

# THE CANADIAN CHEMISTRY CONTEST 2016

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

## PART C: CANADIAN CHEMISTRY OLYMPIAD Final Selection Examination 2016

### 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

Teacher \_\_\_\_\_ Teacher E-Mail \_\_\_\_\_

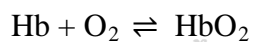
1. (a). The partial pressure of oxygen in inhaled air ( $pO_2(\text{in}) = 159 \text{ mmHg}$ ), and in exhaled air ( $pO_2(\text{ex}) = 116 \text{ mmHg}$ ). If the ambient air pressure is  $760 \text{ mmHg}$ , calculate how many grams of  $O_2$  are transferred from the atmosphere to our alveoli each minute at  $298 \text{ K}$ . Assume normal breathing conditions of 10 inhalations per minute at  $2.0 \text{ L}$  each per inhalation.

3 marks

(b). Oxygen enters our bloodstream from our alveoli, where it binds to the oxygen-binding protein hemoglobin (Hb). Hemoglobin has four oxygen-binding sites. One liter of fully oxygenated blood can carry  $0.18 \text{ L}$  of  $O_2$  measured at  $310 \text{ K}$  and  $1 \text{ atm}$ . Calculate how many hemoglobin molecules are required to transport the  $O_2$  in  $1.0 \text{ L}$  of fully oxygenated blood.

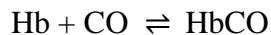
3 marks

(c). The equilibrium between hemoglobin and the O<sub>2</sub> in blood can be represented as:



The equilibrium constant for this reaction is  $9.2 \times 10^{18}$ .

Carbon monoxide (CO) also binds with hemoglobin in the following reaction:



This reaction has an equilibrium constant of  $2.3 \times 10^{23}$ .

Determine the Gibbs energies of reaction for the above two processes at 37°C, and indicate whether each process favours the forward or reverse reaction.

4 marks

(d). Which equilibrium in part (c). lies further towards the products? Does your answer support the argument that carbon monoxide is toxic? Provide an explanation for your answer.

2 marks

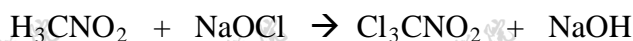
2. Chloropicrin,  $\text{Cl}_3\text{CNO}_2$ , is a volatile pesticide used in agricultural applications. Typically, soil is sealed under a tarp and chloropicrin vapour is pumped into the airtight system and maintained for three to seven days. During the First World War, chloropicrin proved an effective chemical weapon, given that it was less lethal than phosgene ( $\text{COCl}_2$ ).

Chloropicrin is prepared from the reaction of nitromethane and sodium hypochlorite.

(a). Determine the oxidation number of chlorine in sodium hypochlorite ( $\text{NaOCl}$ ).

1 mark

(b). Given the unbalanced chemical equation below, determine the balanced chemical equation for this reaction.



1 mark

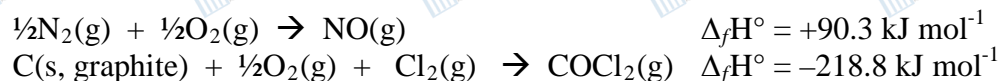
(c). State the chemical reaction type depicted in (b).

1 mark

(d). In 1937 at Queen's University, Canadian professor E.W.R. Steacie and graduate student Walter MacFarlane Smith demonstrated that chloropicrin thermally decomposed to form three gases: phosgene, nitrogen(II) oxide and chlorine. Write a balanced chemical equation for this reaction.

1 mark

(e). The *standard enthalpy of formation* for chloropicrin is  $-78.6 \text{ kJ mol}^{-1}$ . Given the data provided below, calculate the enthalpy change for the thermal decomposition reaction of chloropicrin.



2 marks

(f). In 2009, a research group led by Dr. Abdelwahid Mellouki reported that chloropicrin, when exposed to sunlight at ambient temperature and pressure, undergoes *homolytic* C–N bond breakage to yield  $\text{CCl}_3$  and  $\text{NO}_2$ . Draw the Lewis (electron dot) structures of  $\text{CCl}_3$  and  $\text{NO}_2$ .

1 mark

(g). Using VSEPR (valence shell electron-pair repulsion) theory, sketch the most probable molecular structures for  $\text{CCl}_3$  and  $\text{NO}_2$ .

1 mark

(h). Given its pungent odor, chloropicrin has been used as warning agent, mixed with an odorless fumigant compound (**C**) as a residential fumigant. The following industrial process outlines the synthesis of **C**:

Combustion of finely divided element (**A**) in excess air yields a gaseous, binary compound (**B**) which is an economically important chemical compound. At  $325^\circ\text{C}$ , in the presence of a catalyst, chlorine gas and hydrogen fluoride, **B** is converted to the compound **C**, according to the following balanced chemical equation:



In VSEPR “AXE format” (where E represents a lone pair of electrons), **C** has the molecular geometry  $\text{AX}_4$ , with a two-fold rotational axis of symmetry and two perpendicular planes of symmetry (containing the two-fold rotational axis). **C** is 37.23% fluorine by mass.

