

THE CANADIAN CHEMISTRY CONTEST 2013

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

PART C: CANADIAN CHEMISTRY OLYMPIAD Final Selection Examination 2013

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 2013 Nationality of Passport _____

Teacher _____ Teacher E-Mail _____

INORGANIC CHEMISTRY

1. In 1962 Neil Bartlett synthesized the first noble gas compound, XePtF_6 , at the University of British Columbia. Subsequently, compounds of xenon have proven useful in chemical synthesis: xenon difluoride is used in the preparation of the anti-cancer drug 5-fluorouracil.

(a). State the valence shell electron configuration of xenon.

1 mark

(b). Bartlett's synthesis yielded a mixture of products (among them XePtF_6) which was later reformulated as the salt $[\text{XeF}][\text{PtF}_5]$. Assuming this compound contains platinum(IV), determine the oxidation state of xenon.

1 mark

(c). Subsequent to Bartlett's discovery, Claassen, Selig and Malm reported the synthesis of XeF_4 . Xenon tetrafluoride undergoes hydrolysis to give the highly reactive solid xenon trioxide.

Applying Lewis structures and VSEPR theory, sketch the molecular geometry of XeO_3 , indicating all valence electron pairs.

1 mark

State the name of the molecular geometry for XeO_3 .

1 mark

Estimate the O–Xe–O bond angles to the nearest degree.

1 mark

(d). Using the data provided below, calculate the dissociation enthalpy of an Xe–F bond. Xenon tetrafluoride sublimates at 117°C .

standard enthalpy of formation, $\text{XeF}_4 = -267 \text{ kJ mol}^{-1}$

standard enthalpy of sublimation, $\text{XeF}_4 = +61 \text{ kJ mol}^{-1}$

bond dissociation enthalpy, $\text{F}_2 = +155 \text{ kJ mol}^{-1}$

3'marks

(e). Relative to the lighter noble gases, xenon is approximately 20 times less abundant in the atmosphere than predicted. One theory to explain the missing xenon is that it displaces silicon from quartz (SiO_2) under high temperatures and pressures experienced in the Earth's crust. In 2011, Schrobilgen and Brock reported the first synthesis of XeO_2 at McMaster University.

Carbon dioxide sublimates at -78°C and silicon dioxide melts between 1600 and 1725°C . Account for this difference by comparing and contrasting the bonding in CO_2 and SiO_2 .

2'marks

Xenon dioxide is insoluble in water and has a melting point greater than 0°C . On the Pauling scale, xenon has an electronegativity of 2.6 and oxygen has an electronegativity of 3.4. Draw a structure for XeO_2 that is consistent with all of the information provided.

2'marks

PHYSICAL CHEMISTRY

2. Answer the following questions for the chemical reaction between carbon monoxide and hydrogen gas to produce liquid methanol.



(a). If you increase the temperature of this reaction from 200°C to 250°C, will the equilibrium shift towards the reactants, product, or remain unchanged?

1 mark

(b). If you decrease the volume of the reaction container, will the equilibrium shift towards the reactants, product, or remain unchanged?

1 mark

(c). If you remove methanol from the reaction once it starts to form, will the equilibrium shift towards the reactants, product, or remain unchanged?

1 mark

(d). Given the following standard entropy values: $S^\circ_{\text{CO(g)}} = 198 \text{ J mol}^{-1} \text{ K}^{-1}$, $S^\circ_{\text{H}_2\text{(g)}} = 131 \text{ J mol}^{-1} \text{ K}^{-1}$, and $S^\circ_{\text{CH}_3\text{OH(l)}} = 127 \text{ J mol}^{-1} \text{ K}^{-1}$, is this reaction spontaneous at 25°C?

2 marks

(e). Explain why the spontaneity of this reaction depends on temperature.

2 marks

(f). At what temperatures will the reaction be spontaneous? *Show your calculation for full marks.*

2 marks

(g). Calculate the equilibrium constant (K) for this reaction at both 25°C and 200°C.

