

THE CANADIAN CHEMISTRY CONTEST 2019
for high school and CEGEP students
(formerly the National High School Chemistry Examination)

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2019

Free Response Development Problems (90 minutes)

This segment has five (5) questions. While students are expected to attempt **all** questions for a complete examination in 1.5 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, including this cover page, along with a photocopy of Part A of the examination, is to be returned **IMMEDIATELY** by courier to your Canadian Chemistry Olympiad Coordinator.

— PLEASE READ —	PART A () Correct Answers
1. BE SURE TO COMPLETE THE INFORMATION REQUESTED AT THE BOTTOM OF THIS PAGE BEFORE BEGINNING PART C OF THE EXAMINATION.	25 x 1.6 =/040
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.	PART C
3. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.	1. /012
4. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.	2. /012
5. NOTE THAT A PERIODIC TABLE AND A LIST OF SOME PHYSICAL CONSTANTS WHICH MAY BE USEFUL CAN BE FOUND ON A DATA SHEET PROVIDED AT THE END OF THIS EXAMINATION.	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 2020 Nationality of Passport _____

Teacher _____ Teacher E-Mail _____

POLYMER CHEMISTRY

1. Polyethylene glycol (PEG) is a polymer formed via condensation polymerization which is a form of step-growth polymerization. PEG is a hydrophilic molecule with applications such as acting as a ligand for water insoluble nanoparticles to solubilize them into aqueous solutions.

a) PEG is formed via a condensation polymerization using ethylene glycol (ethane-1,2-diol) as a monomer. Draw the structure of ethylene glycol. *1 mark*

b) Draw the structure of a dimer (two monomers attached) of PEG. *1 mark*

c) Draw PEG represented in polymeric form with n units. *1 mark*

The polydispersity index (PDI) is used to measure the distribution of sizes of polymers in a given sample. It is calculated by the following formula:

$$PDI = \frac{M_w}{M_n}$$

Where M_w is the weight average molecular weight and M_n is the number average molecular weight. M_w is calculated by taking the sums of the squares of the weights of each polymer unit and dividing by the sum of all the weights, whereas M_n is calculated by taking the sums of all the weights and dividing by the number of polymers.

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad M_n = \frac{\sum N_i M_i}{\sum N_i}$$

Below is a table of the weights of different polymeric units of PEG in a given sample.

Counts (N)	Weights (M), $g\ mol^{-1}$
2	502
4	546
6	590
3	634
1	1164

d) Calculate the *PDI* of the PEG sample. 2 marks

e) Calculate how many monomers were used to form the $1164\ g\ mol^{-1}$ unit. 2 marks

A parameter used to show the extent of monomer polymerization is p . For example, $p = 0.5$ would signify 50% monomer polymerization. In the case of step-growth polymerization, such as for PEG, p can be represented in the following ways with respect to M_w and M_n .

$$p = \frac{M_w - M_o}{M_w + M_o} \quad p = \frac{M_n - M_o}{M_n}$$

f) Find an expression for PDI in terms of only p . 2 marks

g) Calculate p for the sample of PEG based on your calculated PDI . 1 mark

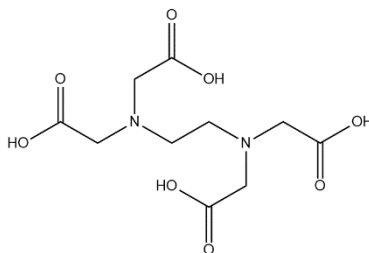
h) What are the maximum and minimum values of PDI ? 2 marks

$PDI_{max} =$

$PDI_{min} =$

ANALYTICAL CHEMISTRY

2. Ethylenediaminetetraacetic acid (EDTA) is a chemical of great industrial and medical importance, due to its potency as a chelating agent for metals. EDTA binds to metals in a 1:1 ratio. The structure of EDTA and the pK_a values of its 4 carboxyl protons are given below.



$$pK_{a1} = 2.0, pK_{a2} = 2.7, pK_{a3} = 6.1, pK_{a4} = 10.3$$

a) Which form of EDTA would you expect to predominate at neutral pH? Draw the structure below. 2 marks

A 1.032g sample of iron ore containing both hematite (Fe_2O_3 , $M=159.688 \text{ g/mol}$) and magnetite (Fe_3O_4 , $M=231.553 \text{ g/mol}$) is contaminated by metal **A** and metal carbonate **BCO₃**. The following procedure is carried out to determine the identity and quantity of contaminants in the ore:

- The sample is dissolved in excess concentrated HCl and chilled in an ice bath, yielding a white precipitate of mass 0.099g with identity **ACl₂**. The filtrate is boiled to remove dissolved carbon dioxide and transferred to a 100.0 mL volumetric flask. Distilled H₂O is added to the mark. At this point, both Fe^{2+} and Fe^{3+} are present in solution.
- A 25.0 mL aliquot of stock solution is titrated with 0.0970M $KMnO_4$ under acidic conditions, requiring 1.32 mL to reach endpoint.
- Excess copper metal is added to a second 25.0 mL aliquot of stock solution to reduce any Fe^{3+} present in solution to Fe^{2+} . Any remaining copper is filtered out, and the titration is repeated, this time requiring 5.19 mL of 0.0970M $KMnO_4$.
- A third 25.0 mL aliquot of stock solution is adjusted to pH 11, forming a white precipitate of iron (II, III) hydroxide. The filtrate is collected and titrated with 0.182M EDTA to a murexide endpoint of 2.38 mL.

b) Write and balance the redox equation for the reaction of KMnO_4 with Fe^{2+} in acidic solution to form Mn^{2+} and Fe^{3+} . *1 mark*

c) From step (ii), calculate the mass of magnetite in the ore sample. (Hint: Fe_3O_4 is equivalent to $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$) *2 marks*

d) From steps (ii) and (iii), calculate the mass of hematite in the ore sample. *2 marks*

e) From step (i), suggest a plausible identity for contaminant **A**, and determine the mass of **A** in the ore sample. *2 marks*

f) From step (iv) and your answers to the questions above, determine the identity of contaminant **B**. *If you did not get an answer for any one or more of (c), (d), or (e), use 0.147g for the mass of BCO_3 in the ore (Note: may not give the same answer for the identity of **B**).* *2 marks*

g) When CO_2 is bubbled through the filtrate from step (iv) (pre-EDTA titration), a white precipitate forms. Write the balanced chemical equation for the formation of this precipitate. *1 mark*

INORGANIC CHEMISTRY

3. Rhodium complexes are commonly used as organometallic catalysts. In the Monsanto process, $cis-[Rh(CO)_2I_2]^-$ is used to catalyze the carbonylation of a methyl halide.

a) Assuming the same electronic state of Rh as above, find a formula for the charge of the complex, n , in terms of a , b and c for the complex $[Rh_a(CO)_bI_c]^n$. *2 marks*

b) $[Rh(CO)_2I_2]^-$ has two isomers: *cis* and *trans*. Draw the two isomers (you do not need to note which is *cis* and which is *trans*). *2 marks*

c) How many valence d electrons does Rh have in $cis-[Rh(CO)_2I_2]^-$? Hint: The $5s$ orbital only contains 1 electron in Rhodium's ground state electronic configuration. *2 marks*

d) Draw and fill in a crystal field splitting diagram for $cis-[Rh(CO)_2I_2]^-$. Assume that CO and I⁻ have similar electronic properties. *3 marks*

e) Circle the correct answer. $cis-[Rh(CO)_2I_2]^-$ is: *1 mark*

Diamagnetic

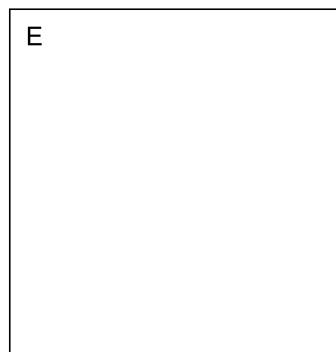
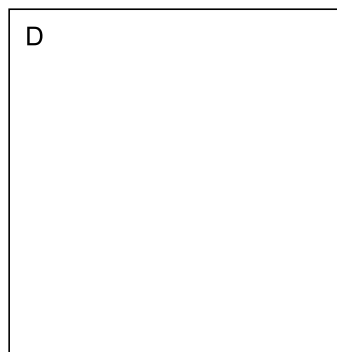
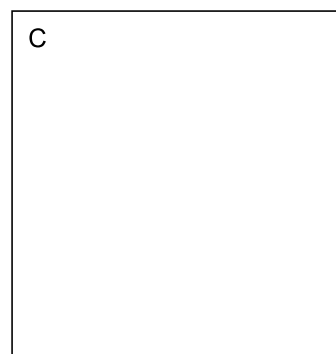
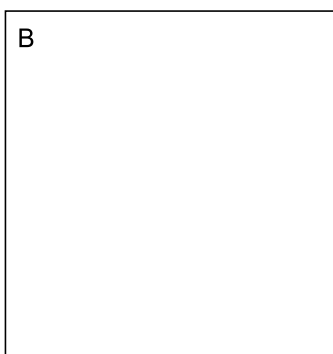
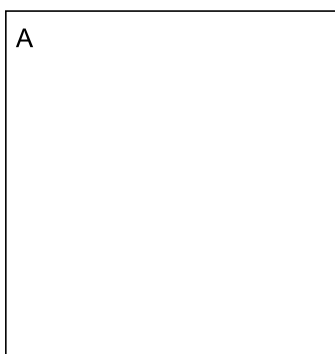
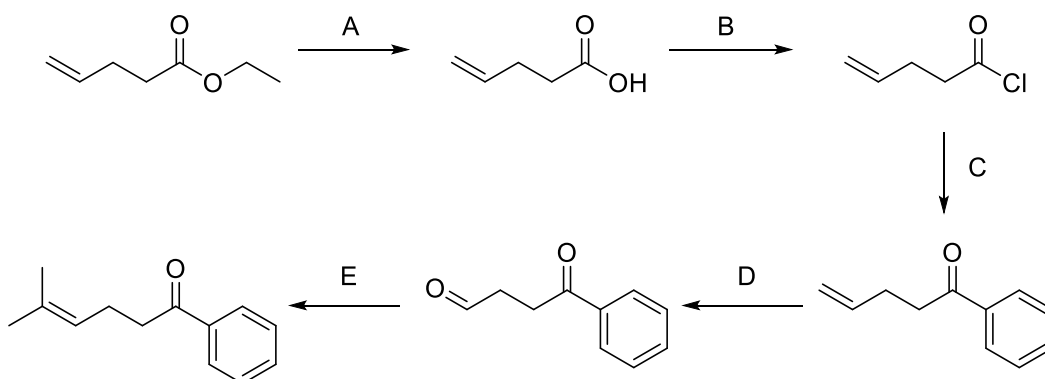
Paramagnetic

Ferromagnetic

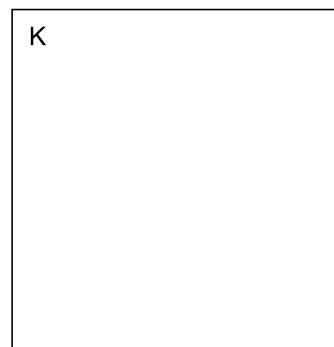
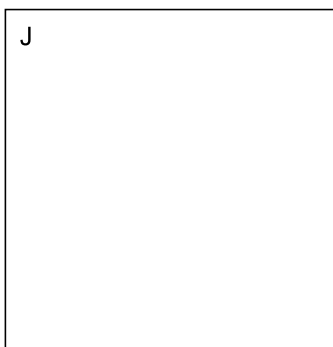
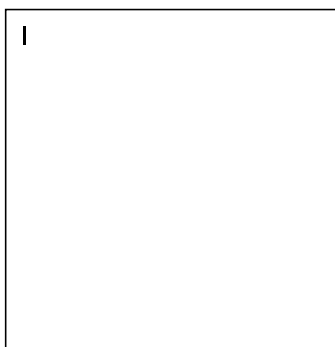
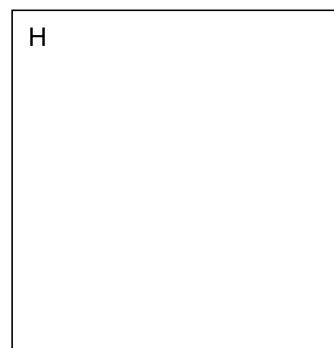
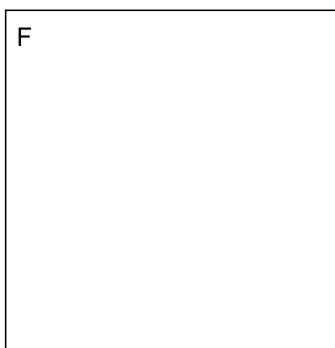
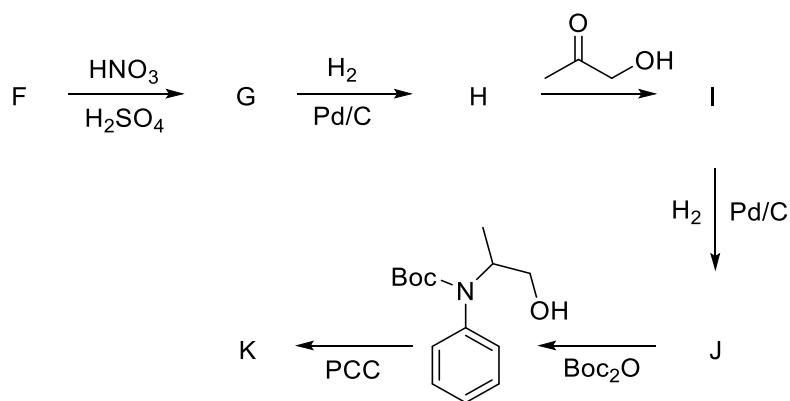
f) Starting from 0 to 10 inclusively, write down EACH number of valence d electrons that would make $cis-[Rh(CO)_2I_2]^n$ diamagnetic assuming the same crystal field splitting properties. *2 marks*