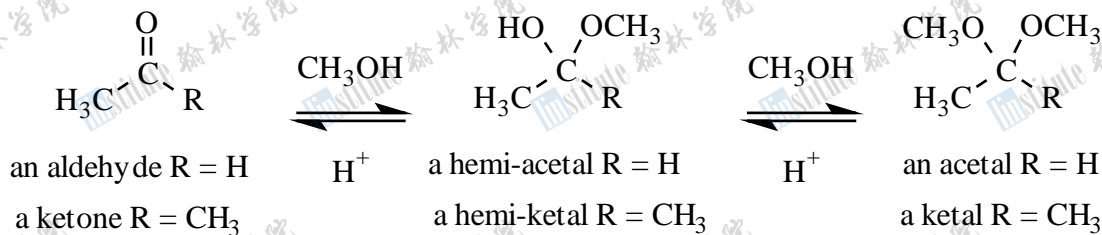
Determine the molecular formula of **A**, **B** and **C**.

3 marks

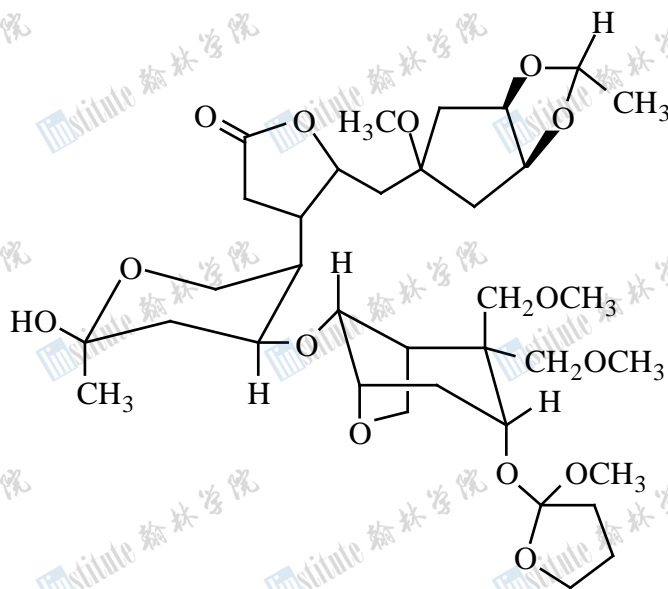
(i). Using VSEPR theory, sketch the molecular structure of **C**.

1 mark

3. (a). Aldehydes and ketones react with alcohols to eventually form acetals and ketals.

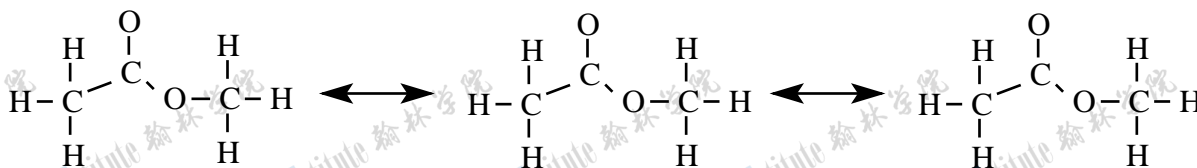


A number of oxygen-containing functional groups are present in the structure below. Using the example above as a guide, indicate the positions of the TWO aldehyde/ketone derivatives by drawing an arrow to the carbon atoms of the former carbonyl (C=O). State whether the group is a hemi-acetal, hemi-ketal, acetal or ketal.



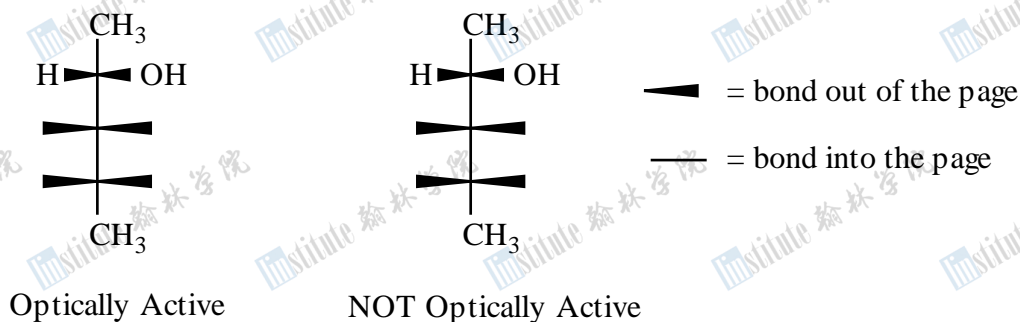
2 marks

(b). A resonance structure is one of several valence-bond structures with localized electrons that approximate the true structure of a compound that has delocalized electrons. Complete the templates below to show three major resonance structures of the ester shown by clearly adding any missing bonds, lone pairs of electrons and formal charges that are present.



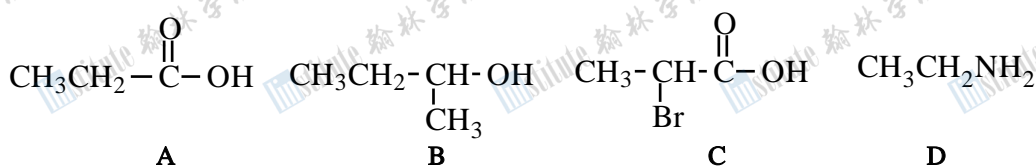
3 marks

(c). Optically active compounds are not superimposable upon their mirror images. Three-dimensional awareness is important in predicting optical activity. Complete the structures below by adding an H and an OH group to each unspecified bond to generate an optically active and a non-optically active compound.



2 marks

(d). Place the following compounds in order of increasing acidity:



\_\_\_\_\_ least acidic

\_\_\_\_\_ most acidic

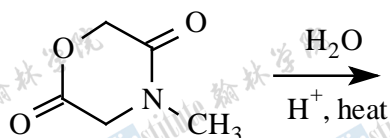
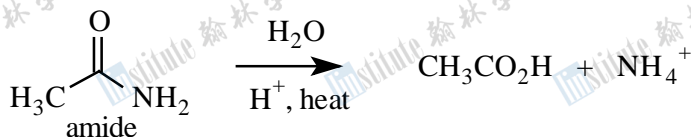
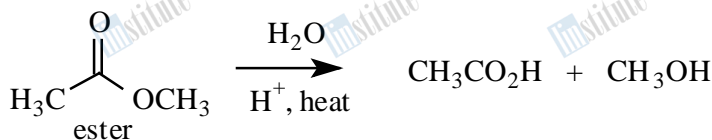
1 mark

(e). A compound that lacks a carbonyl group (C=O) and has the formula  $\text{C}_{14}\text{H}_{24}\text{O}$  reacts rapidly with an excess of  $\text{H}_2$  in the presence of a catalyst to yield a new compound with the formula  $\text{C}_{14}\text{H}_{28}\text{O}$ . The general formula of a non-cyclic alkane is  $\text{C}_n\text{H}_{(2n+2)}$ .

The ORIGINAL compound contained \_\_\_\_\_ ring(s) and \_\_\_\_\_ double bond(s)

2 marks

(f). Esters hydrolyze to form alcohols and carboxylic acids, whereas amides hydrolyze to form amines and carboxylic acids. Write the products of the acidic aqueous hydrolysis of the compound below that incorporates both an ester and an amide functionality.



2 marks

4. The following procedure is used to determine the manganese content of various types of steel, provided that the chromium content is low:

- i. A solution of sodium hydrogen arsenite ( $\text{Na}_2\text{HASO}_3$ ) is first prepared by dissolving 1.230 g of  $\text{As}_2\text{O}_3$  ( $M_m 197.841 \text{ g mol}^{-1}$ ) in concentrated aqueous sodium hydroxide, neutralizing with hydrochloric acid, buffering with sodium bicarbonate, and finally diluting to volume in a 1.000 L volumetric flask.
- ii. Approximately 1 g of the steel sample is weighed accurately into a large conical flask, to which is added a mixture of concentrated sulphuric, phosphoric, and nitric acids. The solution is heated until the sample is fully dissolved and brown fumes cease to evolve.
- iii. The solution is diluted with 50 mL of water, to which is added 5 mL of 0.1 M silver nitrate and 2.5 g of ammonium persulphate. This mixture is boiled for 30 seconds and cooled rapidly to below  $25^\circ\text{C}$ . Any manganese in the sample is now present as  $\text{MnO}_4^-$ .
- iv. A further 75 mL of water is added immediately, together with 5 mL of 0.2 M sodium chloride.
- v. The sample is titrated immediately with the sodium hydrogen arsenite solution to a clear yellow end point that does not change upon further addition of the titrant.

(a). Calculate the concentration of the  $\text{Na}_2\text{HASO}_3$  titrant obtained in step (i) to the correct number of significant figures.

2 marks

(b). The silver ion in step (iii) acts as a catalyst for the ammonium persulphate; why is chloride still added after destroying any residual persulphate?

