CHEMISTRY 1 – Test 2 – Duration: 2 hours

No document allowed. All types of calculators are authorized.

The goal of this problem is to study the composition of a cola. The tag on the can gives the following information: *"carbonated water; sugar, dye: caramel, acidifier: phosphoric acid, vanilla flavor, caffeine."*

Data:

Planck's constant: $h = 6.626\times10^{-34}$ J.s
Speed of light: $c = 2.998\times10^{8}$ m.s^{-1}
Elementary charge: $e = 1.602\times10^{-19}$ C
Avogadro's number: $\mathcal{N}_a = 6.022.10^{23}$ mol^{-1}

Table 1: *Electronegativity of some elements (according to Pauling's scale)*

Element	H	C	N	O	P
Atomic number Z	1	6	7	8	15
Electronegativity	2.1	2.5	3.0	3.5	2.1

Dichloromethane is a slightly polar solvent of dipolar moment 1.14 D

All the different parts of this problem are independent and can be treated in any order.

Part I – Generalities

1. Recall, without justification, the evolution of ionization energies along a particular period of the periodic table.

The first ionization energies of C, N and O atoms are 11.2 eV, 14.5 eV and 13.6 eV, respectively.

2. Do these experimental values follow the expected evolution? If no, give an explanation.

3. Tin (Sn) is located in the same group as C, but on the 5th period. Give its complete electronic configuration.

Part II – Carbonated water and acidifier

Carbonated water is obtained by dissolution of gaseous carbon dioxide (CO_2) in water (H_2O). This dissolution gives the formation of hydrogencarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) in solution.

The acidifier employed is phosphoric acid: H_3PO_4.

5. Write down the Lewis formulas of the following molecules: $\underline{\mathbf{C}}O_2$, $H_2\underline{\mathbf{O}}$, $\underline{\mathbf{C}}O_3^{2-}$, $H\underline{\mathbf{C}}O_3^-$ and $H_3\underline{\mathbf{P}}O_4$ (for the last two compounds, hydrogen atoms are linked to oxygen atoms). Central atoms are indicated in bold and are underlined in the brut formulas.

6. According to VSEPR (Gillespie's theory), give the geometry observed around the central atoms.

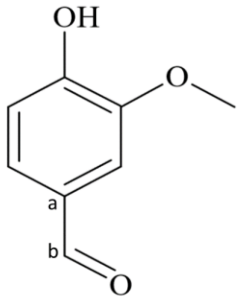
7. Are the two following molecules polar or not: CO_2 and H_2O. Your answer should be clearly justified using some information taken from the previous question.

8. In the carbonate ion (CO_3^{2-}) do we expect to observe the same bond lengths? A clear and justified answer is expected for this question.

Part III – Vanilla flavor

a) Study on the electronic structure of vanillin

The vanilla flavor of the cola is mainly due to vanillin molecule (4-hydroxy-3-methoxybenzaldehyde) of formula:



Molecular Mass

152.15 g.mol^{-1}

Figure 1: *Vanillin formula*

9. Write down the developed formula of vanillin including all the carbon (C) and hydrogen (H) atoms as well as the non-bonding doublets.

10. Give the hybridization states of **every** carbon atoms of vanillin. You can show it directly on the previously drawn structure for answering this question.

11. Deduce the atoms that are coplanar in this molecule. You can justify your answer using the drawing of the unhybridized p orbitals.

12. Is free rotation complete around the C_a-C_b bond (figure 1)? Justify your answer.

Note:

- Representation of an unhybridized p orbital perpendicular to the sheet of paper plane: 

- Representation of an unhybridized p orbital belonging to the sheet of paper plane: 

13. Compare the C_a-C_b bond length to the one bonding carbon atoms in the benzene ring.

To simplify the study of the molecular orbital diagram of vanillin, we will consider the simpler aldehyde molecule: benzaldehyde, of formula:

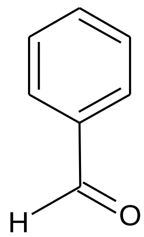


Figure 2: *benzaldehyde formula*

14. How many total **molecular** orbitals are found in the energy diagram of the benzaldehyde? Justify your answer.

15. How many electrons in total do we have to place on this **molecular** energy diagram?

16. Theoretical calculations give the following values for the HOMO and LUMO levels of benzaldehyde: -10.00 and -0.435 eV. Which maximum wavelength absorption do you predict in the UV–visible spectrum?

b) Titration of vanillin by UV-visible spectrometry

To separate vanillin and other compounds from the cola, that is to say for extracting vanillin from the mixture, a water non-miscible solvent is used: dichloromethane $Cl-CH_2-Cl$. Note that dichloromethane is a very good solvent for vanillin.

17. Give precisely the type of interactions explaining the observed high solubility of vanillin in dichloromethane.

After extraction of vanillin in dichloromethane, a second step (not developed here) consists in transferring vanillin back into water. An S_0 aqueous vanillin solution is thus obtained of total volume V_{tot} = 500 mL. **We suppose that all the vanillin initially contained in the can of cola is now present in the S_0 solution. For analyzing S_0, a 10 time dilution is applied.** The spectrum presented in the following figure is obtained, for which $\mathbf{A_{346} = 0.398}$.

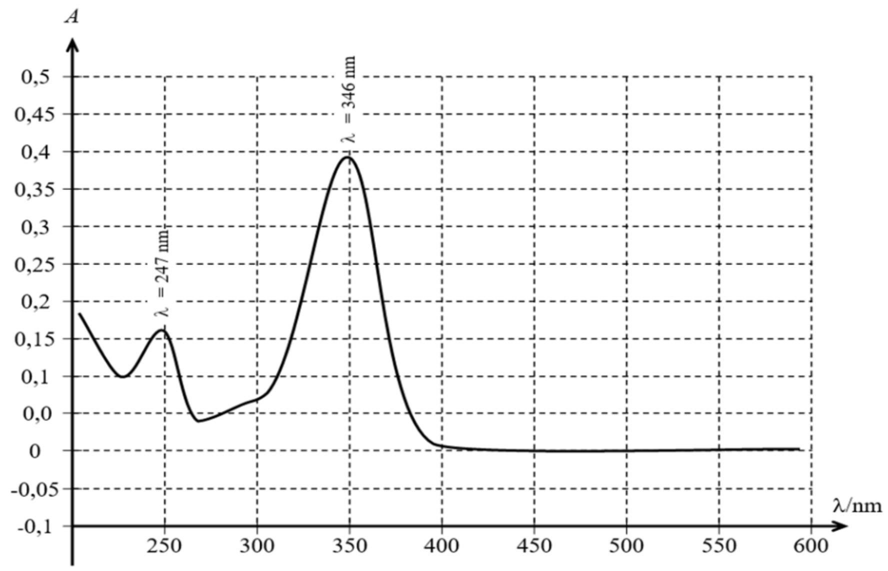


Figure 3: *UV–visible absorption spectrum of the S_0 solution* ***diluted 10 times***

18. Is the aqueous vanillin solution colored? Justify your answer.

19. Recall Beer's law. Give the name and unit of every coefficient of this law.

20. Explain why a 10 times dilution of S_0 was necessary for the correct recording of this spectrum?

A standardization curve is realized starting from a starting solution (solution 1) of vanillin at 6.58×10^{-5} mol.L^{-1}. The obtained results are presented in the following table (measurements were done in a 1.00 cm cuvette):

Table 2 *: Standardization solutions*

Solution number	1	2	3	4	5	6
Vanillin concentrations (in mol.L^{-1})	6.58×10^{-5}	5.26×10^{-5}	$C_{unknown}$	2.63×10^{-5}	1.32×10^{-5}	6.58×10^{-6}
Absorbance at 346 nm	1.859	1.507	0.912	0.714	0.347	0.167

The solution number 3 was prepared according to the following protocol: *using a gauged pipet, take a 25 mL aliquot of solution number 1. Introduce this volume of solution in a 50 mL gauged flask and complete with distilled water until the gauged flask's line is attained.*

