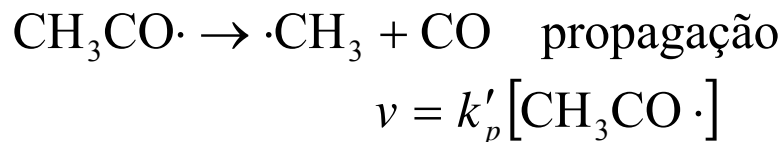
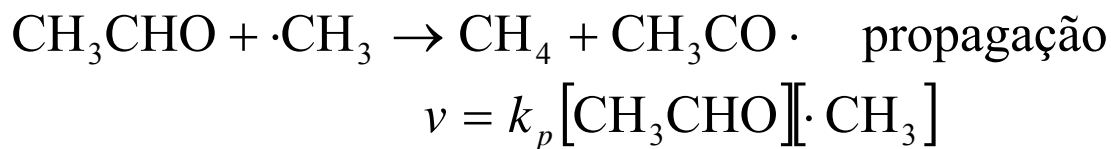
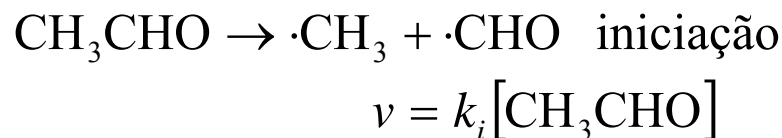
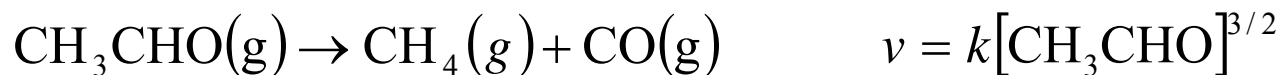


Reações em cadeia

- São reações nas quais o *intermediário em uma etapa gera um intermediário* em uma etapa subsequente, e assim por diante.
- Os *propagadores* da cadeia são os intermediários em uma reação em cadeia.
- Reação em cadeia com radicais: os propagadores são radicais.

Mecanismo da reação de pirólise do acetaldeído: etapas



$$v = k_t[\cdot\text{CH}_3]^2$$

Dedução da lei cinética, usando o método do estado estacionário (permanente, “steady-state”)

$$\frac{d[\cdot\text{CH}_3]}{dt} = k_i[\text{CH}_3\text{CHO}] - k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k'_p[\text{CH}_3\text{CO}\cdot] - 2k_t[\cdot\text{CH}_3]^2 = 0$$

$$\frac{d[\text{CH}_3\text{CO}\cdot]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k'_p[\text{CH}_3\text{CO}\cdot] = 0$$

$$k_i[\text{CH}_3\text{CHO}] - 2k_t[\cdot\text{CH}_3]^2 = 0$$

$$[\cdot\text{CH}_3] = \left(\frac{k_i}{2k_t}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

$$\frac{d[\text{CH}_4]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] = k_p \left(\frac{k_i}{2k_t}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Concorda com a lei cinética experimental, mas não explica a formação de subprodutos: acetona ou propanal

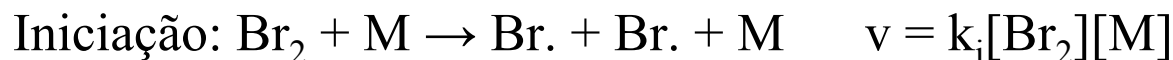
Estequiometria:



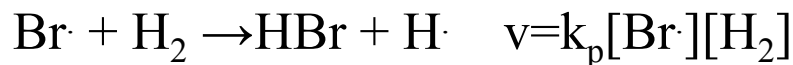
Lei de velocidade:

$$v = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]}$$

Mecanismo proposto:



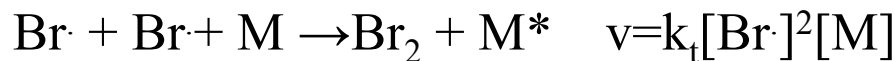
Propagação:



Retardação



Terminação:



Verificação do mecanismo proposto

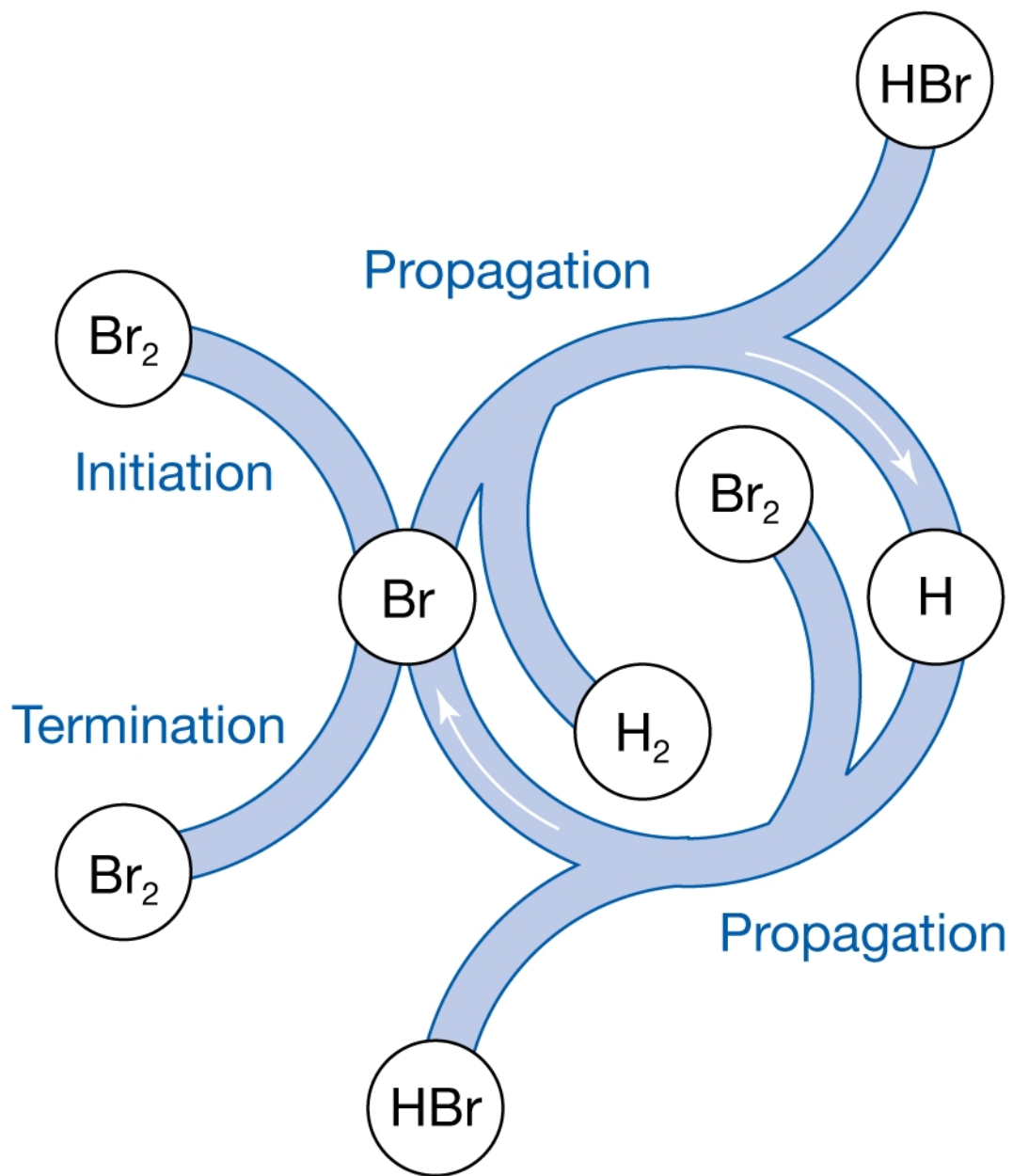
$$\frac{d[\text{H}\cdot]}{dt} = k_p [\text{Br}\cdot][\text{H}_2] - k'_p [\text{H}\cdot][\text{Br}_2] - k_r [\text{H}\cdot][\text{HBr}] = 0$$

$$\frac{d[\text{Br}\cdot]}{dt} = 2k_i [\text{Br}_2][\text{M}] - k_p [\text{Br}\cdot][\text{H}_2] + k'_p [\text{H}\cdot][\text{Br}_2] + k_r [\text{H}\cdot][\text{HBr}] - 2k_t [\text{Br}\cdot]^2 [\text{M}] = 0$$

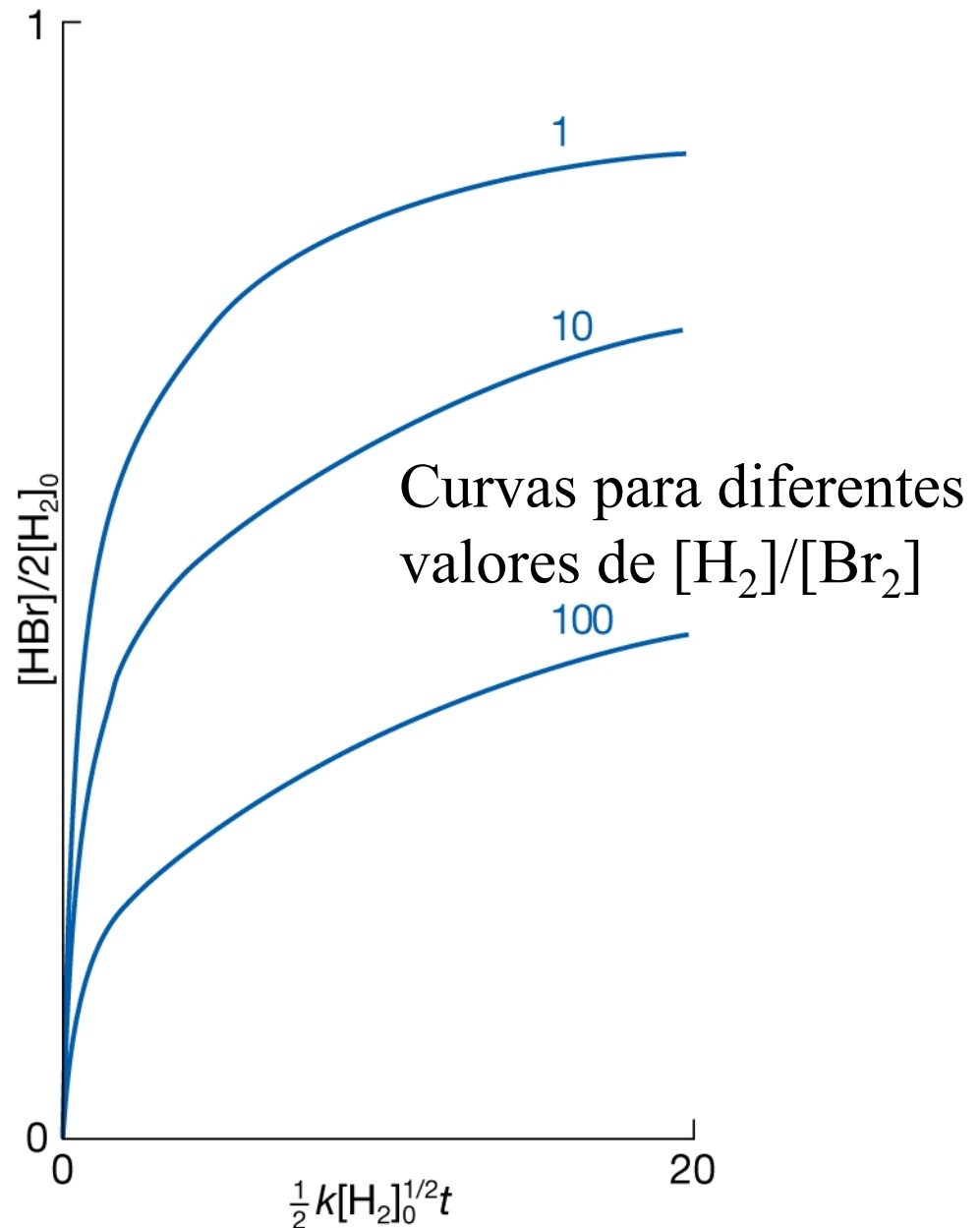
$$[\text{Br}\cdot] = \left(\frac{k_i}{k_t} \right)^{1/2} [\text{Br}_2]^{1/2} \qquad [\text{H}\cdot] = \frac{k_p (k_i / k_t)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2}}{k'_p [\text{Br}_2] + k_r [\text{HBr}]}$$

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_p (k_i / k_t)^{1/2} [\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + (k_r / k'_p)[\text{HBr}]}$$

$$k = 2k_p \left(\frac{k_i}{k_t} \right)^{1/2} \qquad k' = \frac{k_r}{k'_p}$$



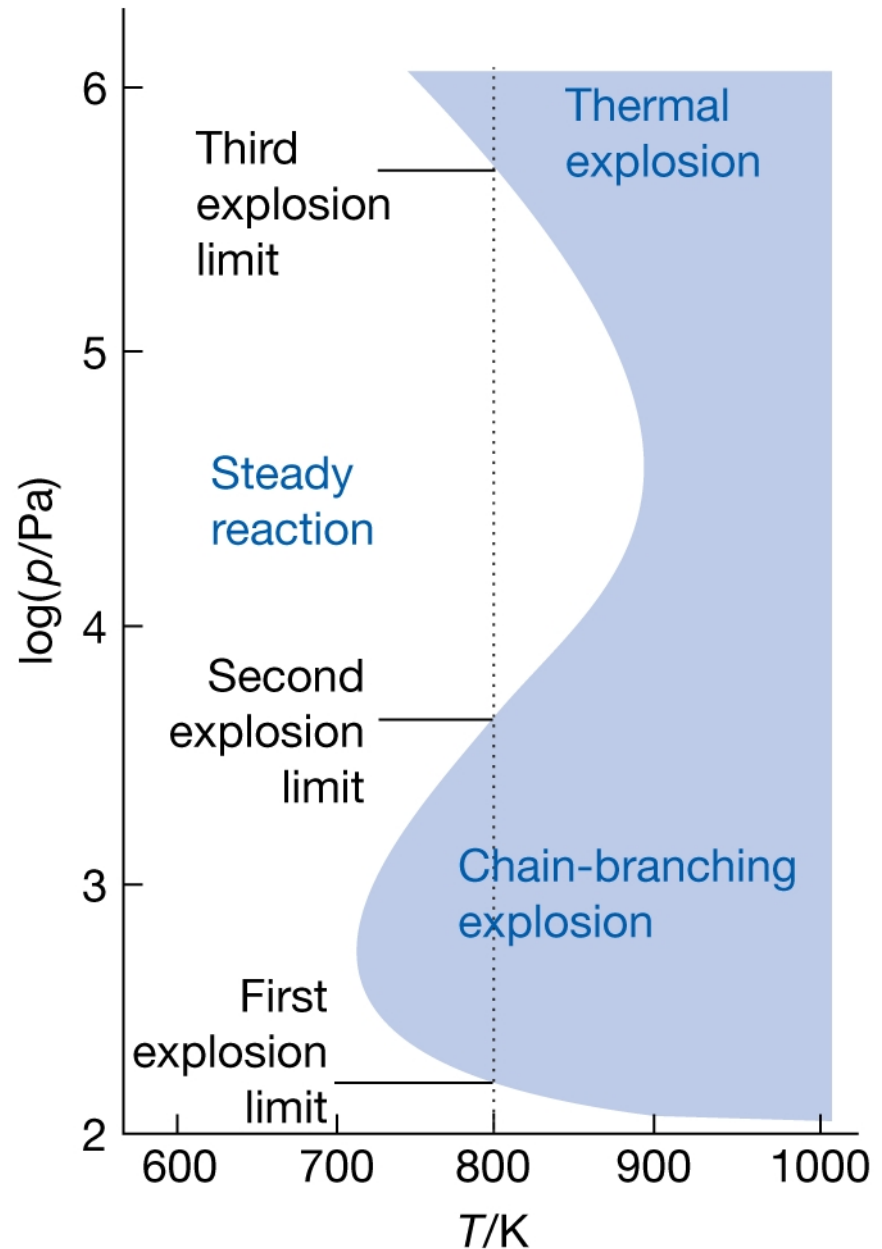
Concentrações
de HBr em
função do
tempo, obtidas
por integração
numérica

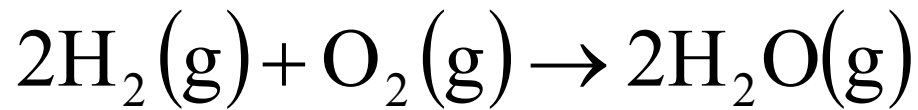


Explosões: reações em cadeia, muito exotérmicas

- $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$
 - Reação simples com mecanismo complexo, ainda incompletamente elucidado
- $$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$$
- $$\text{H}_2 \rightarrow \text{H}\cdot + \text{H}\cdot \quad v = \text{constant}(\alpha_{\text{inicial}})$$
- $$\text{H}_2 + \cdot\text{OH} \rightarrow \cdot\text{H} + \text{H}_2\text{O} \quad v = k_p[\text{H}_2][\cdot\text{OH}]$$
- $$\cdot\text{O}_2\cdot + \cdot\text{H} \rightarrow \cdot\text{O}\cdot + \cdot\text{OH} \quad v = k_b[\cdot\text{O}_2\cdot][\cdot\text{H}\cdot]$$
- $$\cdot\text{O}\cdot + \text{H}_2 \rightarrow \cdot\text{OH} + \cdot\text{H} \quad v = k'_b[\cdot\text{O}\cdot][\text{H}_2]$$
- $$\text{H}\cdot + \text{parede} \rightarrow \frac{1}{2}\text{H}_2 \quad v = k_t[\text{H}\cdot]$$
- $$\text{H}\cdot + \text{O}_2 + \text{M} \rightarrow \text{HO}_2\cdot + \text{M}^* \quad v = k'_t[\text{H}\cdot][\text{O}_2][\text{M}]$$

Abaixo do primeiro limite: reação suave, os propagadores são extintos nas paredes.
Primeiro limite: os propagadores reagem antes de serem extintos nas paredes.
Segundo limite: o aumento na concentração aumenta a velocidade de terminação (aumento de colisões triplas) e a reação se torna suave.
Terceiro limite: reações muito rápidas, comportamento explosivo.





$$v_{\text{rad}} = d[\text{H.}]/dt$$

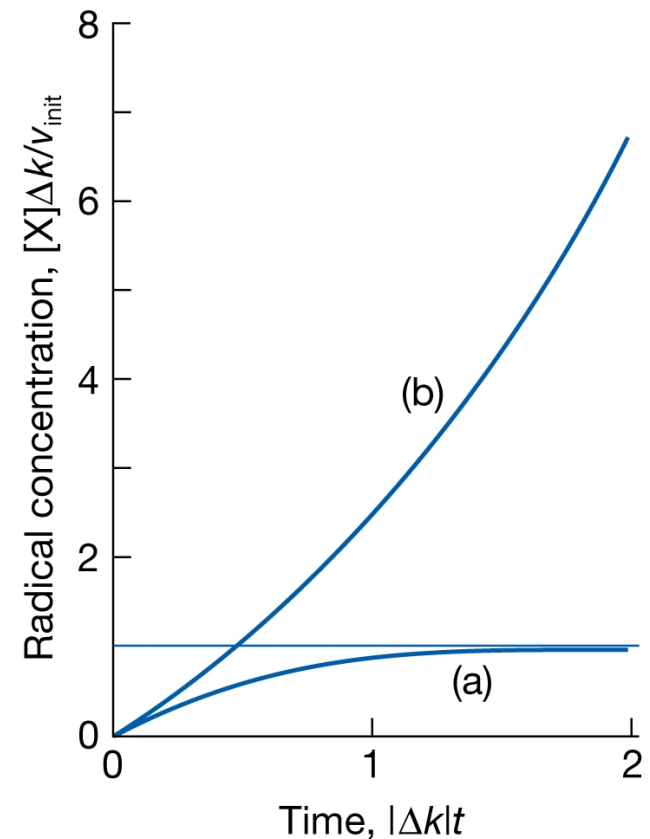
$$v_{\text{rad}} = v_{\text{inicial}} + k_p[\text{OH.}][\text{H}_2] - k_b[\text{H.}][\text{O}_2] + k_b'[\text{.O.}][\text{H}_2] - k_t[\text{H.}] - k_t'[\text{H.}][\text{O}_2][\text{M}]$$

$$v_{\text{rad}} = v_{\text{inicial}} - k_b[\text{O}_2] - k_t - k_t'[\text{H.}][\text{O}_2][\text{M}]$$

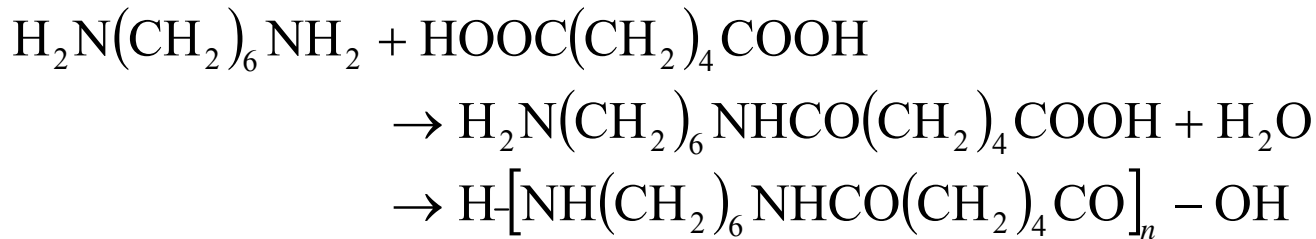
$$v_{\text{rad}} = v_{\text{inicial}} - k_{\text{ram}} - k_t - k_{\text{term}}[\text{H.}]$$

Concentrações baixas de O_2 : terminação domina a ramificação, reação suave

Concentrações altas de O_2 : ramificação Domina, reação explosiva



Cinética de polimerização: condensação



$$\text{Eq.26.5a} \quad \frac{d[A]}{dt} = -k[\text{OH}][A]$$

$$\text{Eq.26.7} \quad p = \frac{[A]_0 - [A]}{[A]_0} = \frac{kt[A]_0}{1 + kt[A]_0}$$

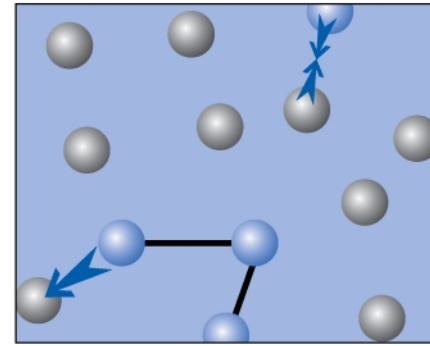
$$\text{Eq.26.5b} \quad \frac{d[A]}{dt} = -k[A]^2$$

$$\text{Eq.26.8a} \quad \langle n \rangle = \frac{[A]_0}{[A]} = \frac{1}{1 - p}$$

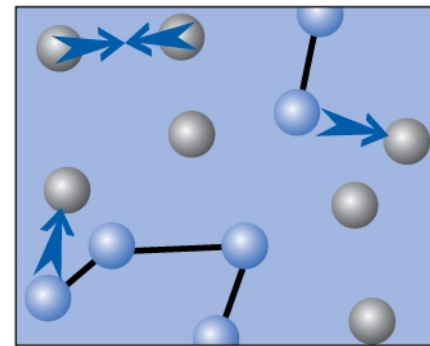
$$\text{Eq.26.6} \quad [A] = \frac{[A]_0}{1 + kt[A]_0}$$

Polimerização por condensação:
poliamida, poliéster, poliuretana,
policarbonato

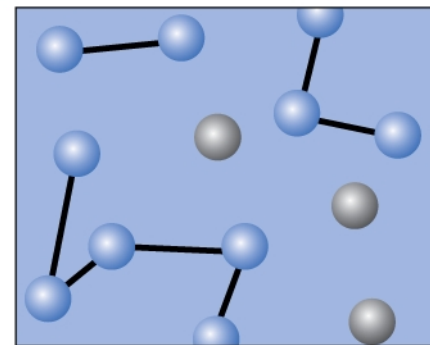
A cadeia é iniciada pela
condensação de dois
monômeros, podendo haver
condensação de oligômeros



