THE CANADIAN CHEMISTRY CONTEST 2014
for high school and CEGEP students

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2014

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 ☐   Passport Valid until November 2014   ☐   Nationality of Passport _____

Teacher _____   Teacher E-Mail _____

ANALYTICAL CHEMISTRY

1. a) A solution is prepared by adding enough water to 560 mg of sodium bicarbonate ($NaHCO_3$) to make up 900 mL of solution. Given that carbonic acid is a diprotic acid where $K_{a1} = 4.45 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$, what is the pH of the resulting solution? *Show your work for full marks*.

(6 marks)

b) Silver nitrate ($AgNO_3$) is often used as a titrant when determining the amount of chloride ions (Cl^-) in drinking water (where the pH is close to 7) *via* formation of a precipitate ($K_{sp} = 1.8 \times 10^{-10}$). At the equivalence point of the titration, neither Ag^+ nor Cl^- will be present in excess in the solution.

(i) Write the precipitation reaction for this titration.

(1 mark)

(ii) How many millilitres of 0.01000 M $AgNO_3$ (aq) are required to titrate 100 mL of water taken from a drinking fountain which has 29.5 mg Cl^-/L?

(2 marks)

(iii) K_2CrO_4 can be used as an indicator in this titration as red-brown Ag_2CrO_4 will begin to precipitate after all of the Cl^- (aq) anions have precipitated (no Ag_2CrO_4 will form until after the equivalence point: $K_{sp} = 9.0 \times 10^{-12}$). What amount of K_2CrO_4 should be added to the original analyte solution to make sure that no Ag_2CrO_4 (s) precipitates until immediately after the equivalence point?

(3 marks)

PHYSICAL CHEMISTRY

2. The efficiency of electric power plants with steam turbines can be modelled using thermodynamics. In a simple model, water takes up heat (q_h) as steam at a high temperature (T_h). Part of this heat is used to carry out work (w), the rest is released to the surroundings at a cooler temperature (T_c). The <u>maximum</u> possible efficiency (ε) is given by the following expression:

$$\epsilon = \frac{|w|}{q_h} \times 100\% = \frac{T_h - T_c}{T_h} \times 100\%$$

a) If the steam leaving the turbine is condensed to liquid water at 45.2 °C (T_c) and the system operates at 35% efficiency, what is T_h (in °C)?

(2 marks)

b) Is this calculated T_h a maximum or minimum value?

(1 mark)

c) The pressure at which the gas phase of a substance is in equilibrium with its liquid phase is called the vapour pressure (p). The Clausius-Clapeyron equation can be used to predict the vapour pressure of a liquid at any temperature if the enthalpy of vapourization and the vapour pressure at some other temperature are known.

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The enthalpy of vapourization of water is 40.656 kJ mol^{-1} at 100.0 °C and exactly 1 bar. Estimate the pressure (in atm) of steam at 241.7 °C, assuming it is in equilibrium with liquid water.

(3 marks)

d) The estimated pressure is not very accurate due to approximations made in deriving the Clausius-Clapeyron equation, one of which is that water vapour behaves as an ideal gas. The van der Waals equation of state is an improved form of the ideal gas law:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

in which V_m is the molar volume and a and b are the van der Waals coefficients. Note that when a and b are zero, the van der Waals equation reduces to the ideal gas law. For water, a = 5.464 atm dm^6 mol^{-2} and b = 3.05 × 10^{-2} dm^3 mol^{-1}. If the ideal gas law predicts a pressure of 40.39 atm for water in the vapour phase at 241.7 °C, what is the pressure (in atm) predicted by the van der Waals equation?

(3 marks)

e) An alternative and frequently more accurate approach to calculating gas pressure is to use a truncated form of the virial equation of state,

$$pV_m = RT\left(1 + \frac{B}{V_m}\right)$$

in which V_m is the molar volume and B is known as the second virial coefficient. The disadvantage is that the value of B is temperature dependent. For water at 570.4 K, B is -117.3 cm^3 mol^{-1}. The density of the gas is 0.01722 kg L^{-1}. What is the pressure (in atm) according to the truncated virial equation?

(3 marks)

ORGANIC CHEMISTRY

3. Although opium has been known for thousands of years, its active constituent, morphine, was not isolated until 1805.

morphine   heroin
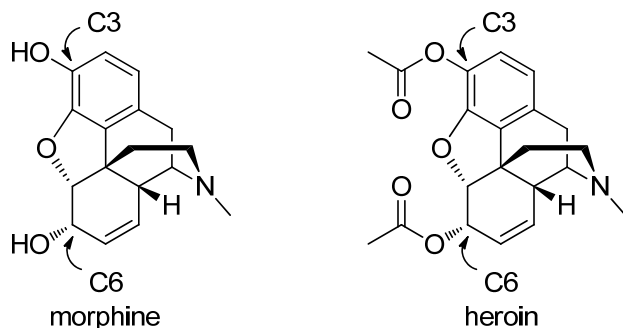
a) How many chirality centres (stereocentres) does morphine have?   What is the absolute configuration of the carbon atom labeled as position 6?

Chirality centres: Configuration at C6:

(2 marks)

b) In an attempt to make a more effective version of morphine, chemists at Bayer created heroin, which was first marketed in 1898. What effect do you expect the acetyl groups placed at carbons C3 and C6 will have on the polarity of heroin?

(1 mark)

c) The nitrogen atom of morphine has a pKa value of approximately 9.
   (i) Draw the form of morphine that you would expect to predominate at physiological pH, 7.4.

(1 mark)

   (ii) What effect does this form have on the overall polarity of morphine?

(1 mark)

d) Cinnamaldehyde is the main constituent of cinnamon oil and is the starting point for the reactions in the scheme shown below. Complete each box to show either the major product of the reaction, or a reasonable set of reaction conditions to effect the transformation shown. Show relative stereochemistry where appropriate.

cinnamaldehyde

Br_2

HCl

CrO_3, H_2SO_4

1. $NaBH_4$
2. H_3O^+

1. MeMgBr (excess)
2. H_3O^+
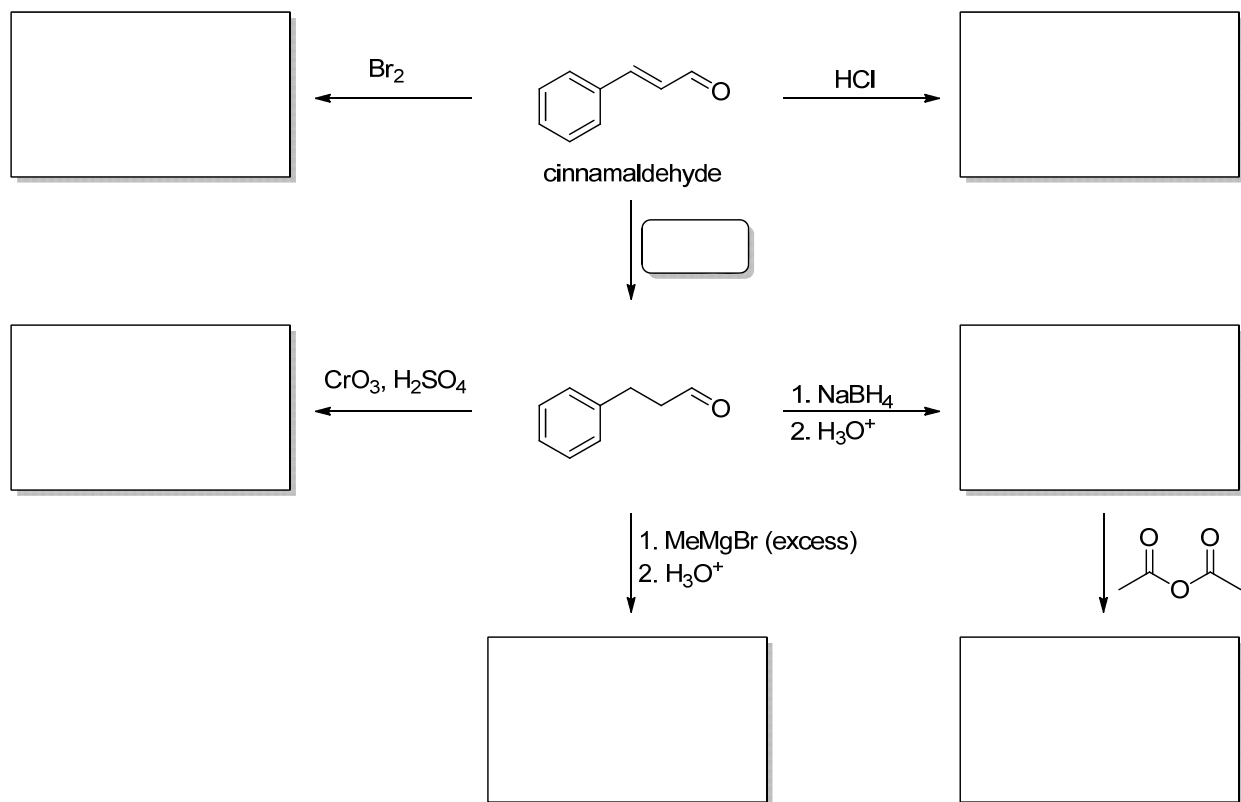
(7 marks)

4. a) The complex ion $[Ti(NCS)_6]^{3-}$ has a single absorbance band at 544 nm.

