kinetics

Chemical kinetics

الكيمياء الحركية

Reaction rates

معدل سرعة التفاعل

Concentration and reaction rates

العلاقة بين تركيز المواد وسرعة التفاعل

Rate equations for single

التفاعل لخطوة واحدة

Step reaction	معادلة السرعة لخطوة واحدة
Reaction mechanisms	ميكانيكية التفاعل
Rate equations and temperature	تأثير درجة الحرارة على سرعة التفاعل
catalysis	المحفزات

Chemical Kinetics

Chemical Kinetics – area of chemistry concerned with rates of reaction .

الكيمياء الحركية – هو الفرع من الكيمياء الذي يهتم بسرعة التفاعلات

Factors that affect rates

العوامل التي تؤثر على سرعة التفاعلات

Concentrations of reactants	التركيز
temperature	درجة الحرارة
Catalyst(s)	المحفزات

Surface area	**مساحة السطح**
Solid reactant	**التفاعلات الصلبة**
liquid reactant	**التفاعلات السائلة**
catalysts	**المحفزات**

Reaction Rates

* reaction rate – change in number of moles of a reactant or product per unit time

$$A \rightarrow B$$

$$\text{Rate} = \frac{\Delta(\text{moles B})}{\Delta t}$$

Progress of reaction

A → B

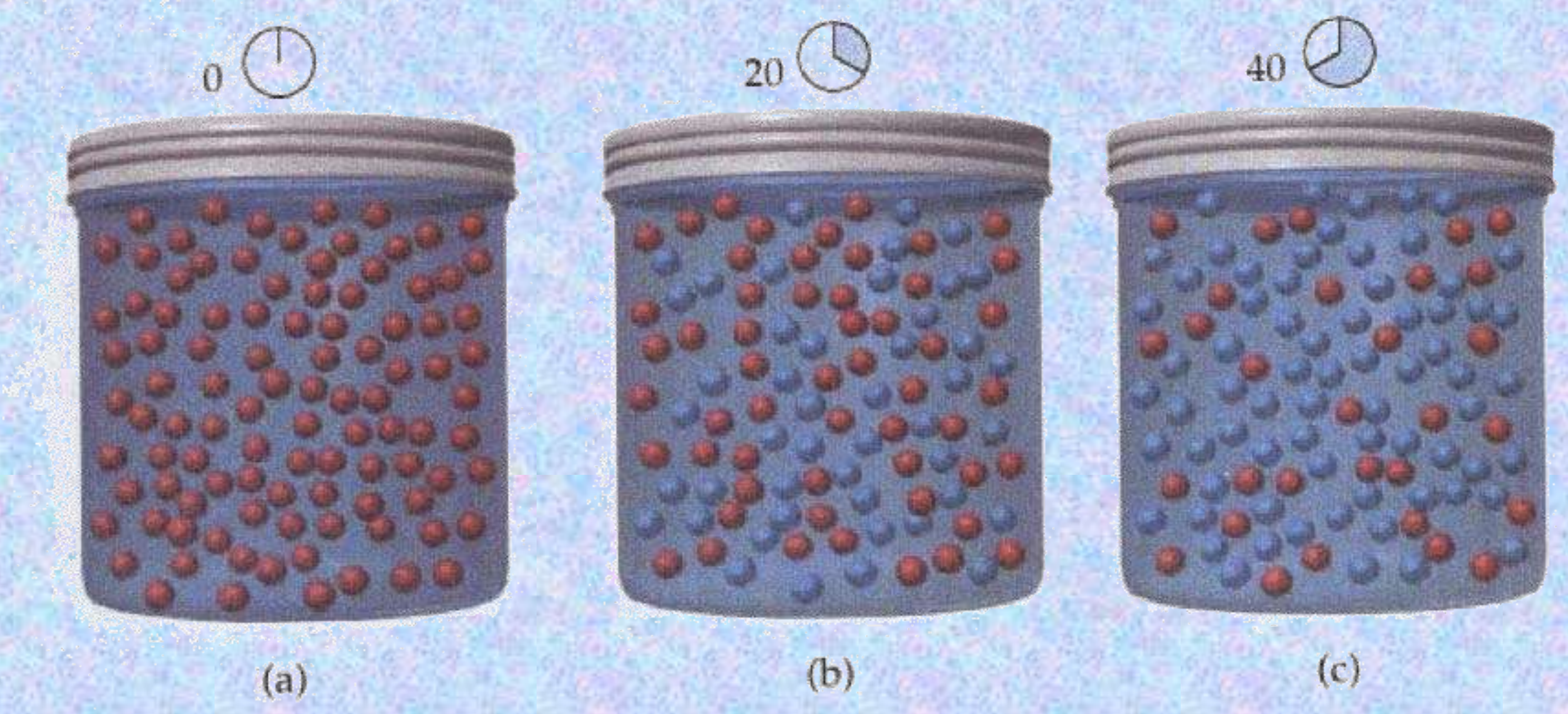
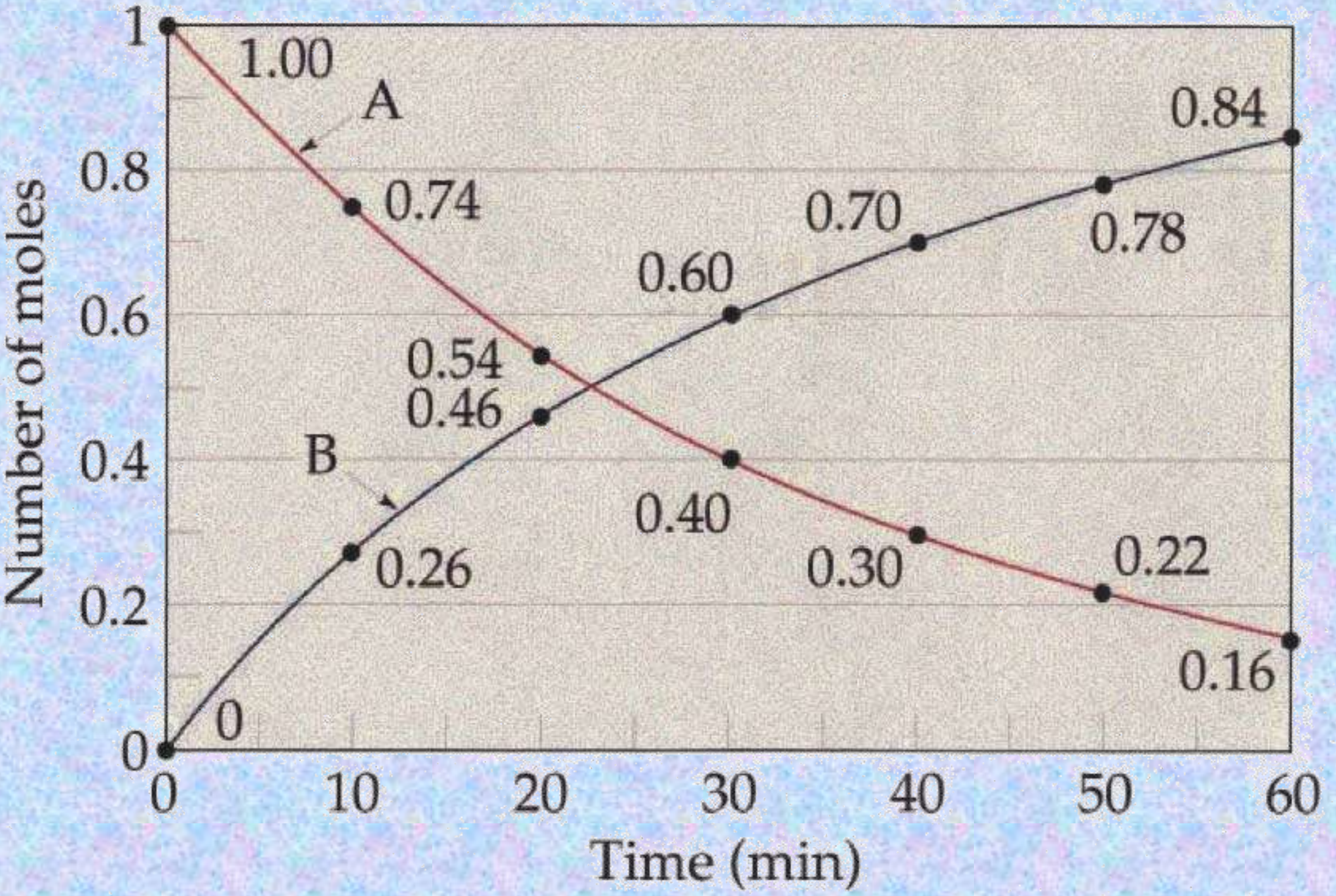


Fig 1 – plots of moles vs Time



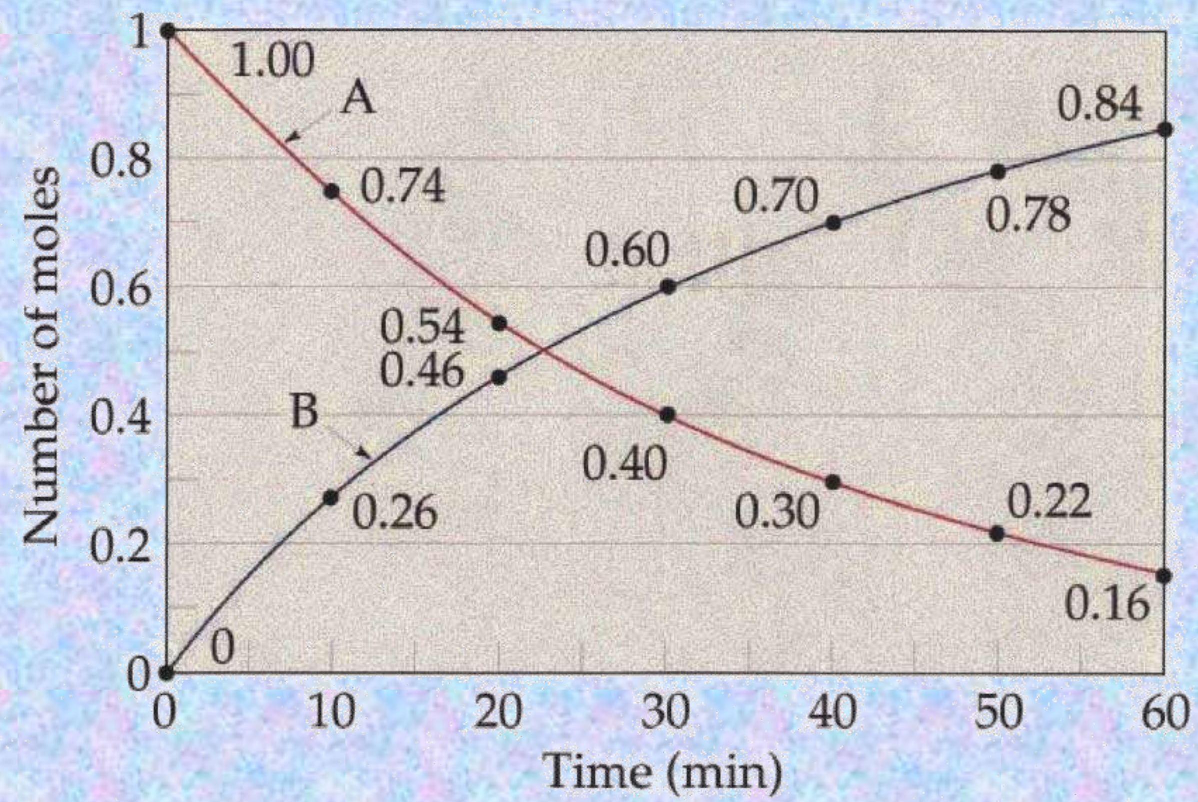
$$R = \Delta(\text{moles B}) / \Delta t = -\Delta(\text{moles A}) / \Delta t$$

Rate of appearance of products (B) is positive

Rate of disappearance of reaction (A) is negative

Rate using concentrations

Reaction rate – change in concentrations of reactant or product per unit time.