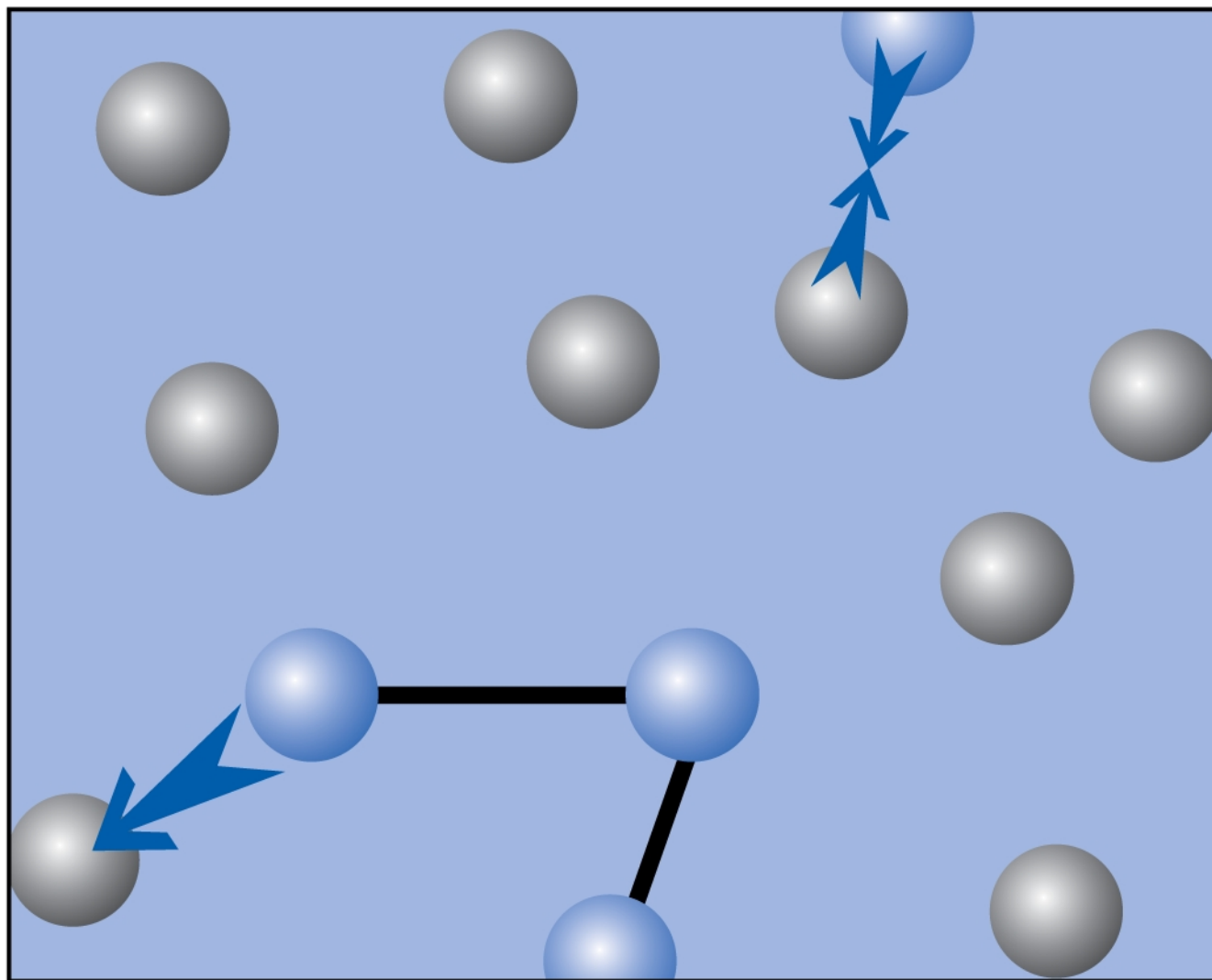
(a)



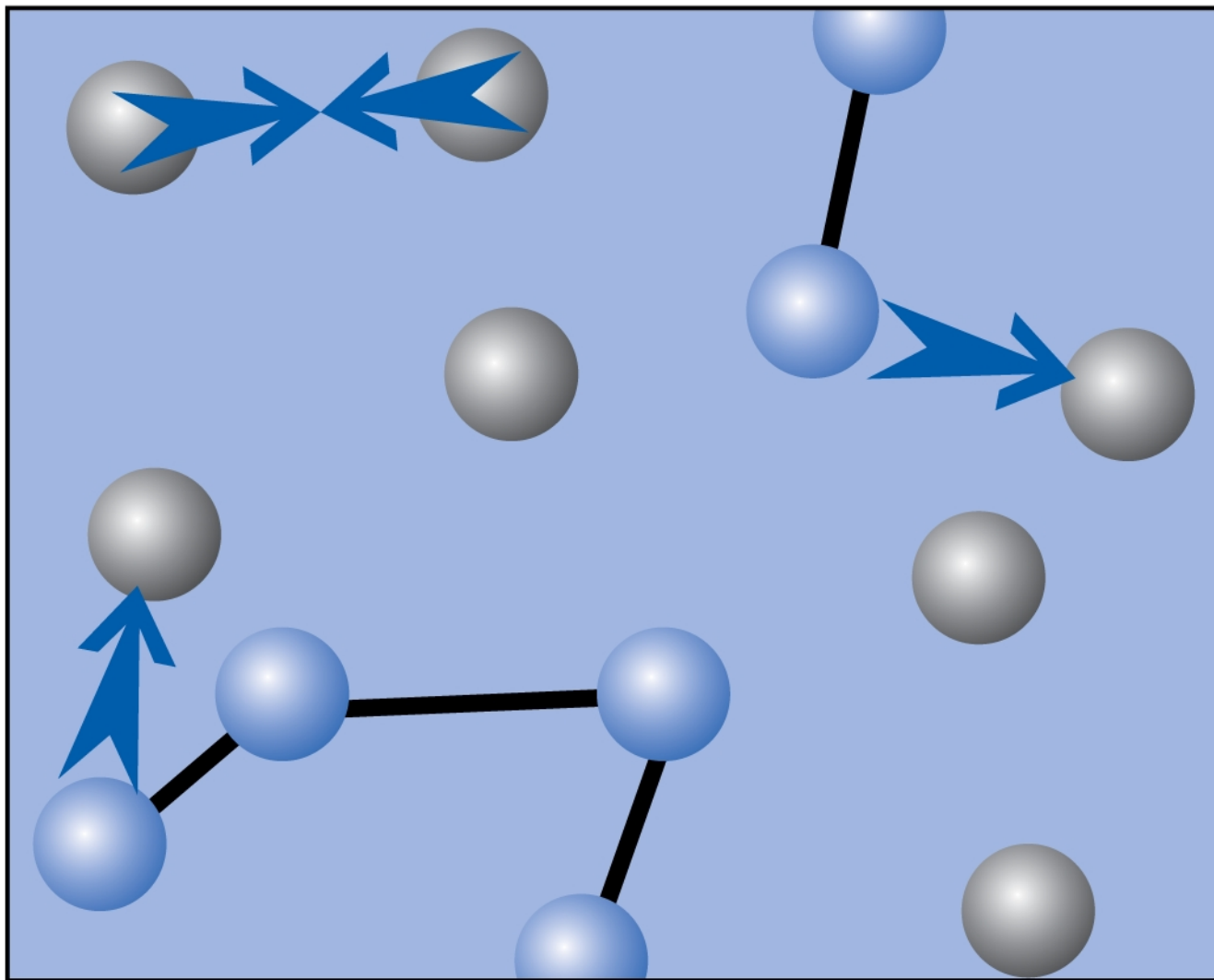
(b)



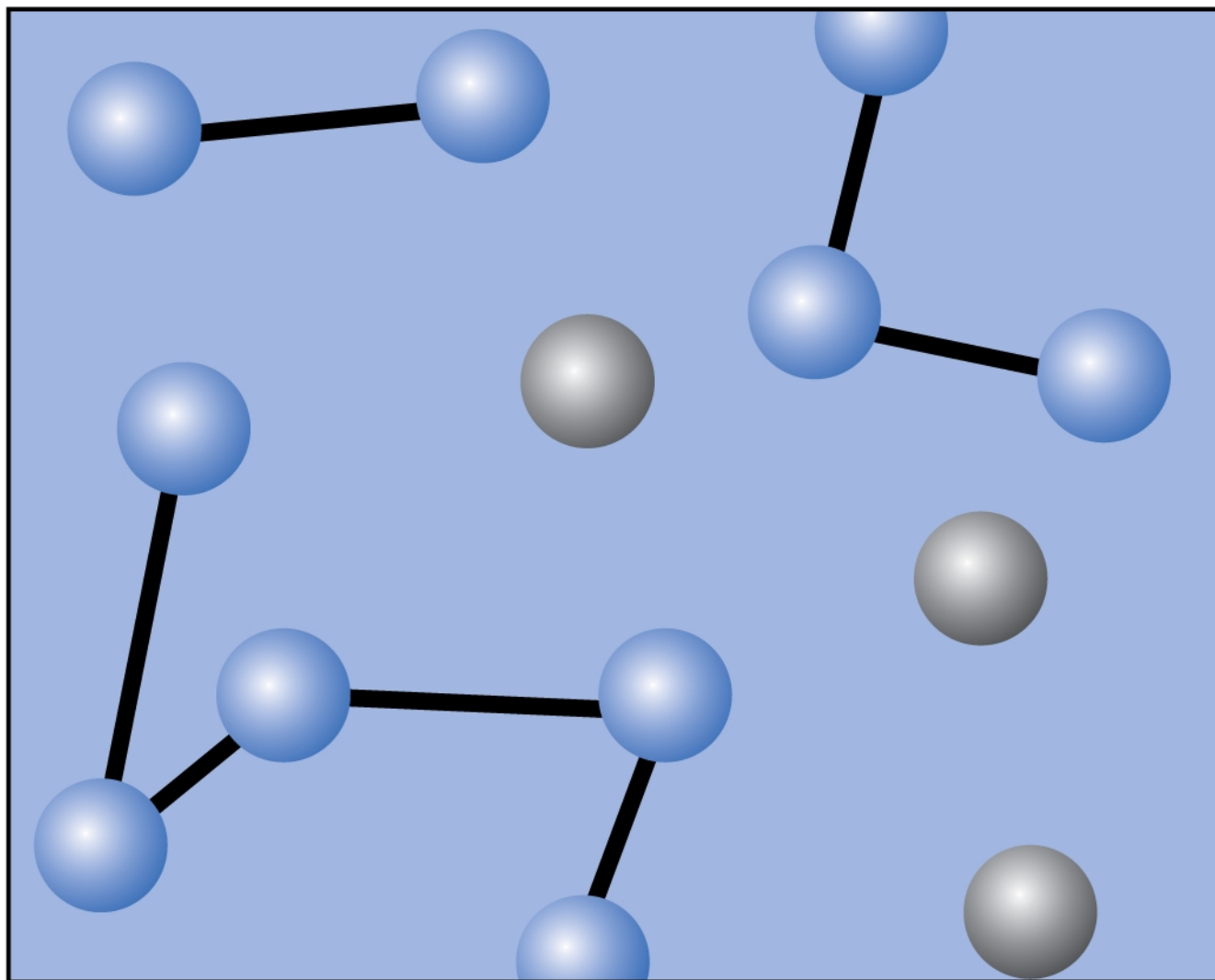
(c)



(a)

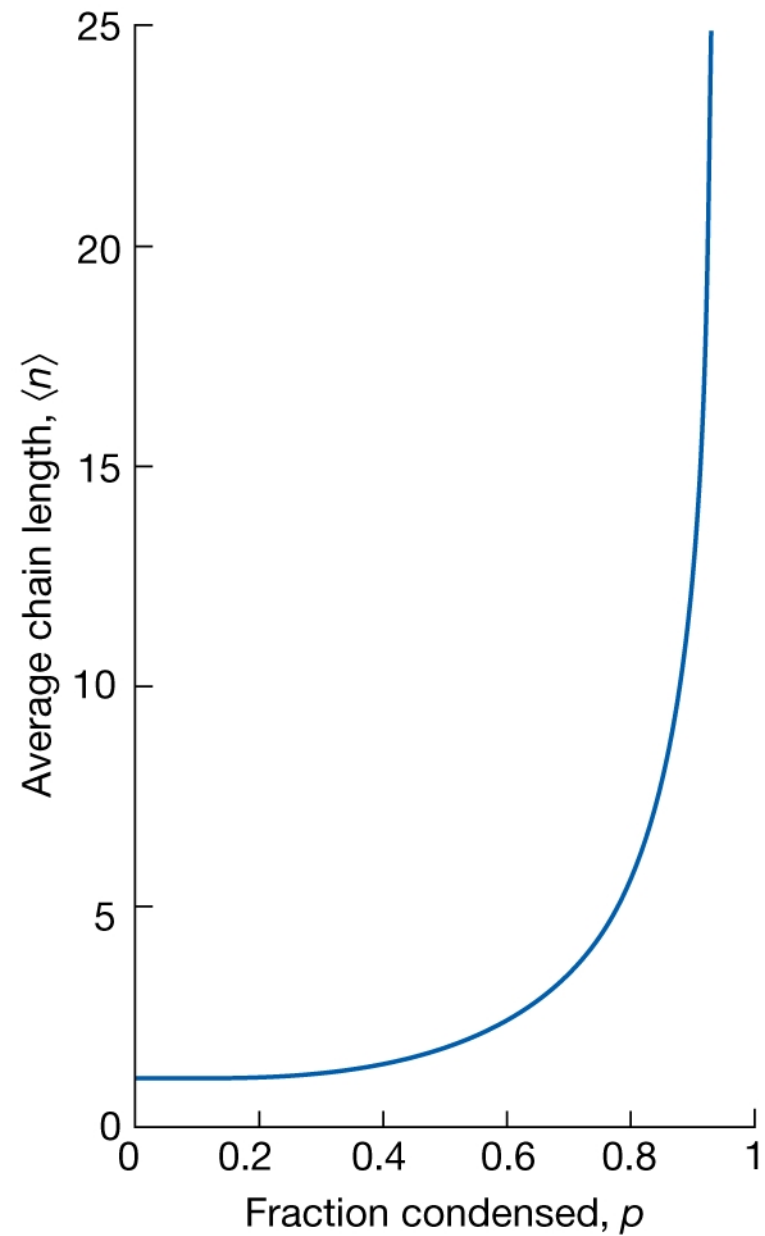


(b)

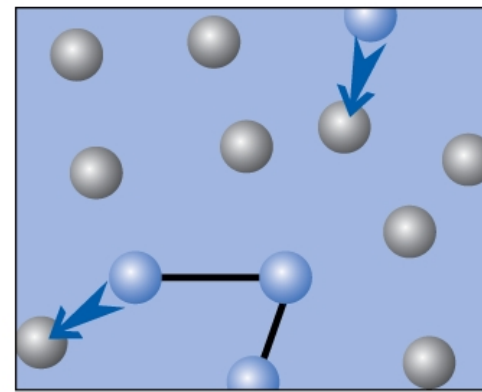


(c)

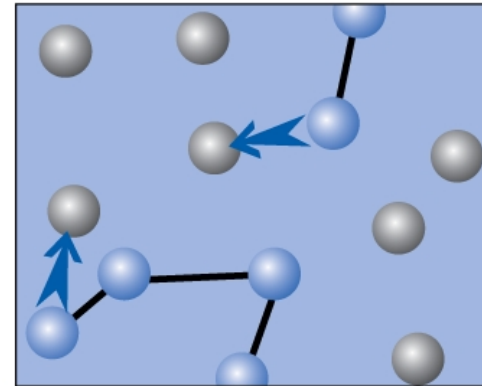
$$\langle n \rangle = \frac{[A]_0}{[A]} = \frac{1}{1-p}$$



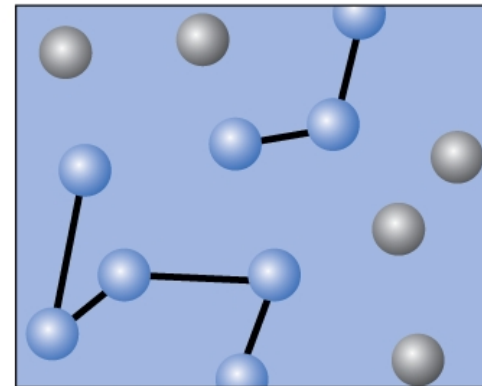
Cinética de polimerização em
cadeia:
as cadeias crescem pela
incorporação de monômeros a
uma cadeia já existente



(a)



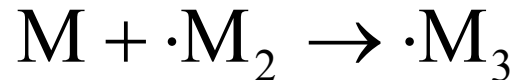
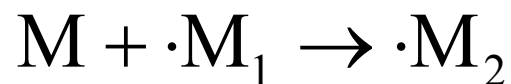
(b)

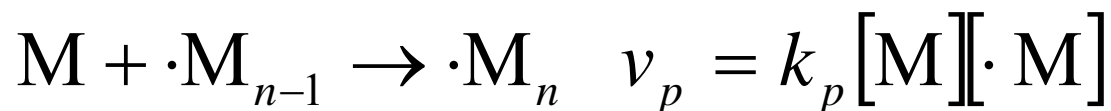


(c)

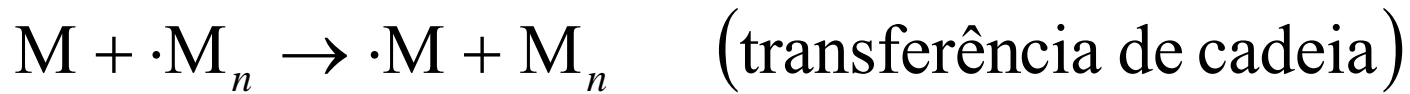
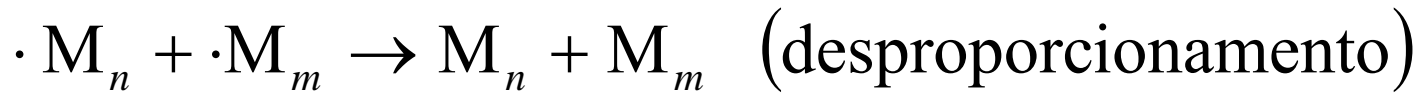


$$v = k[\text{I}]^{1/2}[\text{M}]$$



$$\vdots$$


$$\left(\frac{d[\cdot\text{M}]}{dt} \right)_{\text{produção}} = 2fk_i[\text{I}]$$



$$v_t = k_t [\cdot M]^2$$

$$\left(\frac{d[\cdot M]}{dt} \right)_{\text{terminação}} = -2k_t [\cdot M]^2$$

$$\frac{d[\cdot M]}{dt} = 2fk_i[I] - 2k_t[\cdot M]^2 = 0$$

$$[\cdot M] = \left(\frac{fk_i}{k_t} \right)^{1/2} [I]^{1/2}$$

$$v_p = k_p [\cdot M][M] = k_p \left(\frac{fk_i}{k_t} \right)^{1/2} [I]^{1/2} [M]$$

Comprimento cinético de cadeia e grau de polimerização

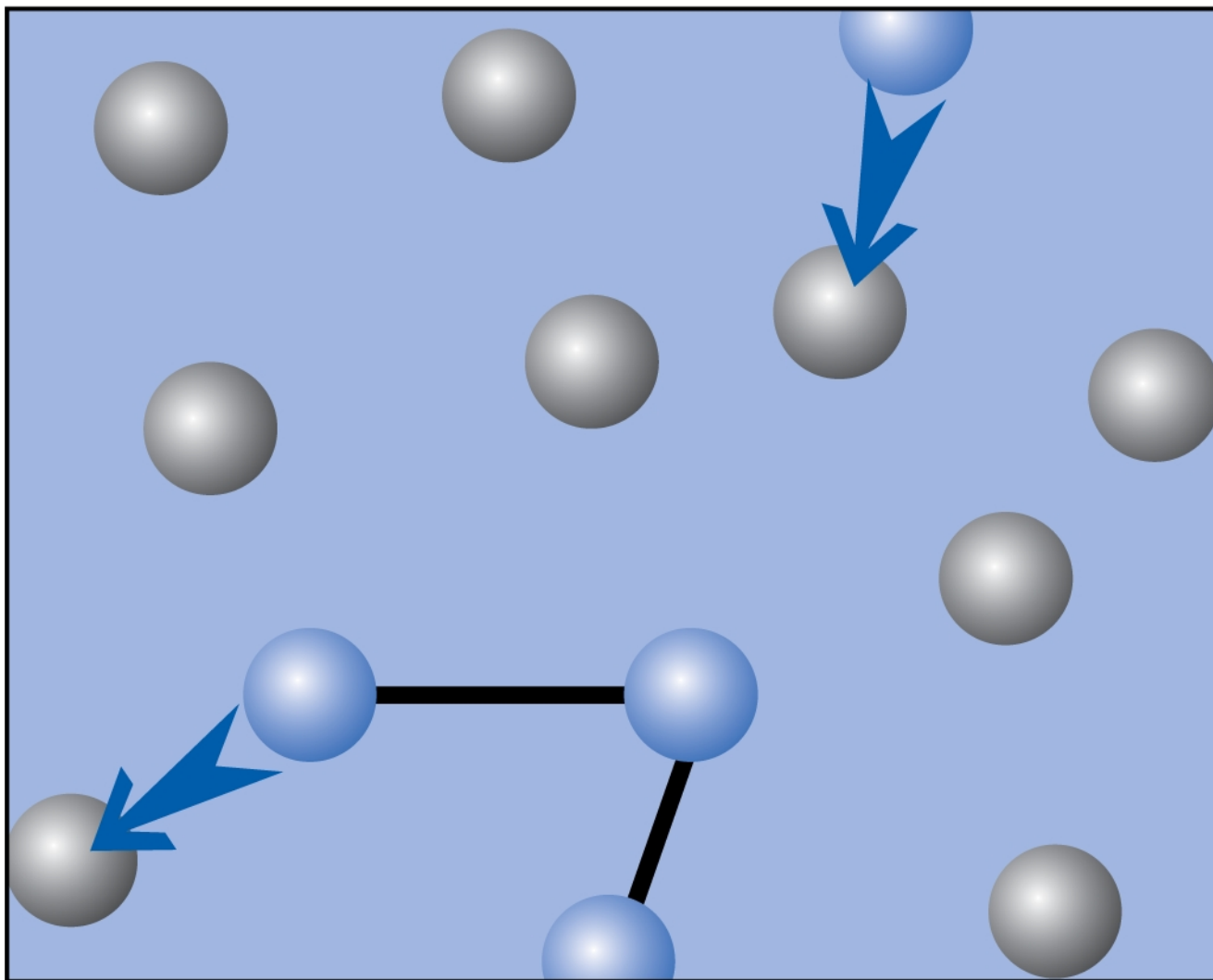
$$\nu = \frac{\text{número de unidades de monômero consumidas}}{\text{número de centros ativos produzidos}}$$

$$\nu = \frac{\text{velocidade de propagação das cadeias}}{\text{velocidade de produção de radicais}}$$

