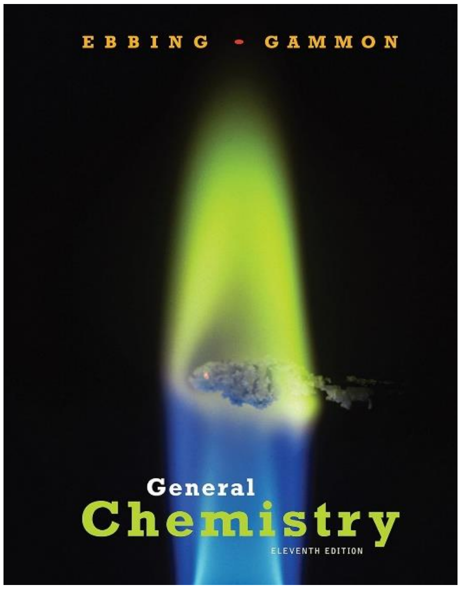


Chapter 13
Chemical Kinetics

The Rate of Reaction

Chemical kinetics: The study of reaction rates, including how reaction rates change with varying conditions and which molecular events occur during the overall reaction.

- **Reaction rate (معدل سرعة التفاعل):** The change in the concentration of a reactant or a product with time (M/s).

- **معدل سرعة التفاعل:** التغير في تركيز المتفاعلات أو النواتج لكل وحدة زمن.

$$A \longrightarrow B$$

$$Rate = -\frac{\Delta[A]}{\Delta t}$$

$$Rate = \frac{\Delta[B]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

$\Delta[B]$ = change in concentration of B over time period Δt

- **وحدة سرعة التفاعل(Rate):**

$$M/s = mol/L \cdot s = mol\,L^{-1}\,s^{-1}$$

Example

إذا كان لدينا المعادلة التالية:

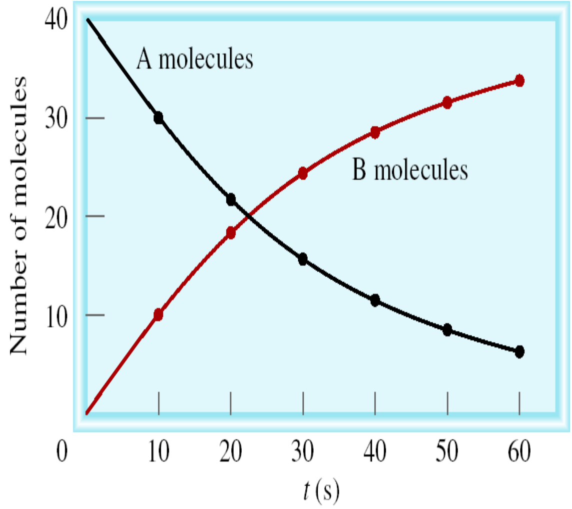
$$aA + bB \rightarrow cC + dD$$

$$So,\ \underbrace{rate = \frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}}_{\text{“Rate expression”}}$$

-الاشارة السالبة تدل على نقصان تركيز المتفاعلات مع الزمن

$$\mathbf{2A \rightarrow B}$$

Rate expression: $rate = \frac{-1}{2}\frac{\Delta[A]}{\Delta t} = \frac{-1}{1}\frac{\Delta[B]}{\Delta t}$



Example 1:

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

1. $2KClO_3 \rightarrow 2KCl + 3O_2$
2. $2KClO_3 + 4KCl \rightarrow 6KCl + 3O_2$
3. $I^- + OCl^- \rightarrow Cl^- + OI^-$

Solution:

1. $Rate = \frac{-1}{2}\frac{\Delta[KClO_3]}{\Delta t} = \frac{1}{2}\frac{\Delta[KCl]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$
2. $Rate = \frac{-1}{2}\frac{\Delta[KClO_3]}{\Delta t} = \frac{-1}{4}\frac{\Delta[KCl]}{\Delta t} = \frac{1}{6}\frac{\Delta[KCl]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$
3. $Rate = \frac{-1}{1}\frac{\Delta[I^-]}{\Delta t} = \frac{-1}{1}\frac{\Delta[OCl^-]}{\Delta t} = \frac{1}{1}\frac{\Delta[Cl^-]}{\Delta t} = \frac{1}{1}\frac{\Delta[OI^-]}{\Delta t}$

Example 2:

Suppose that, at a particular moment during the reaction, molecular NO_2 is formed at the rate of 0.036 M/s.