21. Compute the $C_{\#3}$ in mol.L^{-1}.

22. Which dilution factor was applied to solution 1 for obtaining solution 5?

According to these experimental results, a spreadsheet corresponding to the following figure is realized:

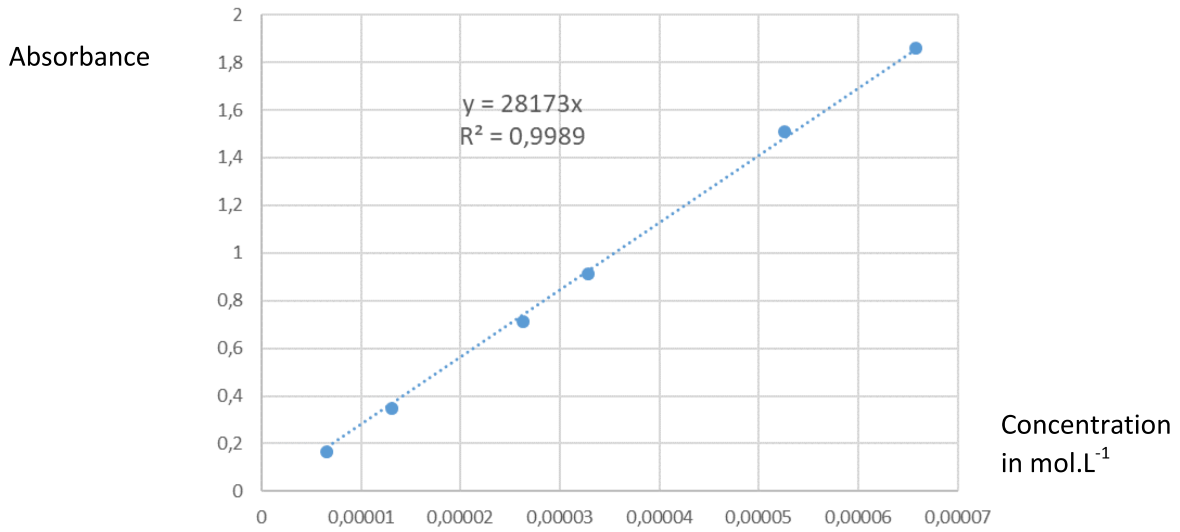


Figure 4*: standardization curve done at 346 nm – on the solutions of vanillin*

23. Compute (in $mol.L^{-1}$) the vanillin concentration of solution S_0.

The approved daily consumption of vanillin is 10 mg/ kg of body weight.

24. Considering that vanilla only has a consumption limit (which is of course false!), compute the maximum number of cola cans that a 70 kg person can drink per day.

Part IV: Constitution of cola cans

Some cola cans are made of an aluminum alloy.

The crystalline structure of aluminum (M(Al) = 27.0 $g.mol^{-1}$) metal is a face centered cubic structure (the motif being made of one atom). Its density is $\rho = 2.70\times10^3$ $kg.m^{-3}$.

25. Draw one cell of aluminum metal.

26. Give the population of the cell.

27. Compute in Å the value of the parameter *a* of the aluminum cell.

28. Calculate in Å the value of R(Al), the atomic radius of aluminum.

29. Calculate the atomic packing factor (APF) of this cell.

30. Give the number of tetrahedral and octahedral holes present in this cell. Represent one of each kind on the question **25**'s answer figure.

31. Give in Å the values of the radii r_T and r_O of atoms that could be inserted without deformation of the structure in the tetrahedral or octahedral holes, respectively.

Aluminum-copper alloys are employed in different applications for their good machinability and also mainly for their excellent resistance to corrosion. Copper radius is 128 pm.

32. Are Al-Cu alloys insertion or substitution alloys? Justify your answer.

We will now focus on an alloy possessing copper atoms located at every vertex of the cubic cell. Aluminum atoms are located at the center of every face.

33. Draw the positions of the atoms located on a plane that cuts the cube in two parts following the diagonal of one face (only one cell should be considered).

34. Give the chemical formula of this particular alloy (using the writing: Al_xCu_y).