EC Chemistry 1 – Test n°2 - Duration : 2h

No document allowed. Any calculators allowed.

Answers must be concisely justified.

The results will be given with the appropriate number of significant digits.

Data

Standard constants: h = 6.626x10^{-34} J.s ; c = 2.998x10^{8} m.s^{-1} ; e = 1.602x10^{-19} C ; m$_e$ = 9.109x10^{-31} kg

Beer-Lambert's law: $\mathrm{I} = \mathrm{I}_0 \exp(-\mu x)$ with μ being the linear absorption coefficient and x the width

Moseley's law: $\sqrt{\nu} = a(Z-b)$ **Selection rules:** Δl = ± 1 and Δj = 0 ; ± 1

Relationship between E and λ (to be used without any demonstration): $E(eV) = 12400/\lambda(\text{Å})$

Slater's model: $E_{n,l} = -13.6\frac{Z_{n,l}^{*2}}{n^2}$ (eV) and $r \propto \frac{n^2}{z^*}$ with $Z_{n,l}^* = Z - \sigma_{n,l}$, and n ≤ 3, $\sigma_{n,l}$: screen constant

Element	H	C	N	O	F	P	S	Cl	Mn	Br	I
Z	1	6	7	8	9	15	16	17	25	35	53
χ	2.20	2.55	3.04	3.44	3.98	2.19	2.58	3.16	1.55	2.96	2.66

χ: Electronegativity value according to Pauling's scale.

Part I : X rays | ~ 20 pts

An X-ray generator that can be used to analyze materials by X-ray fluorescence can be equipped with an anticathode made of chromium (Cr) or copper (Cu). Some discontinuity values for these elements are given in the following table.

Element	Z	λ_K (Å)	λ_{L1} (Å)	$\lambda_{L2,3}$ (Å)	λ_{M1} (Å)	$\lambda_{M2,3}$ (Å)	$\lambda_{M4,5}$ (Å)
Chromium	24	2.070	17.85	21.36	167.3	291.8	5391.0
Copper	29	1.381	11.27	13.18	103.5	168.5	/

We are interested in the case of an anticathode made of copper.

1) Give the electronic configuration of copper. Specify the number of single electrons, as well as the orbitals they are located in.
2) On a Grotrian's diagram, represent all the occupied sublevels.
   For this:
   a) Recall the relationships that connect the quantum numbers that characterize the sublevels,
   b) Specify the value of the quantum numbers for each sublevel.

3) By rigorously justifying your approach, give for copper the set of possible emission lines, with the sublevels involved, corresponding to the transitions associated with different levels ($\Delta n \neq 0$) and having as arrival levels:
   a) The K level,
   b) The L level.
4) What is the minimum tension to be applied to the terminals of the X-ray tube to observe the lines associated with the transitions in the previous question?
5) Calculate the wavelength associated with the K-type lines emitted by the copper anticathode, to within 10^{-3} Å.

Exiting an X-ray tube consisting of an unidentified anticathode, an X-ray beam is composed of two wavelength lines: λ_1 = 1.39 Å and λ_2 = 1.54 Å. The aim is to monochromatize the beam in order to retain (keep) mainly the line with the lower energy. Different filters (F1 to F3) are available, and their linear absorption coefficients as a function of wavelength are gathered in **Table 1**. It will be assumed that the observed discontinuities are associated with the K level.

λ (Å)	1.27	1.29	1.31	1.35	1.37	1.39	1.41	1.43	1.45	1.48	1.50	1.52	1.54	1.56	1.59	1.61
F1	1693	1775	1858	2034	2126	2220	2317	2417	2520	2680	2790	2903	3019	3138	3223	411
F2	1889	1979	2073	2268	2371	2476	2585	2696	2811	2989	370	385	401	417	441	458
F3	2323	290	303	332	347	363	378	395	412	438	456	474	493	513	543	563

Table 1. Values of the linear absorption coefficients (μ in cm^{-1}) at different values of wavelengths

6) Explain the principle of monochromatization of an X-ray beam using a scheme representing the evolution of the absorption coefficient of the filter material, as a function of the wavelength of the incident photons.
7) Which of the different filters available will have to be chosen?
8) Determine the value of the atomic number of the filter.

