

Aula 13 de Março 2023

Cinética Química

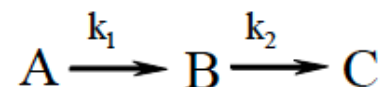
Mecanismos reacionais

Reações consecutivas

Aproximação de estado estacionário

Reacções consecutivas

O mecanismo “complexo” cineticamente mais simples é
a sequência de duas reações de 1ª ordem

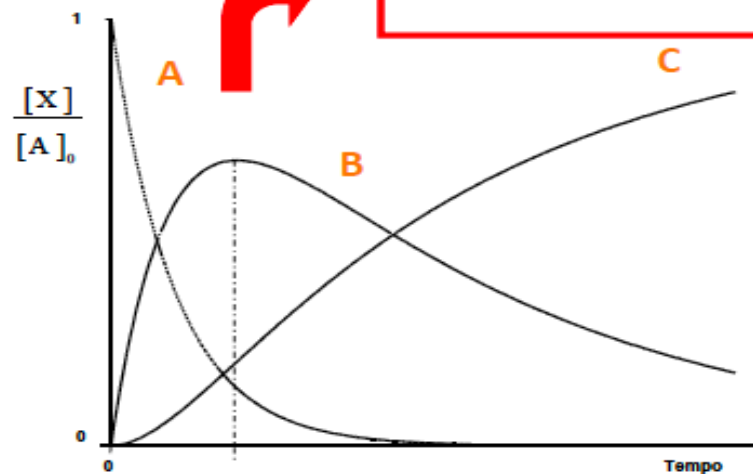


$$\left\{ \begin{array}{l} \frac{d[A]}{dt} = -k_1 [A] \\ \frac{d[B]}{dt} = k_1 [A] - k_2 [B] \\ \frac{d[C]}{dt} = k_2 [B] \end{array} \right. \quad \left\{ \begin{array}{l} [A] = [A]_0 e^{-k_1 t} \\ [B] = \frac{k_1}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t}) \\ [C] = [A]_0 \left(1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right) \end{array} \right.$$

A concentração do intermediário B aumenta e depois diminui
– tem um máximo

$$\frac{d[B]}{dt} = \frac{k_1}{k_2 - k_1} [A]_0 (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}) = 0$$

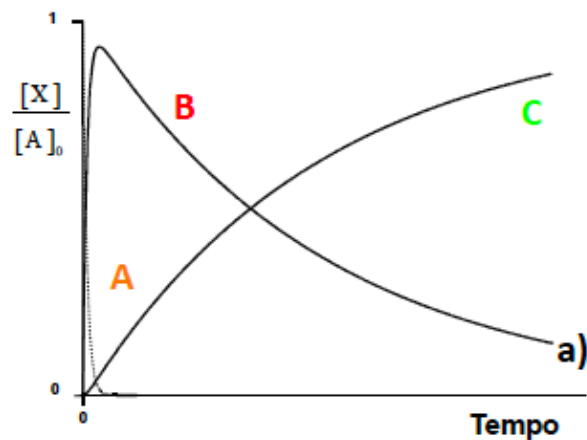
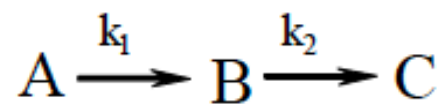
$$[B]_{\text{máx}} = [A]_0 e^{-k_2 t_{\text{máx}}} = [A]_0 \left(\frac{k_2}{k_1} \right)^{\frac{k_2}{k_1 - k_2}}$$



$$t_{\text{máx}} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

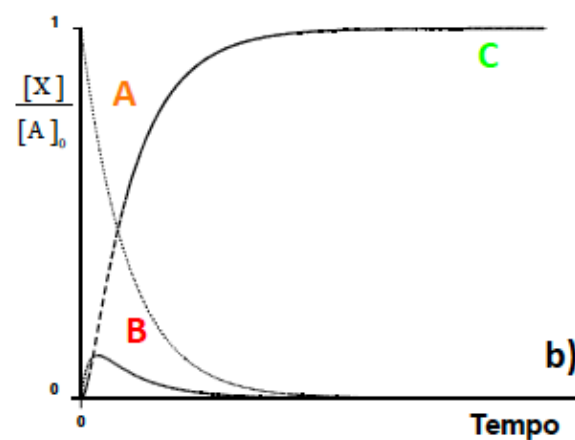
O valor do máximo depende da relação das constantes

k_1 e k_2



$k_1 \gg k_2$

$$[C] = [A]_0 (1 - e^{-k_2 t})$$

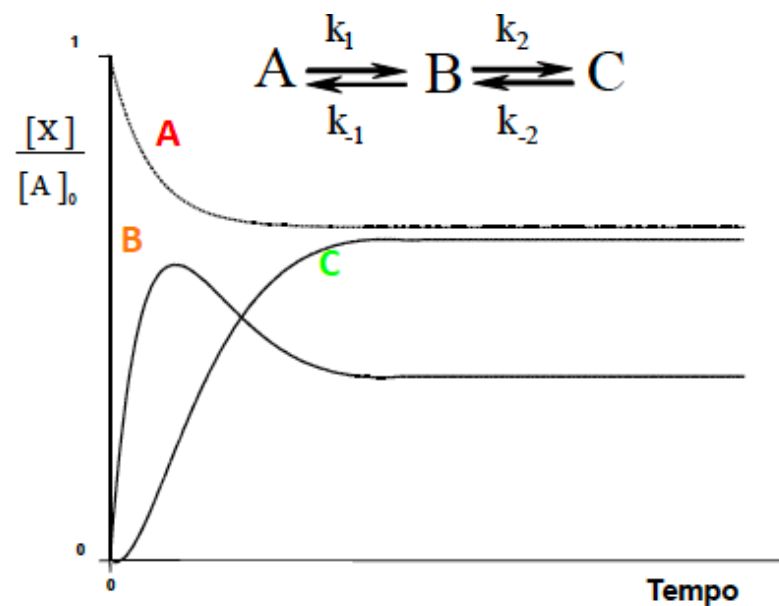


$k_1 \ll k_2$

$$[C] = [A]_0 (1 - e^{-k_1 t})$$

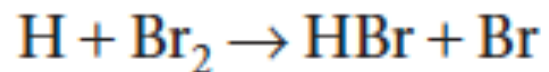
Dois equilíbrios consecutivos

Concentrações de A e B não tendem para 0



$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_{-1}}; \frac{[C]_{\text{eq}}}{[B]_{\text{eq}}} = \frac{k_2}{k_{-2}}; \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

