[illegible]

Chemistry final exam

Mark	Remark
	37,75 → 17,16

H He

Li Be B C N O F Ne

Na Mg Al Si P S Cl Ar

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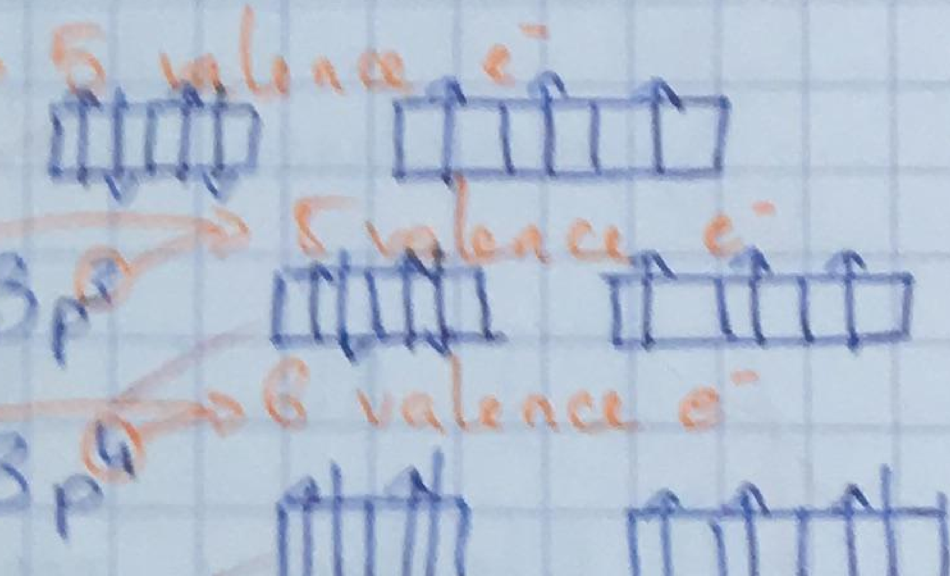
II Lewis structure

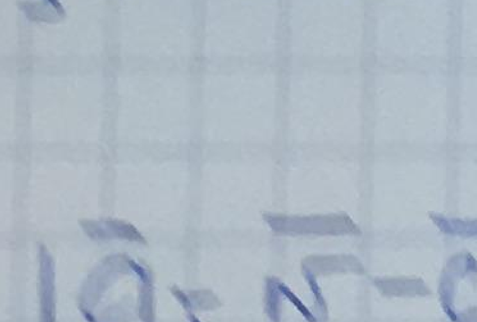
2.1) N : $Z = 7 \Rightarrow 1s^2\,2s^2\,2p^3$ → 5 valence e^-

P : $Z = 15 \Rightarrow 1s^2\,2s^2\,2p^6\,3s^2\,3p^3$ → 5 valence e^-

S : $Z = 16 \Rightarrow 1s^2\,2s^2\,2p^6\,3s^2\,3p^4$ → 6 valence e^-

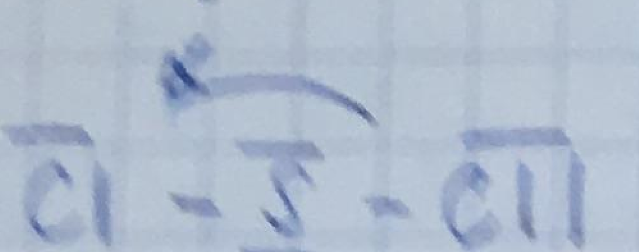


2.2) NCl_3 : $N_{e^-} = 5 + 7 \times 3 = 26\ e^- \Rightarrow 13$ doublets



N is AX_3E_1, thus from VSEPR theory: the geometry is trigonal pyramidal and $\alpha < 109{,}5°$

SCl_2 : $N_{e^-} = 6 + 7 \times 2 = 20\ e^- \Rightarrow 10$ doublets



S is AX_2E_2, thus from VSEPR theory the geometry is bent and $\alpha < 109{,}5°$

