

THE CANADIAN CHEMISTRY CONTEST 2012
for high school and CEGEP students
(formerly the National High School Chemistry Examination)

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2012

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 November 2012 Nationality of Passport _____

Teacher _____ Teacher E-Mail _____

INORGANIC CHEMISTRY

1. The silicate ion (SiO_4^{4-}) is derived from silicic acid, H_4SiO_4 . Silicon-oxygen compounds consist of tetrahedral components which exist in their crystal structures as single molecules, in chains and layers, or in a three-dimensional framework. A general way to write the empirical formula of such silicon-oxygen compounds is $[\text{Si}_x\text{O}_y]^n$.

(a). Derive a formula for the overall charge (n) that is dependent on both x and y.

2 marks

(b). How many corners does one tetrahedron of the anion $(\text{SiO}_3^{2-})_m$ have in common with its neighbours?

1 mark

(c). What is the empirical formula of a silicon-oxygen compound in which four tetrahedrons are connected with their corners to form a chain, and with silver as a cation?

2 marks

Lapis lazuli is a deep blue mineral used for jewellery. It consists of a three-dimensional framework where three out of six Si atoms are substituted by aluminium atoms. The blue colour is caused by S_3^- ions. The ratio of the number of tetrahedrons to the number of S_3^- ions is 6:1. The cations of the mineral are sodium ions.

(d). State the empirical formula of lapis lazuli.

2 marks

(e). Write a balanced ionic equation for the formation of sulfur and hydrogen sulfide if lapis lazuli is treated with hydrochloric acid.

2 marks

(f). Draw a reasonable Lewis structure for the S_3^- ion, including all lone pairs of electrons on each sulfur atom and the formal charge associated with each atom.

3 marks

PHYSICAL CHEMISTRY

2. Svante Arrhenius, a Swedish scientist working at the turn of the 20th century, won the 1903 Nobel Prize in chemistry for his work on the conductivity of electrolyte solutions. However, he is most known today for the Arrhenius equation, which describes how the rate constant of a chemical reaction changes with temperature.

(a). Define and provide one example each of an Arrhenius acid and an Arrhenius base.

Arrhenius acid:

Arrhenius base:

2 marks

(b). The Arrhenius equation can be written as:

$$k = Ae^{-E_a/RT}$$

The fading of the colour of phenolphthalein (an acid-base indicator) in aqueous solution is a second-order reaction. Assuming that its kinetics can be described by the Arrhenius equation, state appropriate and consistent units for k , A , and E_a .

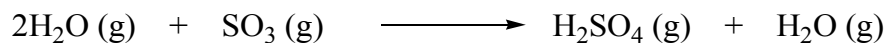
2 marks

In a theoretical derivation of the Arrhenius equation, A is often referred to as the “frequency factor”, referring to the frequency of collisions between (nominally gas-phase) reactant molecules.

(c). Deduce (and justify) whether, in such a derivation, A is constant with respect to temperature.

1 mark

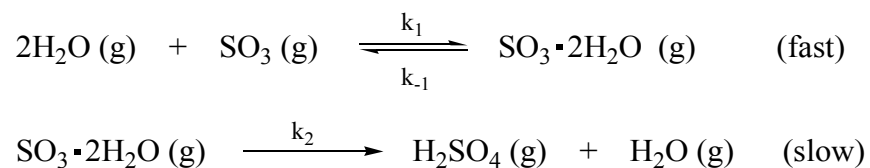
One idea (Proposal A) for the formation of sulfuric acid in the atmosphere is as follows:



Considering the possibility of direct molecular collisions only, which order of reaction would you expect for Proposal A?

1 mark

Proposal A could proceed via a two-step mechanism:



$\text{SO}_3 \cdot 2\text{H}_2\text{O}$ is a complex stabilized by hydrogen bridges.

(d). Assuming that $k_2 \ll k_1$ and k_{-1} , and using the steady-state approximation, derive the respective rate law for the formation of sulfuric acid and state the reaction order of this mechanism.

Rate law:

Reaction order:

4 marks

(e). Quantum-mechanical examinations show that the activation energy for Proposal A is -20 kJ/mol. State the relationship between the rate constant and temperature for Proposal A and predict the temperature dependence of the rate constant.

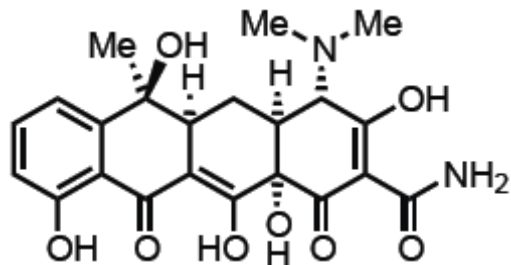
Relationship between rate constant and temperature:

Temperature dependence of rate constant:

2 marks

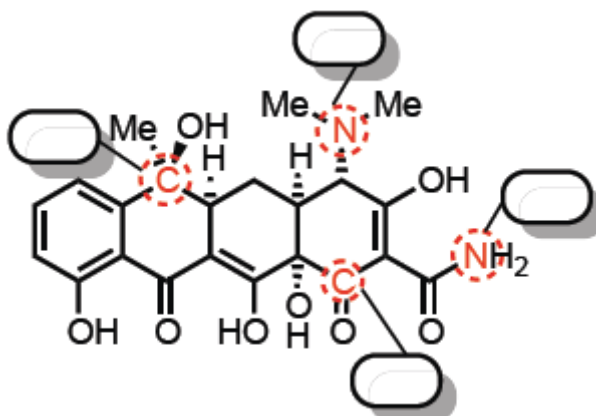
ORGANIC CHEMISTRY

3. (a). The compound shown below is (-)-tetracycline, which is a potent antibiotic. Circle the chiral centres (stereocentres) in (-)-tetracycline directly on the structure.



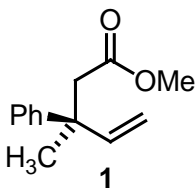
1 mark

(b). In the provided boxes, state the hybridization of the circled atoms on the structure of (-)-tetracycline below.