Elementary reactions

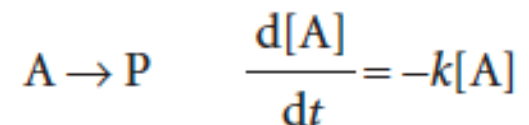


The **molecularity** of an elementary reaction is the number of molecules coming together to react in an elementary reaction.

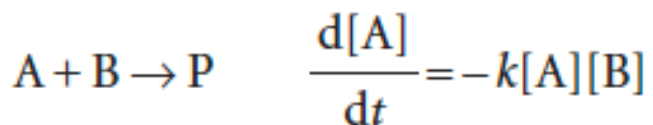
In a **unimolecular** reaction, a single molecule shakes itself apart or its atoms into a new arrangement, as in the isomerization of cyclopropane to propene.

In a **bimolecular** reaction, a pair of molecules collide and exchange energy, atoms, or groups of atoms, or undergo some other kind of change.

The rate law of a unimolecular elementary reaction is first-order in the



An elementary bimolecular reaction has a second-order rate law:

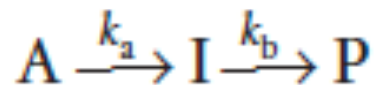


NOTE:

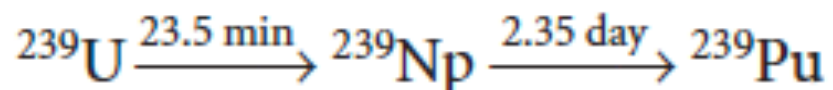
If the reaction is an elementary bimolecular process, then it has second-order kinetics, but if the kinetics are second-order, then the reaction might be complex.

Consecutive elementary reactions

Some reactions proceed through the formation of an intermediate (I), as in the consecutive unimolecular reactions



An example is the decay of a radioactive family, such as



(a) The variation of concentrations with time

The rate of unimolecular decomposition of A is

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

The intermediate I is formed from A (at a rate $k_a[A]$) but decays to P (at a rate $k_b[I]$).

The net rate of formation of I is:

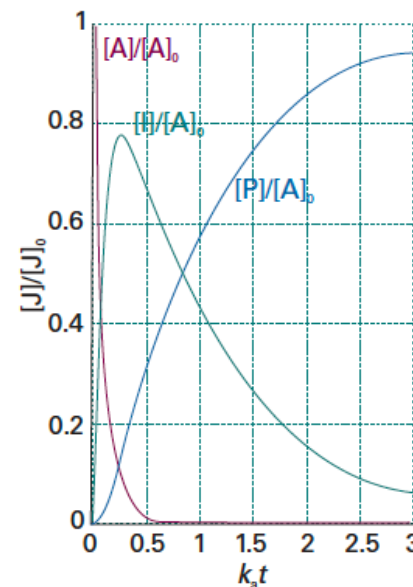
$$\frac{d[I]}{dt} = k_a[A] - k_b[I]$$

The solution of a first-order differential equation with the form

$$\frac{dy}{dx} + yf(x) = g(x)$$

is

$$e^{\int f(x) dx} y = \int e^{\int f(x) dx} g(x) dx + \text{constant}$$



The concentrations of A, I, and P in the consecutive reaction scheme $A \rightarrow I \rightarrow P$. The curves are plots of eqns with $k_a = 10k_b$. If the intermediate I is in fact the desired product, it is important to be able to predict when its concentration is greatest.

The product P is formed by the unimolecular decay of I:

$$\frac{d[P]}{dt} = k_b[I]$$

We suppose that initially only A is present, and that its concentration is $[A]_0$.

$$[A] = [A]_0 e^{-k_a t}$$

After rearrangement:

$$\frac{d[I]}{dt} + k_b[I] = k_a[A]_0 e^{-k_a t}$$

This differential equation has a standard form and, after setting $[I]_0 = 0$, the solution is

$$[I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) [A]_0$$

At all times $[A] + [I] + [P] = [A]_0$, so it follows that

$$[P] = \left\{ 1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a} \right\} [A]_0$$

Analysing consecutive reactions

Suppose that in an industrial batch process a substance A produces the desired compound I which goes on to decay to a worthless product C, each step of the reaction being first-order. At what time will I be present in greatest concentration?

Answer

$$\frac{d[I]}{dt} = -\frac{k_a[A]_0(k_a e^{-k_a t} - k_b e^{-k_b t})}{k_b - k_a}$$

This rate is equal to zero when

$$k_a e^{-k_a t} = k_b e^{-k_b t}$$

Therefore,

$$t_{\max} = \frac{1}{k_a - k_b} \ln \frac{k_a}{k_b}$$

For a given value of k_a , as k_b increases both the time at which [I] is a maximum and the yield of I decrease.

(b) The steady-state approximation

There is a considerable increase in mathematical complexity as soon as the reaction mechanism has more than a couple of steps. A reaction scheme involving many steps is nearly always unsolvable analytically, and alternative methods of solution are necessary (integrate the rate laws numerically or make approximations).

