

THE CANADIAN CHEMISTRY OLYMPIAD 2020

(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, 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.
2. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.
3. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.
4. 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.

Name _____ School _____
(LAST NAME, Given Name; Print Clearly)

Exam Code _____

1. MULTIPLE CHOICE QUESTIONS

Choose the best answer.

12 questions, 1 Mark per question.

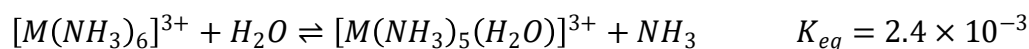
a) Two moles of liquid water initially at 273 K are mixing with three moles of liquid water at 363 K in a perfectly insulated container. Calculate the final equilibrium temperature of the water after mixing.

- a) 298 K b) 307 K c) 318 K d) 327 K e) 358 K

b) Based on VSEPR theory, which of the following has a seesaw molecular geometry?

- a) SF₄ b) CH₄ c) XeF₄ d) BF₃ e) H₂O

c) When a very small amount of complexed metal $[M(NH_3)_6]^{3+}$ is dissolved in a relatively large amount of water, the following ligand substitution reaction occurs:



If approximately 2.7×10^{-7} moles of $[M(NH_3)_6]Cl_3$ was dissolved in 1.0 dm³ of water, what will be the final concentration of NH₃ in the solution?

- a) 6.5×10^{-10} M b) 1.6×10^{-6} M c) 2.7×10^{-7} M d) 2.5×10^{-5} M e) 9.4×10^{-7} M

d) The energy of an electron occupying the n^{th} energy level in a hydrogen-like atom that has a Z number of protons and only **one** electron is given by:

$$E_n = -R_H \frac{Z^2}{n^2}$$

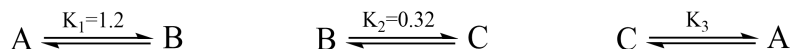
where R_H is Rydberg's constant. Which of the following is a **possible** value for the first ionization energy of helium?

- a) 1.166×10^{-18} J b) 3.146×10^{-18} J c) 8.708×10^{-18} J d) 6.424×10^{-19} J e) 8.991×10^{-18} J

e) Consider the decomposition of ozone occurring in a rigid, isolated container that follows first order kinetics: $2O_3(g) \rightarrow 3O_2(g)$. Let P_f be the final pressure in the container after the decomposition reaction reaches completion, and P_t be the pressure in the container at time t . Find an expression for the rate constant in terms of t , P_f and P_t .

a) $\frac{1}{2t} \ln\left(\frac{3P_f}{4(P_f - P_t)}\right)$ b) $\frac{1}{2t} \ln\left(\frac{2P_f}{4P_f - P_t}\right)$ c) $\frac{1}{2t} \ln\left(\frac{P_f}{3P_f - P_t}\right)$ d) $\frac{1}{2t} \ln\left(\frac{2P_f}{4P_f - 3P_t}\right)$ e) $\frac{1}{2t} \ln\left(\frac{P_f}{3(P_f - P_t)}\right)$

f) Consider the following hypothetical equilibrium system:



If initially only 1.0 M of reactant A was present and began to undergo the above reactions, what will be the final concentration of A when equilibrium has been reached?

a) 0.384 M b) 0.455 M c) 0.833 M d) 0.387 M e) 0.208 M

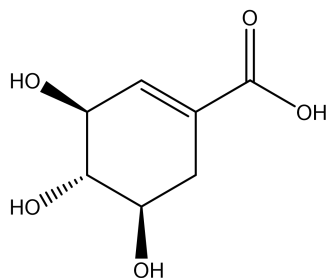
g) A salt of A was mixed with a salt of B in a thermal process to produce 247.24 g of pure product, AB_2O_4 . Elemental analysis of the spinel provided the following data: 65.38 g of metal A and 117.86 g of metal B. The x-ray diffraction data of AB_2O_4 provides a unit cell parameter of 8.085 Å, which is constructed from 8 face centered cubic units (fcc). What is the density of AB_2O_4 ?

a) 6.215 g/cm³ b) 8.860 g/cm³ c) 1.554 g/cm³ d) 7.140 g/cm³ e) 3.107 g/cm³

h) How many compounds have the same molecular formula as 1-butanol? (1-butanol count as one compound, include it in your answer)

