CHEMISTRY 1
Final exam (3 hours)

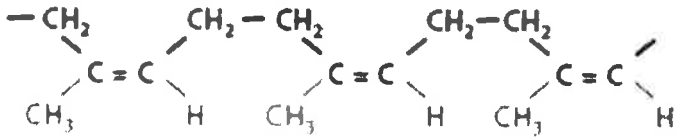
No document allowed. Only « collège » type calculators are authorized.
The four different problems are independent. Every answer must be justified.
Caution: marking is for information only: 40 points

Fighting the HIV/AIDS

"Getting to Zero: Zero new HIV infections. Zero deaths from AIDS-related illness. Zero discrimination" is the multi-year theme (2011-2015) for World AIDS Day. As of 2013, AIDS has killed more than 36 million people worldwide (1981-2012), and an estimated 35.3 million people are living with HIV, making it one of the most important global public health issues in recorded history. In 2012, 6.300 people were infected each day with HIV and 1.6 million people died of HIV-related causes. Among the means to fight against this scourge are the development of preventive and therapeutic means, access to care and treatment for all, the fight against discrimination. The use of condoms remains the only effective preventive measure. Beyond the promotional campaigns of its use, many research and development were / are led around the constituent materials and compounds. It is offered a glimpse into this duty.

I) About polymer materials (2 points)

Natural rubber (« caoutchouc ») is one of the most known polymers. This elastomer is derived from the milky suspension (latex) found in the sap of certain trees. The Mayans and Aztecs already levied this matter from the rubber tree to manufacture waterproof footwear and balls. The latex is isoprene (2 méthyl-1,3 butadiene) whose chemical synthesis leads to different forms. Among them, the Cis 1,4 polyisoprene is used in the manufacture of condoms (chemical formula below). To transform latex in natural rubber, polymer chains are crosslinked.



Cis 1,4 polyisoprene

1) Cite the two morphologies that can be encountered for polymers.
2) What does the glass transition temperature of a polymer correspond to?
3) In your opinion, is the glass transition temperature of rubber well below or well above room temperature ? Explain.
4) How can you explain that natural rubber is not liquid at room temperature?

II) Study of the additives and lubricants

To facilitate storage and handling, plastic products made from natural or synthetic rubber (surgical products, gloves, condoms ...) are coated with non-toxic chemicals that are soluble in water, some of them containing **sodium** and potassium[1].

[1] J. J. Sternlieb, Surgical lubricants. *Brevet* US4143423. 13 mars 1979.

II.A – Atomic sodium: spectroscopy *(7 points)*

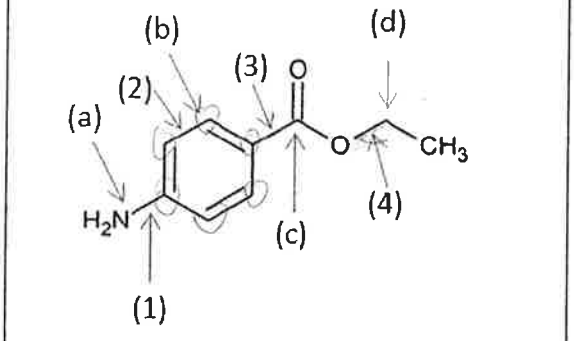
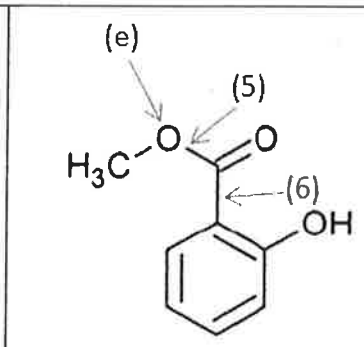
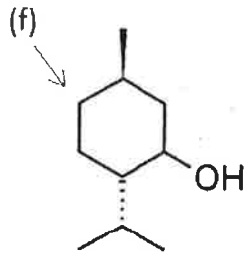
1) Complete the boxes in grey available in the table on page 6 (multiple values are sometimes possible).
2) Vapors of atomic sodium are excited with photons which frequency is between 8.90×10^{14} Hz and 9.20×10^{14} Hz. With an imprecise spectrometer, how many rays will be observed on the emission spectrum? Represent these transitions on a Grotrian's diagram.
3) When using a spectrometer that is sufficiently precise, one can observe on the emission spectrum a highly intense yellow doublet which associated wavelengths are 589.0 nm and 589.6 nm. Explain why this doublet exists. Which levels/sub-levels are involved in the transitions that are characterized by this doublet?
4) One can also observe 2 triplets. What are the levels involved and to which domain(s) of the electromagnetic spectrum do they belong to?

II.B – Sodium carbonate (Na_2CO_3) and sodium acetate (CH_3COONa) *(5 points)*

1) Which ion can be obtained from sodium? Na^+
2) Write down the Lewis structure for the carbonate ion and for the acetate ion (no peroxide-type bonds for these structures).
3) What are the oxidation numbers of the carbon atoms in these ions?
4) Acetic acid (CH_3COOH) and ethanol (CH_3-CH_2OH) form a redox couple. Identify the oxidized and the reduced form for this couple; write down the redox half-reaction in acidic medium, justifying the well-balancing of the reaction through the change in oxidation numbers.
5) The carbonate ion is one of the conjugated base for carbonic acid. Write down the two reactions related to the two acidities of carbonic acid (pKa = 4.8 and 10.3).

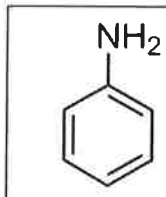
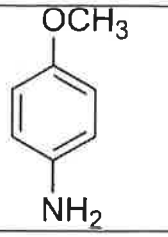
II.C – Benzocaine, methyl salicylate, menthol *(10 points)*

Among the conventional additives found in condoms, one can cite **benzocaine, methyl salicylate** (that acts as local anesthetics, guess why?) and **menthol** (a flavoring additive), which formulas are given below[2] :

		
Benzocaine	Methyl salicylate	Menthol

1) Give the hybridization state, the geometry and the angles found for atoms (a) to (f).
2) Indicate which type (σ and/or π) and compare together the bond lengths for bonds 1, 2, 3 and 4. Qualify your answer.
3) Is free rotation possible around bonds 5 and 6? Qualify your answer.
4) Circle the atoms that are coplanar in the benzocaine molecule
5) Benzocaine owns a basic character due to the amine function. Explain why its pKa value is low (pKa = 2.5).
6) Order by increasing pKa value benzocaine, aniline and anisidine (see following schemes). Qualify your answer.

[2] S. E. Spencer, S. Y. Kim, S. B. Kim, K. A. Schug, *Forensic Science International* 207 (2011) 19–26

	
Aniline	Anisidine

III) Photoluminescent nanoparticles

Among researches made on the development of new highly efficient materials and additives for producing condoms and in order to fight against AIDS virus, one can mention the use of photoluminescent nanoparticles developed in the 80s. The adding of particles was indeed proposed to facilitate the handling of condoms in the dark but they were also proposed as a way to control their integrity after use.[3] Thus **Zinc sulfide nanoparticles doped by metal cations** were then studied and developed. Among others X-ray fluorescence (XRF) and X-ray diffraction (XRD) analytical methods were then used.

III.A X-ray fluorescence analysis *(5 points)*

1) Using a scheme recall the principle of X-ray fluorescence analysis.
2) What information can be learned from the obtained spectrum?
3) Which condition must complete the radiation of the device that emits X-rays in order to produce the K lines of all elements that constitute a given sample (then termed K fluorescence)?

We wish to identify the chemical nature of the doping metallic cation. On the obtained K fluorescence spectrum, one can observe a main doublet of highest intensity at the following wavelengths: 1.540 Å and 1.544 Å.

4) Using the data gathered in the table and the periodic table given on page 5, identify the chemical nature of the element responsible for the production of this characteristic doublet.
5) Write down the electronic configuration of sulfur, zinc and of the doping element (considered here as its neutral atomic state).
6) The doping element can exist in two oxidative states: +I and +II. Rank their radius and compare them to the one of the neutral element (justify your answer).

III.B X-ray diffraction analysis and crystal study *(11 points)*

1) Using a scheme of principle of X-ray diffraction, demonstrate Bragg's law.
2) What are the informations that can be learned from this analysis?
3) Why is it necessary to work with a monochromatized X-ray beam?

In order to monochromatize the beam obtained from a molybdenum anticathode, we wish to use a filter.

4) What condition must complete this filter?
5) Which chemical element would you use?

We will use a 60 µm thick filter. The K-L line emitted by the anticathode is twice as intense as the K-M line. After the filter, the most intense ray represents 98.3% of the total emerging radiation.

6) Compute the difference between the linear absorption coefficients of the constituting filter for the two K-L and K-M lines considered here.

[3] R. W. Etheredge, Novel phosphorescent condoms. *Patent* US5018532. 28 mai 1991.

Two allotropic forms of ZnS exist: "blende" (cubic system) and "wurtzite" (hexagonal system). The X-ray diffraction analysis of the doped ZnS allow the identification of the following four first rays:

(h,k,l)	(1,1,1)	(2,0,0)	(2,2,0)	(3,1,1)
d_{hkl} (Å)	3.121	2.703	1.911	1.630

7) Which allotropic form and which Bravais lattice does the sample belong to? (justify your answer) Compute the cell parameters.

In this structure, sulfur is placed on each node while zinc is located in tetrahedral holes of the lattice.

8) What percentage of the total tetrahedral holes is occupied by zinc? What is the composition of the motif?
9) Give the coordination numbers (not coordinates) of sulfur and zinc in this structure.
10) Draw the first planes of the (1,1,0) and (1,1,1) families (on each scheme should appear the sulfur and zinc at their respective positions).
11) If the crystal was purely ionic, give the contact conditions (radii in function of the cell parameters) between the sulfur and zinc ions in such structure. Compute the cell parameters according to this hypothesis.
12) What can we conclude about the nature of the bonds responsible for the cohesion of the structure?

The doping cation's radius is 0.62 Å

13) From a general point of view, how doping species of different chemical nature can insert into a given lattice?
14) Give and discuss the possible(s) position(s) of the doping cation in this ZnS structure. Use the value of ionic radii for the discussion.

In the other allotropic form of ZnS, the reduced coordinates of sulfur are: (0,0,0) and (2/3,1/3,1/2). In this crystal zinc is also located in tetrahedral holes of the lattice. The densities and atomic packing factors of the two allotropic forms are equal. The distances between the sulfur-sulfur and sulfur-zinc centers are also equal found before for the "blende" structure.

15) What is the Bravais lattice of this structure?
16) Compute the cell parameters and determine the motif composition.
17) Using the value of ionic radii, compute the atomic packing factor of this structure (without doping metal).
18) Compute the density of ZnS (without doping metal).