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 —

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 DATA SHEETS 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 ______________________ 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 ☐ Visa Student ☐

Female ☐ Passport valid until November 2011 ☐

Nationality of Passport ______________________

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

Which formula is incorrect?	$CsSO_4$	$CaCO_3$	$BaZn_2(BO_3)_2$
Which has the lowest melting point?	NaCl	ClF	NaF
Which is the least polar molecule?	PCl_3	PCl_5	ICl_5
Which is the best Lewis acid?	C_2H_6	B_2H_6	N_2H_4
Which is the strongest oxidant?	HCl	HClO	$HClO_4$

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

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.

1 mark

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 electromotive force (V)	0.908	0.875	0.849	0.814

(f). At 25°C, the K_{sp} of $Zn(OH)_2$ in aqueous solution is 3×10^{-17}. Assume that the Leclanché cell was set up so that the electrolyte was fully saturated with $Zn(OH)_2$. 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.

2 marks

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

1 mark

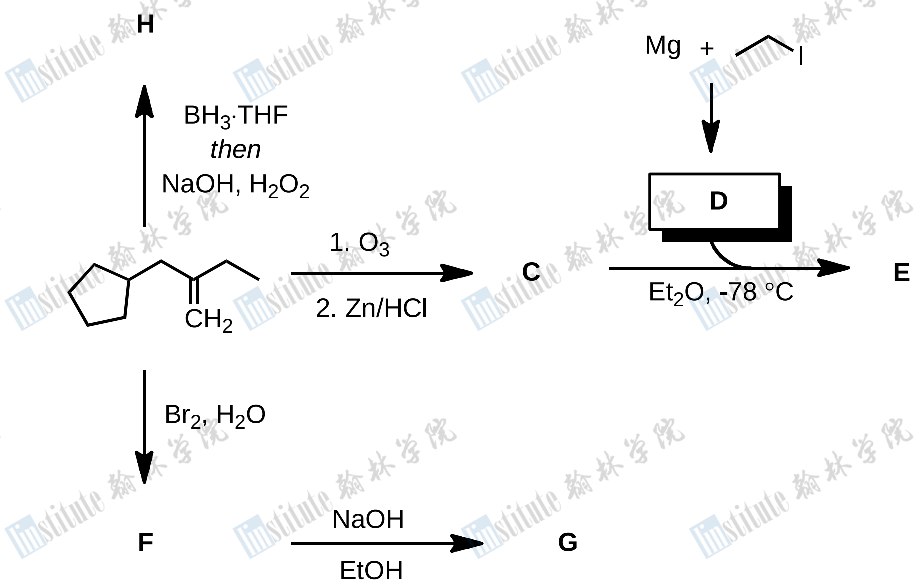
(b). How many chiral centre(s) (stereocentre((s)) are in the above molecule?

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.



C: **D:** **E:**

F: **G:** **H:**

6 marks

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.

1 mark

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

1 mark

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

1 mark

(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*.

2 marks

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

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).

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

(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?

5 marks

--END OF PART C--

Data Sheet
Fiche de données

Relative Atomic Masses (1985 IUPAC)
*For the radioactive elements the atomic mass of an important isotope is given

Masses Atomiques Relatives (UICPA,1985)
*Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	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								

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	1.66054×10^{-27} kg	Unité de masse atomique
Avogadro's number	N	6.02214×10^{23} mol^{-1}	Nombre d'Avogadro
Bohr radius	a_0	5.292×10^{-11} m	Rayon de Bohr
Boltzmann constant	k	1.38066×10^{-23} J K^{-1}	Constante de Boltzmann
Charge of an electron	e	1.60218×10^{-19} C	Charge d'un électron
Dissociation constant (H_2O)	K_w	10^{-14} (25 °C)	Constante de dissociation de l'eau (H_2O)
Faraday's constant	F	96 485 C mol^{-1}	Constante de Faraday
Gas constant	R	8.31451 J K^{-1} mol^{-1} 0.08206 L atm K^{-1} mol^{-1}	Constante des gaz
Mass of an electron	m_e	9.10939×10^{-31} kg 5.48580×10^{-4} amu	Masse d'un électron
Mass of a neutron	m_n	1.67493×10^{-27} kg 1.00866 amu	Masse d'un neutron
Mass of a proton	m_p	1.67262×10^{-27} kg 1.00728 amu	Masse d'un proton
Planck's constant	h	6.62608×10^{-34} J s	Constante de Planck
Speed of light	c	2.997925×10^{8} m s^{-1}	Vitesse de la lumière

1 Å	=	1×10^{-8} cm
1 eV	=	1.60219×10^{-19} J
1 cal	=	4.184 J
1 atm	=	101.325 kPa
1 bar	=	1×10^{5} Pa

IYC 2011
International Year of CHEMISTRY