Kinetic Chemistry (222 C)

By
Prof. Dr. Lobna Abdel-Mohsen Ebaid Nassr

30/3/2020
6/4/2020

Parallel Reactions

Series (Consecutive) First-order Reactions

Parallel Reactions

A **single reactant** may be **converted** into **several** different products **at the same time**.

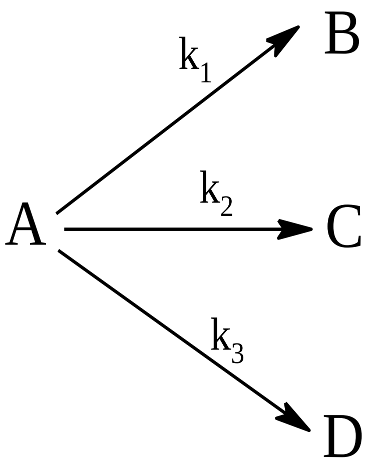
For example, some organic reactions.

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

$$A \xrightarrow{k_3} D$$

or



The rate of the change in [A]:

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] + k_3[A] = (k_1 + k_2 + k_3)[A]$$

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] + k_2[\mathrm{A}] + k_3[\mathrm{A}] = (k_1 + k_2 + k_3)[\mathrm{A}]$$

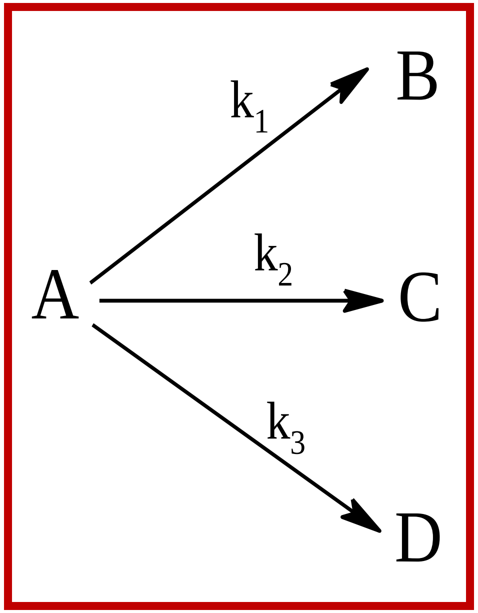
On integration:

$$-\int_{[\mathrm{A}]_o}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = (k_1 + k_2 + k_3)\int_0^t dt$$

$$\ln\frac{[\mathrm{A}]_o}{[\mathrm{A}]} = (k_1 + k_2 + k_3)t$$

$$[\mathrm{A}] = [\mathrm{A}]_o e^{-(k_1+k_2+k_3)t}$$

The rate of the change in [B]:



$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_o e^{-(k_1+k_2+k_3)t}$$

$$k = k_1 + k_2 + k_3 \quad \Rightarrow \quad d[\mathrm{B}] = k_1[\mathrm{A}]_o e^{-kt} dt$$

$$\int_{[B]_o}^{[B]} d[B] = k_1[A]_o \int_0^t e^{-kt}\,dt$$

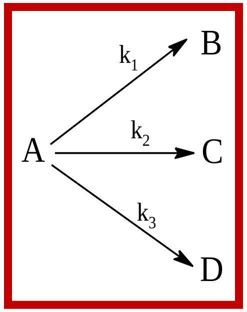
$$[B] = [B]_o + \frac{k_1[A]_o}{k}(1 - e^{-kt})$$

$$[B] = [B]_o + \frac{k_1[A]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t})$$

At the beginning of the reaction, $[B]_o = 0$

$$[B] = \frac{k_1[A]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t})$$

In a similar way,



The rate of the change in [C]:

$$\frac{d[C]}{dt} = k_2\,[A] = k_2\,[A]_o e^{-(k_1+k_2+k_3)t}$$

On integration as in case of [B]

$$[C] = [C]_o + \frac{k_2[A]_o}{k_1 + k_2 + k_3}\left(1 - e^{-(k_1+k_2+k_3)t}\right)$$

The rate of the change in [D]:

$$\frac{d[D]}{dt} = k_3\,[A] = k_3\,[A]_o e^{-(k_1+k_2+k_3)t}$$

On integration as in case of [B]

$$[D] = [D]_o + \frac{k_3[A]_o}{k_1 + k_2 + k_3}\left(1 - e^{-(k_1+k_2+k_3)t}\right)$$

You have to notice that, $[C]_o = [D]_o = 0$

The ratios between the concentration of the products can be as:

$$[B] = \frac{k_1[A]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t})$$

$$[C] = \frac{k_2[A]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t})$$

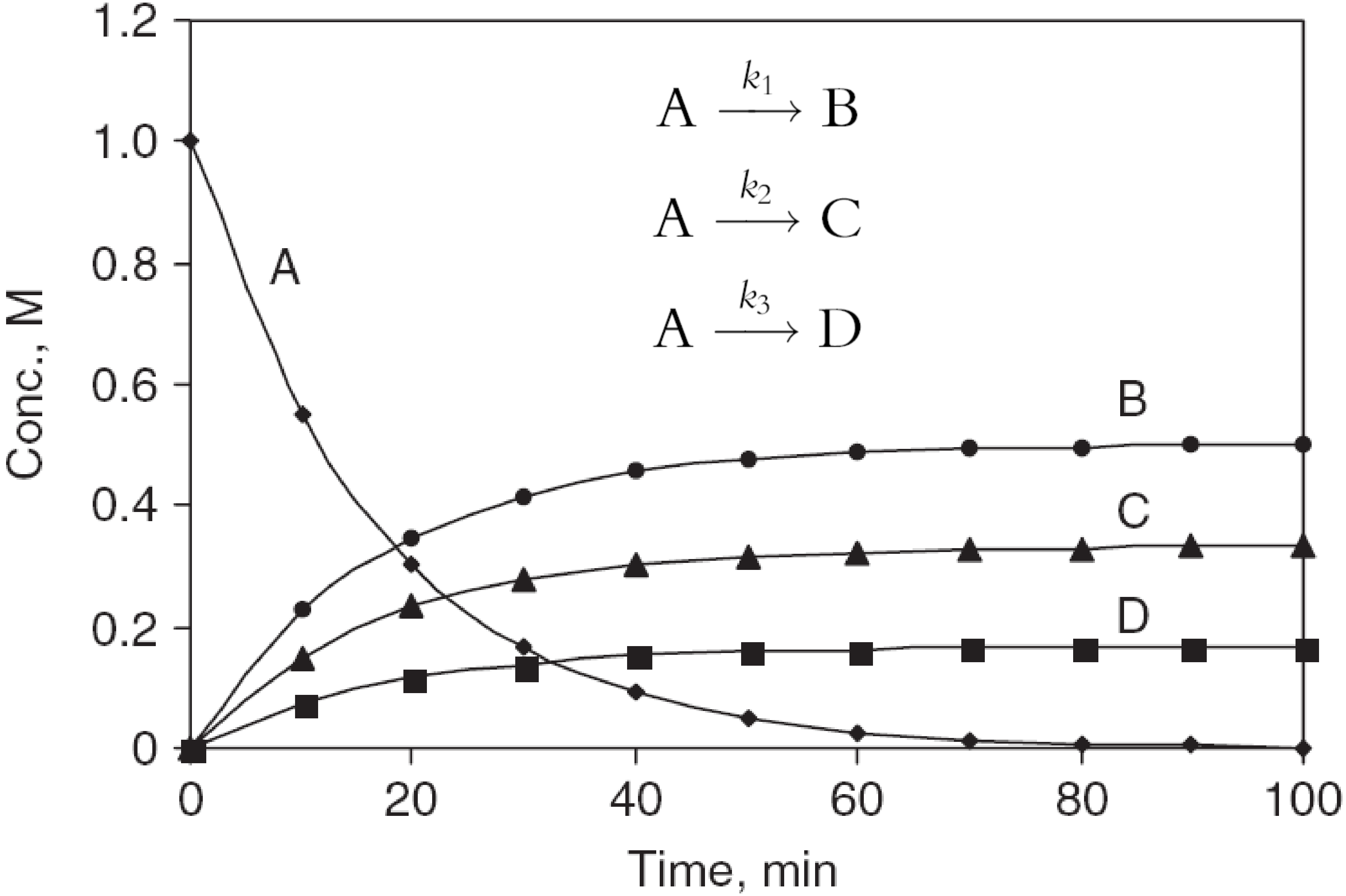
$$[D] = \frac{k_3[A]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t})$$

$$\frac{[B]}{[C]} = \frac{\frac{k_1[A]_o}{k_1 + k_2 + k_3}}{\frac{k_2[A]_o}{k_1 + k_2 + k_3}} \frac{(1 - e^{-(k_1+k_2+k_3)t})}{(1 - e^{-(k_1+k_2+k_3)t})} = \frac{k_1}{k_2}$$

In similar, the ratio between

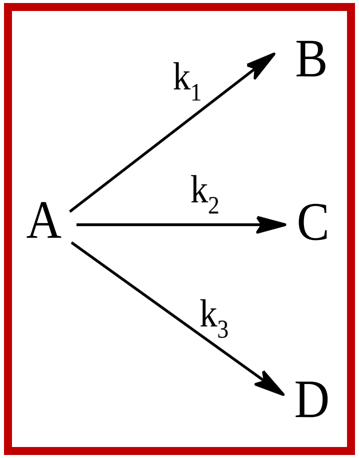
$$\frac{[B]}{[D]} = \frac{k_1}{k_3}$$

The change of [A], [B], [C] and [D] with time:



****Compare between k_1, k_2 and k_3 values****

In parallel reactions



- ✓ **Many products** are formed in **parallel pathways**.
- ✓ **At t = 0**, [B] = $[C]_o$ = $[D]_o$ = 0.
- ✓ **d[A]/dt** is related to both $\mathbf{k_1}$, $\mathbf{k_2}$ **and** $\mathbf{k_3}$
- ✓ **d[Product]/dt** is related only to its corresponding rate constant: $\mathbf{k_1}$ **for [B]**, $\mathbf{k_2}$ **for [C] or** $\mathbf{k_3}$ **for [D].**
- ✓ **The ratios** between the concentrations of the products are related to the rate constant values, such as $\frac{[B]}{[D]} = \frac{k_1}{k_3}$

Series (Consecutive) First-order Reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

During this type of reactions, an intermediate is formed then converted to the final product.

During the reaction, the initial concentration **$[A]_0$** will be divided into **[A]**, **[B]** and **[C]**:

$$[A] + [B] + [C] = [A]_o$$

The rate of **disappearance** of **A**:

$$-\frac{d[A]}{dt} = k_1[A]$$

On integration

$$[A] = [A]_o e^{-k_1 t}$$

The rate of **formation** and **disappearance** of **B**:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[B]}{dt} = k_1[A]_o e^{-k_1 t} - k_2[B]$$

$$\frac{d[B]}{dt} + k_2[B] - k_1[A]_o e^{-k_1 t} = 0$$

It is linear differential equation with constant coefficients

On Integration and rearrangement:

$$[B] = \frac{k_1[A]_o}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

The rate of **formation** of **C**:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

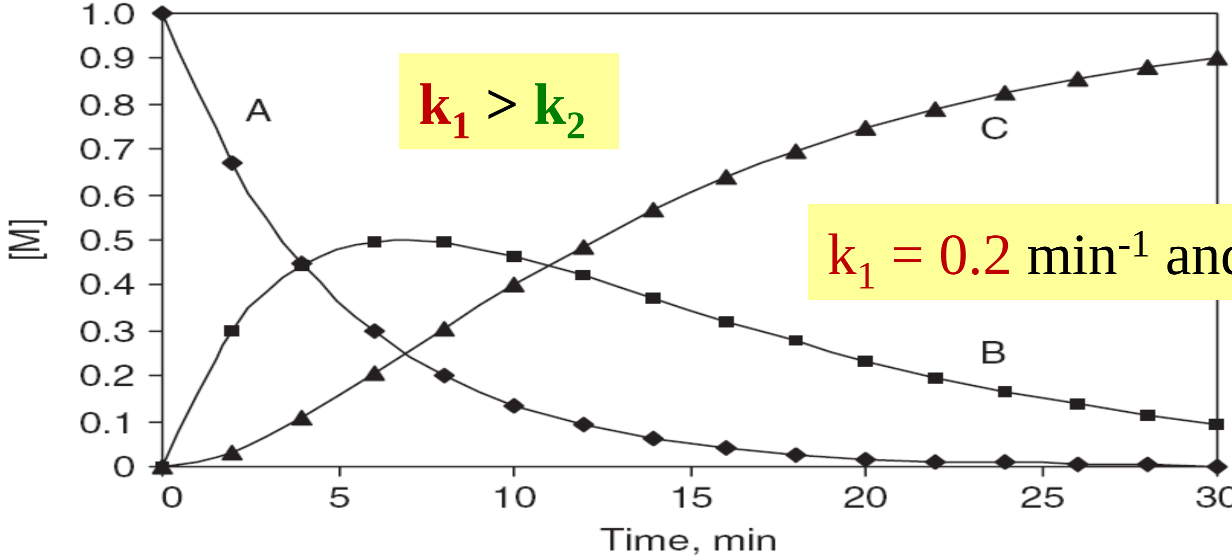
$$\frac{d[C]}{dt} = k_2[B]$$

On Integration and rearrangement, the value of [C] can be determined:

$$[C] = [A]_o \left(1 - \frac{1}{k_2 - k_1}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right)$$

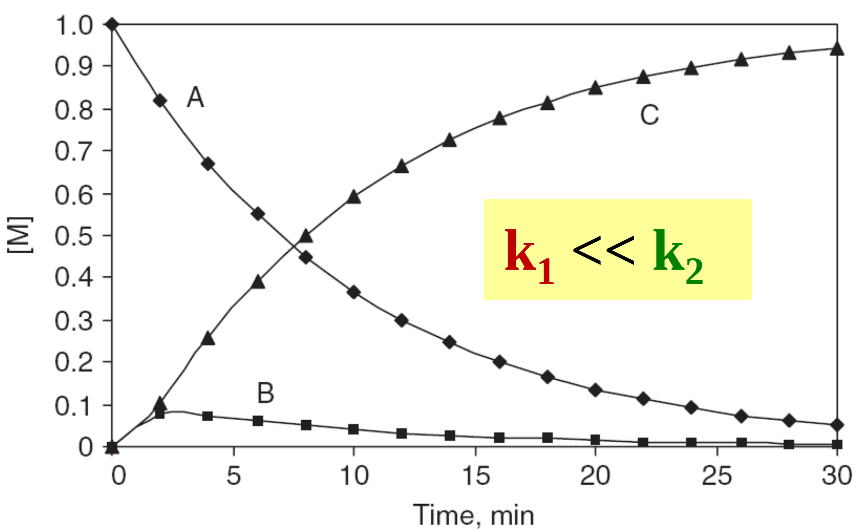
The change of [A], [B] and [C] with time:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$



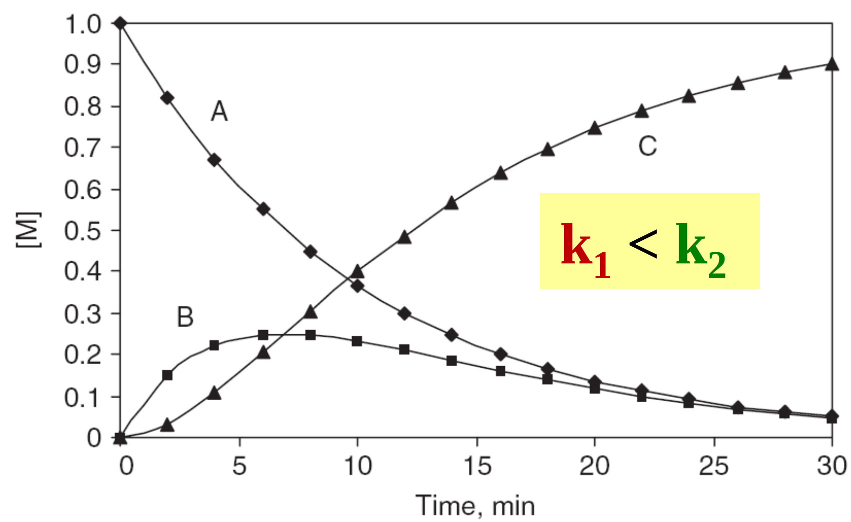
$k_1 > k_2$

$k_1 = 0.2$ min^{-1} and $k_2 = 0.1$ min^{-1}



$k_1 << k_2$

$k_1 = 0.1$ min^{-1} and $k_2 = 1.0$ min^{-1}



$k_1 < k_2$

$k_1 = 0.1$ min^{-1} and $k_2 = 0.2$ min^{-1}

For the intermediate B:

The time necessary to reach its **maximum** concentration (**t_m**):

$$t_m = \frac{\ln \frac{k_1}{k_2}}{k_1 - k_2}$$

In series (consecutive) first-order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- ✓ **An intermediate** is **formed** then **converted** to the **final product**.
- ✓ **After the beginning** of the reaction $[A]_0 = [A] + [B] + [C]$
- ✓ **The concentration of the intermediate,** [**B**] is related to the values of both the rate constant of the first step and the second step (**k_1** and **k_2**).

Parallel Reactions

Series (Consecutive) First-order Reactions

https://staffsites.sohag-univ.edu.eg/lobna.nassr