وزارة التربية و التعليم العاليمديريّة التعليم الثانوي		ثانوية رمال رمال الدوير الرسمية
رقم الثانويّة في المركز التربوي للبحوث و الإنماء 1157		الصّف : علوم حياة انكليزي
رقم الثانويّة في المنطقة التربويّة 5009		المادّة: كيمياء
التاريخ: 08 / 06 / 2023		مدّة المسابقة : 90 دقيقة

This exam includesof three exercises inscribed on four pages numbered from 1 to 4.
The use of a non-programmable calculator is allowed.
Answer the following three exercises:

Exercise 1 (6 points) Perchloric acid

Perchloric acid is used to separate potassium from sodium, and in many laboratory tests and industrial processes.
On the label of a bottle of commercial solution (S_0) of perchloric acid $HC\ell O_4$, we read the following information:

percentage by mass of $HC\ell O_4$ in the solution: p %
molar mass of $HC\ell O_4$: $M(HC\ell O_4) = 100.5\ g.mol^{-1}$
density of solution : $\rho = 1.67\ g.mL^{-1}$
Document-1-

The aim of this exercise is to determine the percentage by mass of perchloric acid in the commercial solution (S_0).

Given: - The study is carried out at 25°C .
- The ion product of water $K_W = 1\times10^{-14}$ at 25°C .

1- Preparation of a solution (S) of perchloric acid

A solution (S) of perchloric acid $HC\ell O_4$ ($H_3O^+ + C\ell O_4^-$) is prepared by diluting 290 times a commercial solution (S_0) of perchloric acid.

Choose, from document-2-, the convenient set used in the preparation of solution (S).

Set (1)	Set (2)	Set (3)
50 mL beaker	50 mL beaker	50 mL beaker
250 mL volumetric flask	250 mL volumetric flask	250 mL volumetric flask
5 mL graduated cylinder	2 mL volumetric pipet	2 mL graduated pipet

Document-2-

2- Behavior of sodium hydroxide in water

Available in laboratory,a bottle of sodium hydroxide solution $NaOH(Na^+ + HO^-)$ noted (S') of molar concentration $C_b = 6.31\times10^{-2}\ mol.L^{-1}$.
We measure the pH of solution (S'), we find $pH_{(S')} = 12.8$

2.1. Calculate the molar concentration of hydroxide ions ,$[HO^-]$, in the solution (S').
2.2. Deduce that sodium hydroxide is a strong base.

3- pH-metric titration of perchloric acid

A volume $V_a = 10$ ml of solution (S) of perchloric acid, is placed in a beaker then distilled water is added to immerse the electrode of pH-meter. A pH-metric titration is realized by adding progressively into the beaker the solution (S') of sodium hydroxide NaOH of molar concentration $C_b = 6.31\times10^{-2}$ mol.L^{-1} . The volume of NaOH added to reach equivalence is $V_{b.E} = 6.4$ mL.

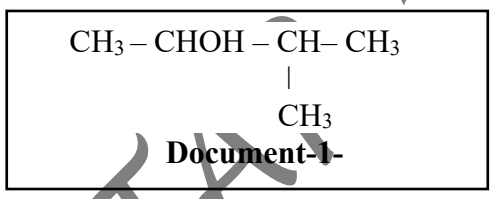
3.1. Write the net-equation of titration reaction.
3.2. Specify the value of pH at equivalence.
3.3. Show that the molar concentration (C_a) of perchloric acid in the solution (S) is equal to 4×10^{-2} mol.L^{-1}.
3.4. Deduce the percentage by mass of perchloric acid in the commercial solution (S_0).
3.5. Determine the pH of the obtained solution after addition of 10 ml of basic solution NaOH .

Exercise 2 (7 points) Esterification Reaction

Esters of general formula RCOOR' are very abundant in nature. Many of them have agreeable characteristic odor and contribute to natural or artificial tastes and flavors of certain fruits, plants, and candies.
The aim of this exercise is to study the preparation reaction of an ester (E).

1. **Study of compound (A)**

The condensed structural formula of monoalcohol (A) is given in **document-1-.**



Document-1-

1.1. Give the systematic name of (A). Indicate the class of this alcohol.

FOR LS

1.2. Show that (A) is a chiral molecule.
1.3. Represent, according to Cram, the two enantiomers of this alcohol.

FOR GS

1.1. Identify a positional isomer of (A).
1.2. Identify a skeletal isomer of (A).

2. **Identification of compound (B)**

Document-2- gives information about compound (B).

- The molecular formula of (B) is in the form of $C_xH_yO_2$.
- The analysis of (B) gives the following percentages by mol:
  % C = 25% and % H = 50%

Document-2-

2.1. Show that the molecular formula of (B) is $C_2H_4O_2$. Deduce the possible families of (B).
2.2. When the compound (B) is dissolved in water, a solution of a pH clearly less than 7 is obtained. Identify (B).

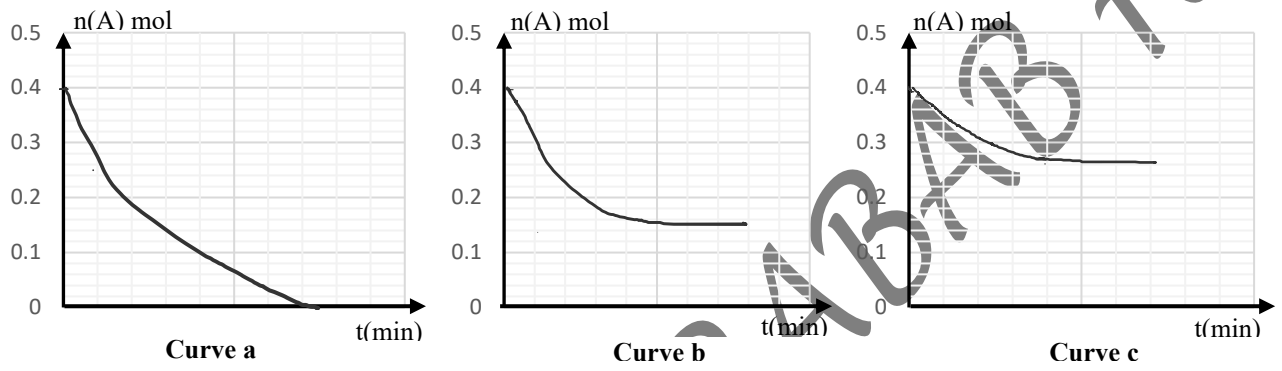
3. Synthesis of ester (E)

In order to synthesize (E), a mixture formed of n_1= 0.5 mol of (B) and n_2= 0.4 mol of (A) is heated to reflux.

3.1. Write ,using condensed structural formula , the equation of esterification reaction . List two of its charateristics.

3.2. Give the systematic name of ester (E).

3.3. Assuming that the esterification yield is 66.75 % .Choose , by justifying, from **document-3-** the curve that corresponds to the evolution of the number of moles of compound (A) as a function of time .



Document-3-

3.4. Determine the equilibrium constant of the reaction.

Exercise 3 (7 points) Kinetic Study of a Slow Reaction

A hydrochloric acid solution $HC\ell$ ($H_3O^+ + C\ell^-$) reacts with calcium carbonate $CaCO_3$ according to a slow and complete reaction as shown by the equation below:

$$2H_3O^+_{(aq)} + CaCO_{3(s)} \longrightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + 3H_2O_{(\ell)}$$

In order to study the kinetic of this reaction, one introduces a mass m g of calcium carbonate in an Erlenmeyer flask.

At instant t = 0, a volume V = 1L of a hydrochloric acid solution (S) HCl ($H_3O^+ + Cl^-$) of molar concentration C = 1 $mol.L^{-1}$ is poured into the Erlenmeyer flask.

Using an appropriate method, the number of moles of carbon dioxide gas $n(CO_2)$ is determined at different instants t.

The results are grouped in the table of **Document-1**:

t (min)	10	20	30	40	60	80	100	120
n (CO_2) 10^{-2} mol	6.0	10	14	17.5	22.5	26.5	29.5	31.0

Document-1

Given:

- Molar mass of calcium carbonate is: $M(CaCO_3)$ = 100 $g.mol^{-1}$
- The study is realized at a temperature T = 25°C.
- H_3O^+ is the only chemical species with acid character in the reacting system.

1- Preliminary study

At the end of the reaction, the pH of the obtained solution is: pH = 0.7

1.1. Deduce that $CaCO_3$ is the limiting reactant.

1.2. Show that at each instant t , the number of moles of CO_2 in mol ,$n(CO_2)_t$,and the pH of solution are related according to the following relation: $n(CO_2)_t = 0.5 - \frac{10^{-pH}}{2}$

1.3. Deduce whether t = 120 min represents the end of reaction time.

2- Kinetic study

2.1. Plot the curve that represents the change in the number of moles of carbon dioxide gas (CO_2) as afunction of time: $n(CO_2) = f(t)$ in the interval of time: [0 -120 min].

Take the following scale:

1 cm for 10 min in abscissa and 1 cm for 2.5×10^{-2} mol in ordinate.

2.2. Determine the average rate of formation of CO_2 between the times t_1=10 min and the time t_2 = 80 min. Deduce the average rate of disappearance of H_3O^+ between t_1 and t_2 .

2.3. Determine, graphically, the half-life time ($t_{½}$) of this reaction.

2.4. The experiment realized at the beginning of the exercise is carried out again but with only modification: the flask is placed in a water bath at temperature T' = 5°C.

Choose, with justification, the correct answer:

2.4.1. The number of moles of CO_2 at instant t = 40 min is:

a) $n(CO_2) > 17.5\times10^{-2}$ mol ; **b)** $n(CO_2) < 17.5\times 10^{-2}$mol ; **c)** $n(CO_2) = 17.5\times 10^{-2}$ mol

2.4.2. the half-life time ($t_{½}$) of this reaction:

a) decreases **b)** increases **c)** remains the same