(i) Calculate the crystal field splitting energy, Δ, in kJ mol^{-1} for this ion.

(*2 marks*)

(ii) The wavelength of 544 nm corresponds to green colour in the visible spectrum. Predict the colour of the $[Ti(NCS)_6]^{3-}$ ion. Briefly explain how you arrived at your answer.

(*2 marks*)

b) In 1968, the coordination compound $[Cr(NH_2CH_2CH_2NH_2)_3][Ni(CN)_5] \cdot 1.5\ H_2O$ was reported in the journal *Inorganic Chemistry*.[1] The compound was interesting because it possessed several unique features at the time, the most notable being that the nickel complex ion was present in the solid in two different 5-coordinate geometries.

(i) If the oxidation state of the chromium is +3, what is the oxidation state of the nickel? Briefly explain how you arrived at your answer.

(*1 mark*)

(ii) Name the ligands present in the coordination compound.

(*1 mark*)

(iii) Is the chromium ion optically active? Support your answer with the aid of suitable diagrams. You may represent the $NH_2CH_2CH_2NH_2$ as N-------N in your diagrams.

(*2 marks*)

[1] Raymond, K.N.; Cornfield, P.W.R.; Ibers, J.A. *Inorg. Chem.*, **1968**, *7*, 1362-1372.

(iv) One of the possible geometries for the 5-coordinate nickel complex is trigonal bipyramidal. Name the other geometry.

(*1 mark)*

(v) Sketch the crystal field splitting diagram for the trigonal bipyramidal geometry. Make sure to label the individual orbitals in the diagram. Complete the diagram by filling the orbitals with the appropriate number of electrons.

(2 *marks)*

(vi) It was unusual to find the nickel ion present in two different geometries in the same solid. The journal article goes on to explain that one of the geometries is nearly perfect in shape while the other is distorted from its ideal shape. Suggest a reason as to why both geometries are observed in the solid.

(*1 mark)*

BIOLOGICAL CHEMISTRY

5. Glutathione (GSH) is a tripeptide whose function is to destroy harmful oxidizing agents in the body by reducing them. In the process, glutathione is oxidized, resulting in the formation of a disulfide bond between two glutathione molecules (GSSG). High cellular levels of GSSG are an indication of oxidative stress. The enzyme glutathione reductase subsequently reduces the disulfide bond, returning glutathione to its original condition so it can react with more oxidizing agents.
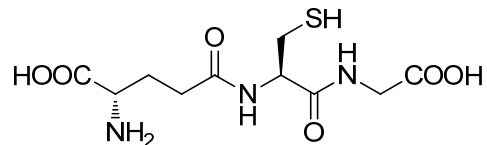
GSH

a) The connection between two of the amino acids that form glutathione is unusual for a peptide, but is important to provide stability from hydrolysis by peptidases. Draw the peptidase-sensitive structure.

(1 mark)

b) From which three amino acids is glutathione formed? Provide either the abbreviation or the full name of each amino acid. (Hint: use the data table provided to identify the side-chains).

(1.5 marks)

c) Draw the form of glutathione that is predominant at pH 7.4 (physiological pH).

(2 marks)

d) Assuming that only one site is ionizable at physiological pH, what is the ratio of the two most predominant forms? *Show your work for full marks*.

(1.5 marks)

e) Given the biochemical standard reduction potentials for the reaction catalyzed by the enzyme glutathione reductase, calculate the standard biochemical free energy change in this reaction. Is this a spontaneous reaction? *Show your calculation for full marks*.

$$\text{GSSG} \ + \ \text{NADPH} \ + \ \text{H}^+ \ \underset{\xleftarrow{\hspace{3cm}}}{\overset{\text{glutathione reductase}}{\xrightarrow{\hspace{3cm}}}} \ 2 \ \text{GSH} \ + \ \text{NADP}^+$$

$$\text{GSSG} + 2 \ \text{H}^+ \ + \ 2 \ e^- \ \longrightarrow \ 2 \ \text{GSH} \qquad E_o' = \text{-0.23 V}$$

$$\text{NADP}^+ + \text{H}^+ \ + \ 2 \ e^- \ \longrightarrow \ \text{NADPH} \qquad E_o' = \text{-0.32 V}$$
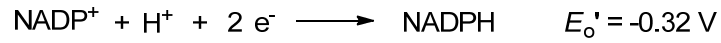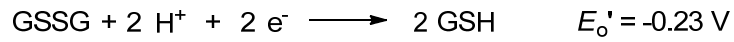
(3 marks)

f) Based on your answer in (e), calculate the equilibrium constant under biochemical standard conditions (these are the same as regular standard conditions except that the pH is 7.0). Are the reactants or products favoured by this equilibrium position? *Show your calculation for full marks*.