a) 3 b) 4 c) 5 d) 6 e) 7

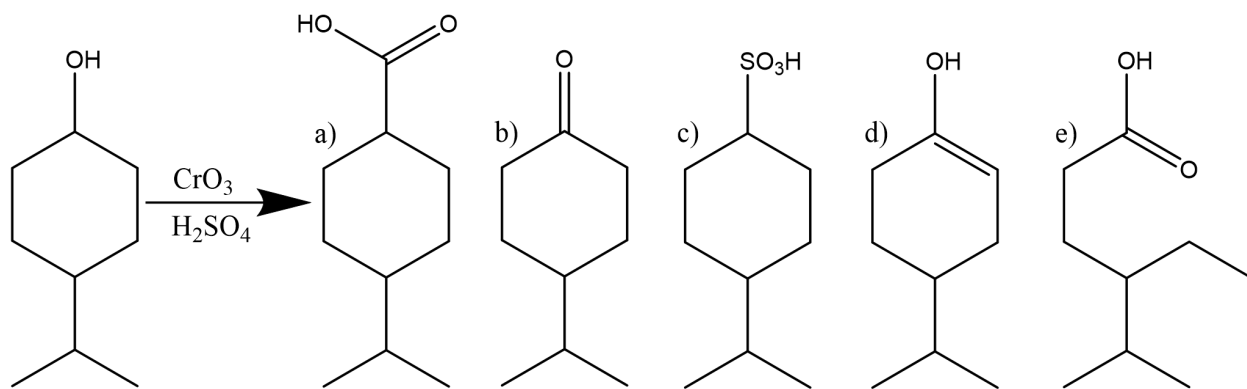
i) Give the number of stereoisomer possible for the compound:



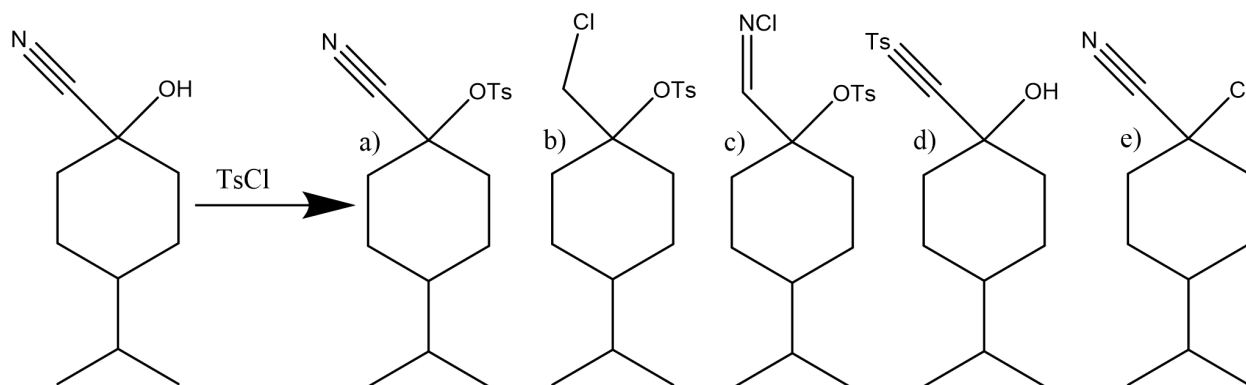
a) 2 b) 4 c) 6 d) 8 e) 16

Identify the **major** product in the following reaction schemes. Choose the best answer.

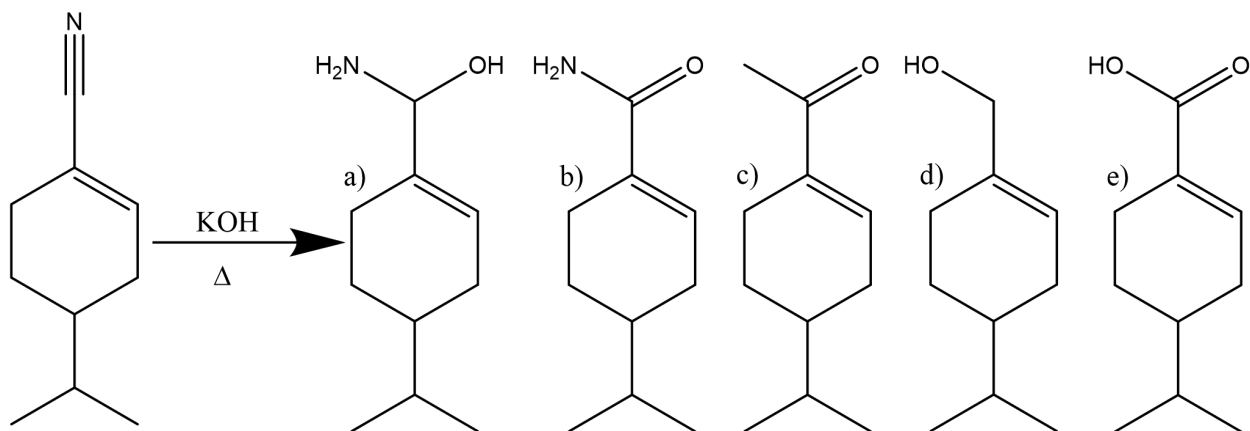
j)



k)



l)



2. ANALYTICAL CHEMISTRY

The major component of bleach powder is calcium hypochlorite. The powder also contains calcium hydroxide, calcium chloride and other impurities.