SF_6 : $N_{e^-} = 6 + 7 \times 6 = 48\ e^- \Rightarrow 24$ doublets

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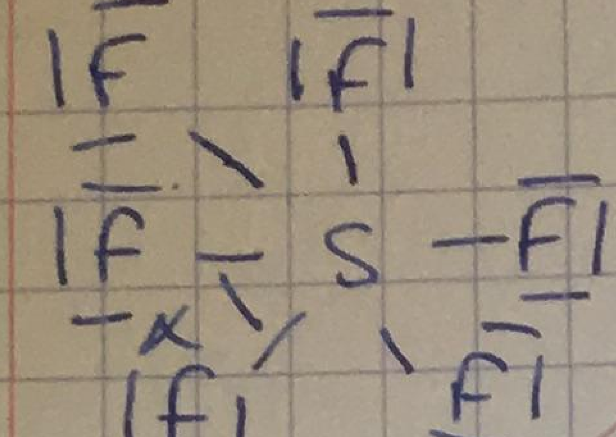

hypervalence is possible since S belongs to the third period.

S is AX_6, thus from VSEPR theory:

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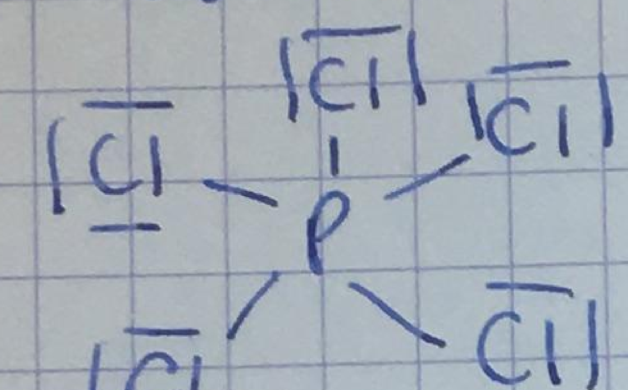
$\alpha = 90°$ and the geometry is octahedral

23) PCl_5 exists, since P belongs to the third period hypervalence is possible and the lewis structure is:



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However, N belongs to the 2^{nd} period, therefore hypervalence isn't possible and NCl_5 doesn't exist.

I) About Tin

1) Electronic configuration: $[Kr]\,5s^2\,4d^{10}\,5p^2$

From its electronic configuration, we can deduce that:

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→ its period is $\boxed{5}$

→ its group is the $\boxed{14^{th}\text{ group}}$ (2^{nd} column of the p-block)

2) Electronic configurations:

Ge: $[Ar]\,4s^2\,3d^{10}\,4p^2$
Pb: $[Xe]\,6s^2\,5d^{10}\,6p^2$
} both of these two elements belong to the second column of the p-block. Hence, we can conclude that they are in the same column than Sn

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3) The first element of this column is ($1s^2 2s^2 2p^2 \Longrightarrow Z = 6$) C.

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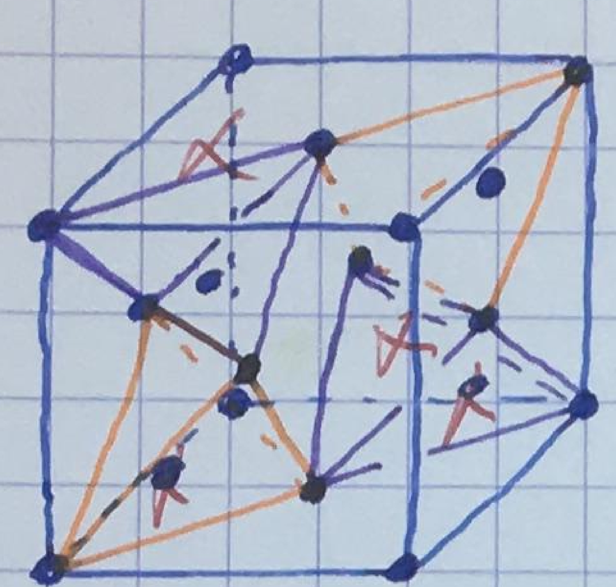
4)



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5) The population of the cell is ($8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 =$) 8 atoms of Sn

Now: $\rho = \dfrac{8 \times M_{Sn}}{N_A \cdot a^3} \Longrightarrow \boxed{a = \left(\dfrac{8 \times M_{Sn}}{N_A \cdot \rho}\right)^{1/3}}$