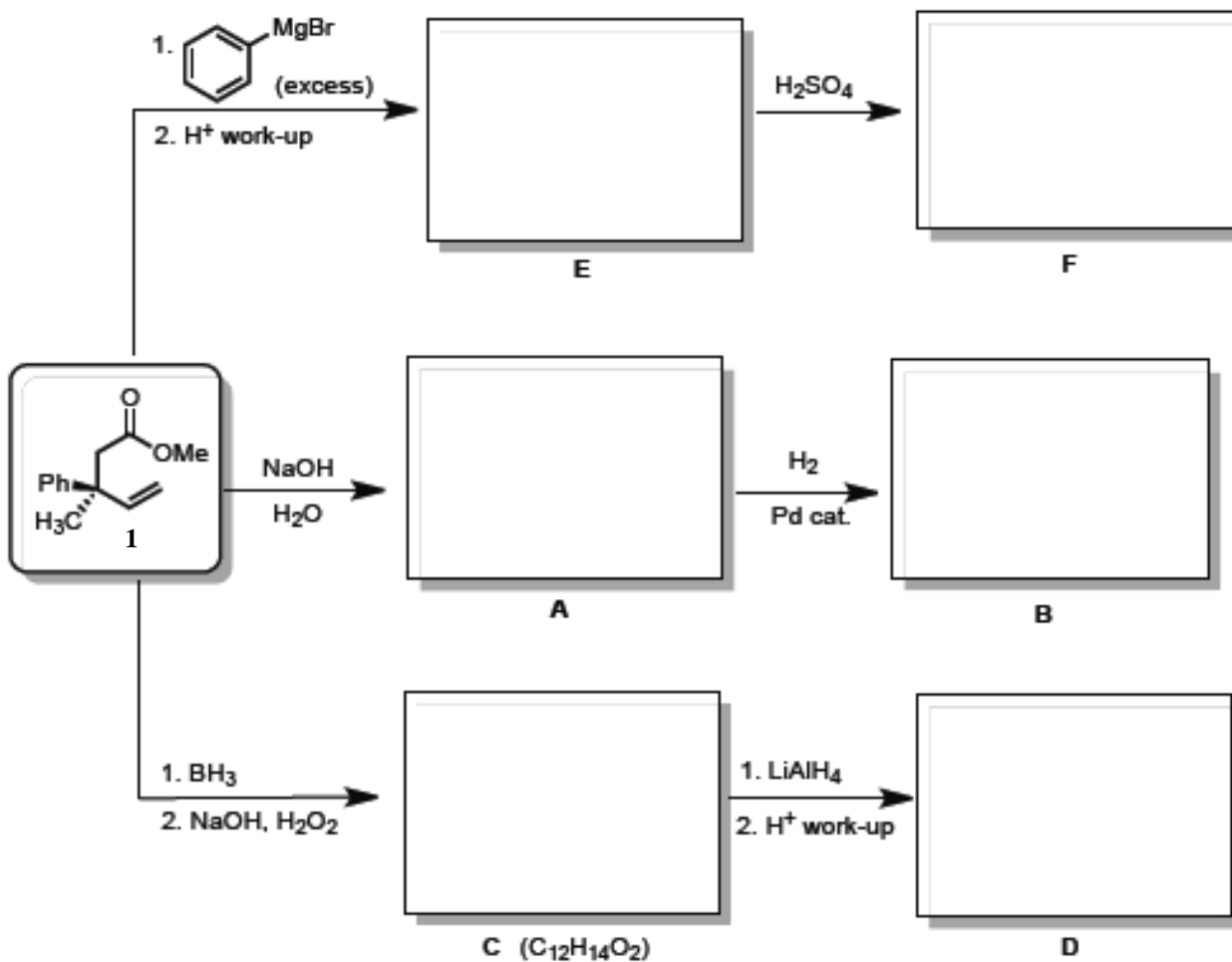
2 marks

Recently, a new antibiotic was synthesized whose structure is shown below (compound **1**). It has broad-spectrum activity but suffers from poor bioavailability. Several transformations were carried out to prepare derivatives of the new antibiotic that exhibit the desired properties.



(c). On the scheme overleaf, and including stereochemistry where important, draw the structures of compounds **A - F**.

6 marks



(d). What is the absolute configuration of the chiral centre (stereocentre) in compound **1**?

1 mark

(e). Draw the structure of the two products formed when **1** reacts with molecular bromine, and state the isomeric relationship between them.

Product structures:

Isomeric relationship:

2 marks

ANALYTICAL CHEMISTRY

4. Manganese may be obtained in the form of manganese dioxide from the ore pyrolusite, a black amorphous solid that may also contain some fraction of manganese carbonate. The determination of manganese in such ore samples may be achieved by various methods, including: (A) reduction in acidic peroxide with quantitation based on the volume of oxygen gas evolved; and (B) reduction by chloride, reaction of the liberated chlorine with iodide to form iodine, then titration using standard sodium thiosulfate. An analyst takes two samples from an amount of finely ground pyrolusite and determines the manganese content by both methods as follows:

Method A:

- Weigh the pyrolusite into a conical flask that is connected to a mercury manometer. Treat the pyrolusite with 10 mL of dilute H_2SO_4 and 20 mL of 10% (v/v) aqueous H_2O_2 . Shake for 2 minutes, and collect all the gas evolved in a mercury manometer.
- 0.1987 g of the pyrolusite sample yielded 53.4 mL of gas at 21.0°C and 1.00 atm.

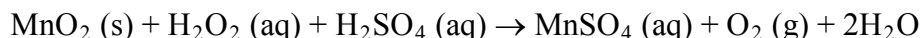
Method B:

- Weigh the pyrolusite into a distillation flask under an inert (oxygen-free) atmosphere. Add concentrated HCl *slowly* while stirring, and then *gently* heat the solution to boiling. Pass the evolved gas through a cooled solution containing 3.5 g of KI in 100 ml of distilled water. Once all the gas has been collected, titrate the I_2 formed with $\text{Na}_2\text{S}_2\text{O}_3$ using starch indicator to the usual end point.
- 0.2234 g of the pyrolusite sample yielded sufficient I_2 to require 19.12 mL of 0.5000 M $\text{Na}_2\text{S}_2\text{O}_3$.

(a). How many moles of gas were evolved from the sample using method A? *Show your calculation for full marks.*

2 marks

(b). The balanced reaction equation for method A is:



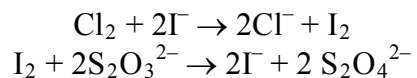
Given this, calculate the % by mass of MnO_2 in the sample obtained by method A. *Show your calculation for full marks.*

2 marks

(c). Write a balanced net ionic equation for the reaction between MnO_2 and chloride under acidic conditions to produce Cl_2 gas and Mn^{2+} .

2 marks

(d). The sequence of reactions involving the chlorine evolved in method B is as follows:



Given this, calculate the number of moles of Cl_2 evolved from the sample using method B. *Show your calculation for full marks.*

2 marks

(e). Calculate the % by mass of MnO_2 in the sample obtained by method B. *Show your calculation for full marks.*

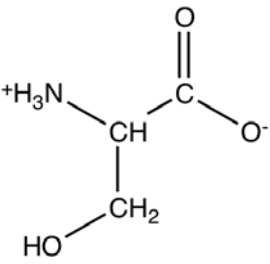
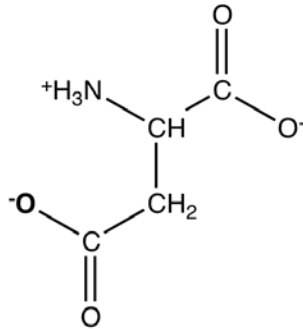
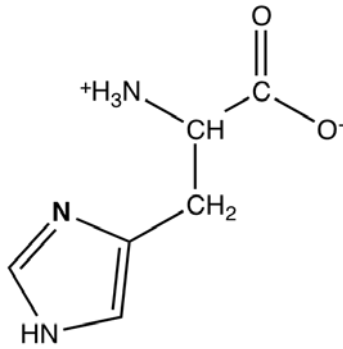
2 marks

(f). What accounts for the discrepancy between the mass % of MnO_2 in the sample obtained by methods A and B? Briefly explain your answer.

2 marks

BIOLOGICAL CHEMISTRY

5. Serine proteases are a group of enzymes that can cleave polypeptides at specific locations, and are some of the most studied molecules for their catalytic mechanism. In general, serine proteases contain the amino acids serine, aspartic acid and histidine in close proximity to each other in order to facilitate the catalytic reaction. The structures of these three amino acids at physiological pH are shown below.

		
serine	aspartic acid (side chain $pK_a = 3.65$)	histidine (side chain $pK_a = 6.04$)

(a). Classify each amino acid above as i) polar or non-polar; and ii) acidic, basic or neutral (circle the correct response in each instance).

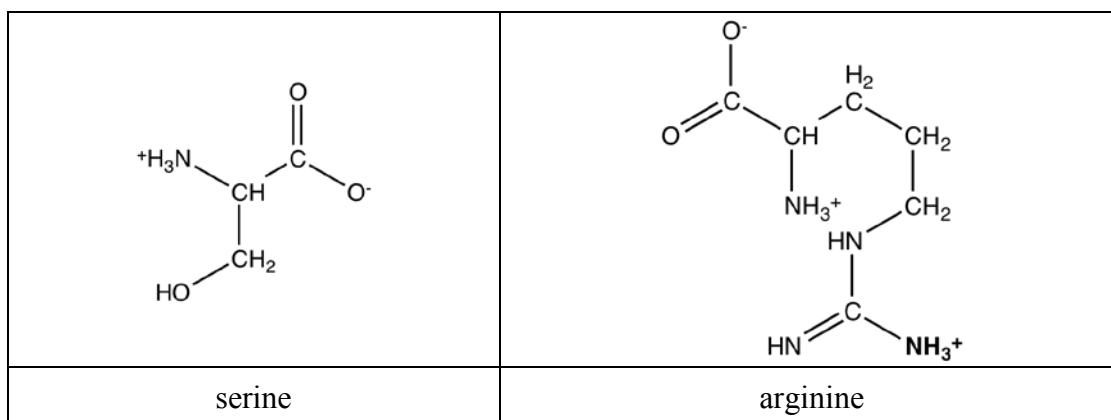
serine:	polar	non-polar	acidic	basic	neutral
aspartic acid:	polar	non-polar	acidic	basic	neutral
histidine:	polar	non-polar	acidic	basic	neutral

