	Problem I : Hydrogen like ions	
Question	**Answer**	**Comments**
1)	« Excitation » involves a transition from n = 1 to a upper level. If we get 10 rays in the subsequent emission spectrum, the upper level is n = 5 (see diagram) as transitions in "cascade" are possible.	- No calculation was needed here, the use of the diagram was enough. - In the Bohr Model, only the main quantum number "n" is relevant: the levels should then be defined by n or En. - A title and captions are compulsory when presenting a diagram (each level should be defined by either n or En).
2)	The identification of the **hydrogen-like** system consists in defining the value of Z, remembering that it contains only 1 electron. Thanks to Ritz-Balmer equation, considering that $R_X = R_H$, and considering the answer of question 1 (transition : 1 →5) we can determine the value of Z: $\frac{1}{\lambda_{1\to5}} = Z^2 . R_X . \left(\frac{1}{1^2} - \frac{1}{5^2}\right)$ with $\lambda_{1\to5}$ = 105.53 Å Value : Z = 3 thus $_3Li^{2+}$	- Error on the equation (see dimension!!) - Error on the manipulation of the equation - Careful: the value of R_X provided is expressed in cm^{-1} while λ is in Å - Some students actually found the value of Z, but the hydrogen-like ion contains only 1 electron!!!

3) | Global demonstration :

$$E_{n \to n'} = = \frac{hc}{\lambda_{n \to n'}} = hcZ^2 . R_X . \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

Ionization : $E_{1 \to \infty} = hcZ^2 R_X = |E_1 - E_\infty|$

Conventions : $E_\infty = 0$ and Energy values being negative

$$E_{1 \to \infty} = -E_1 = hcZ^2 R_X$$

Back to equations :

$$E_{n \to \infty} = -E_n = \left(\frac{hcZ^2 . R_X}{n^2} \right) = \left(-\frac{E_1}{n^2} \right)$$

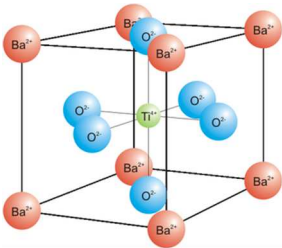To express in eV, it is needed to divide by "e", then the values can be computed

E_1 = - 122.4 eV, E_2 = - 30.6 eV, E_3 = - 13.6 eV,
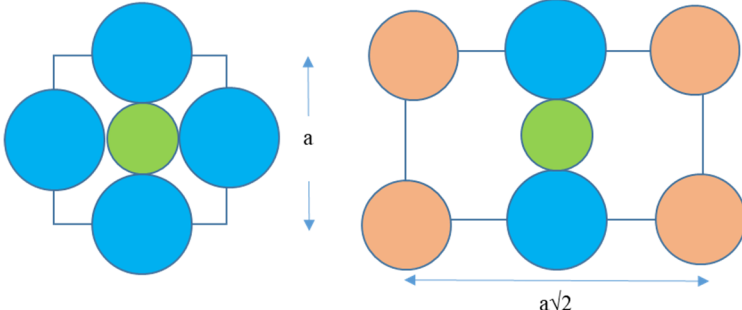
E_4 = - 7.7 eV, E_5 = - 4.9 eV

- « Establish the expression » implies to start from the global equations and to recall the conventions

- Because the values are all negative, $E_{1 \to \infty} = -E_1$ and

$$E_{1 \to \infty} \neq E_1$$

- Too many "arrangements" with equations were observed in this question (a value that was positive that miraculously turns positive etc…) Nothing magical was expected here, only a rigorous demonstration….

	Problem II : Lewis model and VSEPR theory	
Question	**Answer**	**Comments**
1)	Electronic configuration ns^2np^4 (with n=2 for O and n=3 for S). 6 valence electrons for both elements. Thus same column, but different period As n=3 for sulphur, extension of octet rule may apply :	- Globally well answered - However, some of you didn't write the configuration and thus started next questions with a wrong number of valence electrons for S : obviously everything is thus wrong….
2)	 en V, < 120° triangulaire 120° Pyramide base triangulaire < 109,5° -2/3 Tétraédrique 109,5°	- When starting with the correct number of valence electrons, globally well answered. - Some of you wrote structures with respecting strictly the octet rule for S thus with extra charges; however, as the extension of the octet rule is possible, the extension of the octet rule is preferred to limit the number of formal charges: the structures with extra charges are not to be considered anymore (thus wrong answers) - In some answers were sometimes given inconsistent information (examples : a structure can not be linear AND bent at the same time!!! A structure can not be planar AND tetrahedral at the same time!!! A structure that is planar triangular can not have an angle of 109°!!! A structure with 4 bondings groups cannot be trigonal!!! Etc…