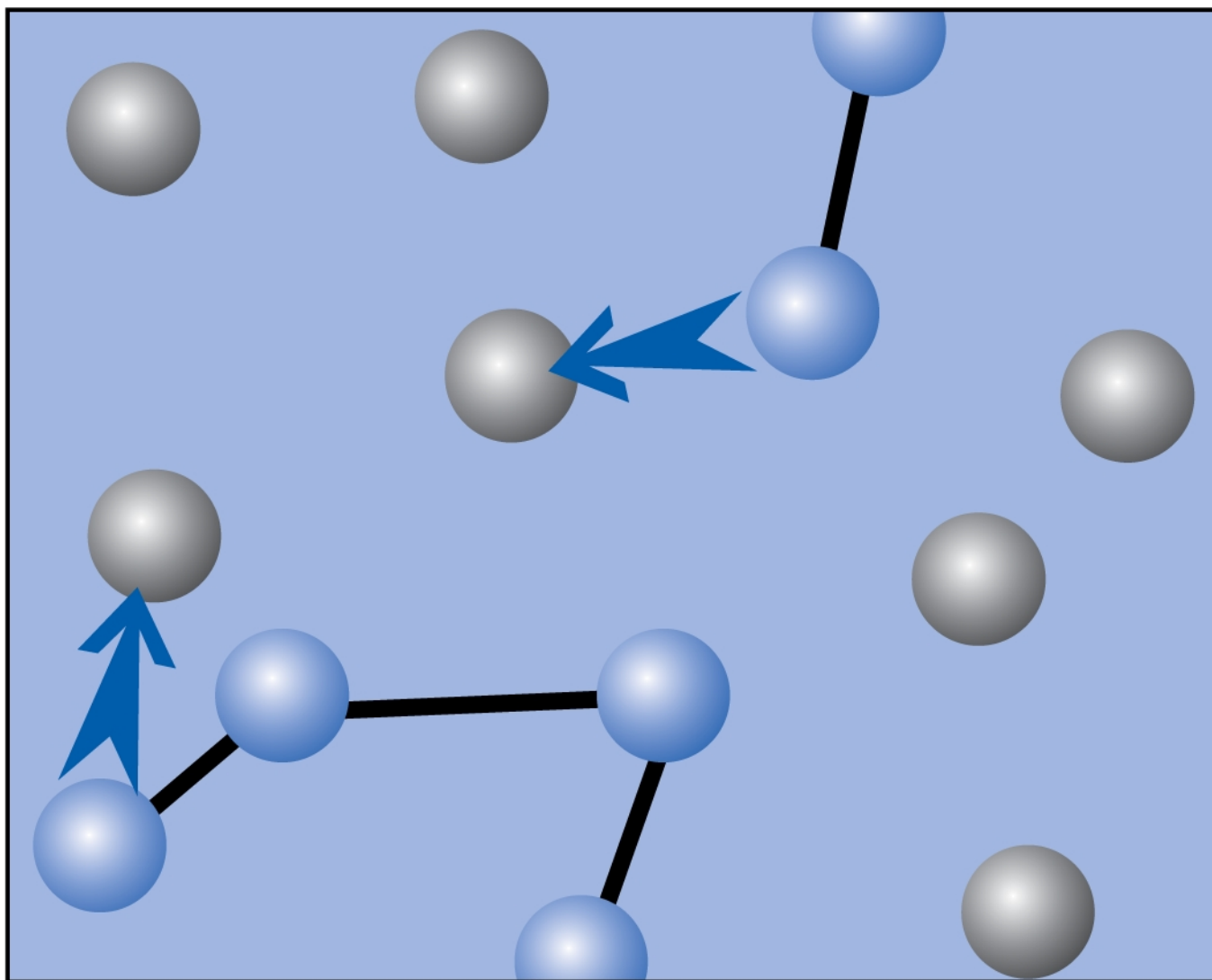
$$\nu = \frac{k_p [\cdot M][M]}{2k_t [M \cdot]^2} = \frac{k_p [M]}{2k_t [\cdot M]}$$

$$\nu = k[M][I]^{-1/2} \quad k = \frac{1}{2} k_p (fk_i k_t)^{-1/2}$$

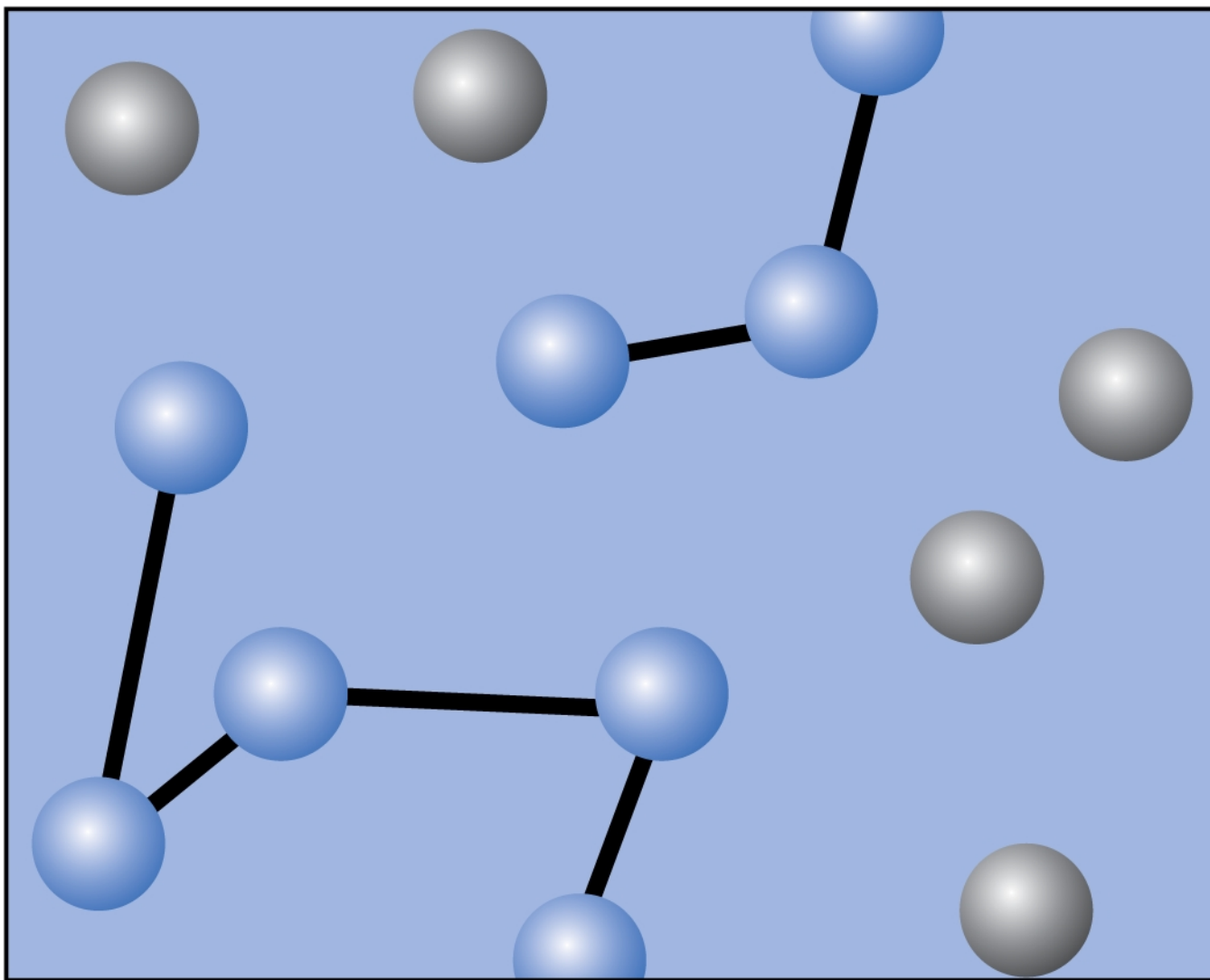
$$\langle n \rangle = 2\nu = 2k[M][I]^{-1/2}$$



(a)



(b)

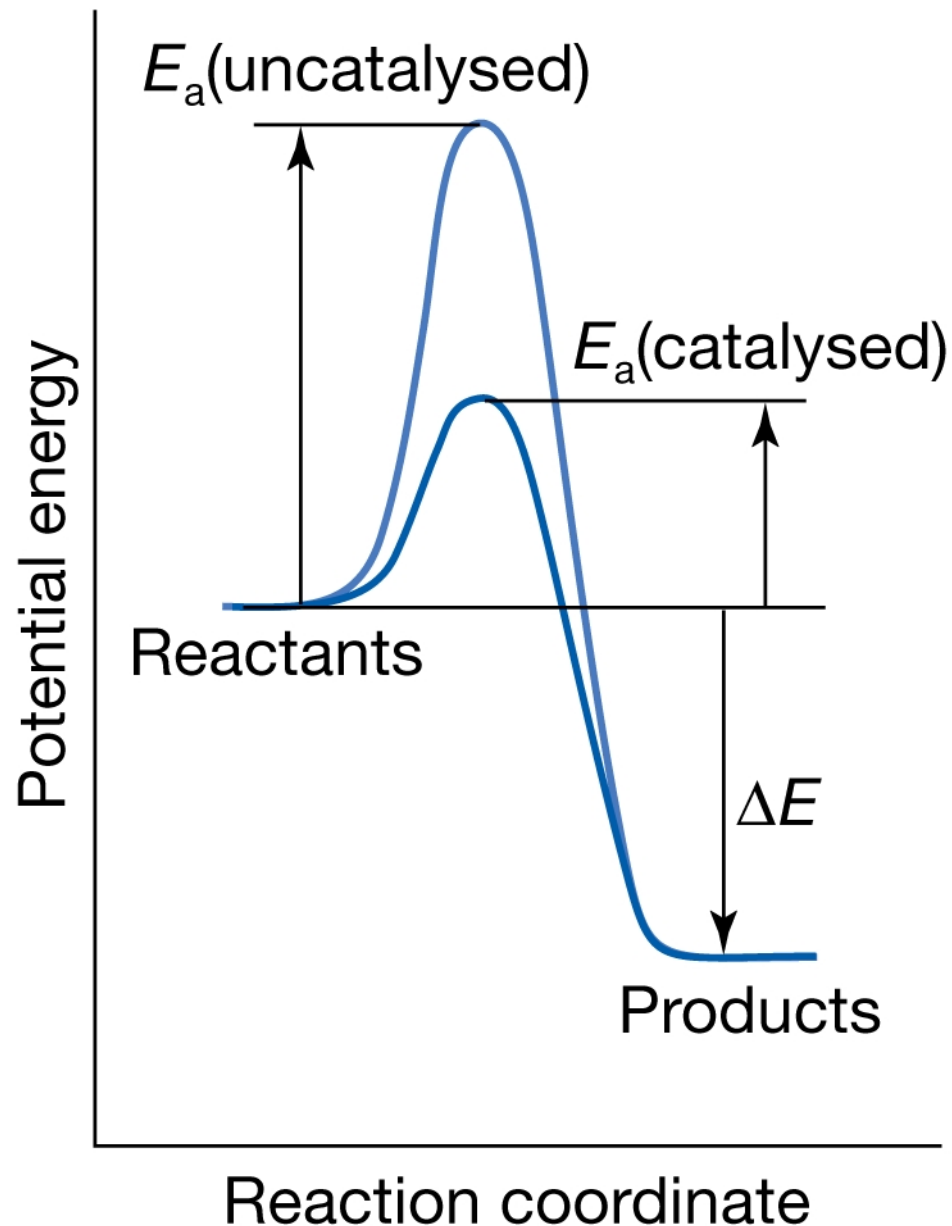


(c)

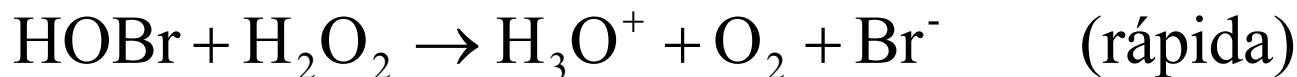
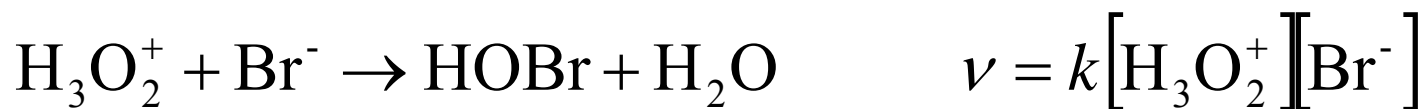
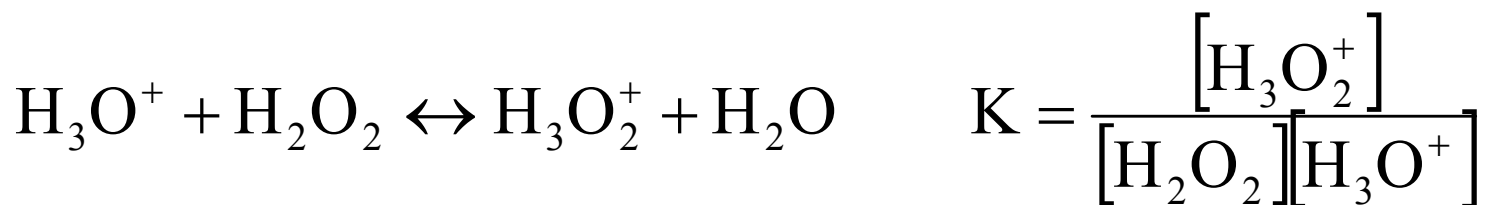
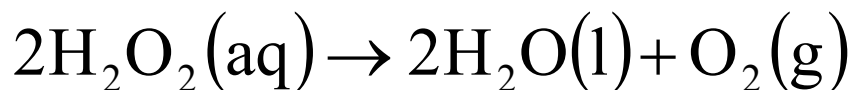
Catálise

Um caminho de reação com energia de ativação menor

Homogênea ou heterogênea



Catálise homogênea



$$\frac{d[\text{O}_2]}{dt} = k_{\text{ef}}[\text{H}_2\text{O}_2][\text{H}_3\text{O}^+][\text{Br}^-]$$



Catálise enzimática: Michaelis-Menten

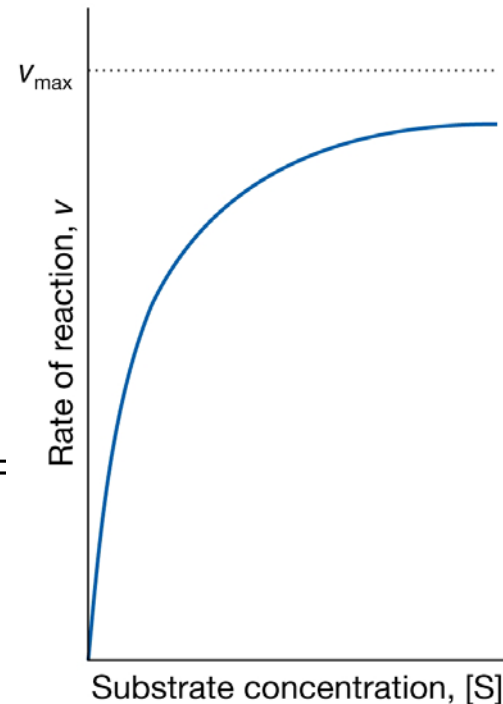


$$v = k_b [ES]$$

$$\frac{d[ES]}{dt} = k_a [E][S] - k'_a [ES] - k_b [ES] =$$

$$[ES] = \left(\frac{k_a}{k'_a + k_b} \right) [E][S] = \frac{1}{K_M} [E][S]$$

$$[ES] = \frac{[E]_0}{1 + \left(\frac{k'_a + k_b}{k_a} \right) \frac{1}{[S]_0}}$$



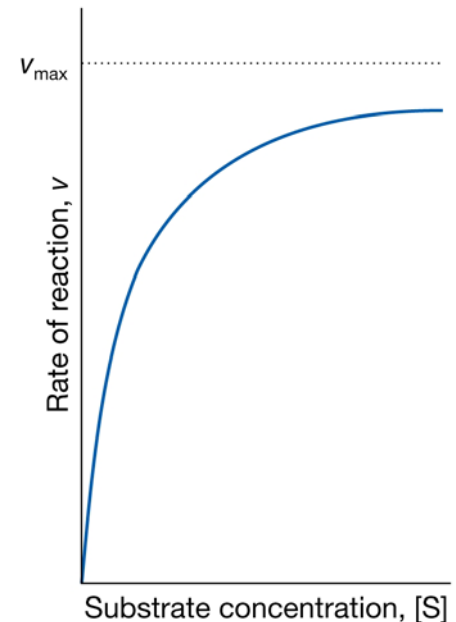
$$v = \frac{k_b [E]_0}{1 + \left(\frac{k'_a + k_b}{k_a} \right) \frac{1}{[S]_0}}$$

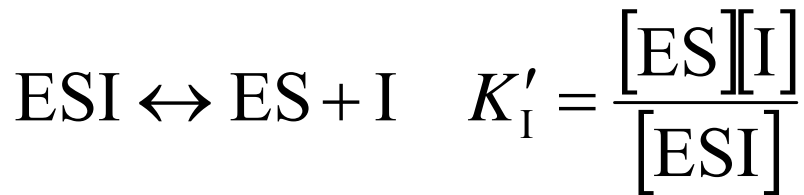
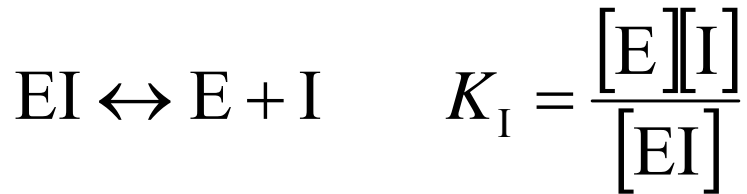
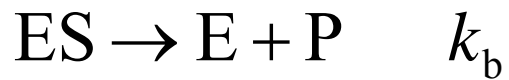
$$se[S]_o \ll K_M : v = \frac{k_a k_b}{k'_a + k_b} [S]_0 [E]_0$$

$$se[S]_o \gg K_M : v = v_{\text{máx}} = k_b [E]_0$$

$$v = \frac{v_{\text{máx}}}{1 + K_M / [S]_0}$$

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

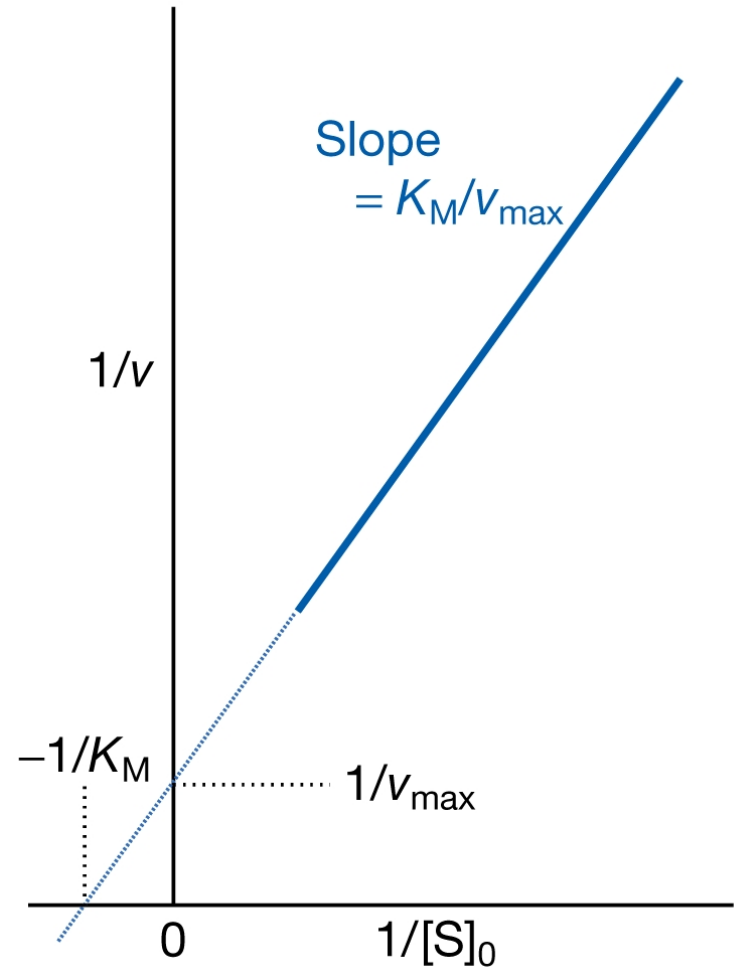




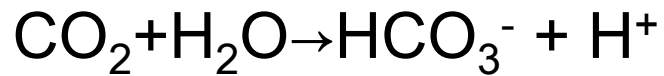
$$v = \frac{v_{\text{máx}}}{\alpha' + \alpha K_M / [S]_0}$$

$$\frac{1}{v} = \frac{\alpha'}{v_{\text{máx}}} + \left(\frac{\alpha K_M}{v_{\text{máx}}} \right) \frac{1}{[S]_0}$$

Gráfico de Lineweaver-Burk

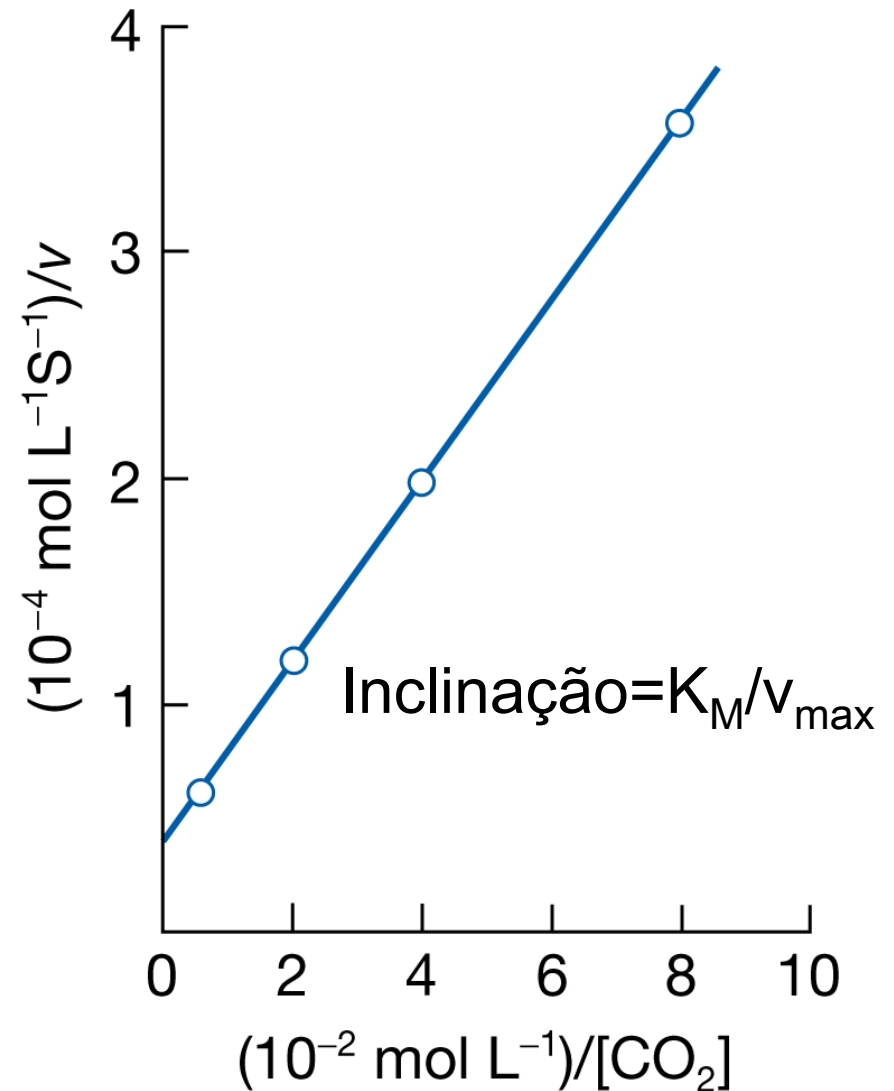


Eficiência da anidrase carbônica (hidrata CO_2 no sangue)



pH = 7,1 T = 273,5K

| $[\text{CO}_2] / \text{mmol/L}^{-1}$ | $v / \text{mol L}^{-1} \text{s}^{-1}$ |
|--------------------------------------|---------------------------------------|
| 1,25 | $2,78 \cdot 10^{-5}$ |
| 2,5 | $5,00 \cdot 10^{-5}$ |
| 5 | $8,33 \cdot 10^{-5}$ |
| 20 | $1,67 \cdot 10^{-4}$ |



$$[E]_0 = [E] + [EI] + [ES] + [ESI]$$

Inibição enzimática

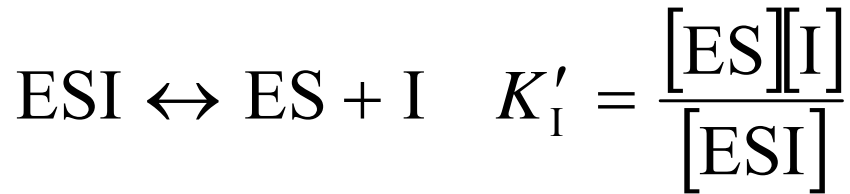
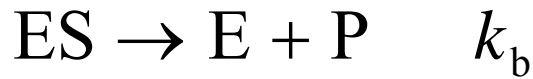
$$\alpha = 1 + \frac{I}{K_I} \quad \text{e} \quad \alpha' = 1 + \frac{[I]}{K'_I}$$

$$[E]_0 = [E]\alpha + [ES]\alpha'$$

$$[E]_0 = \frac{K_M [ES]}{[S]_0} \alpha + [ES]\alpha' = [ES] \left(\frac{\alpha K_M}{[S]_0} + \alpha' \right)$$

$$v = k_b [ES] = \frac{k_b [E]_0}{\frac{\alpha K_M}{[S]_0} + \alpha'}$$

- Inibição enzimática

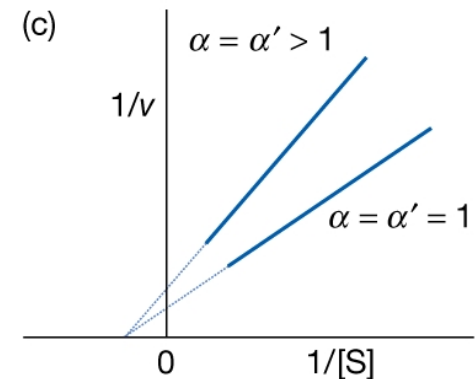
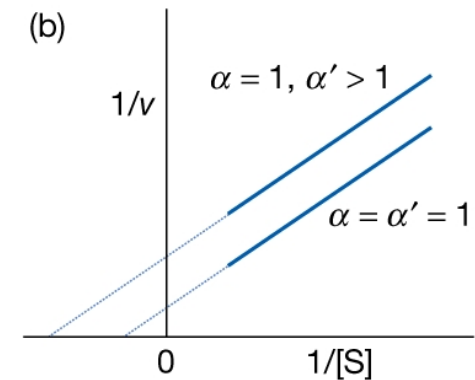
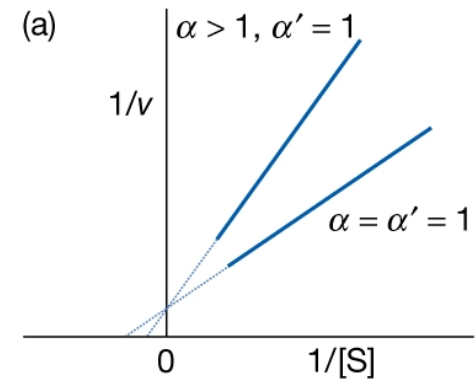


