Chapter 13

Chemical Kinetics

Sections: 13.1 – 13.9

• Definition of Reaction Rate

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.

$$A \longrightarrow B$$

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

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

Δ[A] = change in concentration of A over time period Δt

Δ[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

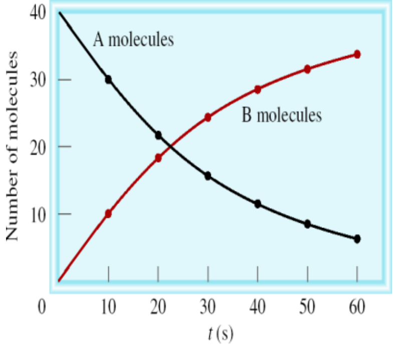
إذا كان لدينا المعادلة التالية:

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

$$So, \quad \boxed{rate = \frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}}$$

"Rate expression"

- الاشارة السالبة تدل على نقصان تركيز المتفاعلات مع الزمن



$$2A \rightarrow B$$

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

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

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

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

• Dependence of Rate on Concentration

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

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

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

$x = order\ of\ A$ 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 3:

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

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

(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:

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. 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 x 10^{-6}
2	0.020	0.010	0.00050	2.30 x 10^{-6}
3	0.010	0.020	0.00050	2.30 x 10^{-6}
4	0.010	0.010	0.00100	1.15 x 10^{-6}

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

$1.15\times10^{-6} = k\times0.010^1\times0.010^1$

$$k = \frac{1.15\times10^{-6}\ M/s}{0.010\ M\ \times0.010\ M} = \mathbf{0.0115\ M^{-1}s^{-1}}$$

$x + y + z = 1 + 1 + 0 = 2$

رتبة التفاعل = 2

c. $rate = k[H_2O_2][I^-] = 0.0115\ \times5\times10^{-3}\times0.03\ \times0.006^0 = \mathbf{1.7\times10^{-6}\ M/s}$

Example 4:

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

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.	$[NO]$	$[H_2]$	(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)

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

• 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
-

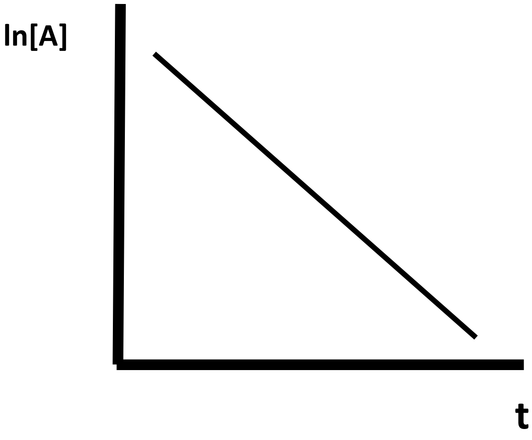
For $\boldsymbol{A \rightarrow Product}$

$$Rate = k[A]$$

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

$$ln[A] = ln[A°] - kt$$

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



[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.

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

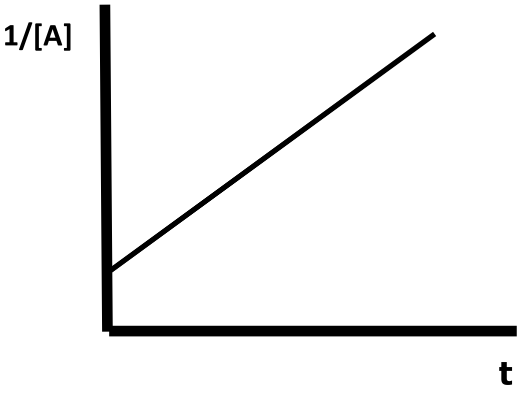
Half-life for first order is:

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

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

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

- **Second-Order Reactions**



$Slope = -k$

$Intercept = [A°]$

$$Rate = k[A]^2$$

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

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

$$T_{1/2} = \frac{1}{k[A°]}$$

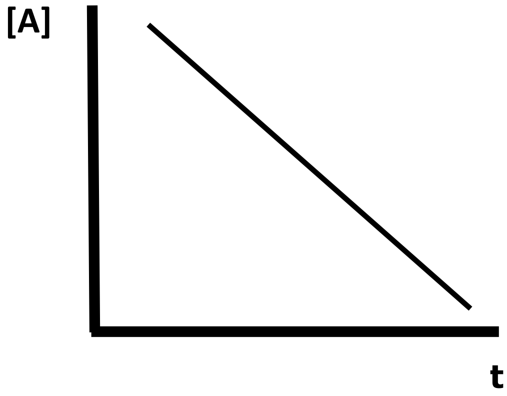
- **Zero-Order Reactions**

$Rate = k$

$k = rate = M/s$

$$[A] - [A°] = -kt$$

$$T_{1/2} = \frac{[A°]}{2k}$$



$Slope = -k$

$Intercept = [A°]$

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 5:

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 takes for the concentration of A to decrease to 0.010 mol/L from its initial value?

Solution:

1. $ln[A] = ln[A°] - kt$

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

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

2. $ln[A] = ln[A°] - kt$

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

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

Example 6:

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 7:

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. $[A] - [A°] = -kt$

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

• Temperature and Rate; Collision and Transition-State Theories

Effect of temperature on the reaction rate:

تأثير درجة الحرارة على سرعة التفاعل:

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

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

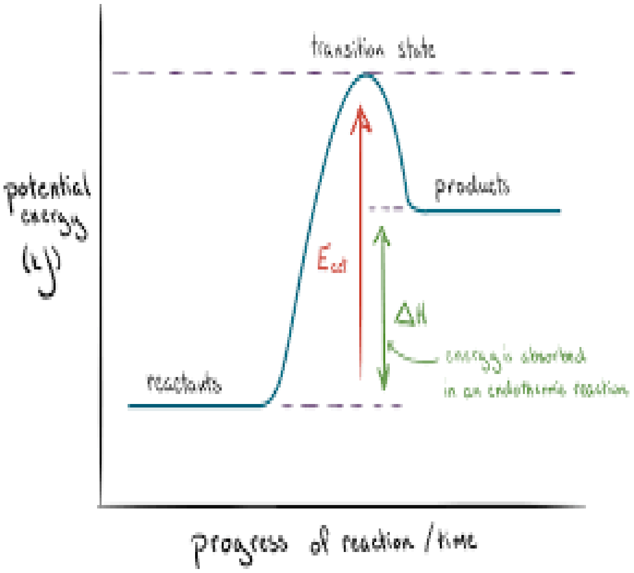
1. The collision frequency (number of collisions per unit time)
2. The fraction of collisions having energy greater than the activation energy (Ea)

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

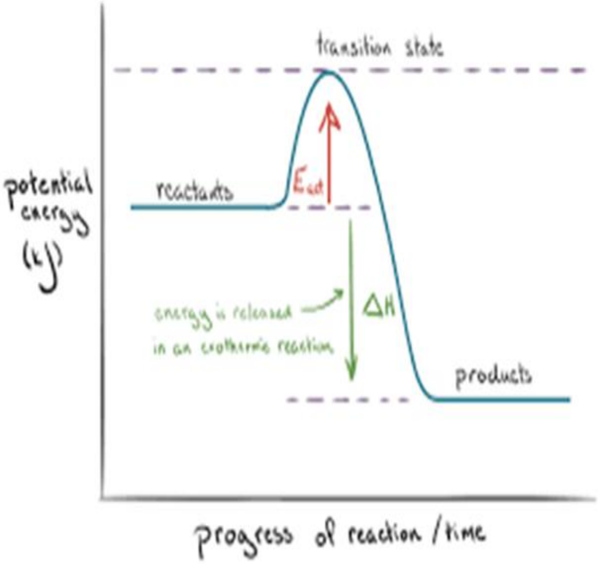
طاقة التنشيط: أقل طاقة لازمة لحدوث التفاعل الكيميائي.