(a) At what rate is N_2O_5 being reacting?

(b) At what rate is O_2 formed?

Solution:

$$Rate = \frac{-1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{1}{1}\frac{\Delta[O_2]}{\Delta t} \quad , \frac{\Delta[NO_2]}{\Delta t} = 0.036\ M/s$$

$a.\quad \frac{-1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} \quad ,$

$$\frac{\Delta[N_2O_5]}{\Delta t} = -2 \times \frac{0.036}{4} = -0.018\ M/s$$

$b.\quad \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{1}{1}\frac{\Delta[O_2]}{\Delta t} \quad ,$

$$\frac{\Delta[O_2]}{\Delta t} = \frac{0.036}{4} = 0.009\ M/s$$

• The Rate Law

Rate law: the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$Rate = k[A]^x[B]^y$

$$aA + bB \rightarrow cC + dD$$

$x = order\ of\ A$ رتبة A

$y = order\ of\ B$ رتبة B

$x + y = order\ of\ the\ reaction$ رتبة التفاعل

$k = Rate\ constant$

(تحديد رتبة التفاعل بطريقتين)

1. $x + y = 0$, *zero order reaction*
2. $x + y = 1$, *first order reaction*
3. $x + y = 2$, *second order reaction*
4. $x + y = 3$, *third order reaction*

Order of the reaction	Units of k
1. Zero order	$mol\ L^{-1}\ s^{-1} = \boldsymbol{M\ s^{-1}}$
2. First order	$\boldsymbol{s^{-1}}$
3. Second order	$L\ mol^{-1}\ s^{-1} = \boldsymbol{M^{-1}\ s^{-1}}$
4. Third order	$L^2\ mol^{-2}\ s^{-1} = \boldsymbol{M^{-2}\ s^{-1}}$

Example 1:

Consider the following data of the oxidation of iodide with hydrogen peroxide:

$$H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2\,H_2O$$

Determine:

(a) the rate law

(b) the rate constant

(c) the rate of the reaction when $[I^-]$ = 0.03 M, $[H^+]$ = 6.0 × 10^{-3} M

and $[H_2O_2]$ = 5.0 × 10^{-3} M

Solution:

Exp. No.	Initial $[H_2O_2]_0$ (M)	Initial $[I^-]_0$ (M)	Initial $[H^+]_0$ (M)	Initial Rate (M/s)
1	0.010	0.010	0.00050	1.15×10^{-6}
2	0.020	0.010	0.00050	2.30×10^{-6}
3	0.010	0.020	0.00050	2.30×10^{-6}
4	0.010	0.010	0.00100	1.15×10^{-6}

a. $rate = k\,[H_2O_2]^x[I^-]^y[H^+]^z$

b. To find k you should know x , y and z

Exp 4 ÷ 1: $\frac{1.15\times10^{-6}=k\,[0.010]^x[0.010]^y[0.00100]^z}{1.15\times10^{-6}=k\,[0.010]^x[0.010]^y[0.00050]^z} \rightarrow$

$$\frac{1.15\times10^{-6}}{1.15\times10^{-6}} = \frac{k}{k}\left(\frac{0.010}{0.010}\right)^x \left(\frac{0.010}{0.0.10}\right)^y \left(\frac{0.00100}{0.00050}\right)^z$$

$\rightarrow 1 = 1^x1^y2^z \;\rightarrow 1 = 2^z \;\rightarrow z = 0$

Exp 3 ÷ 1: $\frac{2.30\times10^{-6}}{1.15\times10^{-6}} = \frac{k}{k}\left(\frac{0.010}{0.010}\right)^x \left(\frac{0.020}{0.\,010}\right)^y \left(\frac{0.00050}{0.00050}\right)^0$

$$2 = 2^y \;\rightarrow y = 1$$

Exp 2 ÷ 1: $\frac{2.30\times10^{-6}}{1.15\times10^{-6}} = \frac{k}{k}\left(\frac{0.020}{0.010}\right)^x \left(\frac{0.010}{0.010}\right)^1 \left(\frac{0.00050}{0.00050}\right)^0$

$$2 = 2^x \;\rightarrow x = 1$$

Let we chose Exp 1: $rate = k\,[H_2O_2]^1[I^-]^1[H^+]^0 \;\rightarrow \boldsymbol{rate = k[H_2O_2][I^-]}$