A chemist performed an experiment to determine the exact component of a batch of this bleach powder. A sample of 7.825 g of the powder was dissolved into water in a 1000 mL volumetric flask to make 1.000 L of the solution.

A 25.00 mL aliquot of the solution was transferred to a 250 mL Erlenmeyer flask. An excess amount of potassium iodide solution and sufficient 1:1 acetic acid solution were added to the flask. This mixture was titrated with a standard aqueous solution of 0.1178 M of sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$. The equivalence point was achieved when 16.93 mL of the $\text{Na}_2\text{S}_2\text{O}_3$ solution were used.

Another 25.00 mL aliquot of the solution was transferred from the volumetric flask to a second Erlenmeyer flask. An aqueous solution of hydrogen peroxide (3%) was added and stirred until there was no more gas produced. The remaining solution was titrated by a 0.1102 M aqueous solution of silver nitrate (AgNO_3). 18.62 mL of the silver nitrate solution was used to reach the chromate end point.

A third 25.00 mL aliquot of the solution was transferred to a 100 mL volumetric flask and water was added to the mark. 25.00 mL of this solution was transferred to a 250 mL Erlenmeyer flask and treated with an aqueous solution of hydrogen peroxide (3%) until there was no more gas produced. The remaining solution was titrated with a 0.02078 M EDTA solution in an ammonia based buffer. 23.37 mL of EDTA was used to reach equivalence point.

a) Calculate the percentage of effective chlorine (Cl_2) in the powder. 2 marks

b) Calculate the total percentage of chlorine (Cl^-) in the powder. *2 marks*

c) Calculate the total percentage of calcium in the powder. *2 Marks*

For the following section, consider:

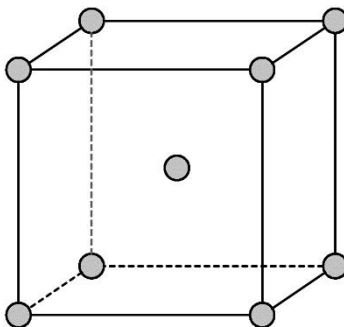
H_2A is a diprotic acid with $\text{pK}_{\text{a}1} = 4.19$ and $\text{pK}_{\text{a}2} = 5.57$ respectively.

d) Calculate the pH of the solution made by dissolving 50.0 mmol of H_2A into water in a volumetric flask filled to the 1000 mL mark. *2 Marks*

e) Calculate the pH of a 1.00 L aqueous solution containing 50.0 mmol of H_2A and 60.0 mmol of NaOH . *4 Marks*

3. INORGANIC CHEMISTRY

Manganese is a metal with a silvery appearance, which exists in the body centered cubic crystal structure, as shown below.

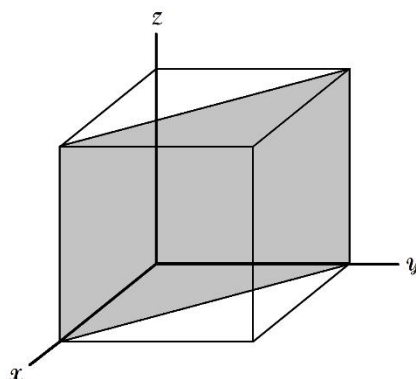


- a) The enthalpy of atomization for Mn is defined as the molar energy required for the process: $Mn_{(s)} \rightarrow Mn_{(g)}$. Given that $\Delta H_{\text{atomization}} = 279.37 \text{ kJ mol}^{-1}$ and considering the number of nearest neighbors for every Mn atom, calculate the dissociation energy of one Mn-Mn bond. *3 marks*

Use the bond dissociation energy calculated in a) to answer question b).

**Use a value of $1.5000 \times 10^{-19} \text{ J}$ if you were unable to calculate the bond dissociation energy in part a).*

The surface energy of a crystal is defined as the energy required to cleave a crystal to generate a certain surface area, units given in J nm^{-2} . The (110) plane dissecting the crystal diagonally is considered:



- b)** Given that the length of the unit cell, $a = 0.8914 \text{ nm}$, calculate the surface energy of the Mn crystal for the (110) plane. Note that atoms intersecting the plane are never split; rather bonds on one side of the plane connected to those atoms are broken. Bonds that are parallel to the plane are not broken. Use the bond energy value you found in question a) for your calculations. *3 marks*

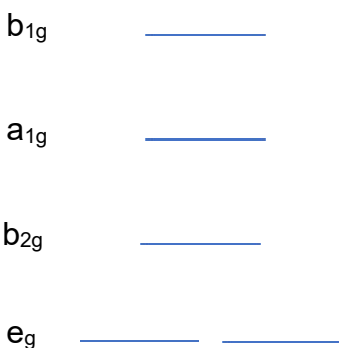
In aqueous solution, metals do not exist as a free ion, but rather in the form of a complex. Mn(III) can exist as the $\text{Mn}(\text{urea})_6^{3+}$ complex, which has octahedral geometry.

