THE CANADIAN CHEMISTRY CONTEST 2018

for high school and CEGEP students
(formerly the National High School Chemistry Examination)

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2018

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 —

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. 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.

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 2019 ☐ Nationality of Passport _____

Teacher _____ Teacher E-Mail_____

ANALYTICAL CHEMISTRY

1. a) Phosphoric acid, H_3PO_4, is a triprotic acid with the following acid dissociation constants: $K_{a1} = 7.5 * 10^{-3}$, $K_{a2} = 6.2 * 10^{-8}$, and $K_{a3} = 2.2 * 10^{-13}$. If a solution of phosphoric acid initially had $[H_3PO_4] = 0.0403$ M, calculate $[PO_4^{3-}]$ at equilibrium. *5 marks*

b) Given the data below at room temperature, estimate the value of the missing equilibrium constant. *3 marks*

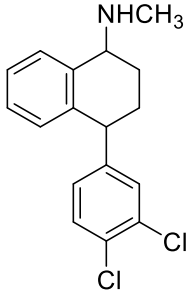
$MX \rightleftharpoons M^+ + X^-$	$K_1 = 4.005$
$RX_2 \rightleftharpoons R^{2+} + 2X^-$	$K_2 = 0.6140$
$2MX + R^{2+} \rightleftharpoons RX_2 + 2M^+$	$K_3 = ?$

c) Using the K values above, calculate the Gibbs free energy of each reaction at room temperature. *2 marks*

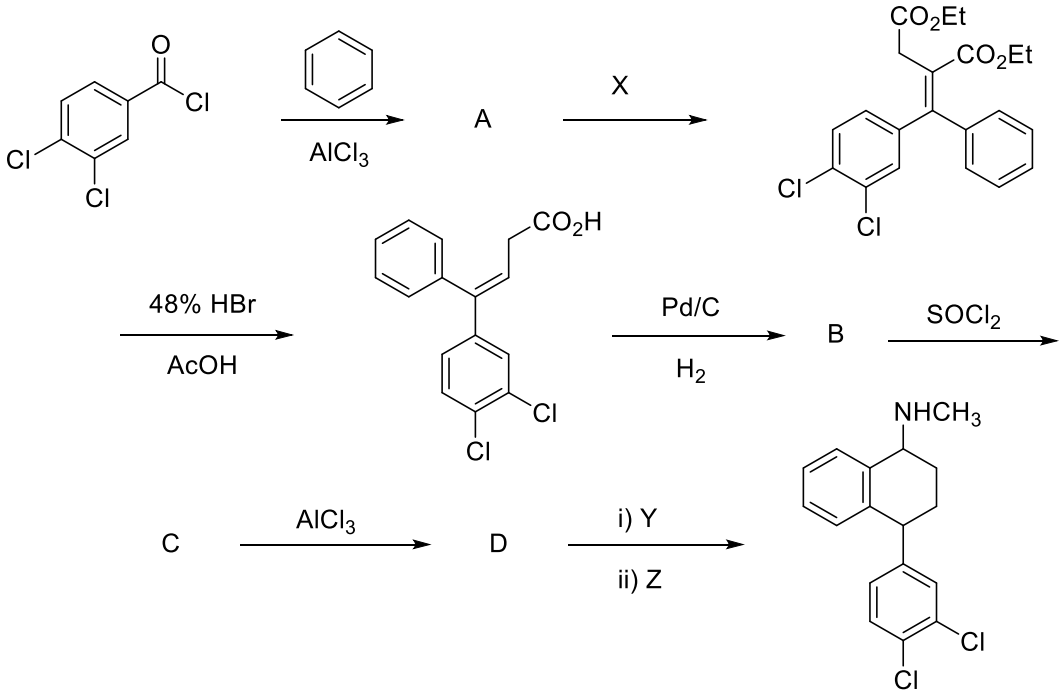
d) Calculate the Gibbs free energy of the third reaction using the Gibbs free energies of the first two reactions and compare it with the value you obtained in part c). Are they different? Similar? Explain why in up to three sentences. *2 marks*

ORGANIC CHEMISTRY

2. Sertraline is a potent pharmaceutical agent for the treatment of depression. It is sold under the name Zoloft and belongs to the class of antidepressants known as selective serotonin reuptake inhibitors (SSRI). Approved for medical use in 1991, it is one of the most prescribed psychiatric medications. The structure is shown below.