ORGANIC CHEMISTRY

4. a) Draw or write reagents **A**, **B**, **C**, **D**, and **E** for the reaction scheme below. Include any necessary conditions. Any aqueous work up is assumed and does not need to be added. *5 marks*



b) Draw the structures of **F**, **G**, **H**, **I**, **J**, and **K** for the reaction scheme below. *6 marks*

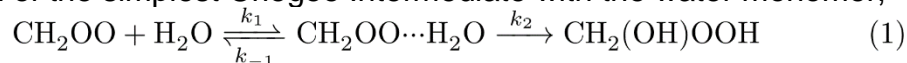


c) Draw the structure of a potential product, **L**, based on the reaction scheme below. Your answer **CAN NOT** be the same as the structure you drew for **K**. There is no box for the answer, please use the space below. *1 mark*

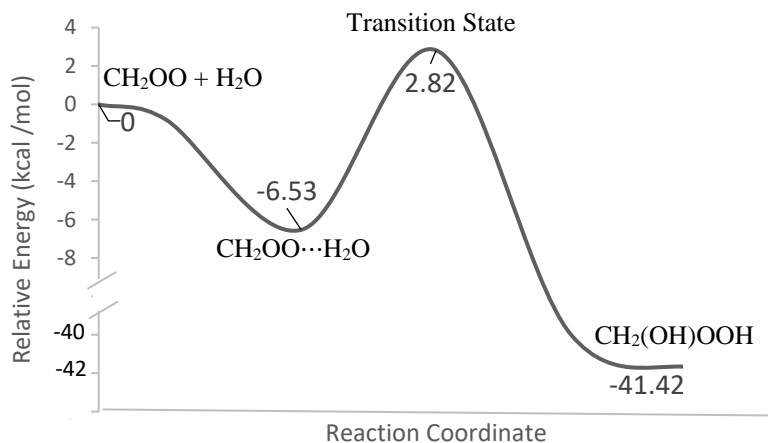


PHYSICAL CHEMISTRY

5. Criegee Intermediates, CH_2OO , have attracted significant interest in recent years due to their critical role in many atmospheric processes. The atmospheric fate of a Criegee Intermediate is largely determined by its reactions with water, due to the high concentration of water in the atmosphere. The following two step reaction and plot show the reaction of the simplest Criegee Intermediate with the water monomer,



where k_1 and k_{-1} are the forward and reverse rate constants for the formation of a weakly bound complex, $\text{CH}_2\text{OO}\cdots\text{H}_2\text{O}$, that then proceeds to the product, $\text{CH}_2(\text{OH})\text{OOH}$, with the rate constant k_2 .



a) Calculate the activation energy of the second step of (1). 1 mark

b) Calculate the overall reaction energy. 1 mark

The rate at which the product is formed is notated $\frac{d[\text{CH}_2(\text{OH})\text{OOH}]}{dt}$. Similarly, the concentration of the weakly bound complex changes at a rate of $\frac{d[\text{CH}_2\text{OO}\cdots\text{H}_2\text{O}]}{dt}$. The expressions for these two rates in terms of their rate constants are:

$$\frac{d[\text{CH}_2(\text{OH})\text{OOH}]}{dt} = k_2[\text{CH}_2\text{OO}\cdots\text{H}_2\text{O}] \quad (2)$$

$$\frac{d[\text{CH}_2\text{OO}\cdots\text{H}_2\text{O}]}{dt} = k_1[\text{CH}_2\text{OO}][\text{H}_2\text{O}] - k_{-1}[\text{CH}_2\text{OO}\cdots\text{H}_2\text{O}] - k_2[\text{CH}_2\text{OO}\cdots\text{H}_2\text{O}] \quad (3)$$

