INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

AMER, SCAN – First year *January 28, 2021*

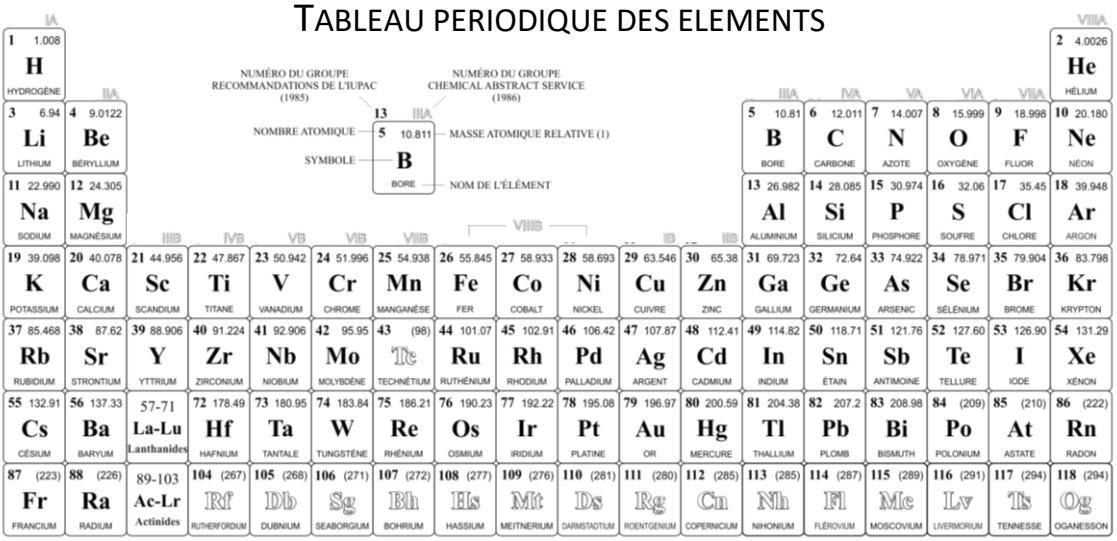
CHIMIE 1 – Final exam - Duration: 3 hours

No document allowed. All type of calculators authorized.

Schedule of mark is for indication only and may be (slightly) adapted
The results will be given with the appropriate number of significant digits.

Data sheet

TABLEAU PERIODIQUE DES ELEMENTS



Standard Constants:

Electronegativity according to Pauling's scale:
χ(H) = 2.1 ; χ (C) = 2.5 ; χ (N) = 3.0 ; χ (O) = 3.5 ; χ (S) = 2.5 ; χ (Mn) = 1.5

h = 6.626 10^{-34} J.s c = 2.998 10^{8} m.s^{-1} e = 1.602 10^{-19} C m_e = 9.109 10^{-31} kg
R_H = R_x Rydberg constant for hydrogen = 109677.80 cm^{-1}
$\mathcal{N}$: Avogadro's number = 6.022.10^{23} mol^{-1}

The following relationship can be used without any demonstration: E(eV) = 12400 / λ(Å)

Standard redox potentials (in V):

$$E^0_{MnO_4^-/Mn^{2+}} = 1.51V \quad ; \quad E^0_{Fe^{3+}/Fe^{2+}} = 0.77V \; ; \quad E^0_{Fe^{3+}/Fe} = -0.04V \quad ; \quad E^0_{Fe^{2+}/Fe} = -0.45V$$

Acidity constant for the couple ($ClCH_2COOH/ClCH_2COO^-$): Ka = $10^{-2,85}$
Autoprotolysis constant for water: Ke = 10^{-14}

Problem I: Hydrogen like ions (3.5 pts)

Following its excitation by a photon of wavelength λ = 105.53 Å, a hydrogen like ion produces 10 emission lines.

1) What is the level reached during the excitation? Justify your answer with the help of a diagram.
2) What is this hydrogen like ion? Give the answer using the following formula $_zX^{y+}$.

3) Establish the expression of the energy of a level noted E_n. Compute the energy in eV of the involved levels to within 10^{-1} eV.

Problem II: Lewis model and VSEPR theory (4.5 pts)

1) Identify the common point(s) and difference(s) between the possible electronic configurations of oxygen and sulfur.
2) Give the Lewis structure, the geometrical shapes and the observed angles deduced from the VSEPR theory for the following molecules or ions: sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfite ion (SO_3^{2-}) and sulfate ion (SO_4^{2-}). If applicable, give the resonance hybrid.

Problem III: Undulatory model of bonding, intermolecular interactions (2 pts)

The molecule shown below has the following empirical formula $C_{10}H_{13}N_3OS$ (M = 223.29 g.mol^{-1}). Figure 1 shows its Lewis formula without the non-bonding doublets. Figure 2 shows its structure established from the Xray diffraction of a crystal.

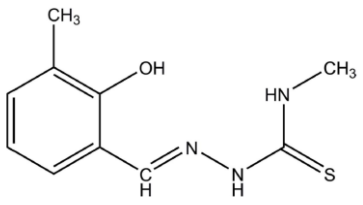


Figure 1 Lewis Formula

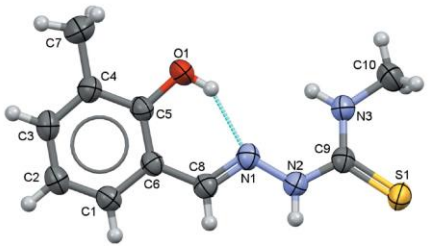


Figure 2 Structure obtained from the Xray diffraction

1) Give the hybridization states of atoms C1, C7, C8, C9, C10.
2) Give the hybridization state of atom N1 and give the type(s) of bond(s) observed between C8 and N1 as well as the orbitals involved.
3) Give the type of interaction that involves nitrogen N1.

Problem IV: Crystallography (12 pts)

A ceramic of composition $BaTiO_x$ adopts a cubic lattice at 125 °C. The radii of the ions composing this structure are the following: rBa^{2+}=135 pm, rTi^{4+}=68 pm and rO^{2-}=140 pm.

1) Give the x value expected in the $BaTiO_x$ formula and explain how you obtained it.
2) Give the type of bond observed in this structure.

Ba^{2+} ions are located on vertices of the structure, Ti^{4+} ions are located at the center of the cube and O^{2-} ions occupy the centers of the faces.

3) Represent the cell structure by clearly identifying the different ions observed.
4) Give the population of the cell.
5) Considering a, the parameter of the cell and using the ions radii, give the cation/anion tangency conditions as well as the non-tangency conditions observed for Ba^{2+}/Ti^{4+} and O^{2-}/O^{2-}.
6) Using the ions radii values, compute the only cell parameter a possible for this cell. Can you conclude on the tangency of one of the cations with the O^{2-} ions?
7) Give the cation/anion coordination numbers of Ba^{2+} and Ti^{4+} ions.
8) Give the Atomic Packing Factor (APF) definition and compute its value for this cell.
9) Compute its density in $g.cm^{-3}$.
10) According to your answers at questions 5) and 6), represent a plane parallel to 2 opposite faces of the cube and passing through the edges in a/2. Then, represent a plane cutting the cube in 2 and passing through 2 opposite edges.

Problem V: Chemical transformations (3.5 pts)

Let's consider the following chemical reaction in water:

$$CH_3COOH_{(aq)} + HCOO^-_{(aq)} \rightleftarrows CH_3COO^-_{(aq)} + HCOOH_{(aq)}$$

At 25°C the equilibrium constant is: $K^0_{298K} = 0.1$

1) For the following operating conditions performed on a total volume of V = 1 L, indicate:

- If a change occurs or not
- If yes, what is the direction of the reaction (forward or backward)?

Answers must be clearly detailed and justified.

a) $[CH_3COOH]_0 = [HCOOH]_0 = [CH_3COO^-]_0 = 0.10$ mol.L^{-1}, $[HCOO^-]_0 = 0$
b) $[CH_3COOH]_0 = [HCOOH]_0 = [HCOO^-]_0 = [CH_3COO^-]_0 = 0.10$ mol.L^{-1}
c) $[CH_3COOH]_0 = 0.10$ mol.L^{-1} and $[HCOOH]_0 = [HCOO^-]_0 = [CH_3COO^-]_0 = 0.010$ mol.L^{-1}
d) $[CH_3COOH]_0 = [HCOO^-]_0 = [CH_3COO^-]_0 = 0.10$ mol.L^{-1}, $[HCOOH]_0 = 0$

Problem VI: Redox reactions (7 pts)

We want to determine the amount (in mg) of Iron (II) Sulfate $FeSO_4$ contained in a given sample (noted S1). To do this, a redox experiment is carried out in an acid medium by reacting the iron cations resulting from the dissolution of $FeSO_4$ with permanganate ions (MnO_4^-). The reaction is considered as total.

1) Knowing that iron (II) sulfate is a strong electrolyte in water, give the equation of dissolution reaction of $FeSO_4$ in water.
2) Give the 2 redox half-reactions equilibrated in acidic medium. The oxidation numbers are required. Indicate the oxidation and reduction half reactions.
3) Give the overall redox reaction indicating the oxidizing and reducing species of this reaction. Give the number of electron moles exchanged per mole of permanganate ions.

The reaction is carried out as follows: One chemist weighs 1.00 g of solid S_1 that contains the iron (II) sulfate and dissolves it in 10.0 mL of acidified water. Finally, a solution containing permanganate ions of initial concentration 0.0250 $mol.L^{-1}$ is added. The exact volume added for the complete reaction of iron ions is 25.0 mL.

4) Give in grams the quantity of iron (II) sulfate present in 1.00 g of solid S_1.

Problem VII: acid-base reactions (7.5 pts)

Let's consider a V = 1.00 L of a chloroacetic acid ($ClCH_2COOH$) solution of initial concentration in water of 0.0500 $mol.L^{-1}$. The influence of self-dissociation of water can be neglected here.

1) Write down the dissociation reaction of this acid in water. Give the expression of the equilibrium constant $K°_T$ and compute its value.
2) Calculate the concentration of all the chemical species present in solution at equilibrium (including HO^-).
3) Give then the pH of the solution. Illustrate the state of the system using a predominance diagram given as a function of the pH.
4) Give (in %) the conversion of chloroacetic acid when the equilibrium is reached.
5) What should be the initial concentration of this acid to obtain a 50% dissociation ratio at equilibrium? What would be the value of the pH?