	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 8:

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:

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

$T_1 = 0°C \rightarrow 273\ K$, $T_2 = 37°C \rightarrow 310\ K$

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

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

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

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

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

Example 9:

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:

$$k_1 = 1.2 \times 10^{-3}\ mol/L \cdot s,\ \ k_2 = 2.8 \times 10^{-2}\ mol/L \cdot s$$
$$T_1 = 400\ K\ ,\quad T_2 = 450\ K$$
$$E_a = ??\ ,\ \ R = 8.314\ J/K \cdot mol$$

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

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

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

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

$$k_1 = 1.2 \times 10^{-3}\frac{mol}{L} \cdot s,\ \ k_2 = ??$$
$$T_1 = 400\ K\ ,\quad T_2 = 500\ K$$
$$E_a = 94280\ J\ ,\ \ R = 8.314\ J/K \cdot mol$$

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

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

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

• 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**:

$$\left.\begin{array}{ll} NO_2 + F_2 \rightarrow NO_2F + F & \text{Elementary reaction 1} \\ F + NO_2 \rightarrow NO_2F & \text{Elementary reaction 2} \end{array}\right\} \text{Reaction mechanism}$$

$$\begin{array}{ll} \hline 2NO_2 + F_2 \rightarrow 2NO_2F & \text{Overall reaction} \end{array}$$

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

Example 10:

Consider the following elementary reactions

$Cl_2 \rightleftharpoons 2Cl$

$Cl + CHCl_2 \rightarrow HCl + CCl_3$

$Cl + CCl_3 \rightarrow CCl_4$

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

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

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 11:

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.

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 12: 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:

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

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

Intermediate: ClO

Catalysis: Cl

Example 13:

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. $\underline{F}$
E. None of these

Example 14:

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 15:

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:

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

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

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

Solution:

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

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

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

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

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 16:

The reaction

$3A + B \longrightarrow C$

Given the following mechanism:

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

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

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

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

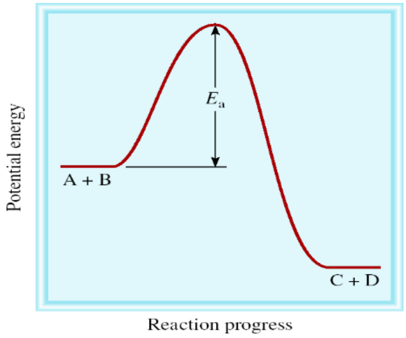
- A. $k[A]^3[B]$
- B. $k[B]^2$
- C. $\underline{k[A][B]^2}$
- D. $k[A]^2[B]^3$
- E. $k[A]$

• Catalyst

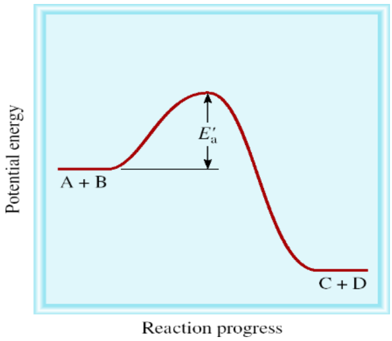
Catalyst: is a substance that increases the rate of a chemical reaction without itself being **consumed.**

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

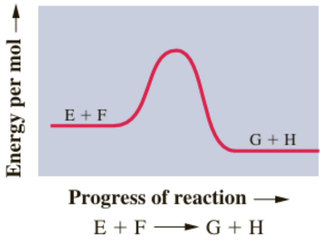
3. **Enzymes**

The substance whose reaction the enzyme catalyzes is called the **substrate.**

Problems:

1) Consider the reaction $E + F \longrightarrow G + H$, which has the following reaction coordinate diagram.

Which one of the following statements is true?



a) The activation energy is greatest for the forward reaction.
b) The reactants are at a lower energy than the products.
c) The reaction is endothermic.
d) The rate of the forward reaction would be slowed by an increase in temperature.
e) If the rate law for the reaction is Rate = $k[E]^2[F]$, then doubling the concentration of E will cause the rate to increase by a factor of 4 (that is, the reaction will proceed four times faster).