- c)** Draw the crystal field splitting diagram of d orbitals for $\text{Mn}(\text{urea})_6^{3+}$ and fill in the orbitals with electrons. Assume that the pairing energy is relatively high. *1.5 marks*

To become more stable, certain transition metal complexes are able to break symmetry in such a way that occupied orbitals become lower in energy. This effect is known as the Jahn-Teller Distortion. Mn(urea)_6^{3+} is a complex that undergoes Jahn-Teller Distortion, and the distorted crystal field splitting diagram for tetragonal elongation is given below.

- d)** Label the given diagram with appropriate d-orbital labels and fill the orbitals with electrons (recall that the pairing energy is high). *1 mark*

Note: In tetragonal elongation, the 2 ligands on the z axis have longer bond lengths, while the 4 ligands on the x-y plane have shorter bond lengths.



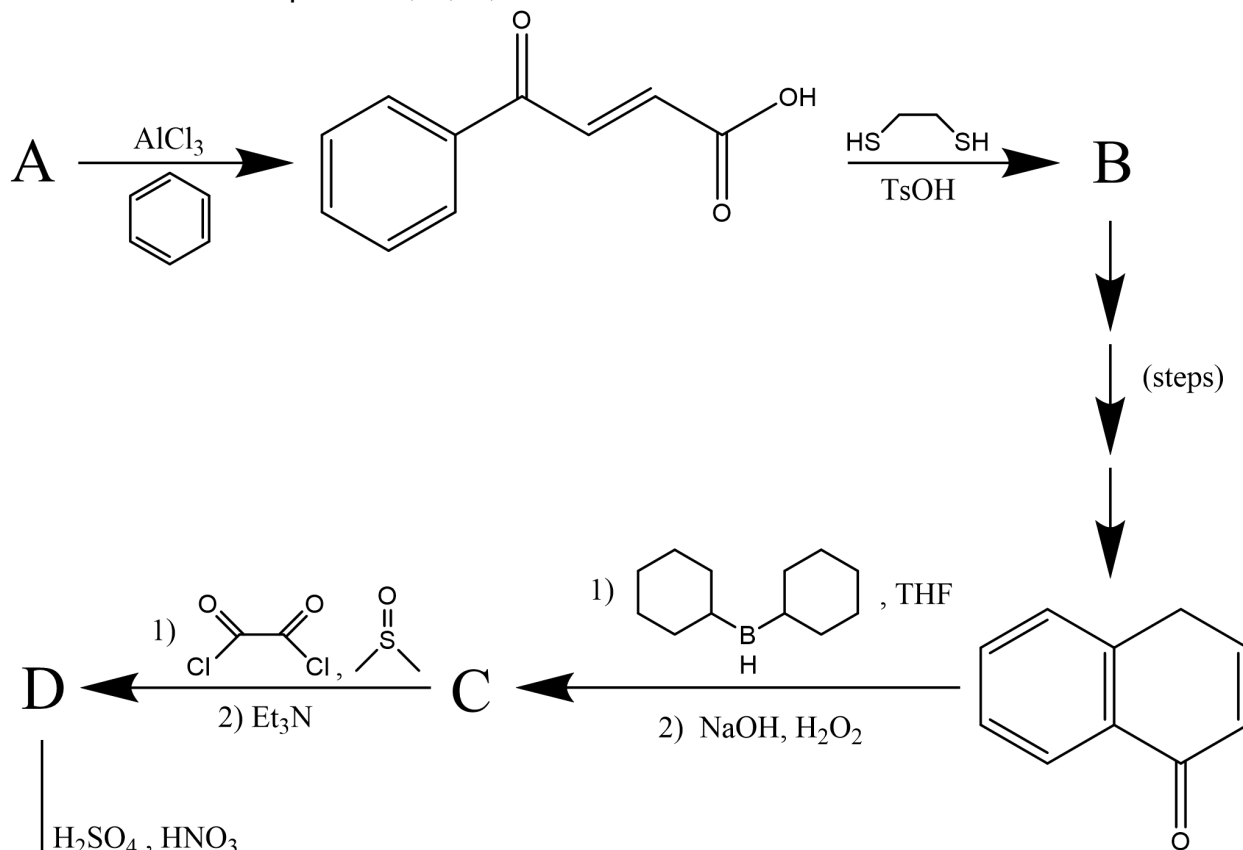
- e)** Given that the transition from e_g to b_{2g} requires 0.867 eV, b_{2g} to a_{1g} requires 1.453 eV, and the e_g set lies 1.317 eV below the 3d energy level of ground state Manganese, calculate the energy in eV that is required for the transition from a_{1g} to b_{1g} . *1.5 marks*

f) Calculate the crystal field splitting energy of the distorted complex in eV. *0.5 marks*