	Problem III : Undulatory model of bonding, intermolecular interactions	
Question	**Answer**	**Comments**
1)	C1,C8, C9 : 3 groups thus sp^2 C7, C10: 4 groups thus sp^3	Generally well answered

2)	With Z = 7, the electronic configuration is $1s^2\ 2s^2\ 2p^3$
	
	N owns thus 5 valence electrons (a pair of electrons + 3 single electrons), and should strictly verified at best the octet rule (n = 2).
	
	In the structure, we see that N is involved in a double bond with C8 and in a single bond with N2 . The lone pair is not presented but obviously exists!!
	
	Thus: N1 3 groups (2 bondings + 1 lone pair) : sp^2 ,
	
	Between C8 and N1 : double bond thus **1σ and 1 π** bonds, Each atom being hybridized sp^2
	  - σ bond involves **sp^2-sp^2**
	  - π bond involves **p_z-p_z**
		Many of you did not consider the lone pair of electrons on N, counting only the 2 bonding groups…
		
		In some answers were sometimes given inconsistent information (examples: sp^3 AND a double bond???)
		sp^1 AND (1 double bond + 1 single bond)
		
		Regarding the π bond, it involves unhybridized p orbitals that are necessarily parallel with each other, thus along the same axis (for example, can't be $p_x - p_y$,).

3)	Hydrogen interaction with the H of the **OH group**	

	Problem IV : Crystallography	
Que stion	**Answers**	**Comments**
1)	The crystal is neutral, we thus need as many positive charges as negative ones: because there is a total of 6 positive charges, we need **x = 3**	
2)	Ionic bonds are involved	In the description of the structure, it is said that ions are involved!
3)		Globally well represented
4)	Thanks to the description of the cell, there are : Ba^{2+} : $8*1/8 = 1$ Ti^{4+} : 1 O^{2-} : $6*1/2 = 3$ Considering that the ceramic is $BaTiO_3$, there is thus 1 $BaTiO_3$/cell	
5)	**Tangency :** $a\sqrt{2} = (2r_{Ba2+} + 2r_{O2-})$ thus $a = (2 \times 135 + 2 \times 140)/ \sqrt{2}$ = **389 pm** $a = (2r_{O2-} + 2r_{Ti4+})$ thus $a = 2 \times 140 + 2 \times 68$ = **416 pm**	Here "tangency" means that the we must have equality: the sign is indeed **strictly equal** (=) and can't be superior or equal (≥)
	Non Tangency : $a\sqrt{3} > 2r_{Ba2+} + 2r_{Ti4+}$ thus $a > (2 \times 135 + 2 \times 68)/ \sqrt{3}$ → **a > 234 pm** $(a\sqrt{2})/2 > 2r_{O2-}$ thus $a > (4 \times 140)/ \sqrt{2}$ → **a > 395 pm**	Here "non tangency" means that the we can't have equality: the sign is indeed **strictly superior** (>) and can't be superior or equal (≥) Regarding the O^{2-} tangency: some of you took the edge (as the anions are at the centre of two opposite faces):

		but there is the Ti^{4+} at the centre of the cube which makes it impossible for the O^{2-} to be tangent along this direction! With the help of the scheme (question 2): you should consider the distance between the centres of two faces sharing one edge, which can be determined using either Pythagorean or Thales theorems…
6)	The only parameter value that suits all the 4 previous conditions (tangency and non-tangency) is the biggest one: **a = 416 pm**. This means that O^{2-} and Ti^{4+} are tangent while **Ba^{2+} and O^{2-}** are not	
7)	<u>Regarding **Ba^{2+}**</u>: as this type of cations occupy a corner of a cube, (shared by 8 cubes) one Ba^{2+} is thus equidistant with 3 O^{2-} anions per cube (the ones located at the centre of the faces making the corner); as each face is shared by two cubes, the anions counts for a total of (3/2) anions per cube (indeed we need to divide by 2 other we would count each O^{2-} twice!!). Because a corner is shared by 8 cubes, there is a total of (3/2) x 8 = 12 O^{2-} anions equidistant to one Ba^{2+}. The coordination number of **Ba^{2+}** is thus 12. <u>Regarding **Ti^{4+}**</u>: as this type of cation occupies the centre of the cube, it is thus equidistant to the 6 anions located at the centre of the faces making the cube. No other oxygens were equidistant. The coordination number of **Ti^{4+}** is thus 6.	While the coordination number for Ti^{4+} was globally well answered, the one for Bi^{2+} was more difficult.
8)	The atomic packing factor or compacity, is the **fraction** of volume in a crystal that is occupied by constituent particles. It is	Knowing the definition, this question uses the result of Q.2 (population) and Q.6 (the cell parameter).

	calculated by comparing the volume of the atoms/ions occupying the cell and considered as **hard spheres** to the volume of the cell. $C = 4/3\pi((rBa^{2+})^3 + (rTi^{4+})^3 + 3(rO^{2-})^3)/a'^3$ $= 4/3\pi(135^3 + 68^3 + 3 \times 140^3)/ \cancel{401^3} \underline{416^3} = \mathbf{0{,}\cancel{71564}}$	Here you should remember that you may have 5 ions per cell which are different from each other! You should thus consider separately the volume occupied by the Ti^{4+} (1 per cell) Bi^{2+} (1 per cell) and O^{2-} (3 per cell) ions, respectively.
9)	$\rho = (Z_{(BaTiO3)} \times M_{BaTiO3})/(N_A x a'^3)$ with $a' = 416$ pm and Z = 1 formula per cell $\rho = [1 \times (137{,}33 + 47{,}867 + 15{,}999 * 3)]/[6{,}022.10^{23}.(416.10^{-10})^3]$ $= 5.38$ g/cm^3	Here, the result was required in g/cm^3 (see text…)
10)		Globally well represented here

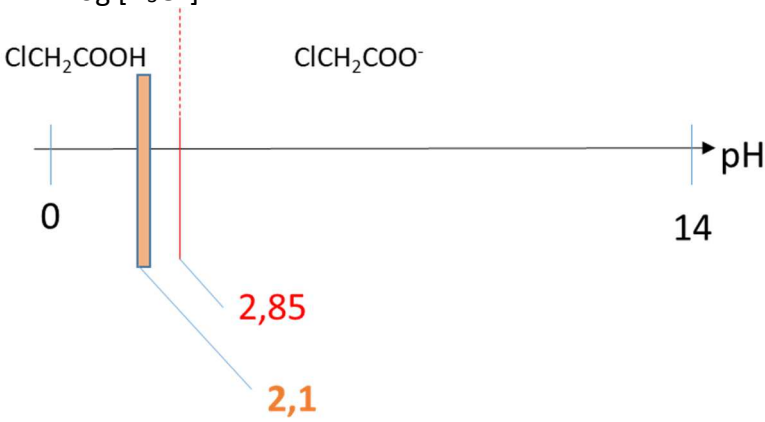| | | Problem V : Chemical transformations | |
|---|---|---|
| **Question** | **Answer** | **Comments** |
| | To see whether there is a change or not, we must compare the value of Q to K with $$Q_0 = \frac{[CH_3COO^-].[HCOOH]}{[CH_3COOH].[HCOO^-]}$$ - If $Q_0 < K_{298}$: a change occurs from left to the right if all the reagents on the left are present
 - If $Q_0 = K_{298}$: no change
 - If $Q_0 > K_{298}$: a change occurs from the right to the left if all the reagents on the right are present | Generally well-answered

 Remember though that $$K^0_{298} = \frac{[CH_3COO^-]eq.[HCOOH]eq}{[CH_3COOH]eq.[HCOO^-]eq}$$ The value provided (0.1) was thus for this literal expression |
| **1)a)** | $Q_0 \rightarrow +\infty$ and $Q_0 > K_{298}$: there is a change, from the right to the left -hand side | - Q_0 doesn't need to have a finite value.

 When Q_0 tends to infinity, it is obviously bigger than K_{298} : thus the system tends to evolve to the left, as long as the reagents on the right are present!!!

 - Some of you had reasoned with writing the reaction in the other way around (see below reaction 2)! Good idea!!

 $CH_3COO^- + HCOOH \leftrightarrow CH_3COOH + HCOOH$ (reaction 2)

 However, remember then that not only the literal expression of Q is inverted in that case (for reaction written in way 2, it becomes $$Q_0 = \frac{[CH_3COOH].[HCOO^-]}{[CH_3COO^-].[HCOOH]}$$ |

		but the one of the equilibrium constant is also inverted!!! Thus, the equilibrium constant of reaction 2 should be (1/ $K_{298}°$) the value of which is thus 10!!
1)b)	$Q_0=1$ and $Q_0>K_{298}$: there is a change, from the right to the left -hand side	
1)c)	$Q_0=0.1 = K_{298}$: no change ; system does not evolve (at « equilibrium)	
1)d)	$Q_0=0$ and $Q_0<K_{298}$: there is a change, from the left to the right-hand side	Some of you said that as $Q_0 = 0$, nothing would happen. Again the condition is on the comparison between Q_0 and K_T : ($Q_0 = 0$ is not a particular situation!!)

	Problem VI – Redox reactions	
	Answer	**Comments**
1)	$FeSO_4 \rightarrow Fe^{2+} + SO_4^{2-}$	Some weird answers were given here… weird in particular considering that in Problem II, the formulae of the sulfate ion was provided in the text!
	As a result, in the condition of the exercise, when the reaction is carried out, we have in presence at the same time the following species: - K^+ and MnO_4^- resulting from the dissolution of $KMnO_4$ - Fe^{2+} and SO_4^{2-} resulting from the dissolution of $FeSO_4$ Then, to identify which reaction takes place, you should be logical and congruent with your own answer (Q1). At this stage, Fe^{2+} is the only species involving iron : there is no neutral iron (Fe)!! But many of you wrote after a reaction involving Fe as a reactant with MnO_4^- ????	
2)	$MnO_4^- + 8H_3O^+ + 5e^- \rightarrow Mn^{2+} + 12H_2O$ Oxidation number of [Mn] in MnO_4^- : +VII Oxidation number of [Mn] in Mn^{2+}: +II As the oxidation number of Mn is reduced, the half-reaction is **Reduction** $Fe^{2+} \rightarrow Fe^{3+} + e^-$ **Oxidation** Oxidation number of [Fe] in Fe^{2+} : +II Oxidation number of [Fe] in Fe^{3+} : +III As the oxidation number of [Fe] increases, the half-reaction is Oxidation	There was nothing to invent here, just be logical and use the data provided. The only redox couple involving MnO_4^- is MnO_4^-/Mn^{2+}, where MnO_4^- is the oxidized form. Because MnO_4^- is the reactant (see text!), it disappears into Mn^{2+} along the reduction process. As a redox reaction is matched set, there is an oxidation half-reaction that involves the other reactant that is necessarily Fe^{2+} (see Q1, plus no redox couple involving SO_4^{2-}). As a consequence, Fe^{2+} should be the reduced form of the other redox couple. Among the 3 couples provided involving "iron species", there is one and only one that uses Fe^{2+} as the reduced form : the Fe^{3+}/Fe^{2+} couple.

3)	$MnO_4^- + 5Fe^{2+} + 8H_3O^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 12H_2O$	No penalty if the reaction was equilibrated without using $8H_3O^+$ but rather $H^+_{(aq)}$
	MnO_4^- is the oxidized form of the redox couple with the highest standard potential : it is the oxidant or oxidizing species of the reaction.	
	In the meantime, Fe^{2+} is the reductant or reducing species of the reaction	
	According to the half-reaction of reduction, 5 moles of electrons are exchanged per mole of MnO_4^- : 5	
4)	According to the global redox reaction, the relationship between the number of moles of Fe^{2+} and the one of MnO_4^- upon reaction is : $(nFe^{2+})/5 = (nMnO_4^- /1)$ As the reaction is total, by determining the amount of $nMnO_4^-$ needed to completely react with Fe^{2+}, we can get the amount of $FeSO_4$. **$nMnO_4^-$** =[MnO_4^-] x $V(MnO_4^-)$ = 0.025x25 = =**0.625mmol** Thus **nFe^{2+}**=5 x $nMnO_4^-$ = 3.125 mmol According to Q1, because $FeSO_4$ is a strong electrolyte : **nFe^{2+} = n $FeSO_4$** = 3.125 mmol $mFeSO_4$= n $FeSO_4$ x $M(FeSO_4)$= 3,125x**151,9** = **474,7 mg =475 mg** In 1.00 g of S1, there is actually 475 mg of $FeSO_4$.	Many confusions were observed here: - Confusions in the concentration and volume of permanganate to determine the corresponding number of moles - The most often encountered error was about the molar mass: Again, the question was about the weight of $FeSO_4$ and thus require the use of your result in Q1 and the molar mass of $FeSO_4$. Too many of you used the molar mass of Fe here (with some explanations on how we could neglect the weight loss associated to the loss of two electrons!!!)

	Problem VII – acid-base reactions	
	Answer	**Comments**
1)	$ClCH_2COOH + H_2O \leftrightarrow ClCH_2COO^- + H_3O^+$ $K^{\circ}_T = \dfrac{[ClCH2COO-]eq[H3O+]eq}{[ClCH2COOH]eq} = Ka = 10^{-2.85}$	Here it is about whether you know or not the definition of: - The dissociation reaction of an acid in water or not - The expression of the equilibrium constant of the corresponding reaction. Note that here water is not only a reactant but it is also the solvent: as a consequence, its activity is 1 and thus it doesn't appear in the expression of the equilibrium constant (and please, do not write that the concentration of water is 1 mol/L which is totally wrong!!! Indeed, in a diluted solution where the main component is water, in 1 liter of solution we have around 1000 g of water, which leads to a concentration of 55.6 mol/L!!)
2)	$ClCH_2COOH + H_2O \leftrightarrow ClCH_2COO^- + H_3O^+$ V=1L <table><tr><td>t₀</td><td>0.0500</td><td>-</td><td>/</td><td>/</td></tr><tr><td>t_eq</td><td>0.0500-x</td><td>-</td><td>x</td><td>x</td></tr></table> As V = 1L $K^{\circ}_T = \dfrac{x^2}{0{,}0500-x} = 10^{-2.85}$ thus $x^2 + K^{\circ}_T x - 0.0500 K^{\circ}_T = 0$	The ICE table can be considered in either number of moles or concentration as the volume is constant and set at 1 L.

	The only possible solution among the two is x = 0.007727 M | t_eq	0.0423	-	0.00773	0.00773 | $[ClCH_2COOH]_{eq}$=42.3mM $[ClCH_2COO^-]_{eq}=[H_3O^+]$=7.73mM (3 cs) $[HO^-] = \dfrac{Ke}{[H_3O^+]} = \dfrac{10^{-14}}{0.00773} = 1.29.10^{-12}$ M	Because we can neglect the impact of self-dissociation of water on providing some H_3O^+, the ICE table is quite simplified here Unfortunately, many numerical errors were found here in particular because of a misuse of your calculator (which means that most of you are not familiar with the manipulation of the calculator)
3)	pH = - log $[H_3O^+]$ = 2.1 	Look at the answer and realize that the predominance diagram must include the following information: - What is presented along the abscissae scale (in other word, "pH") - The extrema values (0, 14) - The pKa for the couple - The species that predominates in its corresponding domain - Obviously the pH value
4)	τ = x/n₀ τ = 0,00773/0,0500 = 0.0155 = 15.5%	Here again the question is whether you know what the "conversion" of a reactant means: it is nothing but "how much has actually being converted" (in other word, how much as disappeared) compared to the maximum amount that can be converted considering the operation conditions (the limiting reactant when applicable etc…)
5)	$ClCH_2COOH + H_2O \leftrightarrow ClCH_2COO^- + H_3O^+$ (V=1L)	

t0	C_0	-	/	/
teq	$C_0/2$	-	$C_0/2$	$C_0/2$

If the conversion is 50%, then we know the composition of the system at equilibrium (see ICE table). Accordingly, using the expression of the equilibrium constant:

$$K°_T = \frac{\left(\frac{C_0}{2}\right)*\left(\frac{C_0}{2}\right)}{\frac{C_0}{2}} = \frac{C_0}{2} = 10^{-2.85}$$

Meaning that $C_0 = 0.00283M$

Th pH of the solution would then be:
pH = -log[H_3O^+] = -log($C_0/2$) = pKa=2.85