$$v = \frac{v_{\text{máx}}}{\alpha' + \alpha K_M / [S]_0}$$

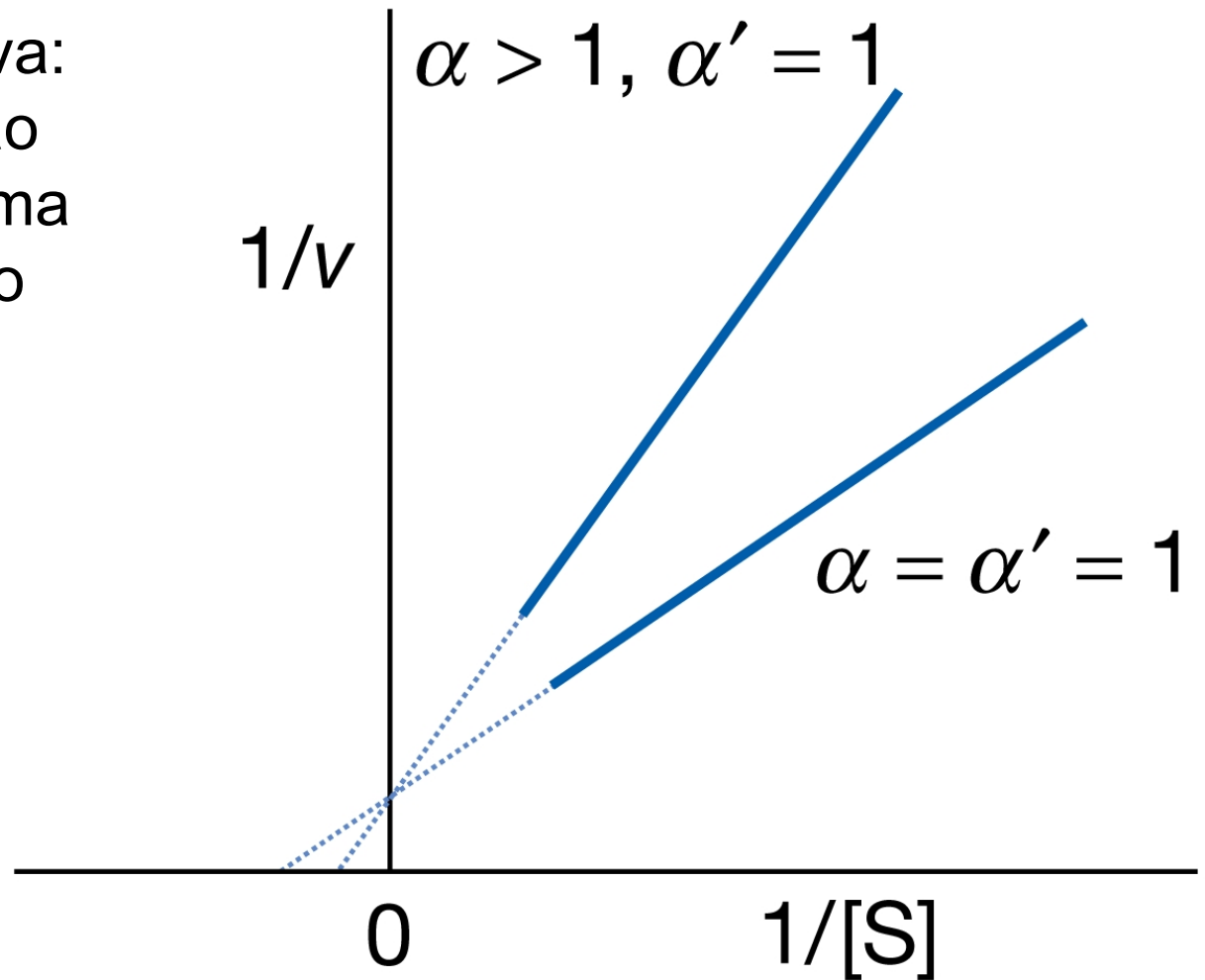
$$\text{onde : } \alpha = 1 + [I] / k_I$$

$$\text{e : } \alpha' = 1 + [I] / k'_I$$

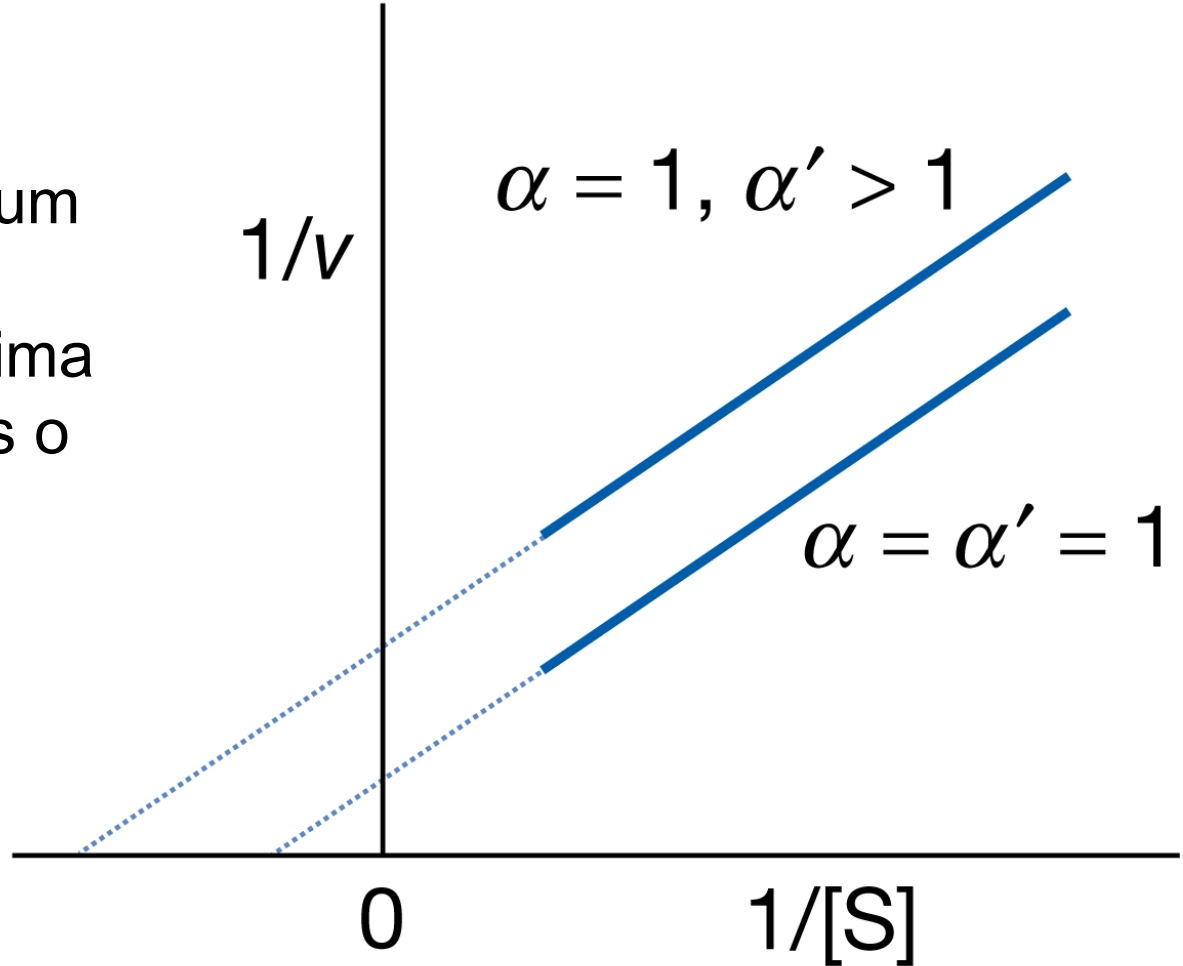
$$\frac{1}{v} = \frac{\alpha'}{v_{\text{máx}}} + \left(\frac{\alpha K_M}{v_{\text{máx}}} \right) \frac{1}{[S]_0}$$



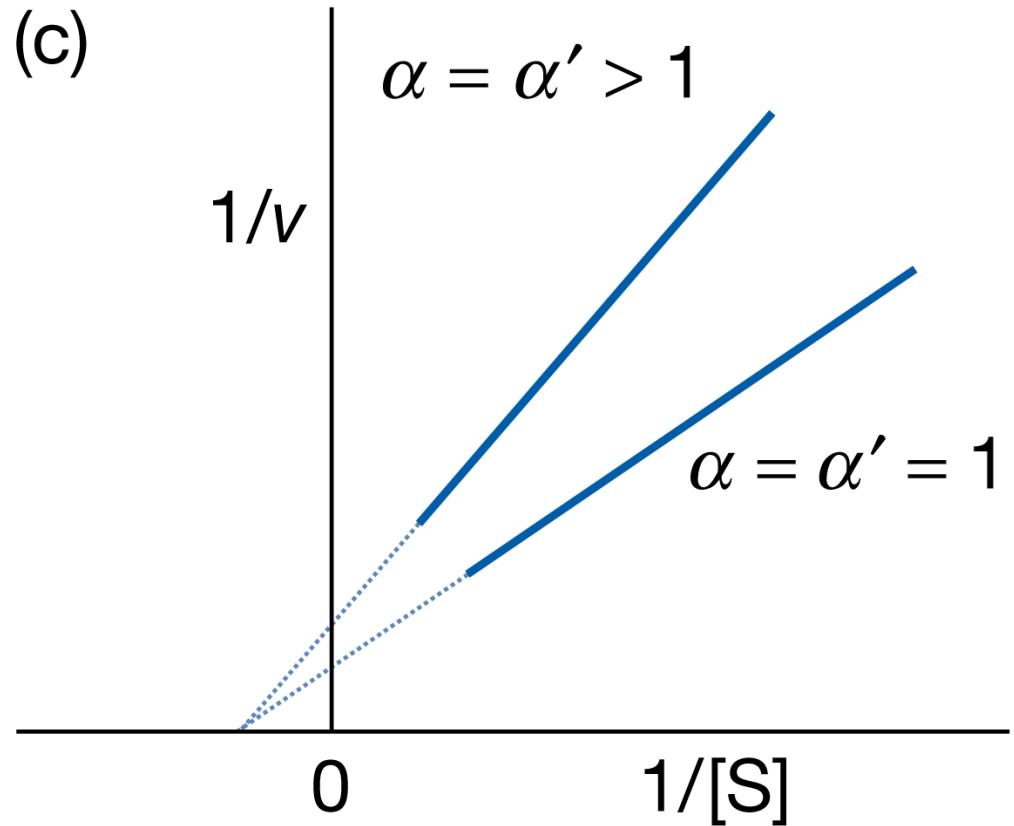
Inibição competitiva:
o inibidor se liga ao
sítio ativo da enzima
e impede a ligação
do substrato



Inibição sem competição: o inibidor se liga a um sítio afastado do sítio ativo da enzima mas apenas após o substrato estar presente



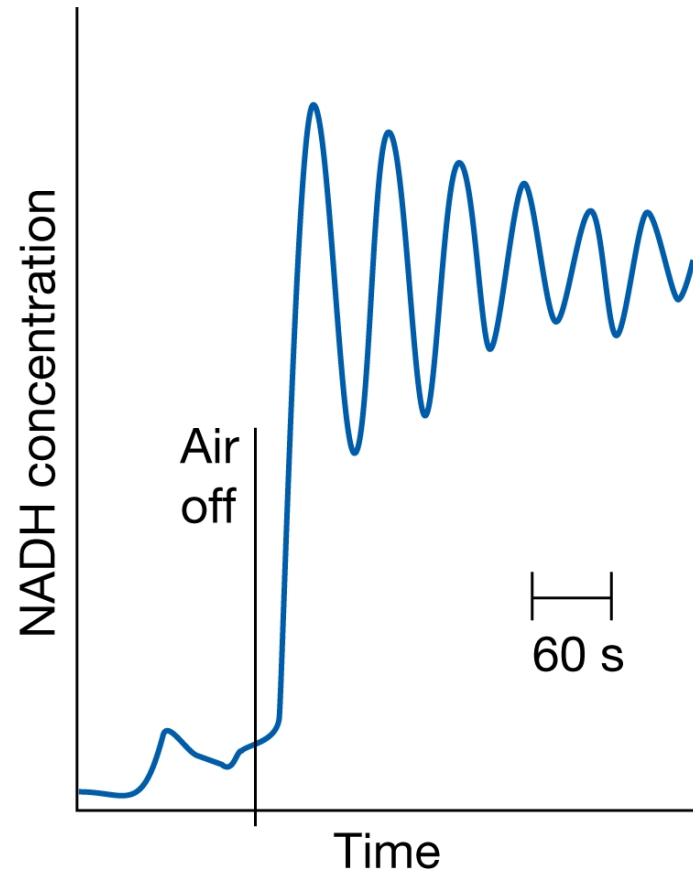
Inibição não-competitiva ou mista: o inibidor se liga a um sítio distinto do sítio ativo da enzima e a sua presença reduz a capacidade do substrato em ligar-se ao sítio ativo



Reações oscilantes

Concentração de NADH em células de levedura devido a:

- i) Inibição da fosfofrutoquinase por altas concentrações de ATP
- ii) Ativação da fosfofrutoquinase por baixas concentrações de ATP



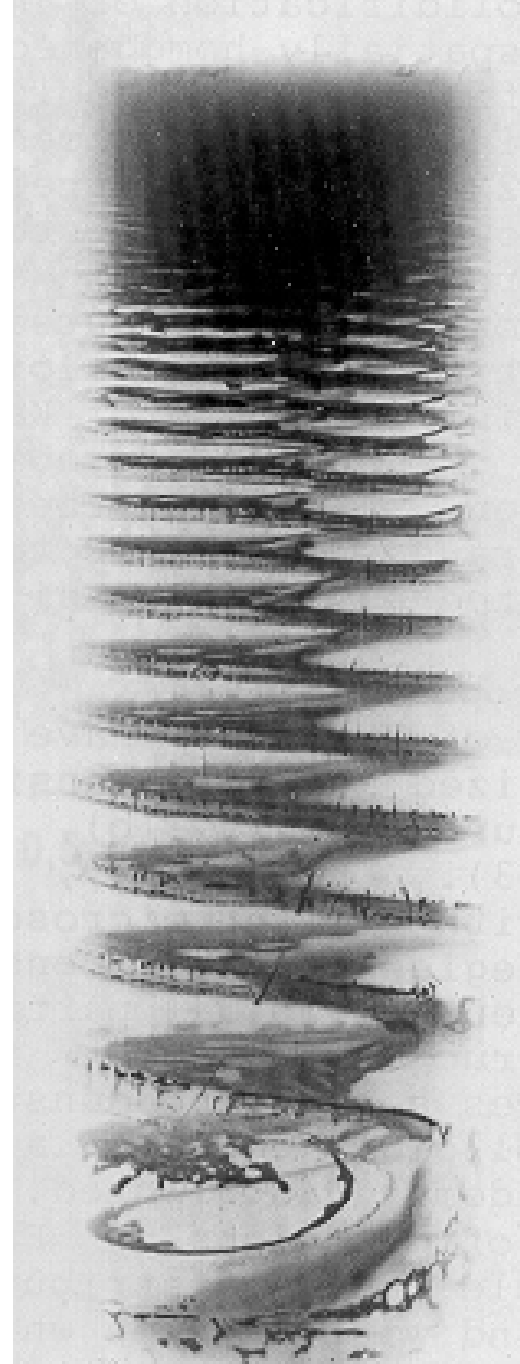
Os problemas clássicos

- Reações-relógio
- Anéis de Liesegang
- Estruturas convectivas (células de Bénard)
- Auto-catálise (Lotka e Volterra)

Chemical waves in the Belousov-Zhabotinsky reaction: Picture Gallery
Department of Biophysics, Otto-von-Guericke University Magdeburg

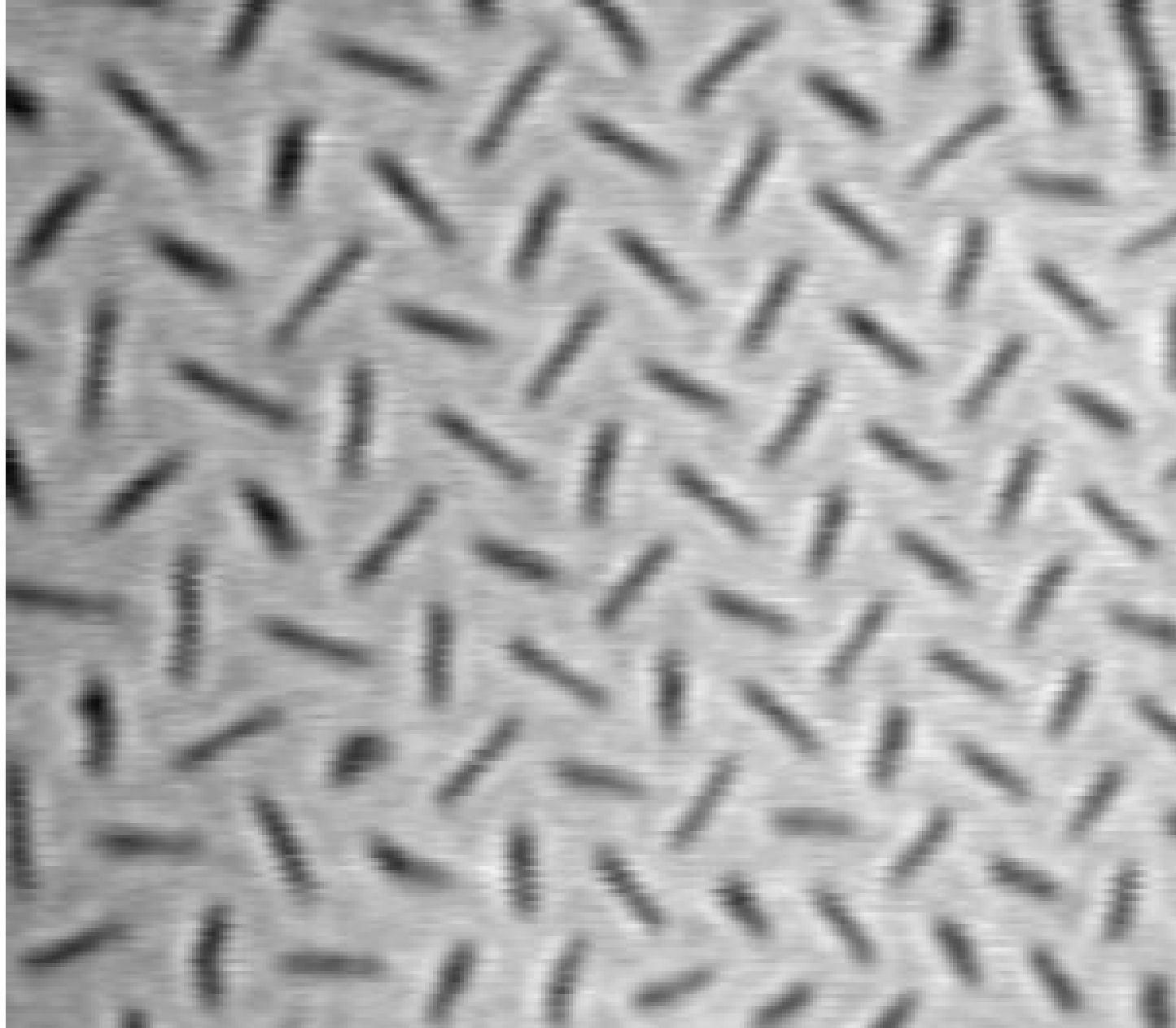
Muitas situações- problema

- Oscilações em reações químicas, explosões
- Formação de franjas, bordas, raias..., em filmes e revestimentos
- Auto-ordenamento
- Fenômenos de *stick-slip*
- Irreprodutibilidades em processo



Precipitação helicoidal de PbI_2 em agar (banda de Liesegang)

“Alfinetes”
formados na
reação de azul
de metileno com
oxigênio

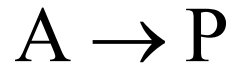
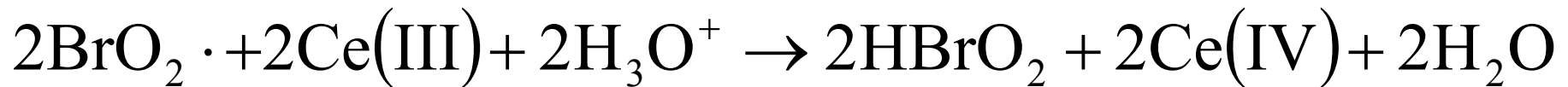


<http://www.uni-magdeburg.de/abp/picturegallery.htm>

Auto-catálise

reação de Belousov-Zhabotinskii: bromato de potássio + ácido malônico + sal de cério (IV)

$$v = k[A][P]$$



$$v = -d[A]/dt$$

$$[A] = [A]_0 - x, [P] = [P]_0 + x$$

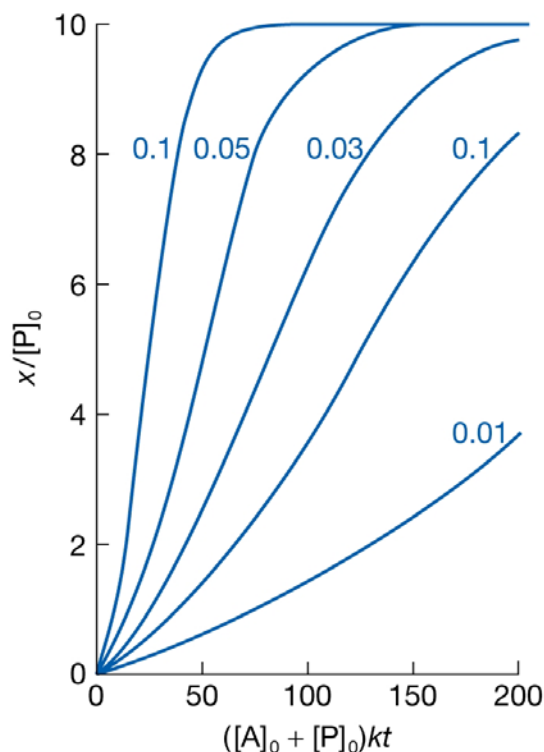
$$\frac{dx}{dt} = k([A]_0 - x)([P]_0 + x)$$

$$\frac{1}{([A]_0 - x)([P]_0 + x)} = \frac{1}{[A]_0 + [P]_0} \left(\frac{1}{[A]_0 - x} + \frac{1}{[P]_0 + x} \right)$$

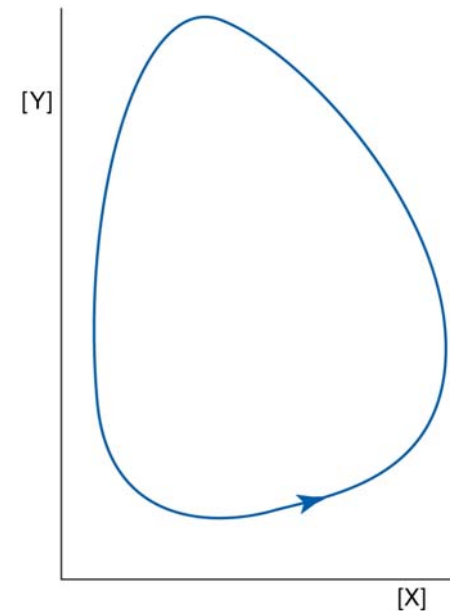
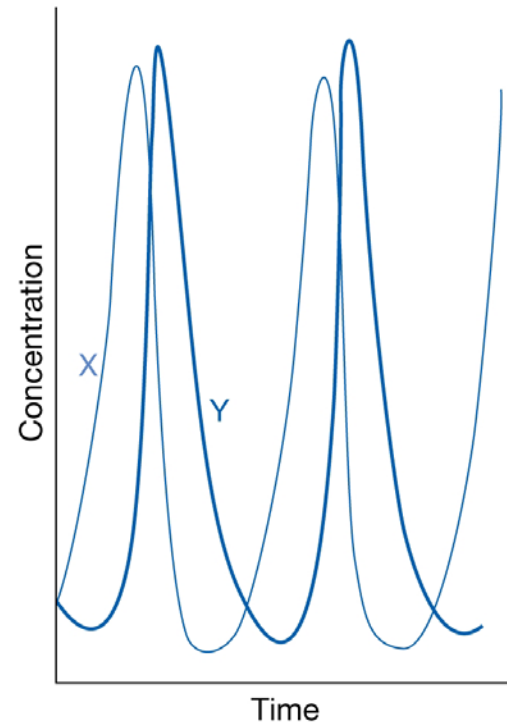
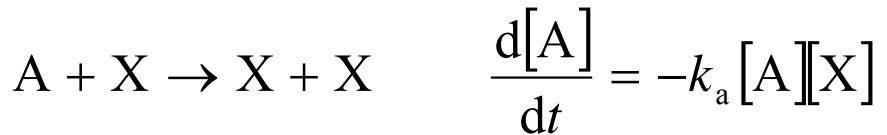
$$\frac{1}{[A]_0 + [P]_0} \ln \left(\frac{([P]_0 + x)[A]_0}{[P]_0([A]_0 - x)} \right) = kt$$

$$\frac{x}{[P]_0} = \frac{e^{at} - 1}{1 + be^{at}}$$

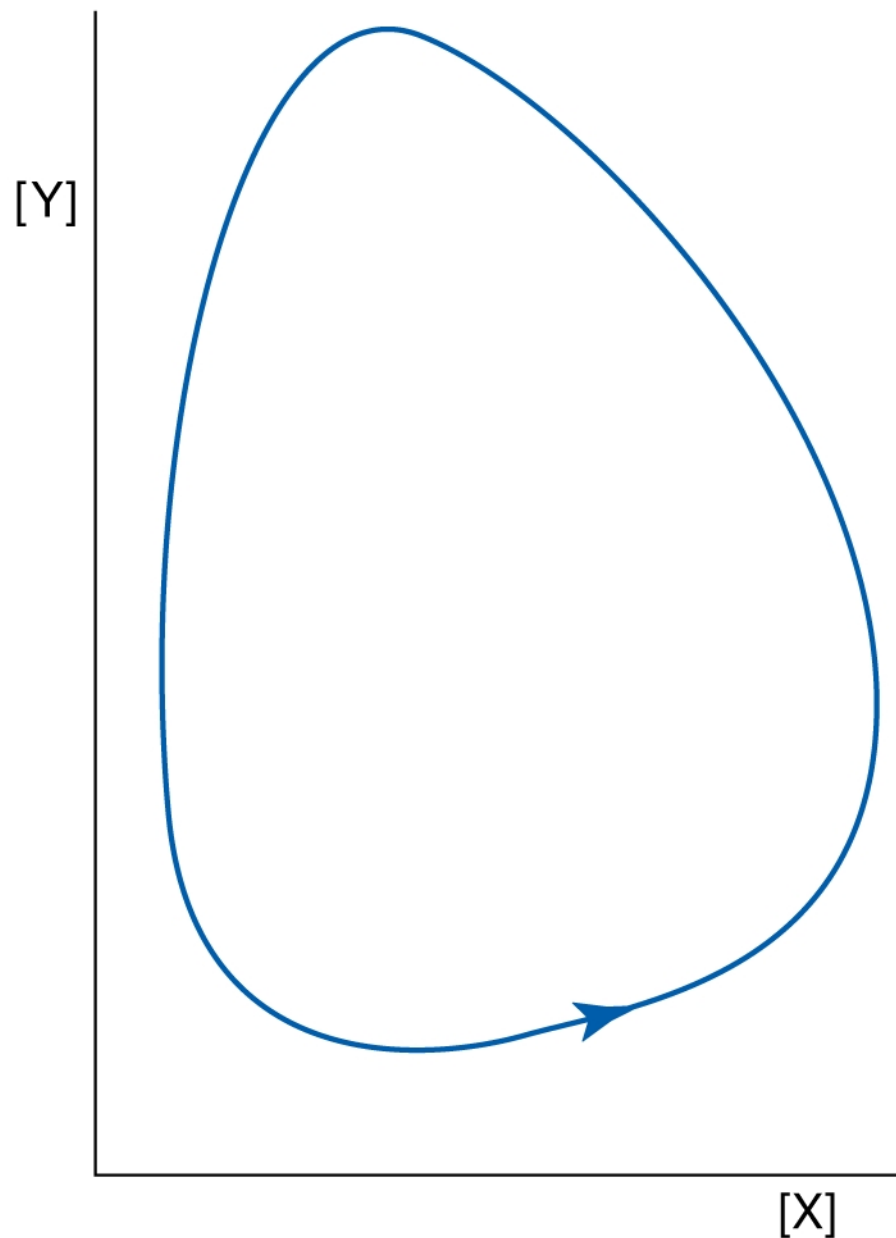
onde : $([A]_0 + [P]_0)k e b = [P]_0 / [A]_0$.



