INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON PCC, Amerinsa, Asinsa, Scan 1st year *December 8th 2017*

CHEMISTRY 1 - Test2 - Duration: 2 hours

No document allowed. Only « collège » type calculators are authorized.
The scale of mark is indicative and may be adjusted.

Data :

$h = 6.626 \times 10^{-34}$ J.s $c = 2.998 \times 10^{8}$ m.s^{-1} $e = 1.602 \times 10^{-19}$ C $N_A = 6.02 \times 10^{23}$ mol^{-1}

You can use the following relationship without any demonstration: E(eV) = 12400 / λ (Å)

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

Lambert-Beer's law: $I = I_0 \exp(-\mu x)$ with x the thickness and m the linear attenuation coefficient

Average wave length (example): $\lambda_{K\text{-}L_{2,3}} = (\lambda_{K\text{-}L_2} + \lambda_{K\text{-}L_3})/2$

Slater's rule: Orbital energy (for n≤3): $E_{n,l} = -13,6\frac{Z_{n,l}^{*2}}{n^2}\ (eV)$ with $Z_{n,l}^* = Z - \sigma$; σ: screening constant

The contribution of the electrons localized in the n' orbital on the screening constant which applies on an electron localized in the orbital n:

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

Experimental values of successive ionization energies of Al (in eV) :

Ionization #	1st	2nd	3rd	4th
Ei (eV)	5.990	18.83	28.45	120.0

The three exercises are independent
Numerical applications should be given with the appropriate number of significant digits

Exercise I: Periodic table – polyelectronic atoms (5 points, indicative value)

The five following elements are belonging to the same column of the periodic table (ordered from top to bottom): $_5$B (boron), Al (aluminium), $_{31}$Ga (gallium), In (indium) and Tl (thallium).

1. Give the atomic number of aluminium, indium and thallium (for the latter, the sub-layer 4f is completely filled). Give the group number of these elements and their corresponding period.

2. To which block do these 5 elements belong to? Are they all metallic elements? Order them by increasing atomic radius (justify).

3. Give the electronic configuration of aluminium. How many valence electrons does it possess?

4. According to Slater's rule, give the screening constant (σ) and the nuclear effective charge (Z*) for:

   a) an electron from the valence shell of Al
   b) an electron from the valence shell of Al^+

5. Give the expression of the energies of the valence shell electrons E(Al) et de E(Al^+), respectively. Deduce from it the value of the first ionisation energy (Ei_1) of aluminium. (Reminder: the energy of a polyelectronic structure is assimilated to the sum of the orbital energies associated to each electron).

6. Compare and comment the Ei_1 value obtained to the experimental one (see in the table above).

7. What explains (in few words) the very different ionization energies measured for the 3^{rd} and 4^{th} ionization of Al?

Exercice II : Lewis structures and VSEPR theory (5 points + 1 bonus, indicative value)

Chlorine, Cl (Z = 17), is located in the same period as aluminum. It exists as a mixture of two isotopes, namely ^{35}Cl and ^{37}Cl. The molecular weight of the natural element is 35.5 $g.mol^{-1}$.

1. Give the composition in elementary particles of each isotope's nucleus.

2. Give the atomic percentage of each isotope in the natural element (we assume that the molar mass of each isotope can be taken as its number of mass).

3. Give the electronic configuration of chlorine. To which group does it belong to?

4. Chlorine gas (Cl_2) reacts with aluminum to produce aluminium trichloride ($AlCl_3$) according to the following equation: $2Al + 3Cl_2 \rightarrow 2AlCl_3$

   a) Give the Lewis structure of $AlCl_3$, give its geometry according to VSEPR theory and deduce the value of the observed bonding angles.

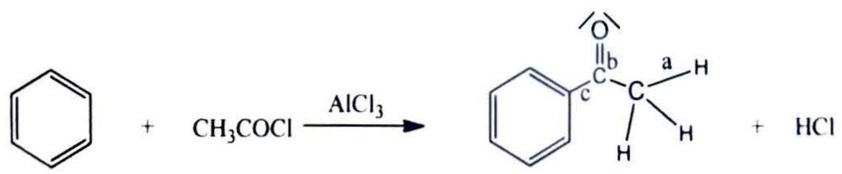
   b) Does aluminium verify the octet rule? What is the consequence on its reactivity?

5. Oxygenated species of chlorine such as perchlorate ions ClO_4^- are observed (for which Cl is the central atom).

   a) Give the most representative Lewis formula of this structure. Give its eventual mesomeric formulas and a representation of corresponding resonance hybrid.

   b) Give the shape of the ClO_4^- ion as well as the predicted value of the bonding angles.

6. The Friedel-Crafts reaction employs $AlCl_3$ as catalysis of the reaction between benzene (C_6H_6) and Acetyl Chloride (CH_3COCl) according to the following reaction:



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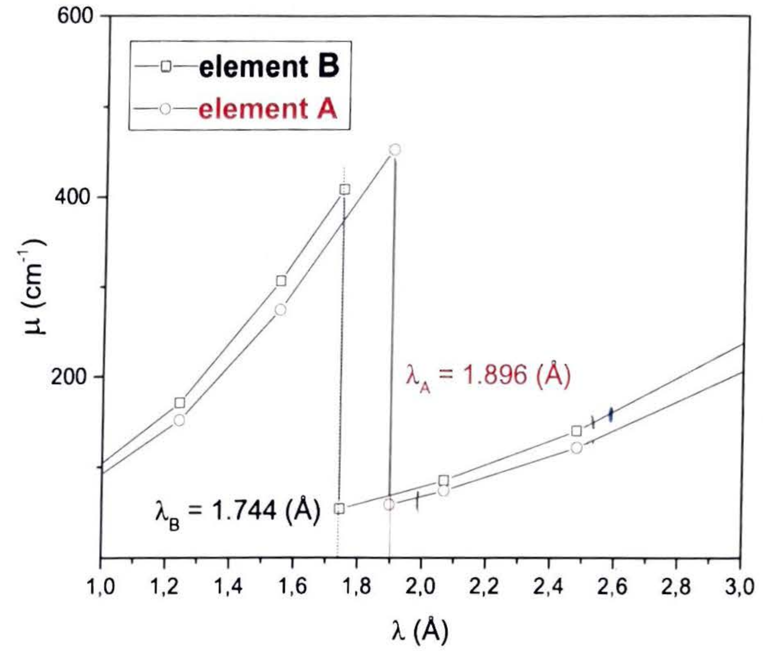
   a) What is the hybridization state of carbon atoms in benzene? Give a representation showing the orbital recovery responsible for the geometry of the molecule.
   b) Give the nature of the **a** and **b** bonds in compound **1**. Give the atomic orbitals used for giving access to the corresponding molecular orbitals.
   c) Is complete free rotation around **c** possible? Justify.

<u>Exercice III : X Rays</u> (10 points, indicative value)

Absolute value of the energies of the K and L levels (in eV):

	K	L_1	L_2	L_3
Cr	5989	696.0	583.8	574.1
Co	7709	925.1	793.2	778.1

Linear attenuation coefficient variation of <u>metals A and B</u>



<u>For the Xrays emitted by the chromium (Cr) anticathode</u>:

- The linear attenuation coefficient of beryllium for K-L ray photons: $\mu_{K\text{-}L} = 1.870\ cm^{-1}$,
- The linear attenuation coefficient of beryllium for K-M ray photons: $\mu_{K\text{-}M} = 1.430\ cm^{-1}$.

A. A X-ray tube is a device allowing the production of X-rays. In a material study laboratory, you have access to 2 different tubes. The first one is equipped with an anticathode made of chromium (Cr, Z=24) and the second one of cobalt (Co, Z=27). Depending on the intended application (chemical or crystallographic X-ray diffraction analysis), either tube will be used. The absolute values of the energies of the K and L levels are given in the above table.

1. Schematically draw the energy diagram by representing the levels K, L and M of the Cr and Co anticathodes. Specify for each of them the quantum numbers n, l and j relative to the electrons present on the different levels. Represent on this diagram the possible transitions from the L and M levels down to the K layer. Calculate the average wavelengths $\lambda_{K\text{-}L}$ of the allowed transitions for the two anticathodes.

2. A potential difference of 7.200 kV is applied between the cathode and the (Cr or Co) anticathode. Give a scheme of the emission spectra (I = f (λ)) of X-rays emitted between 0 and 3 Å for both cases. Explain the global appearance of the two spectra by specifying, in particular, the value of the threshold wavelengths.

3. The wavelengths of the L_I-M transitions of Cr and Co are respectively 23.10 Å and 17.13Å. It will be assumed that all the electrons of the M layer have the same energy.

a) Compute the energies corresponding to the K-M transitions of Cr and Co.

b) Give the associated wavelengths.

B. When exiting the tube, X-rays pass through a beryllium window (Be, Z = 4) which was selected for its vacuum resistance and low X-ray absorption. The value of the intensity I of the transmitted beam through beryllium follows the Beer-Lambert's law.

4. a) For the chromium anticathode, knowing the intensity of the incident X-ray beam $I_{0\ K\text{-}L}$ is 7.4 times greater than the intensity $I_{0\ K\text{-}M}$ before passing the beryllium window, give the value of the $I_{K\text{-}L}/I_{K\text{-}M}$ ratio after passing this window with thickness 2.0 mm.

b) For obtaining a transmitted intensity of the K-L radiation representing 98% of its incident intensity $I_{0\ K\text{-}L}$, give, to within 0.1µm, the maximum thickness of the window.

C. After passing through the beryllium window, the K-L and / or K-M radiations are used for two experiments: for chemical analysis of materials purpose or for crystallographic analysis by X-ray diffraction according to the chosen anticathode:

-for chemical analysis, the radiations from the anticathode must indeed cause the K fluorescence of the elements.

-for crystallographic analysis, the K fluorescence phenomenon should be avoided.

The figure on the previous page shows the observed variation of the linear attenuation of X-ray intensity for two unknown metals A and B.

5. a) What does the discontinuity correspond to? Which energy level is involved?

b) Explain the K fluorescence phenomenon (in few words).

c) Compute the atomic number of the two metals A and B.

d) Without calculations, justify whether metal B can serve as a filter to remove the $\lambda_{K\text{-}M}$ rays from chromium and / or cobalt.

e) Which anticathode (Cr or Co) can be used to perform:

- a crystallographic analysis of the metal A (when K fluorescence has to be avoided)?
- a chemical analysis of the same metal A (when K fluorescence is desired)?

Justify your answers without calculation.