Sertraline can be prepared according to the following scheme:



a) Draw the structures of intermediates A, B, C and D in the boxes below. *4 marks*

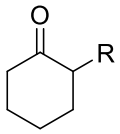
A	B	C	D

b) Provide the reagents X, Y, Z below. *1.5 marks*

X | Y | Z

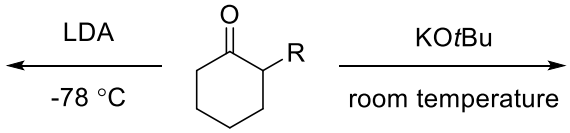
c) Circle all the stereocenters in sertraline. State how many stereoisomers of sertraline exist. *2 marks*

d) Circle the two most acidic sites in the molecule depicted below. *1 mark*



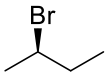
R ≠ H

e) Deprotonation results in the formation of an enolate. There are two possible enolates. The reaction conditions dictate which enolate will form. Draw the corresponding enolate. *1.5 marks*



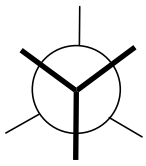
R ≠ H

f) Circle the correct stereochemical marker of the molecule below. *0.5 marks*



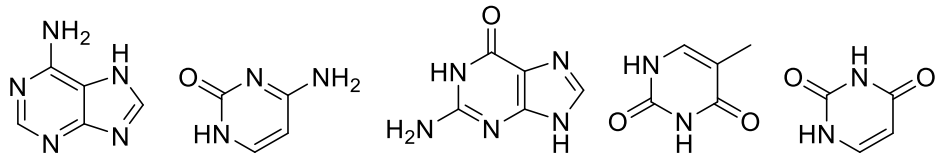
R or S (CIRCLE ONE)

g) Using the template provided, draw the corresponding Newman projection along the C2 - C3 bond. *1.5 marks*



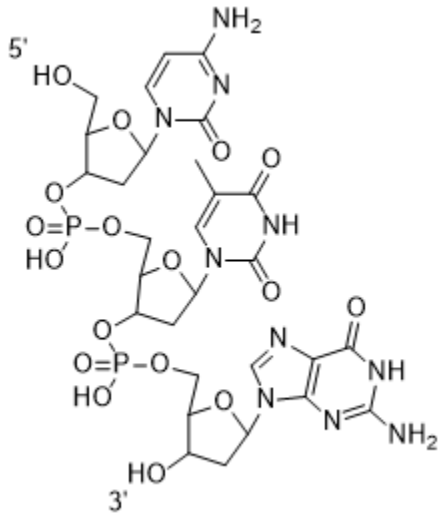
BIOLOGICAL CHEMISTRY

3.



adenine (A) cytosine (C) guanine (G) thymine (T) uracil (U)

DNA and RNA comprise of connected nucleobases: adenine, cytosine, guanine, thymine, and uracil as shown above. Many genetic disorders are caused by trinucleotide repeats. Myotonic dystrophy is caused by a trinucleotide repeat of the following trinucleotide.

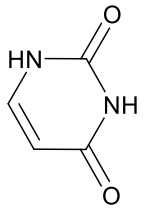


a) Write the code (e.g. 5' – AAA – 3') that corresponds to the trinucleotide. *1 mark*

b) Write the complementary DNA sequence. *1 mark*

c) Write the mRNA sequence that would be transcribed from the initial trinucleotide. *1 mark*

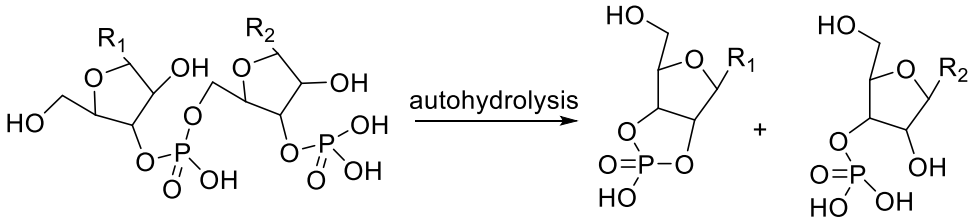
d) Draw the hydrogen bonding between uracil and its base pair on the template below. *3 marks*



uracil (U)

e) Circle the atom(s) that participate as Lewis base(s) in uracil on the template above. *1 mark*

f) DNA and RNA can undergo autohydrolysis. Below is an example of a section of a RNA strand and its product after autohydrolysis.