Numerical application: $\boxed{a \simeq 6{,}49 \cdot 10^{-10}\, m \simeq 6{,}49\, Å}$

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6) Atoms are tangent in the tetrahedral holes, thus we can conclude that the contact condition is:

$2 R_{Sn} = \dfrac{\sqrt{3}}{4} a$, thus: $\boxed{R_{Sn} = \dfrac{\sqrt{3}}{8} a}$

Numerical application: $\boxed{R_{Sn} \simeq 1{,}41 \cdot 10^{-10}\, m \simeq 1{,}41\, Å}$

$APF = \dfrac{8 \times \frac{4}{3} \pi R_{Sn}^3}{a^3} \simeq 0{,}34 < 0{,}74$ and $0{,}68$

Conclusion: This structure is neither compact nor semi-compact. In fact, it is less compact than a semi-compact structure. This is due to the fact that Sn atoms are located in tetrahedral sites.

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8) Half the number of atoms as in the cubic cell, hence the population is 4 Sn.

Sow: $\boxed{\rho = \frac{4 \cdot M_{Sn}}{N_A \times a^2 \times c}} \simeq \boxed{7{,}32.10^3\ kg.m^{-3}}$

$$\boxed{APF = \frac{4 \times \frac{4}{3}\pi R_{Sn}^3}{a^2 \times c} \simeq 0{,}43}$$

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9) $m = 1{,}00\ kg$

In the α-form: $\rho_\alpha = 5{,}77.10^3\ kg.m^{-3}$, thus:

$$\boxed{V_{\alpha\text{-occupied}} = \frac{m}{\rho_\alpha} \simeq 1{,}73.10^{-4}\ m^3}$$

In the β-form: $\rho_\beta \simeq 7{,}32.10^3\ kg.m^{-3}$, thus

$$\boxed{V_{\beta\text{-occupied}} = \frac{m}{\rho_\beta} \simeq 1{,}37.10^{-4}\ m^3}$$

10) This observation might be due to the metastable aspect of the α-form. Indeed, the α-form transformat[ion] might be favored thermodynamically but blocked kinetically. Hence, after several months the consequences of the transformation can be observed.

11) Half equations:

$$\boxed{SnO_2 + \underset{+I}{4H^+} + 2e^- \longrightarrow \underset{+II}{Sn^{2+}} + 2H_2O}$$

no(Sn) = ~~+XI~~

no(O) = ~~-I~~

no(H) = +I

no(O) = -II

$$\boxed{Pb_{(s)} \longrightarrow Pb^{2+} + 2e^-}$$

no(Pb) = 0   no(Pb^{2+}) = +II

* Hence, we can deduce that the number of moles of $SnO_{2(s)}$ introduced initially is equal to the number of moles of Sn^{2+} produced: $\boxed{n_{0\,SnO_2} = n_{Sn^{2+}}}$

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Global reaction:

$$\boxed{SnO_{2(s)} + Pb_{(s)} + 4H^+ \longrightarrow Pb^{2+} + Sn^{2+}} + 2H_2O$$

For half equations: 2 moles of electrons are exchanged per mole of SnO_2

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2) $E°(SnO_2 / Sn^{2+}) = 0,14\,V$
$E°(Pb^{2+}/Pb) = -0,13\,V$

$\Rightarrow \Delta E° = 0,27 > \frac{0,4}{2} = 0,2$

Thus the reaction can be considered as total *

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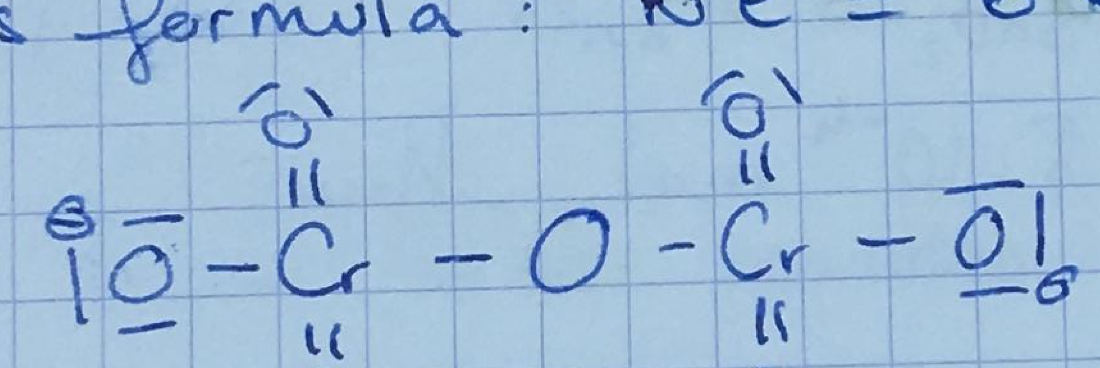
3) Equation of dissolution:

$$\boxed{K_2Cr_2O_7 \xrightarrow{H_2O} 2K^+ + Cr_2O_7^{2-}}$$

Lewis formula: $N_{e^-} = 6\times7 + 6\times2 + 2 = 56\,e^- \Rightarrow 28$ doublets



4) Half equations: $Sn^{2+} + 2H_2O \longrightarrow SnO_2 + 4H^+ + 2e^-$ $(\times 3)$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

+I +III

no(Cr) = +VI
no(–O–) = –II = no(=O) = no(–O⁻)

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Global reaction:

$$3Sn^{2+} + 6H_2O + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3SnO_2 + 12H^+ + 2Cr^{3+} + 7H_2O$$

$$\boxed{3Sn^{2+} + Cr_2O_7^{2-} + 2H^+ \longrightarrow 3SnO_2 + 2Cr^{3+} + H_2O}$$

From half equations: the number of moles of electrons exchanged per mole of $Cr_2O_7^{2-}$ is $\boxed{6\text{ moles}}$

~~16) $n_{Sn^{2+}} = 3\, n_{Cr_2O_7^{2-}} = 3\ \cancel{C}.V$ (from 14)~~

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15) $E°(SnO_2 / Sn^{2+}) = 0{,}14$; $E°(Cr_2O_7^{2-}/Cr^{3+}) = 1{,}33$ $\Big\}\ \Delta E° = 1{,}19 > \frac{0{,}4}{6}$, thus

the reaction can be considered as total

Hence, we can deduce that $\boxed{n_{Sn^{2+}} = 3\, n_{Cr_2O_7^{2-}}}$

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16) $\boxed{n_{Sn^{2+}} = 3\, n_{Cr_2O_7^{2-}} = 3 \times C \times V}$

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17) $\boxed{m\% = \frac{n_{SnO_2} \times M_{SnO_2}}{m}}$ with m% the weight percent.

Now, from 12) : $n_{SnO_2} = n_{Sn^{2+}}$, thus from 16)

$n_{SnO_2} = 3 \times C{\times}V \simeq 1{,}5.10^{-4}$ mol, thus:

$\boxed{m\% = 5\%}$

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18)