2) Identify the **INCORRECT** statement below concerning chemical kinetics:

a) The rate of a chemical reaction changes with time.
b) The rate constant of a reaction generally depends on the concentrations of species.
c) The rate of a chemical reaction is affected by the temperature of the reaction.
d) The rate law of a chemical reaction bears no relationship with the balancing coefficients of the overall reaction.
e) The rate law expresses how the rate varies with concentration of species.

3) The hypothetical reaction $A + B + C \longrightarrow D + E$ has the rate law $Rate = k[A]^2[B]$.

Which of the following changes would have the **least** effect on increasing the rate of this reaction?

a) Doubling [A]0 while keeping [B]0 and [C]0 constant.

b) Doubling [B]0 while keeping [A]0 and [C]0 constant.

c) Doubling [C]0 while keeping [A]0 and [B]0 constant.

d) Increasing the rate constant by running the reaction at a higher temperature.

e) Adding a catalyst to the reaction mixture.

Ch 13

4) The rate law for the iodine clock reaction is given by: $Rate = k[IO_3^-][I^-]^2[H^+]^2$

a) This reaction is first order with respect to IO_3^- and third order overall.
b) This reaction is second order with respect to I^- and 3rd order overall.
c) This reaction is first order with respect to IO_3^- and fifth order overall.
d) This reaction is third order with respect to H^+.

5) Consider the following kinetic data collected at the very beginning of a reaction:

Which of the following is an appropriate expression for the rate law and rate constant?

Exp. No.	**$[A]$(M)**	**$[B]$ (M)**	**(M/s)**
1	**0.1**	**0.1**	**0.009**
2	**0.2**	**0.1**	**0.036**
3	**0.1**	**0.2**	**0.018**

a) $Rate = k[A]^2[B];\ k = 9.0\ L^2/mol^2 \cdot s$
b) $Rate = k[A]^2[B];\ k = 0.9\ L^2/mol^2 \cdot s$
c) $Rate = k[A]^4[B]^2;\ k = 9.0 \times 10^3\ L\ /\ mol \cdot s$
d) $Rate = k[A][B];\ k = 0.9\ L\ /\ mol \cdot s$

6) Of the following factors, which cannot affect the rate of a chemical reaction?

a) all can affect the rate
b) Temperature
c) presence of a catalyst
d) concentration of reactants of the forward reaction
e) physical state or state of subdivision of solid reactants

7) Consider the following rate law expression: $Rate = k[A]^2[B]$. Which of the following is **NOT TRUE** about the reaction having this expression?

a) The reaction is overall third order.
b) The reaction is first order in B.
c) Doubling the concentration of A doubles the rate.
d) The reaction is second order in A.

8) The gas phase reaction $A + B \longrightarrow C$ has a reaction rate which is experimentally observed to follow the relationship $Rate = k[A]^2[B]$. If the concentration of A is tripled and the concentration of B is doubled, the reaction rate would be increased by a factor of:

a) 9 b) 6 c) 18 d) 12 e) 24

9) The collision theory of reaction rates:

I. helps to expose how temperature affects the rate
II. assumes that the rate depends on the frequency at which reactants collide.
III. assumes that reactants must be in correct orientation to react.
IV. assumes that only collisions with energy above the activation energy are successful

a) I, II, and III are correct. IV is incorrect. b) I, III, and IV are correct. II is incorrect.
c) II, III, and IV are correct. I is incorrect. d) All are correct statements.

Ch 13

10) The relationship between the rate constant and temperature is expressed by the:

a) Arrhenius equation. b) rate law.

c) integrated rate equation. d) reaction mechanism

11) Identify the **INCORRECT** statement below:

a) The rate of a typical reaction doubles with a 10° C rise in temperature.
b) The overall rate of reaction is determined by the rate of the fastest elementary step.
c) The reaction mechanism is a step-by-step pathway by which reaction occurs.
d) The reaction mechanism is typically a series of elementary reaction steps.
e) Reaction orders for a single elementary step are equal to the balancing coefficients for that step.

12) Which of the following statements about catalysts are **FALSE**?

a) In homogeneous catalysis the catalyst is in the same phase as the reactants.
b) Catalyst is often transition metals and transition metal oxides.
c) A catalyst can make a nonspontaneous reaction spontaneous.
d) A catalyst speeds up both the forward and reverse reaction.
e) A catalyst lowers the activation energy.

Ch 13

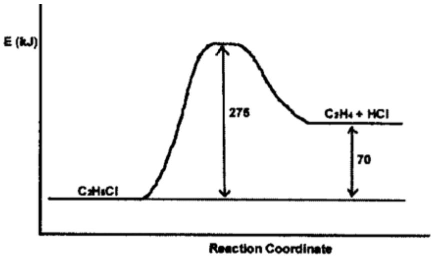
13) Consider the following reaction: $2\ N_2O(g)\ \longrightarrow\ 2\ NO(g)\ +\ O_2(g);\ rate\ =\ k[N_2O]$ If the half-life for the reaction is $0.910\ s$, the rate constant is:

- $a)$ $1.1\ s^{-1}$
- $b)$ $0.69s^{-1}$
- $c)$ $1.3s^{-1}$
- $d)$ $0.32\ s^{-1}$
- $e)$ $0.76\ s^{-1}$

14) A reaction profile (not to scale!) for the reaction is shown below: $C_2H_5Cl\ \longrightarrow\ C_2H_4\ +\ HCl$

What is the activation energy of the **REVERSE** reaction, and is the **FORWARD** reaction exothermic or endothermic?

- $a)$ $70\ KJ$ *and endothermic forward reaction*
- $b)$ $205\ KJ$ *and exothermic forward reaction*
- $c)$ $275\ KJ$ *and endothermic forward reaction*
- $d)$ $275\ KJ$ *and exothermic forward reaction*
- $e)$ $205\ KJ$ *and endothermic forward reaction*



15) A proposed mechanism for one of the pathways for the destruction of ozone in the atmosphere is:

$slow:\ O_3 + NO\ \longrightarrow\ NO_2 + O_2$

$fast:\ NO_2 + O\ \longrightarrow\ NO + O_2$

Which species acts as a catalyst, intermediates and Which rate law for the overall reaction is consistent with this mechanism? **(In order)**

- $a)$ $O_3,\ \ O,\ \ k[O_3][NO]$
- $b)$ $NO,\ \ NO_2,\ \ k[O_3][NO]$
- $c)$ $NO,\ \ O_2,\ \ k[O][O_3][NO]$
- $d)$ $O\ ,\ \ NO_2,\ \ k[NO_2][O]$
- $e)$ $NO_2,\ \ O_3,\ \ k[O_3][NO][O]$

Answers:

1) **e (If the rate law for the reaction is Rate = $k[E]^2[F], \dots\dots\dots\dots.$)**

2) **b (The rate constant of a reaction generally depends on the concentrations of species)**

3) **c (Doubling [C]0 while keeping [A]0 and [B]0 constant)**

4) **c (This reaction is first order with respect to IO_3^- and fifth order overall)**

5) **a ($Rate = k[A]^2[B]$; $k = 9.0\ L^2/mol^2 \cdot s$)**

6) **a (all can affect the rate)**

7) **c (Doubling the concentration of A doubles the rate)**

8) **c (18)**
9) **d (All are correct statements)**
10) **a (Arrhenius equation)**
11) **b (The overall rate of reaction is determined by the rate of the fastest elementary step)**
12) **c (A catalyst can make a nonspontaneous reaction spontaneous)**
13) **e ($0.76\ s^{-1}$)**
14) **e ($205\ KJ$ and endothermic forward reaction)**
15) **b (NO, NO_2, $k[O_3][NO]$)**