This Exam Includes **Three Exercises.** It Is Inscribed On Three Pages Numbered From **1** to **3**.
The Use of a Non-programmable Calculator Is Allowed.

Answer the Following Three Exercises:

First Exercise (7 points)
A Study of a Scale Removal, ˝W. C. NET ˝

On the label of a scale removal ˝ W. C. NET ˝, the following information is noted: contains hydrochloric acid of 13.5 % by mass.
The determination of the density of this liquid gives the following value: d = 1.07 $g.mL^{-1}$.
The purpose of this exercise is to verify the indication 13.5 % by titration using pH - meter.

Given :

- $M_{HCl} = 36.5\ g.mol^{-1}$.
- $pK_a (H_3O^+/H_2O) = 0$; $pK_a (H_2O/HO^-) = 14$.

I- Dilution of the Scale Removal

1- Show, according to the above indication, that the concentration of hydrochloric acid in the scale removal is $C_0 = 3.92\ mol.L^{-1}$.

2- To perform the titration of the above scale removal, it is required to dilute this product 50 times. Choose, among the following list, the convenient glassware used to perform this dilution. Justify your choice.
 - 50, 100 and 200 mL beakers;
 - 5, 10 and 20 mL volumetric pipets;
 - 100, 200 and 500 mL volumetric flasks.

The obtained diluted solution is called (S_a).

II- Carrying Out Titration

A volume V_a = 10 mL of solution (S_a) is titrated with a sodium hydroxide solution of concentration $C_b = 7.8x10^{-2}\ mol.L^{-1}$.

1- Write the equation of the titration reaction and calculate its constant K_R.

2- The results of the pH-meter titration are given in the following table:

V_b(mL)	0	2	4	6	8	9	9.5	10	10.5	11.5	12	12.5	14	16
pH	2.4	2.5	2.6	2.7	2.9	3.1	3.3	3.5	4.4	9.6	10.0	10.3	10.6	10.8

Plot, on the provided graph paper, the curve pH = f(V_b).
Take the following scale: abscissa (1 cm for 2 mL); ordinate (1 cm for 1 pH unit).

3- Determine:
  a) The coordinates of the equivalence point by the parallel tangents method.
  b) The concentration of solution (S_a).

4- Deduce, according to the titration results, the percentage by mass of HCl in the scale removal “W. C. NET.” Specify if the information on the label is verified when the acceptable range of error is up to 5 %. .

Third Exercise (6½ points)
Kinetic of the Oxidation of Iodide Ions by Hydrogen Peroxide

It is suggested to study the oxidation of iodide ions by hydrogen peroxide solution. This slow reaction takes place according to the following equation:

$$2\,I^- + H_2O_2 + 2\,H_3O^+ \rightarrow I_2 + 4\,H_2O.$$

At time t = 0, a volume V_1 = 60 mL potassium iodide solution of concentration C_1 = 0.1 mol.L^{-1} is mixed , in a beaker, with a volume V_2 = 40 mL of an acidified hydrogen peroxide solution of concentration C_2 = 0.06 mol.L^{-1}.

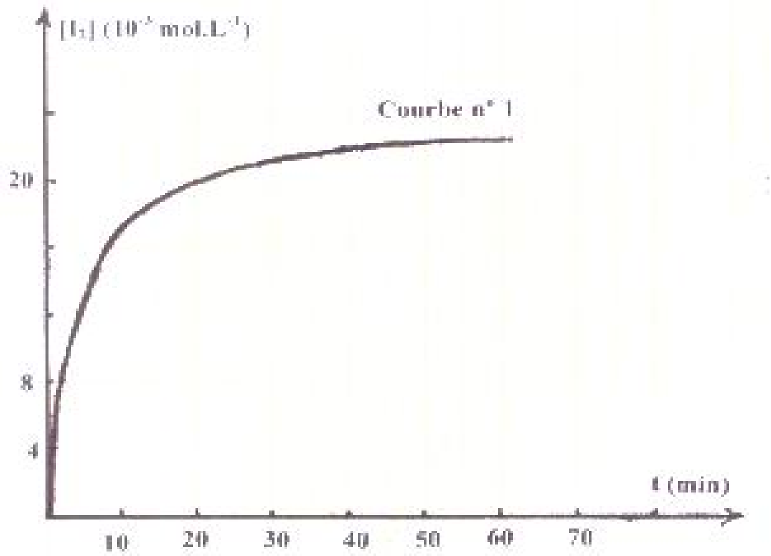
I- Preliminary Study

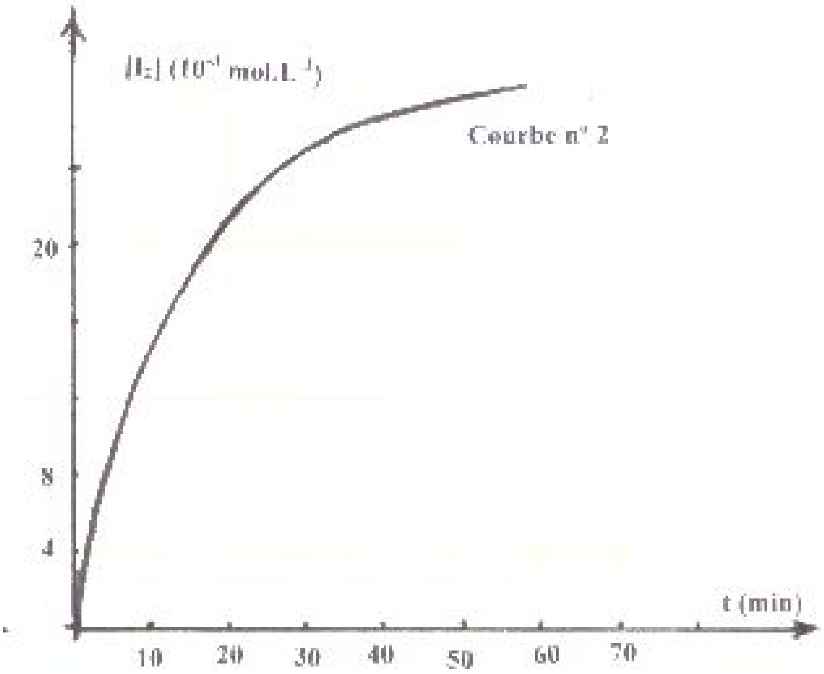
1- Calculate the concentration of iodide ions, $[I^-]_0$, and of hydrogen peroxide, $[H_2O_2]_0$, in the mixture at t = 0.

