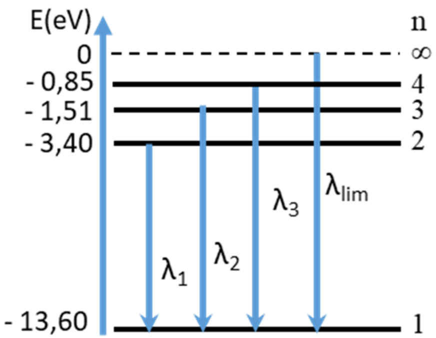
Chimie 1 – Test 1 – October 15, 2021

<u>**I. Atomic spectrum of Hydrogen**</u>	**Comments**
1. The spectrum provided corresponds to one of the series for hydrogen; by definition, a series gathers all transitions in the emission spectrum that arrive to a given energy level noted n which value is not known. Let's note it (n). Long wavelength limit λ_1= 1216 Å associated to the transition involving levels that are the closest to each other: from (n+1) down to (n). Short wavelength limit λ_{lim} = 911.8 Å associated to the transition involving levels that are the furthest to each other: from (∝) down to (n)	Many confusions, shortcuts found here: - In the text it is said that we deal with emission spectrum: thus transitions from a *further* level to a *closer* level (to the nucleus), not the opposite! - Some of you said that the short wavelength limit was the transition from (∝) down to (n = 1). That would be true if we were to deal with the *complete* emission spectrum, while here we work with one of the series: we don't know what is the arrival level (yet).
2. 911.8 Å < $\lambda_{emission}$ < 1216 Å thus wavelength associated to the UV domain	Values were provided in Å, not in nm!!!!
3. Two possibilities to answer this question: a/ As the limits of the series belong to the UV domain for hydrogen, it corresponds to the Lyman's series that gathers all the transitions down to n = 1. b/ From the short wavelength limit λ_{lim} This wavelength is associated to the transition from ($\propto \rightarrow$n). According to Ritz-Balmer, $\frac{1}{\lambda_{\text{lim}}} = R_H\left(\frac{1}{n^2} - \frac{1}{\infty}\right) = \frac{\mathrm{R_H}}{\mathrm{n^2}}$ thus $n = \sqrt{R_H \times \lambda_{\text{lim}}} = 1$	Method b/ it is compulsory to express R_H and λ_{lim} in coherent units (λ_{lim} in cm if you keep R_H in cm^{-1}), or (R_H in $Å^{-1}$ if λ_{lim} expressed in Å).
4. $\Delta \mathrm{E}_{\propto \rightarrow 1}(\boldsymbol{eV}) = \frac{\mathbf{h \times c}}{\mathbf{e} \times \lambda_{\text{lim}}} = \mathrm{E}_\infty - \mathrm{E}_1$ with $\mathrm{E}_\infty = 0$ by convention and energy being negative $\mathrm{E}_1 = -13.60$ eV 4 significant figures as λ_{lim} contains 4	Demonstration was required here, convention rules recalled
5. According to the text: Text :"The lines of the wavelengths $\lambda_1, \lambda_2, \lambda_3$ are those with the highest values for this series".	A rigorous demonstration was expected here, whatever the method selected

We said earlier that the Long wavelength limit λ_1= 1216 Å was associated to the transition (n+1) down to (n). As n = 1, this is the transition from (2) down to 1. As $\lambda_2 < \lambda_1$ with the second lowest wavelength value, it is associated to the second lowest difference in terms of energy. As a consequence, λ_2 corresponds to the transition from (3) down to (1). By the same reasoning, λ_3 is associated to the transition between (4) down to 1. We need the energy of each level (see text). 2 methods (at least) can be envisioned here: a/ $$\Delta E_{2\to1} = E_2 - E_1 > 0 \text{ thus } E_2 = E_1 + \Delta E_{2\to1} = E_1 + \frac{\mathbf{h} \times \mathbf{c}}{\mathbf{e} \times \lambda_1} = -3.40 \text{ eV}$$ $$\Delta E_{3\to1} = E_1 - E_3 > 0 \text{ thus } E_3 = E_1 - \Delta E_{3\to1} = E_1 + \frac{\mathbf{h} \times \mathbf{c}}{\mathbf{e} \times \lambda_2} = -1.51 \text{ eV}$$ $$\Delta E_{4\to1} = E_1 - E_4 > 0 \; thus \; E_4 = E_1 - \Delta E_{4\to1} = E_1 + \frac{\mathbf{h} \times \mathbf{c}}{\mathbf{e} \times \lambda_3} = -0.85 \text{ eV}$$ b/ We can demonstrate that $E_n = E_1/n^2$ $$\Delta E_{\propto\to1}(\boldsymbol{eV}) = h.c.R_H\left(\frac{1}{n^2} - \frac{1}{\infty}\right) = h.c.R_H = E_\infty - E_1 = -E_1$$ $$\Delta E_{\propto\to n}(\boldsymbol{eV}) = h.c.R_H\left(\frac{1}{n^2} - \frac{1}{\infty}\right) = \frac{h.c.R_H}{n^2} = E_\infty - E_n = -E_n$$ By identification: $$E_n = \frac{E_1}{n^2}$$ As we know E_1 from question 4, we can deduce the value of the energy levels whatever n is, including n = 2, 3, 4	The expected precision was given in the text (to within 0.01 eV) In terms of representation, the transitions involve emission phenomenon: the transition are thus downward….