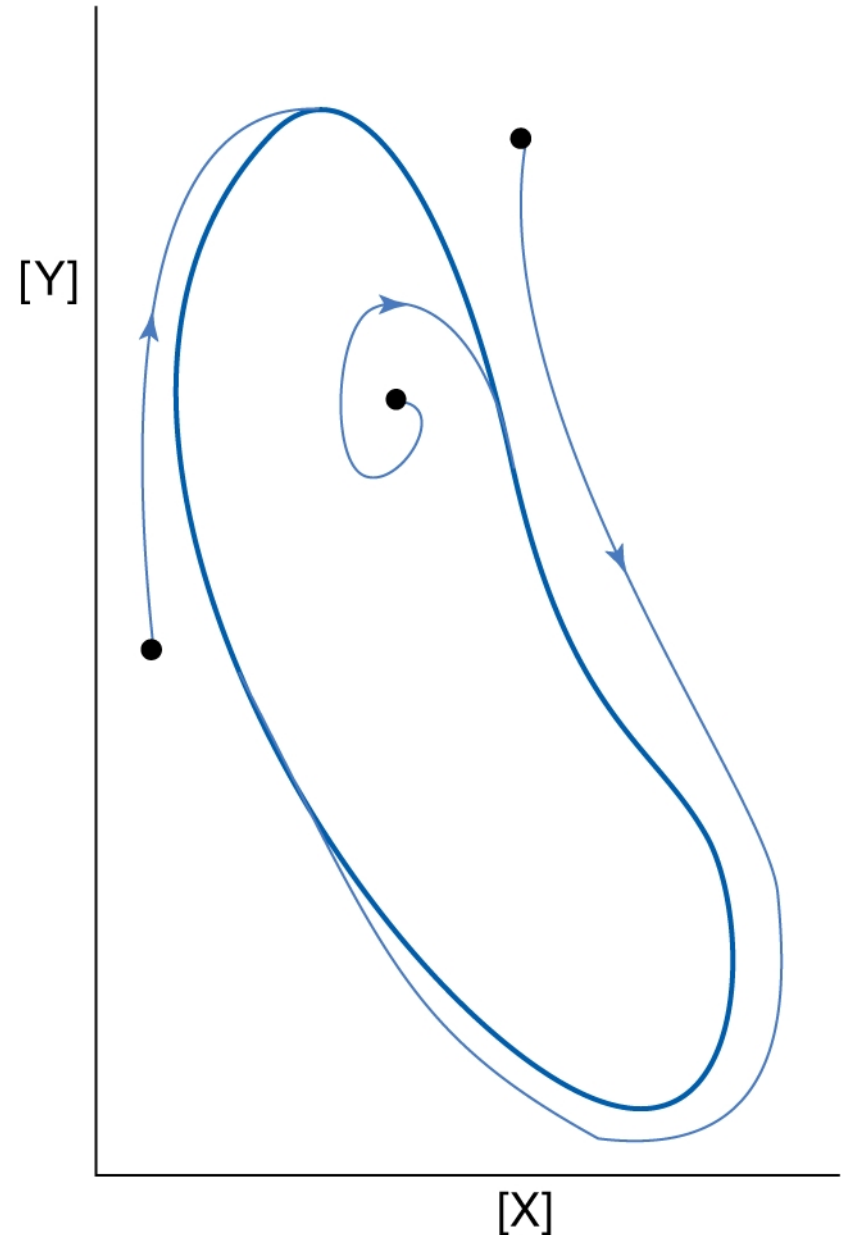
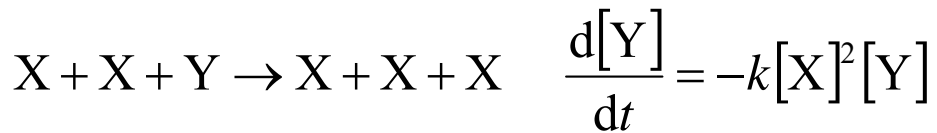
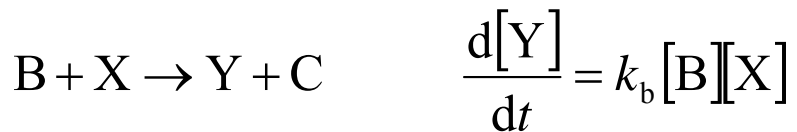
O mecanismo de Lotka-Volterra



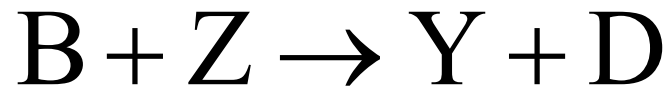
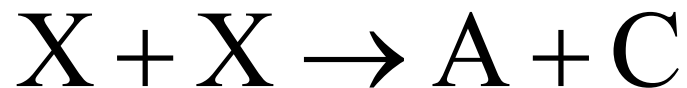
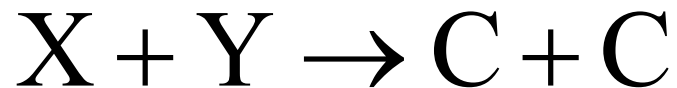
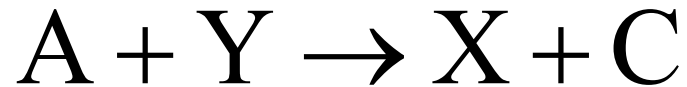
Uma representação
usada com
frequência, em
reações oscilantes



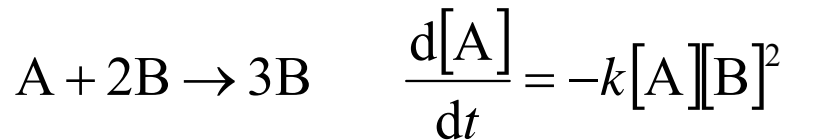
O ciclo limite do bruxelador



O oregonador



Biestabilidade: múltiplos estados estacionários com composições químicas diversas

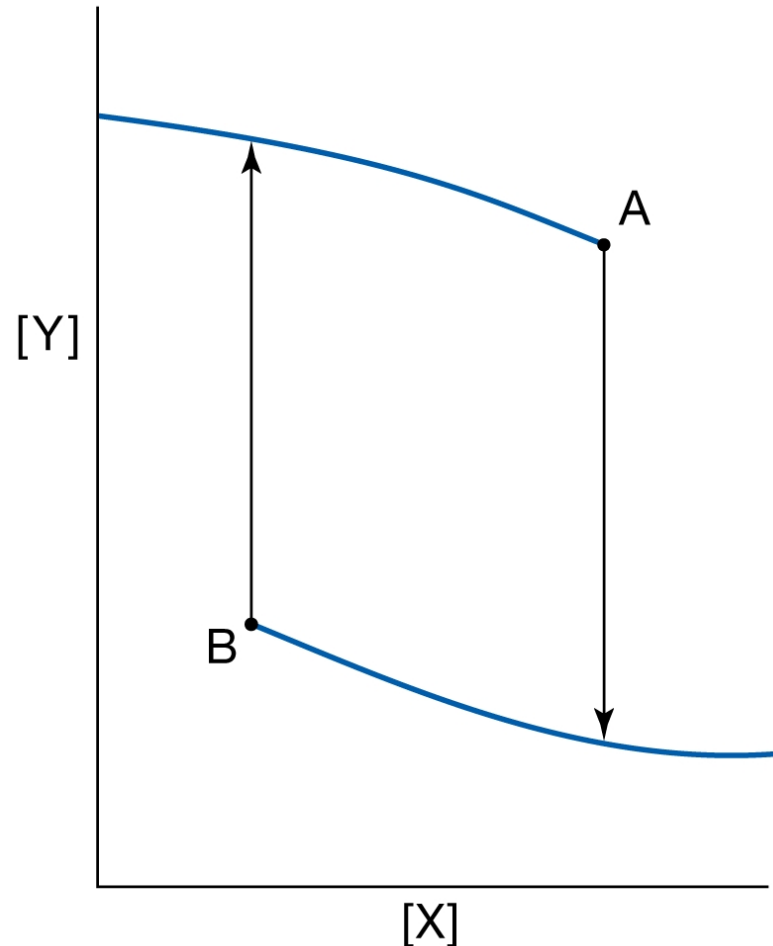


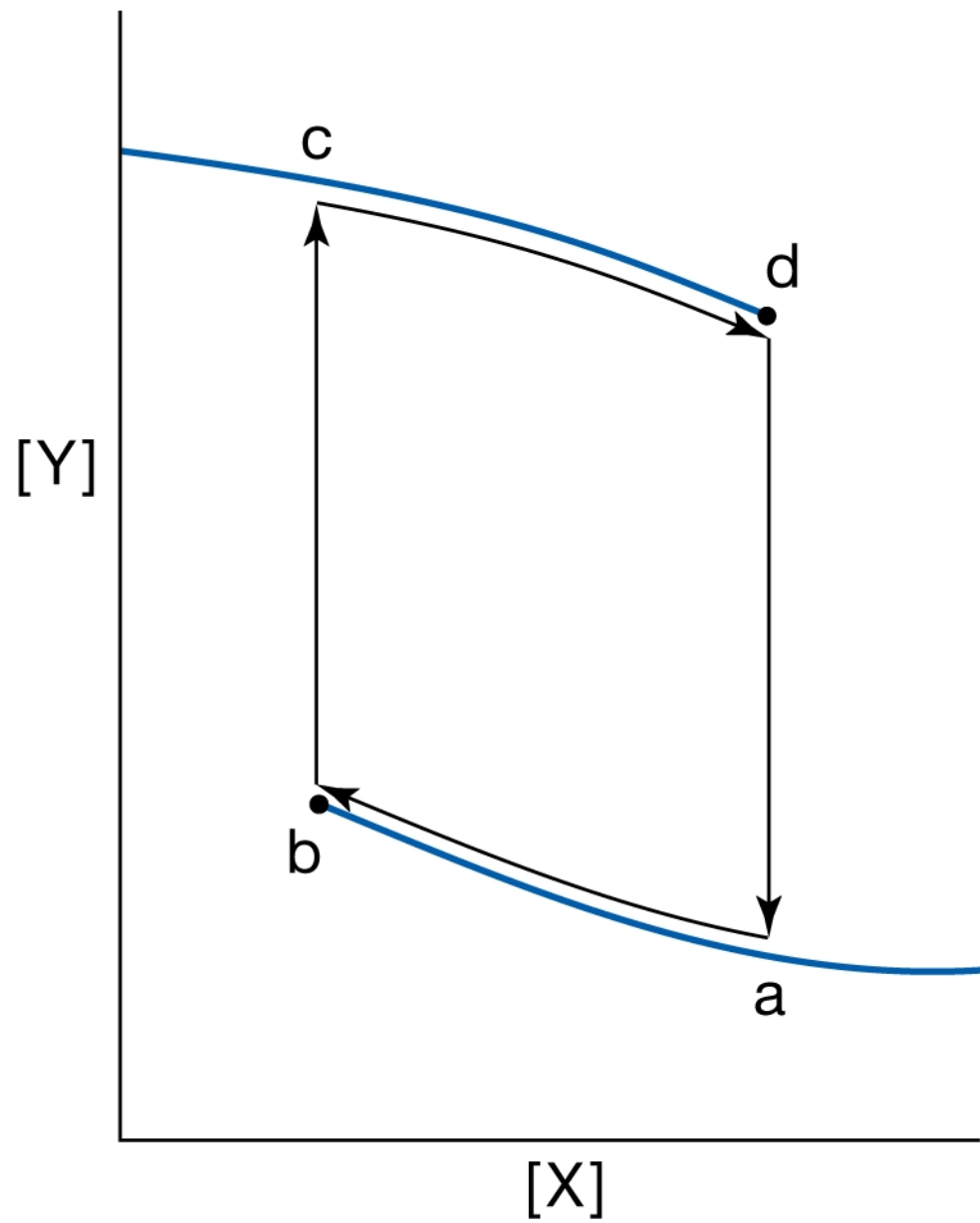
$$\frac{d[A]}{dt} = -k[A][B]^2 + k_0[A]_0 - k_0[A]$$

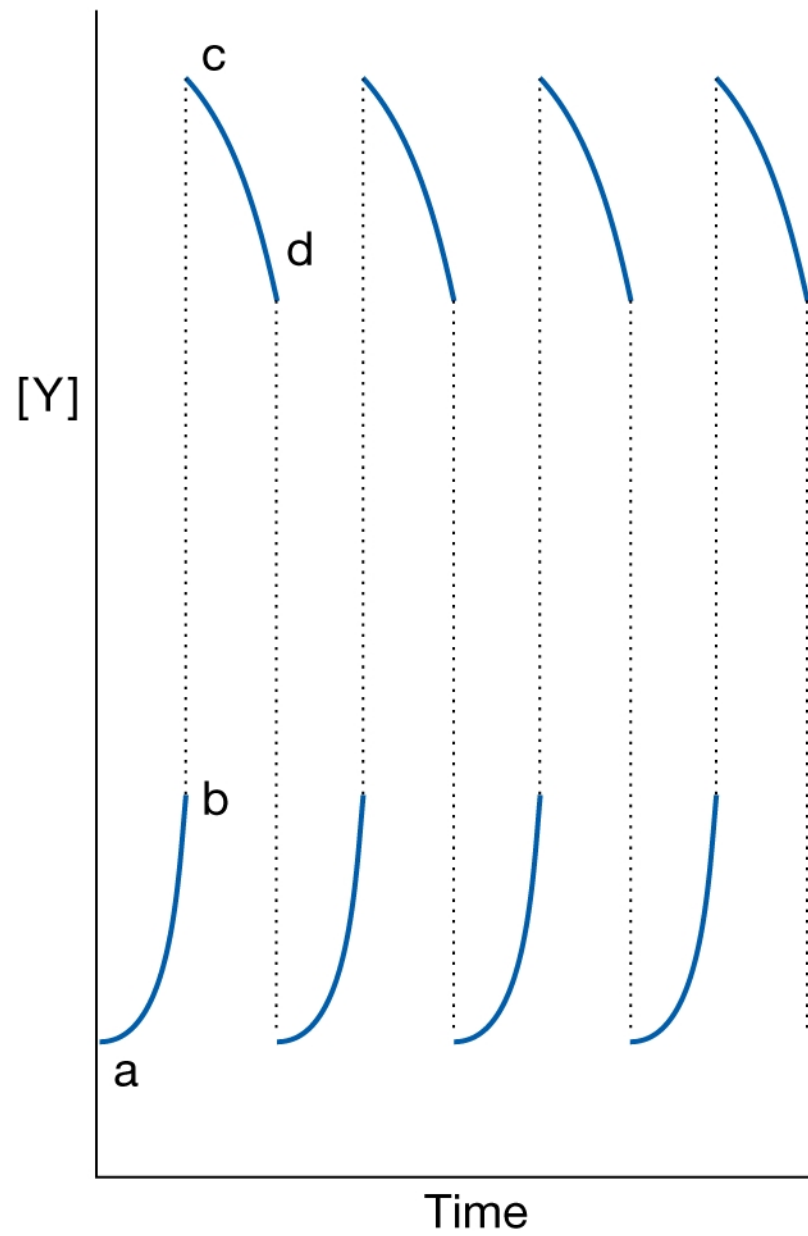
$$([A]_0 - [A])\{k_0 - k[A]([A]_0 - [A])\} = 0$$

$$k[A]^2 - k[A]_0[A] + k_0 = 0$$

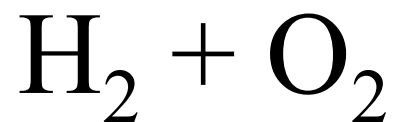
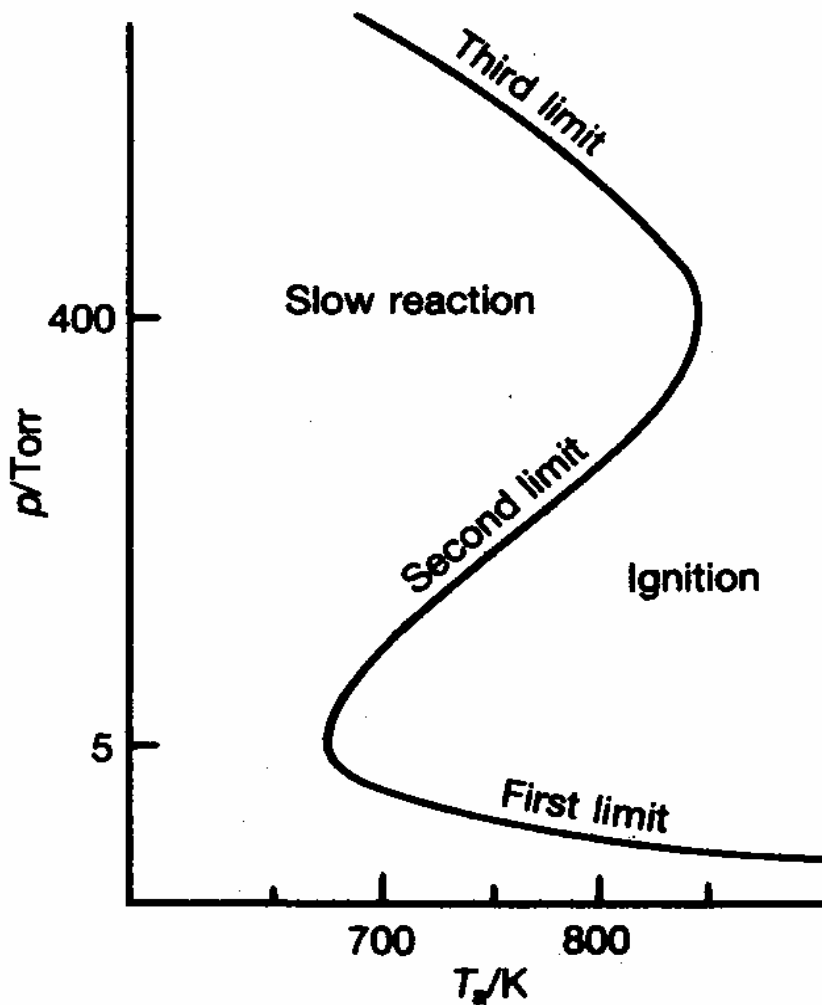
$$[A]_{ep} = \frac{1}{2}[A]_0 \pm \frac{(k[A]_0^2 - 4k_0)^{1/2}}{2k^{1/2}}$$





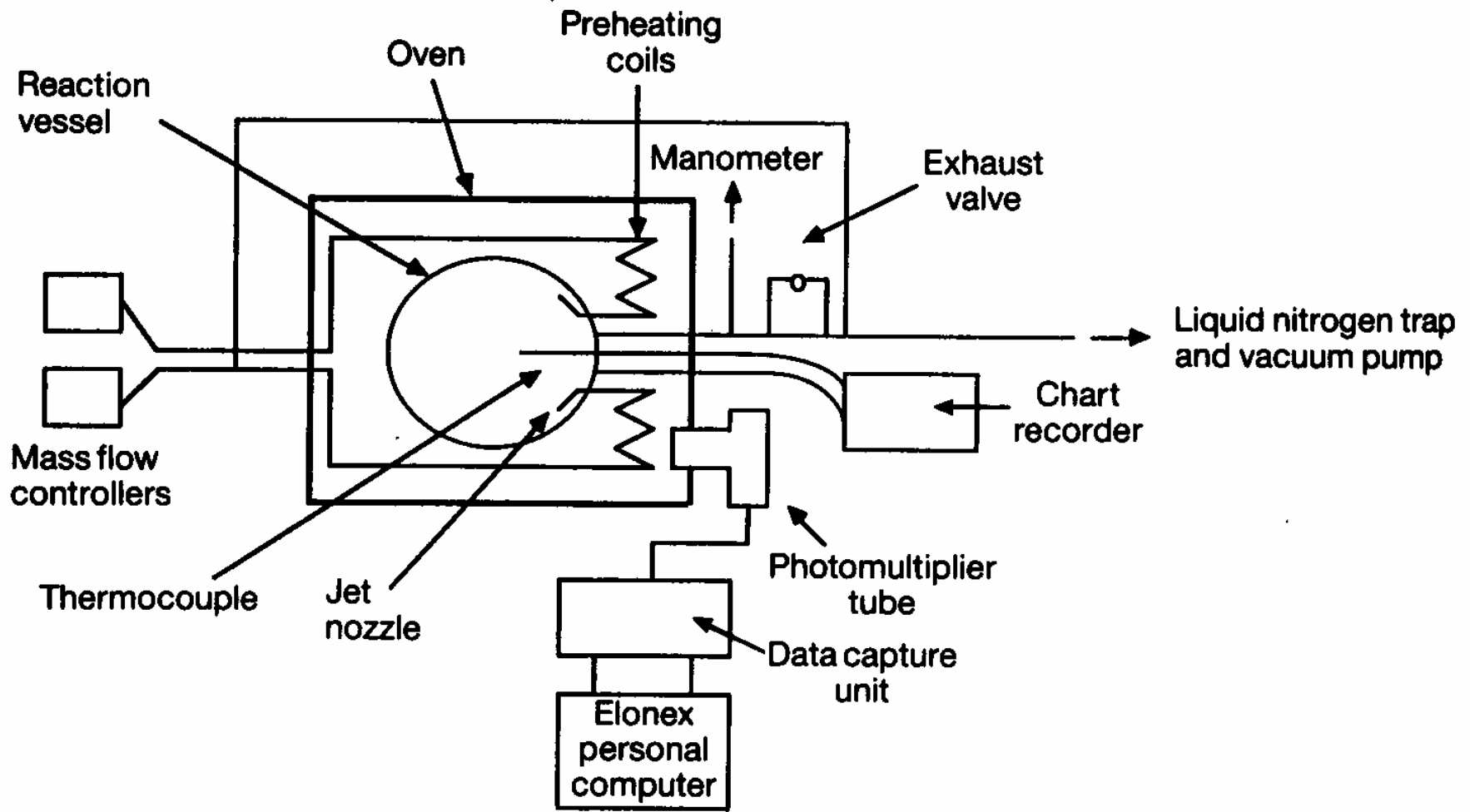


Caos

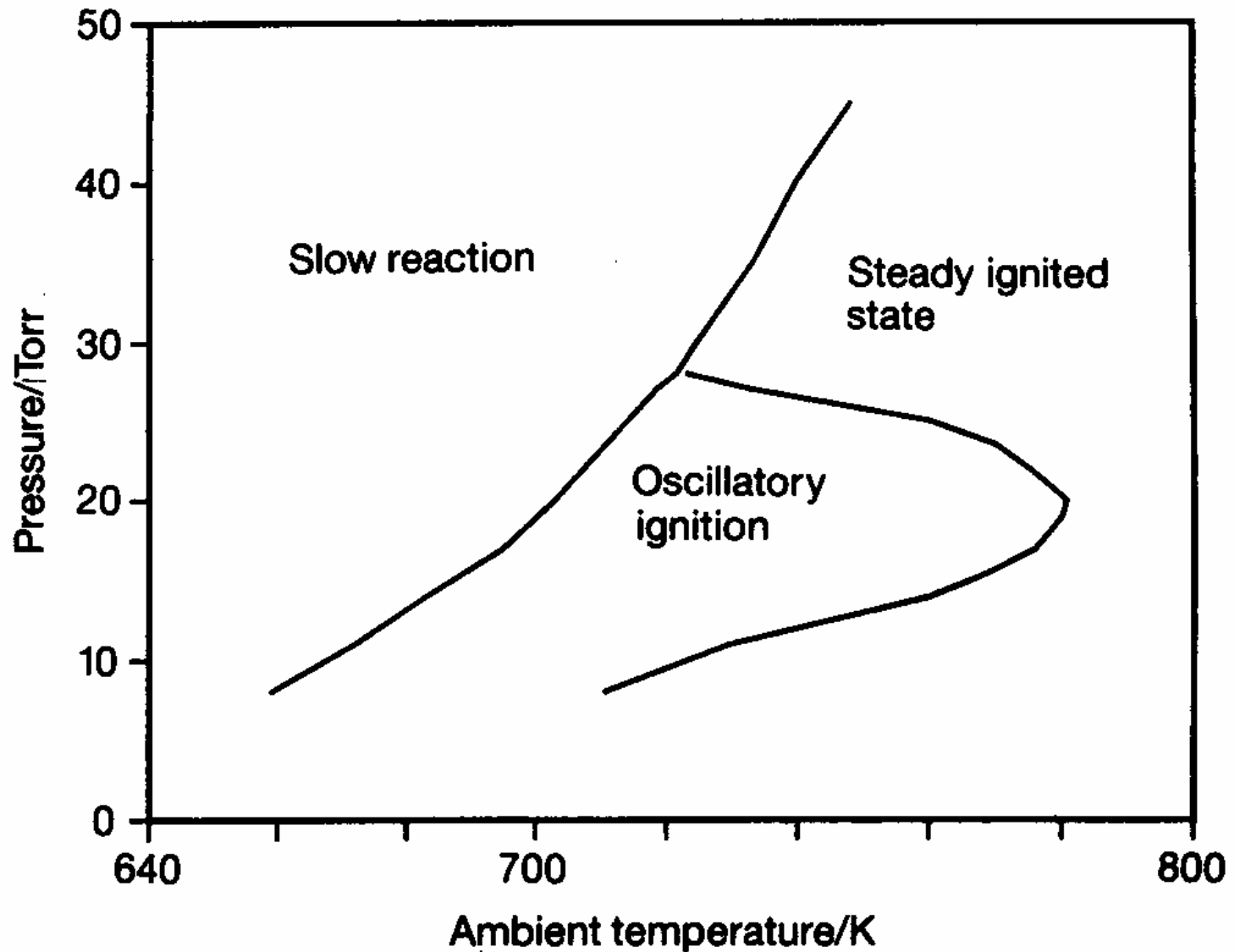


uma reação
simples, pode
provocar
explosões.
Essencial em
uma “economia
do hidrogênio”.

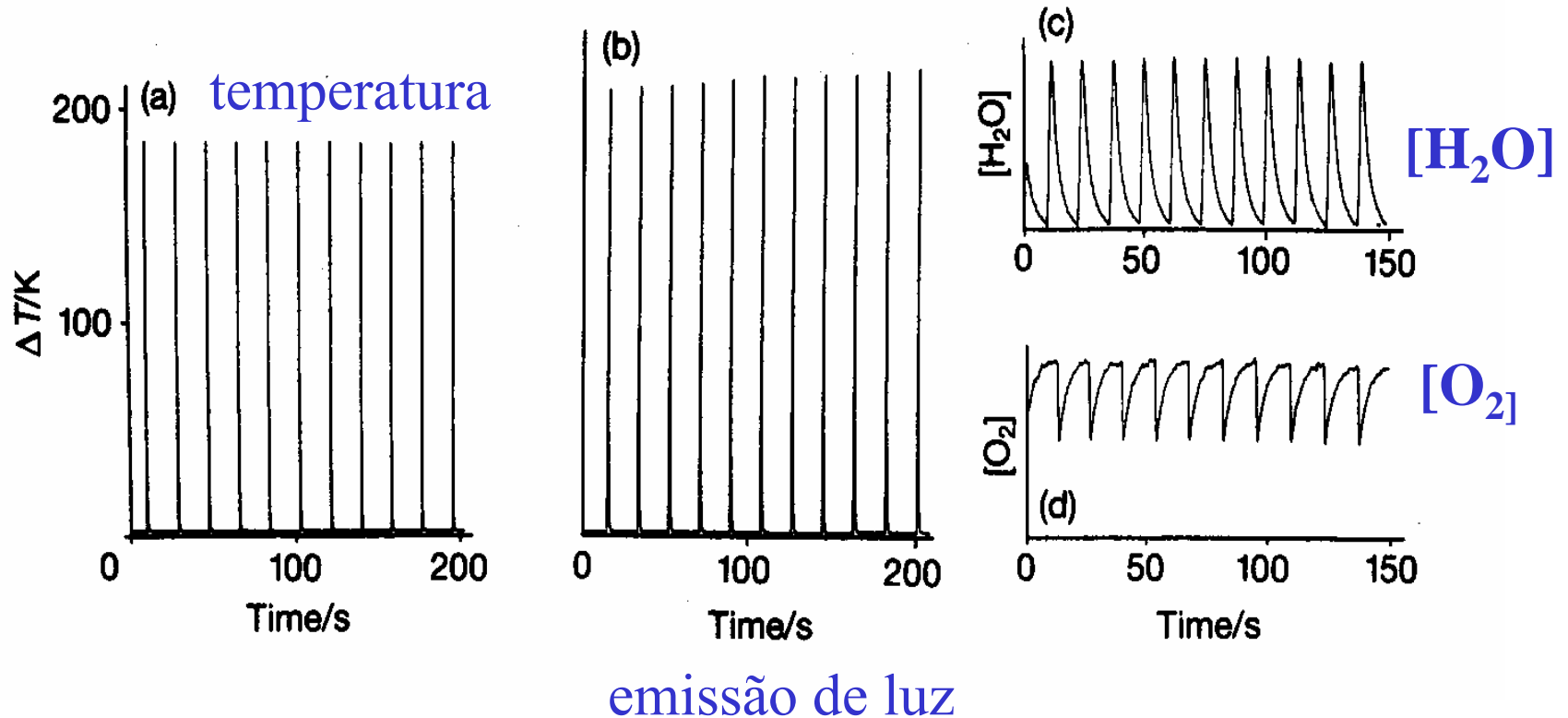
Um reator apropriado: contínuo, com mistura eficiente e controle de temperatura

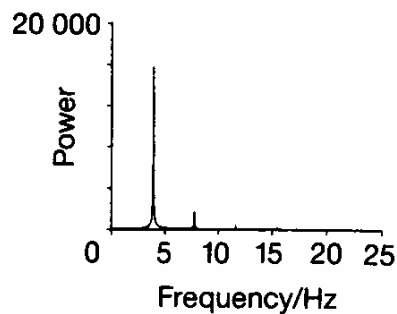
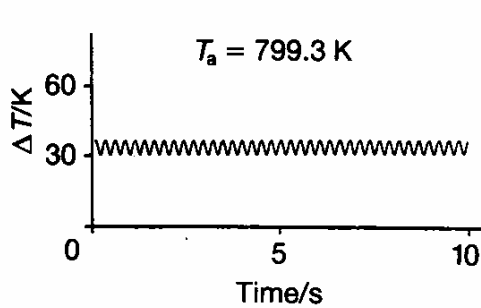
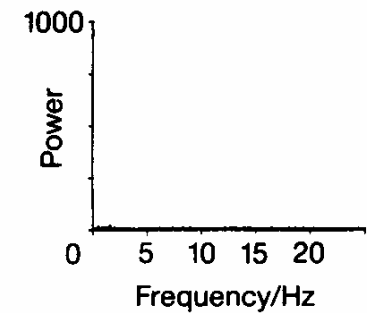
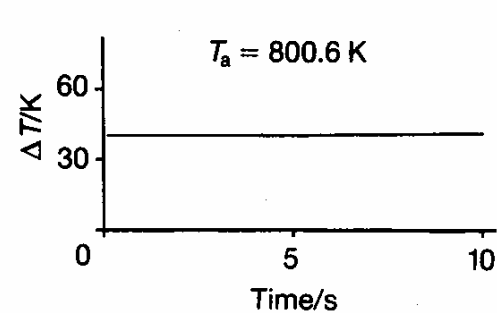
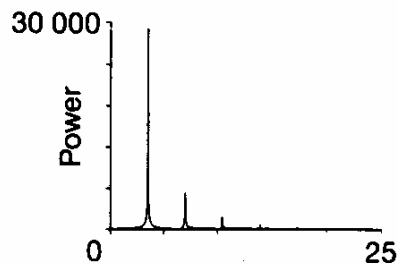
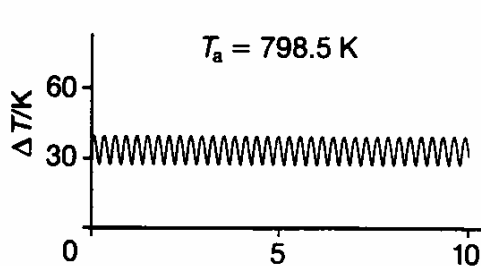
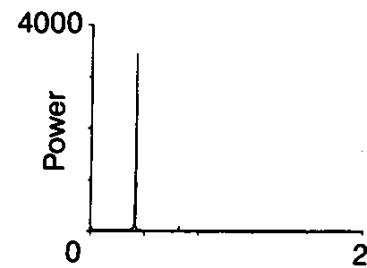
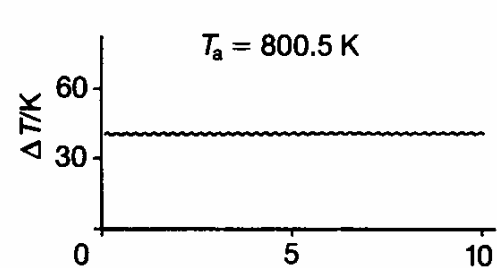
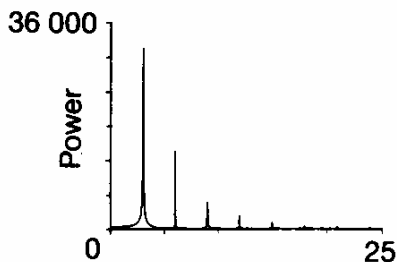
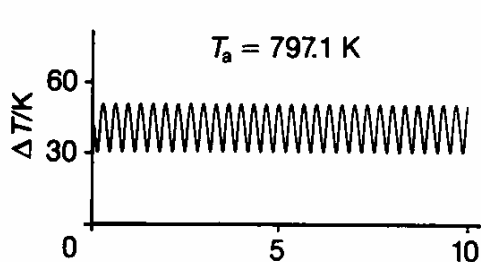
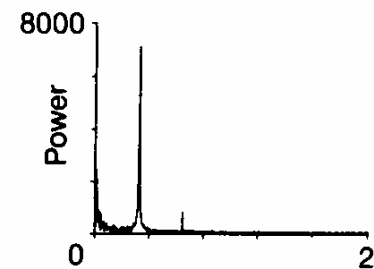
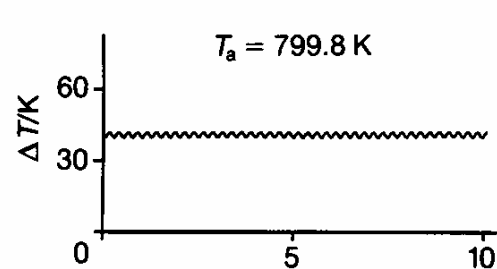
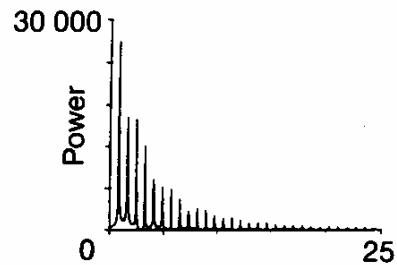
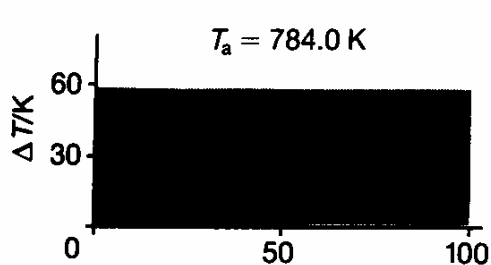


A região do segundo limite, ampliada



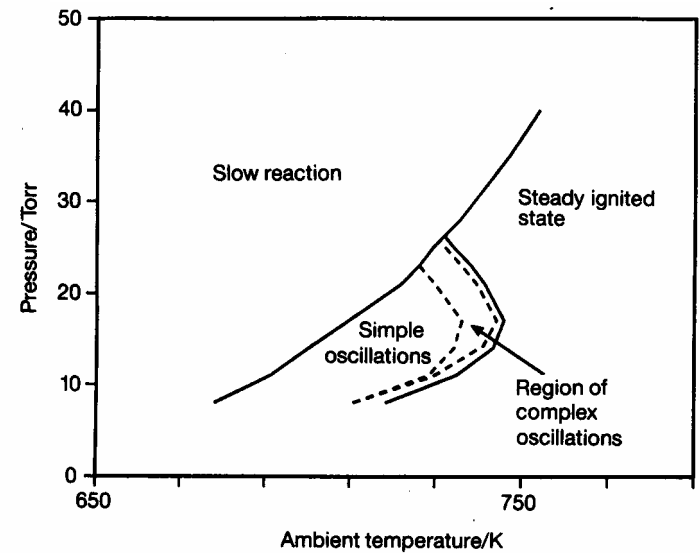
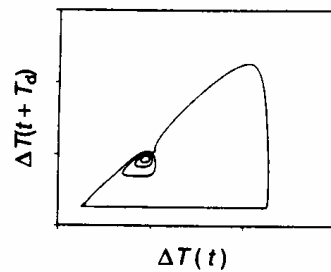
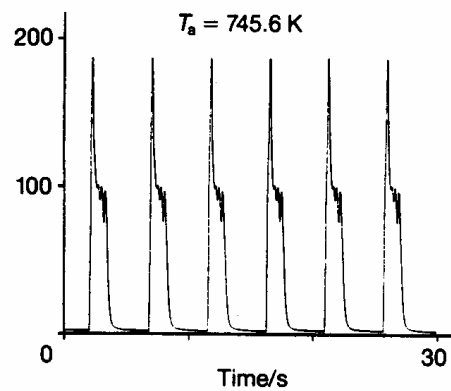
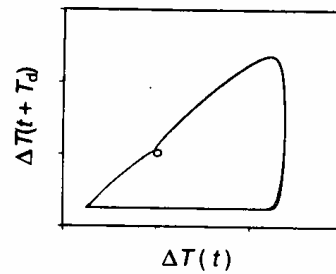
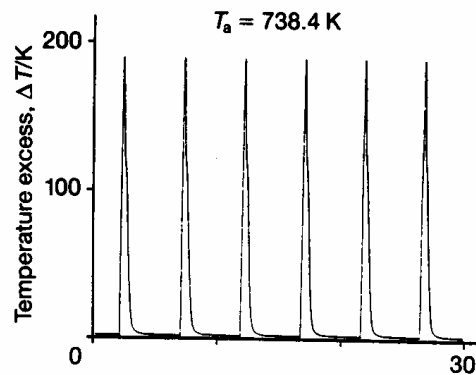
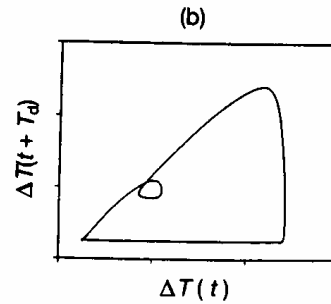
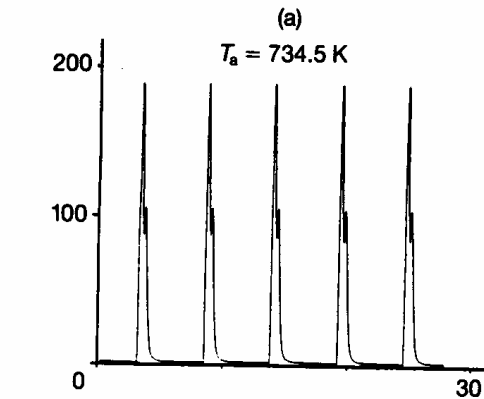
Séries temporais: concentrações, emissão de luz, calor





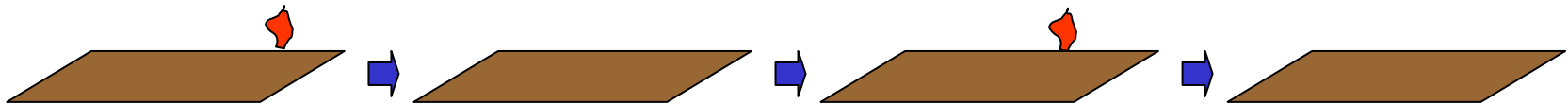
Supressão de
oscilações

Oscilações complexas



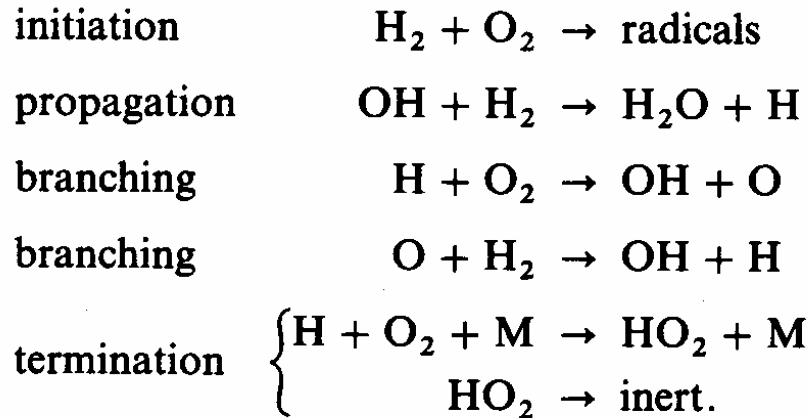
Você também pode observar isto...

- ...na queima de madeira ou carvão, em uma churrasqueira, como pontos de chama intermitente

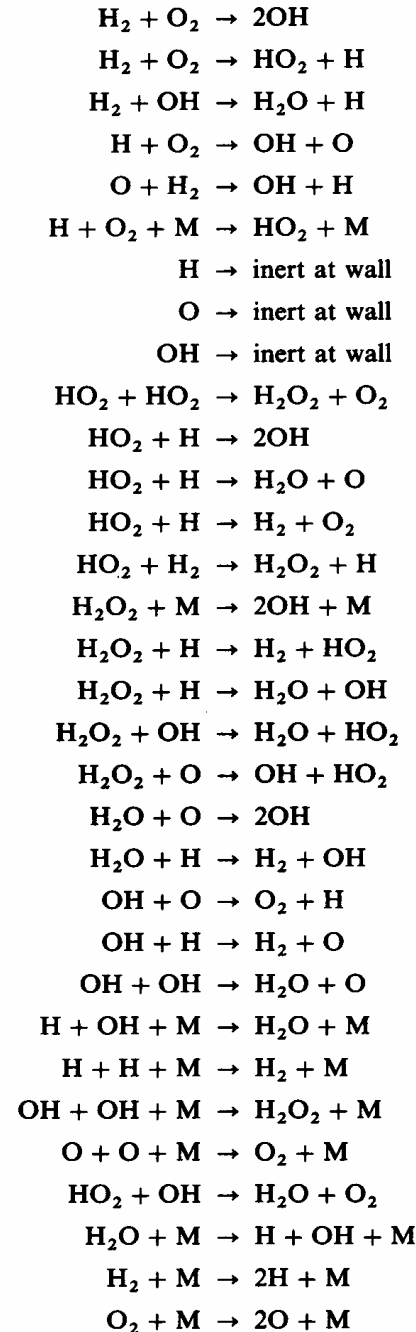


Modelagem

Um modelo simples



Oscilações complexas, aparentemente, só são descritas considerando-se a exotermicidade da reação e a realimentação do sistema através do aquecimento (exotermicidade)

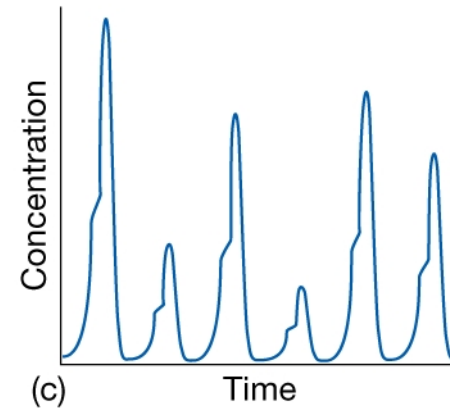
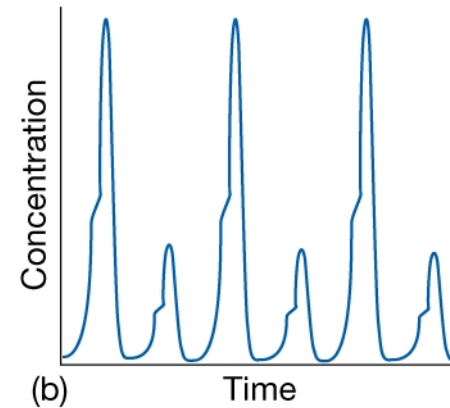
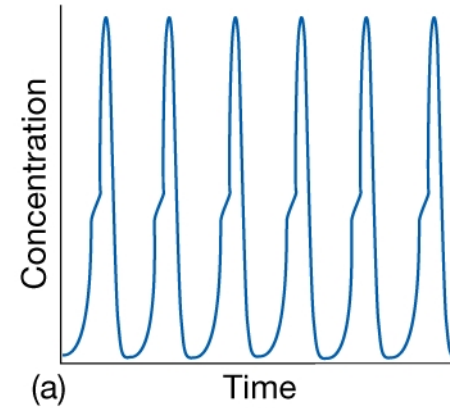