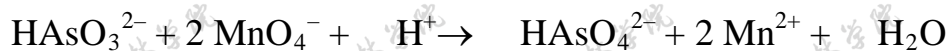
2 marks

(c). Why would *high* chromium content in the steel interfere with this method?

2 marks



(d). Write the balanced equation for the titration reaction:



2 marks

(e). An analyst tests a 0.9875 g sample of steel using this procedure, and obtains an end point volume of 25.32 mL. What is the mass of manganese obtained from the steel sample? Show your calculation for full marks.

4 marks

5. When  $\text{H}_2\text{S}$  is dissolved in water it is almost saturated at a concentration near 0.1 M. Three species containing sulfur exist in this solution ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$  and  $\text{S}^{2-}$ ). Their proportions depend on the acidity of the solution. Given the following equilibrium constants:



(a). What is the concentration of the sulfide ion,  $[\text{S}^{2-}]$ , in a saturated 0.100 M solution of  $\text{H}_2\text{S}$  when the solution pH = 2.0?

5 marks

(b). A solution contains the cations  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ag}^+$  at an original concentration of 0.010M each. Which of these ions will precipitate when the solution is saturated in  $\text{H}_2\text{S}$  and the pH adjusted to 2.0 by adding HCl? Explain your answer.

Given:

$$\text{MnS } K_{sp} = 2.5 \times 10^{-10}$$

$$\text{CoS } K_{sp} = 4.0 \times 10^{-21}$$

$$\text{Ag}_2\text{S } K_{sp} = 6.3 \times 10^{-50}$$

3 marks

(c). How many grams of lead(II) sulfide, PbS, will precipitate from 1.00 L of a saturated solution of lead(II) sulfate, PbSO<sub>4</sub>, if the concentration of sulfide ion, [S<sup>2-</sup>], is adjusted to give a concentration of 1.00 x 10<sup>-17</sup> M?

Given:



4 marks

--END OF PART C--



1 H 1.008																	2 He 4.003					
3 Li 6.941	4 Be 9.012	<b>Relative Atomic Masses (2012, IUPAC)</b> *For the radioactive elements the atomic mass of an important isotope is given										<b>Masses Atomiques Relatives (IUPAC, 2012)</b> *Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important					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 30.97	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 65.38	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 95.96	43 Tc (98)	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 183.9	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)	85 At (210)	86 Rn (222)					
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (269)	111 Rg (272)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (292)	117 Uus	118 Uuo (294)					

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	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 175.0
90 Th 232.0	91 Pa (231.0)	92 U (238.0)	93 Np (237)	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 (262)

**Symbol**      **Value**  
**Symbole**      **Quantité numérique**

Atomic mass unit	<i>amu</i>	$1.66054 \times 10^{-27}$ kg	<i>Unité de masse atomique</i>
Avogadro's number	<i>N</i>	$6.02214 \times 10^{23}$ mol <sup>-1</sup>	<i>Nombre d'Avogadro</i>
Charge of an electron	<i>e</i>	$1.60218 \times 10^{-19}$ C	<i>Charge d'un électron</i>
Dissociation constant (H <sub>2</sub> O)	<i>K<sub>w</sub></i>	$1.00 \times 10^{-14}$ (25°C)	<i>Constante de dissociation de l'eau (H<sub>2</sub>O)</i>
Faraday's constant	<i>F</i>	96 485 C mol <sup>-1</sup>	<i>Constante de Faraday</i>
Gas constant	<i>R</i>	$8.31451$ J K <sup>-1</sup> mol <sup>-1</sup>	<i>Constante des gaz</i>
		$0.08206$ L atm K <sup>-1</sup> mol <sup>-1</sup>	
Mass of an electron	<i>m<sub>e</sub></i>	$9.10939 \times 10^{-31}$ kg	<i>Masse d'un électron</i>
Mass of a neutron	<i>m<sub>n</sub></i>	$1.67493 \times 10^{-27}$ kg	<i>Masse d'un neutron</i>
Mass of a proton	<i>m<sub>p</sub></i>	$1.67262 \times 10^{-27}$ kg	<i>Masse d'un proton</i>
Planck's constant	<i>h</i>	$6.62608 \times 10^{-34}$ J s	<i>Constante de Planck</i>
Speed of light	<i>c</i>	$2.997925 \times 10^8$ m s <sup>-1</sup>	<i>Vitesse de la lumière</i>
Rydberg constant	<i>R<sub>∞</sub></i>	$1.097 \times 10^7$ m <sup>-1</sup>	<i>Constante de Rydberg</i>

1 Å	= 1 x 10 <sup>-10</sup> m
1 atm	= 101.325 kPa
1 bar	= 1 x 10 <sup>5</sup> Pa

<b>STP/TPN</b>	<b>SATP/TPAN</b>
273.15 K	298 K
100 kPa	100 kPa