$1.15\times10^{-6} = k \times 0.010^1 \times 0.010^1$

$$k = \frac{1.15\times10^{-6}\;M/s}{0.010\;M\;\times 0.010\;M} = \mathbf{0.0115\;M^{-1}s^{-1}}$$

$$\boxed{\begin{array}{c} x + y + z = 1 + 1 + 0 = 2 \\ \text{رتبة التفاعل} = 2 \end{array}}$$

c. $rate = k[H_2O_2][I^-] = 0.0115\;\times 5\times10^{-3}\times 0.03\;\times 0.006^0 = \mathbf{1.7\times10^{-6}\;M/s}$

Example 2:

The reaction of nitric oxide with hydrogen at 1280°C is

$$\mathbf{2NO + 2H_2 \rightarrow N_2 + 2H_2O}$$

If the rate constant is $2.5 \times 10^2\ M^{-2}s^{-1}$,find the rate of the reaction when

$[NO] = 0.055\ M\ and\ [H_2] = 0.01\ M$

Exp. No.	$[NO]$(M)	$[H_2]$ (M)	(M/s)
1	0.005	0.002	1.3×10^{-5}
2	0.01	0.002	5×10^{-5}
3	0.01	0.004	10×10^{-5}

Solution:

$rate = k[NO]^x[H_2]^y$

Firstly we should find x and y , Exp 2 ÷ 1: $\frac{5\times10^{-5}}{1.3\times10^{-5}} = \frac{k}{k}\left(\frac{0.01}{0.005}\right)^x \left(\frac{0.002}{0.002}\right)^y \rightarrow\ \cong\ 4 = 2^x \rightarrow\ x = 2$

From rate constant: $M^{-2}s^{-1}$, so order of the reaction is third order (3 = رتبة التفاعل)

$$\boxed{\begin{array}{c} x + y = 3 \\ 2 + y = 3\,,\ \ y = 1 \end{array}}$$

$rate = k[NO]^2[H_2] = 2.5 \times 10^2 \times 0.055^2 \times 0.01 = 7.56 \times 10^{-3}\ M/s$

• Change of Concentration with Time

To calculate the concentration of a reactant (or product) after some time of starting the reaction

We use Integrated Rate Laws (Concentration—Time Equations)

كيفية حساب التركيز في التفاعل بعد مدة معينة من الزمن من بدأ التفاعل

• First-Order Reactions

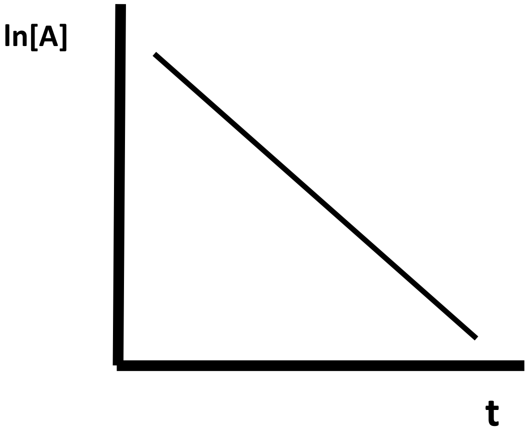
For $\boldsymbol{A \rightarrow Product}$

$$Rate = k[A]$$

$$k = \frac{rate}{[A]} = \frac{M/s}{M} = s^{-1}$$

$$ln[A] = ln[A°] - kt$$

$$or, \ln\left(\frac{[A]}{[A°]}\right) = -kt$$



[A] is the concentration of A at any time t

$[A]_0$ is the concentration of A at time t=0

$$Slope = -k$$

$$Intercept = \ln\,[A°]$$

Half-life, $t_{1/2}$

is the time required for the concentration of a reactant to decrease to half of its initial concentration.

الزمن اللازم لخفض تركيز المادة المتفاعلة إلى نصف تركيزها الأول.

$$t_{1/2} = t \ , \ when \ [A] = \frac{[A°]}{2}$$

Half-life for first order is:

$ln[A] = ln[A°] - kt \ \rightarrow kt_{1/2} = \ln[A°] - \ln[A]$

$$\rightarrow kt_{1/2} = \ln\left(\frac{[A°]}{[A°]/2}\right) = kt_{1/2} = \ln 2$$