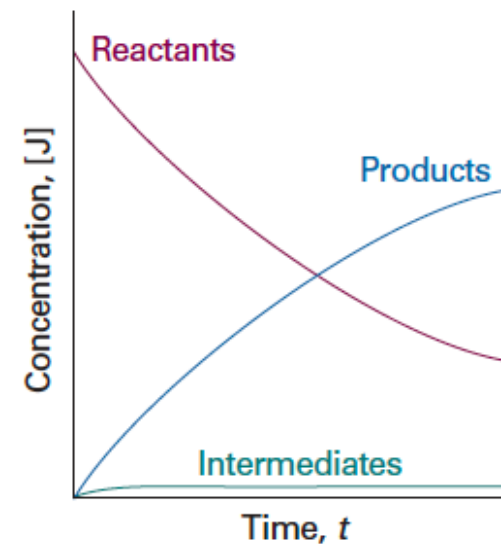
The **steady-state approximation** (which is also widely called the **quasi-steady-state approximation**, QSSA, to distinguish it from a true steady state) assumes that, after an initial **induction period**, an interval during which the concentrations of intermediates, I , rise from zero, and during the major part of the reaction, the rates of change of concentrations of all reaction intermediates are negligibly small

$\frac{d[I]}{dt} \approx 0$ apply the approximation to the consecutive first-order mechanism

$$k_a[A] - k_b[I] \approx 0 \Leftrightarrow [I] \approx (k_a/k_b)[A]$$

we require $k_a/k_b \ll 1$ (so that, even though $[A]$ does depend on the time, the dependence of $[I]$ on the time is negligible). On substituting this value of $[I]$ into $\frac{d[P]}{dt} = k_b[I]$, that equation becomes

$$\frac{d[P]}{dt} = k_b[I] \approx k_a[A]$$



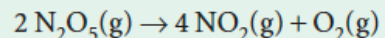
The basis of the steady-state approximation. It is supposed that the concentrations of intermediates remain small and hardly change during most of the course of the reaction.

P is formed by a first-order decay of A, with a rate constant k_a , the rate constant of the slower, rate-determining, step. We can write down the solution of this equation at once by substituting the solution for [A], and integrating:

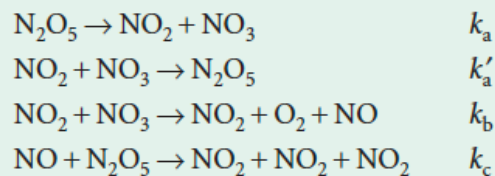
$$[P] = k_a[A]_0 \int_0^t e^{-k_a t} dt = (1 - e^{-k_a t})[A]_0$$

Using the steady-state approximation

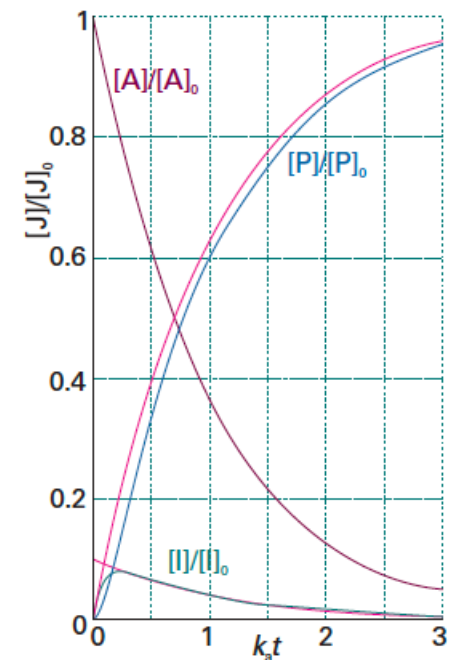
Devise the rate law for the decomposition of N_2O_5 ,



on the basis of the following mechanism:



A note on good practice Note that when writing the equation for an elementary reaction all the species are displayed individually; so we write $A \rightarrow B + B$, for instance, not $A \rightarrow 2 B$.



A comparison of the exact result for the concentrations of a consecutive reaction and the concentrations obtained by using the steady-state approximation (red lines) for $k_b = 20k_a$. (The curve for [A] is unchanged.)

Method First identify the intermediates (species that occur in the reaction steps but do not appear in the overall reaction) and write expressions for their net rates of formation. Then, all net rates of change of the concentrations of intermediates are set equal to zero and the resulting equations are solved algebraically.

Answer The intermediates are NO and NO₃; the net rates of change of their concentrations are

$$\frac{d[\text{NO}]}{dt} = k_b[\text{NO}_2][\text{NO}_3] - k_c[\text{NO}][\text{N}_2\text{O}_5] \approx 0$$

$$\frac{d[\text{NO}_3]}{dt} = k_a[\text{N}_2\text{O}_5] - k'_a[\text{NO}_2][\text{NO}_3] - k_b[\text{NO}_2][\text{NO}_3] \approx 0$$

The net rate of change of concentration of N₂O₅ is

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_a[\text{N}_2\text{O}_5] + k'_a[\text{NO}_2][\text{NO}_3] - k_c[\text{NO}][\text{N}_2\text{O}_5]$$

and replacing the concentrations of the intermediates by using the equations above gives

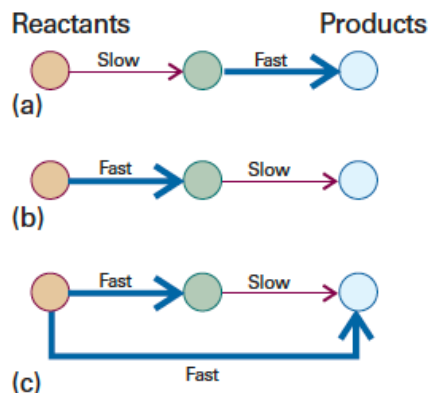
$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -\frac{2k_a k_b [\text{N}_2\text{O}_5]}{k'_a + k_b}$$

(c) The rate-determining step

when $k_b \gg k_a$, then the formation of the final product P depends on only the smaller of the two rate constants. That is, the rate of formation of P depends on the rate at which I is formed, not on the rate at which I changes into P. For this reason, the step $A \rightarrow I$ is called the '**rate determining step**' of the reaction. Its existence has been likened to building a six-lane highway up to a single-lane bridge: the traffic flow is governed by the rate of crossing the bridge.

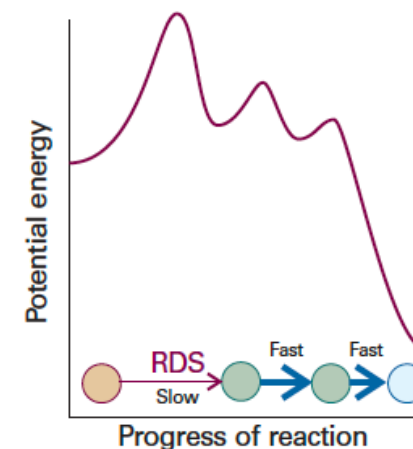
In general the rate-determining step is the slowest step in a mechanism and controls the overall rate of the reaction

The rate-determining step is not just the slowest step: it must be slow and be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be side-stepped



In these diagrams of reaction schemes, heavy arrows represent fast steps and light arrows represent slow steps.

- (a) The first step is rate-determining;
- (b) the second step is rate-determining;
- (c) although one step is slow, it is not rate-determining because there is a fast route that circumvents it.

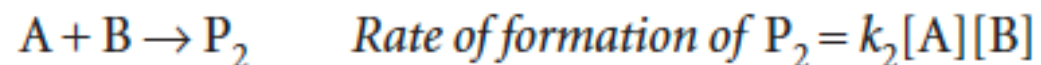
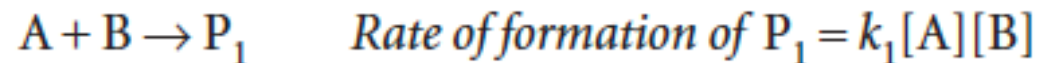


The reaction profile for a mechanism in which the first step (RDS) is rate-determining.

A rate-determining step may also stem from the low concentration of a crucial reactant and need not correspond to the step with highest activation barrier.

(d) Kinetic and thermodynamic control of reactions

Suppose two products, P_1 and P_2 , are produced by the following competing reactions:



The relative proportion in which the two products have been produced at a given stage of the reaction (before it has reached equilibrium) is given by the ratio of the two rates, and therefore of the two rate constants:

$$\frac{[P_2]}{[P_1]} = \frac{k_2}{k_1}$$

This ratio represents the **kinetic control** over the proportions of products, and is a common feature of the reactions encountered in organic chemistry where reactants are chosen that facilitate pathways favouring the formation of a desired product. **If a reaction is allowed to reach equilibrium**, then the proportion of products is determined by **thermodynamic rather than kinetic considerations**, and the ratio of concentrations is controlled by considerations of the standard Gibbs energies of all the reactants and products.

(e) Pre-equilibria

From a simple sequence of consecutive reactions we now turn to a slightly more complicated mechanism in which an intermediate I reaches an equilibrium with the reactants A and B:



A pre-equilibrium can arise when the rate of decay of the intermediate back into reactants is much faster than the rate at which it forms products; thus, the condition is possible when $k'_a \gg k_b$ but not when $k_b \gg k'_a$.

$$K = \frac{[I]}{[A][B]} \quad K = \frac{k_a}{k'_a}$$

The rate of formation of P

$$\frac{d[P]}{dt} = k_b[I] = k_b K[A][B]$$

This rate law has the form of a second-order rate law with a composite rate constant:

$$\frac{d[P]}{dt} = k[A][B] \quad k = k_b K = \frac{k_a k_b}{k'_a}$$

Repeat the pre-equilibrium calculation but without ignoring the fact that I is slowly leaking away as it forms P.

Method Begin by writing the net rates of change of the concentrations of the substances and then invoke the steady-state approximation for the intermediate I. Use the resulting expression to obtain the rate of change of the concentration of P.

Answer The net rates of change of P and I are

$$\frac{d[P]}{dt} = k_b[I]$$

$$\frac{d[I]}{dt} = k_a[A][B] - k'_a[I] - k_b[I] \approx 0$$

The second equation solves to

$$[I] \approx \frac{k_a[A][B]}{k'_a + k_b}$$

When we substitute this result into the expression for the rate of formation of P, we obtain

$$\frac{d[P]}{dt} \approx k[A][B] \quad k = \frac{k_a k_b}{k'_a + k_b}$$

Mecanismos complexos, com vários produtos
intermediários

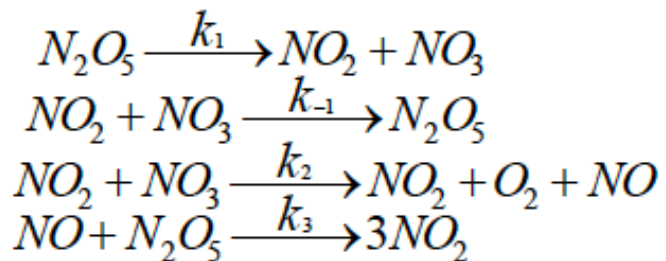
Aproximação do Estado Estacionário

Admite-se que os compostos intermediários (Int)
mais reativos mantêm concentrações baixas e
praticamente constantes durante a reação

$$d[\text{Int}]/dt = 0$$



Reação de 1ª Ordem



**Mecanismo reacional
proposto**



**Aplicação da
aproximação
de Estado Estacionário
a NO_3 e NO**

$$\begin{cases} \frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] = 0 \\ \frac{d[\text{NO}]}{dt} = k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{N}_2\text{O}_5] = 0 \end{cases}$$

$$\begin{cases} [\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}_2]} \\ [\text{NO}] = \frac{k_2[\text{NO}_2][\text{NO}_3]}{k_3[\text{N}_2\text{O}_5]} = \frac{k_1 k_2}{(k_{-1} + k_2) k_3} \end{cases}$$

Aproximação do Estado Estacionário

$$v = -\frac{1}{2} \frac{d[N_2O_5]}{dt} \quad \text{e} \quad \frac{d[N_2O_5]}{dt} = -k_1[N_2O_5] + k_{-1}[NO_2][NO_3] - k_3[NO][N_2O_5]$$

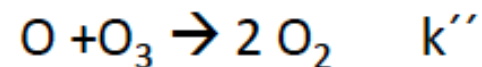
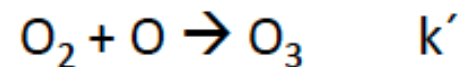
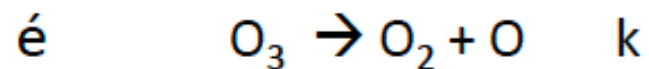
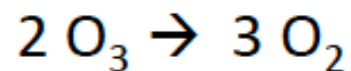
$$\frac{d[N_2O_5]}{dt} = -\frac{2k_1k_2[N_2O_5]}{k_{-1} + k_2}$$

$$v = k'[N_2O_5] \quad \text{com} \quad k' = \frac{k_1k_2}{k_{-1} + k_2}$$

1ª ordem com mecanismo reacional complexo

Problema

- O mecanismo proposto para a reação



Use a aproximação do estado estacionário para o radical O para chegar à seguinte equação de velocidade:

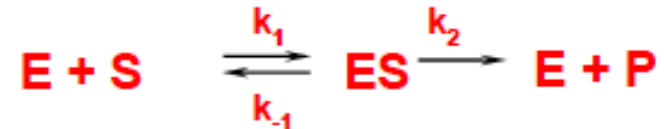
$$\frac{d[\text{O}_3]}{dt} = -\frac{2kk''[\text{O}_3]^2}{k'[\text{O}_2] + k''[\text{O}_3]}$$

Aplicações do método do estado estacionário

Mecanismos de reação em:

- Catálise enzimática – Michaelis-Menten
- Reações unimoleculares – Lindemann-Hinshelwood

Mecanismo de Michaelis-Menten



Aplicação da aproximação de
Estado Estacionário a ES

$$\frac{d[\text{ES}]}{dt} = k_1[\text{E}][\text{S}] - k_{-1}[\text{ES}] - k_2[\text{ES}] = 0 \quad \text{logo } \Rightarrow$$

$$[\text{ES}] = \frac{k_1[\text{E}][\text{S}]}{k_{-1} + k_2}$$

$$[\text{ES}] = \frac{1}{K_M} [\text{E}] [\text{S}]$$

$$\text{and } K_M = \frac{k_{-1} + k_2}{k_1}$$

Como $[\text{E}]_0 = [\text{E}]_{\text{total}} = [\text{E}] + [\text{ES}]$

$$[\text{ES}] = \frac{k_1([\text{E}]_0 - [\text{ES}])[\text{S}]}{k_{-1} + k_2} = \frac{k_1[\text{E}]_0[\text{S}]}{k_{-1} + k_2 + k_1[\text{S}]}$$

$$\frac{d[\text{P}]}{dt} = k_2[\text{ES}] = \frac{k_1 k_2 [\text{E}]_0 [\text{S}]}{k_{-1} + k_2 + k_1 [\text{S}]} = k' [\text{E}]_0 \quad \text{com} \quad k' = \frac{k_1 k_2 [\text{S}]}{k_{-1} + k_2 + k_1 [\text{S}]}$$

$$\frac{d[ES]}{dt} = 0 \Rightarrow k_1 [E] [S] = (k_{-1} + k_2) [ES]$$

como

$$[E] + [ES] = [E]_0 \Rightarrow [E] = [E]_0 - [ES]$$

tem-se :

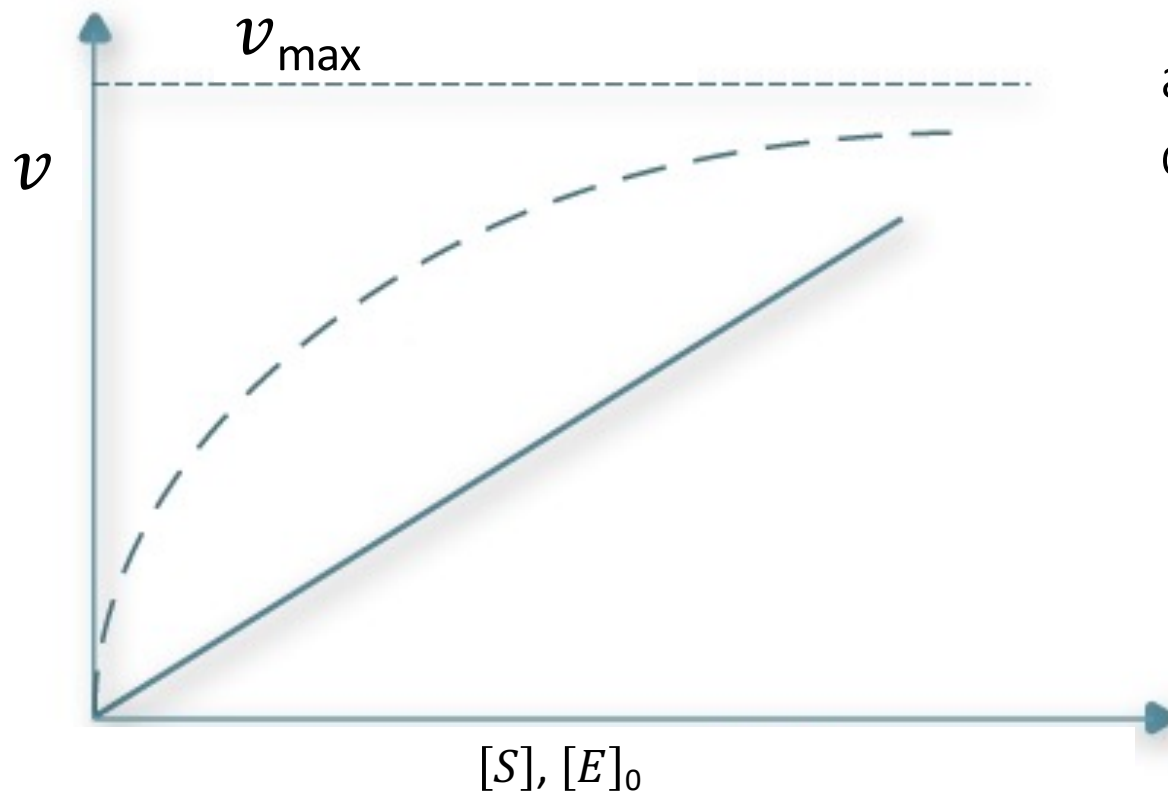
$$k_1 ([E]_0 - [ES]) [S] = (k_{-1} + k_2) [ES]$$

