THE CANADIAN CHEMISTRY CONTEST 2017

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

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2017

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 February 2018 ☐ Nationality of Passport __________

Teacher ___________________________ Teacher E-Mail ___________________________

1. Sulfur dioxide (SO_2) is produced by volcanoes and in various industrial processes. Since coal and petroleum often contain sulfur compounds, their combustion generates sulfur dioxide. Further oxidation of SO_2, usually in the presence of a catalyst such as NO_2, forms H_2SO_4, and thus acid rain. This is one of the causes for concern over the environmental impact of the use of these fuels as power sources.

(a). Draw the best *two* resonance structures for sulfur dioxide, SO_2, which *do not* involve sulfur using its *d*-orbitals in "hypervalency". Be sure to include all formal charges (should they exist) and lone pairs of electrons in your structures.

4 marks

(b). Draw the best resonance form for sulfur dioxide in which sulfur *does* use its *d*-orbitals in bonding. Be sure to include all formal charges (should they exist) and lone pairs of electrons in your structure.

2 marks

(c). What is the hybridization of the sulfur atom in SO_2?

2 marks

(d). Write a reaction involving SO_2 which illustrates how its sulfur atom may act as a Lewis base in reaction with a Lewis acid. In your reaction, designate the Lewis acid as “A”.

2 marks

(e). Write a reaction involving SO_2 which illustrates how its sulfur atom may serve as a Lewis acid in reaction with a Lewis base. In your reaction, designate the Lewis base as "B".

2 marks

2. Electrons moving back and forth in a one-dimensional box may only occupy discrete energy levels given by the formula

$$E = n^2 \frac{h^2}{8mL^2} \qquad n = 1, 2, 3...$$

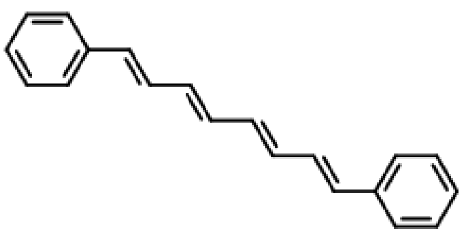
in which n is the energy level, h is Planck's constant, m is the mass of the electron, and L is the length of the box.

(a). Calculate the energy of an electron in the second energy level of a box with length 1.00 nm.

1 mark

Pi electrons in a linear, conjugated molecule or section of a molecule can be modeled after the one-dimensional box system.

(b). In the molecule 1,8-diphenyl-1,3,5,7-octatetratriene shown below, how many pi electrons are part of the linear, conjugated system between the two phenyl groups?



number of pi electrons: ______

1 mark

(c). The linear, conjugated system in 1,8-diphenyl-1,3,5,7-octatetratriene can be modeled roughly after a one-dimensional box. How many orbitals do the pi electrons in the system occupy when the molecule is in the ground state?

1 mark

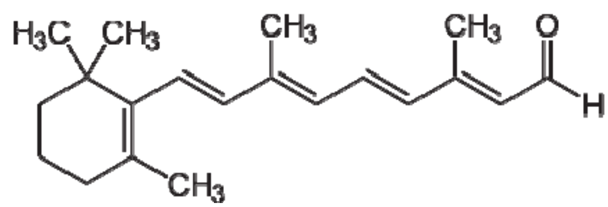
(d). The Highest Occupied Molecular Orbital, or "HOMO", is the highest energy level orbital that is occupied by electrons in ground state. Given a linear, conjugated system with N electrons, what is the equation for the energy of the HOMO in terms of h, m, and L?

1 mark

(e). The Lowest Unoccupied Molecular Orbital, or "LUMO", is the lowest energy level orbital that is not occupied by electrons in ground state. Given a linear, conjugated system with N electrons, what is the equation for the energy difference between the HOMO and LUMO in terms of h, m, and L?

2 marks

Retinal is a form of Vitamin A produced by oxidative cleavage of carotenoids. Retinal has the following structure:



(f). The conjugated system in retinal can be roughly modeled as a one-dimensional box. Given that the average length of a C – C bond in the system is 0.140 nm and the average length of a C =O double bond is 0.123 nm, estimate the length of the box.

2 marks

(g). Calculate the wavelength of light that retinal can absorb to reach an excited state.

4 marks

3. Titanium is an economically important element used principally in the aerospace industry, but also in medical prosthetics and as an industrial pigment. For example, the white lettering on *Skittles* and *M&M* candies is made with titanium dioxide, which was recently declared a possible carcinogen in humans by the *International Agency for Research on Cancer* (IARC).

(a). Among its minerals, titanium most commonly occurs with an oxidation number of +4. State the *complete* electron configuration for titanium, corresponding to this oxidation number. *Do not use short-hand notation*.

