Chemistry 1 - test 2 - Duration : 2hours

No document allowed. All types of calculators are authorized
Each answer should (concisely) be justified
Schedule of mark is for indication only and may be (slightly) adapted

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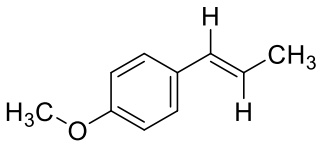
Data:
Nickel: Atomic Numbers, Z_{Ni} = 28; Molecular mass, M_{Ni} = 58.7 g.mol^{-1}; Atomic radius: R_{Ni} = 124 pm
Avogadro's number: N_A = 6,022×10^{23} mol^{-1}
The following relationship can be used without any demonstration: E(eV) = 12400 / λ(Å)

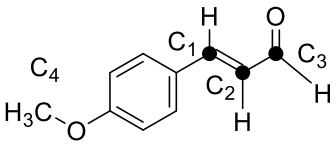
Exercise 1: Let's combine C, N and O (~12 points) ~

1. Knowing that Z_C = 6, Z_N=7 and Z_O=8,
   a. Give the electronic configurations of C, N and O with specifying the valence electrons. Represent their valence shell with the corresponding quantum boxes.
   b. Compare, justifying your answer, the electronegativity of these three atoms.
   c. Compare and discussed their ionization energy.
2. Write down the possible Lewis formulas of the following diatomic edifices: CO, CN^- and NO. For CO and CN^-, compare the contribution of each mesomeric form.
3. The combination of O, C and N may lead to the cyanate ion OCN^-. Propose two mesomeric Lewis formulas specifying the most contributing one. According to VSEPR (Gillespie's theory), give the geometry observed around the central atoms. Does the ion possess a dipole moment?
4. The fulminate ion is this time the anion in which the combination of atoms is O, N and C. When combined with the silver ion Ag^+, it forms silver fulminate, AgONC, which is a neutral, highly reactive compound used in Christmas crackers.
   a. The atomic number of silver is Z = 47. Give its electronic configuration and propose an explanation for the preferential formation of the Ag^+ ion over possible multiple charged species.
   b. Tin (Sn), Antimony (Sb) and Tellurium (Te) are in the same period as silver and in the same groups as C, N and O, respectively. Deduce their atomic number. Justify your answer.
5. The semi-structural formula of methyl nitrate is CH_3ONO_2
   a. Write down the two possible mesomeric formulas and indicate their resonance hybrid.
   b. Experimental measurements indicate an angle of 105° and N-O bond lengths equal to 126 or 136 pm. Assign these values to the corresponding angle and bond lengths. Justify your answer.

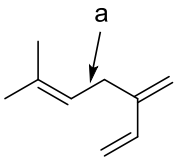
Exercise 2: Cinnamon and star anise (~17 points)



Anethol



para-Methoxy-cinnamaldehyde



β-Myrcene

Anethol, para-methoxy cinnamaldehyde and β-myrcene are natural organic molecules. They give to anise, cinnamon, lemon or cloves their flavor and smell.

1. Insaturated molecules (~11 points)

a. Write down the complete developed formulas of the three molecules, showing all atoms and the non-bonding doublets.

b. In the molecule of para-methoxy cinnamaldehyde:

   i. Give the hybridization states of carbons C_1, C_2, C_3 and C_4. Justify your answer.

   ii. Indicate on the previously drawn structure, the different σ and π bonds. Specify the different overlap for the atomic orbitals that are involved to form the following bonds:

   - C_4-H bond
   - C_2-C_3 bond
   - C_3-O double bond
   - C_3-H bond.

   iii. Specify (and justify) whether free rotation is possible around the bond between C_2 and C_3.

c. Is free rotation possible around the bond **a** (β-myrcene)?

d. For each of the three molecules, give the number of π electrons they possess.

e. How many molecular orbitals are there in the molecule of anethol?

f. The maximum absorption wavelength λ_{max} of anethol is observed on its absorption spectra at 260 nm.

   i. How are called the orbitals involved in the absorption phenomenon?

   ii. Compute in eV (within 0.01 eV) the energy associated to this transition.

   iii. Give the name of the electromagnetic range to which this λ_{max} belongs.

   iv. Compare the structures of the three molecules above and discuss the consequences on the **maximum absorption wavelengths** measured by acquiring their UV-Visible spectrum. Sort these wavelengths in ascending order.

2. UV-Visible spectrometric titration of anethol (~6 points)

The label of a bottle of aniseed drink containing anethol indicates a mass concentration of 1.90 g.L^{-1} ($M_{anethol}$ = 148 g.mol^{-1}). For the titration, the drink is diluted 50 times to give ***solution S_1***.

In order to plot the calibration curve, 5 standard solutions are prepared from a starting S_0 which concentration is ***C_0 = 0.1375 mol.L^{-1}***. The absorbance values for the standard solutions and for the **solution S_1** are gathered in the following table:

	Standard 1	**Standard 2**	**Standard 3**	**Standard 4**	**Standard 5**	**S_1**
Absorbance	0.433	0.650	0.866	0.899	1.299	0.800
Volume (µL) of the solution S_0	50	75	100	125	150	
Total volume (mL) of the flask	50	50	50	50	50	

1. Recall Beer's law. Give the name and unit of every coefficient of this law.
2. Is the relationship between the absorbance and the concentration of the solution verified for the calibration range? Justify your answer.
3. Compute (in mol. L^{-1}) the concentration of anethol in the bottle. Does it comply with value indicated on the label?

Exercise 3: Nickel (~11 points)

Metallic nickel (Ni) crystallizes in a face-centered cubic lattice (close-packed structure with one motif being made of one atom). The atoms are tangent along the diagonal of a face.

1. Give the electronic configuration of Nickel in its fundamental state and indicate the number of single electrons.
2. Represent one cell of this structure and indicate the parameter of the cell **a**.
3. What is the population of the cell?
4. Compute the density of Nickel. Your approach should be clearly explained.
5. Calculate the Atomic Packing Factor.
6. Give the number of tetrahedral and octahedral holes present in this cell. Represent one of each kind on two distinct figures.

ANNEX to be used for Beer's Law plotting (to be given back)

Name:

Group: