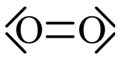
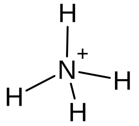
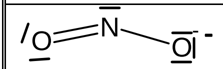
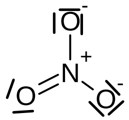
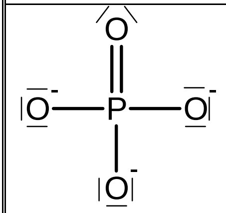
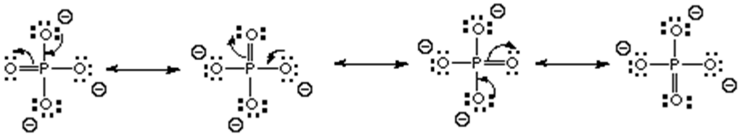
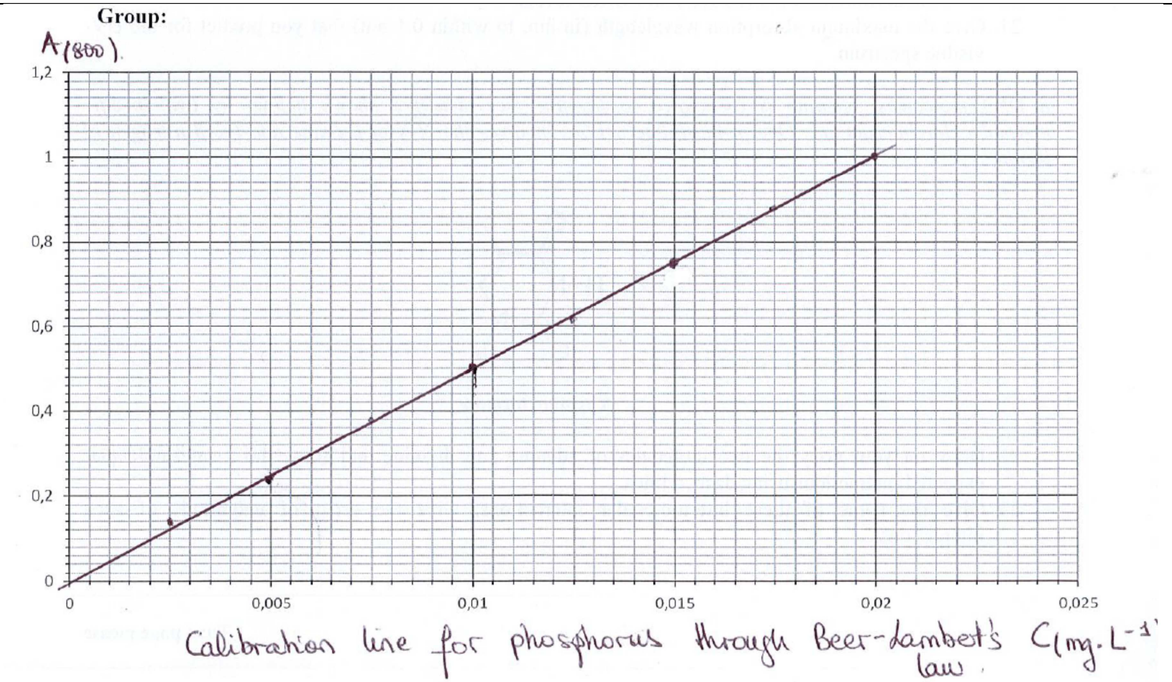
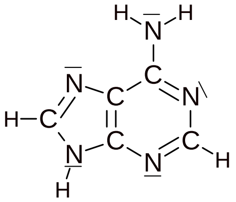
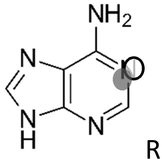
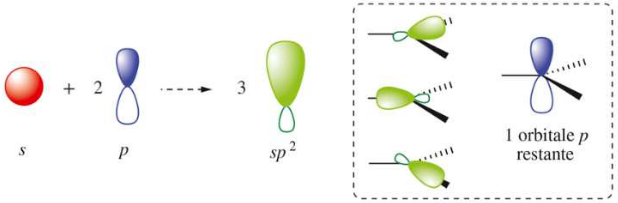
TEST 2 SCAN AMERINSA – CHEMISTRY 2019-2020

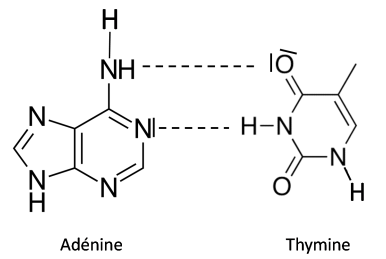
Part A	**Phosphorus**	
Questions	**Answers**	**Comments**
1.	$_{15}P$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ with 5 valence electrons on the 3(s,p) level	For the elements of the p block, the valence electrons are the ones of the outermost shell.
2.	P belongs to the 15th group that starts on the second period. The 5th element of this group appears thus on n=6 and owns 3 electrons on the p subshell. X : n(s,p) ;(n-1)d ;(n-2)f thus $[_{54}Xe]4f^{14}5d^{10}6s^{2}6p^{3}$ (Xe not required) Then, using the building-up principle **Z = 54+14+10+2+3 = 83** (Bismuth : not required)	Because of the building up principle, no elements with electrons on p subshell appear on the 1st line. Thus the groups in the p block starts only at n = 2. Thus the 5th element of the group is not on n = 5 but on n = 6. Moreover, at one point we have the filling of the 4f subshell that requires 14 electrons: thus adding 18 electrons from
3.	$\chi_{15}P$ > $\chi_{83}Bi$ (or X) as the electronegativity decreases along a given column (from top to bottom). For the atomic radius, it increases along a column (from top to bottom).	It is necessary to take into account that the elements are in the same group
4.	For P, the first ionization energy corresponds to the extraction towards ∞ of one valence electron out of the 3p subshell (that is filled after the 3s thus less stable)	It is wrong to say that ionization corresponds to the extraction of the electron (singular) : P owns many electrons !! It is not precise enough to say that it corresponds to the extraction of one of the valence electrons: the latter are split into 3s and 3p subshells that are not of same energy!!
5.	P and S belong to the same period ; as the ionization energy increases along a period, the ionization energy for S should be higher than the one for P. However, the contrary is observed: this is because the p subshell is half-filled for P which makes it very much more stable stable and thus requires a supplementary energy to be destabilized.	

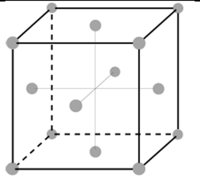
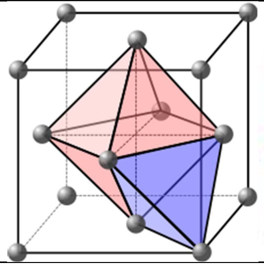
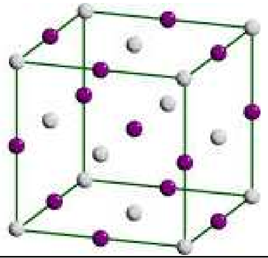
Part B	**Titration of phosphorus in water**		
6. et 7.			**Do not forget the charges on the ions !** **Remember that N and O both belong to the 2nd period: thus they can not sustain more than 8 electrons after bonding** **Thus, any formula where N has two double bonds and a lone pair of electron is not possible.** **P belongs to the 3rd period, so it can exceed the octet of electrons by having a double bond with one of the O (instead of having a lack of electron on P (thus being P+) and 4 oxygens atoms with each an excess of electron (thus being O-));** **Indeed, the rule states that the formula which exceeds the octet rule but lowers the number of charges is to be preferred.**
		AX_4 Tétrahedral shape	
		AX_2E_1 : bent or distorted trangular planar	
		AX_3 Planar triangular	
		AX_4 Tetrathedral	
8.	VSEPR states that the pairs of electrons repulse each other as much as possible, and that a lone pair of electrons occupies more space than a bonding pair of electrons, which means when a lone pair of electrons exists, the angles are lower than for a molecule with only bonding pairs: Thus in NH_4^+ :angles = 109.5 In NO_2^- : angle < 120° In NO_3^- : angles = 120° Thus : $NH_4^+ < NO_2^- < NO_3^-$		