Propose a potential catalyst for this reaction and explain your reasoning in up to two sentences. *1 mark*

g) If the k of autohydrolysis for DNA is ~2 x 10^{-13} s^{-1}, assuming first order kinetics, calculate the half-life of DNA in years. *2 marks*

h) Suppose the oxygen atoms in the above RNA strand were isotopically marked. What would happen to the rate of autohydrolysis? Explain your reasoning in up to two sentences. *1 mark*

i) If the free energy of the products of autohydrolysis are lower than that of the RNA, draw an uncatalyzed AND a catalyzed free energy diagram of the reaction. *2 marks*

INORGANIC CHEMISTRY

4. Vanadium was first discovered in 1830 and was named after the Scandinavian goddess of beauty, due to the striking range of colors which can be found in vanadium-containing compounds. One group of these colorful compounds are the metal aquo complexes formed from vanadium ions in aqueous solutions, including the lilac-colored $[V(H_2O)_6]^{2+}$.

a) What is the geometry around Vanadium in $[V(H_2O)_6]^{2+}$? *1 mark*

b) What is the electron configuration of the Vanadium (II) ion in $[V(H_2O)_6]^{2+}$? *1 mark*

c) What is the Lewis acid in $[V(H_2O)_6]^{2+}$? *1 mark*

The d-orbitals of transition metals like Vanadium are degenerate when observed in individual atoms, but when transition metal ions are bound to ligands in complex ions, the d-orbital electrons repel the lone pair electrons of the ligands. As a result, d-electrons closer to the ligands will be higher in energy than d-electrons further from the ligands, breaking degeneracy of the d-orbitals. This is the basic concept behind Crystal Field Theory and crystal field "splitting" of orbitals.

d) Draw the electron configuration diagram for the d-orbitals and d-electrons of V^{2+} in $[V(H_2O)_6]^{2+}$ with crystal field splitting. *2 marks*

e) Will the crystal-field splitting parameter Δ be larger or smaller in $[V(H_2O)_6]^{3+}$ compared to $[V(H_2O)_6]^{2+}$? *1 mark*

Larger Smaller (CIRCLE ONE)

f) Assuming the same metal ion and other conditions, will the crystal-field splitting parameter Δ be larger or smaller with CN^- ligands compared to H_2O ligands? *1 mark*

Larger Smaller (CIRCLE ONE)

The complex ion $[Co(CN)_6]^{3-}$ follows the same crystal field splitting pattern as $[V(H_2O)_6]^{2+}$. The crystal-field splitting parameter Δ is 4.2 eV and the spin pairing energy of the Co (III) ion is 3.5 eV.

g) Draw the electron configuration diagram for the d-orbitals and d-electrons of Co^{3+} in $[Co(CN)_6]^{3-}$ with crystal field splitting. *(3 marks)*.

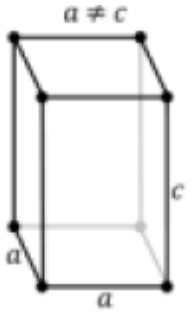
h) Is this a high spin configuration or a low spin configuration? *1 mark*

Low spin High spin (CIRCLE ONE)

i) What is the wavelength in nm of a photon that $[Co(CN)_6]^{3-}$ would readily absorb? *2 marks*

PHYSICAL CHEMISTRY

5. Metal X has been known to humanity for at least 5000 years, mostly in its silvery-white metallic tetragonal β-form. The unit cell of this β-form is shown in the picture below.



a) Identify X given that the density of β-X is 7.29 g/cm^3 and its unit cell contains 4 atoms of X and its parameters are a=0.583 nm and c=0.3181 nm. *3 marks*