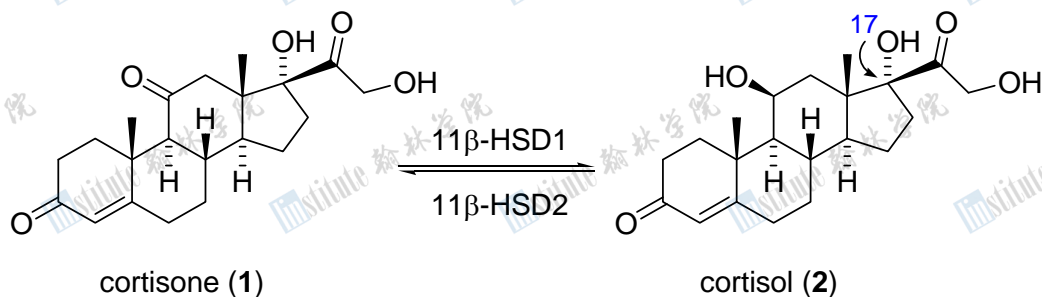
2 marks

(h). Does the magnitude of the equilibrium constant at different temperatures agree with the predicted spontaneity of the reaction at different temperatures?

1 mark

ORGANIC CHEMISTRY

3. As you read this question, or for that matter *whenever* you feel stressed, your adrenal gland releases a concoction of steroidal hormones. This includes cortisol (compound **2**, below) which stimulates gluconeogenesis (the breakdown of glycogen to glucose-1-phosphate) and gives your cells access to stored-up energy.



(a). How many chirality centres (stereocentres) are present in cortisol? What is the absolute configuration of the carbon atom labeled as C17?

Chirality centres:

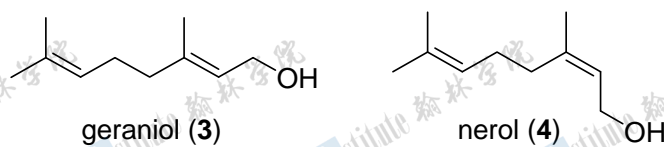
Configuration at C17:

2 marks

(b). State the **type** of reaction being carried out by the enzyme 11 β -hydroxysteroid dehydrogenase Type 1 (11 β -HSD1) during the conversion of **1** to **2**. Propose a laboratory reagent you might use to carry out the same reaction.

2 marks

Due to its ubiquitous availability from nature, geraniol (**3**), the primary component of rose oil, is a commonly used starting material in organic synthesis. Nerol (**4**) is an isomer of geraniol.



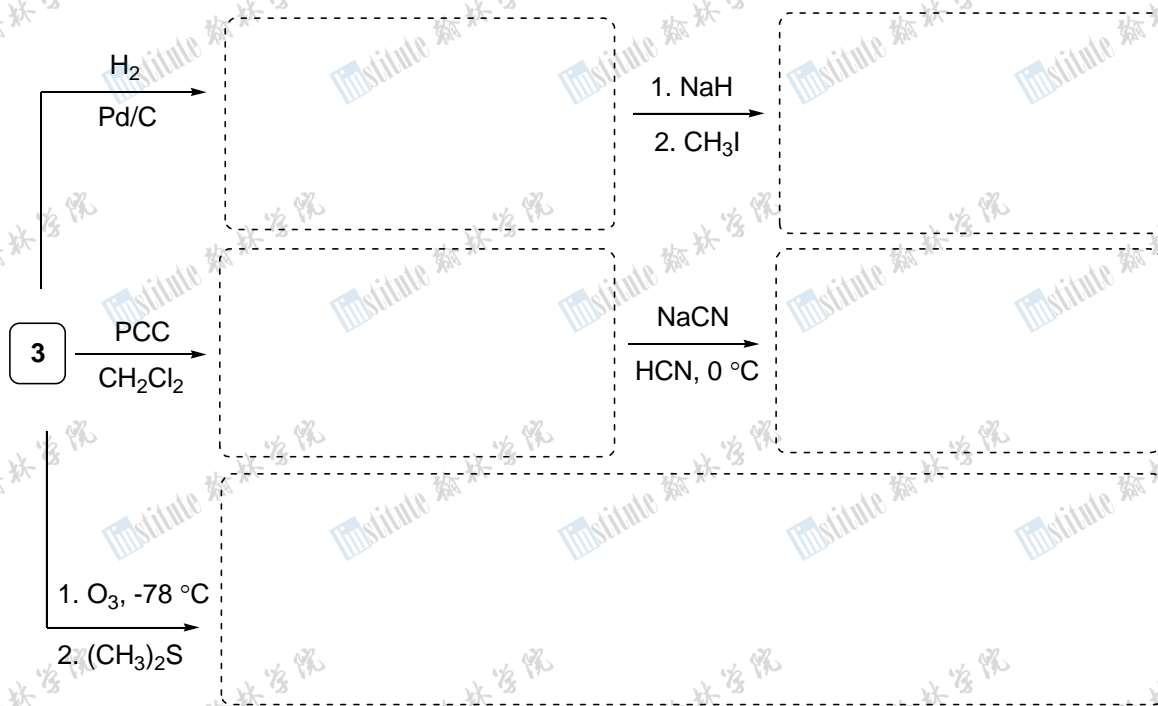
(c). What is the stereochemical relationship between geraniol and nerol?

1 mark

(d). When **3** is treated with one equivalent of *m*CPBA (*meta*-chloroperoxybenzoic acid), a mixture of two compounds having **identical** proton NMR and infra-red spectra are produced in a 1:1 ratio. Draw the structures of these two products.

1 mark

(e). Draw the products for each of the reactions of geraniol shown below (there may be more than one compound required). Note: PCC = pyridinium chlorochromate.



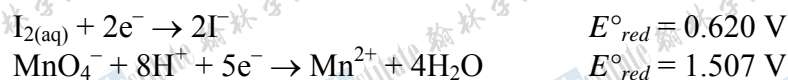
5 marks

(f). Nerol is readily converted into an achiral cyclic compound (formula $\text{C}_{10}\text{H}_{18}\text{O}$) when exposed to aqueous sulfuric acid. Draw the structure of this compound. Hint: under acidic conditions alcohols can be protonated, making them good leaving groups.

1 mark

ANALYTICAL CHEMISTRY

4. Many redox titrations can be followed potentiometrically using a platinum wire indicator electrode and a suitable reference electrode. For example, iodide (I^-) can be determined by titration in acidic solution with standard permanganate (MnO_4^-), forming manganese(II) (Mn^{2+}) and iodine (I_2). During the titration, the potential recorded by the platinum wire is initially determined primarily by the I^-/I_2 redox couple; after the equivalence point, it is determined primarily by the $\text{MnO}_4^-/\text{Mn}^{2+}$ redox couple. The relevant standard reduction potentials for these species are:



(a). Write a balanced net ionic equation for the reaction of permanganate with iodide.

1 mark

(b). What colour changes might you expect to observe during the course of this titration?

1 mark

(c). In practice, analysts prefer to use a potentiometric measurement rather than exploiting a visual colour change to determine the end-point for this reaction. Explain why this is the case.

1 mark

(d). In order to perform this titration, the analyst needs to add either excess acid or a buffer solution to the sample. Why is this necessary?

2 marks

The potentiometric titration can also be reversed, in the sense that iodide can be used as the titrant in order to determine permanganate. Under such circumstances, a known mass of a sample containing manganese is first treated with ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), then boiled, and then allowed to cool before titrating with standard iodide solution.

(e). What is the purpose of the ammonium persulphate, and why is the solution boiled before the titration?

2 marks

A 0.5697 g sample of a manganese-containing ore is digested in acid, treated with ammonium persulphate, boiled, cooled to 25°C, adjusted to pH 5.56 using by adding a suitable buffer, and titrated with 1.012 M KI solution yielding an equivalence point volume of 31.8 mL.

(f). Using the form of the Nernst equation given below, estimate the reduction potential recorded by the platinum electrode before the equivalence point when *exactly half* of the permanganate has been titrated. Assume that the iodine produced has a negligible effect on this value. *Show your calculation for full marks.*

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{Red}]^b}{[\text{Ox}]^a} \right) \text{ for } a \text{ Ox} + n \text{ e}^- \rightarrow b \text{ Red}$$

3'marks

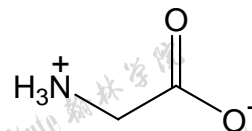
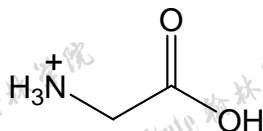
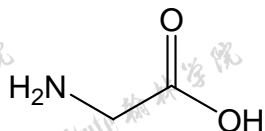
(g). What is the manganese content of the ore sample, expressed as a percentage by weight? *Show your calculation for full marks.*

2 marks

BIOLOGICAL CHEMISTRY

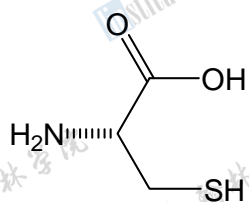
5. Amino acids are one of the basic molecules that serve many purposes in living organisms. They can polymerize to form polypeptides and eventually proteins that serve diverse functions.