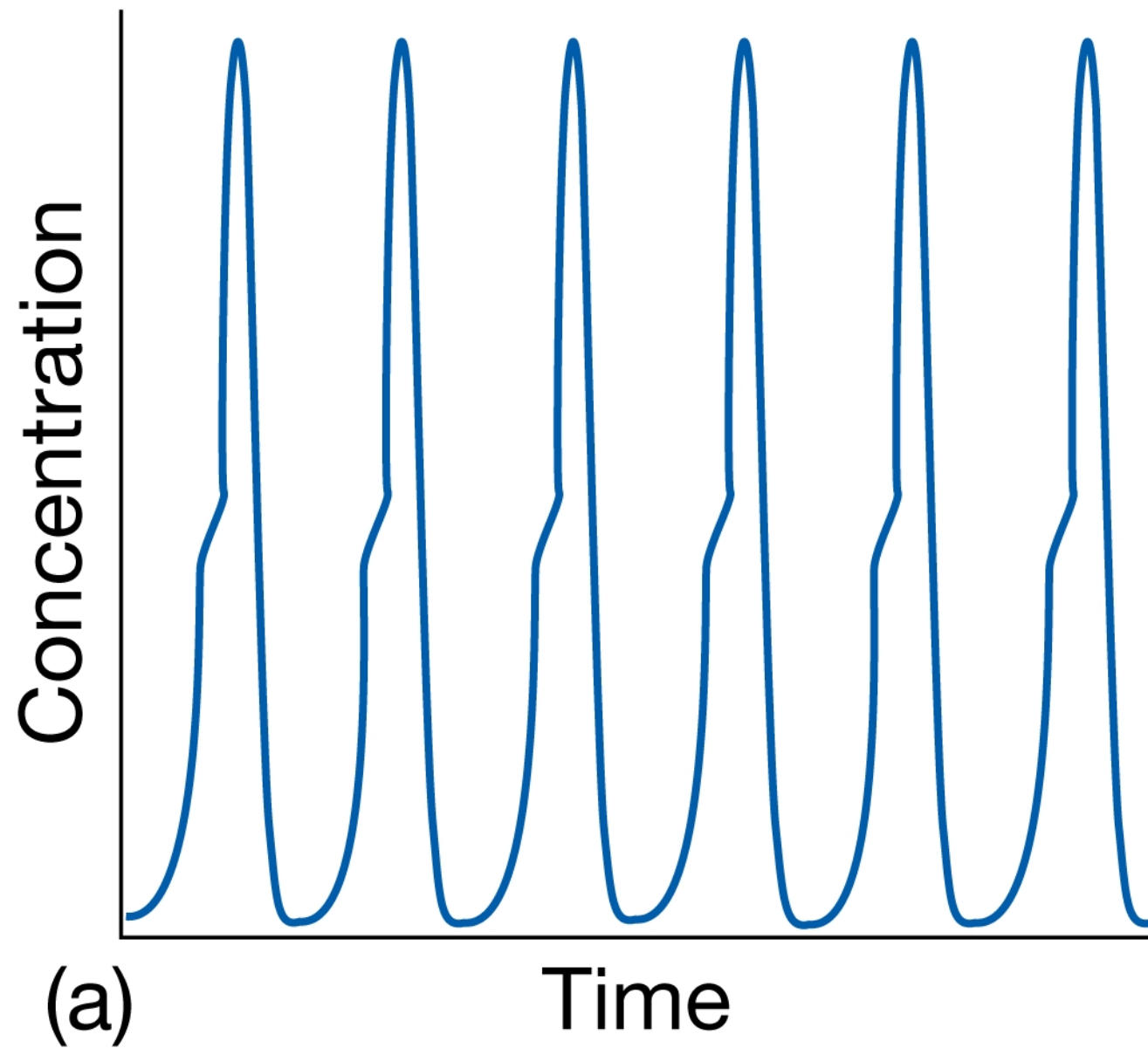
Um
modelo
mais
realístico

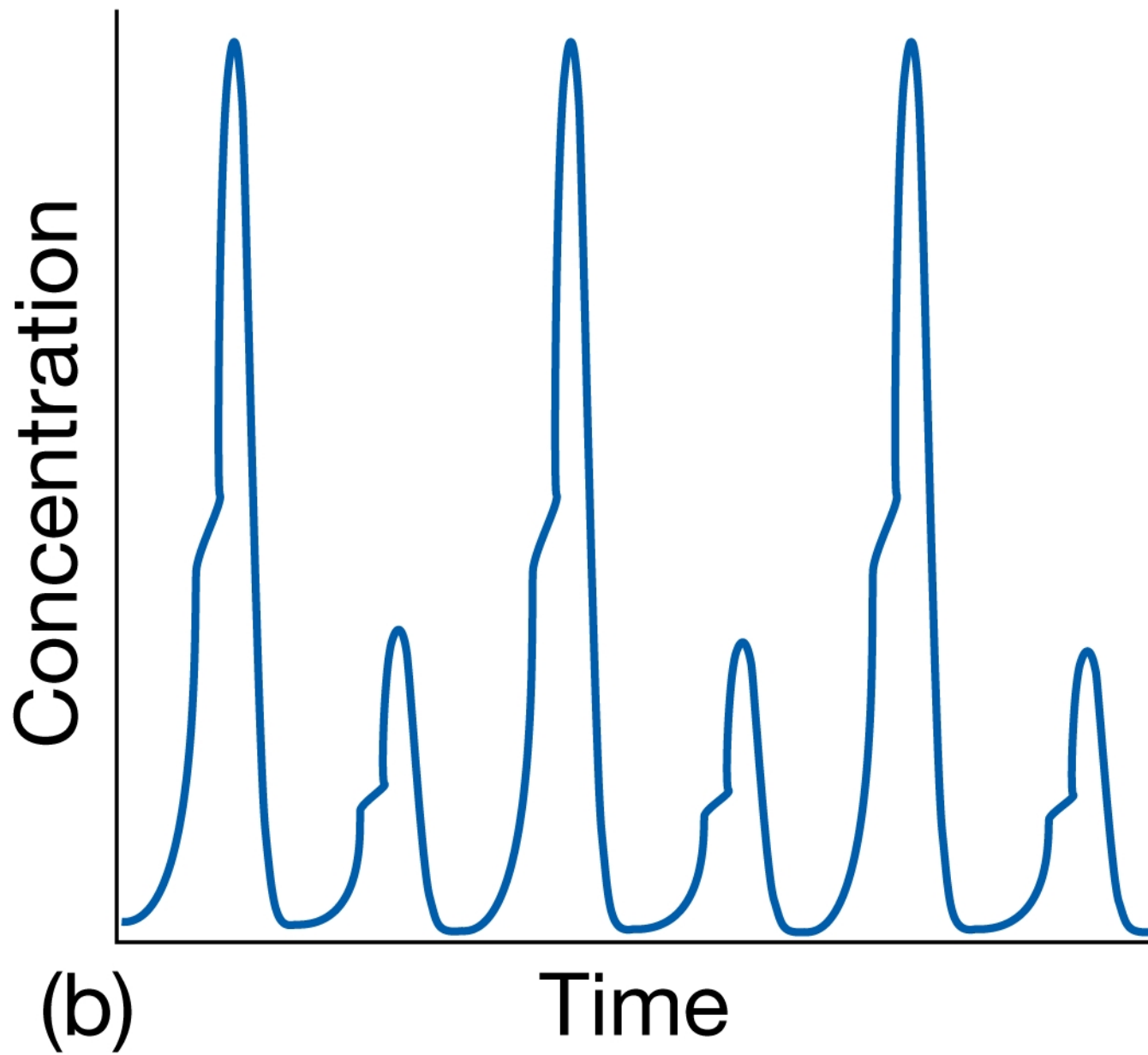
Passagem para o regime
caótico:
Oscilações regulares

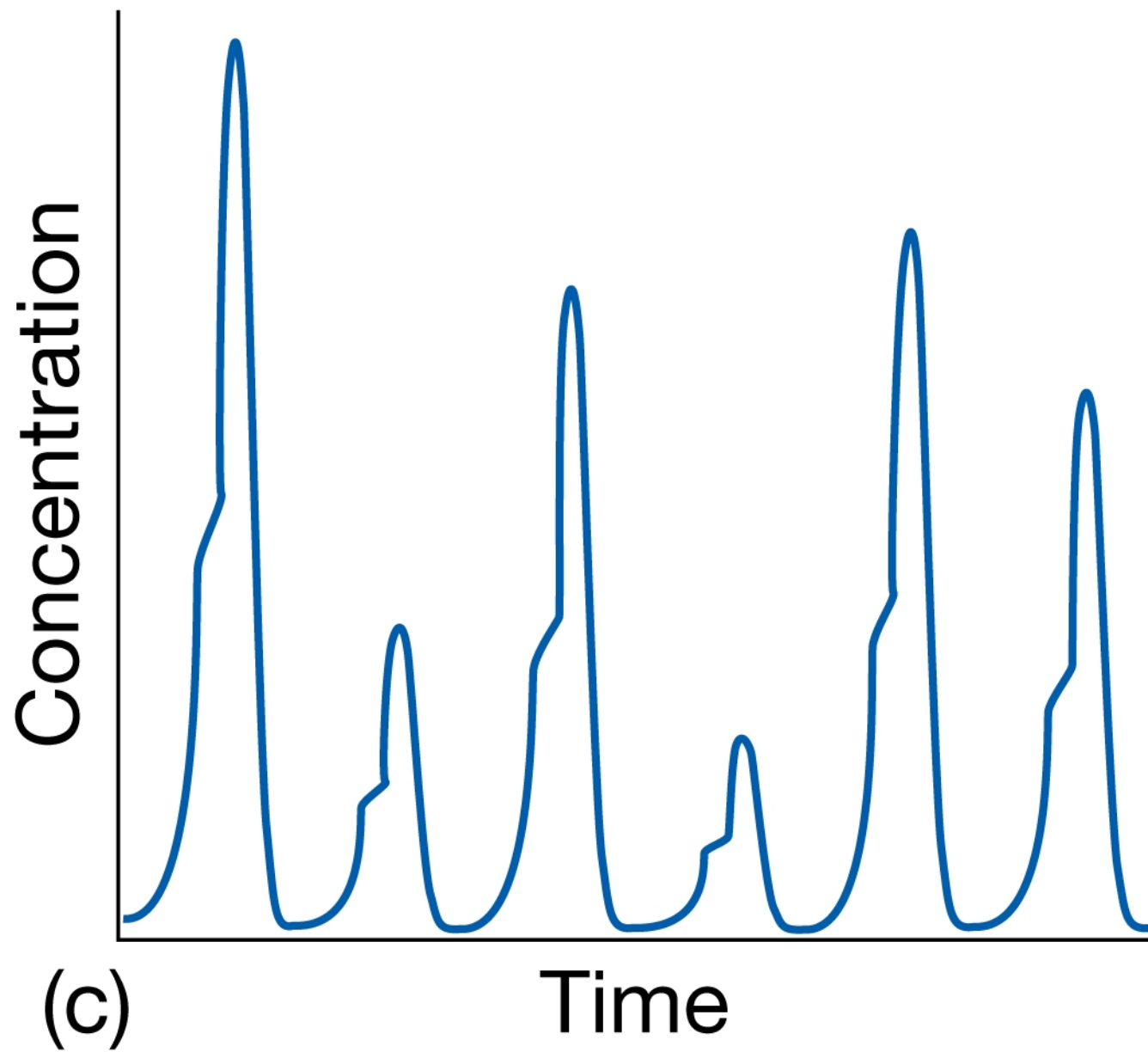
Duplicação do período

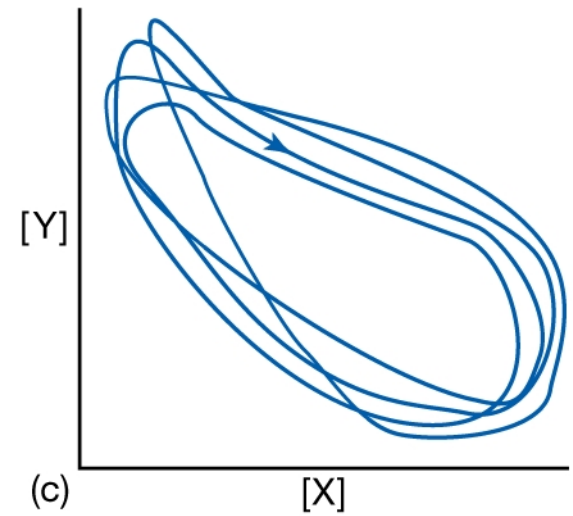
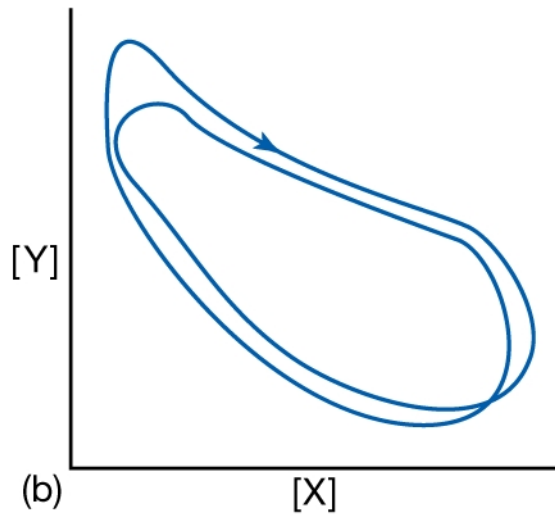
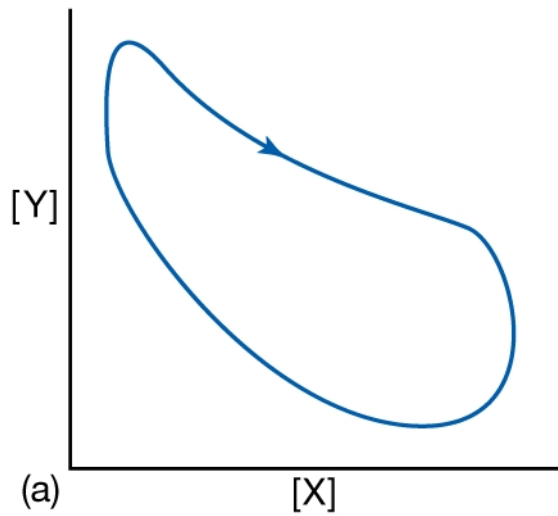
Regime caótico, depois
de muitas duplicações



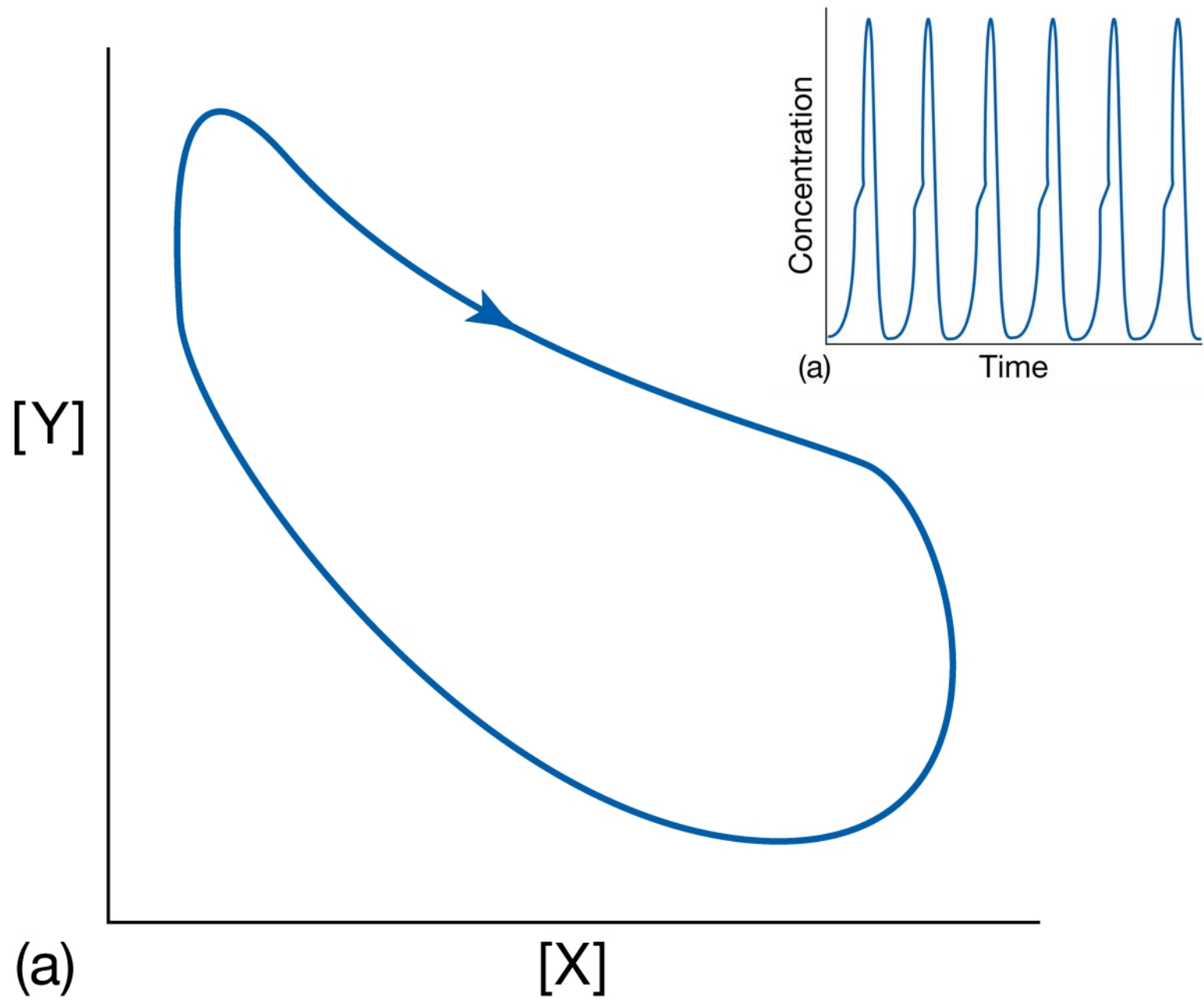


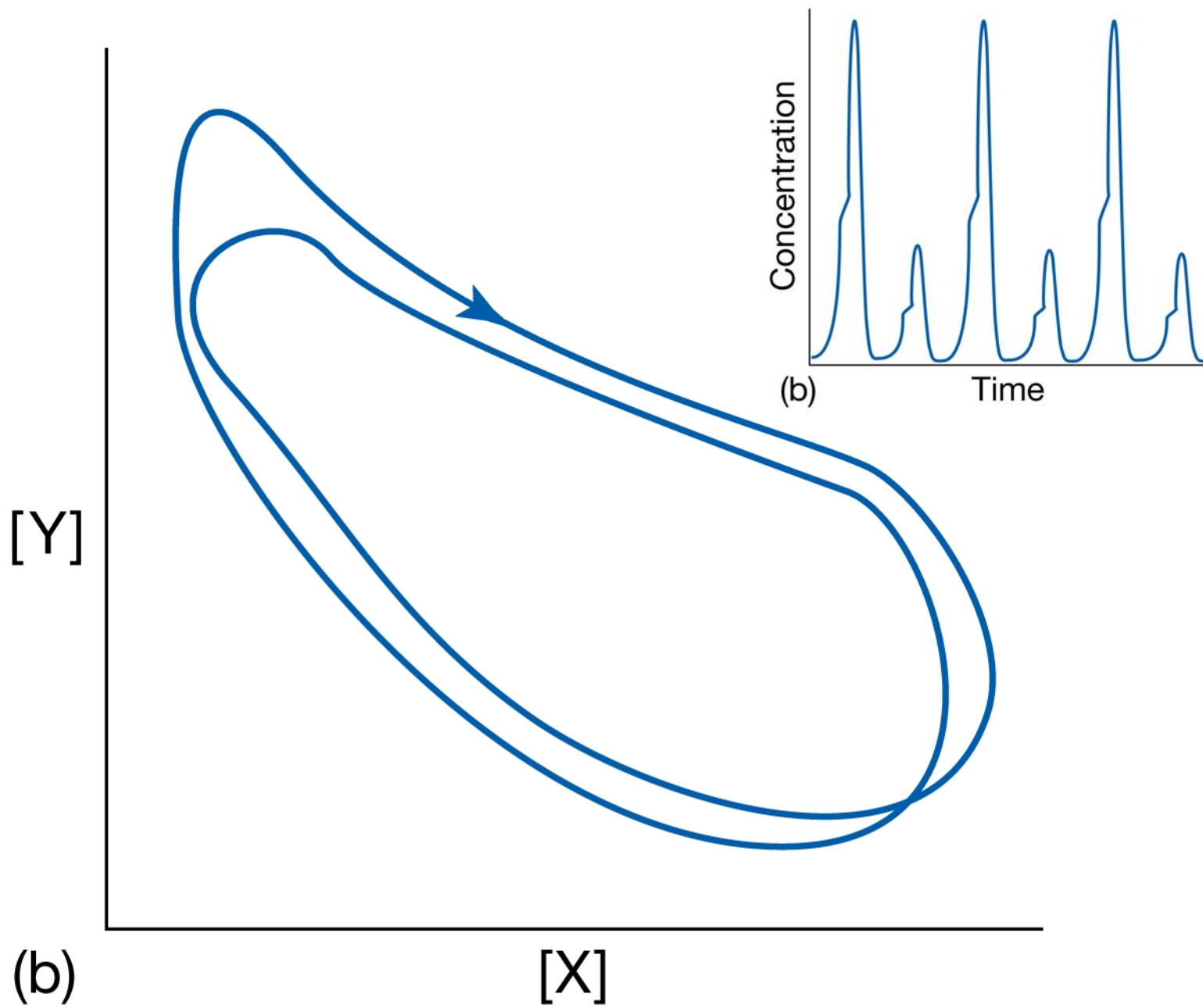


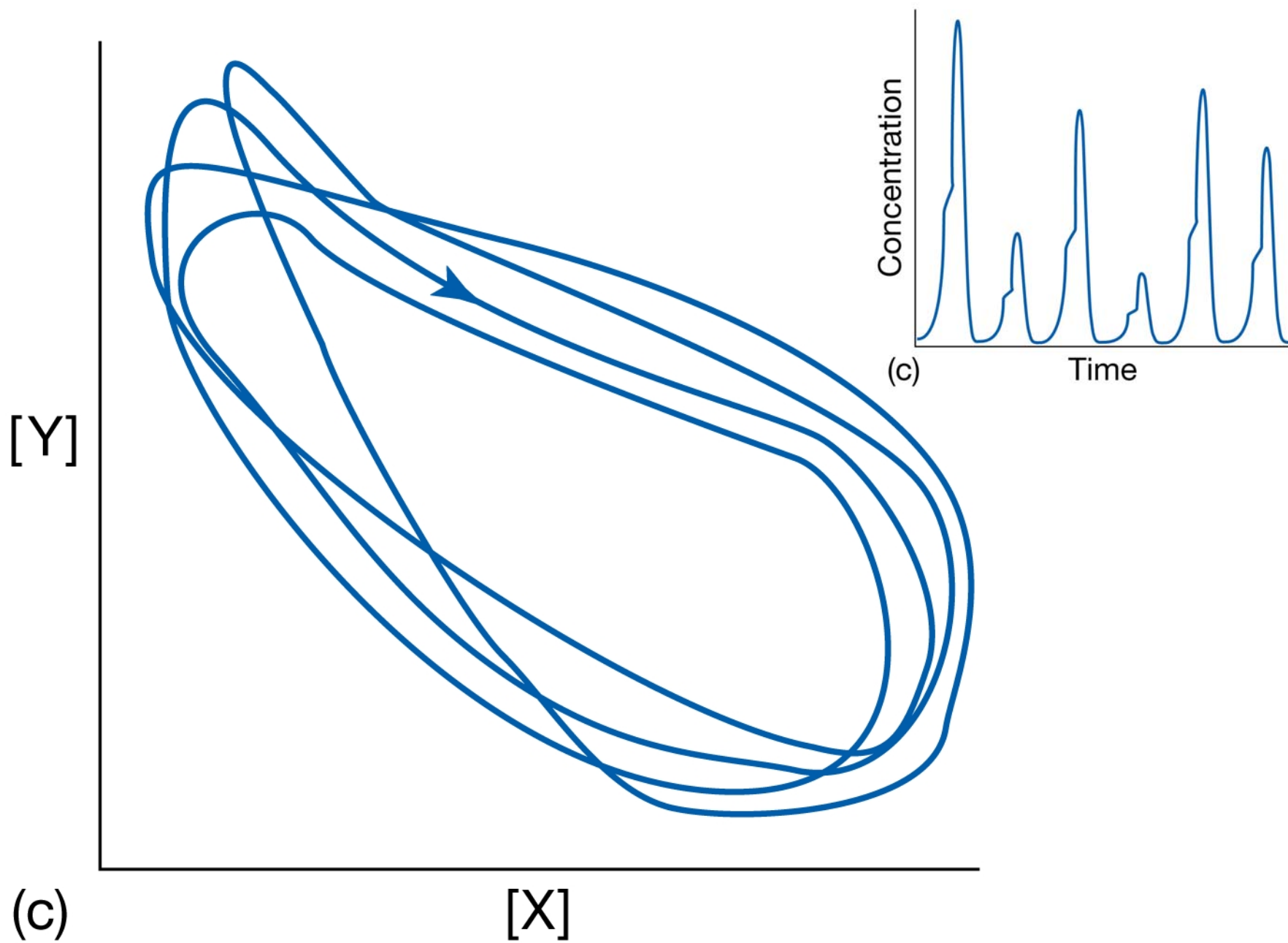




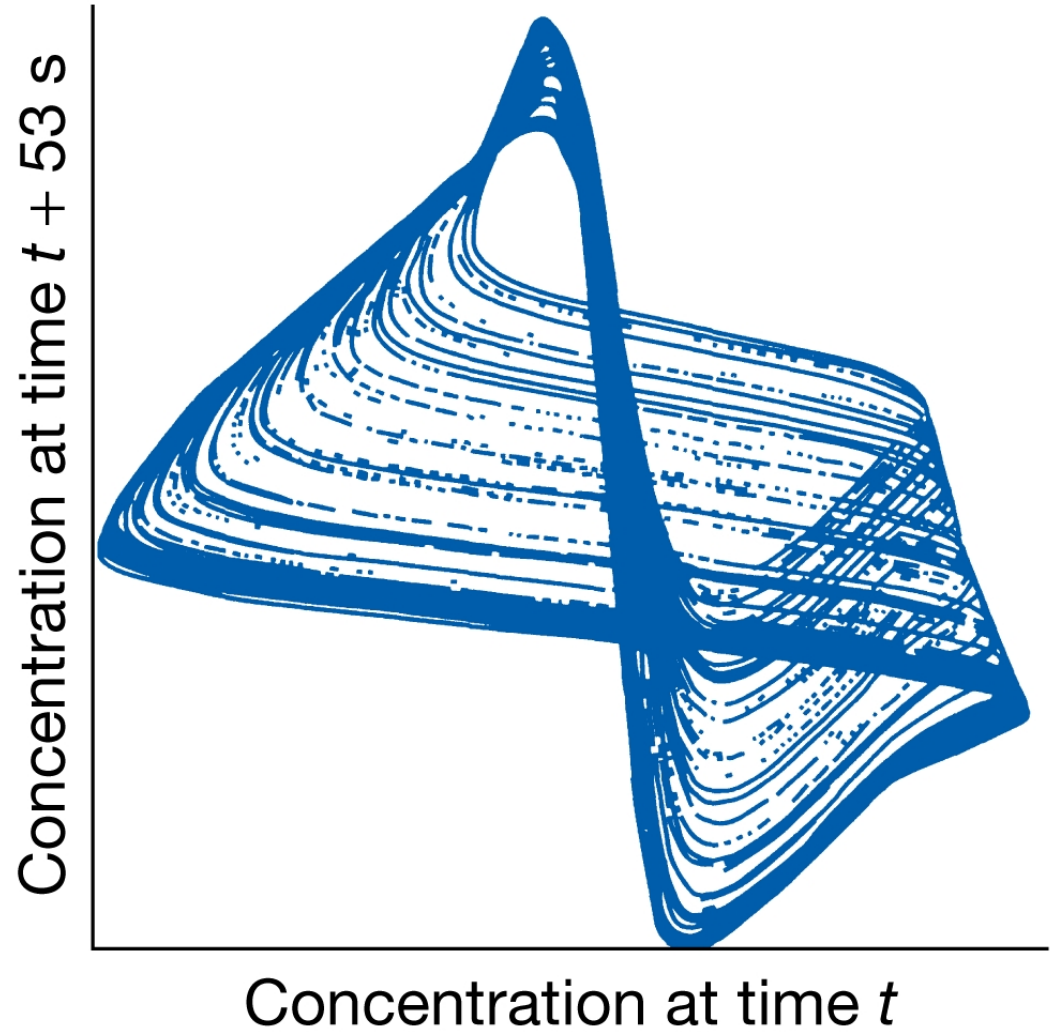
Trajetórias no espaço das concentrações: os atratores