1 mark

(b). *Ilmenite*, $FeTiO_3$, is one of the principal titanium-bearing minerals. An essential step in producing high-purity titanium is the *chloride process*. Balance the chemical equation below for the *chloride process*.

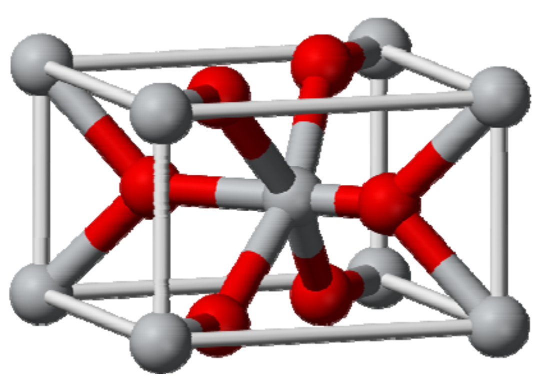
$$\_\_FeTiO_3(s) + \_\_Cl_2(g) + \_\_C(s, graphite) \rightarrow \_\_TiCl_4(l) + \_\_FeCl_3(s) + \_\_CO(g)$$

1 mark

(c). Write a balanced chemical equation for the complete hydrolysis of titanium tetrachloride.

1 mark

Though titanium metal can be produced from *ilmenite* by the *sulfate process*, a higher yield can be obtained by refining the less common mineral *rutile*. The *rutile* unit cell (based upon a body-centred tetragonal arrangement of titanium atoms) is shown below. The oxygen atoms are dark-coloured spheres in the *rutile* unit cell.



(d). Name the localized geometries around oxygen and titanium.

O: ___________________________ Ti: ___________________________

1 mark

(e). Given the dimensions of the unit cell, $a = b = 0.4584$ nm and $c = 0.2953$ nm, calculate the density (in g cm^{-3}) of the *rutile* form of titanium dioxide.

3 marks

(f). Titanium tetrachloride is a liquid at standard ambient temperature and pressure (SATP). Given ΔH_{vap} of +37.5 kJ mol^{-1}, a vapour pressure of 1.70 kPa at SATP and using the *Clausius-Clapeyron* equation (below), calculate the boiling temperature of $TiCl_4$. Assume no change in external pressure.

$$\frac{d\ln P}{dT} = \frac{\Delta H_{vap}}{RT^2} \qquad or \qquad \ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

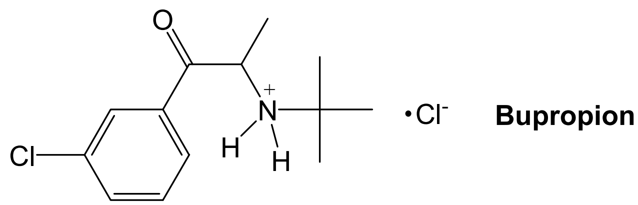
2 marks

(g). High-purity titanium metal can be prepared industrially in a stainless-steel, high-pressure reactor from titanium tetrachloride and magnesium metal, according to the *Kroll process*. Assume the processing temperature is 900°C and a positive pressure (P > 100 kPa) is maintained within the reactor by means of an inert gas. Using the data provided below, explain how titanium metal could be produced by the *Kroll process* with the use of a diagram and a balanced chemical reaction. *If you were unable to obtain an answer from part (f), use 150°C for the boiling point of* $TiCl_4$.

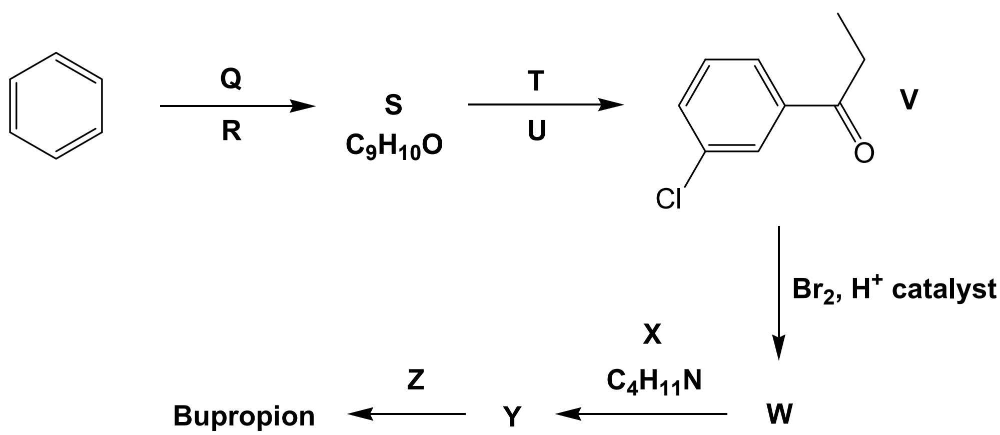
Substance	**Melting point (°C)**	**Boiling point (°C)**	**Density at 25°C (g cm^{-3})**
$TiCl_4$	-24	see part (f)	1.726
Mg	650	1091	1.584
Ti	1668	3287	4.506
$MgCl_2$	714	1412	2.325

3 marks

4. GlaxoWellcome first marketed the pharmaceutical bupropion (structure below) in 1985 under the trade-name Wellbutrin® as a treatment for depression. Many smokers taking the drug reported that after one or two weeks their craving for tobacco ceased and they were able to quit smoking with few withdrawal symptoms. Bupropion therefore began to be marketed in 1997 with a new name (Zyban®) for use as an aid in smoking cessation.



Bupropion can be prepared from benzene according to the following scheme:



(a). Draw the structures of reagents **Q**, **R**, **T**, **U**, **X** and **Z**.

Q =　　　**R** =　　　**T** =

U =　　　**X** =　　　**Z** =

3 marks

(b). Draw the structures of intermediate compounds **S**, **W** and **Y**.

S =　　　**W** =　　　**Y** =

3 marks

(c). State how many stereoisomers of bupropion exist.

0.5 marks

(d). State whether you would expect bupropion to be soluble or insoluble in water, explaining your reasoning **IN LESS THAN TEN WORDS**.

0.5 marks

(e). Draw the major organic product formed when intermediate compound **V** reacts with each of the following five sets of reagents:

$NaBH_4$, ethanol:

(1) CH_3MgBr, ether, then (2) H_3O^+:

H_2, Pt metal:

CH_3NH_2, H^+ catalyst:

$(CH_3)_2NH$, H^+ catalyst:

5 marks

5. The concentration of copper(II) ions in a dilute solution may be determined by a two-step titration procedure as follows:

- the sample is treated with excess potassium iodide, resulting in the formation of copper(I) iodide and iodine
- the iodine formed is titrated with sodium thiosulfate

(a). Balance the net ionic equation for the reaction of copper(II) with iodide.

$$\_\ Cu^{2+}\ (aq)\ +\ \_\ I^{-}\ (aq)\ \rightarrow\ \_\ CuI\ (s)\ +\ \_\ I_2\ (aq)$$

1 mark

(b). Balance the net ionic equation for the reaction of iodine with thiosulfate.

$$\_\ I_2\ (aq)\ +\ \_\ S_2O_3^{2-}\ (aq)\ \rightarrow\ \_\ I^{-}\ (aq)\ +\ \_\ S_4O_6^{2-}\ (aq)$$

1 mark

(c). Using these balanced equations, derive a relationship between the number of moles of copper(II) n_{Cu} in the sample and the number of moles of thiosulfate n_T required to reach the stoichiometric equivalence point for the titration.

2 marks

(d). An excess of iodide is added to 50.00 mL of a solution containing copper(II). The solution is then titrated with 0.1002 M thiosulfate, requiring 32.07 mL to reach the equivalence point. Determine the initial concentration of copper(II) in the sample, making sure to show all steps in your calculation.

2 marks

(e). It is very important that an *excess* of iodide is used in the first step of this procedure. What does the excess iodide do?

2 marks

(f). Suggest a suitable indicator that you could use for this titration. At what point in the procedure would you add this indicator?

2 marks

(g). Titrations involving iodine require a number of precautions. Suggest two possible issues, and the precautions you would take to deal with them.

2 marks

--END OF PART C--

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Data Sheet
Fiche de données

CHEMISTRY **Olympiads** CANADA **Olympiades** CHIMIE

Relative Atomic Masses (2012, IUPAC)
***For the radioactive elements the atomic mass of an important isotope is given**

Masses Atomiques Relatives (UICPA, 2012)
****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 10.81	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											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	*amu*	1.66054×10^{-27} kg	*Unité de masse atomique*
Avogadro's number	N	6.02214×10^{23} mol^{-1}	*Nombre d'Avogadro*
Charge of an electron	e	1.60218×10^{-19} C	*Charge d'un électron*
Dissociation constant (H_2O)	K_w	1.00×10^{-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	*Masse d'un électron*
Mass of a neutron	m_n	1.67493×10^{-27} kg	*Masse d'un neutron*
Mass of a proton	m_p	1.67262×10^{-27} kg	*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*
Rydberg constant	R_∞	1.097×10^{7} m^{-1}	*Constante de Rydberg*

1 Å	= 1×10^{-10} m
1 atm	= 101.325 kPa
1 bar	= 1×10^{5} Pa

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