جامعة الموصل
كلية التربية للعلوم الصرفة
قسم الكيمياء

Chemical Kinatics

Third grade

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The First Lecture

Chemical Kinatics

Third grade

Dr.Noor Al-Taee

- **Scope of Chemical Kinetics**
- Chemical Kinetics deals with the rates of chemical reactions and with how the rates depend on factors such as concentration and temperature. Such studies are important in providing essential evidence as to the mechanisms of chemical processes

- Why study kinetics?

1) To develop a mechanism.
2) To determine steps in a chemical reaction.
3) Ultimately to learn how to make a reaction go faster or slower.
4) To figure out how and why a reaction occurs.

- Chemical Kinetics (what is it?)

The branch of chemistry that is concerned with the rates (or speed) of change in the concentration of reactants with time in a chemical reaction.

The reaction always occur in one main step so we can say that the reaction has a mono or bi molecularity.

- **Kinetics versus Thermodynamics**

Thermodynamics tells us which direction a reaction will go (e.g. at room temperature and standard pressure, carbon is stable in a form of graphite)

- Kinetics can tell us how quickly it will get there (e.g. A diamond will not convert to graphite during your lifetime
- Types of Chemical Reactions

Chemical reaction are divide into two parts according to the state of material.

1) Homogenous reactions

All of the ingredients in this type of reaction are in one case or one phase, as in gaseous and liquid.

Example: reaction of hydrogen gas with nitrogen gas to form the ammonia

$N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$

- **Heterogeneous reaction**

components are common in this type of reaction which exist in two phase or more, and in this case the reaction occur on the surface between the phases.

Examples:

$2H_2O_{(l)} \rightarrow 2H_2O_{(l)} + O_{2\ (g)}$

- **Stoichiometry & Molecularty**

Chemical reaction written in the form of the Stoichiometry equations, which give the ratio between the number of molecules of reactant and product, therefore this statement is a quantitative relationship between reactants and products.

- It not necessary to be representative of the mechanism of reaction For examples the Stoichiometry equation to produce the ammonia

$N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$

- Sometimes Stoichiometry equation refers to the reaction is more simple than of which exists in truth

Examples:

Pyrolysis of nitrozo oxide

$2N_2O \rightarrow 2N_2 + O_2$

This reaction involves two step

- **First:** convert the compound to the oxygen radical and nitrogen atom

$N_2O \rightarrow O{:} + N_2$

- **Second:** involves reaction of oxygen radical with nitrogen give N_2 & O_2

$O{:} + N_2 \rightarrow N_2 + O_2$

- **Reaction Molecularity**

This term can be defined "The number of molecules of starting material or material that participate in the main step of reaction which always form from one or two molecules and sometimes three (the latter is very rare).

- ***Chemical Kinetics:**

The study of the factors affecting the rate of chemical reaction and the elucidation of the mechanism by which a reaction occurs.

- **Rate of Reaction:**

the change in the concentration (conc.) of one of the compounds (reactant or Product) with time.

- *because the rate is continually changing, it must be expressed as a first derivative with respect to time for areaction in which one of the reacting species, A decrease with time.

$$A + B \longrightarrow C + D$$

the rate is: $-\frac{d[A]}{dt}$, $-\frac{d[B]}{dt}$

For one of the product species C, the rate increase with time.

the rate is: $+\frac{d[C]}{dt}$, $+\frac{d[D]}{dt}$

The Second Lecture

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- **Order of Chemical Reactron:**

the sum, of the exponent of the Cone. of the reacting species in the observal rate Law.

- * the order can not be predicate from the over all stoichiometry and must be determind experimentally.

- * the general rate equation can be written as

R= K [Cone.] , n = order of reaction

K = rate of coefficient rate of constant

- Example: to find the rate equation:

$A + 2B \longrightarrow 3C + D$

Reactants products

- A + 2B 3C + D

$$-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt} = \frac{d\{D]}{dt}$$

Rate $= \frac{unit\ of\ conc.}{unite\ of\ time} = \frac{mole/Liter}{sec.} = mole/L.S^{-1}$

R= K[conc.]^{1} : first order reaction

R= K[Conc. R]^{2} : second order reaction.

R= K[R]^{0} : Zero order reaction.

R= K[R]^{112} :one half order reaction.

R= K[R]^{312} : three_half order reaction.

- For the reaction:
- $A + B \longrightarrow C + D$ reaction equation
- $R = K[A][B]$ rate equation
- the reaction is first order with respect to [A]
- the reaction is first order with respect to [B]
- and second order of the over all reaction for the reaction:
- $2A + B \longrightarrow C$
- $R = K[A]^2[B]$
- The reaction is the second order with respect to [A] and First order with respect to [B] and third order for The over all reaction:
- $R = K[A]^{1/2}[B]$
- the reaction is one_half order with respect to [A] and first order with respect to [B] and three_half order for the over all reaction.

The order of reaction refer to the over all reaction and can only determined experimentally.

- For an elementary process the order molecularity are idenical.
- The determination of a mechanism of a reaction can not be described briefly because many type of chemical ideas are involved.

- Kinetic data are one of must useful types of information for determination mechanism.
- The mechanism must Yield the observerate Law.

- **First order reaction:**

Only one substance affect the value for reaction **A** $\longrightarrow$ **P**

Ex:	H_2O_2	$\xrightarrow{MnO_2}$	H_2O +	½ O_2
t=0	(a)		(0)	(0)
t=t	(a-x)		(x)	(x)

a: initial conc. Of thr reaction.

t: conc. Of produce at time = t

a-x: the remaining conc. Of the reaction after time.

$$\frac{dx}{dt} = K(a-x)$$

$$\int_0^x \frac{dx}{(a-x)} = K\int_0^t dt$$

- ❖ **نوجد قيمة الثابت عندما تكون المتغيرات تساوي صفر**

$-\ln(a-x) = Kt + I$ ……….. ❶ X= 0 , t= 0 عندما

$$-\ln(a-0) = K*(0) + I$$
$$-\ln a = I$$
$$I = -\ln a$$

- ❖ ❶ في العلاقة رقم $(\boldsymbol{I = -\ln a})$ بـ***I***وبالتعويض عن قيمة

$$-\ln(a-x) = Kt + I$$

$-\ln(a-x) = Kt + (-\ln a)$ نحصل على

$$-\ln(a-x) = Kt - \ln a$$

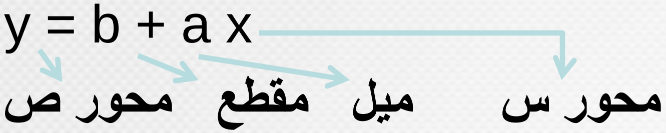
- ❖ **وبترتيب العلاقة**

$$-\ln(a-x) + \ln a = Kt$$

- ➢ المعادلة النهائية

$$\ln a - \ln(a-x) = Kt \quad \boldsymbol{\ln\frac{a}{a-x} = Kt}$$

- وعند رسم العلاقة بين نحصل على خط مستقيم يمر من نقطة الاصل ميلهُ t مقابل الزمن $\ln\frac{a}{a-x}$ يساوي K.
- ان المعادلة النهائية تشبه معادلة الخط المستقيم:



y = b + a x

محور ص مقطع ميل محور س

$$\ln\frac{a}{a-x} = K_1 t$$

- *K= Slope* , $y = \ln\frac{a}{a-x}$, *t = x* , *b = 0*

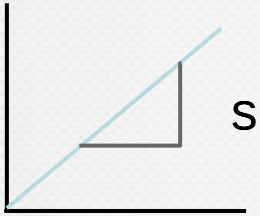
- By multiplying the integrated equation by (-1) being:-

$$\ln(a-x)-\ln a=-K_1t\ldots\ldots\ldots\ldots\ldots$$ ②

$$\ln(a-x)=\ln a-K_1t$$

$y=\ln(a-x)$, $t=x$, $slope=-K$, $b=\ln a$

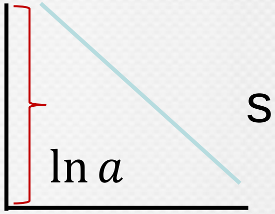
- $\ln\frac{a}{a-x}$



slope = K

t

$\ln(a-x)$



slope = K

t

- **Half Life of First order reaction:**

the time required to reduce the initial conc. of the reaction to half, its orginal value.

$$A \longrightarrow P \qquad \mathbf{\ln\frac{a}{a-x} = Kt \ldots\ldots\ldots} ❶$$

	A	P
t=0	a	0
t=t	(a-x)	x
$t=t_{1/2}$	$\frac{a}{2}$	$\frac{a}{2}$

at $t= t_{1/2}$ $x=\frac{a}{2}$

substitution the value in equation 1

$$\ln\frac{a}{a-\frac{a}{2}} = Kt_{0.5}$$

$$\ln 2 = Kt_{0.5}$$

$$t_{0.5} = \frac{\ln 2}{K}$$

unit of K =[conc.]$^{1-n}$.(Time)$^{-1}$

- Ex: of first order reaction

Decomposition of Hydrogen peroxide (H_2O_2).

$H_2O_2 \xrightarrow{MnO_2} H_2O + \frac{1}{2} O_2$

$2N_2O_{5\,(g)} \longrightarrow 4NO_{2\,(g)} + O_{2\,(g)}$

The Third Lecture

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- **Second Order Reactions**

when two species of similar approximately similar conc. affect the rate of reaction:-

$A + B \longrightarrow C$ Or $A + A \longrightarrow C$

R= K[A][B]

	A	+	A	$\longrightarrow$	C
t=0	*a*		*b*		*0*
t=t	*a-x*		*b-x*		*x*

$$\frac{dx}{dt} = K(a-x)(b-x)$$

After integrate:-

$$\frac{a-(a-x)}{a(a-x)} = Kt$$

$$\frac{x}{a(a-x)} = K_2t$$

- When *a = b*

$$\frac{dx}{dt} = K(a-x)^2$$

$$\int_0^x \frac{dx}{(a-x)^2} = K\int_0^t dt$$

$\frac{1}{a-x} = Kt + I$ *بعد التكامل نحصل على:-*

وعند زمن قدره *(t = 0)* فان *(x = 0)*وبالتالي فان قيمة I تساوي:-

$$\frac{1}{a-x} = Kt + I \xrightarrow{\qquad\qquad} \frac{1}{a-0} = K(0) + I$$

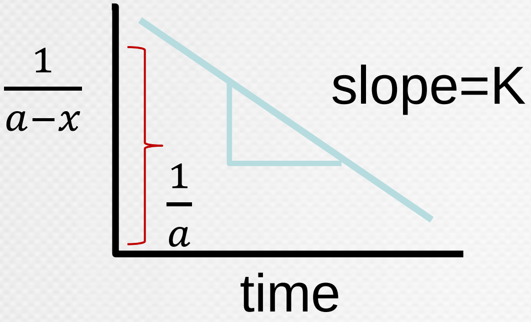
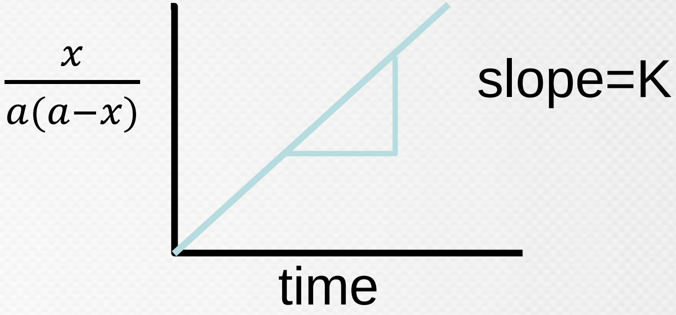
$$I = \frac{1}{a}$$

وبالتعويض عن $(I = \frac{1}{a})$ في العلاقة $\left[\frac{1}{(a-x)} = Kt + I\right]$ ينتج:-

$$\frac{1}{(a-x)} = Kt + \frac{1}{a}$$

- $\boldsymbol{K_2 t = \frac{1}{(a-x)} - \frac{1}{a}}$ ***Or*** $\boldsymbol{\frac{x}{a(a-x)} = K_2 t}$

➢ المعادلة النهائية

-  

- **Half live of second order reaction:-**

$$a=\frac{a}{2} \quad , \qquad x=\frac{a}{2} \quad , \qquad (a-x)=\frac{a}{2} \quad , \qquad t=t_{0.5}$$

$$\frac{x}{a(a-x)}=Kt \qquad\qquad \frac{\frac{a}{2}}{a(\frac{a}{2})}=Kt_{0.5}$$

$$\frac{2a}{2a^2}=Kt \qquad\qquad \frac{1}{a}=Kt_{0.5}$$

$$t_{0.5}=\frac{1}{aK}$$

- **When a ≠ b**

$$\frac{dx}{dt} = K(a-x)(b-x)$$

$$\frac{dx}{(a-x)(b-x)} = Kdt$$

يجب ان نفرض علاقة بين متغيرين او نجد علاقة بينهما, سوف نفرض ثابتين معروفين لنا هما Constant A,B

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$$

$$\frac{1}{(a-x)(b-x)} = \frac{A(b-x)+B(a-x)}{(a-x)(b-x)}$$

$$1 = A(b-x) + B(a-x)$$

$$1 = Ab - Ax + Ba - Bx$$

$$1 = Ab + Ba - x(A+B)$$

At the beginning of reaction: $x = 0$

$1 = Ab + Ba$………….❶

$0 = A + B$……………❷

$A = -B$ …………….❸

$$1 = -Bb + Ba$$

$1 = B(a-b)$ $\qquad B = \frac{1}{a-b}$, $\qquad A = \frac{-1}{a-b}$

$$\frac{dx}{dt} = K(a-x)$$

$$\int_0^x \frac{dx}{a-x} = K\int_0^t dt \qquad \int_0^x \frac{dx}{(a-x)(b-x)}$$

$$A\int_0^x \frac{dx}{(a-x)} + B\int_0^X \frac{dx}{(b-x)}$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = \frac{-1}{a-b}\int \frac{dx}{(a-x)} + \frac{1}{a-b}\int \frac{dx}{(b-x)} = K\int_0^t dt$$

$$\frac{-1}{a-b}\left[-\ln(a-x)\right]_0^x + \frac{1}{a-b}\left[-\ln(b-x)\right]_0^x = Kt$$

$$\frac{1}{a-b}\left[\ln(a-x) - \ln a\right] - \frac{1}{a-b}\left[\ln(b-x) - \ln b\right] = Kt$$

$$\frac{1}{a-b}\left[\ln(a-x) - \ln a - \ln(b-x) + \ln b\right] = Kt$$

$$\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = Kt$$

- ***final integrate eq. of second order reaction when a≠b***

- **Third order reaction:**

three species affect the vate of reaction:

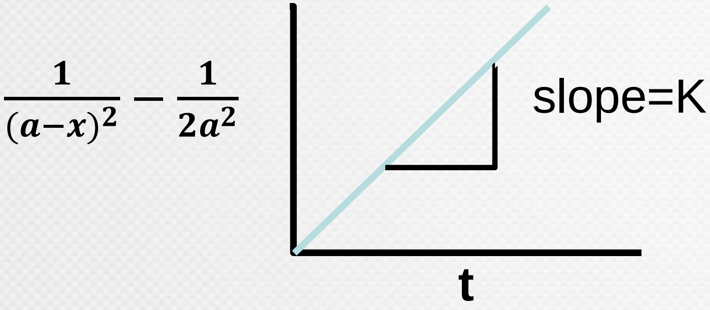
$3A \longrightarrow P$, $2A+B \longrightarrow P$, $A+B+C \longrightarrow P$

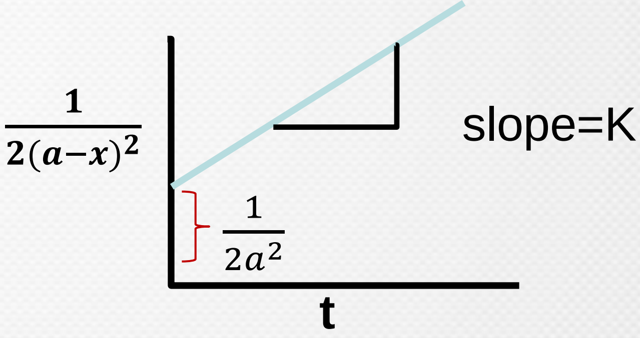
$R=K[A]^3$, $R=K[A]^2[B]$, $R=K[A][B][C]$

- when $a = b = c$

he Final integration equation For third order reaction:

$$\mathbf{Kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}}$$





$$\frac{1}{2(a-x)^2} - \frac{1}{2a^2} = Kt$$

$$\frac{1}{2(a-x)^2} = \frac{1}{2a^2} + Kt$$

- **Half life of third order reaction:-**

$t=t_{0.5}$ when $x=a/2$ or $(a-x)=a/2$

$$\frac{1}{2(a-\frac{a}{2})^2}-\frac{1}{2a^2}=Kt_{0.5} \qquad \frac{4}{2a^2}-\frac{1}{2a^2}=Kt_{0.5}$$

$$\frac{3}{2a^2}=Kt_{0.5} \qquad \boldsymbol{t_{0.5}=\frac{3}{2a^2K}}$$

- The half life of third order reaction is inversely proportional to the sequere value of initial conc. .

	A	+	B	+	C	$\longrightarrow$	P
• T=0	a		b		c		0
• T=t	(a-x)		(b-x)		(c-x)		x

$When\ a = b \neq c$

The integration of itsequation:-

$$\frac{1}{(c-a)^2}\left[\frac{x(c-a)}{a(a-x)} + \ln\frac{c(a-x)}{a(c-x)}\right] = Kt$$

- Case 3:

$When\ a \neq b \neq c$

The integration of itsequation:-

$$\frac{1}{(c-b)(a-x)}\ln\frac{a}{(a-x)} + \frac{1}{(b-a)(b-c)}\ln\frac{b}{(b-x)} + \frac{1}{(c-a)(c-b)}\ln\frac{c}{(c-x)} = Kt$$

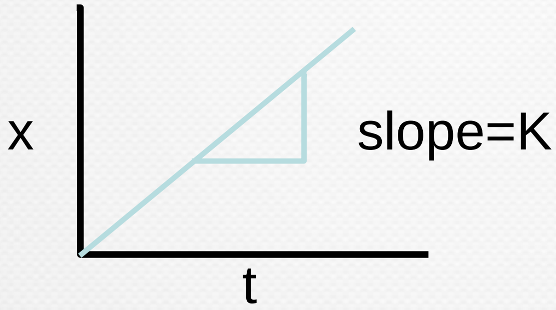
- **Zero order reaction:**

R=K[conc.]^0

$$\frac{dx}{dt} = K[c]^0 \qquad \frac{dx}{dt} = K \qquad dx = Kdt$$

$$\int_0^x dx = K\int_0^t dt \qquad [x]_0^x = K[t]_0^t$$

X=Kt Final integration equation of zero order reaction:



- **Half live of zero order reaction:-**

$t=t_{0.5}$ when $x=a/2$

$X=Kt$

$\frac{a}{2} = Kt_{0.5}$ $a=2Kt_{0.5}$ $t_{0.5} = \frac{a}{2K}$

- Example:- Decomposition of NH_3 gas with the presence of catalyst.

$2NO + O_2 \longrightarrow 2NO_2$

$H_2 + I_2 \longrightarrow 2HI$

Molecularity =2 bimolecular reaction Stiochismetry

- Note: There is no relationship between the stiochiometry and order reaction.

The Fourth Lecture

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- **<u>(n) order reaction</u>**

$$nA \xrightarrow{\qquad} p$$

$$\frac{dx}{dt} = K(a-x)^n$$

$$\int \frac{dx}{(a-x)^n} = K\int dt$$

- اجراء التكامل لها عند $x=x$ عندما $t=t$, و $x=0$ عندما $t=0$

$$\frac{1}{(n-1)(a-x)^{n-1}} = Kt + I$$

$$I = \frac{1}{(n-1)\,a^{n-1}}$$

- نعوض *I* في المعادلة

$$\frac{1}{(n-1)(a-x)^{n-1}} = Kt + \frac{1}{(n-1)\,a^{n-1}}$$

$$\boldsymbol{\frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] = Kt}$$

- يمكن استنتاج قانون عمر النصف بالتعويض عن $t=t_{0.5}$, $x=a/2$

$$t_{0.5}=\frac{1}{(n-1)K}\left[\frac{1}{(a-\frac{a}{2})^{n-1}}-\frac{1}{a^{n-1}}\right]$$

$$t_{0.5}=\frac{1}{(n-1)K}\left[\frac{1}{(\frac{a}{2})^{n-1}}-\frac{1}{a^{n-1}}\right]$$

$$t_{0.5}=\frac{1}{(n-1)K}\left[\frac{2^{n-1}}{(a)^{n-1}}-\frac{1}{a^{n-1}}\right]$$

$$\boldsymbol{t_{0.5}=\frac{2^{n-1}-1}{(n-1)K\,.\,a^{n-1}}}$$

- Determination Method of order reaction there are several method that can be used for determination of order reaction:

These method are:

❑ Integration method
❑ Iselation method
❑ Half life method
❑ Defferntial method

1) **Integration method**: A general method in which the order of reaction can be valuated by substitution of the Kinetic data (conc. Versus time) in an equation of several order.

- The equation which gives constant values of K or a straight line represent the correct order.

الطريقة التكاملية: طريقة عامة يمكن من خلالها حساب قيمة رتبة التفاعل عن طريق تعويض البيانات الحركية (التركيز مقابل الزمن) بعدة معادلات لإيجاد الرتبة.

- المعادلة التي تعطي قيمة ثابت سرعة التفاعل أو تعطي خط مستقيم تمثل المعادلة الصحيحة لمرتبة التفاعل.

2) Isolation method: if the number of reactants is more than one the prossed is followed by Keeping the Conc. for the one or two reactant in high excess as compared with the order one.

طريقة العزل: اذا كان عدد المتفاعلات اكثر من واحد فان الطريقة ستكون بعزل مادة او مادتين من المواد المتفاعلة المتفاعلة وذلك باستخدام زيادة من تركيزه مقارنة بالأخرى.

Ex: for the reaction:-

$A + B + C \longrightarrow P$

$R = K [A] [B] [C]$ to evalute the order of reaction with respect to A

$[B][C] \gg [A]$

we assume

$K' = K'[A]$ $\qquad$ $K' = K [B] [C] = \text{constant}$

to evalute the order with respect to B :

$[A][C] \gg [B]$

$R'' = K'' [B]$ $\qquad$ $K'' = K [A] [C] = \text{Cons.}$

with respect to C:

$[A][B] \gg [C]$

$R''' = K'''[C]$ $\qquad$ $K''' = K[A][B]$

the reaction treated as pseudo First order

- **Half life reaction:** for an (n) order reaction (n≠1) the half life can be expressed by the following equation.

t0.5=conc.(K)an-1 a:- initial Conc. of the reaction

Case1:- if two values of $t_{0.5}$ and initial Conc. are given.

$t_{0.5}$	Conc.
$t_{0.5\ (1)}$	a_1
$t_{0.5\ (2)}$	a_2

$$t_{0.5\ (1)} = \frac{K}{a_1^{n-1}} n\text{-}1$$

$$t_{0.5\ (2)} = \frac{K}{a_2^{n-1}}$$

Divided (1) by (2) gives

$$\frac{t_{0.5\ (1)}}{t_{0.5\ (2)}} = \frac{K/a_1^{n-1}}{K/a_2^{n-1}} = \left[\frac{a_2}{a_1}\right]^{n-1} \Longrightarrow \log\frac{t_{0.5\ (1)}}{t_{0.5\ (2)}} = (n-1)\log\frac{a_2}{a_1}$$

$$(n-1) = \frac{\log\frac{t_{0.5\ (1)}}{t_{0.5\ (2)}}}{\log\frac{a_2}{a_1}} \Longrightarrow n = \frac{\log t_{0.5\ (1)}/t_{0.5\ (2)}}{\log a_2/a_1}$$

- **Case2**:- if several values of $t_{0.5}$ and (a) are available

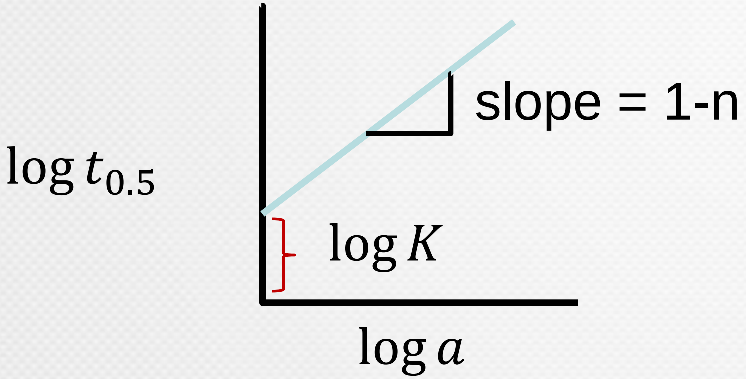
$t_{0.5}$	A
$t_{0.5\ (1)}$	a_1
$t_{0.5\ (2)}$	a_2
$t_{0.5\ (3)}$	a_3
$t_{0.5\ (n)}$	a_n

Scince $t_{0.5} = \frac{K}{a^{n-1}}$

$$\log t_{0.5} = \log \frac{K}{a^{n-1}}$$

$$\log t_{0.5} = \log K - \log a^{n-1}$$

$$\log t_{0.5} = \log K + (1-n) \log a$$



The Fifth Lecture

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4) Differential method: the general rate equation is expressed as follow

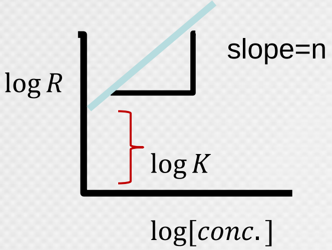
$R = K_n [\text{conc.}]^n$ n= order of reaction

if we take the Log for both side of the equation:-

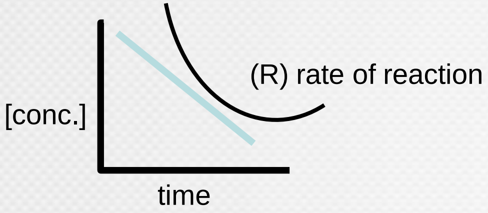
$\text{Log } R = \text{Log } K [\text{conc.}]^n = \text{Log } K + n \text{ Log } [\text{conc.}]$

$\text{Log } R = \text{Log } K + n \text{ Log } [\text{conc.}]$

If we plot Log R versus Log [conc.] given.

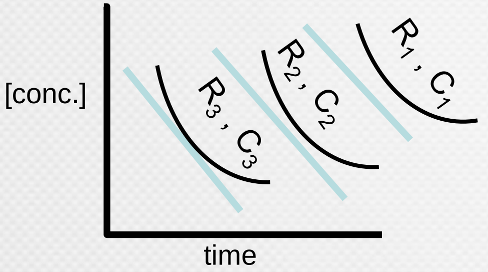


when we plot the [conc.] of the reaction versus time.



experimentally different rate values of reaction, can be evaluted from ploting Conc. versus time.

at various conc. as shown in the figure:-



Initial method

Ex1: the reaction:

$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

is first order reaction with arate constant 2×10^{5} sec^{-1} at 320C° what percentage of SO_2Cl_2 is decomposed on 320C° for 90 min ?

$$Kt = \ln \frac{a}{a-x}$$

$$2 \times 10^{-5} \times 90 \times 60 = \ln \frac{100}{100-x}$$

X=

Ex2: For First order reaction it is Found at 30 min. , 30% of reaction is completed find the value of (K) and the percentage of reaction completed after (5) hours?

	A $\longrightarrow$	P
t=0	100	0
t=30	70	30

Kt= $\ln\frac{a}{a-x}$

K=? %=? After 5 hours

K=$\frac{1}{t}.\ln\frac{a}{a-x}$

K=$\frac{1}{30}.\ln\frac{100}{70}$

K= 0.012 min^{-1}

$$Kt=\ln\frac{a}{a-x}$$

0.012×5 × 60=$\ln\frac{100}{100-x}$

0.012×5 × 60=$\ln 100-\ln(100-x)$

$\ln(100-x)=4.6-3.6$

$\ln(100-x)=1$

- **Q1)**Prove that the decomposition of (HI) in to (H_2) and I_2 is second order if at 500C° the $t_{0.5}$ is (100)min when initial pressure of (HI) is (0.1) atm, where as the $t_{0.5}$ is (600)sec. when initial pressure is (1) torr?

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