For reaction

$A_2 + B_2 \rightarrow 2AB$

Rate of disappearance of $A_2 = - \Delta [A_2] / \Delta t$

Rate of disappearance of $B_2 = - \Delta[B_2] / \Delta t$

Also can be expressed of formation of products:

Rate of appearance of $AB = \Delta[AB] / \Delta t$

Relative rate

$A_2 + B_2 \rightarrow 2AB$

AB is produced as twice as fast of A_2 or B_2

Therefore the relationships between the rates of change for various species are:

$\Delta [A_2] = \Delta [B_2] = \Delta[AB] / 2$

$R = - \Delta[A_2] / \Delta t = - \Delta [B_2] / \Delta t = \frac{1}{2} \Delta[AB] / \Delta t$

Units of Rate = mole / L . s

Relative rates

Ex :

$2HI \rightarrow H_2 + I_2$

The rate of decomposition of HI is twice as fast as the rate of production of H_2 .

The rate of decomposition of HI is twice as fast as the rate of production of I_2

The rate of production of H2 is half as fast as the rate of decomposition of HI.

$$R = -\frac{1}{2}\,\Delta[\mathrm{HI}]/\Delta t = \Delta[\mathrm{H_2}]/\Delta t = \Delta[\mathrm{I_2}]\,\Delta t$$

$$R_{\mathrm{formation}}\ [\mathrm{H_2}] \text{ or } [\mathrm{I_2}] = \frac{1}{2}\,\Delta[\mathrm{HI}]/\Delta t$$

Ex.

i) How is the rate of disappearance of ozone related to the rate of appearance of oxygen in the following equation?

$$2O_3\,(g) \rightarrow 3O_2\,(g)$$

ii) If the rate of appearance of O_2 is 6.0×10^{-5} M/s , what is the value of the rate of disappearance of O_3 ?

Solution

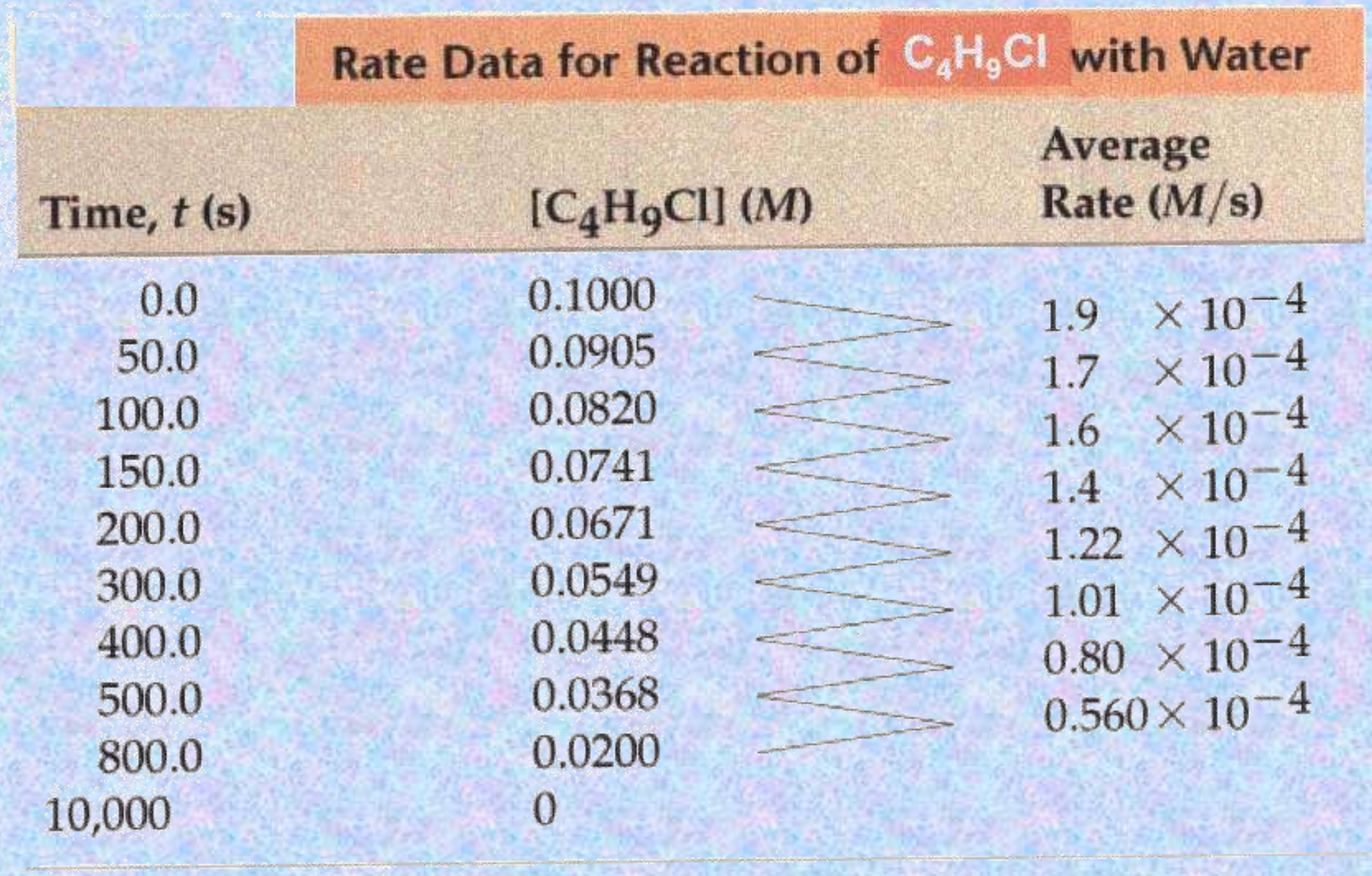
i) $R = \frac{1}{2} \Delta [O_3] / \Delta t = 1/3 \Delta [O_2] / \Delta t$

ii) $R = \frac{1}{2} \Delta [O_3] / \Delta t = 1/3 \times 6.0 \times 10^{-5}$ M/s

$\Delta [O_3] / \Delta t = 2/3 \times 6.0 \times 10^{-5}$

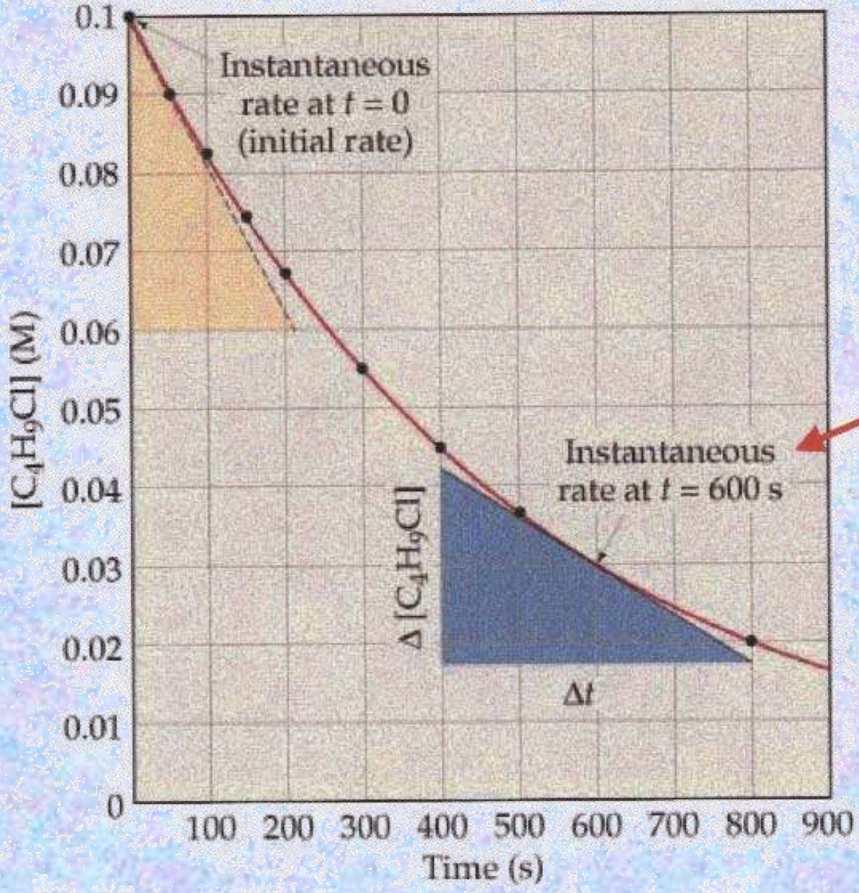
$= 4.0 \times 10^{-5}$ M/s

How we calculate rate from [conc] vs time?



Rate Data for Reaction of C_4H_9Cl with Water

Time, *t* (s)	$[C_4H_9Cl]$ (*M*)	Average Rate (*M*/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	



rate at a particular time - use tangent

Rate Law:

For each chemical reaction there is a mathematical expression , called a rate equation or a rate law ,

Rate law relates the concentrations of reactants to the reaction rate.

$$2N_2\,O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

$$R = k\,[\,N_2O_5]$$

In general:

$aA + bB \rightarrow cC + dD$

$R = k\,[A]^{m}\,[B]^{n}$

Where

k = rate constant

m + n = reaction order

Reaction order and rate constant

- Rate = k [reactant 1 $]^m$ [reactant 2 $]^n$

- Sum of m + n is overall reaction order

- Values of m and n must be determined by experiment – cannot be taken from balanced equation

- Units of the rate constant will vary , depending on the overall reaction order !

Why study the rate Law ?

- It will help us determine possible mechanisms for reaction .

- It will help us learn how to influence reaction conditions to affect rate .

Driving rate Law

Ex:

- **Drive rate Law and k for**

$$CH_3\,CHO\,(g) \rightarrow CH_4\,(g) + CO\,(g)$$

For experimental data for rate of disappearance of CH_3CHO

Exp	[CH3CHO]	R(mol / L .s)
1	0.1	0.02
2	0.2	0.081
3	0.3	0.81
4	0.4	0.318

Ex:

- Drive rate Law and k for

$CH_3\,CHO\,(g) \rightarrow CH_4\,(g) + CO\,(g)$

For experimental data for rate of disappearance of CH_3CHO

Exp	[CH3CHO]	R(mol / L .s)
1	0.1	0.02
2	0.2	0.081
3	0.3	0.81
4	0.4	0.318

solution

$\text{Rate} = k\,[\,CH_3\,CHO\,]^n$

$R_1 = k\,[0.1]^n = 0.02$

$R_2 = k[0.2]^n = 0.081$

$$R_2 / R_1 = (0.081 / 0.02) = (0.2 / 0.1)^n$$

$$= 4 = (2)^n$$

$$= 2^2 = (2)^n$$

$$n = 2$$

R = k [CH3CHO]2

$R_1 = 0.02 = k (0.1)^2$

$0.02 = 0.01 k$

k = 0.02 / 0.01 = 2. 0 L / mol .s

Order of reaction

$R = k\,[A]^{n}$

$n = 0.\ 1, 2, 3\ \ldots$ or fractions

First order reaction

First order RXN – rate depends on the concentration of a single reactant

A → products

$R = k[A]$

Ex : $CH_3NC \rightarrow CH_3CN$

$R = k[CH_3CHO]$

The integrated Rate Law:

1) First order :

Concentration / Time, Relation

$$- d[A] / dt = k [A] \ldots\ldots\ldots (1)$$

Equation (1) can be arranged as

$$-d [A] / [A] = k\, dt \ldots\ldots\ldots\ldots (2)$$

By integration:

$$\int_{[A]_0}^{[A]} d[A]/[A] = k \int_{t_{1=0}}^{t} dt$$

$\ln [A]_0 / [A] = kt$ ……………….. (3)

If we plot $\ln[A]_0 / [A]$ vs. time we get a straight line, with slope equal to k

Ex:

For a reaction

$2N_2O_5\ (s) \rightarrow 4NO_2(g) + O_2\ (g)$

Time	$[N_2O_5]$ M	$\ln[N_2O_5]_0$
0	1.0	0
1.0	0.705	-0.35
2.0	0.497	-0.70
5.0	0.173	-1.75

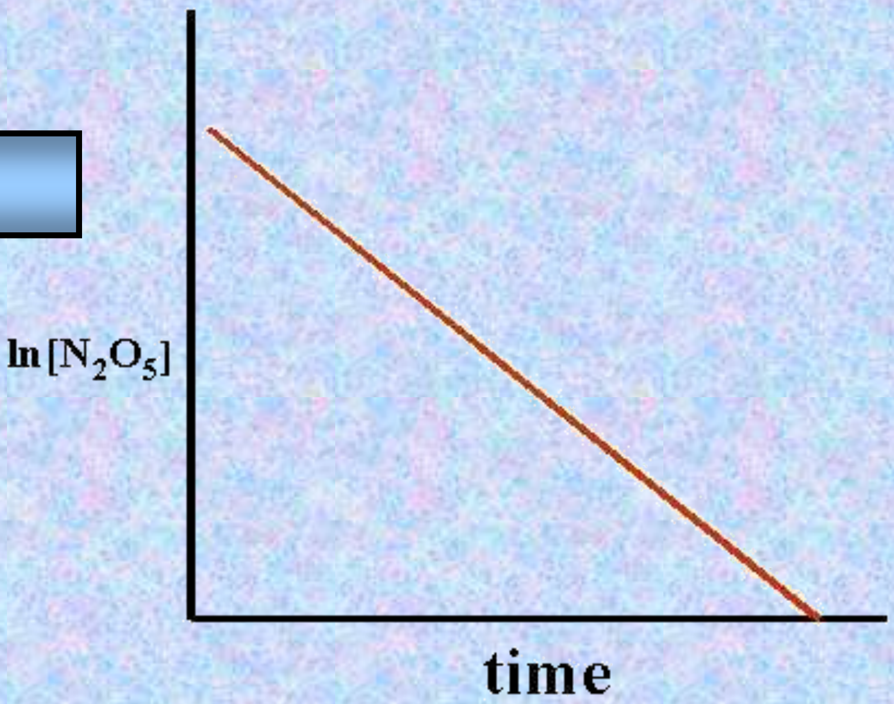
A plot of ln $[N_2O_5]$ vs. time is a straight line

The equation for a straight line is:

$y = ax + b$

$\ln [N_2O_5] = kt + \ln [N_2O_5]_0$

Slope = - k



Half – life

(First order RXN)

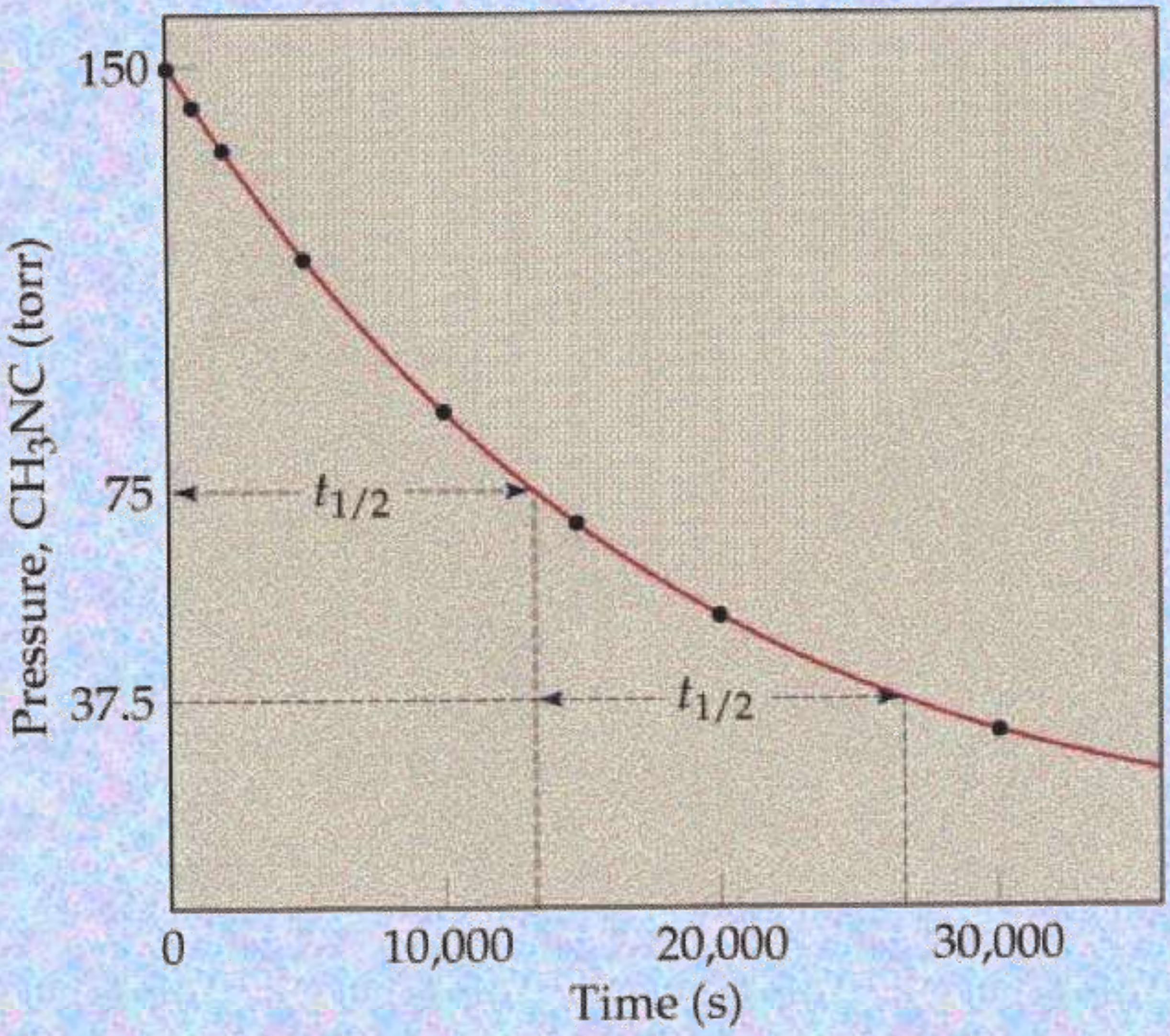
Half – life – time required for a reaction to reach half of its original concentration

$[A] = \frac{1}{2} [A]_o$

$[A]_o / \frac{1}{2} [A]_o = k\, t_{1/2}$

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

Half - Life


150
75
37.5
Pressure, CH_3NC (torr)
$t_{1/2}$
$t_{1/2}$
0
10,000
20,000
30,000
Time (s)

First order Example

- **For the reaction $aA \rightarrow bB$, a plot of ln [A] vs t was linear and gave a slope of – 6.90 x 10^{-2} s^{-1} .**

- **Determine rate law , integrated rate law , and value of the rate constant .**

- **Calculate the half-life**

- **How much time is required for this reaction to be 87.5 % complete ?**

Solution:

i) $R = k [A]$

ii) $k = -$ slope

$= 6.9 \times 10^{-2}\ s^{-1}$

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

$= 0.693 / 6.9 \times 10^{-3} = 100.4\ s$

$$\ln\{ [A]_0 / [A]\} = k\,t$$

$$[A] = 0.125\,[A]_0$$

$$\ln [A]_0 / 0.125\,[A]_0 = 6.9\text{x}10^{-2}\,t$$

$$t = 30.1\text{s}$$

Second order reactions

- Second order RXN – rate depends on the square of the concentration of a single reactant or on the concentration of 2 different reactants .

- A → products or A+ B → products

- $R = k [A]^2$ or $R = k [A] [B]$

Ex:

The following reaction is a second order mechanism

$NO_2 \rightarrow NO + \frac{1}{2} O_2$

$R = k [NO_2]^2$

The integrated rate Law
(second order RXN)

$2A \rightarrow C$

$R = - d[A] / dt = k [A]^2$

$$-\int_{[A]_0}^{[A]} d[A]/[A]^2 = k \int_{t=0}^{t} dt$$

$1 / [A] = 1 / [A]_0 + k t$

- A plot 1 / [A] vs t gives a straight line for second order reaction .

$t_{1/2} = 1 / k[A]_0$, for second order

2nd order Ex:

$2NO \rightarrow 2NO + O_2$

What is the order of reaction

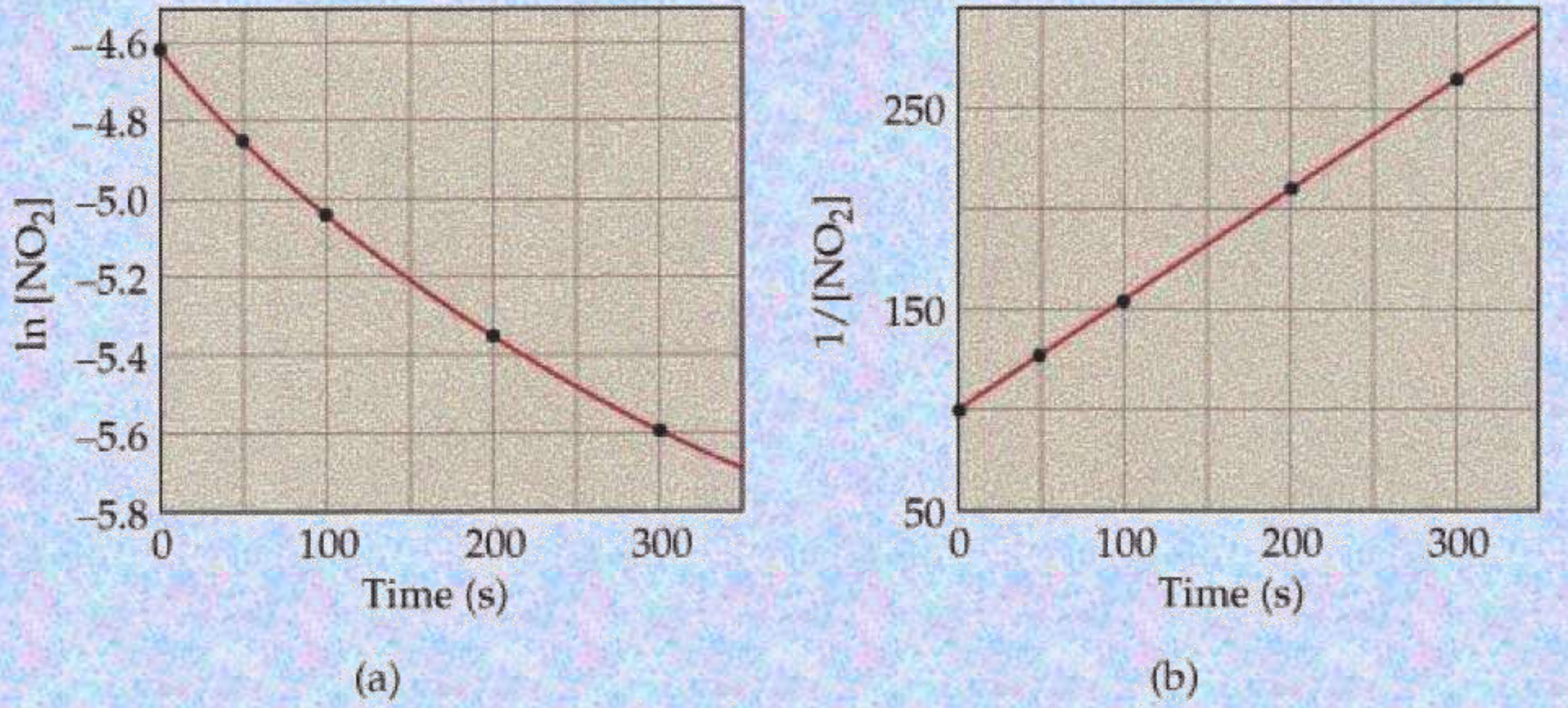
t(s)	$[NO_2]$	$[NO_2]$	$1/[NO_2]$
0	0.01	-4.61	100
50	0.00787	-4.845	127
100	0.00649	-5.038	208
200	0.00481	-5.337	208
300	0.00380	-5.573	263

solution

i) if you do not know the order , make two plots , one ln[NO_2] vs t second 1 / [NO_2] vs t .

ii) The one it is straight line is the order .

Second order plots



(a)

(b)

$NO_2 \rightarrow NO + ½\ O_2$

Zero order reaction

- no dependence on concentration !

- often occurs during catalysis.

$$A \rightarrow p$$

$$R = k\,[A]^{\circ}$$

$$R = k$$

$$- d[A] / dt = k$$

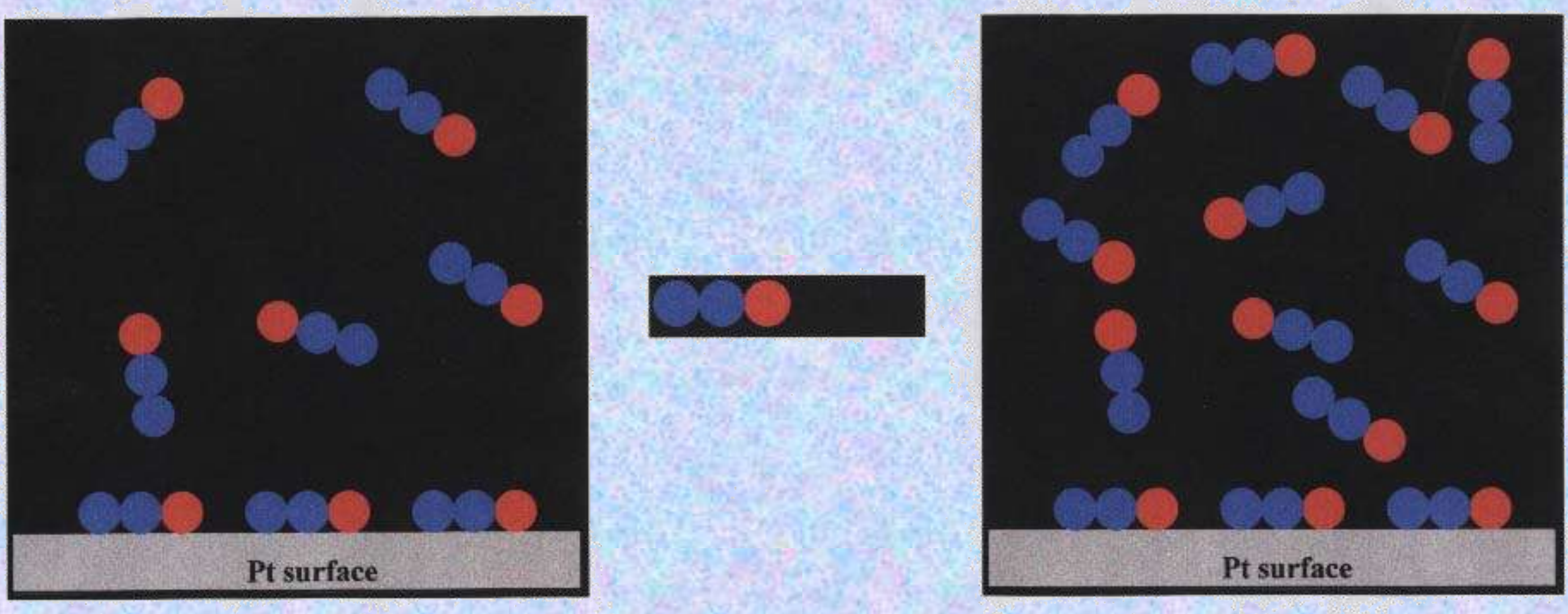
$$-\int_{[A]_0}^{[A]} d[A] = k \int_{t=0}^{t} dt$$

$$[A]_0 - [A] = kt$$

$$t_{1/2} = [A]_0 / 2k$$

Zero – order Example

$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

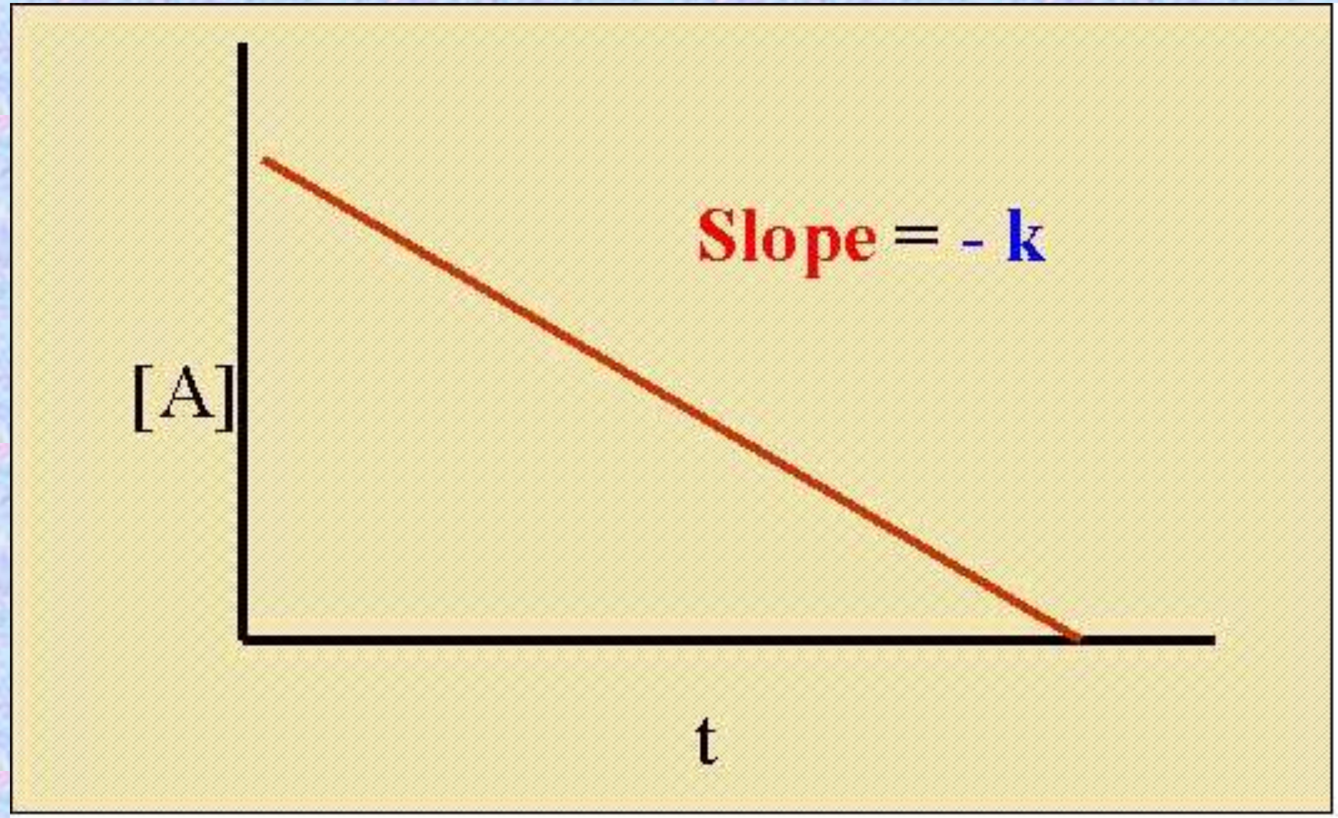


The reaction is catalyzed by Pt and only depends on its surface area – only 3 “slots “ available pictures above .

Increasing the number of N_2O molecules dose not affect rate

Zero – order plot

$[A]_t = -kt + [A]_\circ$



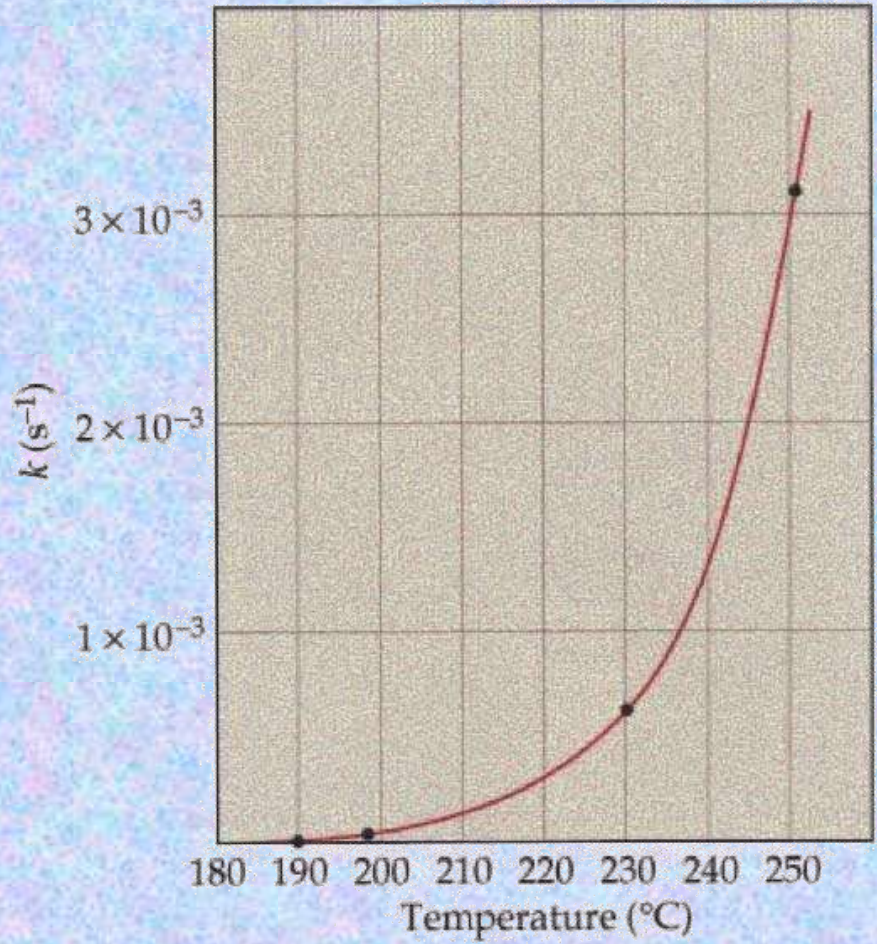
❖Characteristics of zero – first , and second – order reaction of the form $A(s) \rightarrow P$.

