

CHEMISTRY 1 – Test n°3 – Duration : 3 hours

No document allowed. Every calculator types are authorized.

Give your answers with the appropriate number of digits.

Scheme of mark (40 points)

DATA

Planck's constant: $h = 6.626 \times 10^{-34}$ J.s

Light speed: $c = 2.998 \times 10^8$ m.s⁻¹

Avogadro's constant $N_A = 6.022 \times 10^{23}$ mol⁻¹

Elementary charge: $e = 1.602 \times 10^{-19}$ C

E(eV) = 12400 / $\lambda(\text{Å})$ relationship can be used without demonstration

Moseley's Law: $\sqrt{\nu} = a(Z - b)$

Beer-Lambert's Law : $I = I_0 \exp(-\mu l)$ with μ the absorption coefficient

Element	H	He	Li	Be	B	C	N	O	F	Ne
Z	1	2	3	4	5	6	7	8	9	10
A	1.0	4.0	6.9	9.0	10.8	12.0	14.0	16.0	19.0	20.2

Element	Na	Mg	Al	Si	P	S	Cl	Ar	K	Fe	Ti
Z	11	12	13	14	15	16	17	18	19	26	22
A	23.0	24.3	27.0	28.1	31.0	32.1	35.5	40.0	39.1	55.8	47.9

I. CRYSTAL STRUCTURE OF AUSTENITIC IRON (7 PTS)

At 1000 ° C the stable form of iron, termed variety γ , crystallizes in a *face centered cubic* system. Moreover, it crystallizes as a compact structure with a *motif constituted by single iron atom*. Iron atoms are *tangent along the diagonal of a face and the edge of the cubic cell is 3.510 Å long*.

1. Compute the density of Iron γ in g.cm⁻³ (with 3 significant digits)? What is the value of the atomic radius of iron, to within 0.1 pm?
2. Compute the Atom Packing Factor (APF) of this structure.
3. Give the symmetry axes (order and number) characterizing the cubic crystalline system. Draw a figure showing an axis of each type.
4. Give the position (in a few lines or using a diagram) of octahedral and tetrahedral holes. Give their numbers per cell.
5. Compute in pm the maximum radius (termed R_0) of a specie that can be inserted into an octahedral hole without deformation of the crystal structure.

Actually austenitic steel is a carbon insertion alloy in an Iron γ structure.

6. The atomic radius of carbon being 77.0 pm. Show that this atom cannot fit in the octahedral sites of Iron γ without deforming the crystalline structure.
7. What would be the theoretical value in Å of a' , the iron γ cell parameter, if a carbon atom was inserted into an octahedral site while conserving an iron-carbon tangency?

Austenitic steel, of general formula FeC_y , containing 1.33 weight% of carbon is now considered. In fact, this steel has a cell parameter a' of 3.639 Å.

8. Give the density in $\text{g}\cdot\text{cm}^{-3}$ of such steel. Result should be given with 3 significant digits.

II. AUSTENITIC STEEL CORROSION (4 PTS)

The corrosion of steels is mainly due to the oxidation of the iron they contain. In contact with an aqueous solution, the phenomenon is called wet corrosion.

1. Write the electronic half-equation associated to the Fe^{2+}/Fe couple. Identify the oxidized form, the reduced form and determine the respective oxidation numbers

In contact with an aqueous solution, two redox couples can be involved in the oxidation phenomenon of steel:

- In aerated acidic aqueous solution: the $\text{O}_2(\text{aq})/\text{H}_2\text{O}$ couple

- In non-aerated acidic aqueous solution: the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ couple

2. Write down for each of these two redox couples, the associated half-equation in an acidic medium. Identify the oxidized form, the reduced form, and determine the respective oxidation numbers.

3. Give the associated two possible global equations for corrosion of iron in water.

To demonstrate experimentally the corrosion phenomenon of a steel and thus monitor the release of Fe^{2+} ions in the aqueous medium, potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$ is used. By reacting with Fe^{2+} ions, this reagent gives a characteristic blue color to the solution name "Prussian blue". It is due to the presence of a solid which formula is $\text{KFe}[\text{Fe}(\text{CN})_6]$.

4. Which type of ion is preferentially obtained from potassium element (${}_{19}\text{K}$)? Qualify your answer.

5. Give the Lewis formula of cyanide ion (CN^-).

6. Which type of ions, Fe^{2+} or Fe^{3+} , is present initially in potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$? Qualify your answer.

7. Knowing that the "Prussian blue" is an ionic solid, list the ions present in its structure.

III. STUDY OF THE CRYSTAL STRUCTURE OF PRUSSIAN BLUE (RESOLVED BY LUDI IN 1970) (4.25 PTS)

Prussian blue, of formula $\text{KFe}[\text{Fe}(\text{CN})_6]$, is described as a cubic face centered structure of edge value $a = 5.820 \text{ \AA}$, where:

- Iron (II) ions occupy the nodes of the lattice,

- Iron (III) ions occupy the octahedral holes.

- CN ions are located between the Iron (II) and Iron (III) of the structure where the distance $d(\text{Fe}^{2+}-\text{Fe}^{3+})$ is the smallest possible one.

- K^+ ions occupy half of the tetrahedral holes.

1. a) Draw a representation of this structure with only the cations and justify their respective positions.

b) On a second scheme, draw one face of the cubic structure containing also CN^- ions.

2. Compute per cell, the number of ions of each type. Does the formula $KFe[Fe(CN)_6]$ correspond to this structure?
3. Give the coordination number of both Iron (III) and Iron (II) ions with respect to cyanide ions.

IV. X-RAYS (10.5 PTS)

Data:

μ is the absorption coefficient for a given absorption mechanism. It is defined as: $\mu = \beta Z^3 \lambda^3$.

Mechanism of photon absorption by ionization of an electron from the K layer of the absorbing material $\beta = 4.200 \cdot 10^{-2} \text{ cm}^{-1} \cdot \text{\AA}^3$

Mechanism of photon absorption by ionization of an electron from the L_1 layer of the absorbing material $\beta = 5.000 \cdot 10^{-3} \text{ cm}^{-1} \cdot \text{\AA}^3$

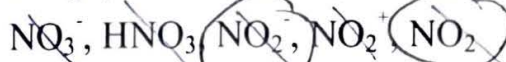
	$ E_K $ (eV)	$ E_{L_1} $ (eV)	$ E_{L_2} $ (eV)	$ E_{L_3} $ (eV)	$ E_{M_{2,3}} $ (eV)
K	3608.4	341.1	295.1	292.1	40.8
Fe	7112.0	846.1	721.1	708.1	52.7

In order to check the iron/potassium molar ratio of Prussian blue ($KFe[Fe(CN)_6]$) and to detect eventual impurities, an EDS (Electron Dispersive Spectroscopy) analysis is performed on a sample using a scanning electron microscope equipped with an electron gun. This technique consists on shooting electrons on the material to be analyzed. These incident electrons are sufficiently energetic to extract core electrons out of the elements of the material. The reorganization of the electronic sub-layers results in the emission of X photons characteristic of these elements. In this exercise, the quantification of the iron/potassium molar ratio will be based on the K-L₃ line of each element.

1. Give the electronic configuration of Iron.
2. Draw a Grotrian's diagram of Iron giving the quantum numbers (n, l, j) of each sub-level that is totally or partially occupied.
 note base (2l+1) - j = |l ± 1/2|
3. Explain (in a few words) the origin of the separation in two energy sub-levels observed for the orbital 2p.
4. Give the possible transitions (emitting photons) that are observed between levels L and M levels.
 Al ± l
5. Compute the minimal potential that has to be applied to the electrons for Iron and Potassium for observing their K-L₃ ray, respectively.
 Δ = 2.0
6. Give the wavelength of the K-L₃ ray of Iron and Potassium emitted by the sample.
7. Propose a way for obtaining that only the photons of the potassium K-L₃ ray hit the detector. You can draw a scheme to justify your answer.
8. Compute the atomic number(s) of the elements which can be used for this purpose (the graphical method is not allowed).
8. The material used for question 7 is Titanium.
9. Compute in μm the width necessary for obtaining an attenuation rate of 99.9% of the K-L₃ ray of Iron.
9. Compute the minimal potential to be applied for the acceleration of electrons in order to quantify the Iron/Potassium stoichiometric ratio if the K-M₃ ray of each element was used.

V. NITROGEN CHEMISTRY (5.75 PTS)

1. Give the electronic configuration of nitrogen and indicate the valence electrons.
2. To which group and period does nitrogen belong to?
3. What are the halogen and alkaline earth elements of the same period?
4. For the following nitrogen containing species, where nitrogen is the central atom:



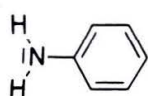
- a) Give the Lewis formula and the eventual mesomeric formulas and resonance hybrid of all the species (hint : NO_2 is a radicalar specie, the radical is located on the nitrogen for the most representative structure).
- b) Give the geometry observed around nitrogen for NO_3^- and HNO_3 .
- c) Using the VSEPR theory, give the angle value of the NO_2^- ion. Same question for NO_2^+ and NO_2 .

VI. AZO DYES (8.5 PTS)

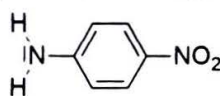
Azo dyes are organic molecules characterized by the presence of a nitrogen-nitrogen double bond (azo group) linking two benzene rings. Azo dyes represent more than half of the dyes used worldwide, all uses combined (food, textiles, paints, plastics, ...). Variation on the structure of the aniline motif is a method to get a wide variety of azo dyes.

1. Basicity of aniline derivatives

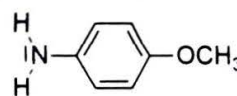
The pK_a of aniline derivatives of structures listed below are 1.0; 4.6 and 5.4. Assign a pK_a to each acid-base couple ($\text{R-NH}_3^+/\text{R-NH}_2$), qualify your answer.



aniline



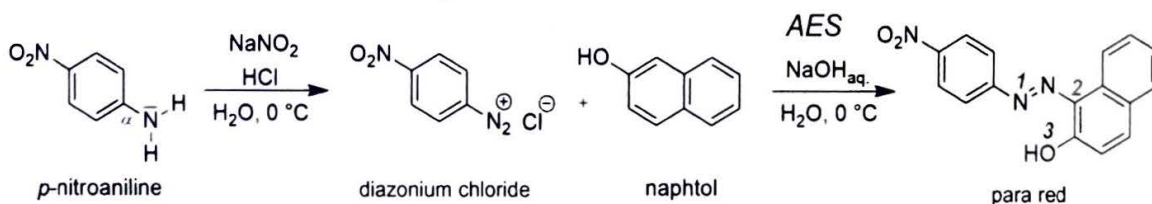
p-nitroaniline



p-anisidine

2. Synthesis of an azo dye: the para red

Para red is an azo dye mainly used for dyeing cellulosic fibers in red. This dye is obtained in 2 steps from *p*-nitroaniline. We will study here only the second electrophilic aromatic substitution (AES) step between diazonium chloride and naphthol in basic medium.



Starting from 5.0 g of diazonium chloride :

- a) What minimum mass of naphthol is necessary for observing a total conversion?
- b) Knowing that the yield of the reaction is 89%, what is the mass of "para red" obtained?
- c) Using mesomeric formulas of *p*-nitroaniline, indicate the number of coplanar atoms. Is complete free rotation observed around the tagged bond (called α) in the previous scheme?
- d) Give the developed formula of "para red", indicating the missing non-bonding doublets. Give the hybridization state of the tagged atoms: 1(N), 2(C) et 3(O).
- e) A diazonium ion has a general formula of R-N_2^+ . Write down the two Lewis formulas of the mesomeric forms corresponding to two different location of the positive charge. Compare the N-N bond length in the two formulas.