$$[E]_0 [S] = [ES] [S] + \frac{1}{k_1} (k_{-1} + k_2) [ES]$$

$$[E]_0 [S] = [ES] \left([S] + \frac{1}{k_1} (k_{-1} + k_2) \right) \Leftrightarrow [ES] = \frac{[E]_0 [S]}{\frac{k_{-1} + k_2}{k_1} + [S]}$$

$$v = - \frac{d[S]}{dt} = \frac{dP}{dt} = k_2 [ES] \quad \text{Logo} \quad v = - \frac{d[S]}{dt} = \frac{dP}{dt} = k_2 \frac{[E]_0 [S]}{\frac{k_{-1} + k_2}{k_1} + [S]}$$

$$v = - \frac{d[S]}{dt} = \frac{dP}{dt} = k_2 \frac{[E]_0 [S]}{\frac{k_{-1} + k_2}{k_1} + [S]}$$



a velocidade aumenta hiperbolicamente com a concentração do substrato,

se $[S]$ muito elevado

$$v = k_2 [E]_0$$

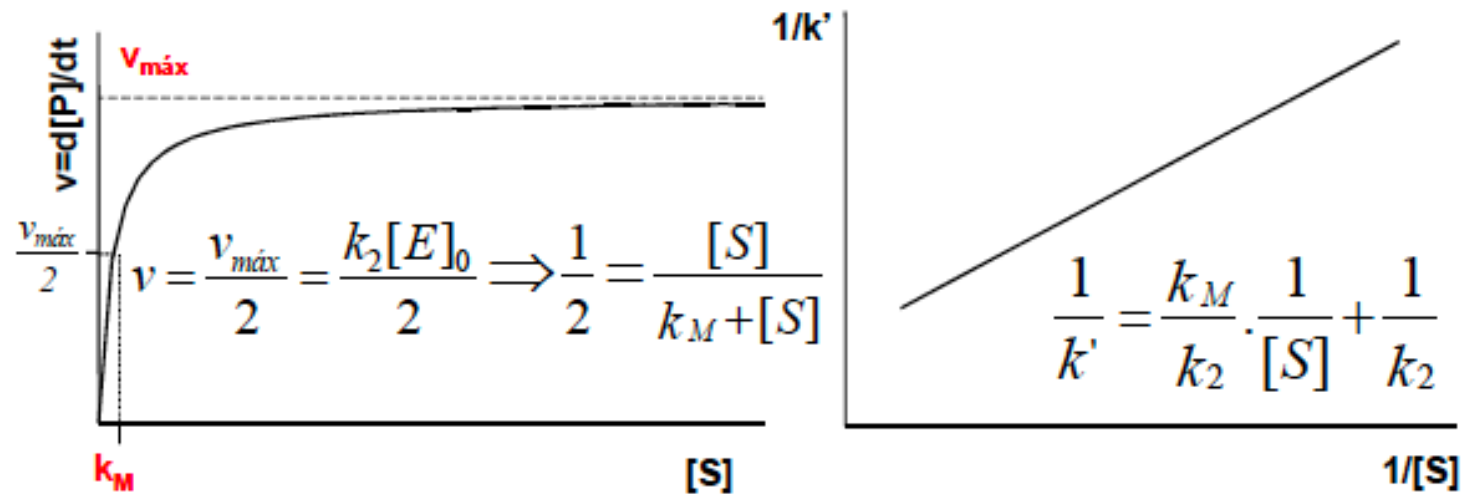
Ordem 0

se $[S]$ é baixa

$$v = k_2 \frac{[E]_0 [S]}{\frac{k_{-1} + k_2}{k_1}}$$

Ordem 1

Mecanismo de Michaelis-Menten k_M



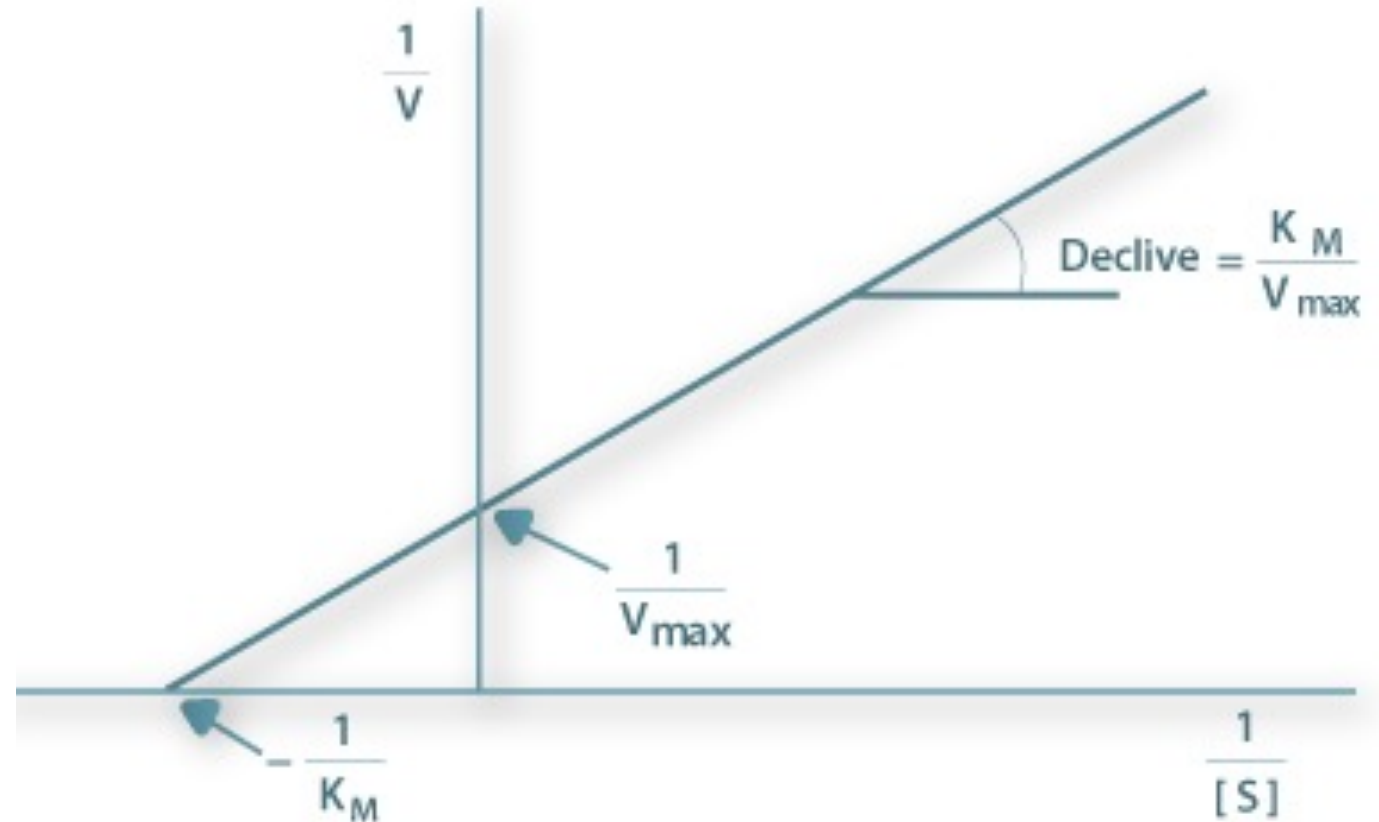
