THE CANADIAN CHEMISTRY CONTEST 2007

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

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2007

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 promptly 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 THE DATA SHEET PROVIDED WITH 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 ___

Number of chemistry courses at a Québec CÉGEP ___

Male ☐ Canadian Citizen ☐ Landed Immigrant ☐ Visa Student ☐

Female ☐ Passport valid until November 2007 ☐

Nationality of Passport ____________________

ANALYTICAL CHEMISTRY

1a. The acids and bases typically used in acid-base titrations (*e.g.* hydrochloric acid and sodium hydroxide) must first be standardised (*i.e.* their concentration accurately determined by experiment) before use. This is done using *primary standards*, such as potassium hydrogen phthalate ($KHC_8H_4O_4$ or KHP, structure below.) Such materials are solids that are easily dried, obtainable in high purity, chemically and physically stable, and have relatively high molar masses. KHP in particular is routinely used to standardise sodium hydroxide. It is dried in an oven at 110 °C for 2 hours to remove any adsorbed water, then cooled in a dessicator before use.

potassium hydrogen phthalate (KHP) **phthalic acid**

(i) Calculate the molar mass of KHP from its molecular formula.

1 mark

(ii) What mass of KHP should be dissolved in 100.0 mL of water to make a 0.100 *M* KHP solution?

1 mark

(iii) Write balanced and net ionic equations for the reaction of KHP with sodium hydroxide. Use HP^- to represent the hydrogen phthalate anion, and P^{2-} to represent the phthalate dianion.

1 mark

(iv) Which of the following statements best explains why KHP is used as a primary standard instead of the diprotic parent compound, phthalic acid? Circle your answer. *1 mark*

(1) Because phthalic acid is hygroscopic and forms anhydride upon drying.
(2) Because it is difficult to calculate a molar equivalent of a diprotic acid.
(3) Because phthalic acid is a weak acid.
(4) Because phthalic acid has a lower molecular weight.

(v) A solution of sodium hydroxide was standardised by accurately transferring 25.00 mL of 0.1006 *M* KHP into a titration flask, adding 3 drops of phenolphthalein indicator, and titrating with the sodium hydroxide solution until the first persistent appearance of a faint pink colour. Calculate the molar concentration of the NaOH titrant, given that 24.05 mL was required to reach the end-point.

2 marks

1b. The sodium hydroxide titrant from question 1(v) was subsequently used to determine the concentration of a dilute phosphoric acid sample: 10.00 mL of the acid was accurately transferred into a titration flask, 3 drops of phenolphthalein indicator added, and the sample titrated with NaOH as described previously.

(i) The acid dissociation constants for the three acidic protons of phosphoric acid are:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_{a1} = 1.1 \times 10^{-2}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad K_{a2} = 7.5 \times 10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad K_{a3} = 4.8 \times 10^{-13}$$

Given this information, write a balanced molecular equation for the reaction between phosphoric acid and sodium hydroxide that will be observed at the phenolphthalein end point, (phenolphthalein changes colour between pH 8.2 and 9.8).

2 marks

(ii) Calculate the molar concentration of the phosphoric acid sample, given that the volume of NaOH required to reach the end point was 25.45 mL.

2 marks

(iii) Another way to perform the titration of phosphoric acid with sodium hydroxide would be to measure the pH of the solution throughout the experiment, and determine the equivalence point from the resulting plot of pH *vs*. volume of titrant added. What is the difference between an equivalence point and an end point?

1 mark

(iv) If the titration were conducted as described in part **1b**(iii), how many equivalence points would be observed?

1 mark

2. This question relates to the reaction between peroxodisulfate(VI) ions and iodide ions in aqueous solution, which takes place according to the following equation:

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightarrow 2\,SO_4^{2-}(aq) + I_2(aq)\ .\ .\ .\ .\ .\ \textbf{Equation 1}$$

This reaction is a second order reaction with a high activation energy.

In addition to values given on your data sheet, you will need to use the following information in order to respond to the questions about this reaction:

Standard reduction potentials

$$I_2(aq) + 2\,e^- \rightleftharpoons 2\,I^-(aq); \quad E^\ominus = +\,0.536\text{ V}$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq); \quad E^\ominus = +\,0.771\text{ V}$$

$$S_2O_8^{2-}(aq) + 2\,e^- \rightleftharpoons 2\,SO_4^{2-}(aq); \quad E^\ominus = +\,2.010\text{ V}$$

Standard free energies of formation

$\Delta G^\ominus_f\{S_2O_8^{2-}(aq)\} = -1114.9$ kJ mol^{-1}; $\Delta G^\ominus_f\{I^-(aq)\} = -\,51.6$ kJ mol^{-1}; $\Delta G^\ominus_f\{SO_4^{2-}(aq)\} = -744.5$ kJ mol^{-1}

Calculation formulae

$\Delta G^\ominus = -\,nFE^\ominus$, 1 Volt = 1 J C^{-1}

and $\log_{10} k = \log_{10} A - E_a/2.3\,RT$ (where k is the rate constant, A is a constant, E_a is the activation energy, and T is the absolute temperature in K)

(a) For the reaction represented by **Equation 1**:

(i) Suggest a **reason** why the activation energy is high.

1 mark

(ii) Calculate the standard cell potential, $E^\ominus$, for the reaction:

1 mark

(iii) Calculate the standard free energy, $\Delta G^\ominus$, of the reaction:

2 marks

(iv) Use the value you obtained in (iii) above to calculate $\Delta G^\ominus_f\{I_2(aq)\}$:

2 marks

(v) After performing a series of experiments on the reaction at different temperatures, a graph of $\log_{10} k$ (y axis) against $1/T$ (x axis) was obtained. The slope of this graph was -9.76×10^3 K. Calculate the activation energy, E_a, for the reaction:

2 marks

(b) The rate of the reaction represented by **Equation 1** can be substantially increased by using $Fe^{3+}(aq)$ ions as catalyst. The reaction now takes place in two steps.

(i) Write a balanced stoichiometric equation for each of these two steps, in the correct order:

<u>First step</u>

1 mark

<u>Second step</u>

1 mark

(ii) What is the value of $\Delta G^\ominus$ for the overall catalyzed reaction?

1 mark

(iii) How does the activation energy change when a catalyst is added to the reaction mixture?

1 mark

3a. The precipitation of iron(III) hydroxide is used to clarify waste waters because the gelatinous compound is very efficient at the entrapment of contaminants. Ignoring the many hydroxoiron(III) species, we can write a simplified equilibrium as:

$$Fe^{3+}(aq) + 3\ H_2O(l) \rightleftharpoons Fe(OH)_3(s) + 3\ H^+(aq)$$

(i) Using the ion product constant for water at 25°C of 1.0×10^{-14}, and given the solubility product for iron(III) hydroxide as 2.0×10^{-39}, provide an expression for provide an expression for the mathematical relationship between $[Fe^{3+}]$ and $[H^+]$.

2 marks

(ii) If iron(III) hydroxide is used to clarify a water supply, what concentration of free iron(III) ions will enter the water system if the water supply has a pH of 6.00 ?

1 mark

(iii) What mass of iron(III) hydroxide will be dissolved during the passage of 1×10^6 L of water ?

1 mark

3b. Note: *Read carefully the whole question before beginning to solve it.* Dilute hydrochloric acid was added to a metallic looking compound **A** (molecular weight 90.756). A colourless gas **B** with a characteristic, unpleasant odour was formed together with a pale green solution of the cation **C**.

The gas **B** was burned in air to give another colourless gas **D** that turned yellow dichromate paper green. Mixing **B** and **D** gave a yellow solid element **E**. Depending on the mole ratios, **E** reacted with chlorine gas to give two chlorides, **F** and **G**, in addition of hydrogen chloride (HCl).

Addition of zinc metal to a sample of the green cation solution **C** gave a metal **H** (with electron configuration of $[Ar]3d^8 4s^2$).

Identify each of the substances and write balanced chemical equations for each reaction.

A = **B =** **C =** **D =**

4 marks

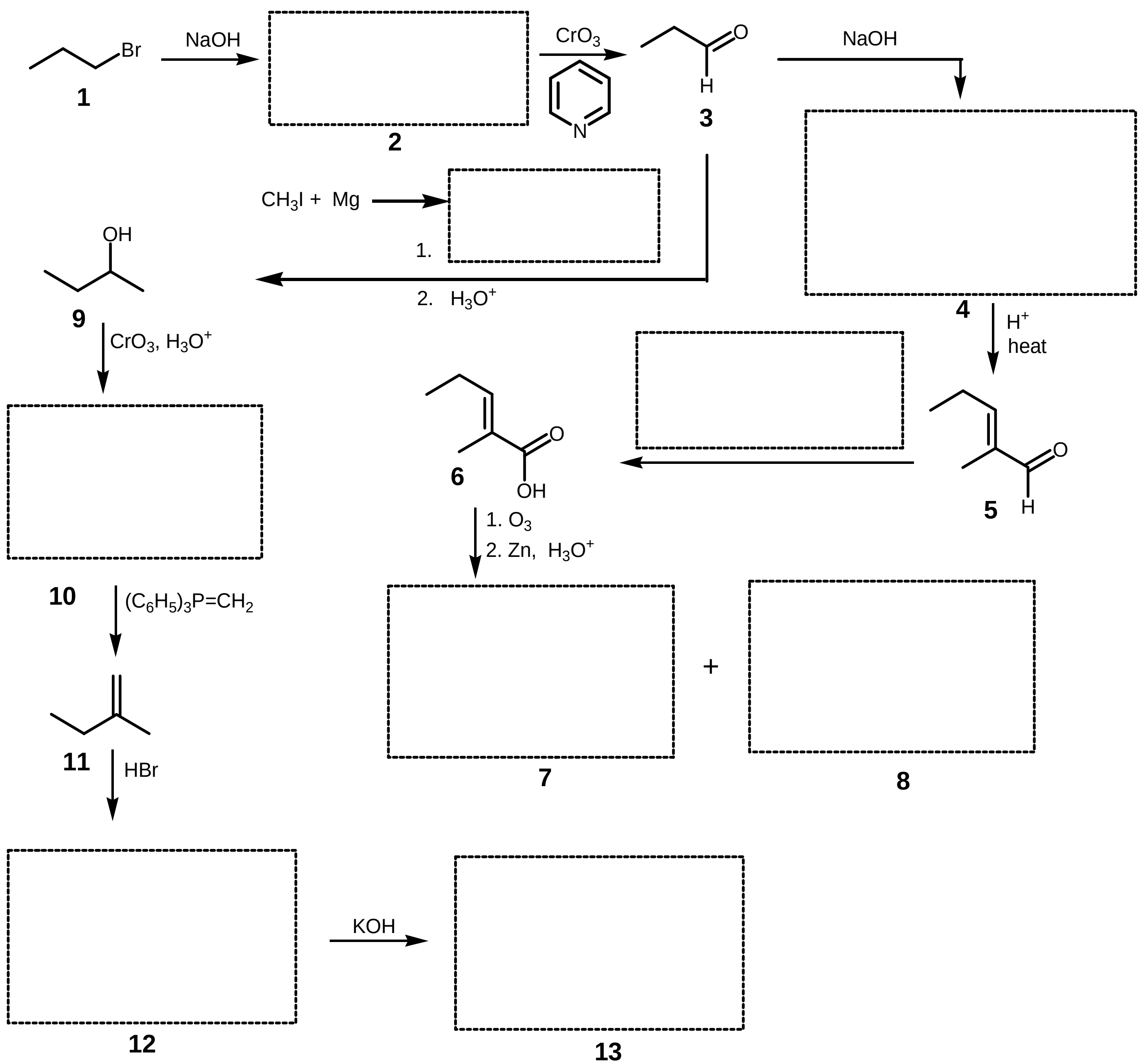
E = **F =** **G =** **H =**

Reactions:

4 marks

ORGANIC CHEMISTRY

4a. Draw structures for the missing intermediates and reagents in the following sequence of reactions (*1 mark* each box) :



4b. Give IUPAC names for the following compounds (*1 mark* each) :

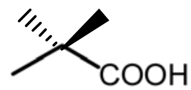
3 –

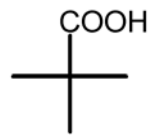
9 –

11 –

BIOLOGICAL CHEMISTRY

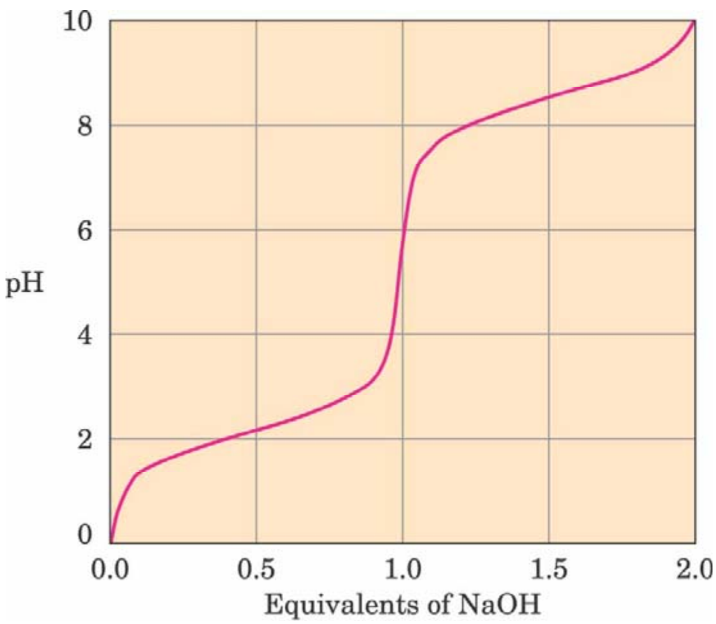
5a. (i) Alanine (Ala) is a simple amino acid [$CH_3CH(NH_2)COOH$] with the *S* configuration. Using the partial structures below, draw the three-dimensional structure and the Fischer projection of alanine.





(*2 marks*)

(ii) The following graph shows a titration curve for an amino acid. What are the approximate values of pK_{a1} and pK_{a2}? What is the isoelectric point (p*I*) for this amino acid? (*3 marks*)



pK_{a1} =

pK_{a2} =

p*I* =

5b. Enzymes are highly efficient catalysts that are found in almost all biological systems. Almost all known enzymes are proteins, which is a class of macromolecules essential to life on earth. A simple enzymatic reaction could be represented as below:

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

where

S = substrate concentration,
E = enzyme concentration
ES = enzyme-substrate complex,
P = product concentration

(i) Define a) rate of product formation, and b) steady state rate constant.

(*2 marks*)

(ii) [ET] (total enzyme concentration) is the sum of both unbound and substrate bound enzyme concentration. Find an alternate expression for rate of product formation using ET.

(*2 marks*)

(iii) Write a balanced equation for the hydrolysis reaction of the simple dipeptide Ala-Ala.

(*3 marks*)

- The End -