EC Chemistry 1 – Final exam – Duration : 3h

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

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Data:

Atomic number: carbon (C, Z=6), nitrogen (N, Z=7), oxygen (O, Z=8), phosphorous (P, Z=15) sulfur (S, Z=16), potassium (K, Z = 19), germanium (Ge, Z=32), tin (Sn, Z=50) and lead (Pb, Z=82).

Electronegativity (according to Pauling): $\chi_O = 3.5$ $\chi_C = 2.5$ $\chi_H = 2.1$ $\chi_{Sn} = 1.8$ $\chi_{Cr} = 1.6$

Molar mass: $M_{Sn} = 118.7$ g.mol^{-1} $M_O = 16$ g.mol^{-1}
$M_N = 14.0$ g.mol^{-1} $M_{Na} = 23.0$ g.mol^{-1}

Planck constant: $h = 6.626 \times 10^{-34}$ J.s
Celerity of light: $c = 2.998 \times 10^{8}$ m.s^{-1}
Avogadro's number: $N_A = 6{,}022 \times 10^{23}$ mol^{-1}
Elementary charge: $e = 1.602 \times 10^{-19}$ C

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

Selection rules for transitions between levels: only the transitions that fulfill both conditions are possible

$$\Delta \ell = \pm 1$$
$$\Delta j = 0 \text{ or } \pm 1$$

Redox couples and standard electrode potential (V):

$Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$	E° = 1.33 V
$SnO_2(s)/Sn^{2+}(aq)$	E° = 0.14V
$Pb^{2+}(aq)/Pb(s)$	E° = - 0.13V

Redox reactions can be considered as total if ΔE° > (0.4/n); n is the number of moles of electrons for the balanced global redox reactions with the stoichiometric coefficients being the smallest possible integer values.

pKa in aqueous solution: HNO_2/NO_2^- pKa =3.30
Self-dissociation of water can be neglected

I. Part I: About tin (Sn) (22 points)

Tin, the leading metal of the Bronze Age, is the chemical element of Symbol Sn (from the Latin Stannum). We propose to examine here some properties of this element.

1. What is the electronic configuration of Tin in its fundamental state? Where is it located in the periodic table of elements (period, group)?
2. Show that Tin belongs to the same column than germanium (Ge) and lead (Pb).
3. What is the first element of the given column?

At atmospheric pressure and at a temperature of 25 ° C, tin exists as a crystalline form called β. Below 13 °C, this form becomes unstable and turns into another crystalline form referred as α.

The α-form, crystallizes in a face-centered cubic structure (with atoms that sits at each corner and at the center of each face), with occupation of one tetrahedral site out of two by another tin atom. It is noted that one atom at each corner and the atom at the center of the related tetrahedral site are tangents. The density of the α-form is 5.77 g.cm^{-3}.

4. Draw the structure of the α-form, representing all the atoms contained in a cell.
5. Determine the cell parameter for the *α-form.*
6. Determine the radius of the tin atom. Calculate then the compacity (or Atomic packing factor APF). Conclusion?

7. With respecting the proportions and conditions of tangency, represent:
    - a plane corresponding to one face of the cube
    - a plane containing two parallel edges but no face of the cube.

Tin as the β-form crystallizes in a tetragonal structure with the following cell parameters: a = b = 0.580nm; c = 0.320 nm; ($\alpha = \beta = \gamma = 90$ °). There is half the number of atoms in this cell as in the cubic cell described in the preceding questions. It is considered that the radius of Tin is the same than in the α-form.

8. Calculate the density of tin in the β-form, as well as the compacity.
9. Let's consider an object made of tin with a mass m = 1.00 kg. What would be the volume occupied by this object in the α-form? In the β-form?
10. (Bonus) When a an object made of tin, initially at 25 °C, is kept several months at -40 ° C, this object is being more fragile, and can even be reduced to powder in some parts. Can you explain briefly this observation?

The preparation of the pure metal Sn is made from SnO_2, which name is "cassiterite" that is extracted from deposits taken from earth crust. The weight content in SnO_2 of a sample can be determined by the following method that involves twos successive reactions.

An initial sample of m = 0.45 g containing some $SnO_{2(s)}$ is suspended in an acidified aqueous solution. Some lead, Pb(s), added in excess, reduces Sn into the $Sn^{2+}{}_{(aq)}$ ion. It is assume that lead does not reduce anything else in the sample.

11. Write down the two half-reactions that are related to the reduction of $SnO_{2(s)}$ by $Pb_{(s)}$, specifying the oxidation numbers of the elements that change. Deduce then the global redox reaction. What is the number of moles of electrons exchanged per mole of $SnO_{2(s)}$?
12. Given the standard potential values of the two concerned redox couples, can the redox reaction be considered as total? Deduce the relationship between the number of moles of $Sn^{2+}{}_{(aq)}$ and the number of moles of initial $SnO_{2(s)}$.

When the reduction is complete, the remaining solid (including excess lead) is separated by filtration and rinsed with water, then added to the rest of the solution (aqueous phase of the reaction + rinsing solution). To this solution is then involved the second reaction in acidic medium. A volume of V = 25 mL of an aqueous solution of potassium dichromate ($K_2Cr_2O_7$), the concentration of which is C = 0.0020 mol/L, is needed to react with all the Sn^{2+} ion.

13. Write the equation of dissolution of potassium dichromate ($K_2Cr_2O_7$) in water, a reaction that is supposed to be total. Give a Lewis formula for the dichromate ion. For this, it is specified that chromium owns six valence electrons, and that the two chromium atoms are at the same oxidation state and connected by a single oxygen atom.
14. Write down the two half reactions that are related to the oxidation of Sn^{2+} ion by the dichromate ion, specifying the oxidation numbers of the elements that change. Deduce then the global redox reaction. What is the number of moles of electrons exchanged per mole of dichromate?
15. Given the standard potential values of the two concerned redox couples, can the redox reaction be considered as total? Deduce the relationship between the number of moles of Sn^{2+} and the number of moles of the dichromate ion.
16. Express literally the relationship between C, the concentration in potassium dichromate of the solution, V, the volume needed, and the number of moles of Sn^{2+}.
17. Express literally the content in $SnO_{2(s)}$, of the solid sample, expressed in weight percent $SnO_{2(s)}$ in the initial sample. Compute then this value.
18. Why is it needed to extract the excess of Pb before carrying out the second reaction?

Many tin derivatives can be used in organic chemistry, for example in the following reaction:

A B C

19. For product C, specify the hybridization state of carbons 1, 2, 3 and 4.
20. Specify (and justify) whether free rotation is possible around the following bonds:
    - Bond (*a*)
    - Bond (*b*).

II. Lewis structure, VSEPR theory (3.5 points)

21. Give the electronic configuration of nitrogen (N), phosphorous (P) and sulfur (S) with specifying the valence electrons. Represent their valence shell in the corresponding quantum boxes.
22. Give the Lewis structure, the shape according to the VSEPR theory and the bond angles for the following molecules: NCl_3, $SC1_2$ and $SC1_6$.
23. Does the NCl_5 and $PC1_5$ molecules exist? Justify succinctly.

III. Spectroscopy of alkaline metals (8 points)

The experiments considered in this problem are carried out on cesium (Cs) in gaseous state.
The values of the energy levels of Cesium (Cs) are listed in the following table:

Niveaux	E (eV)
$6S_{1/2}$	-3.899
$6P_{1/2}$	-2.511
$6P_{3/2}$	-2.443
$5D_{3/2}$	-2.099
$5D_{5/2}$	-2.087
$7S_{1/2}$	-1.598
$7P_{1/2}$	-1.197
$7P_{3/2}$	-1.174

Each level, identified as $\mathbf{n}l_j$ *is described by the three quantum numbers n, l, j*

24. Knowing that the ground level for cesium is $6S_{1/2}$ and that it is populated by a single electron, calculate the atomic number of cesium.
25. Explain why some levels, like 6P levels, are double. For such purpose, recall what the quantum number j represents and how its value is obtained.
26. From the table, compute the ionization energy of cesium (to within 0.001 eV). Will it be higher or lower than that of the element that precedes it in the periodic table (of atomic number Z = Z (Cs) - 1)?
27. Using the selection rules (that are recalled in the first page), give the lines that may be observed in the absorption spectrum considering only the levels listed in the table. Represent them on an energy level diagram.

The name of cesium comes from the Latin word caesius ("sky blue"), because of the light blue color of two lines characteristic of its emission spectrum.

28. Give the transitions and the wavelengths responsible for these two lines (to 1 nm near).
29. In another experiment, if starting from levels $5D_{3/2}$ or level $5D_{5/2}$, give the lines that would be observed in the resulting total emission spectrum.

IV. Acido-basic reaction (10 points)

Chlorhydric acid (which formula is HCl) is a strong acid in water. It is possible to prepare directly an aqueous solution by adding 0.01 mole of HCl in 1 liter of water.

30. Write down the chemical equation that occurs. Define the species that exist in solution after reaction, and give their concentration. What is the pH of the solution?

We intend to prepare an aqueous solution of nitrous acid, HNO_2. However it is not possible to add directly it in water because it is an unstable compound. For such purpose, nitrite salts that contain NO_2^- ions can be used as they are stable compounds.

1 liter of aqueous solution $\mathbf{S_0}$ is prepared by dissolving sodium nitrite $NaNO_2$, a strong electrolyte, in water. The density of the solution which contains 0.5 weight % of sodium nitrite $NaNO_2$ is d = 1.382.

31. Write down the chemical equation that occurs.. Show that the concentration of the solution $\mathbf{S_0}$ is 0.10 mol/L.

To 1 liter of the $\mathbf{S_0}$ solution is added without modification of volume, 0.010 mole of HCl. The final solution is referred as $\mathbf{S_1}$.

32. Write down the reaction that occurs. Express literally the equilibrium constant K_T, then give its value.
33. What is the composition of the solution $\mathbf{S_1}$ at equilibrium? The concentration of all the species should be provided, to within a precision of 0.01 $mol.L^{-1}$. The reasoning and process should be clearly detailed.
34. What is the pH (to within 0.1) of this $\mathbf{S_1}$ solution? Illustrate the state of the system by a predominance diagram as a function of the pH.
35. (Bonus) How much HCl (in mmol) should be added to achieve a nitrite conversion rate greater than 97% in a $\mathbf{S_2}$ solution? Represent the state of this solution on the previous diagram.

End of the exam