Constante de Michaelis $K_M = \frac{k_{-1} + k_2}{k_1} = \frac{\text{desaparecimento de } ES}{\text{aparecimento de } ES}$

A constante K_M é expressa em unidades de concentração e tem um significado tal que quando a concentração do substrato iguala o seu valor a velocidade da reação é igual a metade de v_{\max} (i.e., $[S]_{1/2} = K_M \Rightarrow v = \frac{1}{2}v_{\max}$).

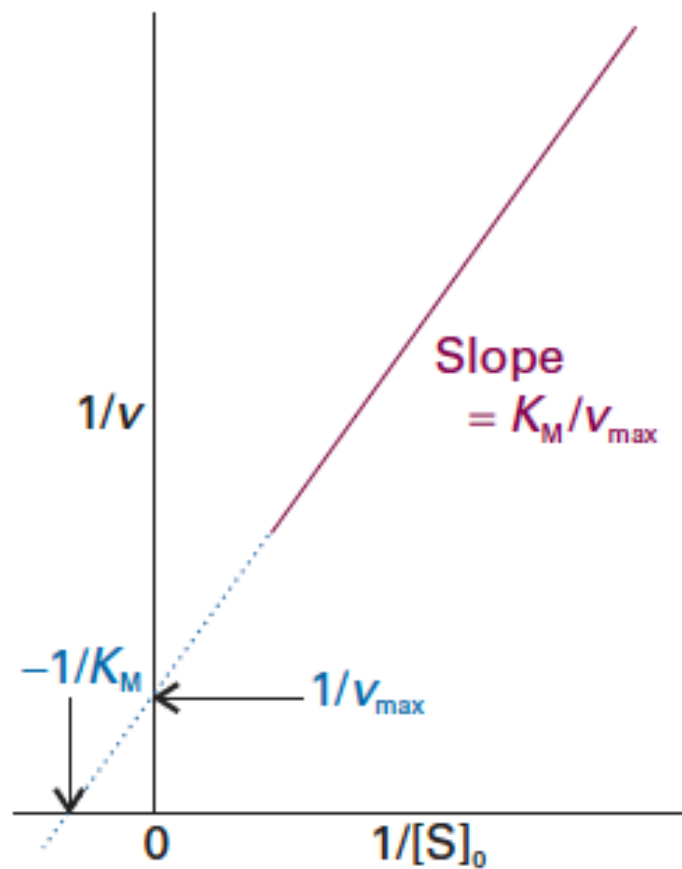
Equação de Lineweaver-Burk:

$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_M}{v_{max}} \cdot \frac{1}{[S]}$$

Da representação gráfica de $1/v$ *versus* $1/[S]$ obtém-se um recta cujo ordenada na origem é $1/v_{max}$ e cujo declive é K_M/v_{max}



Lineweaver–Burk plot



$$[ES] = \frac{[E]_0}{1 + K_M/[S]_0}$$

$$v = \frac{k_b[E]_0}{1 + K_m/[S]_0}$$

$$\frac{1}{v} = \frac{1}{v_{\max}} + \left(\frac{K_M}{v_{\max}} \right) \frac{1}{[S]_0}$$

When $[S]_0 \ll k_M$,
the rate is proportional to $[S]_0$:
 $v = k_2/K_M [S]_0[E]_0$

When $[S]_0 \gg k_M$,
the rate reaches its maximum value
and is independent of $[S]_0$:
 $v = v_{\max} = k_2[E]_0$

The enzyme carbonic anhydrase catalyses the hydration of CO_2 in red blood cells to give bicarbonate (hydrogencarbonate) ion:



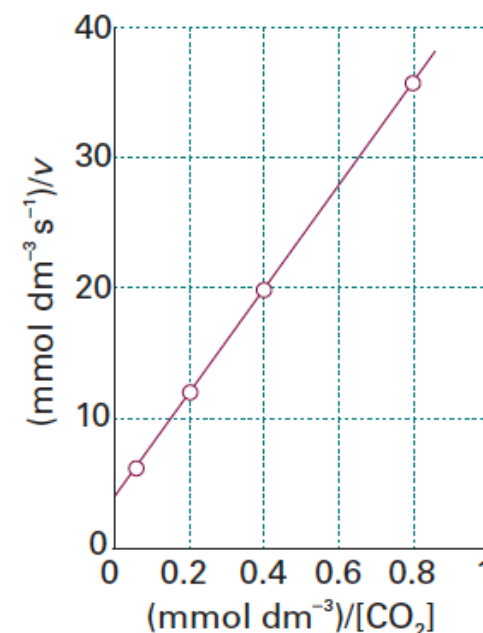
The following data were obtained for the reaction at $\text{pH} = 7.1$, 273.5 K , and an enzyme concentration of 2.3 nmol dm^{-3} :

$[\text{CO}_2]/(\text{mmol dm}^{-3})$	1.25	2.50	5.00	20.0
rate/ $(\text{mmol dm}^{-3} \text{ s}^{-1})$	2.78×10^{-2}	5.00×10^{-2}	8.33×10^{-2}	1.67×10^{-1}

Determine the catalytic efficiency of carbonic anhydrase at 273.5 K .

[Solutions: $v_{\text{max}} = 0.250 \text{ mmol dm}^{-3} \text{ s}^{-1}$, $K_{\text{M}} = 10.0 \text{ mmol dm}^{-3}$

$$k_2 = 1.1 \times 10^5 \text{ s}^{-1} \quad \epsilon = k_2 / K_{\text{M}} = 1.1 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$



The enzyme α -chymotrypsin is secreted in the pancreas of mammals and cleaves peptide bonds made between certain amino acids. Several solutions containing the small peptide N-glutaryl-L-phenylalanine-*p*-nitroanilide at different concentrations were prepared and the same small amount of α -chymotrypsin was added to each one. The following data were obtained on the initial rates of the formation of product:

$[S]/(\text{mmol dm}^{-3})$	0.334	0.450	0.667	1.00	1.33	1.67
$v/(\text{mmol dm}^{-3} \text{ s}^{-1})$	0.152	0.201	0.269	0.417	0.505	0.667

Determine the maximum velocity and the Michaelis constant for the reaction.

[Solutions: $v_{\text{max}} = 2.80 \text{ mmol dm}^{-3} \text{ s}^{-1}$, $K_{\text{M}} = 5.89 \text{ mmol dm}^{-3}$]

Reações Unimoleculares

Reações que envolvem uma só
espécie molecular reagente

Reacção	$\ln (A/s^{-1})$	E_a (kJ mol ⁻¹)
<u>Isomerizações</u>		
Ciclopropano \rightarrow propeno	35.7	274
Ciclopropeno \rightarrow propino	29.9	147
$CH_3NC \rightarrow CH_3CN$	31.3	131
<u>Dissociações</u>		
ciclobutano \rightarrow eteno + eteno	35.9	262
cloreto de etilo \rightarrow HCl + eteno	32.2	244
iodeto de etilo \rightarrow HI + eteno	32.5	221
éter isopropílico \rightarrow propeno + isopropanol	33.6	266

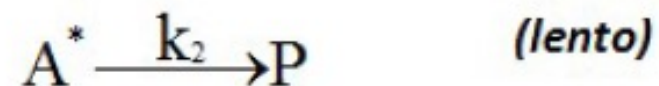
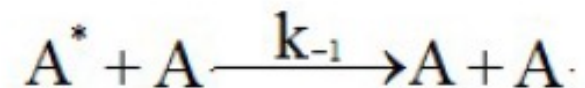
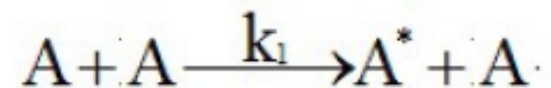
Reações unimoleculares em fase gasosa

- Estas reações são de 1ª ordem, embora o único mecanismo reacional concebível seja o choque entre duas moléculas a fornecer energia suficiente para uma delas se transformar.
- Como é que um acontecimento **bimolecular** simples dá origem a uma **ordem 1**?

Mecanismo proposto por Lindemann, modificado por Hinshelwood

Moléculas são activadas por choque com outras moléculas iguais

As moléculas ativadas A^* podem desativar-se por um novo choque ou reagir, passando ao produto P



Aplicando o método do estado estacionário à molécula ativada A^*

$$d[A^*]/dt = 0 = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*]$$

$$[A^*] = k_1[A]^2 / \{k_{-1}[A] + k_2\}$$

Como a velocidade da reação é a de passagem ao produto

$$d[P]/dt = k_2[A^*]$$

$$\frac{d[P]}{dt} = k'[A] \quad \text{com} \quad k' = \frac{k_1 k_2 [A]}{k_{-1}[A] + k_2}$$

A pseudo-constante de velocidade depende da concentração a pressões intermédias