So, $\boldsymbol{t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}}$

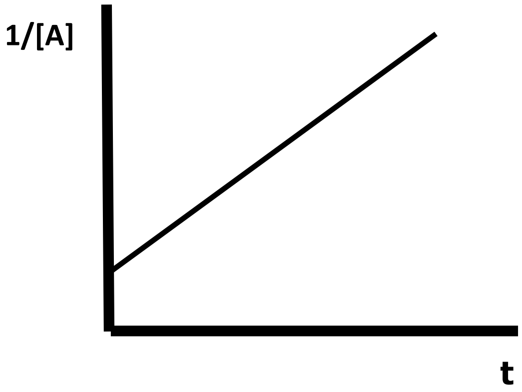
- ## Second-Order Reactions

$Rate = k[A]^2$

$k = \frac{rate}{[A]^2} = \frac{M/s}{M^2} = M^{-1}\, s^{-1}$

$$\frac{1}{[A]} - \frac{1}{[A°]} = kt$$

$$T_{1/2} = \frac{1}{k[A°]}$$



$Slope = -k$

$Intercept = [A°]$

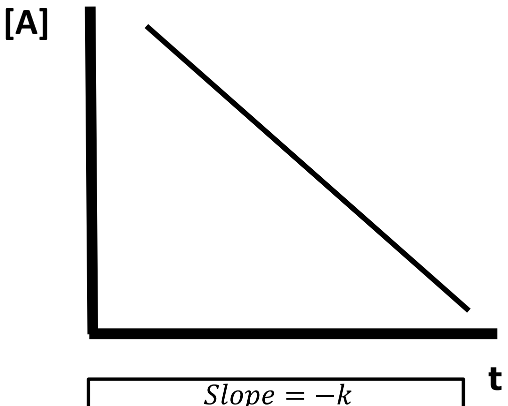
- **Zero-Order Reactions**

$Rate = k$

$k = rate = M/s$

$$[A] - [A°] = -kt$$

$$T_{1/2} = \frac{[A°]}{2k}$$



$Slope = -k$

$Intercept = [A°]$

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order of the reaction	Order	Rate law	Units of k	Concentration time equation	Half-Life	Straight-Line Plot
Zero order	0	$Rate = k$	$M\ s^{-1}$	$[A] - [A°] = -kt$	$T_{1/2} = \frac{[A°]}{2k}$	$[A]\ vs\ t$
First order	1	$Rate = k[A]$	s^{-1}	$\ln[A] = \ln[A°] - kt$	$T_{1/2} = \frac{ln2}{k}$	$\ln[A]$ vs t
Second order	2	$Rate = k[A]^2$	$M^{-1}\ s^{-1}$	$\frac{1}{[A]} - \frac{1}{[A°]} = kt$	$T_{1/2} = \frac{1}{k[A°]}$	$\frac{1}{[A]}\ vs\ t$

Example 1:

The hydrolysis of a certain compound A follows first-order kinetics with a rate constant of $2.5 \times 10^{-3}\ s^{-1}$ at 25°C. If the initial concentration of A is 0.020 mol/L, determine:

1. The concentration of A after 300 seconds.
2. How long in minutes it take for the concentration of A to decrease to 0.010 mol/L from its initial value?

Solution:

1. $ln[A] = ln[A°] - kt$

$$\ln[A] = \ln[0.020] - 2.5 \times 10^{-3} \times 300$$

$$\ln[A] = -4.66 \quad \rightarrow \quad [A] = e^{-4.66} = 9.45 \times 10^{-3}\ M$$

2. $ln[A] = ln[A°] - kt$

$$\ln[0.010] = \ln[0.020] - 2.5 \times 10^{-3} \times t$$

$$t = \frac{\ln[0.010] - \ln\,[0.020]}{-2.5 \times 10^{-3}} = 277\ s = 4.6\ min$$

Example 2:

A second-order reaction is 46% complete at the end of 33 minutes. What is the length of the second half-life of this reaction?

A. 2225 s
B. 40 min
C. 27 min
D. 39 min
E. 38.8 s

Solution:

$$\frac{1}{[A]} - \frac{1}{[A°]} = kt$$

$$k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A°]}\right) = \frac{1}{33\ min \times 60\ s/min}\left(\frac{1}{54} - \frac{1}{100}\right) = \frac{1}{1980\ s} \times 8.52 \times 10^{-3}\ M^{-1} = 4.3 \times 10^{-6}\ M^{-1}\ s^{-1}$$

$$T_{1/2} = \frac{1}{k[A°]} = \frac{1}{4.3 \times 10^{-6} \times 100} = 2325.6\ s = \mathbf{38.8\ min}$$

Example 3:

The decomposition of compound A is a reaction with a rate constant of 1.8×10^{-2} M/s at 30°C. determine:

a. How long it takes for the concentration of A to decrease from 0.058 M to 0.004 M ?
b. How long (in minutes) will it take to convert 63 percent of the starting material?
c. Calculate the half-life of the reaction if the initial concentration of A is 0.0055 *M* and if it is 0.001 *M*.

