## THE CANADIAN CHEMISTRY CONTEST 2011 for high school and CEGEP students (formerly the National High School Chemistry Examination)

# PART C: CANADIAN CHEMISTRY OLYMPIAD Final Selection Examination 2011

## **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 —	PARTA ( )
1. BE SURE TO COMPLETE THE INFORMATION REQ THE BOTTOM OF THIS PAGE BEFORE BEGINNING THE EXAMINATION.	Correct Answers G PART C OF $25 \times 1.6 = \dots /040$
<ol> <li>STUDENTS ARE EXPECTED TO ATTEMPT ALL QU PART A AND PART C. CREDITABLE WORK ON A NUMBER OF THE QUESTIONS MAY BE SUFFICIEN AN INVITATION TO THE NEXT LEVEL OF THE SE PROCESS.</li> <li>IN QUESTIONS WHICH REQUIRE NUMERICAL CA BE SURE TO SHOW YOUR REASONING AND YOU</li> <li>ONLY NON-PROGRAMMABLE CALCULATORS M ON THIS EXAMINATION.</li> <li>NOTE THAT A PERIODIC TABLE AND A LIST OF S PHYSICAL CONSTANTS WHICH MAY BE USEFUL FOUND ON DATA SHEETS PROVIDED AT THE EN EXAMINATION.</li> </ol>	JESTIONS OF A LIMITED NT TO EARN LECTION       PART C         1.
Name (LAST NAME, Given Name; Print Clearly	School
City & Province	Teacher
Date of birth	E-Mail
Home Telephone ( )	Years at a Canadian high school
Number	of chemistry courses at a Québec CÉGEP
Male 🗆 Canadian Citizen 🗆	Landed Immigrant
Female  Passport valid	until November 2011
	Nationality of Passport

#### INORGANIC CHEMISTRY

**1.** (a). Circle the correct answer to each of the following questions:

Which formula is incorrect?	CsSO <sub>4</sub>	CaCO <sub>3</sub>	$BaZn_2(BO_3)_2$
Which has the lowest melting point?	NaCl	ClF	NaF
Which is the least polar molecule?	PCl <sub>3</sub>	PCl <sub>5</sub>	ICl <sub>5</sub>
Which is the best Lewis acid?	$C_2H_6$	$B_2H_6$	$N_2H_4$
Which is the strongest oxidant?	HC1	HClO	HClO <sub>4</sub>

5 marks

(b). Write the chemical formulae of the lettered compounds in the reaction scheme below.

When 1.00 g of a white solid **A** is strongly heated, 0.78 g of another white solid, **B**, and a gas are obtained. An experiment is carried out on the gas, showing that it exerts a pressure of 209 mmHg in a 450 mL flask at 25°C. Bubbling the gas into a solution of  $Ca(OH)_2$  forms another white solid, **C**. If the white solid **B** is added to water, the resulting solution turns red litmus paper blue. Addition of aqueous HCl to the solution of **B** and evaporation of the resulting solution to dryness yields 1.055 g of a white solid **D**. When **D** is placed in a Bunsen burner flame, it colours the flame green.

A: \_\_\_\_\_ D: \_\_\_\_\_

**B**:

**C**:

7 marks

### PHYSICAL CHEMISTRY

**2.** The Leclanché cell was developed by Georges Leclanché, a French electrical engineer, in the mid-1800s. It was one of the first electrical batteries and, as such, a precursor to today's dry cell batteries. However, as opposed to dry cell batteries, the Leclanché cell was a **wet-cell** battery, which meant that the electrolyte in the battery was in the liquid phase.

(a). Identify one advantage that dry-cell batteries have over wet-cell batteries.

The anode in the Leclanché cell was pure zinc metal. The other half-cell contained both manganese (III) and manganese (IV) in their oxide forms; the electrode in this half-cell was also a manganese oxide. The cell operated under *basic* conditions.

(b). Write the line notation of this electrochemical cell.

1 mark

(c). Write the net chemical reaction of the Leclanché cell in the *spontaneous* direction.

2 marks

The electrolyte in the Leclanché cell is an aqueous solution of ammonium chloride,  $NH_4Cl_{(aq)}$ . Unlike wet-cells that you may have created in the laboratory, the Leclanché wet cell was a "one-pot" cell. Instead of requiring a salt bridge, the half cells were in direct contact through a porous membrane.

(d). Briefly explain why a salt bridge is needed in electrochemical cells.

1 mark

Under normal operating conditions, it was very difficult to recharge the Leclanché cell – in other words, once the reaction had run its course, it could not be reversed.

(e). Write an equation to justify the observation on the previous page. The equation should *not* involve manganese. Remember that the cells are in contact through a porous membrane.

### 1 mark

The electromotive force of the Leclanché cell was measured at a variety of temperatures, as shown in the table below.

Temperature (°C)	25	50	75	100
Standard	0 908	0.875	0 849	0.814
electromotive force (V)	0.700	0.075	0.017	0.011

(f). At 25°C, the K<sub>sp</sub> of Zn(OH)<sub>2</sub> in aqueous solution is  $3 \times 10^{-17}$ . Assume that the Leclanché cell was set up so that the electrolyte was fully saturated with Zn(OH)<sub>2</sub>. Using data from the table above, determine the electromotive force of this cell.

4 marks

Electrochemical cells are often treated as if kinetic considerations do not matter, but there may be kinetic limitations on the rate at which charge -i.e. the current - that can be produced.

(g). For a given mass of a metal electrode, in order to maximize current, state whether one would rather a densely-packed metal electrode *or* a porous metal electrode. Explain your reasoning.

#### ORGANIC CHEMISTRY

**3.** (a). Draw the structure of the molecule 2-chloro-3-methylpent-1-ene (A) in the box below.



1 mark

(b). How many chiral centre(s) (stereocentre((s)) are in the above molecule?

1 mark

(c). Reduction of **A** with hydrogen gas and a palladium catalyst affords compound **B** as a mixture of stereoisomers. Draw *all* of the possible stereoisomers of B that are formed. What is (are) the stereochemical relationship(s) between them?

4 marks

(d). For the reaction scheme below, complete the boxes overleaf to indicate each of the substances C, D, E, F, G and H. Be sure to include stereochemistry where appropriate.



G:

D:

H:

E:

6 marks

## ANALYTICAL CHEMISTRY

4. Hydrochloric acid may be standardized by direct titration of a known mass of sodium carbonate dissolved in pure water using phenolphthalein indicator to provide a first end-point in the pH range 8.2–9.8, and methyl orange indicator to provide a second end-point in the pH range 3.1–4.4. To achieve a sharp methyl orange end-point, it is necessary to boil the titration mixture after the first end-point to remove carbon dioxide. This is referred to as a "modified methyl orange end-point".

(a). Write a single balanced reaction equation for the complete neutralization of sodium carbonate with hydrochloric acid.

end-point.

(c). Write a balanced net ionic equation showing how carbon dioxide is formed during the titration after the first (phenolphthalein) end-point.

(d). Why would the carbon dioxide cause the methyl orange end-point to not be as sharp as needed for an accurate titration?

2 marks

(e). An analyst titrates 0.4773 g of pure sodium carbonate with hydrochloric acid to a modified methyl orange end-point of 30.15 mL. What is the molar concentration of the hydrochloric acid? (The formula weight of sodium carbonate is 105.99 g/mol). Show your calculation for full marks.

(b). Write a single net ionic equation for the reaction that gives rise to the first (phenolphthalein)

1 mark

1 mark

1 mark

Sodium carbonate can coexist with either sodium hydroxide or sodium bicarbonate, but not both simultaneously. A sample of sodium carbonate contaminated with one of these two compounds is titrated with the hydrochloric acid from part (e). The phenolphthalein end-point volume is 15.07 mL and the modified methyl orange end-point volume is 50.32 mL (35.35 mL beyond the phenolphthalein end-point).

(f). What is the contaminant, sodium hydroxide or sodium bicarbonate? Give clear and concise reason(s) for your answer.

2 marks

(g). What is the mole fraction of contaminant in the sample?

3 marks

BIOLOGICAL CHEMISTRY

**5.** Enzymes are protein catalysts found in biological systems. Consider the following reaction where an enzyme (E) converts a particular substrate (S) into a product (P) via a transition state (ES).

$$E + S \xrightarrow{k_1} ES \xrightarrow{k_2} E + P$$

(a). Express the rate of product formation by writing a kinetic expression.

2 marks

(b). Write a steady state expression  $(K_{eq})$  for this system.

2 marks

(c). If [ET] = the total enzyme concentration (sum of both unbound enzyme concentration and substrate-bound enzyme concentration), write an alternative expression for the rate of product formation, using [ET] at steady state.

3 marks

(d). If enzyme A binds to the substrate 25 times stronger than enzyme B, what is the ratio of the catalytic rate between enzyme A and enzyme B if the energy of the two transition states is identical? What is the difference in activation energy between the two reactions?

