INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

Formation initiale aux métiers d'ingénieurs
SCAN FIRST

December 13th 2019

Chemistry 1 - test 2 - Duration : 2hours

No document allowed. All types of calculators are authorized
Each answer should (concisely) be justified
Schedule of mark is for indication only and may be (slightly) adapted

Data:
Atomic Numbers: Hydrogen (H, Z=1), Nitrogen (N, Z=7), Oxygen (O, Z=8), Aluminum (Al, Z=13), Phosphorus (P, Z=15)

Molecular mass: M_{Al} = 27.0 g.mol^{-1} M_O = 16.0 g.mol^{-1} M_H = 1.0 g.mol^{-1}
M_N = 14.0 g.mol^{-1} M_P = 31.0 g.mol^{-1}

Atomic radius: R_{Al} = 128 pm R_P = 108 pm

Planck's constant: $h = 6.626\times10^{-34}$ J.s Speed of light: $c = 2.998\times10^{8}$ m.s^{-1}
Avogadro's number: $N_A = 6.022\times10^{23}$ mol^{-1} Elementary charge: $e = 1.602\times10^{-19}$ C

Part A: Phosphorus (~ 4 points)

Phosphorus was discovered by Hennig BRANDT in 1669 in Hamburg (Germany). He obtained a white material shining in the dark and burning with a bright light when in contact with air. Thus, its name comes from the Greek phosphoros, "which brings, or carries, light".

1. Give the electronic configuration of Phosphorus in its fundamental state. Precise the valence electrons.
2. Give the atomic number of the fifth element of the phosphorus group? Justify your answer.
3. Compare, justifying your answer, the electronegativity and the atomic radii of this element with the one of phosphorus.

The first ionization energies (EI_1) of the elements of the phosphorus period were measured:

element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
Z	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*
EI_1 (kJ.mol^{-1})	*496*	*738*	*777*	*786*	*1012*	*1000*	*1251*	*1520*

4. Define the first ionization energy of phosphorus.
5. Explain why the first ionization energy of phosphorus is higher than the one of sulfur.

Part B: Titration of Phosphorus in water (~ 14.5 points)

The European standards for the residual concentrations of chemicals from wastewater treatment plants are the following:

	Biological oxygen demand	Chemical oxygen demand	Suspended matter	Total Nitrogen	Total phosphorus
Maximum concentration limits	25 mg.L^{-1}	125 mg.L^{-1}	35 mg.L^{-1}	10 mg.L^{-1}	1 mg.L^{-1}

The total phosphorus corresponds mainly to the concentration of phosphate ions PO_4^{3-} in water.
The total nitrogen corresponds to the concentration of ammonium NH_4^+, nitrite NO_2^- and nitrate NO_3^-.

6. Write down the Lewis formula of the following molecules: O_2, **N**H_4^+, **N**O_2^-, **N**O_3^- and **P**O_4^{3-}. Central atoms are indicated in bold and are underlined in the brut formulas.

7. According to VSEPR (Gillespie's theory), give the geometry of for the ions: $\underline{\mathbf{N}}H_4^+$, $\underline{\mathbf{N}}O_2^-$, $\underline{\mathbf{N}}O_3^-$ and $\underline{\mathbf{P}}O_4^{3-}$.
8. Classify the bond angles in the following ions: ammonium NH_4^+, nitrite NO_2^- and nitrate NO_3^- in ascending order. Justify your answer.
9. In the phosphate ion ($\underline{\mathbf{P}}O_4^3$) do we expect to observe the same bond lengths? A clear and justified answer is expected for this question.

The concentration of Phosphorus in water can be determined by spectroscopy. The principle of this method is based on the reaction of ammonium molybdate named "reagent M" with phosphate ions. ***This reaction is total and the molybdophosphoric acid, which has a blue color, is thus formed quantitatively****.*
Note: no knowledge on the structure of molybdophosphoric acid is requested to address the questions bellow

10. Recall Beer's law. Give the name and unit of every coefficient of this law.
11. Between the following two wavelengths: 450 nm and 800 nm, which one is the most suitable for carrying out the analysis of the samples. Justify your answer.

