2021-2022 CORRECTION AND COMMENTS – Test 2 CHEMISTRY 1

Questions	Answers and comments	
Exercise I : 4 points		
1.	Population : Atoms A : (8 x 1/8 + 6 x ½) = 4 Atoms B: (12 x ¼ + 1) = 4	Globally well answered. (even if some of you have not considered the B atom located at the very centre of the cube…)
2.	**APF :** fraction or percentage of the volume really occupied by the atoms then assimilated to spheres compared to the total volume of the cell **APF value =** $\dfrac{4\times\frac{4}{3}\pi(r_A{}^3+r_B{}^3)}{a^3} = \dfrac{4\times\frac{4}{3}\pi\times(1.81^3+0.97^3)}{5,56^3} = \mathbf{67\%}$	Definition is important : atoms are considered as hard spheres (otherwise how to express the volume of the atoms?) And careful with the expression of the volume of a sphere!! (many errors here!!) Moreover some of you have computed the value of the cell parameter considering that the atoms of A were tangent - Value a was provided in the text!! - It is not said that the A atoms are tangent in a ny direction, or that the A atoms organize in a close-packed structure : you can't consider the tangency condition then! Some of you got an APF value bigger than 1. Considering the definition, is that logical???

3.	Definition of density $\rho = \dfrac{m}{V} = \dfrac{n_A \times M_A + n_A \times M_A}{V}$	Many errors found here !
	with : n_A and n_B = population of atoms A and B in the cell, respectively	Just to make sure : there are 4 atoms of A and 4 atoms of B. It is true that there is a total of 8 atoms in the cell.
	M_A and M_B = molar mass of A and B in g/mol	
	N_A = Avogadro's number = 6.022 10^{23} mol^{-1}	HOWEVER: $(4M_A + 4M_B) \neq 8\,(M_A + M_B)$
	V = volume of the cell = a^3	
	$$\rho = \frac{4 \times (M_A + M_B)}{N_A \times (a)^3} = \frac{4 \times (23 + 35,5)}{6,022\ 10^{23} \times (5,56x10^{-8})^3} = 2,26\ g.cm^{-3}$$	

Exercise II : 15 points

1.	Z=37 : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$	
	the highest layer of n (5s) contains only 1 electron so it is an alkaline (ns^1)	
2.	Let x and y be the relative abundance of the ^{85}Rb and ^{87}Rb isotopes, respectively	
	We have a set of two equations such that :	
	x+y=1	
	84.9118x+86.9092y=85.4678	
	The mathematical solution of are such that :	
	x=0.7216 and y = 1-x = 0.2784	
	Natural rubidium is thus made up to 72.16% of ^{85}Rb and 27.84% of ^{87}Rb	
3.	By definition, ionization is the transition of one outermost electron to infinite. Because there is only one electron that occupies the 5s level, the resulting ionization energy is: $$E_i = E_\infty - E_{5S_{\frac{1}{2}}} = -E_{5S_{\frac{1}{2}}} \text{ as } E_\infty = 0 \text{ by convention}$$	Here, part of the answer consists in remembering that ionization energy, as for any transition, is the difference of energy between 2 levels.

	As $E_i = 4.177 eV = -E_{5S_{\frac{1}{2}}}$, we confirm that $E_{5S_{\frac{1}{2}}}$=-4.177 eV If Level 5S$_{1/2}$ is defined thanks to the reciprocal of its wavelength $\frac{1}{\lambda_{5S_{\frac{1}{2}}}}$, it means that $\left| E_{5S_{\frac{1}{2}}} \right| = hc.\frac{1}{\lambda_{5S_{\frac{1}{2}}}}$ Thus $5S_{1/2} : \dfrac{E_{5S_{\frac{1}{2}}}}{hc} = \dfrac{1}{\lambda_{5S_{\frac{1}{2}}}}$ Using the correct units, we find back that 1/λ=33685cm^{-1}	The relationship between λ and E was only part of the answer!!
4.	The Sr, located to the right of the Rb in the same period, will have an ionization energy greater than this one because : - it owns one more proton in its core that Rb, it will exert a stronger attraction on its most distant electrons and - the electron which it has in more in its electronic cloud will have a weaker screening constant (because it is located on the same layer: cf Slater) The Cs is located below Rb so its electronic configuration will be terminated by 6s^1. It will have a whole layer of electrons more compared to Rb ; all the extra electrons of the 5th layer will have a high screen constant. Thus E$_i$(Cs)=3.894 eV < E$_i$(Rb)=4.177 eV < E$_i$ Sr=5.695 eV	
5.	Some levels are doubled because of the spin orbit coupling, defined by the fifth quantum number j. $j = \left| l \pm \frac{1}{2} \right|$ For S levels (l = 0)there is only one possible value for j = ½, while for any other value levels, there are 2 possible values. Ex: for P levels, as l = 1, j = ½ or j = 3/2. The levels is thus doubled, defined as 5P$_{1/2}$ and 5P$_{3/2}$ All the transitions are not possible as only the ones that verify the selection rules (provided!!!!) may exist	