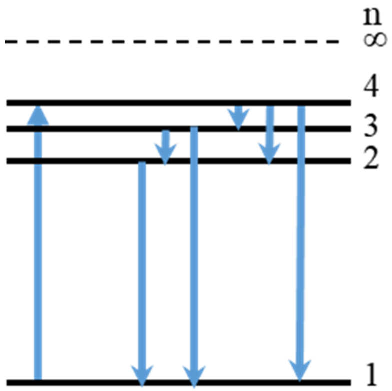
<table>
<tr><td>
</td><td>“Values of the associated quantum numbers”
With the Bohr’s model, the levels are defined exclusively by the main quantum number n.

Many of you gave numerous values of the quantum numbers: (n, l, ml, ms) : this doesn’t apply here!!</td></tr>
<tr><td>II. About boron</td><td></td></tr>
<tr><td>1a.
n : main quantum number : positive non-zero integer value
ℓ : secondary quantum number : integer value such that $0 \leq \ell \leq$ n-1
m_ℓ : magnetic quantum number : integer value such that $-\ell \leq m_\ell \leq +\ell$</td><td>It was compulsory here to specify that the {n, l and ml} values are INTEGER values

Some of you gave as an answer, what each quantum number value represent (shell, orbitals, orientation); it’s good to know this, but it was not the answers to the question…</td></tr>
<tr><td>1b.
<table>
<tr><th>n</th><th>ℓ</th><th>m_ℓ</th><th>Subshell or orbital</th></tr>
<tr><td>3</td><td>2</td><td>-2</td><td>yes 3d</td></tr>
<tr><td>2</td><td>0</td><td>0</td><td>yes 2s</td></tr>
<tr><td>2</td><td>3</td><td>-3</td><td>Not possible</td></tr>
</table></td><td>To the question:” is there an atomic orbital that would correspond to each set of values”? Obviously the expected answers were not only:” yes”…</td></tr>
<tr><td>2a. Number of protons = 5
Number of neutrons = 6
Number of electrons = 5</td><td>Generally well answered</td></tr>
<tr><td>2b. Valence electrons are on the outermost shell, with the highest n: $2s^2\,2p^1$</td><td>As answered by many of you, it’s true that there are 3 valence electrons. But the question was not on the number of valence electrons!</td></tr>
</table>

2c. 1 single electron	Thanks to the building up principle, 2 electrons are paired in the 2s orbital, thus only 1 single electron (on 2p)
3. A hydrogen-like system contains one electron only, as for hydrogen. Starting from a total of 5 electrons, the atom thus needs to lose 4 electrons: $_5B^{4+}$	Both parts of the answers were expected
4a. By definition, ionization energy according to the Bohr's model corresponds to the transition from **level 1 to ∝.** Using Ritz-Balmer equation: $$E_i^Z = Z^2 \times hc \times R_X\left(\frac{1}{1^2} - 0\right)$$ And $$E_i^H = hc \times R_H\left(\frac{1}{1^2} - 0\right)$$ As $R_X = R_H$ (according to the text) :$E_i^Z = Z^2 \times E_i^H$	Obviously, the demonstration starts with the recall of what ionization energy corresponds to…
4b. $$E_i^Z = \frac{Z^2 \times hc \times R_X}{e} = \frac{5^2 \times 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 10967700}{1.602 \times 10^{-19}} = 340.0\ eV$$ Or $E_i^Z = Z^2 \times E_i^H = 5^2 \times 13.60 = 340.0\ eV$ $$E_i^Z = E_i^Z = Z^2 \times hc \times R_X = 5^2 \times 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 10967700$$ $E_i^Z = 5.447 \times 10^{-17}$J $$E_i^Z = Z^2 \times hc \times R_X N_A$$ $$= 5^2 \times 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 10967700 \times 6.022 \times 10^{23}$$ $E_i^Z = 3.280.10^4$ kJ.mol^{-1}	Answers were expected in 3 different units