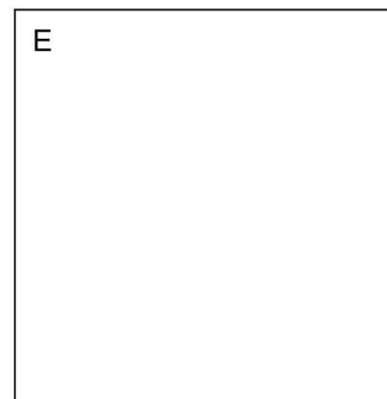
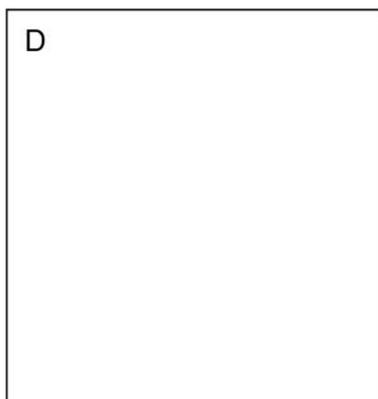
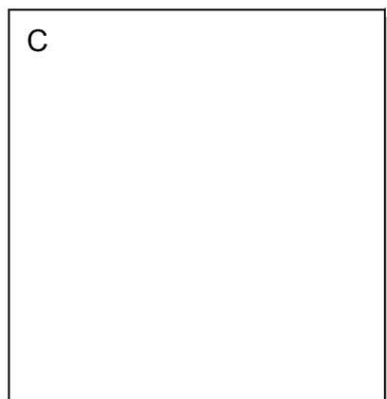
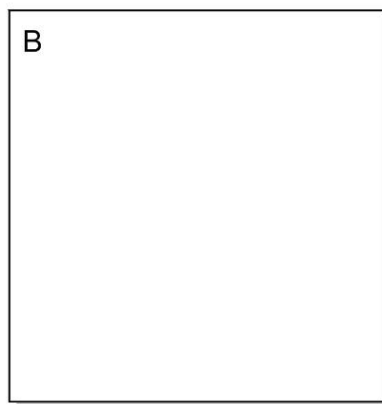
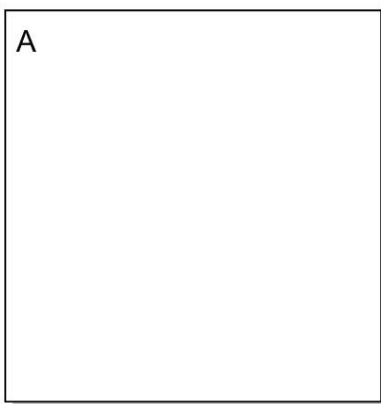
g) Given that the crystal field splitting energy of the non-distorted octahedral complex is 2.702 eV, calculate in eV the stabilization energy of both complexes. This calculation should show that the tetragonal complex is more stable. By how many eV is the tetragonal complex more stable? *1.5 marks*