Solution:

a. $[A] - [A°] = -kt$

$$0.004 - 0.058 = -1.8 \times 10^{-2} \times t \rightarrow t = \frac{0.004 - 0.058}{-1.8 \times 10^{-2}} = \mathbf{3\ s}$$

b. $[A] - [A°] = -kt$

$$37 - 100 = -1.8 \times 10^{-2} \times t \rightarrow t = \frac{37 - 100}{-1.8 \times 10^{-2}} = 3500\ s = \mathbf{58\ min}$$

c. $t_{1/2} = \frac{[A°]}{2k} = \frac{0.0055}{2 \times 1.8 \times 10^{-2}} = \mathbf{0.15\ s}$

$$t_{1/2} = \frac{[A°]}{2k} = \frac{0.001}{2 \times 1.8 \times 10^{-2}} = \mathbf{0.028\ s}$$

• Activation Energy

Effect of temperature on the reaction rate:

تأثير درجة الحرارة على سرعة التفاعل:

$Temperature \uparrow \rightarrow$	$Kinetic\ energy \uparrow \rightarrow$	$number\ of\ collision \uparrow \rightarrow$	$rate\ of\ the\ reaction \rightarrow$	$rate\ constant\ (k) \uparrow$
درجة الحرارة	الطاقة الحركية	عدد التصادمات	سرعة التفاعل	ثابت سرعة التفاعل

In collision theory, the rate constant (*k*) for a reaction depends on:

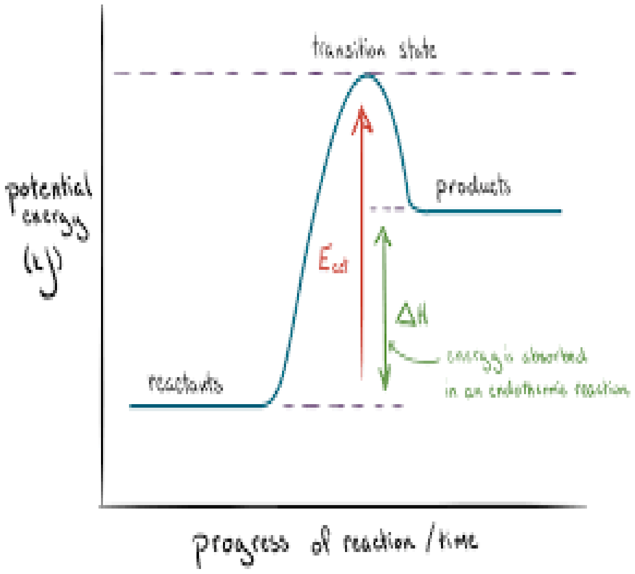
1. The collision frequency (number of collisions per unit time)
2. The fraction of collisions having energy greater than the activation energy (Ea)

activation energy (E_a) (طاقة التنشيط): The minimum amount of energy required to initiate a chemical reaction.

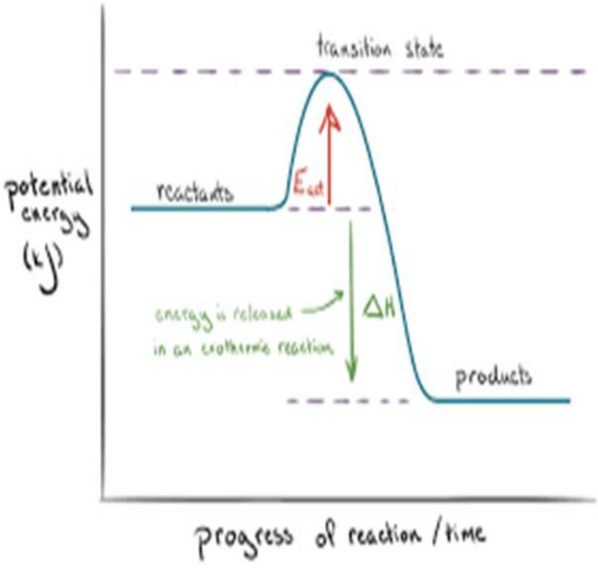
طاقة التنشيط: أقل طاقة لازمة لحدوث التفاعل الكيميائي.