2- Determine the limiting reactant.

II- Kinetic Factors

1- Choose the curve that represents the variation of the concentration of I_2 as a function of time. Justify





2- The kinetic study of this reaction is performed with an appropriate setup. The curve that represents the variation of the concentration of iodine versus time is drawn. Two tangents are drawn on this curve at two different points and then their corresponding slopes are calculated. The obtained values are : $S_8 = 6.3 \times 10^{-4}$ mol.L^{-1}.min^{-1} at t = 8 min and $S_{20} = 2 \times 10^{-4}$ mol.L^{-1}. min^{-1} at t = 20 min.

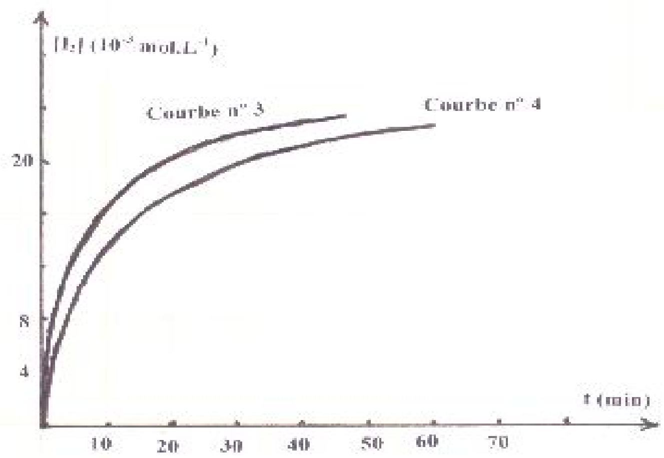
a) Based on this information, deduce the rate of disappearance of I^- at t = 8 min and t = 20 min.

b) By comparing the two rates, specify the involved kinetic factor.

3- Determine at $t_{1/2}$, the half-life of the reaction, the concentration of $[I^-]_{1/2}$.

4- We repeat, by using the same initial mixture, the kinetic study of the reaction at two different temperatures: θ_A = 25 ºC and θ_B = 35 ºC. The two curves (nº 3 and nº 4) that represent the concentrations of I_2 versus time, at the two temperatures, are shown on the graph below.

- Attribute the curve that corresponds to each temperature and justify.



Second Exercise (6½ points)
A Chlorination Agent : PCl_5

The phosphorous pentachloride, PCl_5 is a white solid, at room temperature. It is a strong chlorination agent used in organic chemistry.

Given:
Molar atomic mass in $g.mol^{-1}$: $M_H = 1$; $M_C = 12$; $M_O = 16$; $M_P = 31$; $M_{Cl} = 35.5$.
Molar mass of air is 29 $g.mol^{-1}$.

I- PCl_5 Is an Unstable Compound

At 100 ºC and above, gaseous phosphorous pentachloride decomposes according to the following equation: $PCl_{5\,(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$.

1 mol of PCl_5 is introduced in a thermal reactor where the temperature could change from 100 ºC to 350 ºC. The decomposition of PCl_5 is followed by determining the density of the gaseous mixture relative to air ***(d)***, at different temperatures. The obtained results are given in the following table (1):

Temperature (º C)	100	150	200	350
Relative density ***(d)***	7.2	5.4	4.3	3.6

1- Rewrite the table (2) below, on the answer sheet, and complete it in terms of α, where α is the degree of dissociation of PCl_5.

	PCl_5	PCl_3	Cl_2
Initial state (mol)	1	0	0
Equilibrium state (mol)			

2- Show that α and ***d*** are related to each other by the following relation: $d = \dfrac{208{,}5}{29(1+\alpha)}$.

3- Based on the contents of the table (1), deduce if the decomposition reaction of PCl_5 is endothermic or exothermic.

II- Chlorination Agent in Organic Chemistry

Phosphorous pentachloride reacts, at room temperature, with a carboxylic acid A, having a saturated carbon chain, according to the reaction of the following equation:

$$A + PCl_5 \rightarrow B + HCl + POCl_3.$$

1- Determine the molecular formula of A. Write the condensed structural formula of A and of B and give the name of each. $M_A = 60\ g.mol^{-1}$.

2 To prepare an ester having the banana oder, it is required to perform one of the two following reactions:
Reaction (1): the acid A is mixed with the alcohol 3-methyl-1-butanol ;
Reaction (2): the compound B is mixed with the alcohol 3-methyl-1-butanol.
a) Among the following terms, choose the convenient terms that characterize each one of the two reactions (1) and (2): athermic, complete, exothermic, reversible and endothermic.
b) Write the equation of the reaction between the acid A and the alcohol 3-methyl-1-butanol.
c) Deduce the advantage that results from the action of PCl_5 on acid A to give compound B in the preparation of esters.