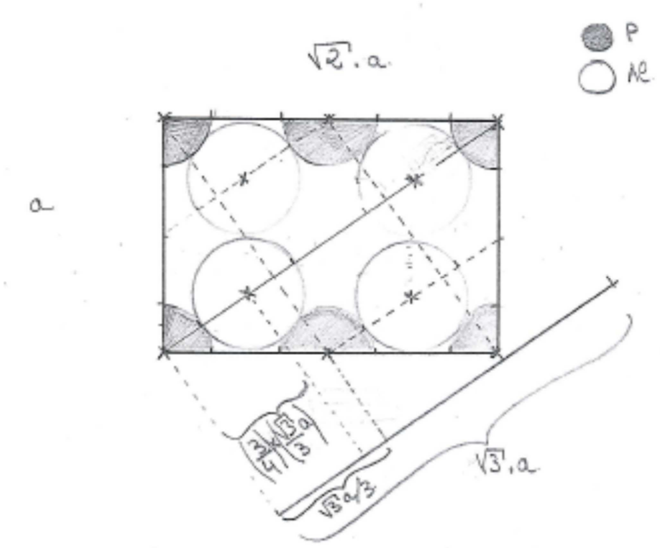
9.	The phosphate ion has 4 mesomeric forms, due to a resonance phenomenon : each bond are thus equal, the value of which being between the one of a double and the one of a single bond 	**One can also represent the resonance hybrid for such phosphate ion**
10.	Beer-Lambert's lawe : Abs = ε.l.c Abs : Absorbance of the solution at a given wavelength ε : Molar extinction coefficient at the given wavelength in L.mol^{-1}.cm^{-1} (or L.mol^{-1}.m^{-1}) l : length of the cuvette used for the experiment in cm (or in m) c : concentration in the solute that absorbs at the given wavelength in mol.L^{-1}	**It is worthnoting here that :** **if Abs = ε.l.c with c in mol/L** **As c (mol/L) = c (g/L) / molar mass (g/mol)** **Then Abs =(ε.l/Molar mass) x c (g/L)** **Thus one can manipulate the values of Absorbance as a function of C (expressed in g/L): if Beer's lambert applies, A is still linear as a function ofc (expressed in g/L) passing through 0.**
11.	The solution **being blue** , it means that it absorbs the complementary color that is red : we should work **at 800 nm**	
12.	In the table where provided the values of absrobance and the corresponding massic concentrations: one can thus directly plot A = f(c (in mg.L^{-1}) As we get a straight line which intercept with the origin is 0; Beer Lambert's law is verified	**Here the captions and a meaningful title were expected** **Careful with the reading of the values of concentrations in the table: For instance, when A = 0.88, the phosphorus mass concentration is c = 0.0175 mg.L^{-1})**

	 Calibration line for phosphorus through Beer-Lambert's law	
13.	For the absorbance of the diluted solution ABS = 0.56, we can find out the associated concentration c = 0.011 mg/L As the mother solution was diluted by a factor 500, its concentration is 500 times larger : c = 5.5 mg/L. As the limit is set at 1.1 mg/L, the solution doesn't comply with the European regulation's limits.	**We can find the concentration of the diluted solution by various means :** - **Use of the plot directly** - **Use a cross-product as the intercept with the origin is at 0** - **Find the slpoe of the equation using two points (values taken from the table)**
14.	Beer Lambert's law is valid only for Absorbances lower than 1.5. Above this limit, the absorbance is not linear with respect to the concentration anymore. Dilution was compulsory here in order to work in the range of concentrations where the linearity is ensured.	**A precise answer was expected here:** **Sentences like the followings are not satisfactory :** **« Beer Lambert's law does not work"** **"Concentrations need to be low"** **"If not, the measurements are not accurate"…**

Part C	**Phosphate ions in human body**	
15.		**Each N owns a lone pair of electrons; as C and N belong to the 2nd period, around them we should have 8 electrons : it helps to find the number of H.** **The global formula is $C_5H_5N_5$**
16.	All C atoms are hybridized sp^2 , as well as the nitrogen noted β	**The question on Carbons involved Carbons a to e (not only carbons a and e)…**
17.	 Représentation de l'OA p de l'azote Représentation des orbitales hybridées (dans le plan) : 	Because N is hybridized sp^2, it means that the 2s and 2 of the 2p orbitals of N (for example 2p$_x$ and 2p$_y$) hybridize and lead to 3 identical hybridized sp^2 orbitals that are found in a given plane (x0y, according to the 2p orbitals), all separated by an angle of 120°. The remaining 2p$_z$ orbital is perpendicular to the (x0y) plane. Thus, the fate of the orbitals is such that : - 1sp^2 orbital is doubly occupied by 2 valence electrons: it corresponds to the lone pair of electrons - 1s^2 orbital is occupied by one valence electron of N: it is used to frontally overlap with 1 valence electron from C to make a σ bond - 1s2 orbital is occupied by 1 valence of N: it is used to frontally overlap with 1 valence electron from C to make a σ bond - 2pz orbital is occupied by 1 valence electron of N: it is used to overlap with 1 valence electron from C in a sideway fashion to make a π bond
18.	C: 4 valence atomic orbitals (2s,2p) and 5 C atoms in the molecule H: 1 valence atomic orbital (1s) and 5 H in the molecules N : 4 valence atomic orbitals (2s, 2p) and 5 N atoms in the	One should remember that there is as many molecular orbitals (bonding, non-bonding or anti-bonding) as initial atomic orbitals: one should then refer to the number of atomic orbitals for each atom, and count the total number of atoms:

	molecule ➔ (4 x5 + 1 x 5 + 4 x 5= = 45 atomic orbitals that combine to obtain 45 molecular orbitals (MO).	
19.	C: 4 valence electrons ($2s^2$ $2p^2$) and 5 C atoms in the molecule H: 1 valence electron ($1s^1$) and 5 H in the molecule N : 5 valence electrons ($2s^2 2p^3$) and 5 N atoms in the molecule ➔ (4 x5 + 1 x 5 + 5 x 5= = 50 electrons).	The molecule is neutral : the total number of electrons is the sum of the valence electrons of each atoms.
20.	HOMO : Highest Occupied Molecular Orbital LUMO : Lowest Occupied Molecular Orbital	
21.	The smallest difference of energy to observe a transition is the one that exists between the HOMO and LUMO, which wavelength will thus be the highest one $\lambda(m) = \frac{hc}{\Delta E.e} = \frac{6.626.10^{-34} \times 2.998.10^{8}}{\lvert -0.11 + 8{,}77 \rvert \times 1.602.10^{-19}}$ $= 1.432.10^{-7} m \ thus \ 143.2 \ nm \ (to \ within \ 0.1 \ nm)$	
22.		**It is said in the text than one intermolecular interaction involves the Nitrogen β of adenine with the NH of thymine.** **In order to develop another specific interaction taking inco account the first one, we can thus consider the interaction between one H carried by Nitrogen α with one oxygen if Thymine (see example).**
23.	Both interactions involve a H that is bonded to a very electronegative element (N) and a very electronegative element bearing a lone pair of electrons: these are thus Hydrogen	

