INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON AMER, SCAN – First year *January 27, 2022*

CHIMIE 1 – Final exam - Duration: 3 hours

No document allowed. All type of non-connected 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

Standard Constants:

$h = 6.626 \times 10^{-34}$ J.s $c = 2.998 \times 10^{8}$ m.s^{-1} $e = 1.602 \times 10^{-19}$ C $m_e = 9.109 \times 10^{-31}$ kg
$R_x = 109677.80$ cm^{-1} $\mathcal{N}$: Avogadro's number $= 6.022 \times 10^{23}$ mol^{-1}

The following relationship can be used without any demonstration: $\Delta E(eV) = 12400 / \lambda(Å)$

Element	H	C	N	O	Na	P	S	Cl	K	Cr	Fe
Z	1	6	7	8	11	15	16	17	19	24	26
M (g.mol^{-1})	1	12	14	16	23	31	32	35,4	39	52	55,8
χ	2.1	2.5	3.0	3.5	0.9	2.2	2.6	3.2	0.8	1.7	1.8

Z : Atomic number, M : molecular weight, χ : electronegativity according to Pauling's scale

Standard redox potentials: **$E°(Fe^{3+}/Fe^{2+}) = +0.77$ V** **$E°(Cr_2O_7^{2-}/Cr^{3+}) = +1.33$ V**

Redox reactions can be considered as total if $\Delta E° > 0.24/n$ with n the number of moles of electrons exchanged between the oxidant and the reductant.

In water, hydrochloric acid (HCl) and nitric acid (HNO_3) are considered as strong acids.

pKa ($RCOOH/RCOO^-$) = 3.40 for the mandelic acid/mandelate acid base couple
pKe = 14 for the self-dissociation of water at 25 °C

I. Hydrogen like ion (4/40)

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1. The ionization energy of an hydrogen like ion is equal to 1362.38 eV. What is this hydrogen like ion? Give the answer using the following formula $_zX^{y+}$.
2. The energy of the levels 1 to 6 (E_n) are given in the following table. What physical phenomena occur when a sample of this hydrogen like ion is subjected to an electromagnetic radiation which frequency ranges from 3.00×10^{17} to 3.10×10^{17} Hz? Justify clearly your answer.

Levels n	1	2	3	4	5	6
E_n (eV)	- 1362.38	- 340.60	-151.38	-85.15	-54.50	-37.84

3. In the obtained emission spectrum, identify the transition associated to a ray which wavelength equals 6.55 nm.

II. Crystallography (12/40)

Chromite $Fe_xCr_yO_z$ crystallizes in a structure such that: O^{2-} ions form a face-centered cubic lattice (FFC). The cell contains only one formula of FexCryOz.

1. Give the complete electronic configuration of Iron (Fe) and Chromium (Cr).
2. Represent the cell structure by clearly identifying the O^{2-} ions. Determine the number of O^{2-} ions per cell.
3. Give the number of tetrahedral and octahedral holes present in this cell. Represent one of each kind on two distinct figures.
4. Represent the two following planes representing the O^{2-} ions and indicating the position of the center of the interstitial holes:
    a. A plane representing a face of the cube.
    b. A plane cutting the cube in 2 and passing through 2 opposite edges

Fe^{2+} ions occupy 1/8 of the tetrahedral holes and Cr^{n+} ions occupy half of the octahedral holes. The cell parameter is a = 419 pm and radius of the O^{2-} ion is $r(O^{2-})$ = 140 pm.

5. Give the x, y and z values expected in the $Fe_xCr_yO_z$ formula and determine the charge n for the ion Cr^{n+}.
6. Considering the cation/anion tangency conditions, determine the radius of the Fe^{2+} and Cr^{n+} ions in pm.
7. Compute its density in $g.cm^{-3}$ and in $kg.m^{-3}$.

III. Chemical transformations (the three parts are independent)

A. Reduction of nitrate to nitrite by iron (II) in acidic medium (7/40) 7

The transformation of nitrate NO_3^- into nitrite NO_2^- is one of the essential reactions for the assimilation of nitrogen by plants thanks to bacteria with nitrate reductase enzymes. **Here the redox reaction, in aqueous medium, with iron ions will be modeled according to the chemical equation with the reaction constant K_T°.**

$$NO_3^- + 2Fe^{2+} + 2H_3O^+ \rightleftharpoons NO_2^- + 2Fe^{3+} + 3H_2O \qquad K_T^\circ = 681$$

1. Give the Lewis structure of NO_3^- and NO_2^- as well as all possible mesomeric formulas for each ion. *Note that nitrogen is the central atom and that there is no O-O bond in these ions.*
2. According to the VSEPR theory, predict their geometrical shapes and the observed ONO angle value.

3. For the following operating conditions and considering a total volume 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 (recall M = mol.L^{-1}).

a) $[Fe^{2+}]_0$ = 0.10 M; $[NO_3^-]_0$ =0.10 M; $[H_3O^+]_0$ = 0.10 M; $[NO_2^-]_0$ = 0 M; $[Fe^{3+}]_0$ = 0 M

b) $[Fe^{2+}]_0$ = 0.20 M; $[NO_3^-]_0$ = 0.10 M; $[H_3O^+]_0$ = 0.10 M; $[NO_2^-]_0$ =0.50 M; $[Fe^{3+}]_0$ = 0.50 M

c) $[Fe^{2+}]_0$ = 0.10 M; $[NO_3^-]_0$ = 0.037 M; $[H_3O^+]_0$ = 0.010 M; $[NO_2^-]_0$ = 0.010 M; $[Fe^{3+}]_0$ = 0.0502 M

B. Redox titration of ions Fe (II) (8/40)

The dichromate ion $Cr_2O_7^{2-}$ is a classical reagent in chemistry. It oxidizes, in acidic aqueous medium, Fe^{2+} ions into Fe^{3+} ions. We propose to use potassium dichromate ($K_xCr_2O_7$), to titrate the Fe (II) ions contained in a commercial phytosanitary product.

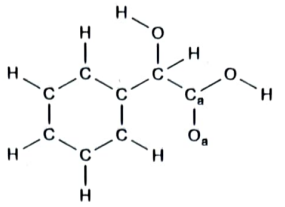
1. Give the value of x in the formula for potassium dichromate ($K_xCr_2O_7$). Justify your answer.
2. $K_xCr_2O_7$ is a strong electrolyte in water, define this term.
3. Give the 2 redox half-reactions equilibrated in acidic medium. The oxidation numbers of the elements involved in the redox process are required.
4. Give the overall redox reaction indicating the oxidant and the reductant of the reaction. Give the number of moles of electrons exchanged per mole of dichromate ions.
5. Using the standard potentials, justify that the reaction is favored in the forward direction and is quantitative.

The commercially available phytosanitary product is found as an aqueous solution, noted S in the following. The label specifies that its density is equal to 1.05 g.cm^{-3} and that its mass percentage in Fe^{2+} ions is 6%. We propose to verify the mass percentage announced by the manufacturer by titrating the Fe^{2+} ions contained in the S solution, with a solution of potassium dichromate $K_xCr_2O_7$.

The reaction of the Fe^{2+} ions, contained in S, with the $Cr_2O_7^{2-}$ ions is carried out as follows: a volume V_1 = 20.0 mL of the commercial solution S, then hydrochloric acid and a sufficient volume of distilled water are added in a beaker. Then, a solution of potassium dichromate with initial concentration $C_2 = 2.00\ 10^{-1}$ mol. L^{-1} is added. In order for all Fe^{2+} ions to react, a volume V_2 = 18.2 mL of the potassium dichromate solution $K_xCr_2O_7$ is required.

6. What is the experimental concentration thus found for Fe^{2+} ions in solution S?
7. Verify the mass percentage of Fe^{2+} ions that was provided on the label of the S solution.

C. Reaction of nitric acid with sodium mandelate (9/40)



Structure of mandelic acid to be completed

1. Complete the structure of mandelic acid given above with bonding and non-bonding pairs of electrons without adding or moving any atoms or adding charge.
2. Indicate clearly on this structure a bond between a sp^2 carbon and a sp^3 carbon. Justify your answer.
3. Describe the nature of the C_a-O_a bond defined on the structure by indicating the atomic orbitals and the type of overlaps involved. No figure is required.

To simplify, we note the mandelic acid / mandelate ion couple: RCOOH/$RCOO^-$.

4. Write the protonation reaction of $RCOO^-$ when reacting with water. Give the expression of the equilibrium constant K'°_T, compute and comment its value.
5. We are interested in the reaction of nitric acid (HNO_3) with a solution of sodium mandelate ($RCOO^-_{(aq)}$, $Na^+_{(aq)}$).
   a) Knowing that nitric acid HNO_3 is a strong acid in water, show that the equation of the reaction, without spectator ion, is then written as followed:

$$RCOO^-_{(aq)} + H_3O^+_{(aq)} \rightleftharpoons RCOOH_{(aq)} + H_2O_{(l)}$$

   b) Give the expression of the equilibrium constant K''°_T, compute and comment its value.

6. To 10.0 10^{-3} mole of sodium mandelate in 100 mL of water, **n** mol of nitric acid is added without change in volume. The obtained solution leveled up to a pH value of 2.8.

a) Establish the ratio [RCOOH]/[$RCOO^-$] at equilibrium and compute its value. Then, illustrate the state of the system using a predominance diagram given as a function of the pH.

b) After establishing the reaction advancement table, determine (in mole) the amount of nitric acid **n** added.

c) Compute the concentration of **all the chemical species** present in solution at equilibrium.

End of the subject