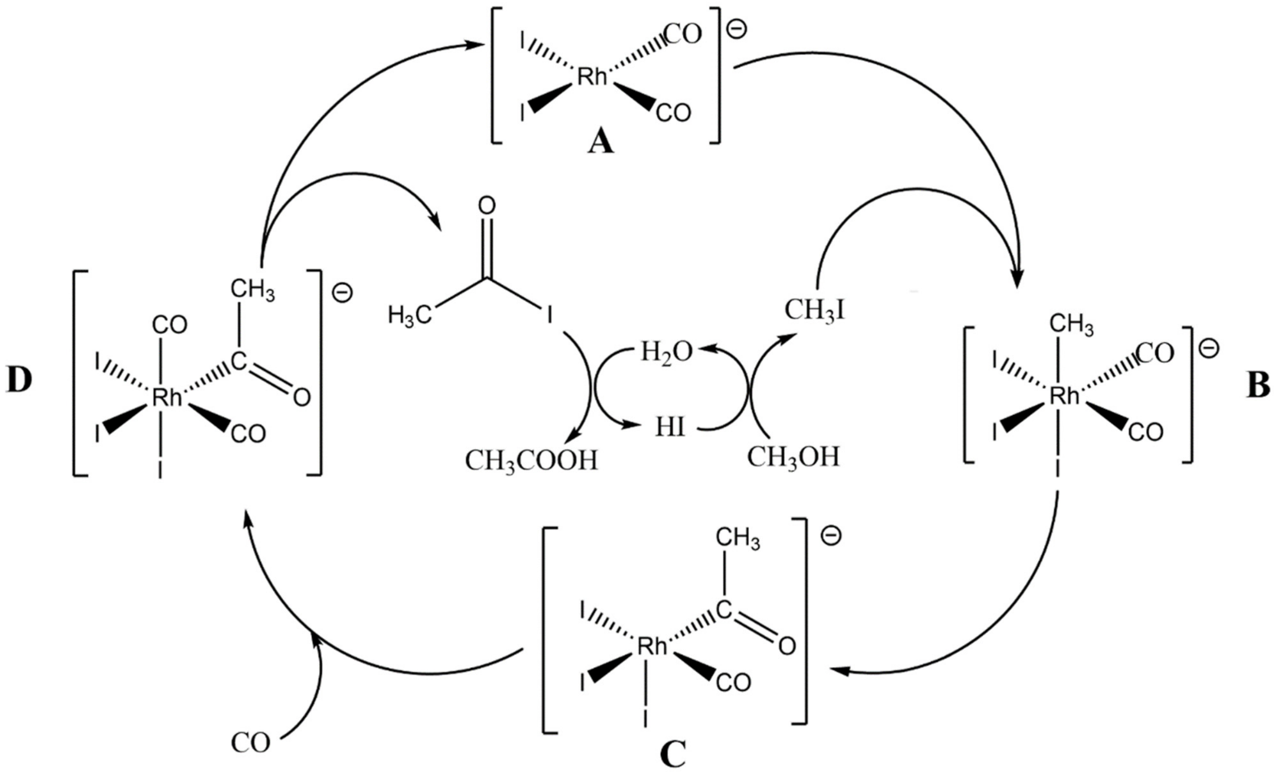
f) If 14.94mL of the titrant is required to reach the equivalence point for a 25.00mL aliquot of the analyte, what is the purity of the Leucine sample?
0.5 mark

0.01494 * 0.100 * 10 *131.17 / 2.000 = **97.98%**

(97.48 ~ 98.48% gets full points)

3. INORGANIC CHEMISTRY

The Monsanto process is a famous industrial catalytic cycle. The process is presented below:



Please answer the following questions pertaining to the Monsanto process:

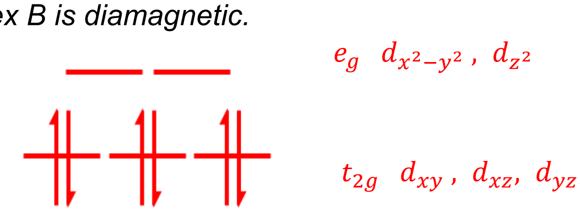
a) Write the *overall* balanced equation for the Monsanto process.
1 mark

$CH_3OH + CO \rightarrow CH_3COOH$

b) For complex A, state which of its ligands are weak field and which are strong field, and also state whether the complex is a cis or trans isomer.
1 mark

iodide is weak field and CO is strong field (0.25 points each). The complex is in cis conformation (0.5 points).

c) For complex B, draw its crystal field splitting diagram, making sure to fill in the electrons and label each d orbital. *Hint: complex B is diamagnetic.*
2 marks



This is just a typical low spin octahedral CFT diagram, with 6 electrons filling the t_{2g} set. 1 point for the d-orbital splitting, 0.5 points for labelling the orbitals correctly, and 0.5 points for filling in the electrons properly.

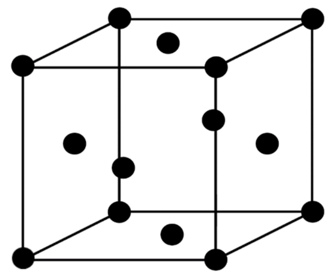
d) For complex C, state its geometry and coordination number.
1 mark

the geometry is square pyramidal (0.5 points) and the coordination number is 5 (0.5 points).

e) For complex D, state the metal's oxidation state and d-electron count.
1 mark

the oxidation state is +3 (0.5 points) and the d-electron count is 6 (0.5 points).

Rhodium, the metal used in the Monsanto process, crystallizes into the face centered cubic structure as shown below:



The lattice parameter (unit cell length) of the crystal is 0.380 nm.

f) State the number of atoms present in the unit cell.
0.5 mark 4

g) State the coordination number of Rh in the crystal.
0.5 mark 12

h) Calculate the density of Rh in g cm^{-3}.
2 marks

mass/volume: $(4 \times 102.9)/(6.02214 \times 10^{23} \times (0.380 \times 10^{-7})^3) = 12.5$ g cm^{-3}
1 point for general mass/volume expression, 0.5 points for correct answer, 0.5 points for correct units.

i) Calculate the volume of empty space in the unit cell of Rh in nm^3.
Hint: the volume of a sphere with radius r is given by: $V = \frac{4}{3}\pi r^3$
3 marks

Rh atomic radius = $0.380 \times \sqrt{2}/4 = 0.134$ nm (1.5 points)

volume occupied by atoms: $4 \times \frac{4}{3}\pi \times 0.134^3 = 0.0406$ nm^3 (0.5 points)

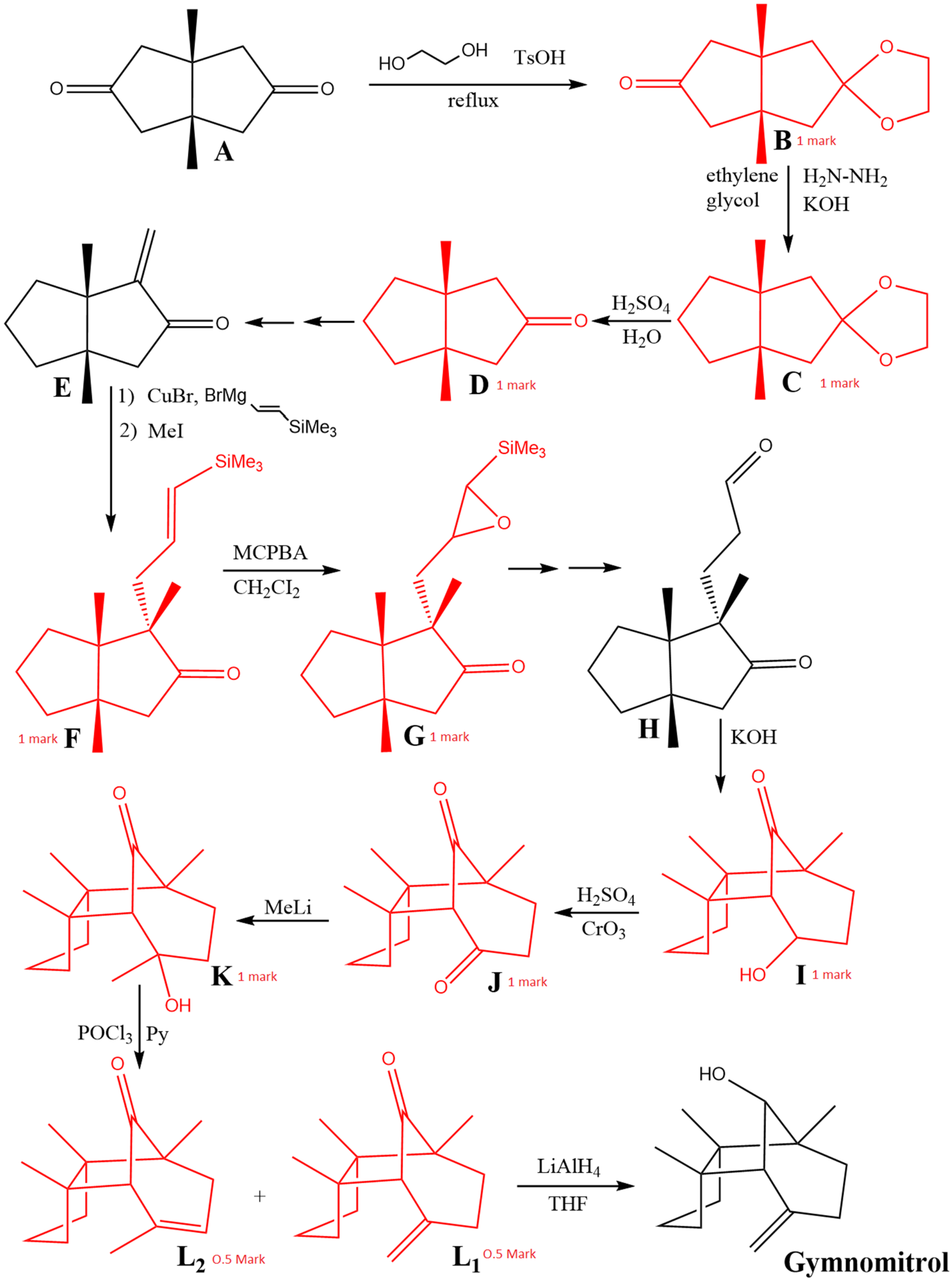
volume of unit cell: $0.380^3 = 0.0549$ nm^3 (0.5 points)

volume of empty space: $0.0549 - 0.0406 = 0.0143$ nm^3 (0.5 points)

4. ORGANIC CHEMISTRY and NMR spectroscopy

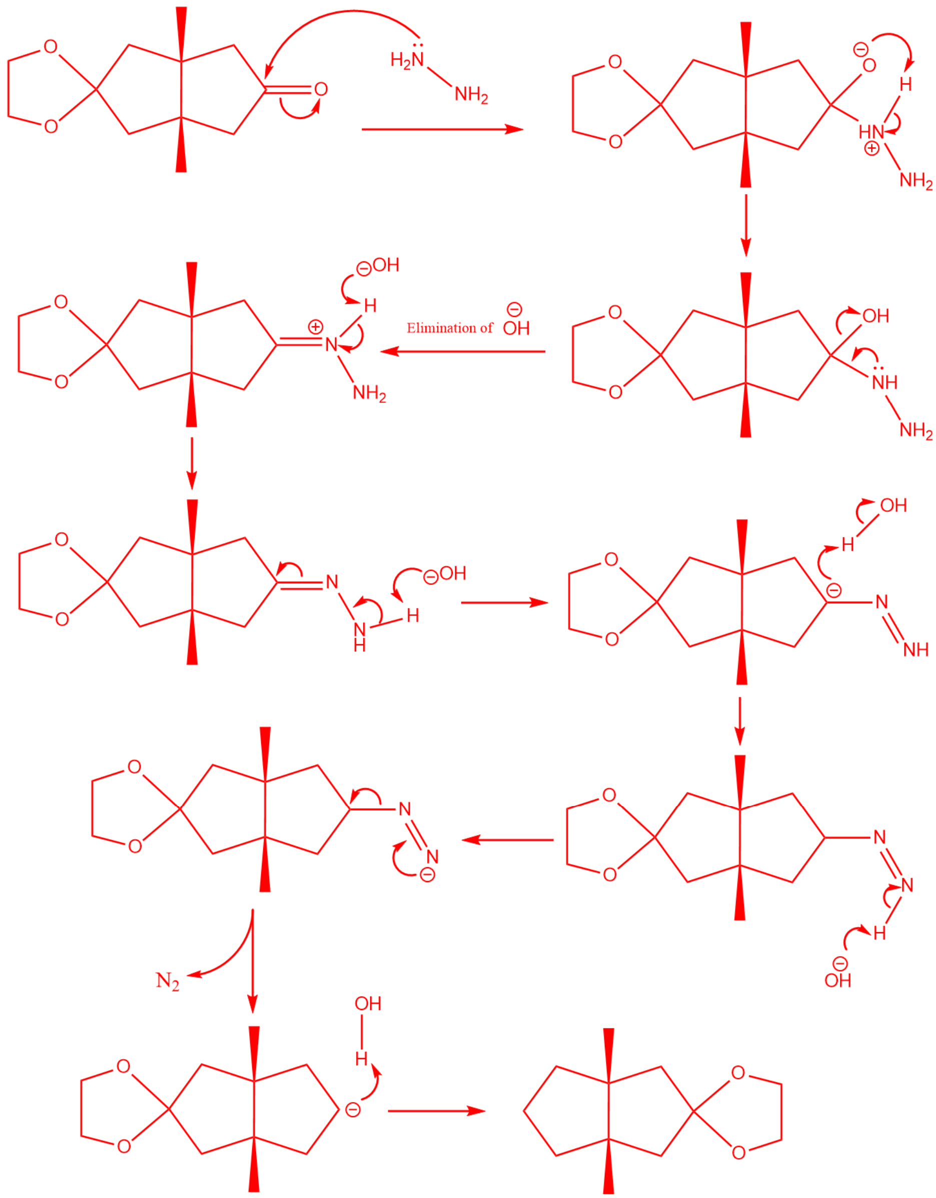
a) The total synthesis of **Gymnomitrol** combines a wide variety of synthesis techniques. In step 1, only one side is reacted. Over the reaction sequence, a Michael addition and enolate attack are performed consecutively. Later in the sequence, an aldol addition is used to further cyclize the molecule. Given starting compound A and the following reaction sequence, identify compounds **C, D, F, G, I, J** and **K.** Structures **L_1** and **L_2** are both possible products from precursor **K**. **<u>Draw</u>** them both and note which one reacts to form Gymnomitrol.

9 marks



b) Step 2 in the synthesis of **Gymnomitrol** is known as a Wolff-Kishner Reduction. **Draw** the complete reaction mechanism.

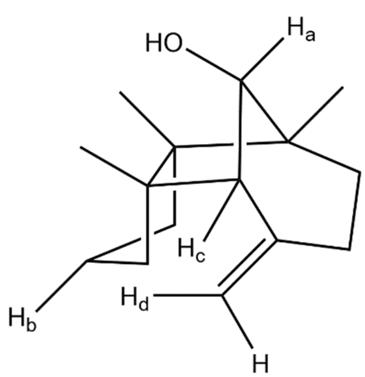
1 mark



1 point; 0.5 points for hydrazone formation, 0.5 points for deprotonation and condensation

c) The selected hydrogen atoms all appear in the condensed H-NMR spectrum. **Fill in the table** with the hydrogen atoms' corresponding H-NMR peaks.

2 marks



Gymnomitrol

Chemical shift options for peaks:
5.00, 3.72, 1.65 and 2.53 ppm

Hydrogen atom	Chemical shift of peak (ppm)
a.	3.72
b.	1.65
c.	2.53
d.	5.00

5. PHYSICAL CHEMISTRY

The following 2nd-order reaction: $A(g) \rightarrow 2B(g)$ was carried out at T = 27 °C in a reaction vessel of constant volume. At the beginning of the reaction, only A(g) at P = 1 atm was present. After 100 minutes of reaction, the total pressure P in the vessel reaches 1.5 atm. Assume that both A(g) and B(g) are ideal gases.

a) Determine the half-life $t_{1/2}$ and the rate constant k of the reaction at 27 °C. State your units in atmosphere and minutes.

3 marks

	A	→	2B	P
I	1 atm		0	1 atm
C	-x		+2x	+0.5
E	1-x		2x	1.5 atm

$1 - x + 2x = 1.5$
$1 + x = 1.5$
$x = 0.5\ atm$
$P_A(100\ min) = 1 - 0.5 = 0.5\ atm$

Or:

$P_B = 2(1 - P_A)$
$P_A + P_B = 1.5 \Rightarrow$
$P_A + 2(1 - P_A) = 1.5\ atm\ at\ 100\ min$
$P_A + 2 - 2P_A = 1.5$
$2 - 1.5 = P_A$
$P_A(100\ min) = 0.5\ atm$

1 mark

$P_A(100\ min) = 0.5 \times P_A(0\ min) \Longrightarrow$
$t_{\frac{1}{2}} = 100\ min$

1 mark

$$2^{nd}\ order\ k = \frac{1}{t_{\frac{1}{2}} P_A(0\ min)} = \frac{1}{100 \times 1} = 0.01\ atm^{-1} min^{-1}$$

1 mark

Remove 0.5 mark for missing or wrong units

b) Give the rate constant k using moles, litres and seconds for the units.

1 mark

$$[A]_0 = \frac{n}{V} = \frac{P_A(0\ min)}{RT} = \frac{1}{0.08206 \times 300} = 0.0406 \frac{mol}{L}$$

$$or \quad = \frac{101325}{8.314 \times 300 \times 1000 L/m^3} = 0.0406 \frac{mol}{L}$$

$$t_{\frac{1}{2}} = 100\ min = 6000\ s$$

$$k = \frac{1}{t_{\frac{1}{2}}[A]_0} = \frac{1}{6000 \times 0.0406} = 4.1 \times 10^{-3}\ mol^{-1} L s^{-1}\ \ or\ 0.0041\ mol^{-1} L s^{-1}$$

Remove 0.5 mark for missing or wrong units

Consider a closed container of fixed size in contact with its surroundings maintained at a temperature of 298 K. The inside of this container is partitioned by a frictionless, movable wall into two compartments labeled 1 and 2, with initial volumes of $V_1 = 5L$ and $V_2 = 1L$, respectively. In compartment 1, there is a gaseous equilibrium mixture of molecules A and B with a total pressure of 1 atm. In compartment 2, there is a gas of only compound C also with a pressure of 1 atm. A piece of metal catalyst of negligible volume is then introduced into compartment 2 which causes gas C to decompose into gaseous product D in an equilibrium reaction. This pushes the wall against compartment 1, which increases V_2 and decreases V_1, also shifting the $A \rightleftharpoons B$ equilibrium as according to Le Chatelier's principle. The wall is pushed until the reactions in both compartments reach a new state of equilibrium. The standard changes in Gibbs free energies for the two equilibria are:

$$A(g) \rightleftharpoons 2B(g) \quad \Delta G_1^o = -5.183\ kJ/mol$$
$$C(g) \rightleftharpoons 3D(g) \quad \Delta G_2^o = -5.636\ kJ/mol$$

Assume all gases are ideal.

c) Calculate the initial number of moles for C.
1 mark

$$n = \frac{PV}{RT} = \frac{1 \times 1}{0.08206 \times 298} = 0.0409\ mol$$

$$or \ = \frac{101325 \times 0.001}{8.3145 \times 298} = 0.0409\ mol$$

Remove 0.5 mark for missing or wrong units

d) Calculate the equilibrium constant for reaction 1 and 2.
1 mark

$$\Delta G^o = -RTln(K) \Rightarrow \ln(K) = \frac{-\Delta G^o}{RT} \Longrightarrow$$

$$K_1 = e^{-\frac{\Delta G_1^o}{RT}} = e^{\frac{5183}{8.3145 \times 298}} = 8.10$$ 0.5 mark

$$K_2 = e^{-\frac{\Delta G_2^o}{RT}} = e^{\frac{5636}{8.3145 \times 298}} = 9.72$$ 0.5 mark

e) Calculate the initial number of moles for A and B.
2 marks

$$K_1 = \frac{P_B^2}{P_A} = 8.1 \quad and \quad P_B + P_A = 1\ atm$$

$$\frac{P_B^2}{P_A} = \frac{P_B^2}{1 - P_B} = 8.1 \quad \Longrightarrow \quad P_B^2 = 8.1 - 8.1P_B \Longrightarrow P_B^2 + 8.1P_B - 8.1 = 0$$

$$use\ quadratic\ equation\ to\ solve\ with\ \ a = 1, b = 8.1\ and\ c = -8.1$$

$$\sqrt{b^2 - 4ac} = 9.9\ the\ solution\ is{:}\ P_B = \frac{-8.1 + 9.9}{2} = 0.9\ atm$$

(The other root gives a negative pressure.)

$$P_A = 1 - 0.9 = 0.1\ atm$$

$$n = \frac{PV}{RT}$$

$$n_A = \frac{P_A V}{RT} = \frac{0.1 \times 5}{0.08206 \times 298} = 0.0204\ mol \quad or \quad \frac{0.1 \times 101325 \times 0.005}{8.3145 \times 298} = 0.0204\ mol$$

$$n_B = \frac{P_B V}{RT} = \frac{0.9 \times 5}{0.08206 \times 298} = 0.184\ mol \quad or \quad \frac{0.9 \times 101325 \times 0.005}{8.3145 \times 298} = 0.184\ mol$$

Remove 0.5 mark for missing or wrong units

We know that V_2 will increase and V_1 will decrease. To get a better idea of how the system may evolve we can define V_{max}, the maximum volume of compartment 2 and V_{min} the minimum volume of compartment 1. To answer f) and g) assume that both compartments are independent from one another and the sum of their volumes is not restricted.

f) Calculate the value of V_{max}, the maximum volume of compartment 2 at 1 atm.
1 mark

$$Initial\ moles\ of\ C, n_C = 0.0409\ mol$$

$$C \rightarrow 3D\ , therefore\ if\ the\ reaction\ is\ complete\ n_D = 3n_C = 3 \times 0.0409 = 0.1227\ mol$$

$$V_{max} = \frac{n_D RT}{P}$$

$$at\ 1\ atm\ and\ 298\ K, \qquad V_{max} = \frac{0.1227 \times 0.08206 \times 298}{1} = 3\ L$$

g) Calculate the value of V_{min}, the minimum volume of compartment 1 at 1 atm.
1 mark

$$Initial\ moles\ of\ A\ and\ B, n_A = 0.0204\ mol\ \ and\ n_B = 0.184\ mol$$

$$2B \rightarrow A\ , therefore\ if\ the\ reaction\ is\ complete\ n_A = 0.0204 + \frac{n_B}{2} = 0.1124\ mol$$

$$V_{min} = \frac{n_A RT}{P}$$

$$at\ 1\ atm\ and\ 298\ K, \qquad V_{min} = \frac{0.1124 \times 0.08206 \times 298}{1} = 2.75\ L$$

h) Once a new state of equilibrium is reached the pressure of the system has changed and the volume of compartment 1 reach 4L. Determine the value of the new equilibrium pressure in the container.
2 marks

$$n_A = 0.0204 + \frac{0.184 - n_B}{2} = \frac{0.0408 + 0.184 - n_B}{2} = \frac{0.2248 - n_B}{2}$$

$$n_A = \frac{P_A V_1}{RT} = 0.16357 P_A \quad and \quad n_B = \frac{P_B V_1}{RT} = 0.16357 P_B$$

$$\Longrightarrow 0.16357 P_A = \frac{0.2248 - 0.16357 P_B}{2}$$

$$P_A = \frac{0.2248 - 0.16357 P_B}{0.32714}$$

$$substitute\ in\ \frac{P_B^2}{P_A} = 8.1 \Longrightarrow \quad \frac{0.32714 P_B^2}{0.2248 - 0.16357 P_B} = 8.1$$

$$\Longrightarrow 0.32714 P_B^2 = 1.82088 - 1.324917 P_B \Longrightarrow 0.32714 P_B^2 + 1.324917 P_B - 1.82088$$

$a = 0.32714$
$b = 1.324917$
$c = -1.82088$
$\sqrt{b^2 - 4ac}$ =2.034

$$P_B = \frac{-1.324917 + 2.034}{2 \times 0.32714} = 1.084\ atm$$

$$P_A = \frac{P_B^2}{8.1} = 0.145\ atm$$

$$P = P_A + P_B = 1.23\ atm$$

(Give 1 mark for 1.084 or 0.145 atm. 2 marks for 1.23 atm)

-END OF PART C-