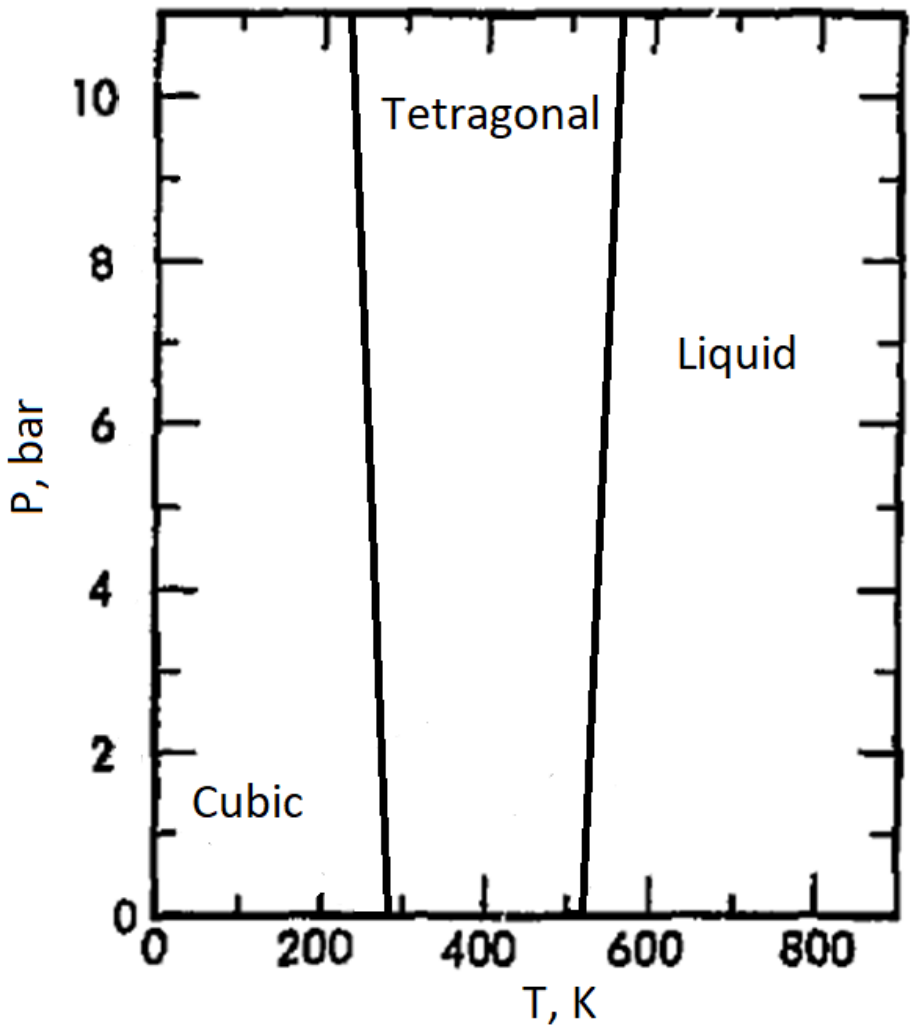
At low temperature this metal undergoes a phase transition to face-center cubic α-form.

b) Draw a unit cell of the α-X and indicate the number of atoms in the unit cell. *2 marks*

c) Atomic radius of X is known to be 0.182 nm. Find the density of α-X. *2 marks*

As a result of this phase transition, ductile and dense metallic β-X turns to brittle α-X. Among non-chemists this transition is known as X pest, since the silvery white metal tarnishes and visible cracks appear on its surface.
Allegedly, it was one of the reasons for failure of the first expedition to South Pole (lead in 1910 by Robert Scott), since food and water containers were affected.

d) The phase diagram of X is displayed below. Estimate the temperature at which β-X turns to α-X on Earth. Is it reasonable to blame X-pest based on your estimate? *1 mark*



Element X has the largest number of stable isotopes at 10 due to its nuclear stability. Its heaviest known isotope only has a half-life of 408 ns. Praseodymium, a different element, has only one known stable isotope, Pr-141.

e) Write down the electron configuration of praseodymium in its ground state. *1 mark*

f) If Pr-122 has a half-life of 0.5 s, and there was initially a mixture of 20% Pr-141 and 80% Pr-122, what would be the atomic weight of Pr before and after 11.2 s has passed? *2 marks*

-END OF PART C-