# THE CANADIAN CHEMISTRY CONTEST 2011 <br> for high school and CEGEP students <br> (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 | $\underset{\text { Correct Answer: }}{( })$ |
| :---: | :---: |
| $25 \times 1.6$ | ........../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 $\qquad$ Teacher $\qquad$
Date of birth $\qquad$ E-Mail $\qquad$
Home Telephone ( ) - $\qquad$ Years at a Canadian high school $\qquad$
Number of chemistry courses at a Québec CÉGEP $\qquad$
Male $\quad \square \quad$ Canadian Citizen $\square \quad$ Landed Immigrant $\square \quad$ Visa Student
Female $\square \quad$ Passport valid until November 2011
$\qquad$

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

| Which formula is incorrect? | $\mathrm{CsSO}_{4}$ | $\mathrm{CaCO}_{3}$ | $\mathrm{BaZn}_{2}\left(\mathrm{BO}_{3}\right)_{2}$ |
| :--- | :--- | :--- | :--- |
| Which has the lowest melting point? | NaCl | ClF | NaF |
| Which is the least polar molecule? | $\mathrm{PCl}_{3}$ | $\mathrm{PCl}_{5}$ | $\mathrm{ICl}_{5}$ |
| Which is the best Lewis acid? | $\mathrm{C}_{2} \mathrm{H}_{6}$ | $\mathrm{~B}_{2} \mathrm{H}_{6}$ | $\mathrm{~N}_{2} \mathrm{H}_{4}$ |
| Which is the strongest oxidant? | HCl | HClO | $\mathrm{HClO}_{4}$ |

5 marks

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

When 1.00 g of a white solid $\mathbf{A}$ is strongly heated, 0.78 g of another white solid, $\mathbf{B}$, 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 $25^{\circ} \mathrm{C}$. Bubbling the gas into a solution of $\mathrm{Ca}(\mathrm{OH})_{2}$ forms another white solid, $\mathbf{C}$. If the white solid $\mathbf{B}$ is added to water, the resulting solution turns red litmus paper blue. Addition of aqueous HCl to the solution of $\mathbf{B}$ and evaporation of the resulting solution to dryness yields 1.055 g of a white solid $\mathbf{D}$. When $\mathbf{D}$ is placed in a Bunsen burner flame, it colours the flame green.
A: $\qquad$ D: $\qquad$

B: $\qquad$

C: $\qquad$

## 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.
(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, $\mathrm{NH}_{4} \mathrm{Cl}_{(a q)}$. 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.

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 ( ${ }^{\circ} \mathbf{C}$ ) | 25 | 50 | 75 | 100 |
| :--- | :---: | :---: | :---: | :---: |
| Standard <br> electromotive force (V) | 0.908 | 0.875 | 0.849 | 0.814 |

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

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.
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 $\mathbf{A}$ with hydrogen gas and a palladium catalyst affords compound $\mathbf{B}$ 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?
(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

## 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.
(b). Write a single net ionic equation for the reaction that gives rise to the first (phenolphthalein) 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?
(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 $105.99 \mathrm{~g} / \mathrm{mol}$ ). Show your calculation for full 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 $50.32 \mathrm{~mL}(35.35 \mathrm{~mL}$ beyond the phenolphthalein end-point).
(f). What is the contaminant, sodium hydroxide or sodium bicarbonate? Give clear and concise reason(s) for your answer.
(g). What is the mole fraction of contaminant in the sample?

## 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).

$$
\mathrm{E}+\mathrm{S} \underset{k_{-l}}{k_{l}} \mathrm{ES} \xrightarrow{k_{2}} \mathrm{E}+\mathrm{P}
$$

(a). Express the rate of product formation by writing a kinetic expression.
(b). Write a steady state expression $\left(\mathrm{K}_{\mathrm{eq}}\right)$ for this system.
(c). If $[E T]=$ 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.
(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 | 2 | Data Sheet |  |  |  |  |  |  |  |  |  | 13 | 14 | 15 | 16 | 17 | 18 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }_{1.008}^{1}$ |  |  |  |  |  |  |  |  |  |  |  | ${ }_{2}^{2}$ |  |  |  |  |
| $\sqrt{6.941}^{3 \mathrm{Li}}$ | $\begin{array}{\|l\|} \hline 4 \\ \mathrm{Be} \\ 9.012 \end{array}$ | Fiche d <br> Relative Atomic Masses (1985 IUPAC) <br> *For the radioactive elements the atomic mass of an important isotope is given |  |  |  |  | e données <br> Masses Atomiques Relatives (UICPA,1985) *Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important |  |  |  |  |  | ${ }_{5}^{5}$ | ${ }^{6}$ | ${ }_{14.007}{ }^{\text {N }}$ | ${ }^{8} 0$ | ${ }_{9}^{9} \mathrm{~F}$ | 10 <br> Ne <br> 20.180 |
|  |  |  |  |  |  |  |  |  |  |  | ${ }^{17}$ | 18 |  |  |  |  |
| 22.990 | 24.305 | 3 | 4 | 5 | 6 | 7 |  |  |  |  |  | 8 | 9 | 10 | 11 | 12 |  | . 086 | 974 | S. 27 | ${ }_{453}$ | ${ }_{39.948}$ |
| ${\underset{39}{19} \mathrm{~K}}_{1988}$ | ${ }_{40.08}^{20}$ | $\begin{array}{\|l\|} \hline 21 \\ \text { Sc } \\ 44.956 \end{array}$ | ${ }_{47,88}^{22} \mathrm{Ti}^{22}$ | $\int_{50.942}^{23}$ | ${ }^{24}{ }_{51.996}^{24}$ | ${ }_{554.938}^{25}$ | ${ }^{26} \mathrm{Fe}$ | ${ }^{27}$ Co | $\begin{array}{\|c\|} \hline 28 \\ \mathrm{Ni} \\ 58.69 \end{array}$ | ${ }^{29} \mathrm{Cu}$ | ${ }_{\text {30 }}^{12}$ | $\left.\right\|_{69.72} ^{\mathrm{Ga}_{3}}$ | ${ }_{72,61}^{32}$ | As <br> 74.92 | $\begin{aligned} & 34 \\ & \mathrm{Se} \\ & 88.96 \end{aligned}$ | $\begin{aligned} & 35 \\ & \mathrm{Br} \\ & 79.904 \end{aligned}$ | 36 <br> Kr <br> 83.80 |
| $\begin{aligned} & { }_{85}^{37} \mathrm{Rb}_{85} \\ & \hline \end{aligned}$ | $38$ | $\stackrel{3}{39} \mathbf{Y}, 906^{\mathbf{Y}}$ | ${ }_{91.22}^{40}$ | $\underbrace{41}_{92.906} \mathrm{Nb}$ | ${ }_{9}^{42} \mathrm{Mo}$ | $\begin{gathered} 43 \\ \text { Tc } \\ \text { (98) } \end{gathered}$ | $\begin{array}{\|l\|} \hline \text { Ru } \\ \text { Ru } \\ \hline 10.07 \end{array}$ | $\left\lvert\, \begin{gathered} 45 \\ R_{102.006} \\ \hline \end{gathered}\right.$ | 46 <br> $\mathrm{Pd}_{106.42}$ | ${\underset{107.87}{47}}^{4 \mathrm{Ag}}$ | ${ }^{48} \mathrm{Cd}$ $\underbrace{}_{112 \cdot 41}$ | $\ln _{114.82}^{49}$ | ${ }_{118.71}^{50}$ | $\left\lvert\, \begin{aligned} & 51 \\ & \text { Sb } \\ & \text { S2 } \\ & \hline \end{aligned}\right.$ | $\begin{gathered} 52 \\ \mathrm{Te}_{127.60} \end{gathered}$ | ${ }_{\text {23 }}^{53}$ | 54 <br> Xe <br> 131.29 |
| $\begin{aligned} & 55 \\ & \mathbf{1 3 2 . 9 0 5} \end{aligned}$ | $\begin{aligned} & 56 \\ & \mathrm{Ba}_{137.33} \\ & \hline \mathrm{Ba} \end{aligned}$ | ${ }_{137}^{57}{ }_{138}^{5 \cdot 9}$ | ${\underset{178.49}{72}}_{\mathrm{Hf}_{1}}$ | $\mathrm{F}_{180.948}^{73}$ | ${\underset{18}{743.85}}^{74}$ | $\begin{aligned} & 75 \\ & \mathrm{Re} \\ & 186.2 \end{aligned}$ | ${ }^{76} \mathrm{Os}$ | ${ }^{77} \begin{aligned} & \text { Ir } \\ & 192 \cdot 2 \end{aligned}$ | $\left\lvert\, \begin{aligned} & 78 \\ & \mathrm{Pat}_{195.08} \end{aligned}\right.$ | ${\underset{196}{ }{ }^{796.967}}^{79}$ | $\begin{aligned} & 80 \\ & { }_{200.59}^{89} \end{aligned}$ | $\begin{gathered} 81 \\ \mathrm{TI}_{204.37} \end{gathered}$ | $8$ | $\left\lvert\, \begin{array}{l\|} 83 \\ \mathrm{Bi}_{20.980} \end{array}\right.$ | $\begin{array}{\|l\|} \hline 84 \\ \text { Po } \\ \text { (209) } \end{array}$ | $\begin{aligned} & 85 \\ & \text { At } \\ & (210) \end{aligned}$ | 86 <br> Rn <br> (22) |
| $\stackrel{i}{(223)}_{87}^{\mathrm{Fr}}$ | $\left.\right\|_{226.03} ^{88}{ }_{20}^{\mathrm{Ra}}$ | 89 <br> AC <br> 227.03 | $\begin{aligned} & 104 \\ & \mathrm{Rf} \\ & (261) \end{aligned}$ | $\int_{(262)}^{105}$ | $\left\lvert\, \begin{aligned} & (106 \\ & \mathrm{Sg} \\ & (263) \end{aligned}\right.$ | 107 <br> Bh <br> $(262)$ | $\begin{gathered} 108 \\ \mathrm{Hs} \end{gathered}$ | $\begin{gathered} 109 \\ \mathrm{Mt} \end{gathered}$ | $\begin{gathered} 110 \\ \text { Ds } \end{gathered}$ |  |  |  |  |  |  |  |  |