(a). Which of the following represents the structure of the amino acid glycine under physiological conditions (pH = 7.4)? Circle the correct answer.

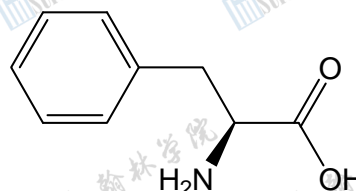


1 mark

(b). Consider the two amino acids shown below. Draw the two possible dipeptides that would result from peptide bond formation between one molecule and the other. Draw each dipeptide in the form it would exist at pH 1.0.



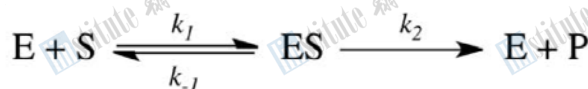
cysteine



phenylalanine

4 marks

A group of enzymes that catalyze peptide bond formation could serve to maintain tight control of many interconnected physiological functions. One way of studying kinetic effects of molecules involved in an enzyme-catalyzed reaction is to use a steady state assumption to simplify kinetic constants involved. Consider the following reaction where an enzyme (E) converts a particular substrate (S) into a product (P) via a transition state (ES).



Assuming steady state exists, a simplified constant (K_m) can be expressed as the following:

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

(c). Explain what is meant by the term “transition state”.

1 mark

(d). How would values of K_m compare between low-affinity and high-affinity enzymes?

1 mark

(e). If enzyme A binds to the substrate 50 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? At physiological temperature (37°C), what is the difference in activation energy between the two reactions?

5 marks

--END OF PART C--



1 H 1.008																	2 He 4.003					
3 Li 6.941	4 Be 9.012	Relative Atomic Masses (2012, IUPAC) *For the radioactive elements the atomic mass of an important isotope is given										Masses Atomiques Relatives (IUPAC, 2012) *Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important					5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95					
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80					
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3					
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)					
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (269)	111 Rg (272)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (292)	117 Uus	118 Uuo (294)					

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa (231.0)	92 U (238.0)	93 Np (237)	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 (262)

Symbol
Symbole

Value
Quantité numérique

Atomic mass unit	<i>amu</i>	1.66054×10^{-27} kg	<i>Unité de masse atomique</i>
Avogadro's number	<i>N</i>	6.02214×10^{23} mol ⁻¹	<i>Nombre d'Avogadro</i>
Charge of an electron	<i>e</i>	1.60218×10^{-19} C	<i>Charge d'un électron</i>
Dissociation constant (H ₂ O)	<i>K_w</i>	1.00×10^{-14} (25°C)	<i>Constante de dissociation de l'eau (H₂O)</i>
Faraday's constant	<i>F</i>	96 485 C mol ⁻¹	<i>Constante de Faraday</i>
Gas constant	<i>R</i>	8.31451 J K ⁻¹ mol ⁻¹	<i>Constante des gaz</i>
		0.08206 L atm K ⁻¹ mol ⁻¹	
Mass of an electron	<i>m_e</i>	9.10939×10^{-31} kg	<i>Masse d'un électron</i>
Mass of a neutron	<i>m_n</i>	1.67493×10^{-27} kg	<i>Masse d'un neutron</i>
Mass of a proton	<i>m_p</i>	1.67262×10^{-27} kg	<i>Masse d'un proton</i>
Planck's constant	<i>h</i>	6.62608×10^{-34} J s	<i>Constante de Planck</i>
Speed of light	<i>c</i>	2.997925×10^8 m s ⁻¹	<i>Vitesse de la lumière</i>
Rydberg constant	<i>R_∞</i>	1.097×10^7 m ⁻¹	<i>Constante de Rydberg</i>

1 Å	= 1 x 10 ⁻¹⁰ m
1 atm	= 101.325 kPa
1 bar	= 1 x 10 ⁵ Pa

STP/TPN	SATP/TPAN
273.15 K	298 K
100 kPa	100 kPa