1101	Endothermic reaction	Exothermic reaction
Reactants and products	Reactants < products	Reactants > products
ΔH إشارة	+	-
E_a	$E_{a_{endo}} > E_{a_{exo}}$	$E_{a_{endo}} > E_{a_{exo}}$
$E_a\ forward\ and\ E_a\ reverse$	$E_a\ forward > E_a\ reverse$	$E_a\ forward < E_a\ reverse$

$$\underbrace{A + B}_{\text{Reactants}} \rightarrow \underbrace{C + D}_{\text{Products}}$$



Endothermic reaction (ماص للحرارة)



Exothermic reaction (طارد للحرارة)

Rate constant is related to temperature with **Arrhenius Equation.**

$$k = Ae^{-E_a/(RT)}$$

$$\downarrow$$

$$ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

A : Constant called the frequency factor.

E_a: Activation energy (J/mol)

R : Gas constant: 8.314 J/mol.K

T : temperature in K

k : rate constant

Example 1:

The rate constant of a first-order reaction is $2.58 \times 10^{-3}\ s^{-1}$ at 0°C.

If the activation energy for the reaction is 45.6 kJ/mol, what is the rate constant at 37°C?

Solution:

$$ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{2.58 \times 10^{-3}}{k_2}\right) = \frac{45600}{8.314}\left(\frac{1}{310} - \frac{1}{273}\right)$$

$$ln\left(\frac{2.58 \times 10^{-3}}{k_2}\right) = -2.4 \quad , \quad \frac{2.58 \times 10^{-3}}{k_2} = e^{-2.4}$$

$$k_2 = \frac{2.58 \times 10^{-3}}{e^{-2.4}} = \mathbf{0.028\ s^{-1}}$$

$$k_1 = 2.58 \times 10^{-3}\ s^{-1} \ , \ k_2 = \ ??$$

$$T_1 = 0°\text{C} \rightarrow 273\ K \quad , \quad T_2 = 37°\text{C} \rightarrow 310\ K$$

$$E_a = 45.6\frac{KJ}{mol} = 45600\frac{J}{mol}, \ R = 8.314\ J/K \cdot mol$$

Example 2:

The rate constant for the decomposition of nitrogen pentoxide into nitrogen dioxide and oxygen is $1.2 \times 10^{-3}\ mol/L \cdot s$ at 400 K and $2.8 \times 10^{-2}\ mol/L \cdot s$ at 450 K.

a. Find the activation energy E_a .
b. Calculate the rate constant at 500 K.

Solution:

$$ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$k_1 = 1.2 \times 10^{-3}\ mol/L \cdot s,\ \ k_2 = 2.8 \times 10^{-2}\ mol/L \cdot s$$

$$T_1 = 400\ K\ ,\quad T_2 = 450\ K$$

$$E_a = \ ??\ ,\ \ R = 8.314\ J/K \cdot mol$$

$$a.\quad \ln\left(\frac{1.2\times10^{-3}}{2.8\times10^{-2}}\right) = \frac{E_a}{8.314}\left(\frac{1}{450} - \frac{1}{400}\right)$$

$$-3.15 = E_a \times -3.34 \times 10^{-5}$$

$$\rightarrow E_a = 94280\, J = \mathbf{94.28\ KJ}$$

$$k_1 = 1.2 \times 10^{-3}\frac{mol}{L} \cdot s,\ \ k_2 = ??$$

$$T_1 = 400\ K\ ,\quad T_2 = 500\ K$$

$$E_a = 94280\, J\ ,\ \ R = 8.314\ J/K \cdot mol$$

$$b.\quad ln\left(\frac{1.2\times10^{-3}}{k_2}\right) = \frac{94280}{8.314}\left(\frac{1}{500} - \frac{1}{400}\right)$$

$$ln\left(\frac{1.2 \times 10^{-3}}{k_2}\right) = -5.67\quad ,\quad \frac{1.2 \times 10^{-3}}{k_2} = e^{-5.67}$$

$$k_2 = \frac{1.2 \times 10^{-3}}{e^{-5.67}} = \mathbf{0.35\ M^{-1}\ s^{-1}}$$

Elementary reactions and reaction mechanism

A balanced chemical equation is a description of the overall result of a chemical reaction.

❑ The overall reaction is actually made from several one-step reactions. Each is called **Elementary reaction**:

$NO_2 + F_2 \rightarrow NO_2F + F$	Elementary reaction 1	Reaction mechanism
$F + NO_2 \rightarrow NO_2F$	Elementary reaction 2	
$2NO_2 + F_2 \rightarrow 2NO_2F$	Overall reaction	

❑ The sequence of **elementary steps** that leads to product formation is the **reaction mechanism**.

Example:

Consider the following elementary reactions

Obtain the net, or overall, chemical equation from this mechanism.

$$Cl_2 \leftrightarrow 2Cl$$

$$Cl + CHCl_3 \rightarrow HCl + CCl_3$$

$$Cl + CCl_3 \rightarrow CCl_4$$

Solution: $Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$

Molecularity of a reaction

molecularity of a reaction: the number of molecules reacting in an elementary step.

- Unimolecular reaction – elementary step with 1 molecule
- Bimolecular reaction – elementary step with 2 molecules
- Termolecular reaction – elementary step with 3 molecules

	Example of reaction	Rate law
Unimolecular reaction	$A \rightarrow products$	rate = k[A]
Bimolecular reaction	$A + B \rightarrow products$ $A + A \rightarrow products$	rate = k[A][B] $rate = k[A]^2$
Termolecular reaction	$A + B + C \rightarrow products$ $2A + B \rightarrow products$ $A + A + A \rightarrow products$	$rate = k[A][B][C]$ $rate = k[A]^2[B]$ $rate = k[A]^3$

Example 1:

What is the molecularity of each step in the following mechanism?

$$Cl_2 \rightleftharpoons 2Cl$$

$$Cl + CHCl_2 \rightarrow HCl + CCl_3$$

$$Cl + CCl_3 \rightarrow CCl_4$$

Solution:

- The forward part of the first step is unimolecular.
- The reverse part of the first step is bimolecular.
- The second step is bimolecular.
- The third step is bimolecular.

• Elementary reactions and reaction mechanism

The rate-determining step (RDS): the slowest step in the sequence of steps leading to product formation.

☐ The rate-determining step should predict the same rate law that is determined experimentally.

- يجب أن يتوافق قانون سرعة التفاعل مع التفاعل البطيئ (RDS) في التفاعل.
- يجب أن تكون مجموع كل المعادلات البطيئة والسريعة (الميكانيكا) تؤدي إلى المعادلة المطلوبة (المعادلة النهائية).

Example: Consider the reaction of NO_2 with F_2 is believed to occur in the

Following steps:

$$2NO_2 + F_2 \rightarrow 2NO_2F \qquad rate = k[NO]^x[F_2]^y$$

$$NO_2 + F_2 \rightarrow NO_2F + F \quad slow \quad rate = k_1[NO][F_2]$$

$$F + NO_2 \rightarrow NO_2F \quad fast \quad rate = k_2[NO][F]$$

The rate of the overall reaction is: $\boldsymbol{rate = k_1[NO_2]^1[F_2]^1}$ (same of slow reaction)

Intermediates (الوسيط): species that appear in a reaction mechanism but not in the overall balanced equation.

An intermediate is always formed in an early elementary step and consumed in a later elementary step.

الوسيط: هو المركب أو العنصر الذي يظهرمع النواتج في المعادلة الأولى في التفاعل ويظهر مع المتفاعلات في المعادلة الثانية ولكن لا يظهر أبداً في المعادلة النهائية للتفاعل.

Catalysis (المحفز): the increase in the rate of a reaction that results from the addition of a catalyst.

Catalysis is always consumed in an early elementary step and formed in a later elementary step.

المحفز يظهر مع المتفاعلات في المعادلة الأولى ويظهر مع النواتج في المعادلة الثانية، ولكن لا يظهر أبداً في المعادلة النهائية للتفاعل.

Ex:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

Solution:

$$O_3 + O \rightarrow 2O_2$$ (المعادلة النهائية للتفاعل)

Intermediate: ClO

Catalysis: Cl

Example 2:

Given the following mechanism:

$NO_2 + F_2 \rightarrow NO_2F + F$

$F + NO_2 \rightarrow NO_2F$

Identify the intermediate in the reaction.

A. NO_2
B. F_2
C. NO_2F
D. F
E. None of these

Example 3:

Given the following mechanism:

$A + B \rightleftharpoons C$

$E + C + A \rightarrow D$

$D + G \rightarrow E + W$

Identify the intermediates and catalysts in the reaction.

A. C is intermediate, E is the catalyst
B. B and D are intermediates, W is the catalyst
C. C and D are intermediates, A is the catalyst
D. G is intermediate, E and D are the catalysts
E. C and D are intermediates, E is the catalyst

Example 4:

Consider the reaction of NO_2 with F_2 is believed to occur in the following steps:

Find the overall rate law for the reaction.