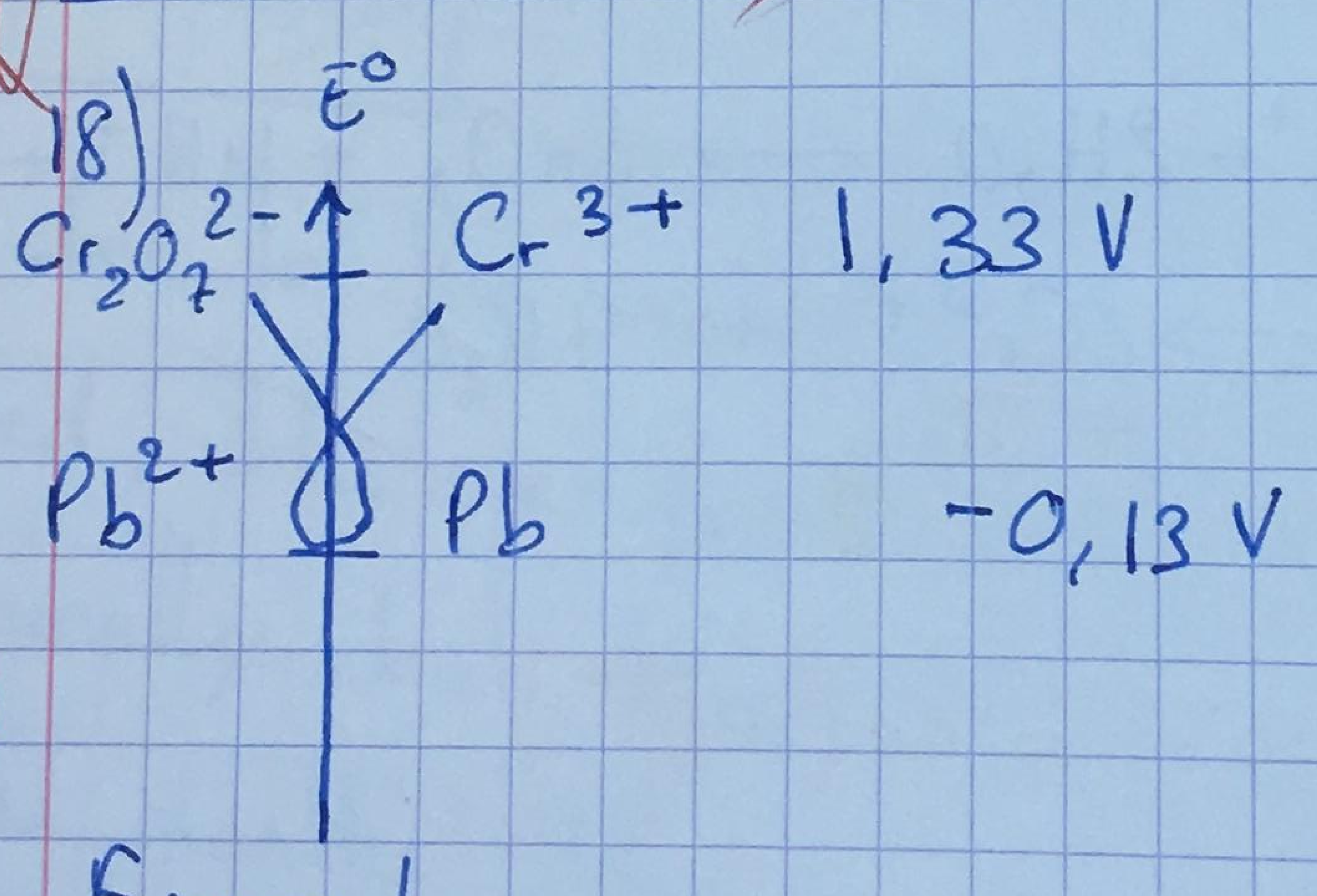

Figure 1

In order to prevent the reaction between $Pb_{(s)}$ and $Cr_2O_7^{2-}$ (Figure 1), it was necessary to extract the excess of Pb.

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19) 1 and 4: hybridization state is $\boxed{sp^2}$

2 and 3: hybridization state is $\boxed{sp^3}$

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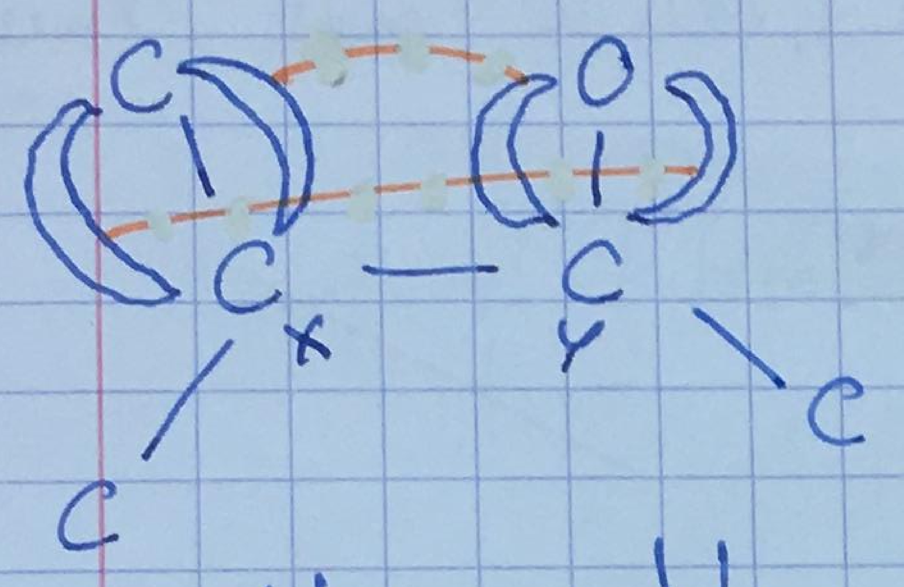
20) b is a pure σ bond, hence free rotation is possible.

For a:



a isn't a pure σ bond since there are some interactions between the non hybridized orbitals of the two C (X and Y), thus free rotation isn't possible.

key: - - - : interaction between the non hybridized orbitals

IV Acido-basic reaction

2

30) HCl is a strong acid ⟹ the reaction is total.

equation: $\boxed{HCl + H_2O \longrightarrow Cl^- + H_3O^+}$

After reaction, the existing species are:

$Cl^{\ominus}$: $[Cl^-] = \boxed{[HCl]_0 = 0{,}01\ mol.L^{-1}}$ the reaction is total

H_3O^+ : $[H_3O^+] = \boxed{[HCl]_0 = 0{,}01\ mol.L^{-1}}$

H_2O : solvant

$\boxed{pH = -\log[H_3O^+] \simeq 2{,}0}$

31) Equation of dissolution:

$\boxed{NaNO_{2(s)} \xrightarrow{H_2O} NO_{2(aq)}^- + Na^+_{(aq)}}$

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$d = 1,382 \Rightarrow \rho_{solution} = 1,382\ kg.L^{-1}$

Now, the volume of S_0 is 1L, thus:

$m_{solution} = 1,382\ kg$, thus:

$m_{NaNO_2} = 6,91.10^{-3}\ kg$, thus:

$$n_{NaNO_2} = \frac{m_{NaNO_2}}{23 + 14 + 2\times 16} = 1,00.10^{-1}\ mol$$, thus:

$$\boxed{[NO_2^-]_0 = \frac{n_{NaNO_2}}{V} = 1,00.10^{-1}\ mol.L^{-1}}$$

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32) Species in the solution:

$[H_3O^+] = 0,01\ mol.L^{-1}$ from 30)

$[NO_2^-] = 0,1\ mol.L^{-1}$

Equation of the reaction:

$NO_2^- + H_3O^+ \longrightarrow HNO_2 + H_2O$

$$k_T = \frac{[HNO_2]}{[NO_2^-][H_3O^+]} = \left(\frac{[NO_2^-][H_3O^+]}{[HNO_2]}\right)^{-1} = \frac{1}{k_a(HNO_2/NO_2^-)}$$

$$\boxed{k_T = 1,00.10^3}$$

3

33)

	NO_2^-	+ H_3O^+	$\longrightarrow HNO_2$	+ H_2O
$t=0$	c_0	c_1	0	
$t=t_{eq}$	$c_0-\xi$	$c_1-\xi$	ξ	

Now: $$k_T = \frac{[HNO_2]_{eq}}{[NO_2^-]_{eq}[H_3O^+]_{eq}} = \frac{\xi}{(c_0-\xi)(c_1-\xi)}$$, thus:

$$\boxed{\xi = 9,94.10^{-3}\ mol.L^{-1}}$$, thus:

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$[NO_2^-]_{eq} = 9,01.10^{-2}\ mol.L^{-1}$

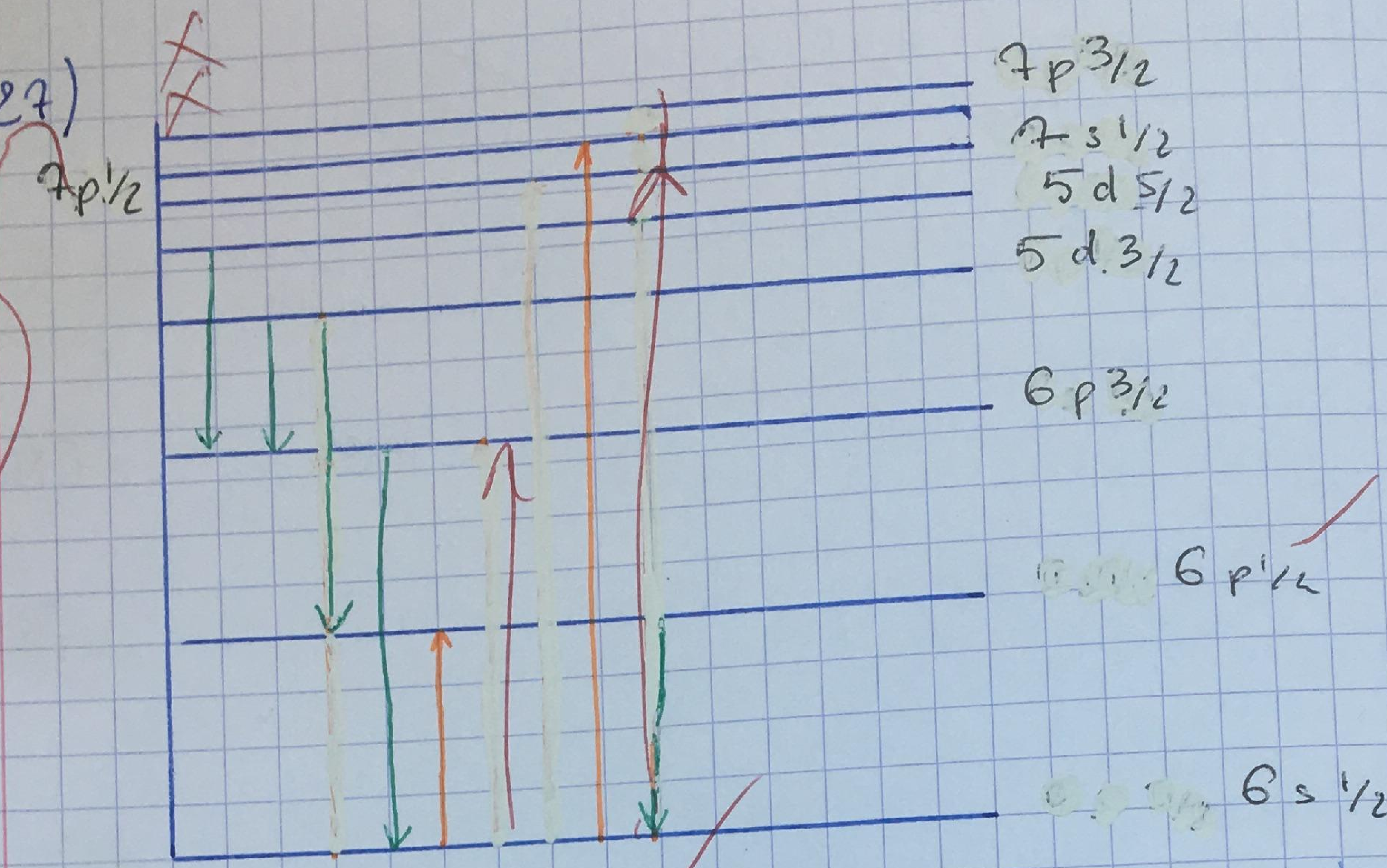
$[H_3O^+]_{eq} = 5,53.10^{-5}\ mol.L^{-1}$

$[HNO_2]_{eq} = 9,94.10^{-3}\ mol.L^{-1}$

Na^+

Cl^-

27)



↑ : corresponding lines to the absorption spectrum.

28) The absorption line between $6s_{1/2}$ and $6p_{1/2}$ corresponds to $\lambda \simeq 893$ nm

The other one corresponds to $\lambda \simeq 459$ nm

29) → (cf 27))

The line that would be observed are represented at 27) on the Grotrian's diagram

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34) $\boxed{pH = -\log([H_3O^+]_{eq}) = 4,3}$

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HNO_2 | NO_2^- → pH

3,30 4,3

This result is consistant since : $[HNO_2]_{eq} << [NO_2^-]_{eq}$

III Spectroscopy of alkaline metals

24)

?

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$\boxed{Z(Cs) = 55}$

25) Some levels are double because of the spin orbit coupling which is induced by the rotation of electrons on themselves. The quantum number j represents this phenomenon. j is obtained thanks to the formula :

$\boxed{j = \left| \ell \pm \frac{1}{2} \right|}$

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26) The ionization energy of Cs will be lower than that of the element tha precedes since this element is a noble gas and therefore it is very stable.

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