

CHEMISTRY 1 – Test 2

Duration 2h

*No document allowed. Only « collège » type calculators are authorized.
The marking-scheme is for information only.*

Some constants and formula are given on page3

I. X Rays (10 pts)

	Z	λ_K (Å)	λ_{L_1} (Å)	λ_{L_2} (Å)	λ_{L_3} (Å)	$\lambda_{M_{2,3}}$ (Å)	$EM_{4,5}$ (eV)
Zn	30						81.0
Ni	28						36.0
Co	27	1.6081	13.391	15.617	15.918	210.17	
Fe	26	1.744					
Mn	25	1.896					

We wish to design an X-ray fluorescence analysis device using cobalt (Co) as a source of X-rays.

- 1) Give the electronic configuration of cobalt. Give its position (period and group) in the periodic table. Which block is it belonging to?
- 2) Compute the wavelengths (to within 10^{-3} Å) of the three main transitions observed between the M/L departure levels and the K arrival level. Give the value of $\lambda_{KL_{2,3}}$, the average of λ_{KL_2} and λ_{KL_3} .
- 3) The anticathode is hit by an electron beam accelerated by either a voltage of 5 kV, or a voltage of 10 kV. Draw schematically, in function of the wavelength the two emission spectra obtained for each applied voltage. Show on the X-axes the meaningful values.
Comment the graphs by indicating the origin of the different elements of the spectra (continuous and discontinuous).

In order to obtain a high quality in the analysis, the X-ray beam that is produced needs to be monochromatized. It is indeed possible to highly reduce the highest energy ray by absorbing it using a well selected filter. We possess two thin sheets in this purpose, one made of iron (Fe) and one made of manganese (Mn). Their absorption characteristics are recorded in the following table:

E (keV)	5.905	6.200	6.492	6.924	7.061	7.470	7.654	8.052
$\mu(\text{Fe})$ (cm ⁻¹)	698.8	613.1	532.1	440.1	418.9	2884.6	2719.6	2420.9
$\mu(\text{Mn})$ (cm ⁻¹)	544.3	475.2	414.7	2916.0	2772.0	2383.2	2239.2	1980.0

- 4) Plot $\mu(\text{Fe})$ et $\mu(\text{Mn})$ in function of the wavelength (graph paper on page 4 can possibly be used but do not forget to give it back). What do those two curves show? To which characteristic wavelength do they give access to?
- 5) a) Draw schematically (no scale asked) the appearance of the emission spectra obtained (accelerating voltage of 10 kV) after the beam has crossed each filter. Conclude on the best filter for our purpose.
b) For cobalt, we have the following incident intensities ratio: $I_{K-M_{2,3}}/I_{K-L_{2,3}}=0.1$. Compute the $I'_{K-M_{2,3}}/I'_{K-L_{2,3}}$ ratio value after the beam has crossed the filter selected in the previous question (its width is 10 μ m).

- 6) We would like to determine the energies of layers K, L and M of cobalt.
In some conditions, it is possible to detect several less intense rays corresponding to transitions between layers M and L. In the case of cobalt, the ray corresponding to the larger wavelength observed between these two levels is 1.829 nm.
- Draw the Grotrian's diagram of cobalt for the K, L and M levels (level N is not asked). The diagram should contain the (n,l,j) triplets corresponding to each level as well as its energy in eV (to within 0.1 eV).
 - Indicate on the diagram the ray corresponding to $\lambda=1.829$ nm and verify that this transition is permitted.

II. Physical properties of elements (2 pts)

Berillium (Be) is located before boron (B) and carbon (C) in the periodic table.

- When Z increases, how does the first ionization energies vary in a raw (period) of the periodic table?
- Compute the first ionization energy of boron using Slater's rules.
- The experimental first ionization energy of beryllium is 9.3 eV, the one of boron is 8.3 eV and the one of carbon is 11.2 eV. Comment this evolution and give an explanation for the difference observed for boron when comparing the experimental value with the one obtain using Slater's rules.

III. Structure and geometry of molecules or ions (6,5 pts)

- 1) Study of some fluorinated molecules.

Draw the Lewis structures; give the Gillespie's formula and the shapes of the following molecules. Indicate the oxidation state (number) of the central atom and the expected angles values according to the VSEPR theory.

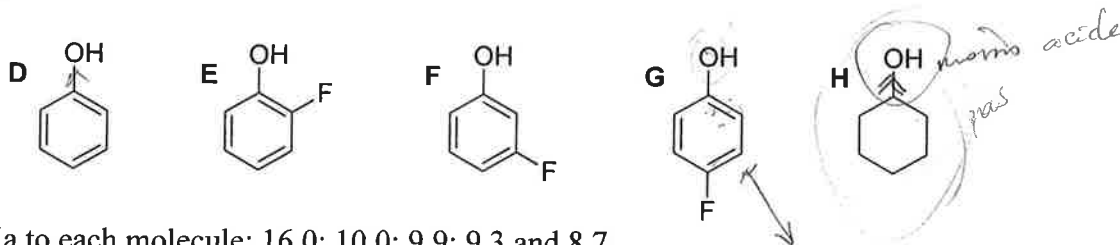


- 2) Three non-cyclic molecules (named **A**, **B** and **C**) are corresponding to the C₂H₂Cl₂ formula.
For **A** and **B** the two carbon atoms have the same oxidation state. **C** has two carbon atoms with different oxidation states.
- Give the structures of **A**, **B** and **C** knowing that **A** possesses no dipole moment and **B** a dipole moment of 1.9 D (Debye).
 - For molecule **A**, give the hybridization states of the carbon atoms.
 - Are all the atoms of molecule **A** coplanar (belonging to the same plane)? Qualify your answer using a little scheme showing the geometry of the orbitals involved in the bonding.
 - Compounds **A** and **B** have different boiling points: one is 60°C and the other is 48°C. Assign the boiling point to each compound and give an explanation for the observed temperature gap.
- 3) Guanidinium thiocyanate is a salt heavily used in biochemistry for protein and nucleic acids denaturation.
- Draw two mesomeric formulas of the thiocyanate ion: SCN⁻.
Give the hybridization states of the carbon atoms in these two structures.
 - The guanidinium formula is C(NH₂)₃⁺ (it contains no N-N bonds).
Draw two types of structures; one with a positive charge on the carbon atom and the other on one of the nitrogen atom.
 - Why is the one with the positive charge on the nitrogen favored? Show that it possess several resonance formulas and give the hybridization states of the carbon atoms in these structures.

- 4) The thiocyanate ion can be obtained by reacting thiosulfate ions with cyanide ions according to the following reaction: $\text{CN}^- + \text{S}_2\text{O}_3^{2-} \rightarrow \text{SCN}^- + \text{SO}_3^{2-}$
- Give the Lewis structure of the cyanide ion (CN^-)
 - Give the Lewis structure of the thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$) in which the sulfur atoms adopt two oxidation numbers: 0 and +IV.
 - Give the Lewis structure and the shape of the sulfite ion (SO_3^{2-})

IV. Chemical reactivity of molecules (2 pts)

We want to rank the following molecules (**D** to **H**) possessing hydroxyl functions (OH) for their relative acidity.



Assign the pKa to each molecule: 16.0; 10.0; 9.9; 9.3 and 8.7.
Qualify your ranking.

Data and formula

Constants: $h = 6.63 \times 10^{-34}$ J.s; $c = 3 \times 10^8$ m.s⁻¹; $e = 1.602 \times 10^{-19}$ C; $N = 6.02 \times 10^{23}$ mol⁻¹

Bragg's law: $2 d_{hkl} \sin\theta = \lambda$

Beer Lambert's law : $I = I_0 \exp(-\mu x)$

Moseley's law : $\sqrt{\nu} = a(Z - b)$

Relationship between E and λ : $E(\text{eV}) = 12400/\lambda(\text{\AA})$

Slater's rules : $E = -13.6 \frac{Z^{*2}}{n^2}$ (eV) with $Z^* = Z - \sigma$

Contribution of the electrons localized in the n' orbital on the screen constant (σ) which applies on an electron localized in the orbital n are gathered in the following table:

Orbital of the electron	$n' < n-1$	$n' = n-1$	$n' = n$	$n' > n$
1s	-	-	0.30	0
ns, np	1.00	0.85	0.35	0
nd	1.00	1.00	1.00 for s and p 0.35 for d	0

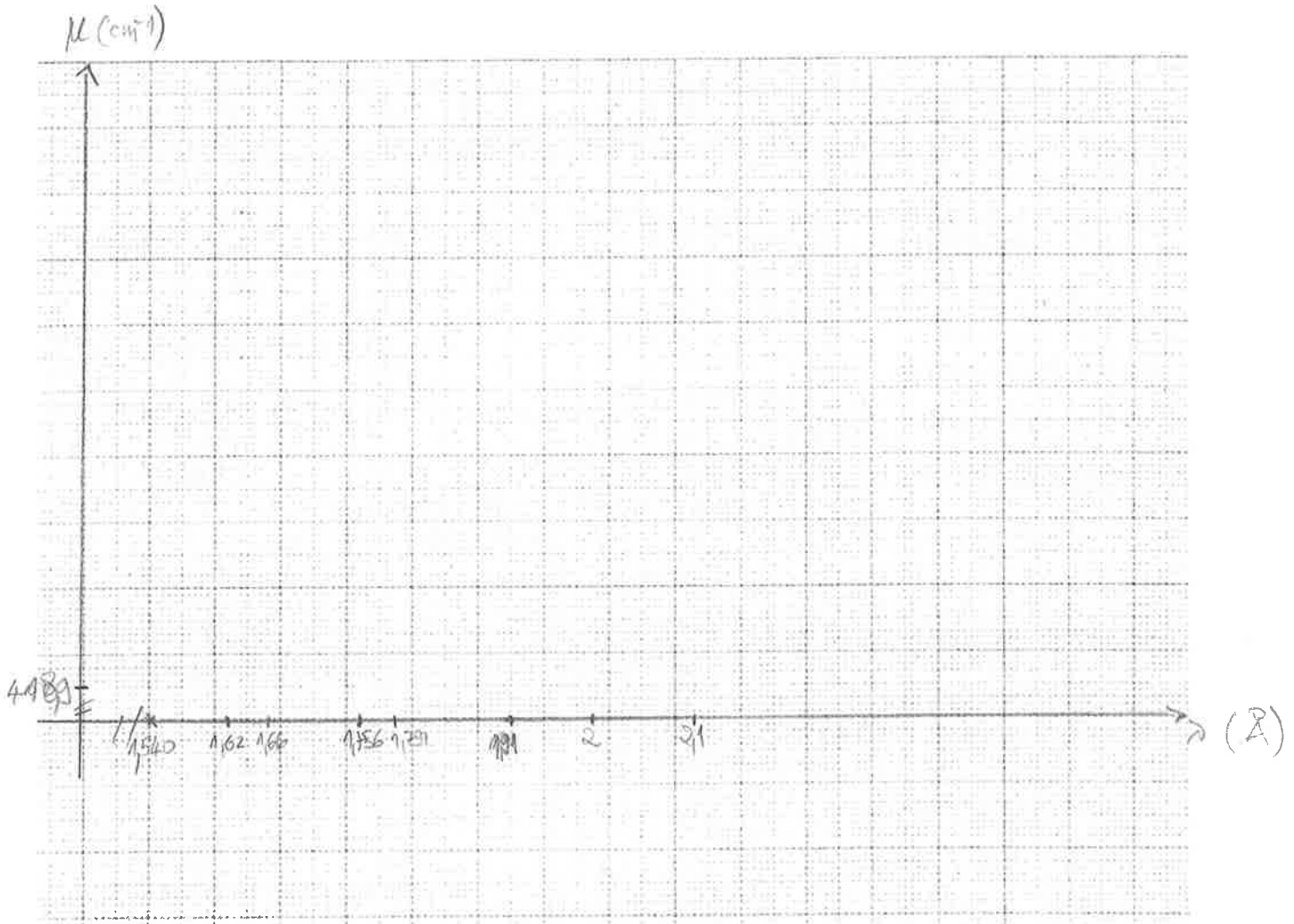
Element	H	Be	B	C	N	O	F	S	Cl
Z	1	4	5	6	7	8	9	16	17
Electronegativity (Pauling)	2.1	1.5	2.0	2.5	3.0	3.5	4.0	2.5	3.0

258 cm⁻¹ → 1 cm

Name:

Surname:

Group:



Do not forget to give back this graph paper sheet.

1,5 → 160 Å