1																	18
1 <b>H</b> 1.008	2				]	Data	a Sh	eet				13	14	15	16	17	2 <b>He</b> 4.003
3 Li <sup>6.941</sup>	4 <b>Be</b> 9.012	Relativ	e Atomic 1	Masses (19	<b>Fic</b>	he d	e do Masses At	onné	<b>es</b> Relatives (	UICPA,19	(85)	5 <b>B</b> 10.811	6 <b>C</b> 12.011	7 <b>N</b> 14.007	8 <b>O</b> 15.999	9 <b>F</b> 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.990	12 Mg 24.305	*For the of an in	e radioactiv nportant isc <b>4</b>	ve elements ptope is giv 5	the atomic en 6	e mass	*Dans le ca atomique fo <b>8</b>	as des élém ournie est c <b>9</b>	ents radioa celle d'un i <b>10</b>	ictifs, la ma sotope imp <b>11</b>	asse ortant <b>12</b>	13 <b>Al</b> 26.982	14 <b>Si</b> 28.086	15 <b>P</b> 30.974	16 <b>S</b> 32.07	17 Cl 35.453	18 <b>Ar</b> 39.948
19 <b>K</b> 39.098	20 <b>Ca</b> 40.08	21 <b>SC</b> 44.956	22 <b>Ti</b> 47.88	23 V 50.942	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.938	26 <b>Fe</b> 55.847	27 <b>CO</b> 58.93	28 <b>Ni</b> 58.69	29 Cu 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 Ge 72.61	33 <b>As</b> 74.922	34 <b>Se</b> <sub>78.96</sub>	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.80
37 <b>Rb</b> 85.468	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.906	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.906	42 <b>Mo</b> 95.94	43 <b>TC</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.906	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53   126.90	54 <b>Xe</b> 131.29
55 <b>CS</b> 132.905	56 <b>Ba</b> 137.33	57 <b>La</b> 138.91	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.948	74 W 183.85	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.967	80 <b>Hg</b> 200.59	81 <b>TI</b> 204.37	82 Pb 207.2	83 Bi 208.980	84 <b>Po</b> (209)	85 At (210)	86 <b>Rn</b> (222)
87 <b>Fr</b> (223)	88 <b>Ra</b> 226.03	89 <b>AC</b> 227.03	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b>	109 <b>Mt</b>	110 <b>Ds</b>								

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.91	144.24	(145)	150.4	151.97	157.25	158.93	162.50	164.930	167.26	168.934	173.04	174.97
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)
								1	1	1	1	1	1

	Symbol Symbole
Atomic mass unit	amu
Avogadro's number	N
Bohr radius	$a_0$
Boltzmann constant	k
Charge of an electron	е
Dissociation constant (H <sub>2</sub> O)	$K_{\rm W}$
Faraday's constant	F
Gas constant	R
Mass of an electron	me
Mass of a neutron	m <sub>n</sub>
Mass of a proton	mp
Planck's constant	h
Speed of light	С

=	1 x 10 <sup>-8</sup> cm
=	1.60219 x 10 <sup>-19</sup> J
=	4.184 J
=	101.325 kPa
=	1 x 10 <sup>5</sup> Pa

Value Quantité numérique 1.66054 x 10<sup>-27</sup> kg 6.02214 x 10<sup>23</sup> mol<sup>-1</sup> 5.292 x 10<sup>-11</sup> m 1.38066 x 10<sup>-23</sup> J K<sup>-1</sup> 1.60218 x 10<sup>-19</sup> C 10<sup>-14</sup> (25 °C) 96 485 C mol<sup>-1</sup> 8.31451 J K<sup>-1</sup> mol<sup>-1</sup> 0.08206 L atm K<sup>-1</sup> mol<sup>-1</sup> 9.10939 x 10<sup>-31</sup> kg 5.48580 x 10<sup>-4</sup> amu 1.67493 x 10<sup>-27</sup> kg 1.00866 amu 1.67262 x 10<sup>-27</sup> kg 1.00728 amu 6.62608 x 10<sup>-34</sup> J s 2.997925 x 10<sup>8</sup> m s<sup>-1</sup>

Unité de masse atomique Nombre d'Avogadro Rayon de Bohr Constante de Boltzmann Charge d'un électron Constante de dissociation de l'eau (H<sub>2</sub>O) Constante de Faraday Constante des gaz

Masse d'un électron

Masse d'un neutron

Masse d'un proton

Constante de Planck Vitesse de la lumière