Monochromatization is considered efficient if the ratio of transmitted intensities is greater than 10 and the attenuation of the line of interest is less than 40%.

9) Considering that the incident intensity ratio $\frac{I_2^0}{I_1^0}$ = 3.0, and a filter of thickness x = 10 μm is available, is the monochromatization efficient?

Part II : Lewis structure, VSEPR, Redox, Hybridization | ~20-pts

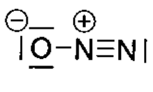
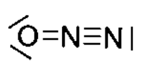
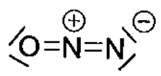
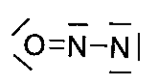
Exercise 1. Lewis structures and VSEPR theory~ 10 pts

Let's consider the following species (in bold, the central atom to which the others are connected to) : **C**O_3^{2-}, **P**OCl_3, **S**O_2, **S**O_4^{2-} and HF

1) Justifying concisely your approach, propose the most probable Lewis formula for each of these species.
2) Write all the mesomeric formulas for CO_3^{2-}, and represent the corresponding resonance hybrid.
3) Give the geometry according VSEPR theory, for **C**O_3^{2-}, **P**OCl_3 and **S**O_2 as well as the angle values about the central atom.
4) Determine and justify whether the $POCl_3$ presents a permanent dipole moment.
5) The values of the boiling temperatures for the hydrogen halides, namely HF, HCl, HBr, HI are given in the table below. How do you explain the observed evolution?

Hydrogen halide	Molar mass ($g.mol^{-1}$)	Boiling temperature (°C)
HF	20.0	20
HCl	36.5	-85
HBr	80.9	-67
HI	127.9	-36

6) Nitrous oxide is a gas with the formula N_2O. When we asked students to represent its Lewis formulas, several answers were given. Justifying concisely your answers, indicate for each following suggestion whether it is correct or not. Finally, identify the most probable formula.

a)  **b)**  **c)**  **d)** 

Exercise 2. Redox reaction ~ 4 pts

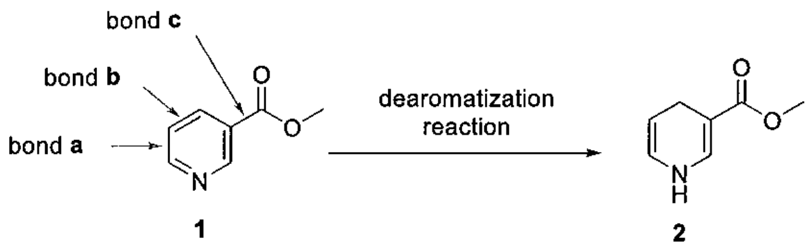
Sulphur dioxide (**S**O_2) is used in wines as a preservative thanks to its antioxidant and antimicrobial properties. However, if the concentration is too high, sulfur dioxide has an unpleasant smell and taste and can even be toxic. It is possible to measure the amount of **S**O_2 contained in the wine by reacting them with **Mn**O_4^- ions in water, in acidic medium.

Redox couples involved: **S**O_4^{2-}/**S**O_2 and **Mn**O_4^-/Mn^{2+}
(the bolded atom is the one to which the others are all bonded to)

1) Write the two balanced halves-reactions specifying the oxidation number of the appropriate element that is involved by the redox process.
2) Write the global redox reaction, specifying the oxidant and the reductant of the reaction.
3) Specify the number of moles of electrons exchanged per mole of SO_2.

Exercise 3. Hybridization ~ 6 pts

Scientists have developed a new methodology for the synthesis of 1,4-dihydropyridines (e.g. molecule **2**) from pyridines (e.g. molecule **1**) under mild conditions (for simplicity's sake, the other reactants are not specified).



1) Write the developed formulas for molecules **1** and **2** by showing all atoms (C, H, O, N) and lone pairs.
2) Specify the hybridization states of carbon and oxygen atoms in each of the previous representations.
3) Compare together the **a** and **b** bond lengths. Justify concisely your answer.
4) Is free rotation around the **c** bond possible? Clearly justify your answer with one or more schemes.
5) Calculate the oxidation numbers of the carbon atoms circled in gray. What can you then deduce about the nature of the involved reaction?

End of the subject.