Order	Rate expression	Conc – time relation	Half life $t_{1/2}$	Liner plot
0	Rate =k	$[A]_\circ - [A]$	$[A]_0 / 2k$	[A] vs.t
1	Rate = k[A]	$Ln[A]_\circ/[A]=kt$	0.693/ k	ln[A] vs.t
2	Rate =$k[A]^2$	$1/[A] – 1/[A]^\circ=kt$	$1/ k[A]_{0^\circ}$	1/[A] vs.t

A Model for chemical Kinetic

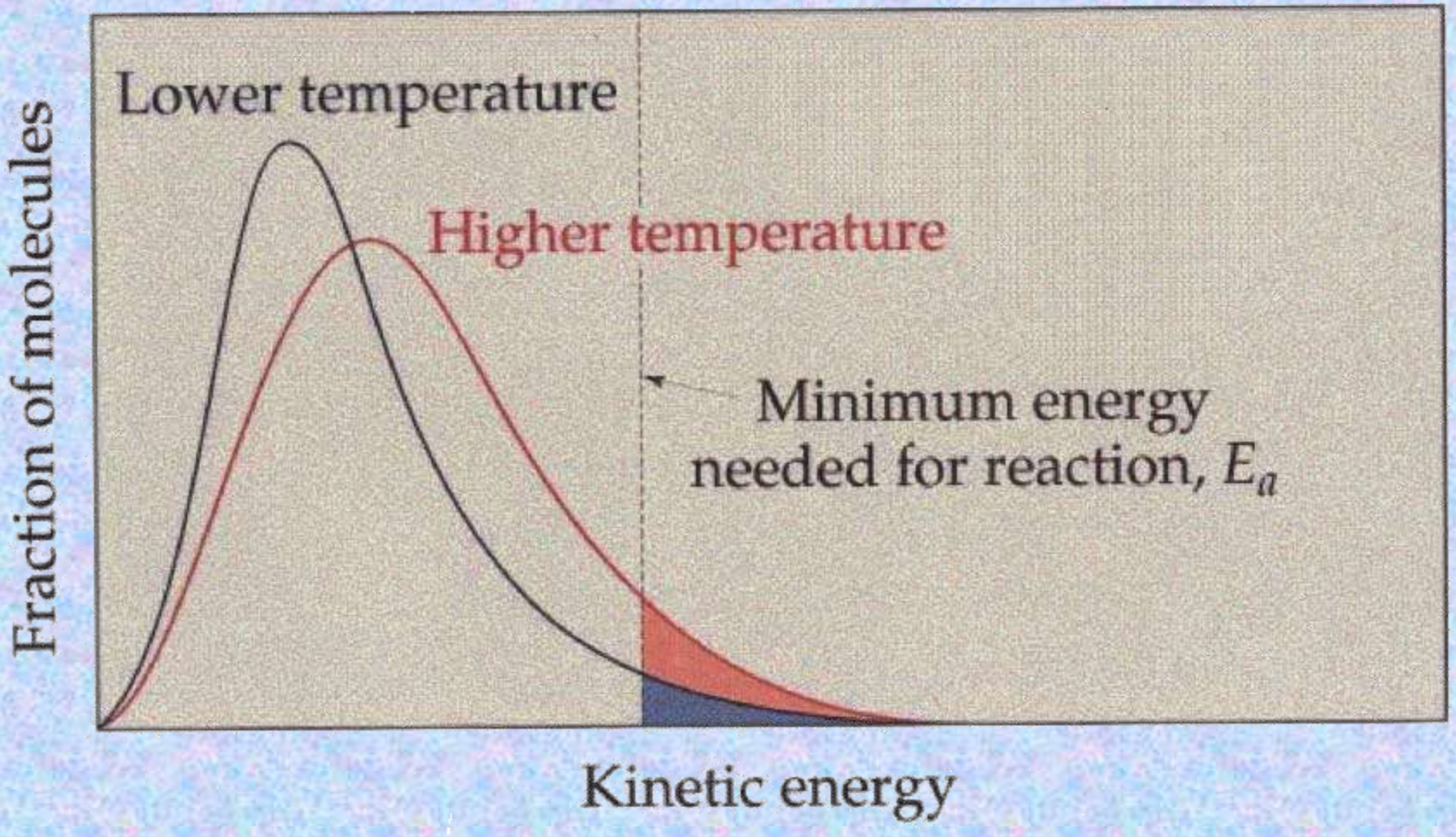
- RXNs speed up when T is increased .
- Molecules must collide to react
- collisions must have sufficient energy .
- During collisions , molecules must have correct orientations .

Rate vs temp



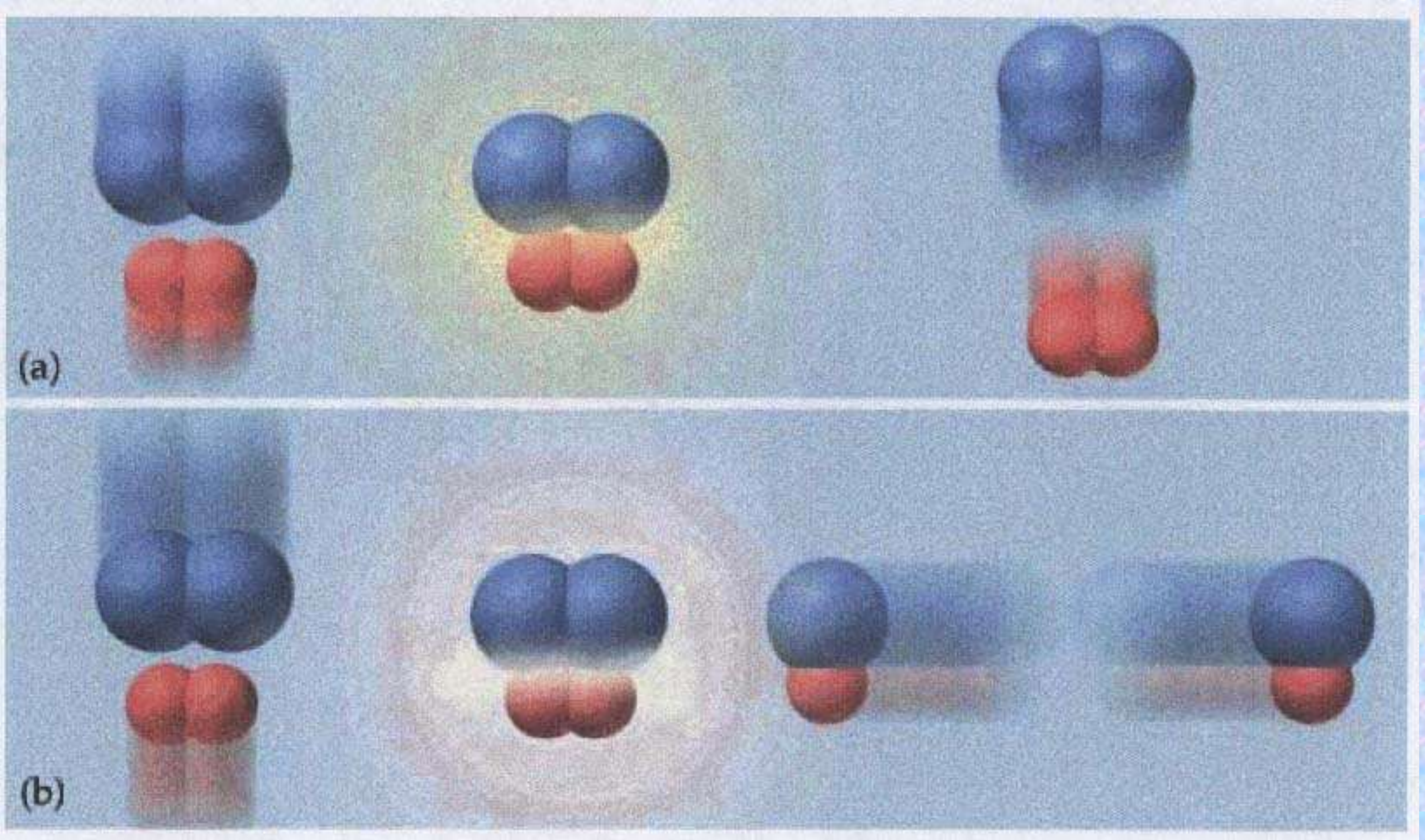
RXNs speed up when T is increased

Distribution of Kinetic Energies



Collisions Must Have sufficient Energy

$A_2 + B_2 \rightarrow 2\,AB$



Too slow

Collision Theory

- Molecules must collide to react .

- More collisions per unit time should lead to faster reaction

- Colliding molecules must have a minimum amount of kinetic energy for a collision result in products (otherwise they just bounce off each other) .

- Minimum collision energy needed is called the activation energy , E_a .

- Raising the temperature of a reaction raises the kinetic energy of the reactants and increases the number of collisions per unit time .

- Raising the temperature should lead to faster reactions .

- At some point , when two molecules collide and react , there is a highest energy state called the transition state This barrier is the activation for the reaction to occur .

Collision orientations

$CI + CINO \rightarrow CI_2 + NO$

(a) Effective collision

(a) Ineffective collision

Activation Energy , Ea

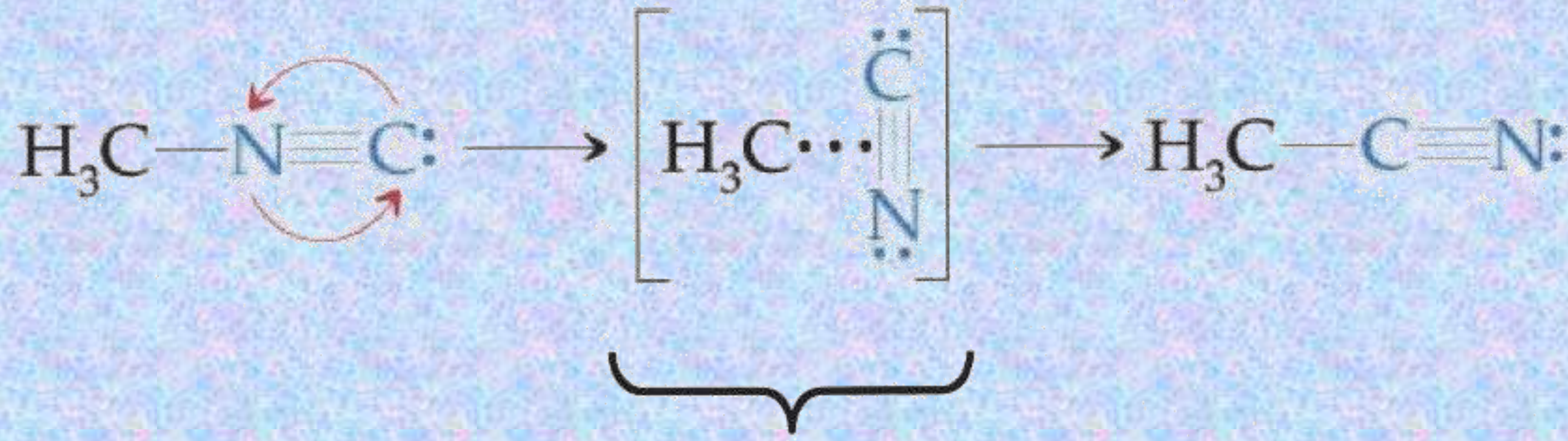
❖E_a = minimum energy required to initiate a chemical reaction

- “ threshold energy “

طاقه محددة

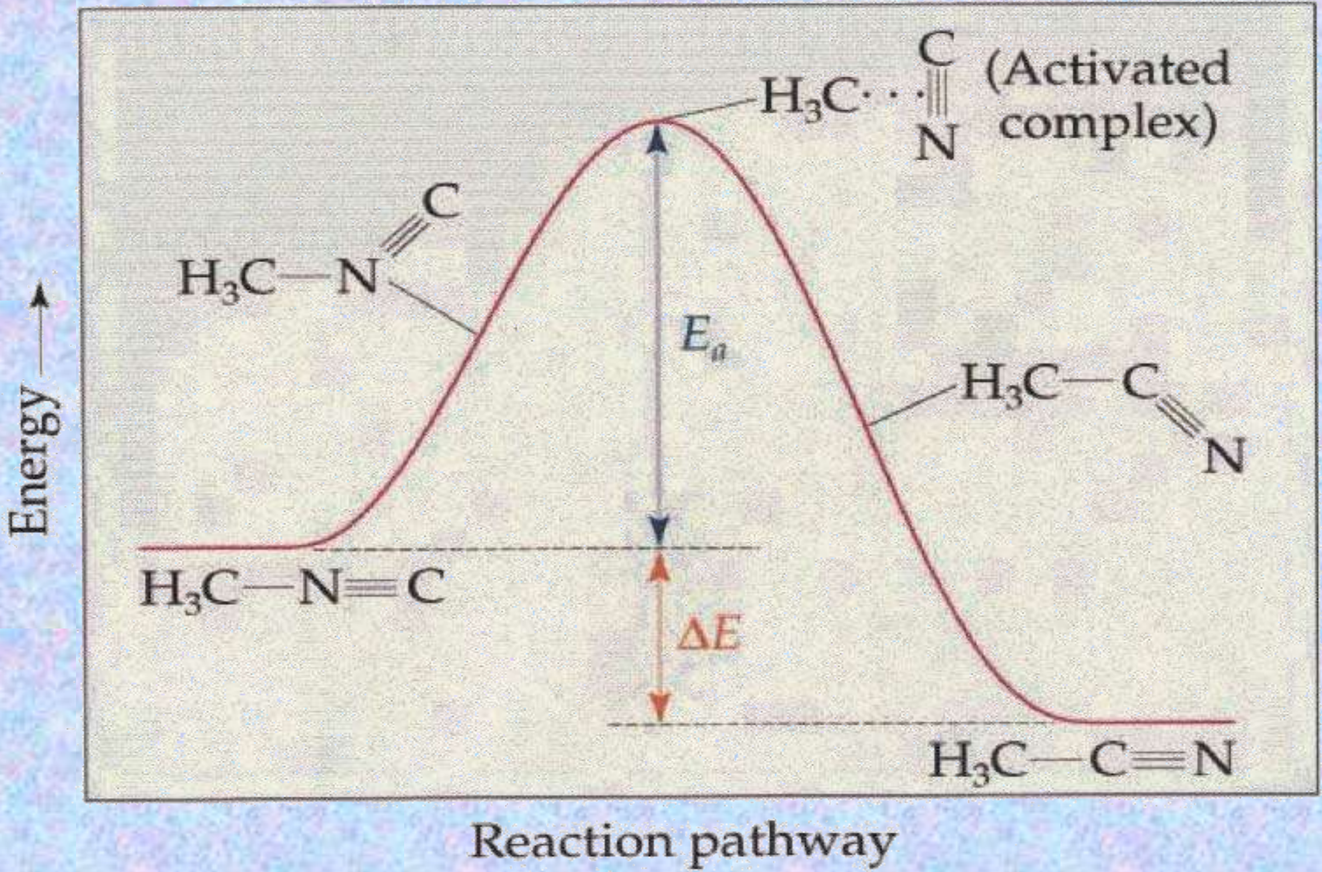
- “ energy hill “

Transition state Example

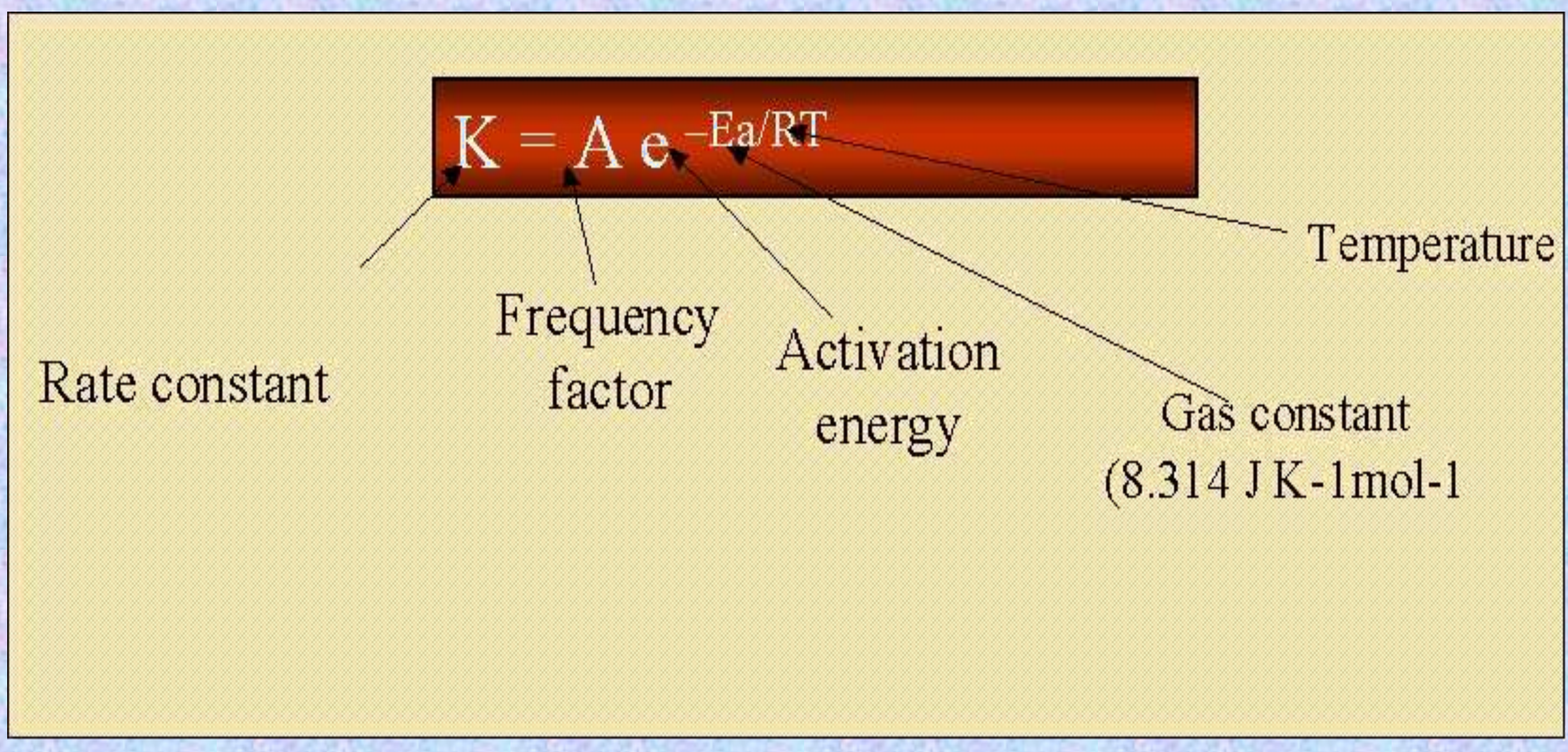


Transition state = activated complex

Energy profile



Arrhenius Equation



$$K = A\,e^{-Ea/RT}$$

Rate constant

Frequency factor

Activation energy

Temperature

Gas constant (8.314 J K-1mol-1

Arrhenius Equation

$k = A\,e^{-Ea / R\,T}$

$\ln k = \ln [A] – Ea / Rt$

It is a linear equation !

Arrhenius plot

2-Arrhenius Equation

$$\ln (k_2/k_1) = Ea / R (T_2 – T_1) / T_2T_1$$

Ex:

- The activation energy of a certain reaction is 76.7 KJ/mol How many times faster will the reaction occur at 50°C than at 0°C ?

Solution

We will use the equation

$$\ln (k_2/k_1) = Ea / R [(T_2 – T_1) / T_2T_1]$$

$$\ln (k_2 / k_1) = [(76.7 \text{ x } 1000) / 8.314] [(323-273)/323\text{x}273]$$

$$\text{Ln } (k_2 /k_{1\,)}= 5.23$$

$$k_2 / k_1 = 187$$

$$k_2 = 187\ k_1$$

Reaction Mechanisms

- Reaction mechanism – process by which a reaction occurs

- Elementary step – single (step) event in a mechanism

- Mechanisms can never be proved .

Molecularity

- Molecularity – number of molecules that participate in an elementary step .

- Unimolecular – 1, $A \rightarrow P$, rate = $k[A]$

- Bimolecular – 2 , $A + A \rightarrow P$, rate = $k[A]^2$

- Termolecular –3 , $A + A + B \rightarrow P$, rate = $k[A]^3$

Multi step Mechanisms

Ex : $NO_2 + CO \rightarrow NO + CO_2$

Proposed mechanism :

1) $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$

2) $NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$

NO_3 is an intermediate

Requirements for a Valid mechanism

- Sum of the elementary steps must give the overall balanced equation .

- Mechanism must agree with the experimentally determined rate law .

Rate laws of Elementary steps

- You can write a rate law directly from the molecularity (stoichiometry) of an elementary step .

From our example :

$$\mathrm{Rate}_1 = k_1[\mathrm{NO_2}]\,[\mathrm{NO_2}] = k_1[\mathrm{NO_2}]^2$$

$$\mathrm{Rate}_2 = k_2[\mathrm{NO_3}]\,[\mathrm{CO}]$$

Rate – Determining step

- Rate – determining step = slow step
- Our example again :

1) $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ **slow**

2) $NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$ **fast**

$\text{Rate}_1 = k_1[NO_2]^2$

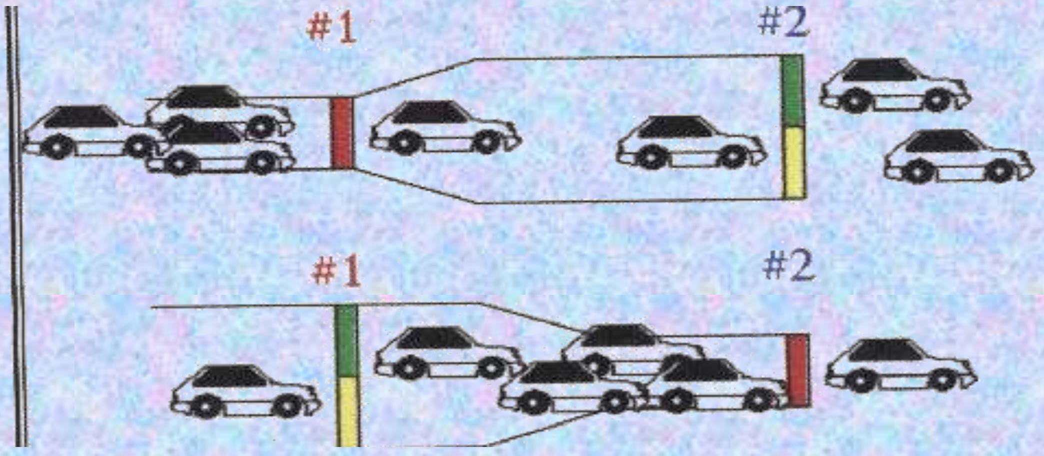
Experiment rate law

$\text{Rate}_{RXN} = k_{RXN}\,[NO_2]^2$

- **Question** : what does a rate law tell us ?

- **Answer** : it gives us information about the elementary steps involved in a reaction

Toll Booth Analogy



1st case : #1 is slow step Rate depends on #1 .

2nd case : #2 is slow step Rate depends on #2

Reactions can work the same way .

Is it a valid Mechanism ?

$NO_2 + NO_2 + NO_3 + CO \rightarrow NO_3 + NO + NO_2 + CO_2$

$NO_2 + CO \rightarrow NO + CO_2$ ✓

$\text{Rate}_{\text{RXN}} = k_{\text{RXN}}[NO_2]^2$

Experimental rate law = $k[NO_2]^2$ ✓

Mechanism with an initial slow step :

$$2NO + F_2 \xrightarrow{k} 2ONF \qquad R = k[NO][F_2]$$

❖ **The suggested mechanism corresponding to bimolecular rate equations is :**

$$1)\ NO + F_2 \xrightarrow{k_1} ONF + F, \qquad R_1 = k_1 [NO] [F_2]$$

slow

$$2)\ NO + F \xrightarrow{k_2} ONF, \qquad R_2 = k_2 [NO] [F]$$

fast

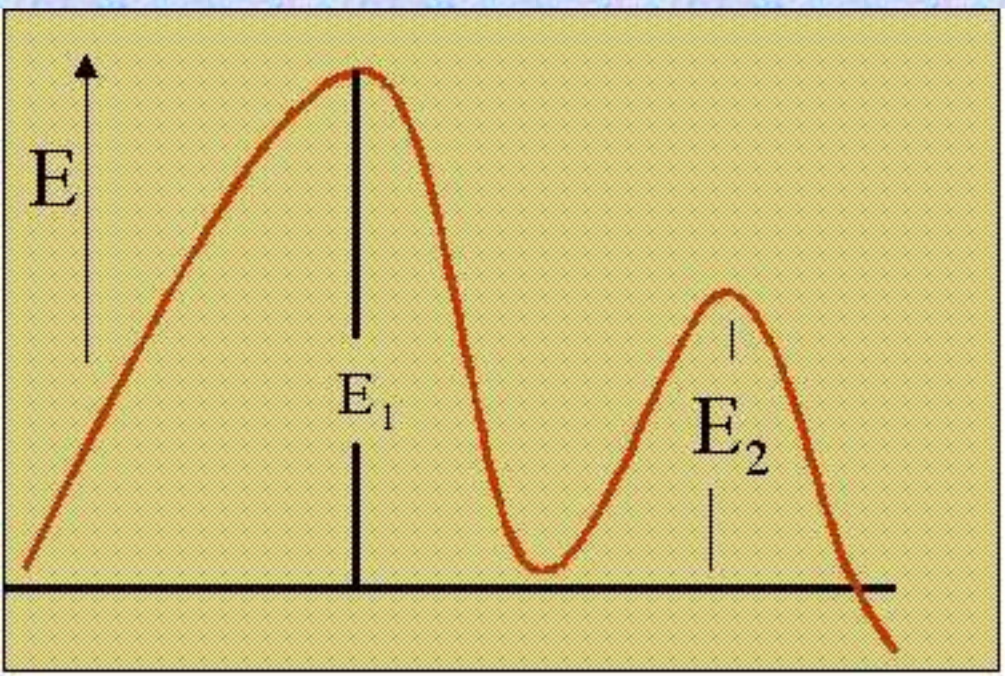
Rate = rate of slowest step

R_1 =R

k_1 [NO] [F_2] = k[NO] [F_2]

Where k_1= k

Energy profile



Mechanism with a final slow step

$$CH_3OH + H^+ + Br^- \xrightarrow{k} CH_3Br + H_2O$$

$$\text{Rate} = k\,[CH_3OH\,]\,[H^+\,]\,[Br^-]$$

1) From the rate equation , the rate tells us the mechanism should occur in one step .

2) But this is not easy to 3 molecule to collision in the same time

3) The reaction believed to occur by three steps none of them is three- body collision .

4) The 3ed step is the slowest one .

i) $CH_3OH + H^+ \xrightarrow{k_1} CH_3OH_2$, $R_1 = k_1[CH_3OH]\ [H^+]$, fast

ii) $CH_3OH_2^+ \xrightarrow{k_2} CH_3OH + H^+$ $R_2 = k_2[CH_3OH^+_2]$, fast

iii) $Br^- + CH_3\ OH^+_2 \xrightarrow{k_3} CH_3\ Rr + H_2O$, $R_3 = k_3[Br^-][CH_3OH^+_2]$, slow

$$R_3 = R$$

$$R = k_3\ [Br^-]\ [CH_3OH^+_2]$$

- **We have $[CH_3\ OH^+_2]$ is the intermediate , we have to eliminate this term from the rate law .**

- **$[CH_3\ OH^+_2]$ can be eliminated by assuming the rate of formation of $[CH_3\ OH^+_2]$ equal the rate of its disappearance .**

- **$k_1 [CH_3\ OH][H^+] = k_2 [CH_3\ OH^+_2] + k_3 [CH_3\ OH^+_2] [Br^-]$ step 2 is two fast than step 3**

Then $k_2 >> k_3$

$k_1 [CH_3OH] [H^+] = k_2[CH^3OH^+_2]$

$[CH_3OH^+_2] = k_1[CH_3OH] [H^+] / k_2$

- By replace $[CH_3OH^+_2]$ in rate equal we get

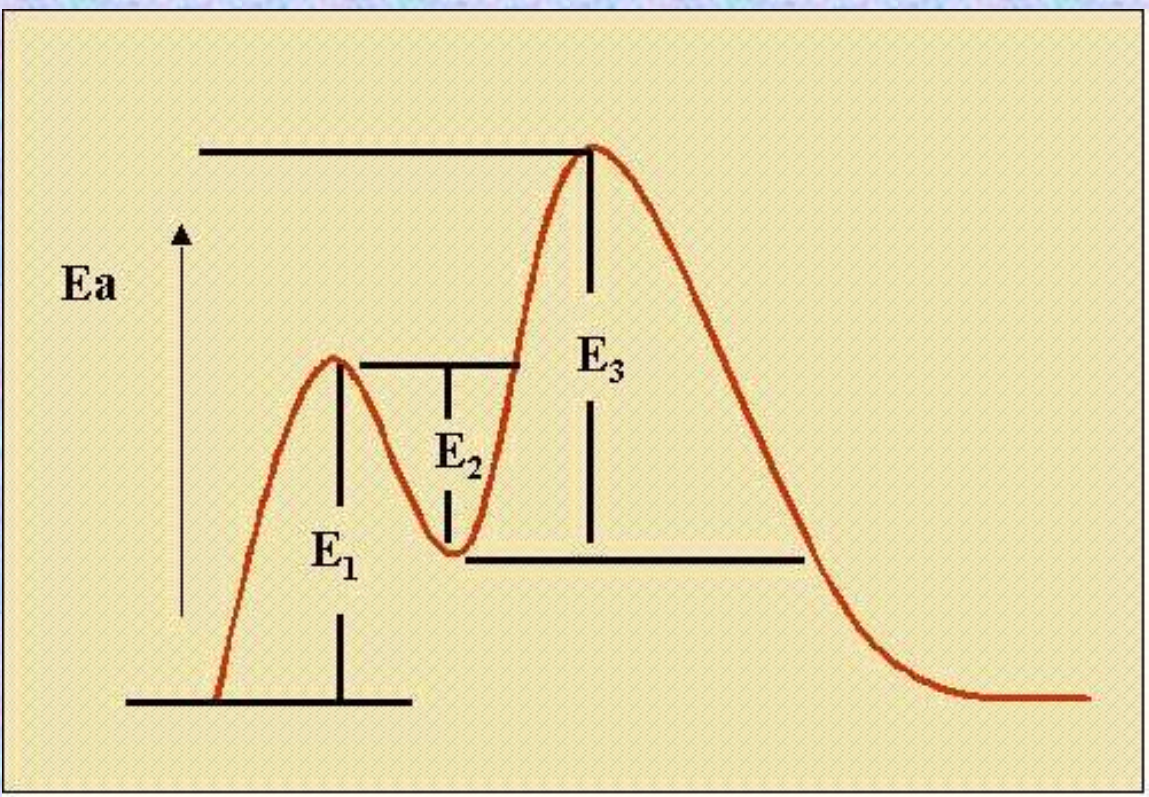
$$\text{Rate} = k_3 [Br^-] R_1 / R_2 [CH_3OH] [H^+]$$

$$= k_3k_1 / K_2 [CH_3OH] [Br^-] [H^+]$$

$$R = k [CH_3OH] [Br^-] [H^+]$$

Where $k = k_1 k_3 / k_2$

Potential energy diagram for three steps mechanism 3ed step is rate determining.



Reaction coordinate

Chain mechanism

$$H_2 + Br_2 \xrightarrow{200^0C} 2H\,Br$$

❖This reaction is occurs according to chain mechanism reaction :

1) $Br_2 \rightarrow 2Br$, chain initiation

2) $Br + H_2 \rightarrow H\,Br + H$ chains

$H + Br_2 \rightarrow H\,Br + Br$ propagate

$Br + H_2 \rightarrow H\,Br + H$

3) $Br + Br \rightarrow Br_2$ chains

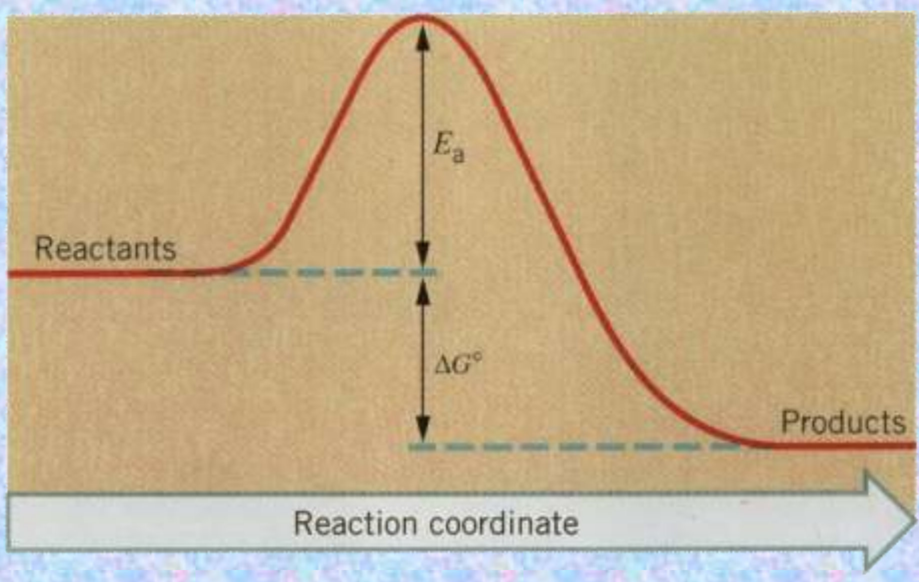
$H + H \rightarrow H_2$ terminate

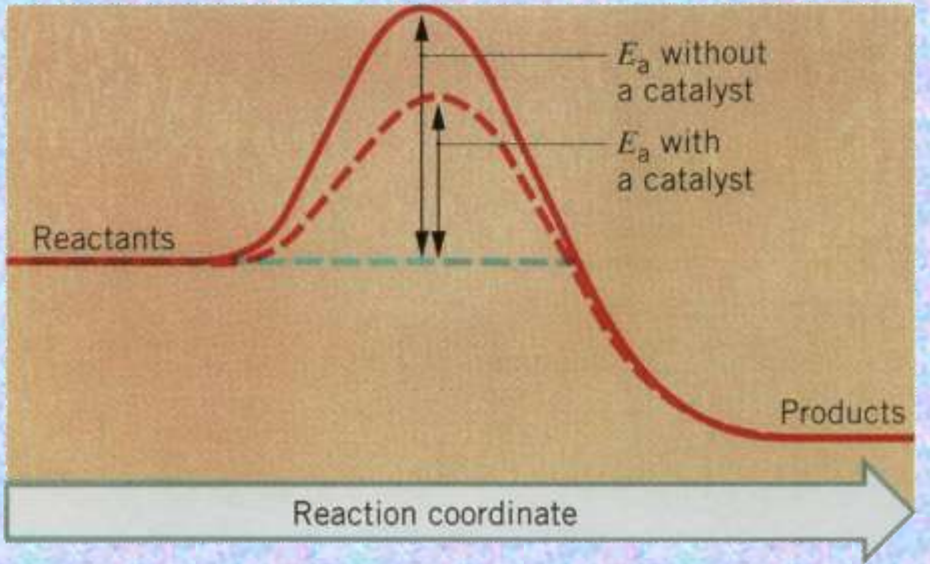
Catalysis

- Catalyst – substance that increases the rate of a reaction without undergoing permanent chemical change itself .

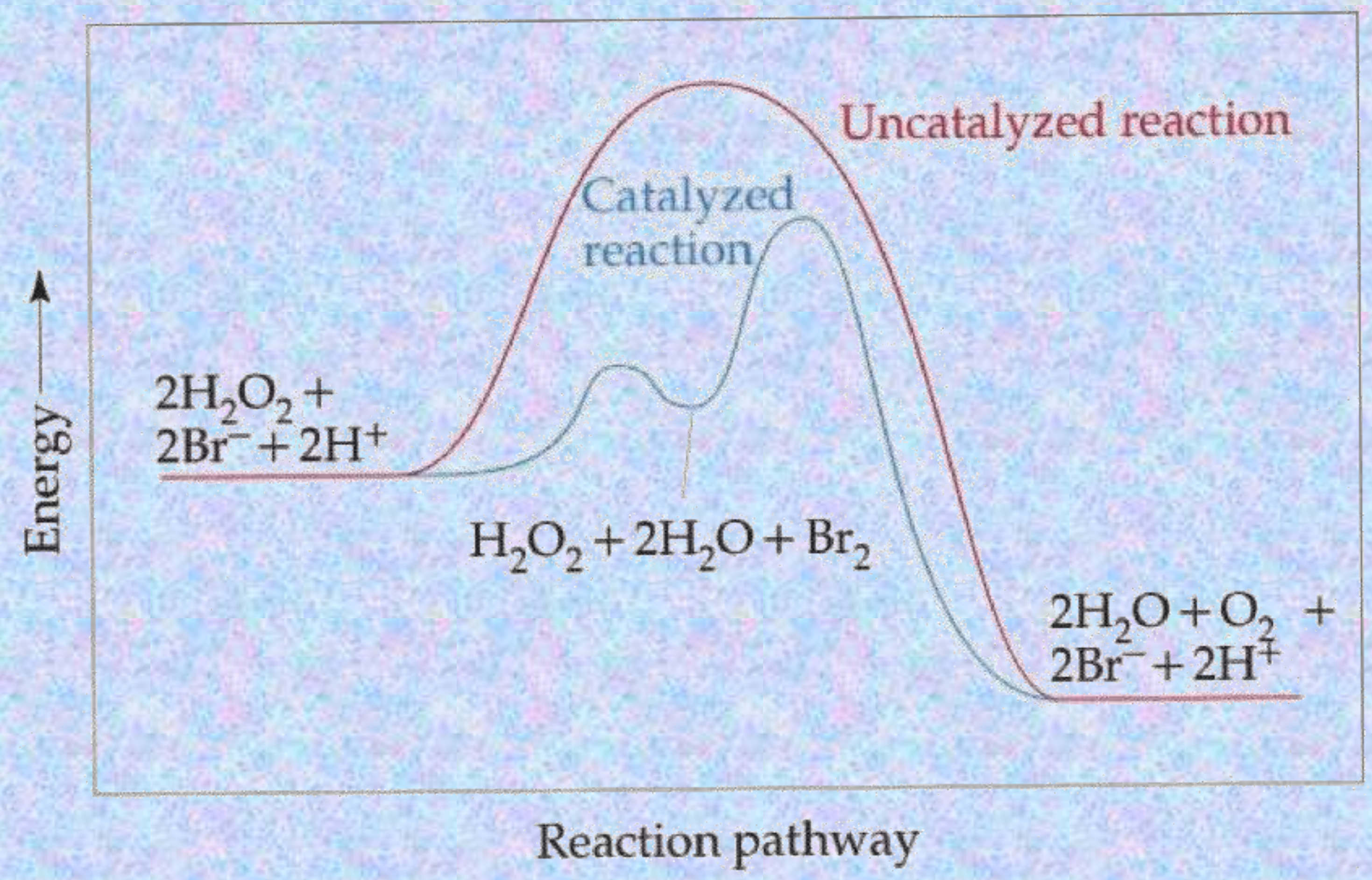
- A catalyst lowers the activation energy for the reaction .

- Usually , by providing a completely different mechanism .


E_a
Reactants
$\Delta G°$
Products
Reaction coordinate


E_a without a catalyst
E_a with a catalyst
Reactants
Products
Reaction coordinate

Catalysis energy profile



Types of Catalysis

- **Homogeneous – catalyst and reacting molecules are in the same phase .**

- **Heterogeneous – catalyst and reacting molecules are in different phases .**

Heterogonous catalyst

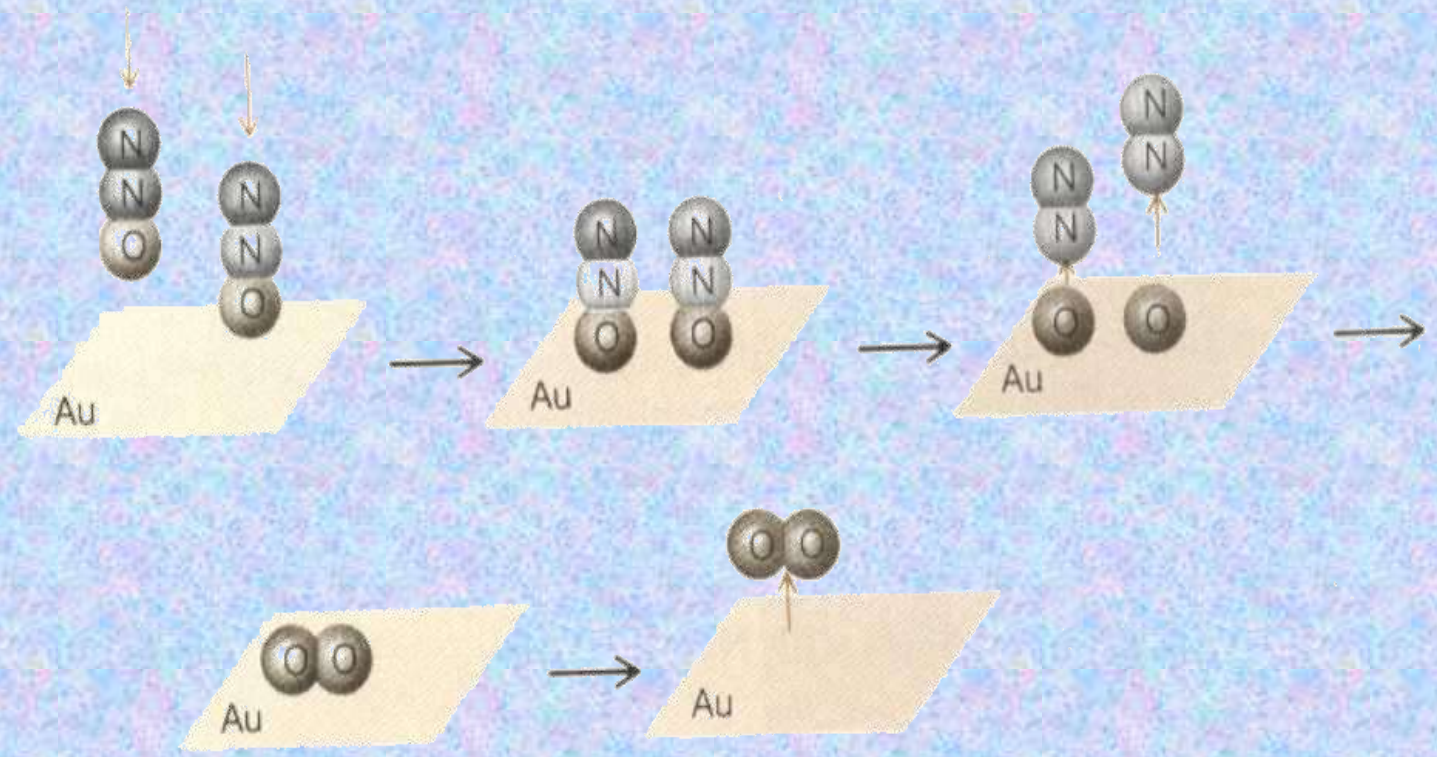
$$N_2O\,(g) \xrightarrow{Au} N_2(\,g) + O_2(g)$$

1) $N_2O(g) \rightarrow N_2O$ (on Au)

2) N_2O(on Au) $\rightarrow N_2$ (g) + O on(Au)

3) O (on Au) + O (on Au) $\rightarrow O_2$

$R = k\,[N_2O]_0 = k$


N
N
O
N
N
O
Au
N
N
O
N
N
O
Au
N
N
O
N
N
O
Au
O O
Au
O O
Au

$2N_2\,O(s) \rightarrow 2N_2\,(g) + O_2\,(g)$, Ea =245 KJ, No catalyst

$2N_2O(s) + \xrightarrow{Cl_2} 2N_2\,(g) + O_2(g) + CL_2$, Ea = 140 KJ ,

homogeneous catalyst.

$2N_2\,O \xrightarrow{Au} 2N_2\,(g) + O_2\,(g)$, Ea =120 KJ ,

heterogeneous.