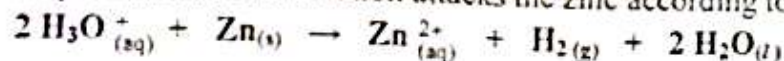


First exercise: Kinetics of the reaction between the hydrochloric acid and zinc (9.5pts)

A hydrochloric acid solution attacks the zinc according to the following reaction equation :



The purpose of this exercise is to study the kinetics of this reaction.

Given:

- Molar atomic mass : $M_{\text{Zn}} = 65.4 \text{ g mol}^{-1}$.

1- Preliminary Study

At time $t = 0$, poured $V_a = 40 \text{ mL}$ of a hydrochloric acid solution of concentration $C_a = 0.500 \text{ mol.L}^{-1}$ in a beaker containing a mass $m = 1 \text{ g}$ of zinc powder . It is assumed that the volume of the reaction mixture remains constant.

The hydrogen gas formed over time was collected and its volume is measured under conditions where the gas is molar volume $V_m = 25 \text{ L.mol}^{-1}$.

1.1- Explain the advantage of using zinc powder and not a strip of zinc in this study.

2- Preparation of the solution (S)

The solution S hydrochloric acid was prepared from a commercial solution of hydrochloric acid contained in a bottle do the label contains the following information:

Percentages by mass : 32% ; Density : $D = 1.14 \text{ g.ml}^{-1}$

$M(\text{HCl}) = 36.5 \text{ g mol}^{-1}$

2.1 - Show that the commercial solution of hydrochloric acid at a concentration close to $C_0 = 10 \text{ mol.L}^{-1}$.

2.2- Describe the procedure to prepare 100 ml of solution (S).

3- Kinetics of the reaction

The results of this experiment are grouped in the following table :

t (s)	0	50	100	150	200	250	300	400	500	750
V_{H_2} (mL)	0	36	64	86	104	120	132	154	170	200

3.1- Justify if the instant $t = 750 \text{ s}$ is the date that marks the end of the reaction.

3.2- Calculate, at each time t , the amount of H_2 "n (H_2) in mol" (Give the results in a table).

Handwritten note: $C_0 = 10 \text{ mol.L}^{-1}$

Handwritten calculation: $\frac{10}{0.55} = 0.270$

3.3- Draw on graph paper, the curve representing the variation of $n(\text{H}_2)$ as a function of time $n(\text{H}_2) = f(t)$.

Take the following scale : abscissa : 1 cm = 50 s abscissa axis:

ordonnée: 1 cm = 0.5×10^{-3} mol ordonnte axis.

3.4- Determine the average rate of formation of H_2 in the interval of time (50s----100s).

3.5.1- The rate of formation of H_2 in the experiment is determined at $t = 0\text{s}$ and $t = 200\text{s}$.

The obtained values are: $r = 1.3 \times 10^{-5} \text{ mol.s}^{-1}$ and $r = 5 \times 10^{-5} \text{ mol.s}^{-1}$.

Relate, by justifying, each rate to its corresponding time.

3.5.2- Deduce the maximum rat of the reaction.

3.6- Determine graphically the half -life reaction.

3.7. Establish the following relation: $[\text{H}_3\text{O}^+]_t = [\text{H}_3\text{O}^+]_0 - 2.10^{-3} V(\text{H}_2)$.

3.8- Draw the shape of the curve $[\text{H}_3\text{O}^+] = g(t)$ specifying the points corresponding to

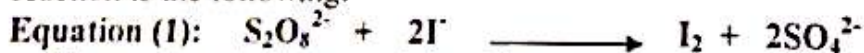
$t = 0$; $t = t_{1/2}$ and $t = 750 \text{ s}$.

3.9- We repeat the experiment with the same mass of zinc, but poured into the flask 40 ml of hydrochloric acid concentration 1 mol.l^{-1} on the same graph in question (3.3), draw the shape of the curve $n(\text{H}_2) = g(t)$ in the time interval 0 ----- 750 s. Justify your answer.

Second exercise: Kinetic of the reaction between iodide ions and peroxydisulfate ions (5pts)

We propose to study experimentally the evolution of rate of reaction of a product in a chemical reaction

In this experiment, we study the rate of formation of iodine with respect to time in the oxidation-reduction reaction between iodide ions I^- and peroxydisulfate ions $\text{S}_2\text{O}_8^{2-}$. The equation of the slow reaction is the following:

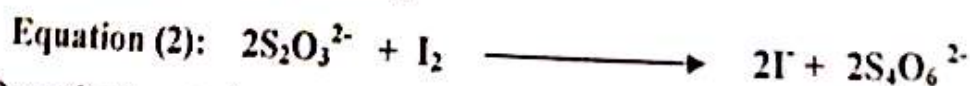


We prepare a beaker containing $V_1 = 400 \text{ mL}$ of potassium peroxydisulfate solution ($2\text{K}^+ + \text{S}_2\text{O}_8^{2-}$) of concentration $C_1 = 0.04 \text{ mol.L}^{-1}$ and in a second beaker containing $V_2 = 400 \text{ mL}$ potassium iodide ($\text{K}^+ + \text{I}^-$) of concentration $C_2 = 0.4 \text{ mol.L}^{-1}$.

At instant $t = 0$, we mix the contents of the two beakers, using a chronometer, we mesure the concentration of I_2 in different interval of time by taking different samples such that:

A few seconds before instant t , we take a sample of volume $V = 5 \text{ mL}$ from the reactional mixture and at instant t , we introduce the sample in a beaker containing 50 mL of glass water, before the titration, we add some drops of starch solution in the beaker. Then to determine the concentration of iodine solution, we add a volume V' of thiosulfate ions $\text{S}_2\text{O}_3^{2-}$ of concentration $C' = 10^{-2} \text{ mol.L}^{-1}$ to the iodine solution to decolorize.

The titration equation is the following:



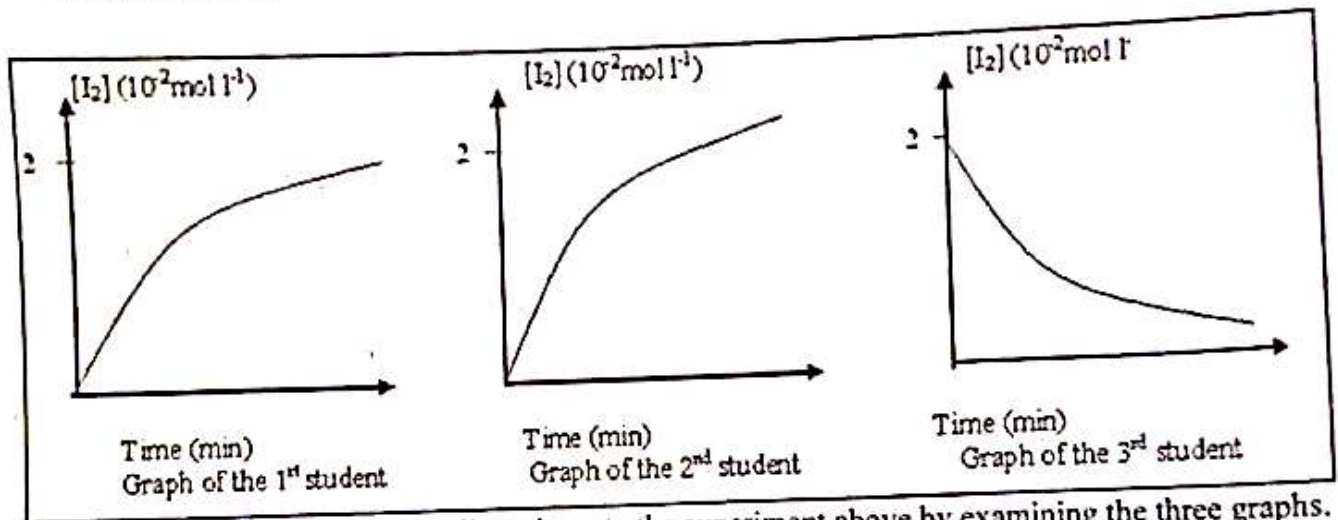
1- Quantitative study:

1.1- Calculate the initial molar concentrations of chemical species $\text{S}_2\text{O}_8^{2-}$ and I^- .

1.2- Determine the maximum concentration of I_2 , Which is produced in the beaker.

2-Kinetic study:

- 2.1- Compare the rate of the two reactions (1) and (2). Specify if we can study the rate of the second reaction.
- 2.2- Give the role of cold water and indicate the kinetic factors involved in this step done before titration.
- 2.3- Establish the following relation: $n(I_2)_t = [S_2O_3^{2-}] \times V_e/2$, knowing that V_e = volume of thiosulfate at equivalence point.
- 2.4- Determine the maximum volume of thiosulfate necessary to titrate a sample of iodine.
- 2.5- Three students plot the following shapes of the curve of concentration of iodine as function of time given above.



Specify the corresponding shape to the experiment above by examining the three graphs.

Third exercise: (5.5 pts)

Esterification reaction

At a constant temperature T_1 , a mixture is prepared consisting of 0.4 mol of ethanoic acid CH_3COOH and (n mol) of ethanol CH_3CH_2OH ($n < 0.4$ mol) in the presence of a few drops of concentrated sulfuric acid.

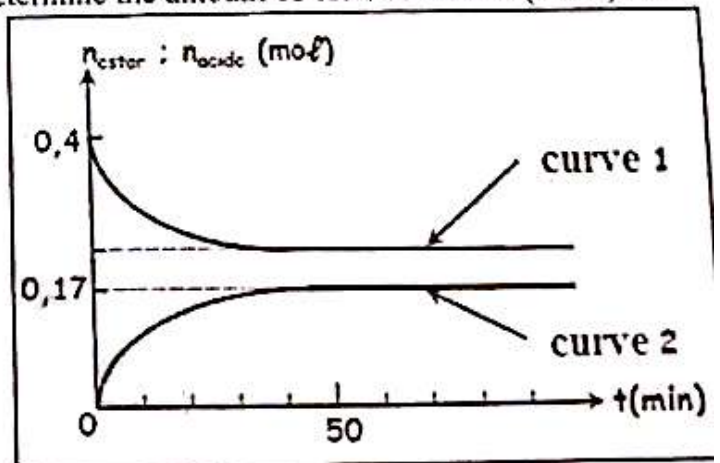
The equation of the reaction is: $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

Using an appropriate experimental procedure, we determine the amount of ester formed n (ester) and acid remaining n (acid) at different times. This helps to draw the curves in the adjacent figure:

Given: Density of ethanol = 0.789 g.ml^{-1} ;
 $M_{\text{ethanol}} = 46 \text{ g.mol}^{-1}$.

1-qualitative study:

- 1.1- Give the role of few drops of concentrated sulfuric acid.



2- Equilibrium reaction:

2.1-Prove that the initial number of mol of alcohol is $n = 0.2 \text{ mol}$, knowing that the volume of alcohol remained at equilibrium is $V = 1.75 \text{ ml}$

2.2- Based on the adjacent figure, draw out two characteristics of this reaction.

2.3-Specify the time when the system is in a state of dynamic equilibrium.

2.4- Determine the molar composition of the mixture when the dynamic equilibrium is reached.

2.5 - Show that the value of the equilibrium constant K_C relating to the esterification reaction is $K_C = 4.188$.

2.6.1-Copy and complete the following table in terms of n and α ; where α is the degree of transformation of ethanol.

	CH_3COOH	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	H_2O
Initial state (mol)	$2n$	n		
Equilibrium state (mol)				

2.6.2- Show that the expression of the constant K_C of this equilibrium, in terms of α is as follows: $K_C = \alpha^2 / (2-\alpha)(1-\alpha)$

2.6.3-The mathematical resolution of the quadratic equation found in the preceding question gives the two following values of α : 0.85 and 3.09 ; deduce the percentage of transformation of alcohol in this reaction.