$2N_2O_5 \rightarrow 4NO_2 + O_2$

Mechanism:

$Step\ 1:\ \ N_2O_5 \rightleftharpoons NO_2 + NO_3 \quad fast$

$Step\ 2:\ \ NO_2 + NO_3 \longrightarrow NO_2 + NO + O_2 \quad slow$

$Step\ 3\ \ NO + NO_3 \longrightarrow 2NO_2 \qquad fast$

Solution:

$Step\ 1:\ \ N_2O_5 \rightleftharpoons NO_2 + NO_3 \quad fast \qquad rate = k_1[N_2O_5]$

$Step\ 2:\ \ NO_2 + NO_3 \longrightarrow NO_2 + NO + O_2 \quad slow \qquad rate = k_2[NO_2][NO_3]$

$Step\ 3:\ \ NO + NO_3 \longrightarrow 2NO_2 \qquad fast \qquad rate = k_3[NO][NO_3]$

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \qquad rate = k[N_2O_5]^x$$

So, $rate = k[NO_2][NO_3] \quad but,\ \boldsymbol{rate = k[N_2O_5]^x}$

In equilibrium (⇌)(Step 1), $\mathrm{k}_1[N_2O_5]^1 = k_{-1}[NO_2][NO_3]$

, $\boldsymbol{x = 1}$

So, $\boldsymbol{rate = k[N_2O_5]}$

Example 5:

The reaction

$3A + B \longrightarrow C$

Given the following mechanism:

$Step\ 1\text{:}\ \ A + B \rightleftharpoons D \quad (fast\ equilibrium)$

$Step\ 2\text{:}\ \ D + B \longrightarrow E$

$Step\ 3\text{:}\ \ E + 2A \longrightarrow C + B$

$If\ step\ 2\ is\ the\ rate - determining\ step,\ then\ the\ rate\ of\ formation\ of\ C\ shouid\ equal:$

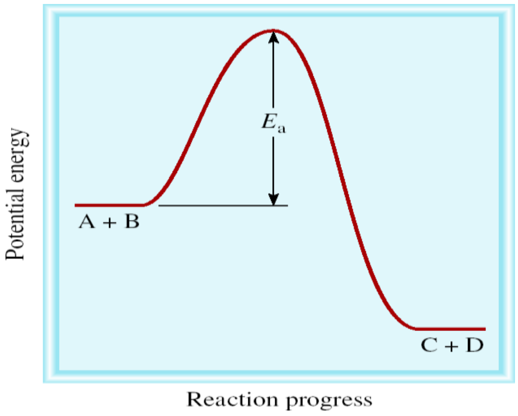
A. $k[A]^3[B]$
B. $k[B]^2$
C. $\underline{k[A][B]^2}$
D. $k[A]^2[B]^3$
E. $k[A]$

• Catalyst

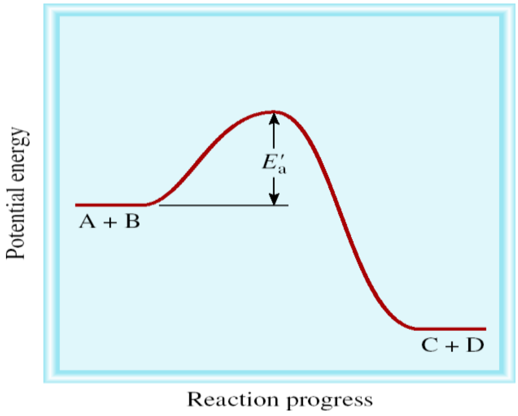
Catalyst: is a substance that increases the rate of a chemical reaction without itself being **consumed.**

Add catalyst ⟶
1. Decrease E_a
2. Increase rate of the reaction
3. Increase rate constant (K)
4. Decrease the time for reaction

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



(*Uncatalyzed)*



(Catalyzed)

Types of catalysts:

1. **Homogenous**: <u>Same</u> phase of catalyst and reaction material.

Ex: $\frac{3}{2}O_{2(g)} \xrightarrow{NO_{(g)}} O_{3(g)}$

2. **Heterogeneous:** <u>Different</u> phase of catalyst and reaction material.

Ex: $C_2H_{4(g)} + H_{2(g)} \xrightarrow{Ni_{(s)}} C_2H_{6(g)}$

3. **Enzymes**
   - ❖ The substance whose reaction the enzyme catalyzes is called the **substrate**.