4. ORGANIC CHEMISTRY

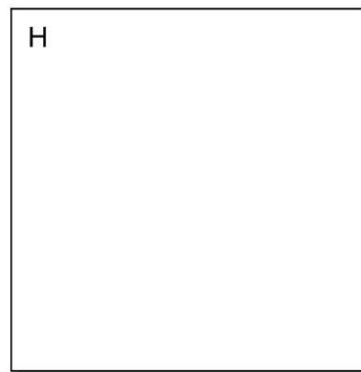
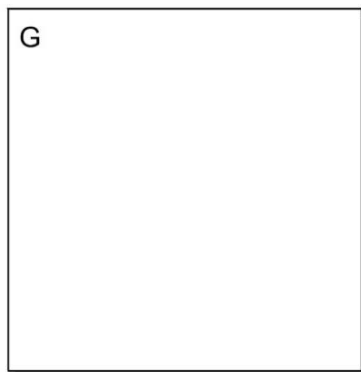
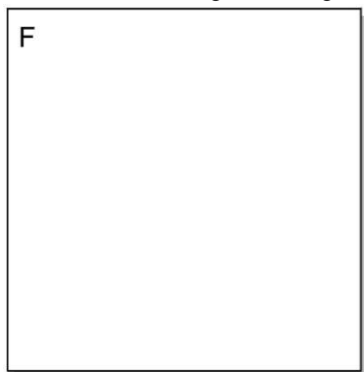
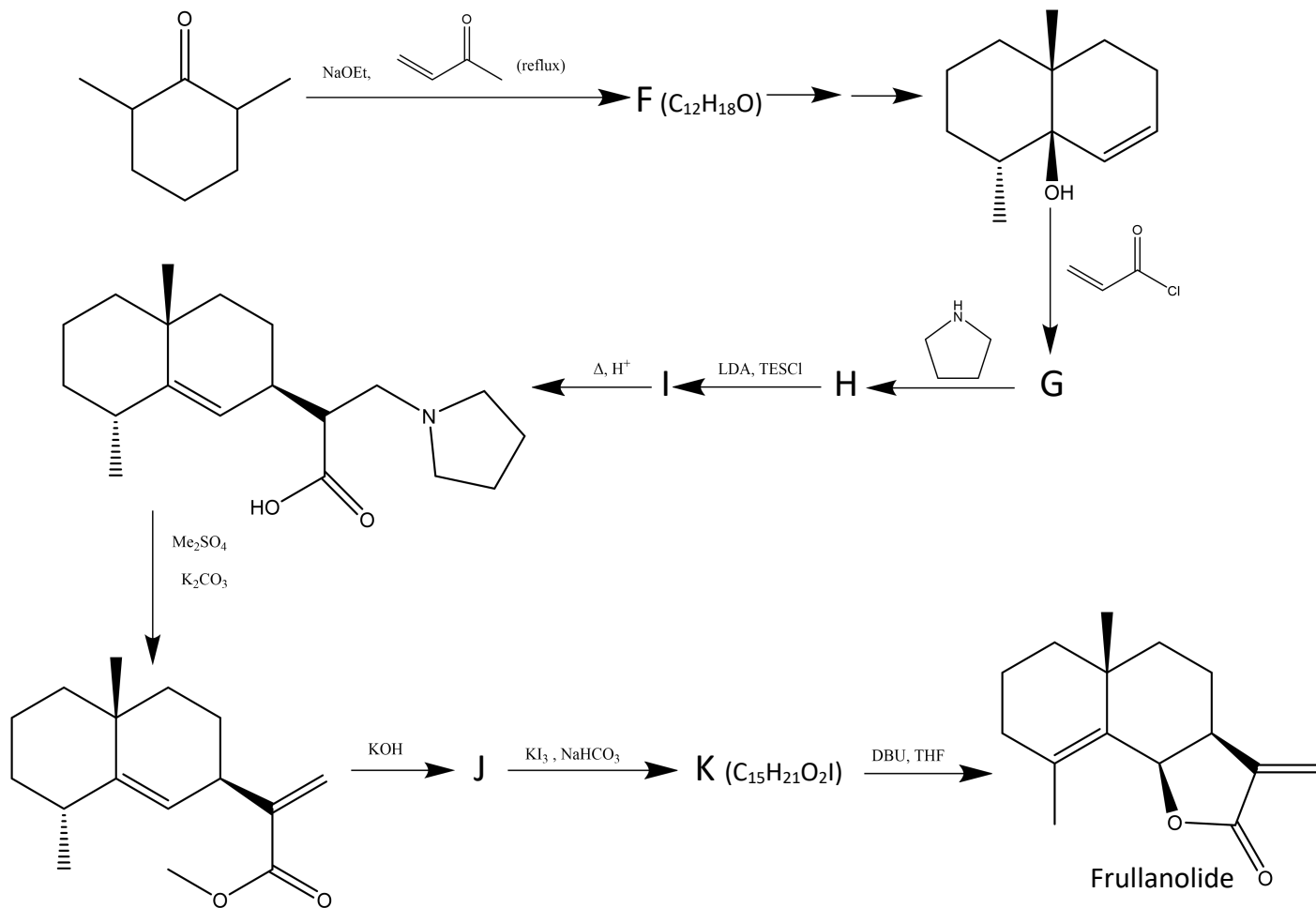
a) The molecular formula of E is $C_{10}H_7NO_4$. Using this information determine the structures of compound A, B, C, D and E. *5 marks*



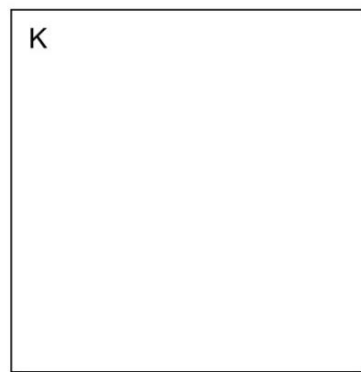
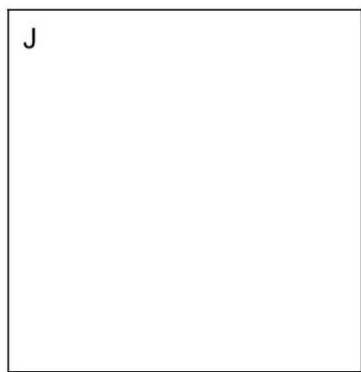
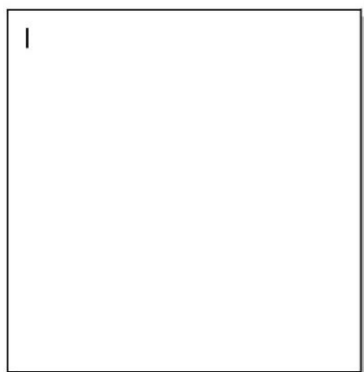
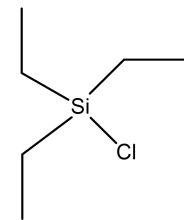
E



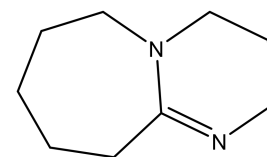
b) The synthesis scheme of Frullanolide is presented below (workup is assumed where necessary). Draw the structures of **F**, **G**, **H**, **I**, **J**, and **K** for the reaction scheme below. 6 marks



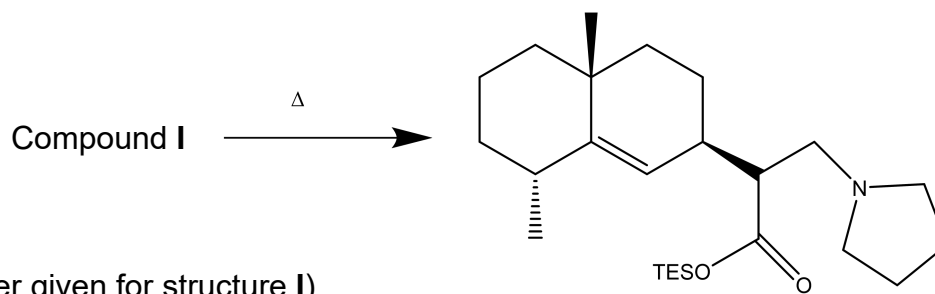
TESCI =



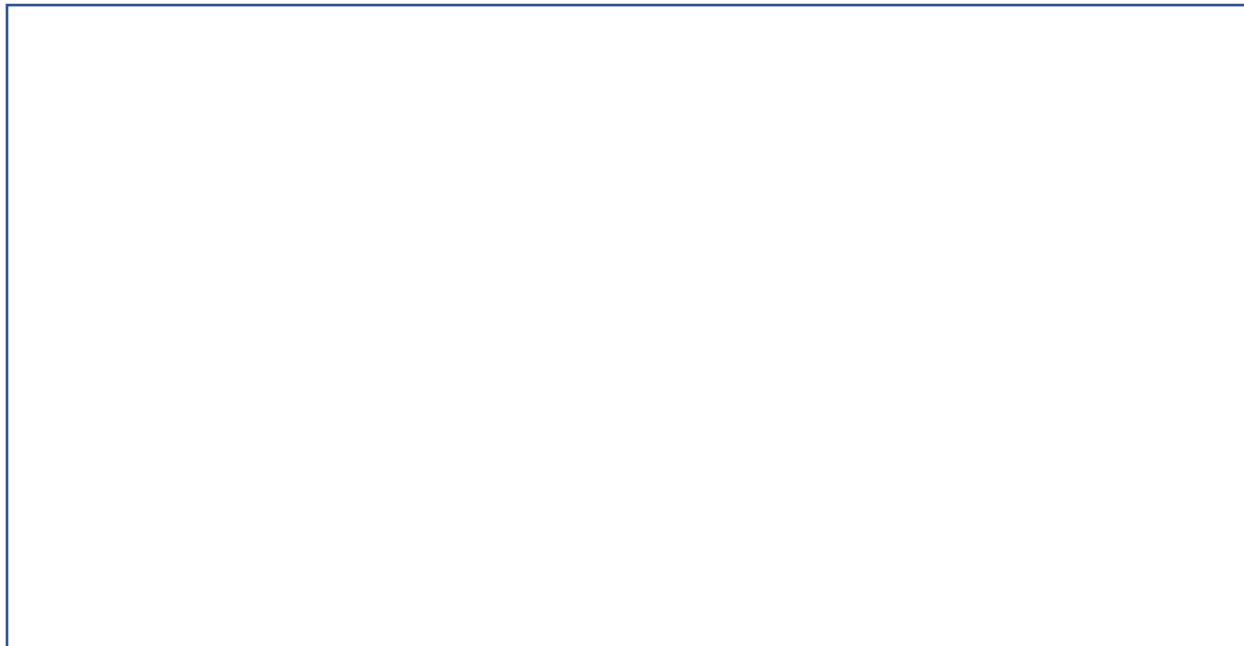
DBU =



- c) The reaction scheme below is part of the synthesis of Frullanolide, depicted on the preceding page. Draw a mechanism with curved arrows to show the transformation of compound I. Write your answer in the box. *1 mark*



(Use the answer given for structure I)



5. PHYSICAL CHEMISTRY

Simple Model for Pi-Electrons in Conjugated Systems.

