Ministry of Higher Education and Scientific Research
AL-Mustaqbal University College of Science
Department of Biochemistry

Physical Chemistry

Lecture 2

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First semester

Type of Reactions

By

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Reaction Orders in Chemistry

The types of orders are zero-order, first-order, second-order, or mixed-order.

- A zero-order reaction proceeds at a constant rate.
- A first-order reaction rate depends on the concentration of one of the reactants.
- A second-order reaction rate is proportional to the square of the concentration of a reactant or the product of the concentration of two reactants.

Factors affecting reaction rate

Depending upon what substances are reacting, the reaction rate varies. Acid/base reactions, the formation of salts, and ion exchange are fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in reactant molecules greatly influence the rate of its transformation into products

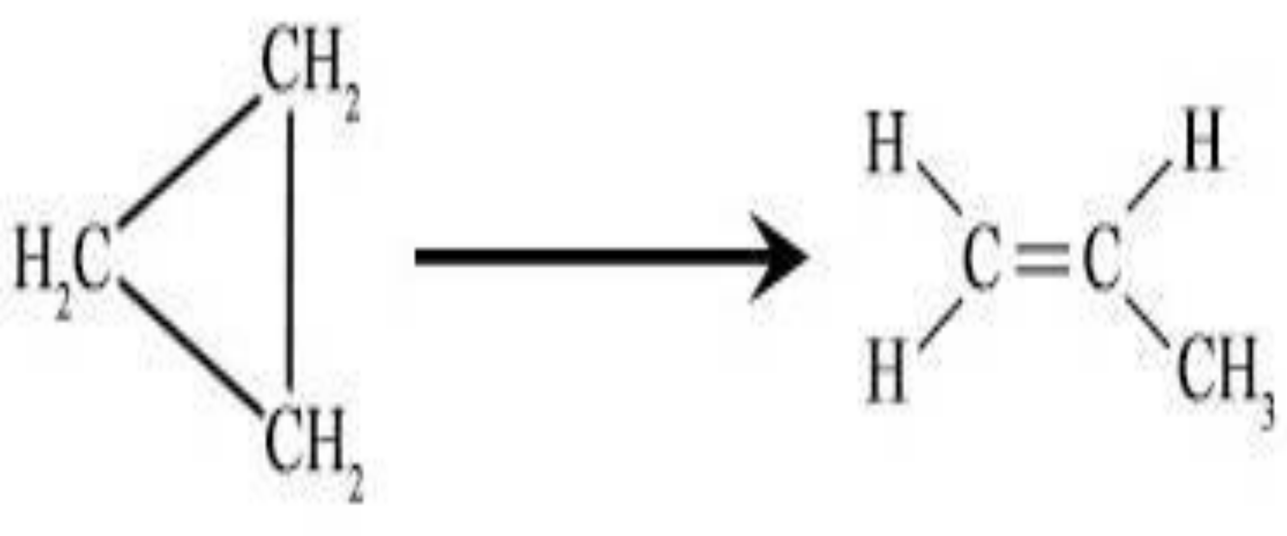
Molecularity

in chemistry is the number of molecules that come together to react in an elementary (single-step) reaction and is equal to the sum of stoichiometric coefficients of reactants in this elementary reaction. Depending on how many molecules come together, a reaction can be unimolecular, bimolecular or trimolecular.

1- Unimolecular reactions

In a unimolecular reaction, a single molecule rearranges atoms forming different molecules. This is illustrated by the equation $\mathbf{A + B \longrightarrow P}$ and is described by the **first order rate law** where [A] is the concentration of species A, t is time, and kr is the reaction rate constant.

An example of a unimolecular reaction, is the isomerization of cyclopropane to propene



Unimolecular reactions can be explained by the Lindeman mechanism.

2- Bimolecular reactions

In a bimolecular reaction, two molecules collide and exchange energy, atoms or groups of atoms. This can be described by the equation $\mathbf{A + B \longrightarrow P}$

which corresponds to the **second order rate law**:

Here, the rate of the reaction is proportional to the rate at which the reactants come together.

An example of a bimolecular reaction is the SN_2-type nucleophilic substitution of methyl bromide by hydroxide ion.

$$\mathbf{CH_3Br + OH^- \longrightarrow CH_3OH + Br^-}$$

3- Trimolecular reactions

A trimolecular reaction in solutions or gas mixtures involves three reactant molecules simultaneously colliding. However the term trimolecular is also used to refer to three body association reactions of the type $\mathbf{A + B \rightarrow M\ C}$

Where the M over the arrow denotes that to conserve energy and momentum a second reaction with a third body is required. After the initial bimolecular collision of A and B an energetically excited reaction intermediate is formed, then, it collides with a M body, in a second bimolecular reaction, transferring the excess energy to it. The reaction can be explained as two consecutive reactions:

1- $\mathbf{A + B \longrightarrow AB*}$ **2-** $\mathbf{AB* + M \longrightarrow C + M}$

These reactions frequently have a pressure and temperature dependence region of transition between second and third order kinetics.

For example, in hydrogenation with a metal catalyst, molecular dihydrogen first dissociates onto the metal surface into hydrogen atoms bound to the surface.

Types of reaction

1- Zero order reactions

Zero-order reactions (where order = 0) have a constant rate. The rate of a zero-order reaction is constant and independent of the concentration of reactants.

	A $\longrightarrow$	Product
T= 0	0	a
T= ?	a-x	x

If the rate law is

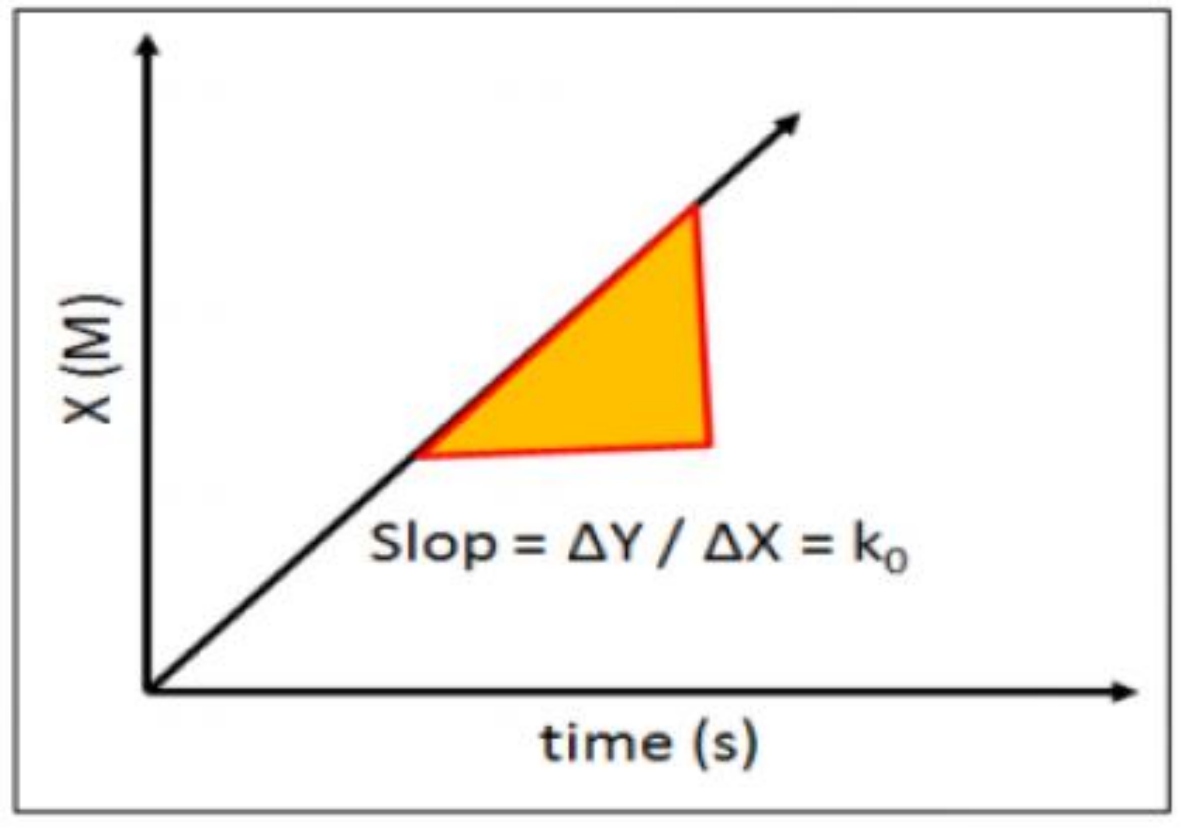
$$\frac{dX}{dt} = K_o \ (a--x)^{n=0}$$

$$\frac{dX}{dt} = K_o$$

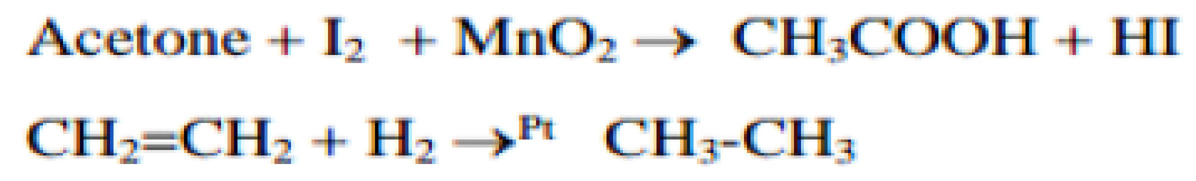
بتكامل المعادلة

$$X = K_o t$$

التمثيل البياني للمعادلة الأخيرة يمثل بالشكل الاتي



من التفاعلات التي تسلك سلوك المرتبة الصفرية:



$\text{Acetone} + I_2 + MnO_2 \rightarrow CH_3COOH + HI$

$CH_2{=}CH_2 + H_2 \xrightarrow{Pt} CH_3\text{-}CH_3$

2- First order reactions

A first-order reaction (where order = 1) has a rate proportional to the concentration of one of the reactants.

	A	$\longrightarrow$	B	+	C
T= 0	a		a		0
T= ?	a-x		x		x

$$\text{Rate} = \frac{dX}{dt} = K_1 \, (a--x)^{n=1}$$

بتكامل المعادلة

$$\int \frac{dX}{(a-x)} = K_1 \int dt$$

$$\text{Ln} \, \frac{a}{(a-x)} = K_1 \, t + C$$

C = كمية ثابتة عندما يكون $t = o , x=0$

معادلة سرعة التفاعل من الدرجة الأولى

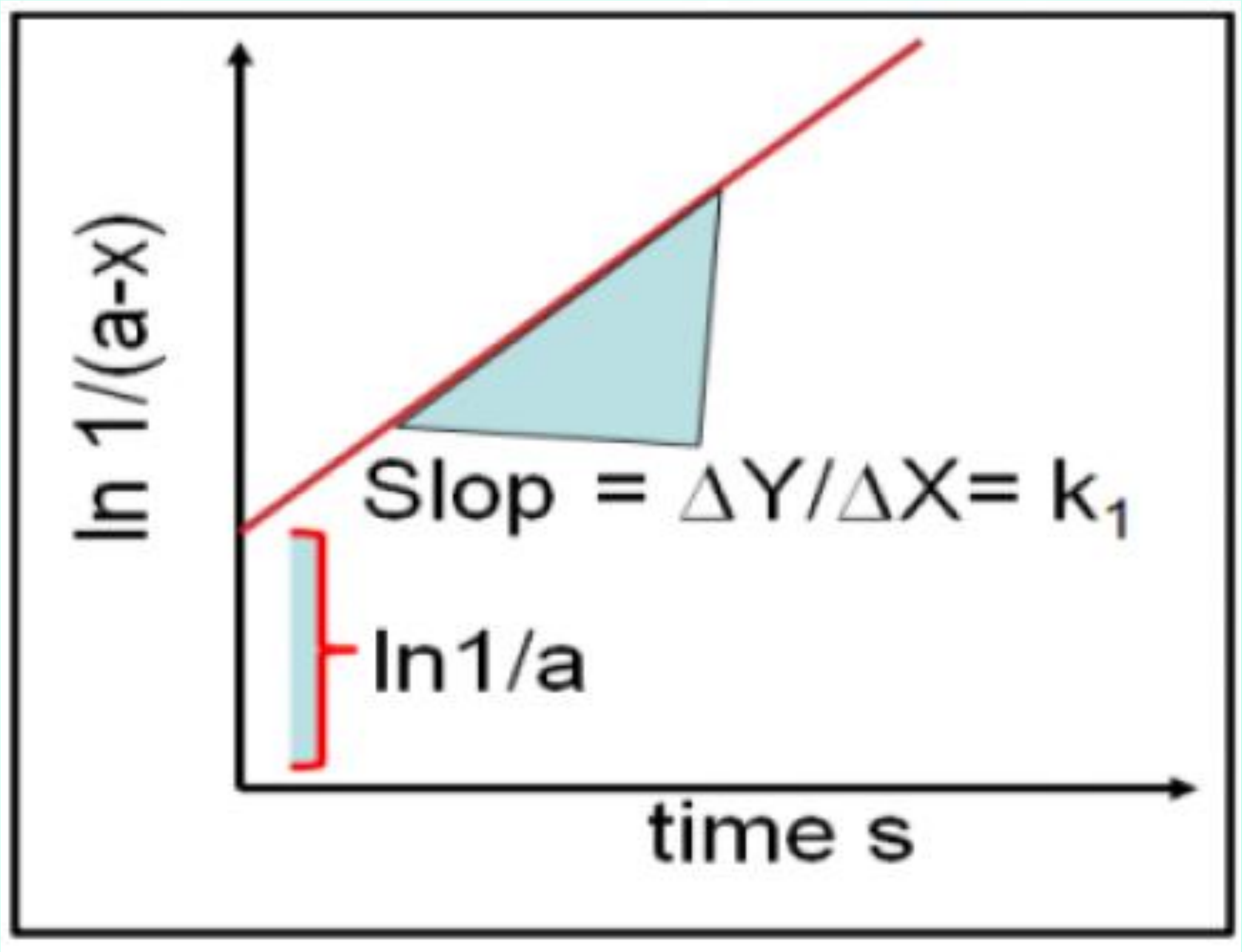
$$\mathrm{Ln}\,\frac{a}{(a-x)} = K_1\,t$$

ويمكن ترتيبها بدلالة اللوغاريتم الأساس

$$k_1 = \frac{1}{t}\,\mathrm{Ln}\,\frac{a}{(a-x)}$$

معادلة سرعة التفاعل من الدرجة الأولى بدلالة اللوغاريتم

$$k_1 = \frac{1}{t}\,\mathrm{Log}\,\frac{a}{(a-x)}$$



من التفاعلات التي تسلك سلوك المرتبة الاولى:

$$CH_3COOC_2H_5 + H_2O + H^+ \rightarrow CH_3COOH + C_2H_5OH$$

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

اما زمن عمر النصف للتفاعل من المرتبة الأولى

$$k_1 = \text{Log}\,\frac{a}{a-x} = \text{Log}\,\frac{a}{(a-\ 1/2\ a)}$$

$$\text{Ln} = \frac{a-x_1}{a-x_2} = k_1\ (t_2 - t_1)$$

$$t_{1/2} = \frac{\text{Ln}_2}{k_1} = \frac{2.303}{k_1}$$

Thank you