5. If the emission spectrum contains 6 rays, the electron of the B^{4+} hydrogen-like ion has first been excited to level n= 4



The frequency band should then:

- Permit the transition from n = 1 to n = 4 : the associated frequency would then correspond to the minimum value
- Not permit the transition from n = 1 to n = 5 (otherwise the emission spectrum would contain more than 6 rays): the associated frequency would then correspond to the maximum value

$$\vartheta_{1-5} = \frac{c}{\lambda} = \mathrm{cR_H Z^2}\left(\frac{1}{1^2} - \frac{1}{5^2}\right) = 7.890.\,10^{16}\mathrm{Hz}$$

Thus : υ should then be strictly lower than υ_{max} = 7.890. 10^{16} Hz

III. Spectroscopy for hydrogen-like systems

1°) The transition associated to the highest energy in the absorption spectrum corresponds to ionization, thus to the transition from (n = 1) to (∝).

Thus :

$$E^{A}_{ionization} = hc \times \frac{1}{\lambda^{A}_{ionisation}} = \frac{6.626\times10^{-34}\times2.998\times10^{8}}{101.3\times10^{-10}} \times 10^{-3} \times 6.022 \times 10^{23} =$$
$$1.181 \times 10^{4}\ \mathrm{kJ/mol}$$

And :

Obviously, it was expected to recall that the highest energy transition was associated to ionization.

Some of you used the equation:

$$E(eV) = \frac{12400}{\lambda(\text{Å})}$$

$E^{B}_{ionization} = hc \times \frac{1}{\lambda^{B}_{ionisation}} = \frac{6.626\times10^{-34}\times2.998\times10^{8}}{25.33\times10^{-10}} \times 10^{-3} \times 6.022 \times 10^{23} =$ 4.723×10^{4} kJ/mol 4 significant figures in agreement with the precision given in the text	Why not, but you need first to demonstrate it!!! Remember that : $E(J) = \frac{h(J.s)\ c\ (m.s^{-1})}{\lambda(m)} = \frac{h(J.s)\ c\ (m.s^{-1})}{10^{-10}.\lambda(Å)}$ $E(eV) = \frac{E(J)}{e}$ $E(kJ.mol^{-1}) = E(J).10^{-3}.N_A$ The energy expressed in $kJ.mol^{-1}$ is for a mole of event: it is thus N_A times bigger than for 1 event…
2°) By applying Ritz-Balmer equation to both hydrogen-like systems that own the same value of Rydberg's constant ($R_A = R_B = R_x$) and for the ionization phenomenon: $\frac{1}{\lambda^{A}_{ionization}} = R_x \times Z_A^2 \times \left(\frac{1}{1^2} - 0\right) = R_x \times Z_A^2$ $\frac{1}{\lambda^{B}_{ionisation}} = R_x \times Z_B^2$ Thus : $\frac{Z_B}{Z_A} = \sqrt{\frac{\lambda^{A}_{ionization}}{\lambda^{B}_{ionization}}} = 2$	Some of you intended to use the equation demonstrated in exercise 2, question 4a) that lead to : $E_i^Z = Z^2 \times E_i^H$ However, this equation was obtained considering that $R_X = R_H$ … which is not verified here (see text)!!!
3°) We need to have the energy of the emitted radiation for the transition (4 →2) for Z_B strictly equals to the ionization energy for Z_A : $R_x \times Z_B^2 \times \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = R_x \times Z_A^2 \times \left(\frac{1}{1^2} - \frac{1}{\infty}\right)$ thus $\left(\frac{Z_B}{Z_A}\right)^2 = \frac{16}{3}$ $\frac{Z_B}{Z_A} = \frac{4}{\sqrt{3}} = 2.3$ According to question 2, this is not verified.	