The free electron model is a crude approximation for conjugated molecules. In this model, several approximations are considered:

1. The Pi-electrons are assumed independent of all other electrons (core, lone pairs, and sigma bonds) and do not interact among themselves.
2. The total energy of the molecule is the sum of sigma-bond energies and kinetic energies of the Pi electrons.
3. The Pi-Electrons are considered to be moving freely in a 1D box whose length is $L = n_C \times 1.40 \text{ \AA}$ where n_C is the number of C atoms from the conjugated Pi-system.
4. The energy of a Pi-electron cannot be arbitrary. If the conjugated system is not cyclic the only allowed values are called energy levels and are given by the formula:

$$E_n = n^2 \frac{h^2}{8mL^2}$$

Where m is the mass of an electron, L is the box length, h is Planck's constant and n can be any positive integer.

On the other hand, if the conjugated system is cyclic the energy levels are given by the formula:

$$E_n = n^2 \frac{h^2}{2mL^2}$$

where n can be any integer number.

Furthermore, the energy levels are filled with electrons starting with the ones having the smallest energy. A maximum of two electrons of opposite spin can populate each energy level.

Consider the hexa-1,3,5-triene molecule and assume that the free Pi electron model is valid.

a) Draw an energy diagram, fill the Pi electrons and calculate the energies of the occupied levels. *2 Marks*

b) Calculate the total energy of the conjugated system. *1 Mark*

c) Determine the wavelength of the light (in nm) that is required to excite an electron from the highest-occupied level (HOMO) to the lowest unoccupied level (LUMO).
1 Mark

Consider now the benzene molecule, C_6H_6 .

d) Calculate the energy of the conjugated system in the benzene molecule and compare it with that of hexa-1,3,5-triene. Explain the differences. *2 Marks*

e) Calculate the energy required to excite an electron from the highest occupied to the lowest unoccupied energy level for benzene. Compare with hexa-1,3,5-triene and explain the differences. *2 marks*

Consider now the molecule of cyclobuta-1,3-diene. Experimentally one finds that this molecule is highly unstable and difficult to isolate in its singlet state, when the numbers of electrons of spin alpha and beta are equal. Nevertheless, some derivatives of cyclobuta-1,3-diene can be studied in their triplet states (Kostenko et al., 2017), when the number of alpha electrons exceeds by two that of beta electrons.

- f)** Using the free Pi electrons model explain why the triplet cyclobuta-1,3-diene, which adopts a square geometry, is a diradical. Use this information to explain why it would be challenging to isolate the triplet cyclobuta-1,3-diene, although its derivative tetrakis(trimethylsilyl) cyclobuta-1,3-diene was isolated as a solid at room temperature. *2 Marks*

Consider now the molecules B_2 , C_2 , N_2 , O_2 and F_2 .

- g)** The only molecules in the above-mentioned series that are diradicals are B_2 and O_2 . How can this experimental observation be reconciled with a simple free Pi electron model? *2 Marks*

-END OF PAPER-



1 H 1.008																	18 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 Nh (284)	114 Fl (289)	115 Mc (288)	116 Lv (292)	117 Ts (294)	118 Og (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 **Value**
Symbole **Quantité numérique**

Atomic mass unit	<i>amu</i>	1.66054 x 10 ⁻²⁷ kg	Unité de masse atomique
Avogadro's number	<i>N_A</i>	6.022 x 10 ²³	Nombre d'Avogadro
Charge of an electron	<i>e</i>	1.60218 x 10 ⁻¹⁹ C	Charge d'un électron
Dissociation constant (H ₂ O)	<i>K_w</i>	1.00 x 10 ⁻¹⁴ (25°C)	Constante de dissociation de l'eau (H ₂ O)
Faraday's constant	<i>F</i>	96 485 C mol ⁻¹	Constante de Faraday
Gas constant	<i>R</i>	8.31451 J K ⁻¹ mol ⁻¹ 0.08206 L atm K ⁻¹ mol ⁻¹	Constante des gaz
Mass of an electron	<i>m_e</i>	9.10939 x 10 ⁻³¹ kg	Masse d'un électron
Mass of a neutron	<i>m_n</i>	1.67493 x 10 ⁻²⁷ kg	Masse d'un neutron
Mass of a proton	<i>m_p</i>	1.67262 x 10 ⁻²⁷ kg	Masse d'un proton
Planck's constant	<i>h</i>	6.62608 x 10 ⁻³⁴ J s	Constante de Planck
Speed of light	<i>c</i>	2.997925 x 10 ⁸ m s ⁻¹	Vitesse de la lumière
Rydberg constant	<i>R_H</i>	1.096 x 10 ⁷ m ⁻¹	Constante de Rydberg

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

Scratch Paper

Scratch Paper