3 marks

(b). Calculate the isoelectric point of a 1.00 M solution of serine ($pK_{a1} = 2.19$, $pK_{a2} = 9.12$). The isoelectric point is defined as the pH at which an amino acid is exactly balanced between anionic and cationic forms and exists as a neutral zwitterion. *Show your calculation for full marks.*

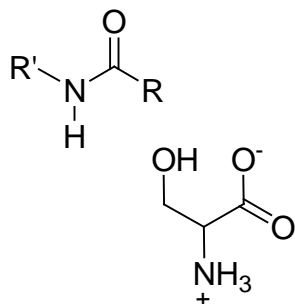
2 marks

(c). A single point mutation can convert a serine residue into an arginine residue as shown below. Assuming that a serine residue initiates polypeptide cleavage via nucleophilic attack, and that the structure of the catalytic groove is not affected by such a mutation, state and briefly explain the likely effect the mutation would have on catalytic activity.



3 marks

(d). Write a mechanism to show how a serine residue helps to cleave a polypeptide under aqueous conditions. Include curved arrows to show movement of electrons and show important intermediate structures. Use the molecules below as the polypeptide substrate for the reaction and the serine residue, respectively.



4 marks

--END OF PART C--

1											18													
1 H 1.008																		2 He 4.003						
3 Li 6.941	4 Be 9.012																		5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305																		13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.07	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80							
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29							
55 Cs 132.905	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)							
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs	109 Mt	110 Ds															

Data Sheet

Fiche de données

Relative Atomic Masses (1985 IUPAC)

Masses Atomiques Relatives (UICPA, 1985)

*For the radioactive elements the atomic mass of an important isotope is given

*Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
90 Th 232.038	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

	Symbol Symbole	Value Quantité numérique	
Atomic mass unit	amu	1.66054 x 10 ⁻²⁷ kg	Unité de masse atomique
Avogadro's number	<i>N</i>	6.02214 x 10 ²³ mol ⁻¹	Nombre d'Avogadro
Bohr radius	<i>a</i> ₀	5.292 x 10 ⁻¹¹ m	Rayon de Bohr
Boltzmann constant	<i>k</i>	1.38066 x 10 ⁻²³ J K ⁻¹	Constante de Boltzmann
Charge of an electron	<i>e</i>	1.60218 x 10 ⁻¹⁹ C	Charge d'un électron
Dissociation constant (H ₂ O)	<i>K</i> _w	10 ⁻¹⁴ (25 °C)	Constante de dissociation de l'eau (H ₂ O)
Faraday's constant	<i>F</i>	96 485 C mol ⁻¹	Constante de Faraday
Gas constant	<i>R</i>	8.31451 J K ⁻¹ mol ⁻¹ 0.08206 L atm K ⁻¹ mol ⁻¹	Constante des gaz
Mass of an electron	<i>m</i> _e	9.10939 x 10 ⁻³¹ kg	Masse d'un électron
Mass of a neutron	<i>m</i> _n	1.67493 x 10 ⁻²⁷ kg 1.00866 amu	Masse d'un neutron
Mass of a proton	<i>m</i> _p	1.67262 x 10 ⁻²⁷ kg 1.00728 amu	Masse d'un proton
Planck's constant	<i>h</i>	6.62608 x 10 ⁻³⁴ J s	Constante de Planck
Speed of light	<i>c</i>	2.997925 x 10 ⁸ m s ⁻¹	Vitesse de la lumière

1 Å	=	1 x 10 ⁻⁸ cm
1 eV	=	1.60219 x 10 ⁻¹⁹ J
1 cal	=	4.184 J
1 atm	=	101.325 kPa
1 bar	=	1 x 10 ⁵ Pa

