

***Experimental Of Physical Chemistry***  
***(Chemical Kinetics)***

***Third Year***  
***First Course***

***Produced by***

***Barakat A. F. Kamel (Lecturer)***

***Amal S. Mahdi( Lecturer)***

***Waeel M. Haumud ( Lecturer)***

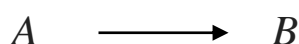
***Jaleel Sh. Taher (Assistant Lecturer)***

# Introduction

**Chemical Kinetics:** is a studying 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



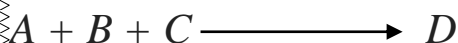
$$R = \frac{d[B]}{dt}$$

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).

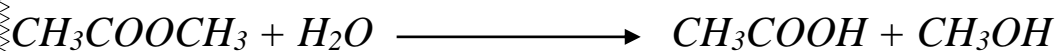
**Rate Constant (k):** Is the change in the concentration of reactants or products substances in the unit of time, the unit of rate constant is  $[(\text{mol/L})^{1-n} \cdot \text{time}^{-1}]$ .

**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.

# **Experiment (I)**

## **Determination the rate constant (k) 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:

$$\ln(a/a-x) = kt \quad \text{or} \quad \ln(V_\infty / V_\infty - V_t) = kt$$

This reaction is (pseudo first order)

The unit of (k) is  $[\text{min}^{-1}]$

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

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

### **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.
- 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 ( $V_\infty$ ) 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 ( $t = 0$ )

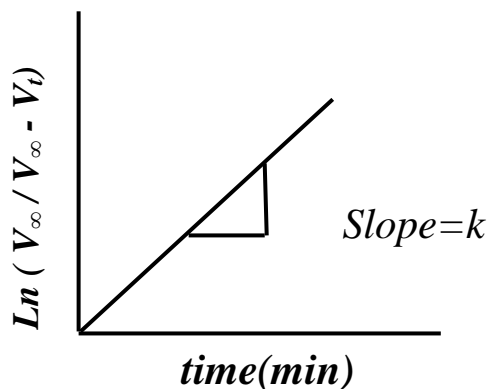
$V_t$  : volume of NaOH descending from the burette at( $t = t$ )

$V_\infty$  : 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)	$V_\infty$ (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					

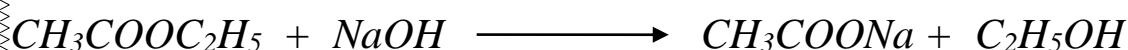
2- Plot a graph of  $\text{Ln} ( V_\infty / V_\infty - V_t)$  against ( $t$ ) and from the slope determine the rate constant ( $k$ ), then determine the half-life time( $t_{1/2}$ ).



## **Experiment (2)**

### **Determination the rate constant (k) 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:

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

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

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

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

#### **Procedure:**

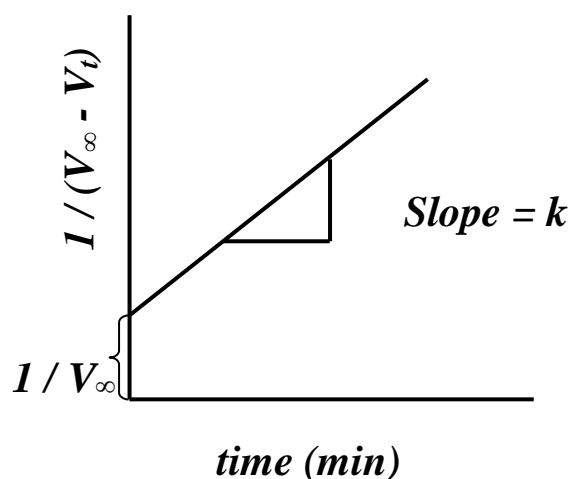
- 1- Take (50)ml of (0.05N) ethyl acetate, put it in the beaker then add (50)ml of (0.05N) NaOH and start recording the time at the beginning of the reaction.
- 2- After (3)min of the reaction beginning withdraw (10)ml from the mixture to the conical flask, add (10)ml of (0.025N) HCl and (10)ml distilled water (D.W.) (slows down 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)	$V_\infty$ (ml)	$(V_\infty - V_t)$ (ml)	$(V_\infty / V_\infty - V_t)$	$1 / (V_\infty - V_t)$
3					
6					
9					
12					
15					

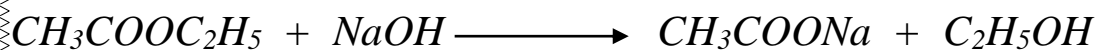
2- Plot a graph of  $1 / (V_\infty - V_t)$  against  $(t)$  and from the slope determine the rate constant ( $k$ ), then determine the half-life time ( $t_{1/2}$ ).



## **Experiment (3)**

### **Determination the rate constant (k) 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:

$$\ln [b(a-x) / a(b-x)] = (1/a - b)kt$$

#### **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 of (0.025N) HCl and (10)ml distilled water (D.W.) (slows down 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- Calculate the concentration of  $\text{CH}_3\text{COOC}_2\text{H}_5$  in the reaction mixture at ( $t = 0$ ) by dilution law:

$$\begin{aligned} N_1 \cdot V_1 &= N_2 \cdot V_2 \\ 0.08 \times 50 &= N_2 \times 100 \\ N_2 &= 0.04 = b \end{aligned}$$

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

$$\begin{aligned} N_1 \cdot V_1 &= N_2 \cdot V_2 \\ 0.05 \times 50 &= N_2 \times 100 \\ N_2 &= 0.025 = a \end{aligned}$$

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

$$N_1 \cdot V_1 = N_2 \cdot V_2$$

$$0.025 \times (10 - V_t) = N_2 \times 10$$

$$N_2 = (a-x)$$

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

4- Calculate( $x$ ) value which represent  $\text{CH}_3\text{COONa}$ :

$$a - x = \text{from step 3}$$

$$a = \text{from step 2}$$

$$x = ?$$

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

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

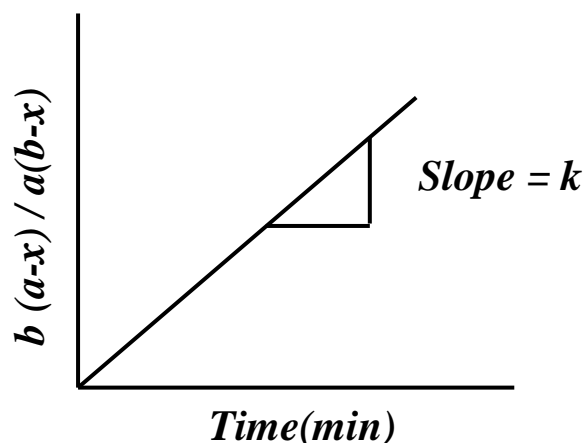
$$b - x = 0.04 - \text{value step 4}$$

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

6- Arrange the results according to the following table:

Time(min)	$V_t$ (ml)	( $b-x$ )	$x$	( $a-x$ )	$b(a-x) / a(b-x)$
3					
6					
9					
12					
15					

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

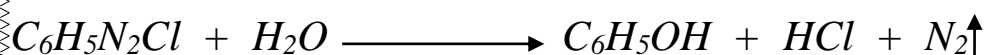




## **Experiment (4)**

### **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:

$$\ln(a-x) = -kt + \ln a \quad \text{or} \quad \ln(V_\infty - V_t) = -kt + \ln V_\infty$$

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

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

#### **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 outflow 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 ( $V_\infty$ ): put the conical flask which contain the reaction mixture in the water bath at temperature of  $90C^\circ$  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

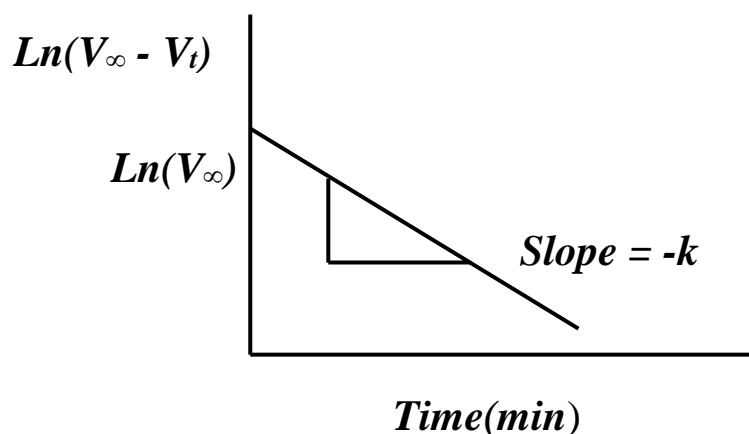
conical flask again in the water bath at  $90^{\circ}\text{C}$  and cool down again, take the average and measure ( $V_{\infty}$ ).

### Calculations and graph:

1- Arrange the results according to the following table:

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

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

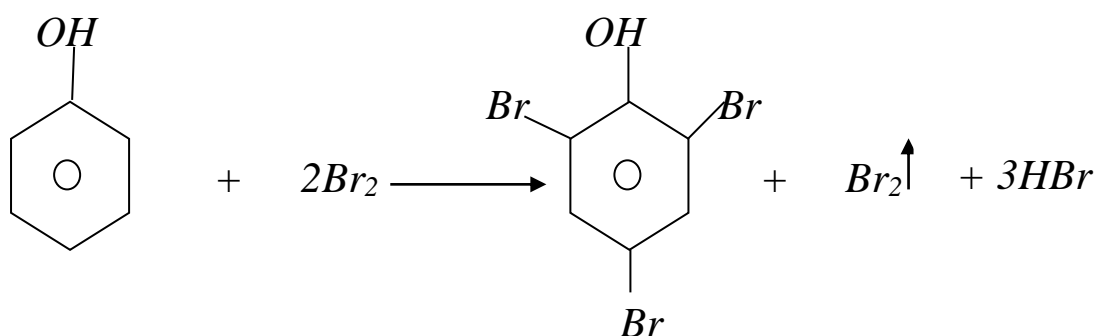


# Experiment (5)

## 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 reason of adding phenol to the reaction mixture to indicate the end of the reaction. The excess of bromide change the mixture color.

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

$$\boxed{\ln k = \ln A - E_a / RT}$$

$$k = 1/t$$

$$\boxed{\ln 1/t = \ln A - E_a / RT}$$

### Procedure:

- 1- Add (2.5)ml of [KBr + KBrO<sub>3</sub>]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<sub>2</sub>SO<sub>4</sub> and 2 drops of red methyl indicator to the test tube number 2.
- 3- Put the two test tubes in water bath at (40)C<sup>o</sup> 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 pink color.

4- Repeat steps (1-3) by different temperatures (50, 60, 70)C°.

### Calculations and graph:

1- Arrange the results according to the following table:

Temperature (C°)	Temperature (K°)	1 / T	time	1 / t	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

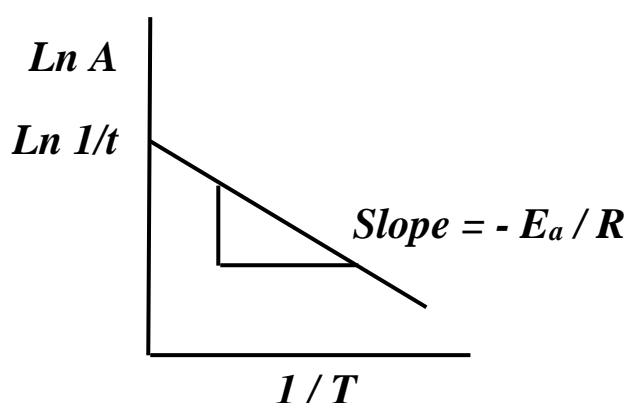
$t$ : time

$E_a$  : activation energy (J/mol) or (KJ/mol)

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

$T$ : temperature

A: frequency factor ( take the unit of  $k$  )



## **Experiment (6)**

### **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 expect that the reaction order is fourth order but

Experimentally, it was found zero order reaction.

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

$$k t = x$$

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

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

#### **Procedure:**

##### **A- Determination of the initial concentration (a):**

1- Add (6)ml of  $\text{I}_2$  then (5)ml of (0.1)N  $\text{H}_2\text{SO}_4$  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):

$$\begin{aligned} N_1 \cdot V_1 &= N_2 \cdot V_2 \\ 0.1 \times V_o &= N_2 \times 5 \implies N_2 = a \end{aligned}$$

### **B- Determination the remain concentration (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 ):

$$N_1 \cdot V_1 = N_2 \cdot V_2$$
$$0.1 \times V_t = N_2 \times 5 \implies N_2 = (a-x)$$

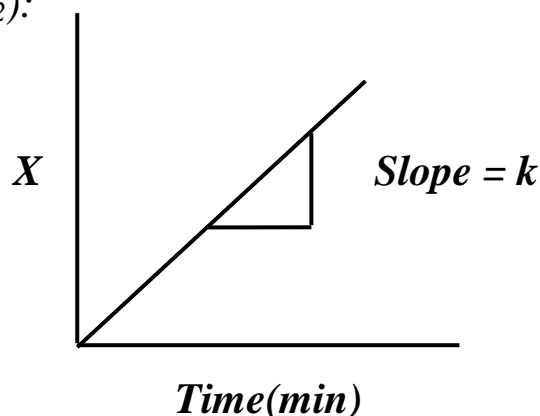
5- Repeat steps (2-4) every (5)min at interval time (5, 10, 15, 20, 25).

### **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( $t_{1/2}$ ):



# **Experiment (7)**

## **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:

$$\boxed{\ln[a / (a-x)] = k t}$$

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

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.
- 2- Measurement of librated 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 ( $a$ ):

$$\boxed{\begin{array}{l} N_1 \cdot V_1 (KMnO_4) = N_2 \cdot V_2 (mixture) \\ 0.05 \times V_o = N_2 \times 5 \implies N_2 = a \end{array}}$$

**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):

$$N_1 \cdot V_1 (KMnO_4) = N_2 \cdot V_2 (mixture)$$
$$0.05 \times V_t = N_2 \times 5 \implies N_2 = (a-x)$$

**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)	$[a / (a-x)]$ (mol/l)	$Ln[a / (a-x)]$
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( $t_{1/2}$ ):