The steady state approximation assumes that the weakly bound complex reacts as quickly as it is produced (the concentration is constant). This gives a second expression for the rate of change of the weakly bound complex:

$$\frac{d[\text{CH}_2\text{OO}\cdots\text{H}_2\text{O}]}{dt} = 0 \quad (4)$$

c) Using these expressions, solve for the rate at which the product is formed in terms of only the initial reactants $[\text{CH}_2\text{OO}]$ and $[\text{H}_2\text{O}]$ and the rate constants k_1 , k_{-1} , k_2 . *3 marks*

d) For bimolecular reactions with an activated complex, we can often assume that the forward step for formation of the activated complex is much slower than the backwards step ($k_2 \ll k_{-1}$). This means $k_{-1} + k_2 \approx k_{-1}$. Simplify your final expression from part c based on this assumption. *1 mark*

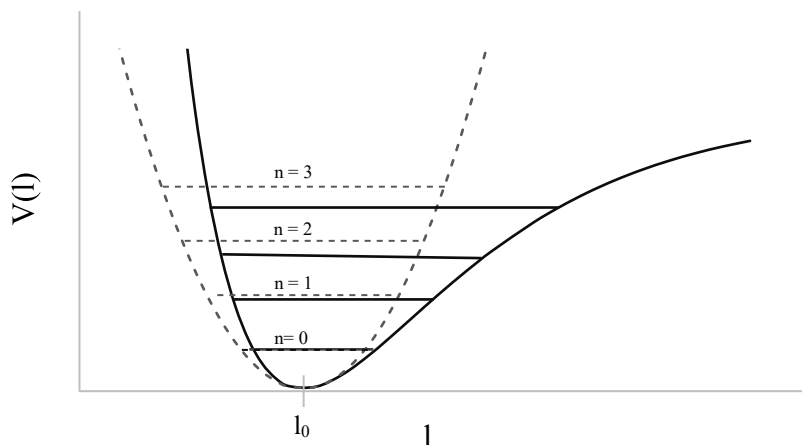
We can determine rate constants, like k_2 , with statistical mechanics and accurate descriptions of a molecule's energy levels. The following questions investigate the vibrational energy levels of HCl. The simple harmonic oscillator is a common approximation for the vibration of a diatomic molecule and follows Hooke's Law. The harmonic oscillator potential, $V(l)$, is given below (l is the displacement of the H-Cl bond from its equilibrium length, l_0). The corresponding energy, E_n , for each of its vibrational energy levels, n , is also given.

$$V(l) = \frac{k}{2}(l - l_0)^2 \qquad E_n = h\nu(n + \frac{1}{2})$$

The bond stretching frequency, ν , is related to the force constant, k , and h is Planck's constant. As the displacements, l , grow larger, the harmonic-oscillator potential begins to diverge from the true potential. A better approximation is given by the Morse potential:

$$V(l) = D_e(1 - \exp^{\beta(l-l_0)})^2 \qquad E_n = h\nu[(n + \frac{1}{2}) - \chi_e(n + \frac{1}{2})^2]$$

where D_e is the dissociation energy of the molecule, β is a measure of the curvature of $V(l)$ around its minimum, and χ_e is the anharmonic constant. An example of these potentials with energy levels, n , is shown in the figure below. The dotted lines correspond to a harmonic potential and the solid to a Morse potential. (Note that \exp is equivalent to Euler's number, e)



e) The ground state energy, $n=0$, of a molecule is E_0 . If the transition from $n=0 \rightarrow 2$ for HCl has energy $E_{2 \rightarrow 0} = E_2 - E_0 = 5668 \text{ cm}^{-1}$, estimate the ground state energy of HCl using the harmonic approximation. *2 marks*

f) If $E_{3 \rightarrow 0} = 8347 \text{ cm}^{-1}$, what should be the ground state energy of HCl using the harmonic approximation? *1 mark*

g) Your values from parts e and f should be different due to anharmonicity. Use $E_{2 \rightarrow 0}$ and $E_{3 \rightarrow 0}$ to estimate the anharmonic constant, χ_e . *3 marks*

-END OF PART C-