(3 marks)

--END OF PART C--

Data Sheet

Physical Constants

Name	Symbol	Value
Avogadro's constant	N_A	6.0221×10^{23} mol^{-1}
Boltzmann constant	k_B	1.3807×10^{-23} J K^{-1}
Gas constant	R	8.3145 J K^{-1} mol^{-1}
Faraday constant	F	96485 C mol^{-1}
Speed of light	c	2.9979×10^8 m s^{-1}
Planck's constant	h	6.6261×10^{-34} J s
Standard pressure	$p°$	1×10^5 Pa = 1 bar
Atmospheric pressure	p_{atm}	1.01325×10^5 Pa
Zero of the Celsius scale		273.15 K

Amino Acids

Small

H₂N–CH(H)(H)–COOH
Glycine (Gly, G)
MW: 57.05

H₂N–CH(CH₃)–COOH
Alanine (Ala, A)
MW: 71.09

Nucleophilic
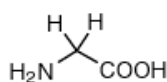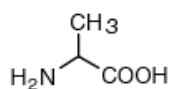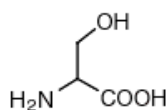
H₂N–CH(CH₂OH)–COOH
Serine (Ser, S)
MW: 87.08, pK$_a$ ~ 16
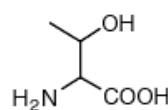
H₂N–CH(CH(OH)CH₃)–COOH
Threonine (Thr, T)
MW: 101.11, pK$_a$ ~ 16
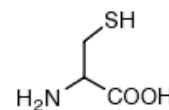
H₂N–CH(CH₂SH)–COOH
Cysteine (Cys, C)
MW: 103.15, pK$_a$ = 8.35

Hydrophobic
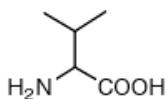
Valine (Val, V)
MW: 99.14
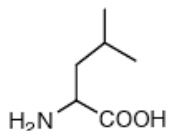
Leucine (Leu, L)
MW: 113.16
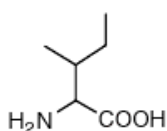
Isoleucine (Ile, I)
MW: 113.16
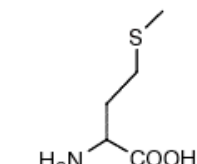
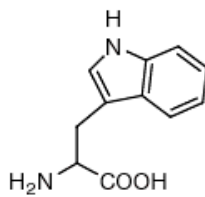Methionine (Met, M)
MW: 131.19
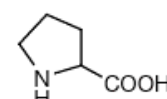
Proline (Pro, P)
MW: 97.12

Aromatic
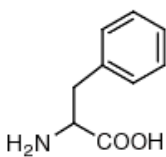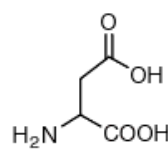
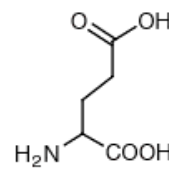Phenylalanine (Phe, F)
MW: 147.18
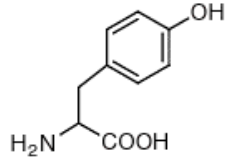
Tyrosine (Tyr, Y)
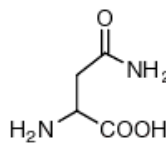MW: 163.18

Tryptophan (Trp, W)
MW: 186.21

Acidic

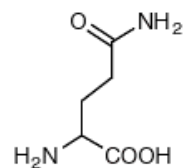Aspartic Acid (Asp, D)
MW: 115.09, pK$_a$ = 3.9

Glutamic Acid (Glu, E)
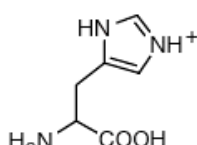MW: 129.12, pK$_a$ = 4.07
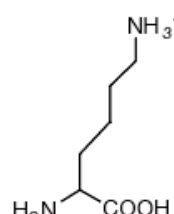
Amide

Asparagine (Asn, N)
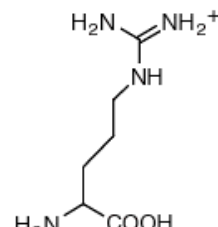MW: 114.11

Glutamine (Gln, Q)
MW: 128.14

Basic

Histidine (His, H)
MW: 137.14, pK$_a$ = 6.04

Lysine (Lys, K)
MW: 128.17, pK$_a$ = 10.79

Arginine (Arg, R)
MW: 156.19, pK$_a$ = 12.48