	interactions The associated energy is in the range of 5 to 40 $kJ.mol^{-1}$	
Part D	**Phosphorus in a pesticide**	
24.	 In a face-centered cubic system, the atoms are located at each vertex + at the center of each face: thereis thus a total of (1 + 6x ½)= 4 atoms.	It is said here that the atoms are not tangent: the condition seen in the lecture (for a compact structure) does not apply then!
25.	In this structure, there are tetrahedral (in blue) and octahedral holes (in pink), respectively T holes : one at each vertex, thus 8 O holes (purple in the second figure) : at the very center of the cube + 1 at the center of each edge shared by 4 neighboring cubes, thus a total of (12x1/4 + 1) = 4	 
26.	Using the tangency condition: For a T hole, the geometrical condition is: $\frac{a\sqrt{3}}{4} = R_P + R_{iT}$ Indeed, the T holes are located at 3/4 of the height of the regular tetrahedron in blue, itself corresponding to 1/3 of the (long) diagonal of the cube which equals √3a For a O hole, the geometrical condition is $a = 2R_P + 2R_{iO}$	**1/ Using the tangency condition means it is the strict equality that applies here!!** **2/ By the way, some of you wrote that** the *geometrical condition* that applied was ($a\sqrt{3} = 4R + 4R_{iT}$) (equation 1) which *numerically* leads to ($\frac{a\sqrt{3}}{4} = R + R_{iT}$), (equation 2). (equation 1) would mean that along the diagonal of the cube, 2 atoms of phosphorus and 2 atoms of aluminum would be tangent, which is wrong!! (see scheme below that represents the plane cutting the cube along the diagonal of a face)

		(Scheme respecting the proportions between R_P, R_{Al} and a)  **Thus, the real demonstration is that the geometrical constraint is $\left(R + R_{iT} = \frac{3}{4} \times \frac{a\sqrt{3}}{3} = \frac{a\sqrt{3}}{4}\right)$ (R_{iT} is a the center of gravity of the regular tetrahedron which vertices are occupied by P) (equation 2), which then gives $(a\sqrt{3} = 4R + 4R_{iT})$ (I*f* a hypothetical P atom was at the very center of the cube *which is not the case*, then 2 atoms of P and 2 atoms of Al would be tangent along the long diagonal of the cube *which is not the case*).**
27.	Because we have a ratio of 1 Al for 1 P, and because we have a total of 4 P in the cube (see question 24), we have thus 4 Al in the cube: If the Al occupy the O holes, because there is a total of 4 of them in the cube: 100% of the O holes would be occupied. If the Al occupy the T holes, because there is a total of 8 of them in the cube: 50% of the T holes would be occupied.	
28.	If Al were to occupy the T holes:	

	$: a = \left(\frac{4\times(rAl+rP)}{\sqrt{3}}\right) = \left(\frac{4\times(128+108)}{\sqrt{3}}\right) = 545pm$ If Al were to occupy the O holes : $: a = 2\times(rAl+rP) = 2\times(128+108) = 472pm$	
29.	One method consists in computing the density that would be observed in each case, and compare it to the real one If Al were to occupy the T holes: $\rho_T = \frac{nb_{AlP}\times MM_{AlP}}{N_A\times a^3} = \frac{4\times(31+27)}{6{,}022.10^{23}\times(545.10^{-12})^3} = 2.38\ g.cm^{-3}$ If Al were to occupy the O holes: $\rho_O = \frac{nb_{AlP}\times MM_{AlP}}{N_A\times a^3} = \frac{4\times(31+27)}{6{,}022.10^{23}\times(472.10^{-12})^3} = 3.66\ g.cm^{-3}$ As the density is lower than 3 g.cm^{-3}, the Al occupy the 50% of the T holes and a = 545 pm.	
30.	C= $\frac{nb_{Al}\times\frac{4}{3}\pi\times R_{Al}{}^3+nbP\times\times\frac{4}{3}\pi\times R_P{}^3}{a^3} = \frac{4\times\left(\frac{4}{3}\right)\pi(128^3+108^3)}{545^3}$ = 0.34 Al occupy the T holes, they are thus surrounded by 4 atoms of P : the coordination number is 4.	**As a consequence, P located at each vertex has 8 tetrahedral holes around it but only 50% of them are occupied: the coordination number of P is 4.** see scheme below that represents the plane cutting the cube along the diagonal of a face for the AlP crystal (remember the notion of repeating motif (here made of 1 P and 1 Al) which composition and internal organization should be kept the same in the crystal).