In order to plot the calibration curve, the eight following standard solutions are prepared from a starting S_0 solution of phosphorus at a concentration of $\boldsymbol{C_0 = 5.00\ 10^{-2}\ mg.L^{-1}}$:

Solution number	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
Volume of the S_o solution (mL)	*0.50*	*1.0*	*1.5*	*2.0*	*2.5*	*3.0*	*3.5*	*4.0*
Volume of the "reagent M" (mL)	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Total volume of the flask (mL)	*10*	*10*	*10*	*10*	*10*	*10*	*10*	*10*
Phosphorus mass concentrations (10^{-2} mg.L^{-1})	*0.25*	*0.50*	*0.75*	*1.00*	*1.25*	*1.50*	*1.75*	*2.00*
Absorbance	*0.14*	*0.24*	*0.38*	*0.50*	*0.62*	*0.74*	*0.88*	*1*

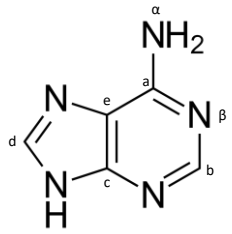
12. Verify graphically using the attached graph paper the validity of Beer's law.

A water sample from a wastewater treatment plant is analyzed to determine if the water meets the European standards. The sample is diluted 500 times and the absorbance of the resulting solution S is $\boldsymbol{A = 0.56}$*.*

13. Compute (in mg. L^{-1}) the concentration of phosphorus in the sample. Does it comply with the European regulation's limits?
14. Explain why a 500 times dilution of the sample was necessary for the correct recording of this spectrum?

Part C: Phosphate ions in human body (~ 10 points)

In the human body, adenosine triphosphate (ATP) is a molecule essential for energy transfer. It consists in a triphosphate unit combined with adenine whose structure is given below:



Adenine Formula

15. Write down the complete developed formula of adenine, showing all carbon atoms C, hydrogen H, nitrogen N and the nonbonding doublets.
16. Give the hybridization states of carbons **a** to **e** as well as nitrogen $\boldsymbol{\beta}$.

Remarks:

- Representation of an unhybridized p orbital perpendicular to the plane of the sheet: 

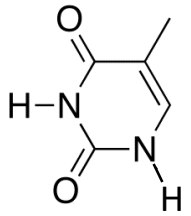
- Representation of an unhybridized p orbital in the plane of the sheet: 

17. Represent hybridized and unhybridized orbitals of nitrogen β.
18. How many molecular orbitals are expected on the complete energy diagram of this molecule?
19. How many electrons in total must be placed to complete this molecular orbital diagram?

Theoretical computations give estimated values for the HOMO and LUMO energy levels of adenine of -8.77 and -0.11 eV, respectively.

20. Give the definition of the HOMO and LUMO levels.
21. Give the maximum absorption wavelength (in nm, to within 0.1 nm) that you predict for the UV-visible spectrum.

In DNA molecules, adenine is associated to thymine (see structure shown below) by two specific intermolecular interactions. One of these interactions involves the H-N of thymine and the β nitrogen of adenine.



Thymine formula

22. Draw on your copy the two molecules of adenine and thymine and show the 2 intermolecular expected interactions using dashed lines.
23. Give the name of these intermolecular interactions. Give the order of magnitude of such interactions.

Part D: Phosphorus in a pesticide (~ 10 points)

*Phosphorus can form an alloy with aluminum called aluminum phosphide of formula **AlP (ratio: 1 atom P for 1 atom Al)**. This solid is usually used as a pesticide.*

24. In this structure, Phosphorus crystallizes according to a cubic arrangement. Phosphorus atoms are located on the vertices of the cube and on the center of each face. Knowing that Phosphorus atoms are not tangent to one another, represent one cell of this structure.

25. Indicate, by naming them, the two types of interstitial holes present in structures of this type. Give how many holes of each kind are present (justify your answer).

26. Let's define R_i as the radius of an interstitial hole considered as a sphere. Establish, for each type of interstitial holes and using the tangency condition, the relationships between R_i, R_P (the radius of phosphorus atoms) and a (the cell parameter).

In this crystal structure, aluminum atoms occupy one type of interstitial holes studied previously. Phosphorus and aluminum atoms are tangent to one another.

27. Specify for each interstitial hole type the percentage of sites occupied by aluminum atoms.

28. Compute in pm (10^{-12}m) the cell parameters of the possible structures.

29. Given that the density of the AlP compound is smaller than 3 g.cm^{-3} and using calculations, find the actual structure of the crystal.

30. Give the APF of this structure and give the coordination numbers of Al/P.

ANNEX to be used for Beer's Law plotting **(to be given back)**

NAME:

Group: