

Experiments in Physical Chemistry
(Chemical Kinetics)

Third Stage
First Course

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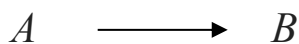
2024 -2025

Introduction

Kinetic Chemistry: is a study of the speed and mechanics of chemical reactions.

Rate of reactions(R): Is the average of change in the concentration of reactants or products in the unit of time(M/min).

Reactants $\longrightarrow$ Products



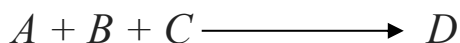
$$R = \frac{d[B]}{dt}$$

Since reactants go away with time:

$$R = - \frac{d[A]}{dt}$$

Rate Law: The rate of reaction is directly proportional to the concentration of the reactants raised to certain bases called (reaction order)

Example:



$$R \propto [A]^{\alpha} [B]^{\beta} [C]^{\gamma} \longrightarrow R = k[A][B][C]$$

$$n = \alpha + \beta + \gamma$$

R: reaction rate

k: rate constant

n: reaction order

Reaction Order(n): Is the sum of the forces of the concentration limits in the differential equation of the law of reaction rate and can be (0 or 1 or 2 or 3 or fractional number).

Rate Constant (k): Is the change in the concentration of reactants or products substances in the unit of time, the unit of rate constant is $[(\text{unite})^{1-n} \cdot \text{time}^{-1}]$ where (unite = (mol/L) or (ml) or (atm) etc.

Half – life Time ($t_{1/2}$): Is the time required to complete 50% of the reaction or the time required to consume half of the reactant substance.

So what is the benefit of each terms that mentioned?

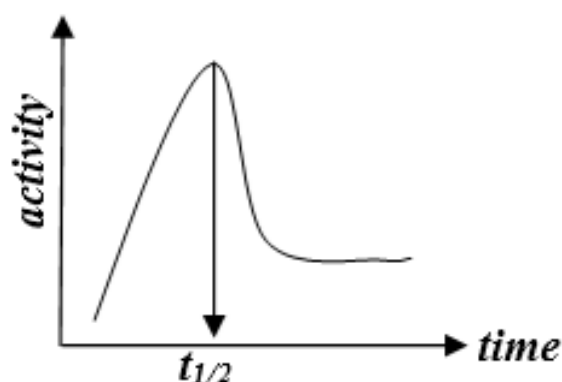
1) Rate of reactions(R): *In order to know whether the reaction is fast or not?*

Through the law $R = \frac{\Delta[]}{\Delta t}$, since R is inversely proportional to time.

2) Reaction Order(n): *To know the reactants or participate in the reaction.*

3) Rate Constant (k): *To find out whether the reaction is occurring or not.*

4) Half – life Time ($t_{1/2}$): *To find out the time required for half of the reactants to be consumed. Therefore, we extract the half-life, not the total life, because the reactant's effectiveness is great and increasing for a certain period of time, then the effectiveness of the reactants decreases because their concentration decreases.*



Experiment (1)

Determination the rate constant (k_1) and half-life time ($t_{1/2}$) of the hydrolysis of methyl acetate in acid medium:

Theory: methyl acetate is readily hydrolyzed to give methanol and acetic acid:



The reaction is catalyzed by hydrogen ions. The rate constant for first order reaction can be calculated from the following equation:

$\text{Ln} (a / a-x) = k_1 t$	or	$\text{Ln} (V_\infty / V_\infty - V_t) = k_1 t$
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This reaction is (pseudo first order)

The unit of (k_1) is [time^{-1}] or [min^{-1} , sec^{-1} , hr^{-1} , ect.]

The half-life time ($t_{1/2}$) can be calculated from the following equation:

$t_{1/2} = 0.693 / k_1$

Procedure:

1- Take (5)ml from stock solution of methyl acetate, put it in the beaker then add (100)ml of (0.1N) HCl but not opposite (be sure not losing any volume of methyl acetate on the wall of glass) and start recording the time at the beginning of the reaction. Put the mixture in water bath at (30-35°C).

2- After (5)min of the reaction beginning withdraw (10)ml from the mixture to the conical flask, add (20)ml of distilled water (D.W.) (slows down the reaction) and add (2) drops of phenolphthalein indicator.

3- Titrate with (0.1N) NaOH and record the volume of NaOH that descending from the burette immediately after appearance of pink color.

4- Repeat steps (2 and 3) every (5)min to calculate (V_t) according to these times (5, 10, 15, 20, 25)min.

5- To calculate (V_∞) these are two ways:

a-(Condensation): Take (10)ml from the reaction mixture from the beginning reaction in to dry conical flask, connected to condenser, start the reaction for 1hr, then rise the condenser from up end of the conical flask, add (2) drops of phenolphthalein indicator and titrate against (0.1N) NaOH.

b- Leave the reaction mixture for 24hr, then add (2) drops of phenolphthalein indicator and titrate against (0.1N) NaOH.

Calculations and graph:

V_o : volume of NaOH descending from the burette at ($t = 0$)

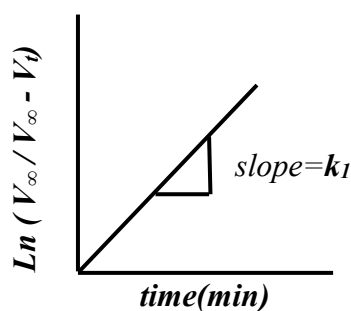
V_t : volume of NaOH descending from the burette at($t = t$)

V_{∞} : volume of NaOH descending from the burette at the end of reaction

1- Arrange the results according to the following table:

Time (min)	V_t (ml)	V_{∞} (ml)	$(V_{\infty} - V_t)$ (ml)	$(V_{\infty} / V_{\infty} - V_t)$	$\text{Ln} (V_{\infty} / V_{\infty} - V_t)$
5					
10					
15					
20					
25					

2- Plot a graph of $\text{Ln} (V_{\infty} / V_{\infty} - V_t)$ against (t) and from the slope determine the rate constant (k_1), then determine the half-life time($t_{1/2}$).



Discussion:

- 1) The order reaction of hydrolysis methyl acetate is pseudo first order. Why?
- 2) H_2O takes part in the reaction but not in the rate law. Why?
- 3) During titration, NaOH reaction with CH_3COOH not with HCl. Why?
- 4) Add (100ml) HCl (0.1M) to (5ml) of methyl acetate, not opposite. Why?
- 5) Add (20ml) cold D.W. to the mixture titration?



Experiment (2)

Determination the rate constant (k_2) and half-life time ($t_{1/2}$) of the saponification of ethyl acetate and sodium hydroxide at equal concentration

Theory: the saponification of ethyl acetate is taking place according to the following equation:



The rate constant for second order reaction can be calculated from the following equation:

$$1/(a - x) = 1/a + k_2 t \quad \text{or} \quad 1/(V_\infty - V_t) = 1/V_\infty + k_2 t$$

The unit of (k_2) is $[\text{mol}^{-1} \cdot \text{L} \cdot \text{min}^{-1}]$ or $[\text{ml}^{-1} \cdot \text{min}^{-1}]$

The half-life time ($t_{1/2}$) can be calculated from the following equation:

$$t_{1/2} = 1/a k_2 \quad \text{or} \quad t_{1/2} = 1/V_\infty k_2$$

Procedure:

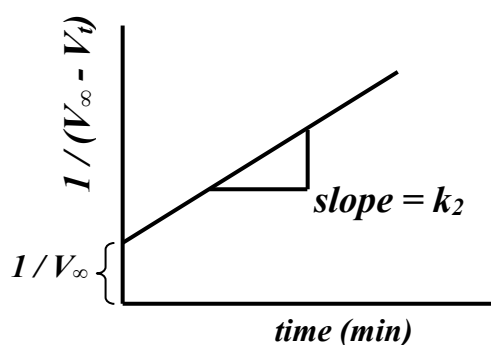
- 1- Take (50)ml of (0.05N) ethyl acetate, put it in the beaker then add (50)ml of (0.05N) NaOH and start recording the time at the beginning of the reaction. Put the mixture in water bath at (30-35°C).
- 2- After (3)min of the reaction beginning withdraw (10)ml from the mixture to the conical flask, add (10)ml distilled water (D.W.) (slows down the reaction) and (10)ml of (0.025N) HCl (stop the reaction) then add (2) drops of phenolphthalein indicator.
- 3- Titrate with (0.025N) NaOH and record the volume of NaOH that descending from the burette immediately after appearance of pink color.
- 4- Repeat steps (2 and 3) every (3)min to calculate (V_t) according to these times (3, 6, 9, 12, 15)min.

Calculations and graph:

- 1- Arrange the results according to the following table:

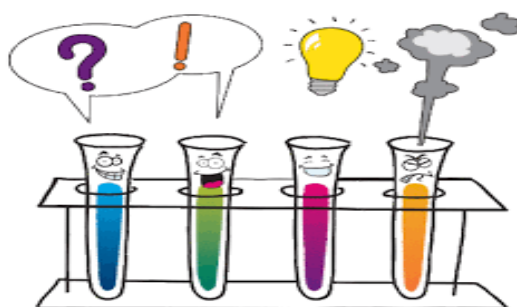
Time (min)	V_t (ml)	V_∞ (ml)	$(V_\infty - V_t)$ (ml)	$1 / (V_\infty - V_t)$ (ml) ⁻¹
3				
6				
9				
12				
15				

2- Plot a graph of $1/(V_\infty - V_t)$ against (t) and from the slope determine the rate constant (k_2), then determine the half-life time($t_{1/2}$).



Discussion:

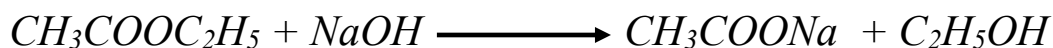
- 1) The saponification of ethyl acetate is second order reaction. Why?
- 2) What is the purpose of adding (10 ml) HCl (0.025M) to (10 ml) of reaction mix?
- 3) Calculate the concentration of reactants after mixed. Why?
- 4) In saponification of ethyl acetate, we recorded (V_t) value each (3min.) while in hydrolysis of $\text{CH}_3\text{COOCH}_3$ each (5min.). why?



Experiment (6)

Determination the rate constant (k_2) of ethyl acetate and sodium hydroxide at different concentration

Theory:



This reaction is a second order. The rate constant can be calculated from the following equation:

$$\ln [b(a-x) / a(b-x)] = (a-b) k_2 t$$

Procedure:

- 1- Take (50)ml of (0.08N) ethyl acetate, put it in the beaker then add (50)ml of (0.05N) NaOH and start recording the time at the beginning of the reaction.
- 2- After (3)min of the reaction beginning withdraw (10)ml from the mixture to the conical flask, add (10)ml distilled water (D.W.) (slows down the reaction) and (10)ml of (0.025N) HCl then add (2) drops of phenolphthalein indicator.
- 3- Titrate with (0.025N) NaOH and record the volume of NaOH that descending from the burette immediately after appearance of pink color.
- 4- Repeat steps (2 and 3) every (3)min to calculate (V_t) according to these times (3, 6, 9, 12, 15)min.

Calculations and graph:

- 1- Calculate the concentration of $\text{CH}_3\text{COOC}_2\text{H}_5$ in the reaction mixture at ($t = 0$) by dilution law:

$$\begin{aligned} N_1 \times V_1 &= N_2 \times V_2 \\ 0.08 \times 50 &= N_2 \times 100 \\ N_2 &= 0.04 \text{mol/L} = a \end{aligned}$$

- 2- Calculate the concentration of NaOH in the reaction mixture at ($t = 0$) by dilution law:

$$\begin{aligned} N_1 \times V_1 &= N_2 \times V_2 \\ 0.05 \times 50 &= N_2 \times 100 \\ N_2 &= 0.025 \text{mol/L} = b \end{aligned}$$

- 3- Calculate the concentration of NaOH remaining ($b-x$) using dilution law at ($t = t$)

$$\begin{aligned} N_1 \times V_1 &= N_2 \times V_2 \\ 0.025 \times (10 - V_t) &= N_2 \times 10 \end{aligned}$$

Repeat this step every (3, 6, 9, 12, 15) min

4- Calculate (x) value which represent CH_3COONa :

$$\begin{aligned} b-x &= \text{from step 3} \\ b &= \text{from step 2} \\ x &= ? \end{aligned}$$

repeat this step every (3, 6, 9, 12, 15)min

5- Calculate the remaining concentration of $\text{CH}_3\text{COOC}_2\text{H}_5$ (a-x):

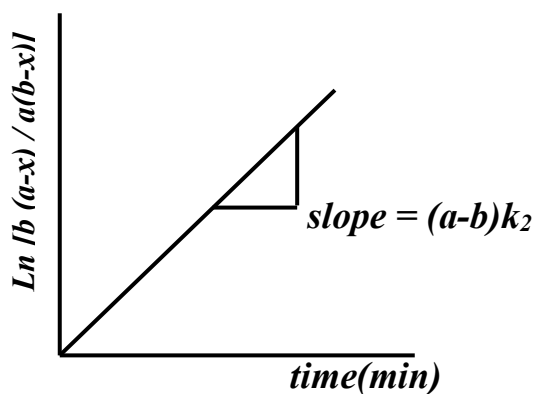
$$a-x = 0.04 - \text{value step 4}$$

repeat this step every (3, 6, 9, 12, 15)min.

6- Arrange the results according to the following table:

Time(min)	V_t (ml)	(b-x)	X	(a-x)	$b(a-x) / a(b-x)$	$\text{Ln}[b(a-x) / a(b-x)]$
3						
6						
9						
12						
15						

7- Plot a graph of $[b(a-x) / a(b-x)]$ against (t) and from the slope determine the rate constant (k_2).



Discussion:

1- Can we find the half-life time($t_{1/2}$) for this experiment? Why?

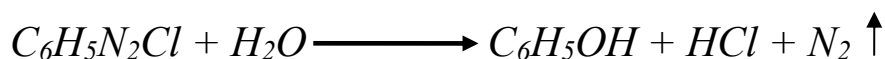
2- If used NaOH with high volume, the reaction will be first or second order?



Experiment (7)

Determination the rate constant (k) and half-life time ($t_{1/2}$) of the Decomposition of Benzene Diazonium Chloride

Theory: Benzene diazonium chloride is hydrolyzed in water according to the following equation:



This reaction is a pseudo first order. The rate constant for the first order can be calculated from the following equation:

$$\text{Ln}(a-x) = \text{Ln } a - k_1 t \quad \text{or} \quad \text{Ln}(V_\infty - V_t) = \text{Ln } V_\infty - k_1 t$$

The half-life time ($t_{1/2}$) can be calculated from the following equation:

$$t_{1/2} = 0.693 / k_1$$

Procedure:

By use the (Hempel as burette):

1- The level of the water inside the two burette should be the same, put burette A near burette B (which is closed) that the level of the solution inside burette A should be at level 50ml while burette B at level zero.

2- The conical flask is closed with rubber which led to decrease the solution level inside burette B. make the level inside two burette equal, record (V_o) (it's the out flow of the system, it represent to the different between the two burette caused from pressure different), its value subtracted from the measured values, that it measure volume (V_t).

3- Add (5)ml of benzene diazonium chloride then (10)ml distilled water inside conical flask and close by rubber.

4- After the reaction is proceed with shaking , calculate the beginning reaction time. Measure (V_t). for each 5min (5, 10, 15,20,25)min to be five reading.

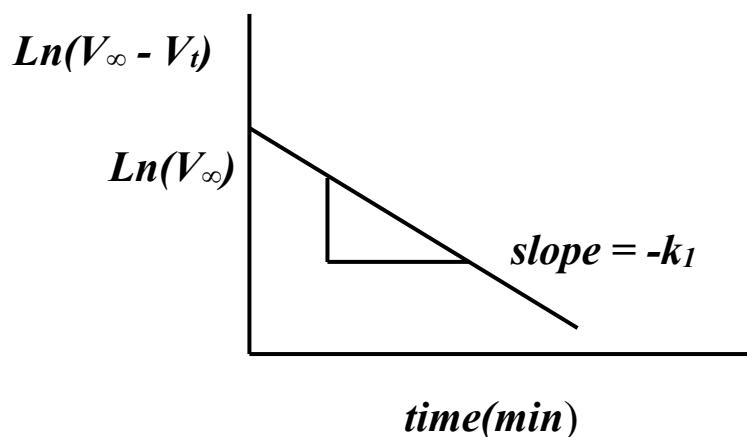
5- Measure (V_∞): put the conical flask which contain the reaction mixture in the water bath at temperature of 90°C to decompose all the salt, until the solution in burette reach to (50)ml, then cool down the conical flask in cold water bath. Put the conical flask again in the water bath at 90°C and cool down again, take the average and measure (V_∞).

Calculations and graph:

1- Arrange the results according to the following table:

<i>Time (min)</i>	<i>V_o (ml)</i>	<i>V_∞ (ml)</i>	<i>Ln(V_∞)</i>	<i>(V_t-V_o) (ml)</i>	<i>(V_∞ -V_t) (ml)</i>	<i>Ln(V_∞ - V_t)</i>
5						
10						
15						
20						
25						

2- Plot a graph of [Ln(V_∞ - V_t)] against (t) and from the slope determine the rate constant (k₁), then determine the half-life time(t_{1/2}).



Experiment (4)

Effect of Temperature on the Rate Reaction

(Calculation the Activation Energy and Frequency Factor)

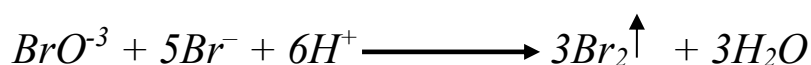
Theory: Bromide is reacted with bromate according to the following equation:



The rate equation of this reaction is represented by:

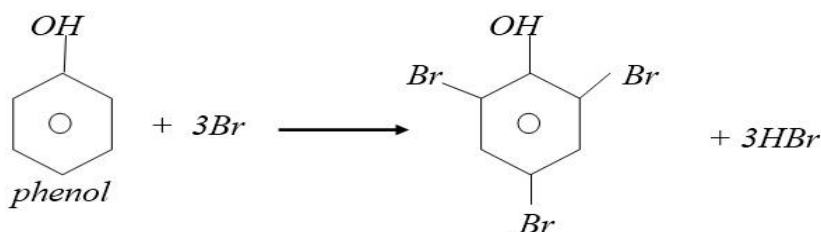
$$-d[\text{BrO}^-] / dt = k [\text{BrO}^-]^x [\text{Br}^-]^y [\text{H}^+]^z$$

In order to better understand the bromate-bromide reaction, it is important to take note of the stoichiometric equation, which is noted as:



This reaction couples with the reaction of Br_2 and methyl orange, which produces bleach. By combining the two reactions, the basis is built for determining the rate of the reaction. As bromate BrO^- and bromide Br^- react, they produce Br_2 , which then reacts with methyl orange to dissipate the color of the solution and show completion of the reaction. This dissipation of color can be timed and used for calculation.

However, this reaction happens very quickly, and under normal circumstances would not be able to be timed. By adding phenol to the solution, the reaction of Br_2 with methyl orange can be slowed down with the following side reaction:



This reaction of Br_2 with phenol slows down the reaction with methyl orange enough that it is able to be timed and indicate the end of the reaction by change the mixture color.

The rate constant can be calculated by (Arrhenius equation):

$$k = A \cdot e^{-E_a / RT} \implies \ln k = \ln A - E_a / RT$$

the time required to remove the color of reagent after mixing the reactants is inversely proportional with the rate of reaction:

$$\text{Rate} \propto 1/t$$

1

When this reaction takes place at different temperature, its activation energy can be calculated as follows:

Total Mass
22.17226
120.00000
0.00000
0.00000
0.00000
0.00000
0.00000
142.17226

$$\text{Rate} = A \cdot e^{-E_a / RT} \implies 1/t = A \cdot e^{-E_a / RT}$$

1

$$\ln 1/t = \ln A - E_a / RT$$

Ion Type	# of Atoms	Mass	Total Mass
Hydrogen	22	1.00783	22.17226
Carbon	10	12.00000	120.00000
Nitrogen	0	14.0031	0.00000
Oxygen	0	15.9949	0.00000
Sulfur	0	31.9721	0.00000
Bromine	0	78.9183	0.00000
Exact Mass			142.17226

Procedure:

1- Add (2.5)ml of $[\text{KBr} + \text{KBrO}_3]$ mixture and (2.5)ml of (0.01)N phenol to the test tube number 1.



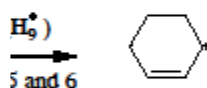
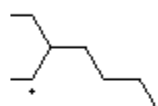
2- Add (6)ml of (0.3)N H_2SO_4 and 2 drops of red methyl indicator to the test tube number 2.



3- Put the two test tubes in water bath at $(40)^\circ\text{C}$ until reaching the thermal equilibrium, then add the test tube number 2 to the test tube number 1 and note the time until disappearance of red color to yellow.

Ion Type	# of Atoms	Mass	Total Mass
Hydrogen	18	1.00783	18.14094
Carbon	10	12.00000	120.00000
Nitrogen	0	14.0031	0.00000
Oxygen	0	15.9949	0.00000
Sulfur	0	31.9721	0.00000
Bromine	0	78.9183	0.00000
Exact Mass			138.14094

4- Repeat steps (1-3) by different temperatures $(50, 60, 70)^\circ\text{C}$.



Calculations and graph:

1- Arrange the results according to the following table:

Temperature (°C)	Temperature (K)	$1/T$ (K) ⁻¹	t (time)	$1/t$ (time) ⁻¹	$\ln (1/t)$
40					
50					
60					
70					

2- Plot a graph of $[\ln 1/t]$ against $[1/T]$ and from the slope calculate the activation energy (E_a) and determine frequency factor (A).

Where:

k : rate constant

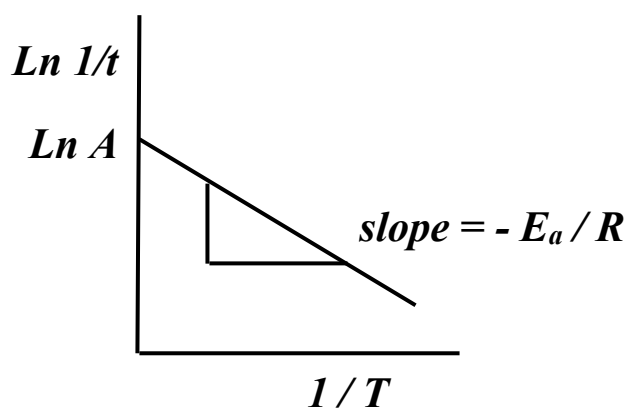
t : time

E_a : activation energy (J/mol) or (kJ/mol)

R : gases constant (8.314 J/mol.K)

T : temperature

A : frequency factor (time⁻¹)



Discussion:

1- Define the activation energy and Arrhenius equation.

2- What is the purpose of adding the phenol to the reaction between bromate & bromide?

Experiment (3)

Determination of Rate Constant (k) and Half-life time ($t_{1/2}$) of Acetone and Iodine

Theory: In aqueous solution acetone reacts with iodine according to the following equation:



The reaction is catalyzed by acids and bases. This reaction is called (Self-stimulation).

Theoretically, it was expecting that the reaction order is third order but experimentally, it was found zero order reaction.

The rate constant can be calculated according to the following equation:

$$k_0 t = x \quad \text{where } k_0 = \text{mol. L}^{-1}.\text{time}^{-1}$$

The half-life time can be calculated according to the following equation:

$$t_{1/2} = a / 2k_0$$

Procedure:

A- Determination of the initial concentration of I_2 (a):

- 1- Add (6)ml of I_2 in volumetric flask (50)ml, complete the volume with D. W.
- 2- Withdraw (5)ml from the mixture, put it in the conical flask and add 2 drops of starch indicator until blue color is appearance.
- 3- Titrate the mixture against (0.1)N sodium thiosulfate until the color disappearance.
- 4- Use the equivalent law to determine (a):

$$N_1 \times V_1 = N_2 \times V_2$$

$$0.1 \times V_0 = N_2 \times 5 \implies N_2 = a$$

B- Determination the remain concentration of I_2 (a-x):

1- In volumetric flask (50)ml, add (6)ml I_2 and (5)ml of (0.1)N H_2SO_4 then add (6)ml acetone after addition of acetone record the time to calculate the beginning of reaction time then add D. W.

2- After (5)min from the addition of acetone withdraw (5)ml from the mixture and add (5)ml of (0.025)N sodium acetate (to stop the reaction) then add 2 drops of starch indicator.

3-Titrate the mixture against (0.1)N sodium thiosulfate until the color disappearance.

4- Use the equivalent law to determine (a-x) at ($t = t$):

$$\begin{array}{l} N_1 \times V_1 = N_2 \times V_2 \\ 0.1 \times V_t = N_2 \times 5 \quad \implies \quad N_2 = (a-x) \end{array}$$

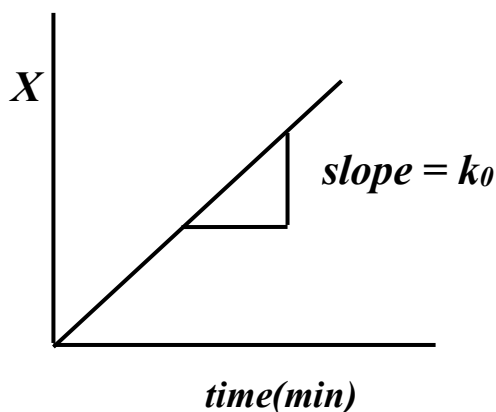
5- Repeat steps (2-4) every (5)min at interval time (5, 10, 15, 20, 25).

Calculations and graph:

1- Arrange the results according to the following table:

time (min)	V_o (ml)	a (mol/L)	V_t (ml)	$a-x$ (mol/L)	$X = a - (a-x)$ (mol/L)
5					
10					
15					
20					
25					

2- Plot a graph of $[X]$ against $[t]$ and from the slope calculate the rate constant(k) and half-life time($t_{1/2}$):



Discussion:

- 1- The reaction between acetone & I_2 is zero order. Explain.*
- 2- This reaction is called (Self-stimulation). Why?*
- 3- Why calculated the initial concentration (**a**) of I_2 ?*



Experiment (5)

Hydrolysis of Hydrogen Peroxide by Manganese Dioxide (MnO_2)

Theory: Hydrogen peroxide is hydrolyzed slowly to O_2 and H_2O :



To increase the hydrolysis process is used the catalyst (MnO_2). This is called (Heterogeneous Catalysis). The reaction is a first order and to calculate the rate constant (k) and half-life time ($t_{1/2}$) according to the following equation:

$$\boxed{\text{Ln}[a / (a-x)] = k_1 t}$$

$$\boxed{t_{1/2} = 0.693 / k_1}$$

There is two ways to follow the reaction:

- 1- Titration the remain of H_2O_2 ($a-x$) during periods of time against potassium permanganate in acidic media.
- 2- Measurement of liberated oxygen volume during periods of time.

Procedure:

A- Determination of initial concentration of H_2O_2 (a):

- 1- Take (5)ml of H_2O_2 and add (5)ml of (1M) H_2SO_4 and titrate against of (0.05)M potassium permanganate KMnO_4 .
- 2- Use the equivalent law to determine (a):

$$N_1 \times V_{1(\text{KMnO}_4)} = N_2 \times V_{2(\text{mixture})}$$

$$0.05 \times V_o = N_2 \times 5 \quad \Longrightarrow \quad N_2 = a$$

B- Determination of remain concentration of H_2O_2 (a-x)

1- Take (50)ml of H_2O_2 and add (0.017)g of MnO_2 , after (5)min withdraw (5)ml from the mixture and add (5)ml of (1M) H_2SO_4 then titrate against of (0.05)M potassium permanganate $KMnO_4$.

2- Use the equivalent law to determine (a-x) at (t=t):

$$N_1 \times V_{1(KMnO_4)} = N_2 \times V_{2(mixture)}$$

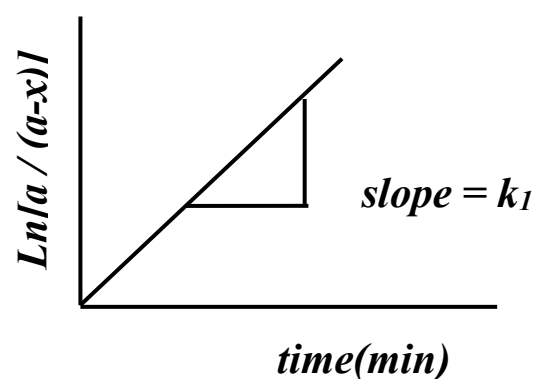
$$0.05 \times V_t = N_2 \times 5 \quad \Rightarrow \quad N_2 = (a-x)$$

Calculations and graph:

1- Arrange the results according to the following table:

time (min)	V_o (ml)	a (mol/L)	V_t (ml)	a-x (mol/L)	$[a / (a-x)]$	$Ln[a / (a-x)]$
5						
10						
15						
20						
25						

2- Plot a graph of $Ln[a / (a-x)]$ against [t] and from the slope calculate the rate constant(k) and half-life time($t_{1/2}$):



Discussion:

1- What is the type of titration in this experiment?

2- In this experiment, was an indicator used?

3- Is it possible to use HCl acid instead of H_2SO_4 acid?

4- What did the reaction rate depend on?