6.	At this stage the accessible data are those which $1/\lambda$ is provided. Moreover, it is possible to express the energy as a function of the reciprocal of the wavelength $E(eV) = 12400.\frac{1}{\lambda(cm^{-1})}.10^{-8}$:	

Level	$1/\lambda$ (cm^{-1})	E(eV)
$4D_{3/2}$	14338	-1.778
$4D_{5/2}$	14326	-1.776
$6S_{1/2}$	13553	-1.681

7.	Here it is asked to give the lines that would appear on the absorption spectrum for Rb. Absorption is associated to a transition from the energy level where the outermost electron is located (for Rb it is in the $5S_{1/2}$ level) to a furthest subshell such that the selection rules will apply (such that $\Delta l = \pm 1$ AND $\Delta j = (0 \ or \pm 1)$.	It is always important to read carefully what is asked. Here the question was NOT about all the possible lines that will be observed considering only the levels listed in the table, but rather "all the possible lines that will be observed in the **absorption spectrum** considering only the levels listed in the table.
	Thus, the only possible transitions in the absorption spectrum are the following: $5S_{1/2}$-$5P_{1/2}$: $5S_{1/2}$-$5P_{3/2}$: $5S_{1/2}$-$6P_{1/2}$: $5S_{1/2}$-$6P_{3/2}$:	And this was in bold in the text…

8.		Because the levels were ordered in increasing energies in the table, it was possible to order them in the corresponding energy level diagram. To be complete, the energy scale should be provided with the origin level (infinite). At this stage it was possible to provide the values in black in the table. Transitions on the absorption spectrum all started from level $5S_{1/2}$ according to question 7.
9.	According to the selection rules, only 4 lines can be found in the absorption spectrum involving the levels gathered in the table. As we know how the energy levels order between them (as compared to $5S_{1/2}$, $6P_{3/2}$ is the furthest then comes $6P_{1/2}$ then $5P_{3/2}$ then $5P_{1/2}$) we can order the transitions between each other in terms of energy: $E(5S_{1/2}, 6P_{3/2}) > E(5S_{1/2}, 6P_{1/2}) > E(5S_{1/2}, 5P_{3/2}) > E(5S_{1/2}, 5P_{1/2})$. This means that the wavelengths associated to the transitions can be ordered according to : $[\lambda_{5S_{1/2}\rightarrow 6P_{3/2}}] < [\lambda_{5S_{1/2}\rightarrow 6P_{1/2}}] < [\lambda_{5S_{1/2}\rightarrow 5P_{3/2}}] < [\lambda_{5S_{1/2}\rightarrow 5P_{1/2}}]$	It is true that in the table, as a data, 3 levels were described with their values of $1/\lambda$. This means that applying $E(eV) = 12400/\lambda$ will provide directly the absolute value of the associated energy level. But to answer question 9, what was provided were the wavelength of an absorption line, which corresponds to a transition from one energy level to another one. As a consequence, when applying $E(eV) = 12400/\lambda$, you do not get

The values for the transitions are provided in the text we can thus ascribe them to the associated transitions:

$[\lambda_{5S_{1/2} \to 6P_{3/2}} = 420 \text{ nm }] < [\lambda_{5S_{1/2} \to 6P_{1/2}} = 421 \text{ nm}] < [\lambda_{5S_{1/2} \to 5P_{3/2}} = 780 \text{ nm}] < [\lambda_{5S_{1/2} \to 5P_{1/2}} = 794 \text{ nm}]$

Finally, the energy of a transition is nothing but the exact difference between the two energy levels involved. As an example:

$$\Delta E_{5S_{1/2} \to 6P_{3/2}} = E_{6P_{3/2}} - E_{S_{\frac{1}{2}}} = \frac{12400}{\lambda_{5S_{\frac{1}{2}} \to 6P_{\frac{3}{2}}}} = \frac{12400}{4200} = 2.952 eV$$

Thus : $E_{6P_{3/2}} = \frac{12400}{\lambda_{5S_{1/2} \to 6P_{3/2}}} + E_{S_{\frac{1}{2}}} = \frac{12400}{4200} - 4.177 = -1.225 eV$

Same reasoning is applied to the other levels:

$E_{6P_{\frac{1}{2}}} = \frac{12400}{\lambda_{5S_{\frac{1}{2}} \to 6P_{\frac{1}{2}}}} + E_{S_{\frac{1}{2}}} = \frac{12400}{4210} - 4.177 = -1.231 eV$

$E_{5P_{\frac{3}{2}}} = \frac{12400}{\lambda_{5S_{\frac{1}{2}} \to 5P_{\frac{3}{2}}}} + E_{S_{\frac{1}{2}}} = \frac{12400}{7800} - 4.177 = -2.587 eV$
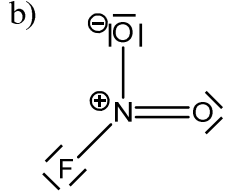
$E_{5P_{\frac{1}{2}}} = \frac{12400}{\lambda_{5S_{\frac{1}{2}} \to 5P_{\frac{1}{2}}}} + E_{S_{\frac{1}{2}}} = \frac{12400}{7940} - 4.177 = -2.615 eV$

Then the energy level values could be added to the Grotrian's diagram (question 8) values were added in blue color.

To fill the table, once we have the energy of each level, we can then compute $1/\lambda$ for each level

the value of the energy level but the difference between the two energy levels!!!

Around 10% of you have remembered this and thus answered properly this question (while this was the topic of the tutorials made on: spectroscopy of hydrogen, spectroscopy of hydrogen-like systems, and obviously spectroscopy of alkaline metals that has been the topics of 4 or 5 sessions)

Level	$1/\lambda$ (cm^{-1})	E(eV)
5P$_{1/2}$	21109	-2.615
5P$_{3/2}$	20863	-2.587
6P$_{1/2}$	9927	-1.231
6P$_{3/2}$	9879	-1.225

10.	After absorption occurs, transitions involving the same levels will be observed in the <u>emission spectrum</u>, meaning that the transitions are opposite. Because two of them are in the red (794 and780 nm) and two of them are blue (420 and 421 nm), blending them make purple!	Here it is important to realize that what is seen by the audience are the photons **emitted** by rubidium.

Exercise III : 16 points

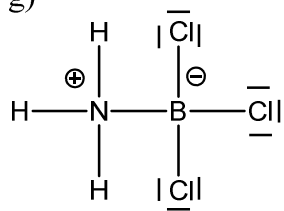|		
1.	Electronic configurations: B $1s^22s^22p^1$ C $1s^22s^22p^2$ N $1s^22s^22p^3$ O $1s^22s^22p^4$ F $1s^22s^22p^5$	Globally well-answered
2.	Electronegativity increases in aperiod from left to right B<C<N<O<F	
	a) Right: 2 electrons about each H (duet rule), 8 about each C and the Cl (octet rule), no charge b) Wrong as there are 10 electrons about the N which belongs to the 2nd period and which can not sustain more than 8 electrons (strict octet rule) b) c) Right : duet rule for H, octet rule for C, O, negative charge on oxygen d) Wrong : while duet (H) and octet rule (C, N) apply for the atoms, one of the nitrogen has only 4 valence electrons and should thus own a positive charge	a) Well, one of the atom was a chlorine Cl (and not a carbon…)

d)
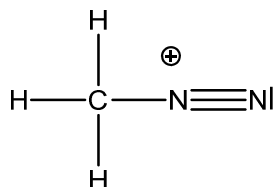
e) Correct : aluminium is on the same group as Boron and owns the same Lewis structure (3 valence electrons and own empty box), 6 electrons after bonding, octet for F, no charge.

f) Correct : duet rule for H, octet rule for C, S, O, charges correctly ascribed to S and O (O more electronegative than S) but still not **the most representative**. Indeed, S belongs to the same column as O but is in the 3rd period, can thus sustain more than 8 electrons. Extension of the octet rule, that leads to a S=O double bond, will lower the number of formal charges that is to be preferred.
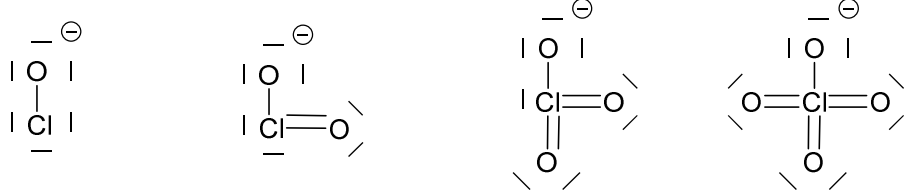
f)
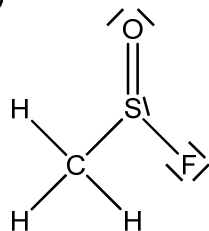
g) Wrong : absence of charges on N (4 electrons to make single bonds while N owns 5 valence electrons: should own a positive charge) and B (4 electrons to make single bonds while B owns 3 valence electrons: should own a negative charge).
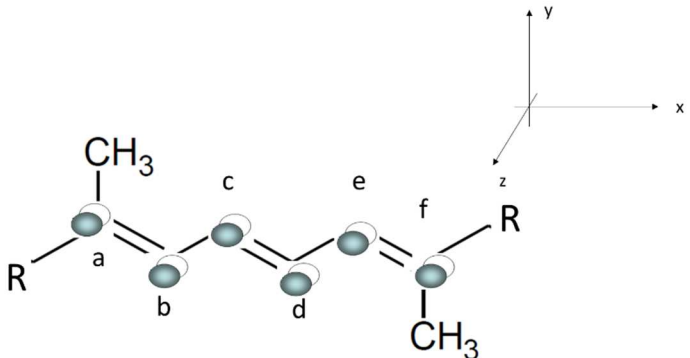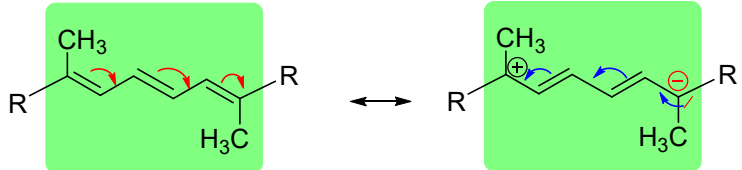
g)

3.	As Cl belongs to the same column as F, it owns 7 valence electrons ; as it is in a period which (n >2), it can sustain more than 8 electrons (extension of the octet rule).	
	Because O is more electronegative than Cl, O should own the negative charge. As the global ion owns one negative charge only, it is on the oxygen atom that thus make a single bond with Cl. The following ions can thus be considered :	
	No superior ions that would own one negative charge only.	
	b) For the 2nd ion : AX_2E_2 : bent ; $\alpha < 109°$	When you have a diatomic assembly, stop talking about the shape!!!!
	For the 3rd ion, AX_3E_1 : trigonal pyramidal $\alpha < 109$	
	For the 4th ion, AX_4 : tetrahedral $\alpha = 109$	
	c) Mesomeric forms exist	
	for the 2nd ion: 2	
	for the 3rd: 3	
	for the 4th, 4	
4.	In a given ion, the bond length are all equal due to mesomeric formulas	
	Between ions, the bond length are not equal:	
	The longest one is the single bond, found in ion 1.	
	Because of mesomeric formulas, the bond lengths in the other ions are a mix between a single bond and double bond but they are again different:	
	- In the 2nd ion, the real bond length is the exact average between 1 single bond and 1 double bond	

	- In the 3rd ion, the real bond length is the exact average between 1 single bond and 2 doubles bonds; because a double bond is shorther than a single bond, the averaged value for ClO_3^- has to be lower than for ClO_2^- Thus, the shortest one is for the 4th ion, which is the closest one to a full double bond (average between 1 single bond and 3 double bonds).	
5.		

exercise IV : 15 points

1.	Hybridization state for Carbons from (a) to (f): sp^2 Hybridization state for Carbon in the CH$_3$ group: sp^3	
2.	 Hybridization state sp^2 : result of mixong and recombination of 2s, 2p$_x$ and 2p$_y$ (for example) to form 3 hybridized orbitals sp^2 in the (x,y) plane (as 2p$_x$ and 2p$_y$ were involved) There is one unhybridized 2p$_z$ orbital on each related carbon The unhybridized p$_z$ orbitals of the 6 Carbons (a to f) organizes such that they are parallel to have a lateral overlap; all these carbons and the H they are bonded to are thus co-planar. Regarding the C of the methyl groups; the frontal overlap between their sp^3 orbital and one sp^2 orbital of carbons (a) and (f) necessarily implies that these C of the methyl are also coplanar to all the other carbons.	

	However, for the methyl groups, C is hybridized sp^3, thus this carbon is at the center of tetrahedron-shaped geometry. Thus the Hydrogens can not all be in the same plane as the other atoms. There is still free rotation between C(a) and C(methyl), which makes it possible to have at best 1 hydrogen in the same plane. As a conclusion : all the atoms highlighted in green on the Figure are coplanar except at least 2 of the 3 H of the methyl groups	
3.	The free rotation around the C$_b$ - C$_c$ bond is impossible because this rotation would lead to the breaking of the lateral overlap represented previously (π bond). The free rotation around the bond C$_f$ - CH$_3$ is possible because it does not break the axial overlap of hybrid orbitals involved in this bond.	Orbital representation not required in this second case
4.	Let write the mesomeric formulas involving the delocalization of three π-bonds This was enough to justify that the molecule owns 3 conjugated double bonds	Instead of the scheme, it was also possible to describe with words the delocalization of the 6 π electrons
5.	These 5 bonds are in fact identical contrary to what the formula represented in the text suggested (alternating single and double bonds). The resulting bond length is greater than that of a double bond but lower than that of a single bond.	
6.	Some double bonds are not conjugated in each of the molecule!! We count the number of double bonds involved in an exact alternation of double/single bonds. Phytoene : 3 / Phytofluene 5 / Carotene : 7 / Lycopene : 11	No representation of any mesomeric formula was expected as the justification
7.	Energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).	
8.	Litteral formula : $\lambda_{abs} = \dfrac{hc}{\Delta E_{HOMO-LUMO}}$ Phytoene : 287 nm / Phytofluene : 348 nm / Carotene : 395 nm / Lycopene : 502 nm	

	It can be seen that as the energy difference HOMO-LUMO decreases, the absorption wavelength increases and shifts into the visible range (for carotene and lycopene). It can also be related to the number of conjugated double bonds…	
9.	Calculation of the lycopene concentration in the commercial sample : $$C_{Lycopène} = \frac{w_{Lycopene} \times m_{total}}{M_{Lycopene} \times V_{total}} = \frac{0.05 * 0.600}{536.9x1} = 5,59 \times 10^{-5} mol.L^{-1}$$ Let F be the dilution factor to be applied such that $A^{502nm}_{Lycopene} = \varepsilon^{502nm}_{Lycopene} = 0.633$ The diluted solution (which concentration is noted $C'_{Lycopene}$) should then verify both equations: - $C'_{Lycopene} = \frac{C_{Lycopene}}{F}$ - $A^{502nm}_{Lycopene} = \varepsilon^{502nm}_{Lycopene} \times l \times C'_{Lycopene}$ Thus $F = \frac{\varepsilon^{502\,nm}_{Lycopène} \times l \times C_{Lycopene}}{A^{502nm}_{Lycopene}} = 15$	