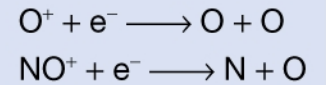
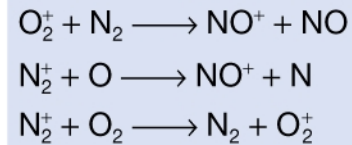
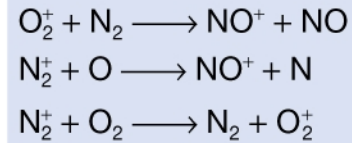
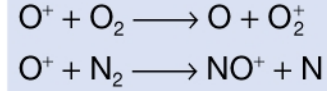
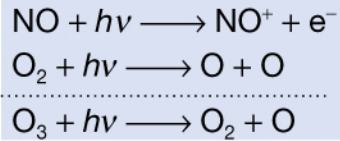
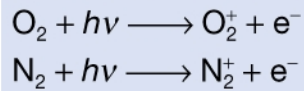
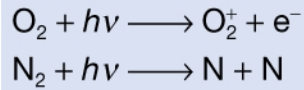
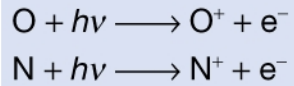
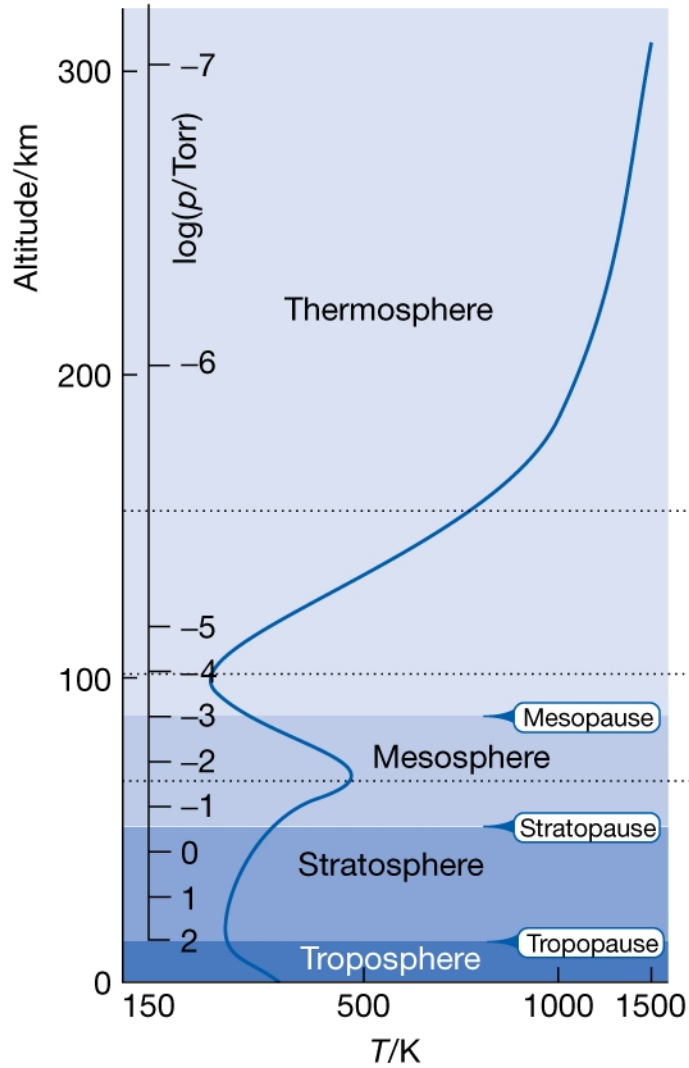


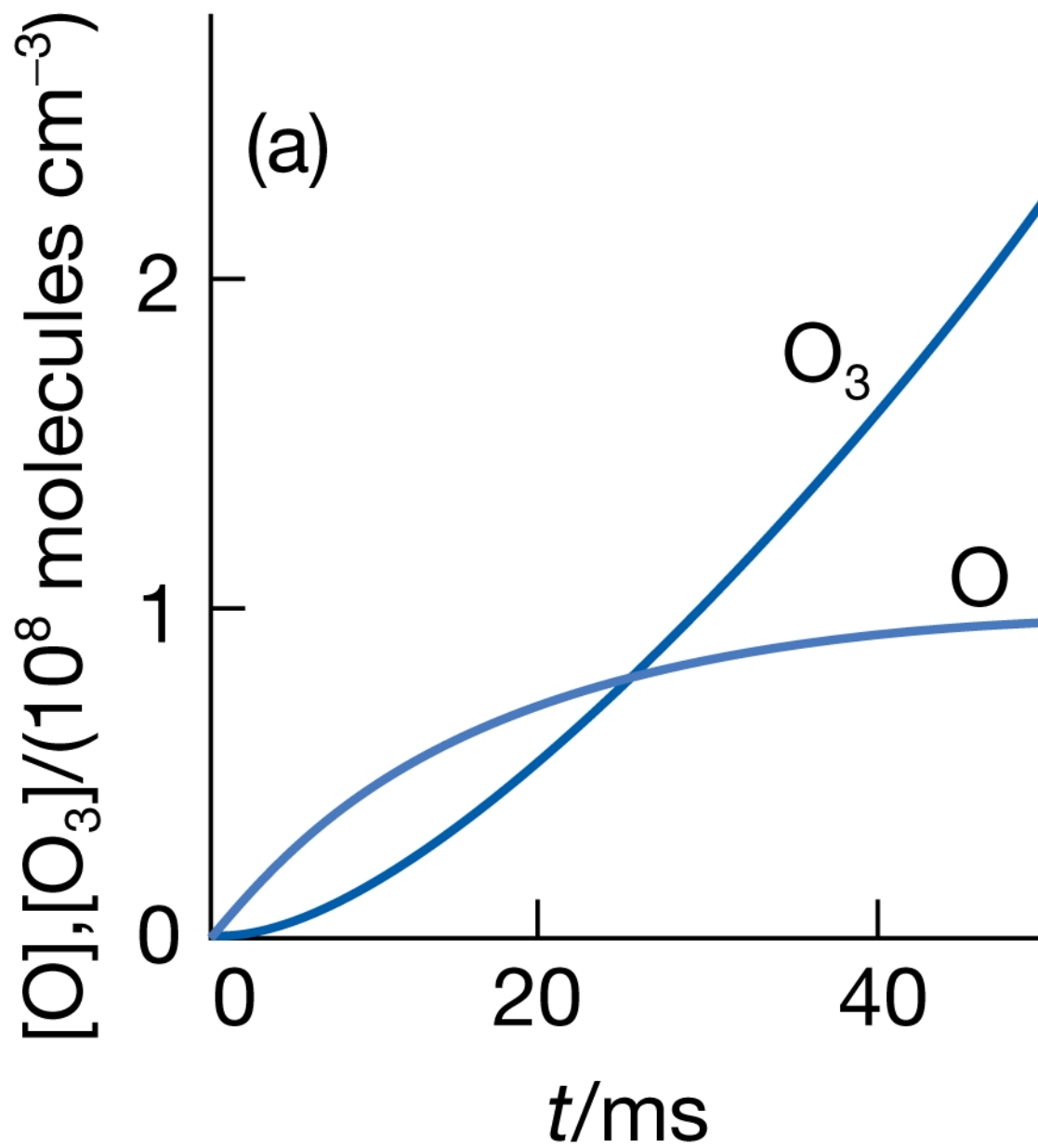


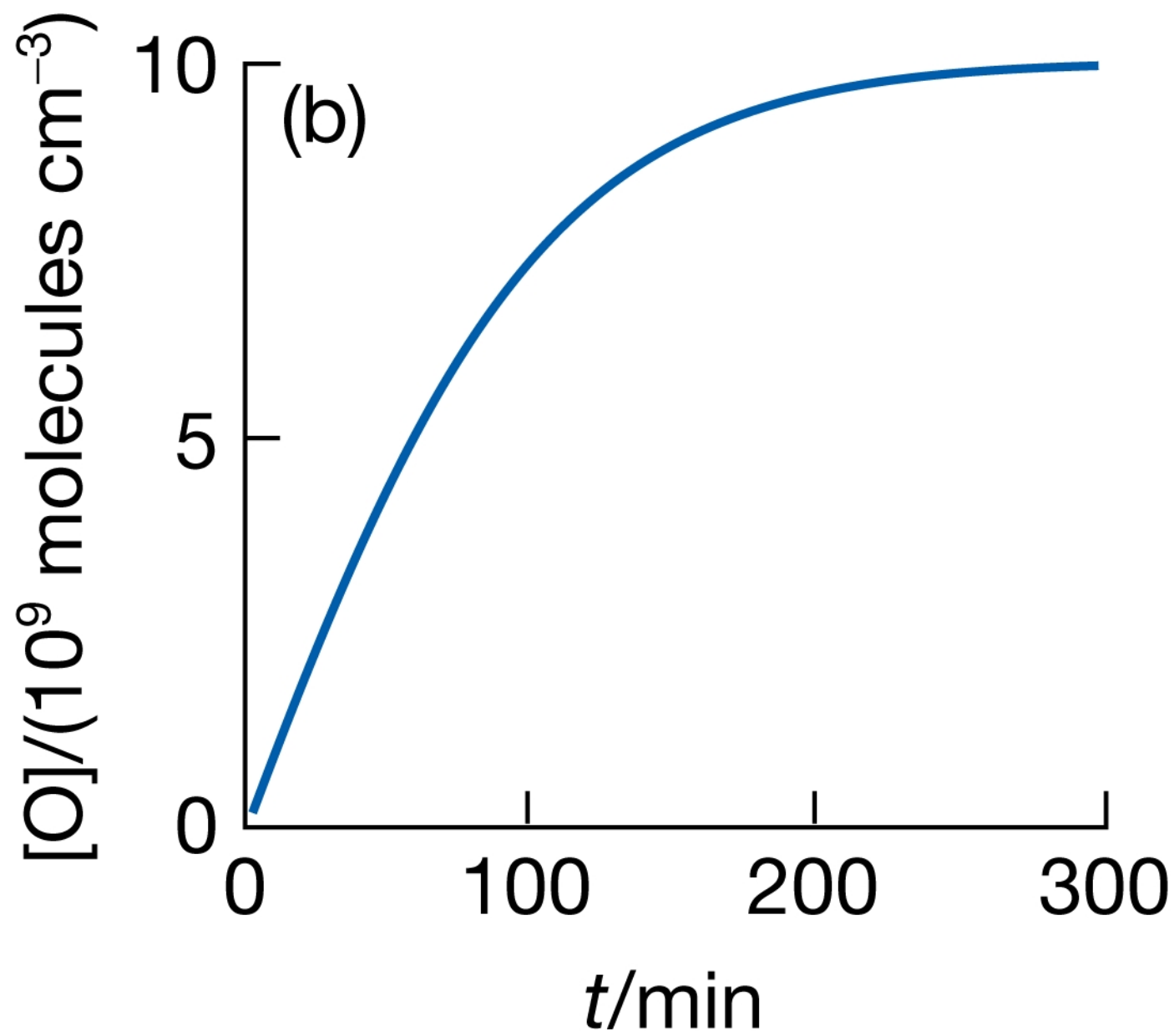


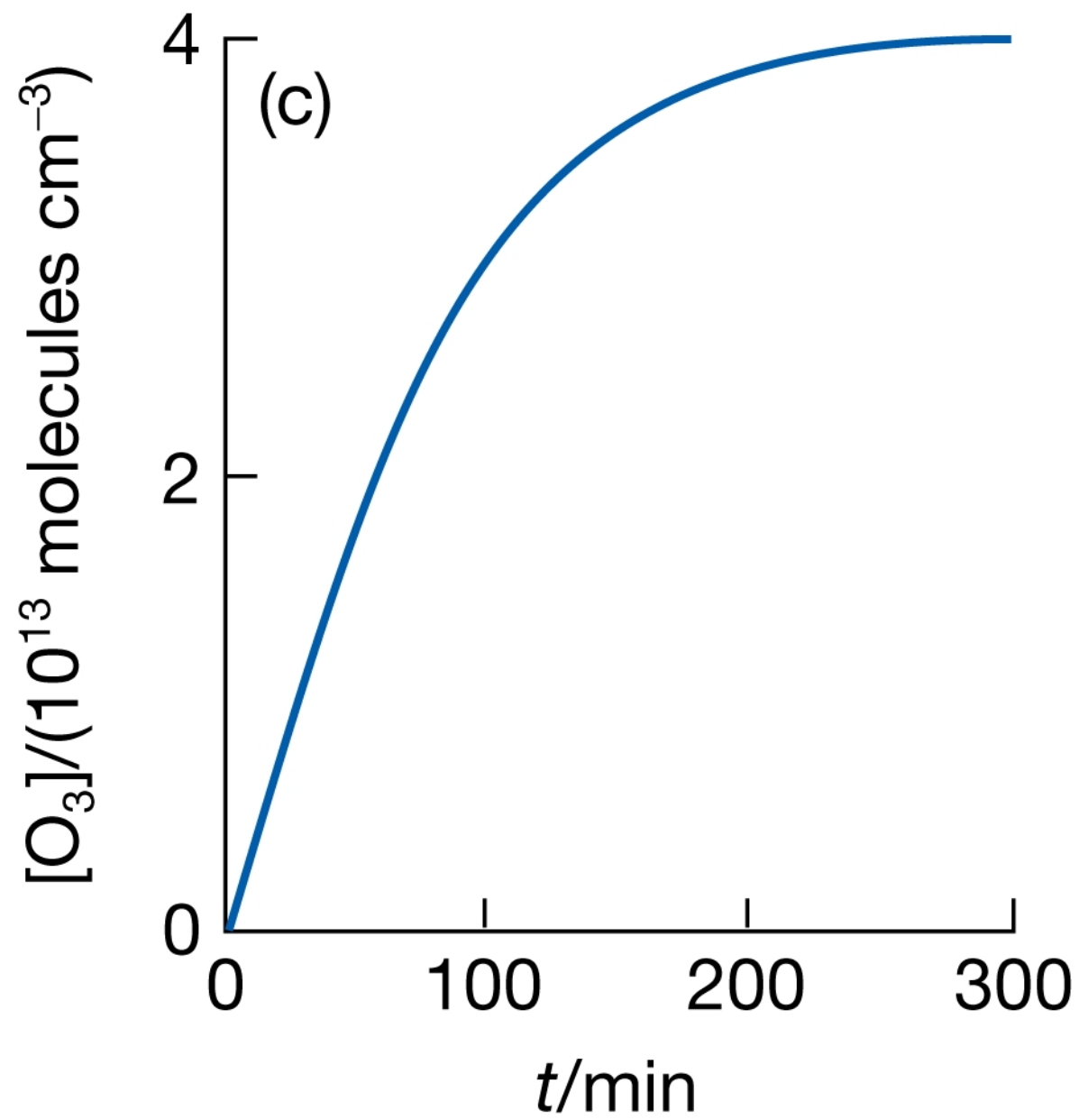
Um atrator
estranho:
regime caótico

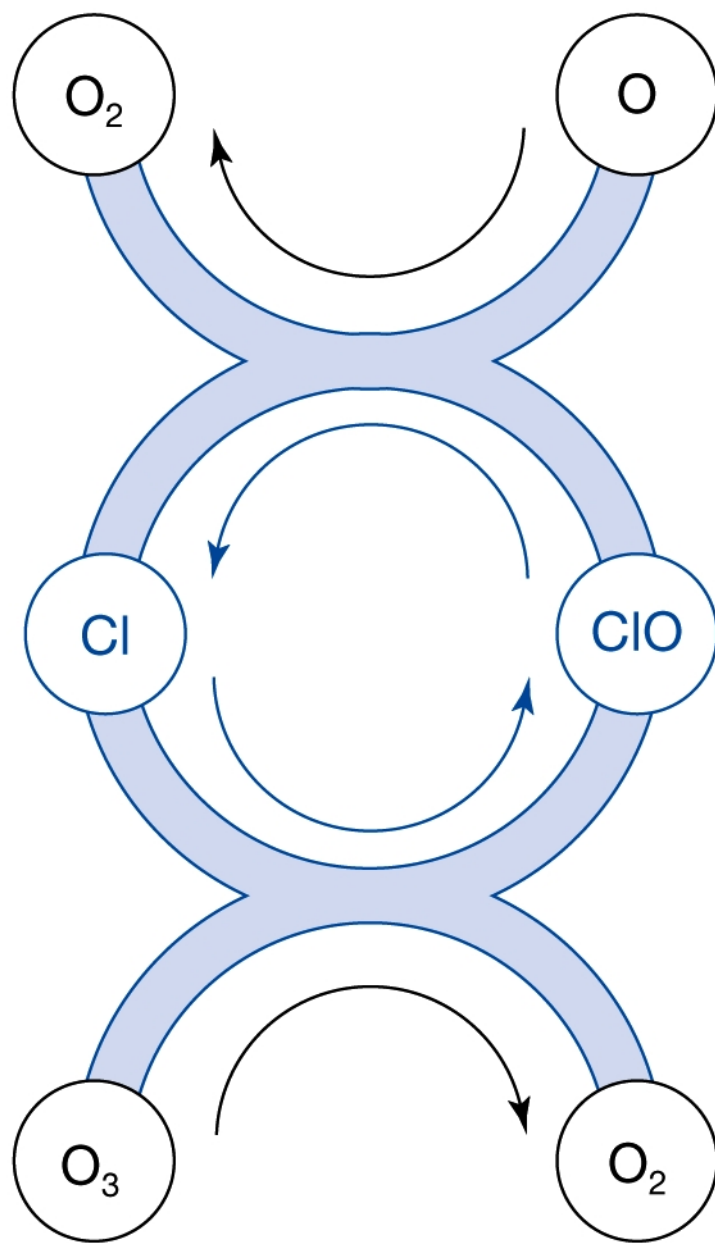


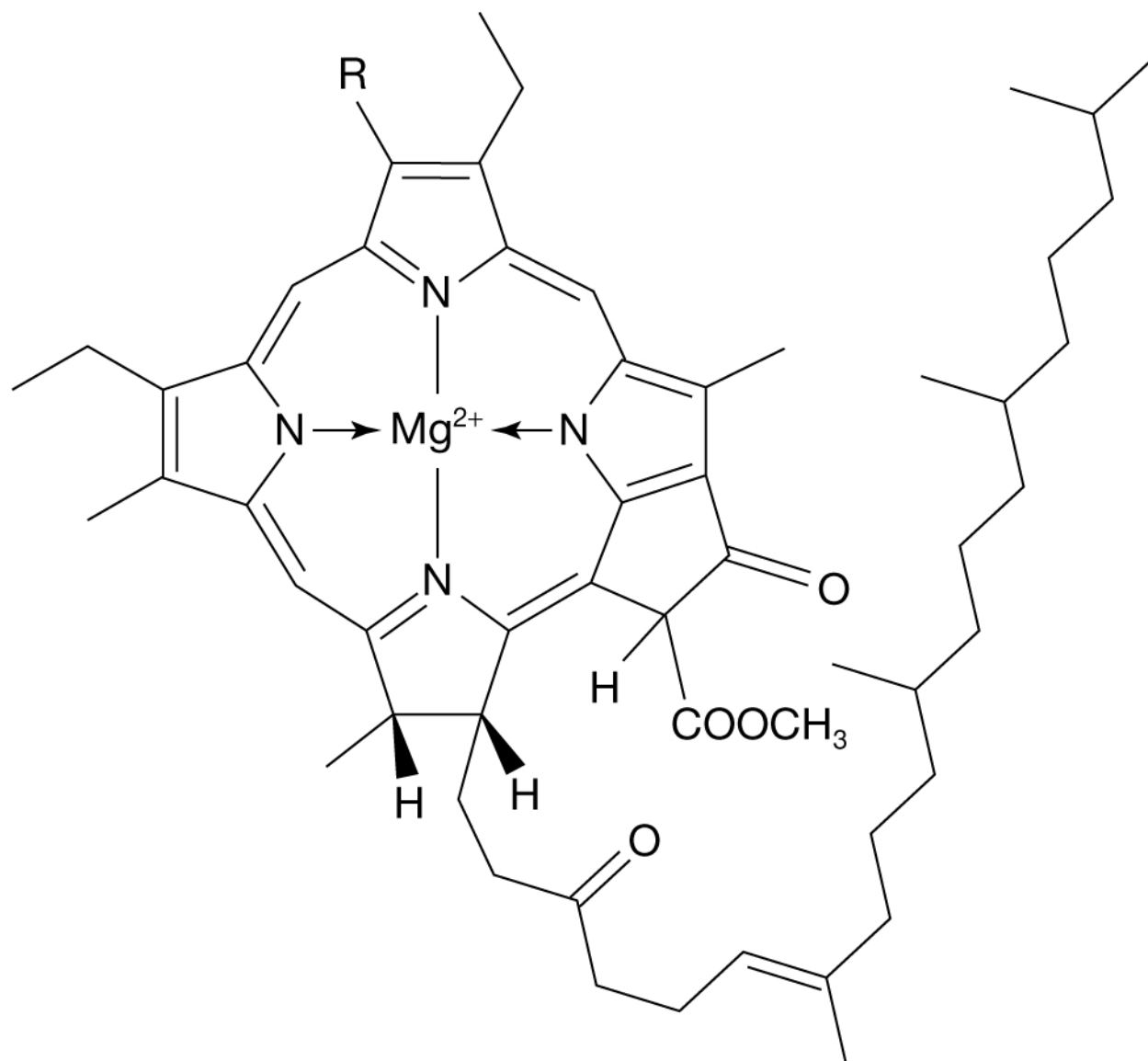




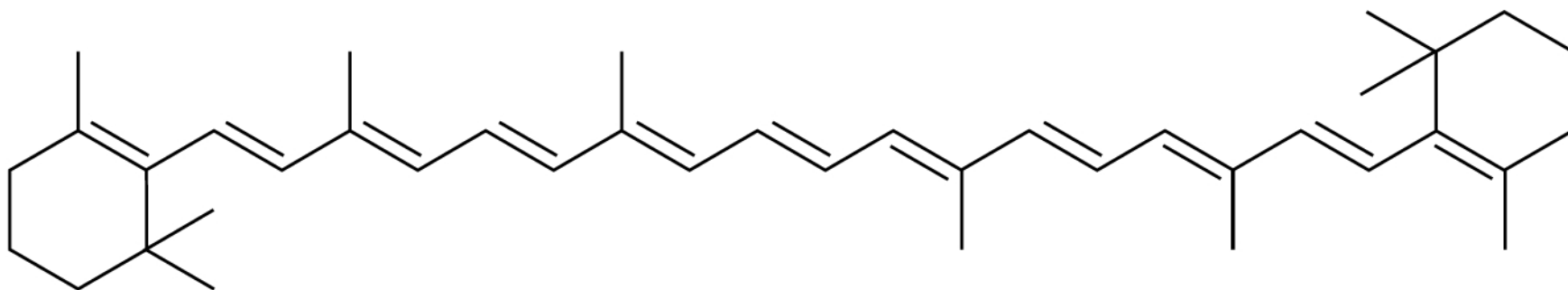




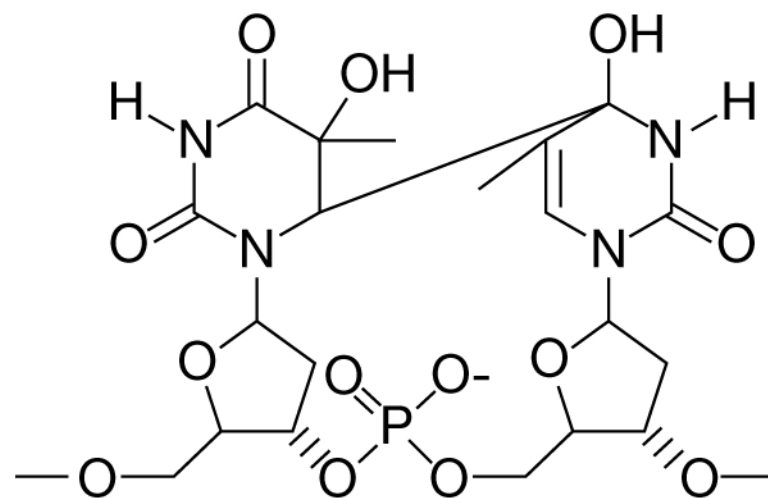
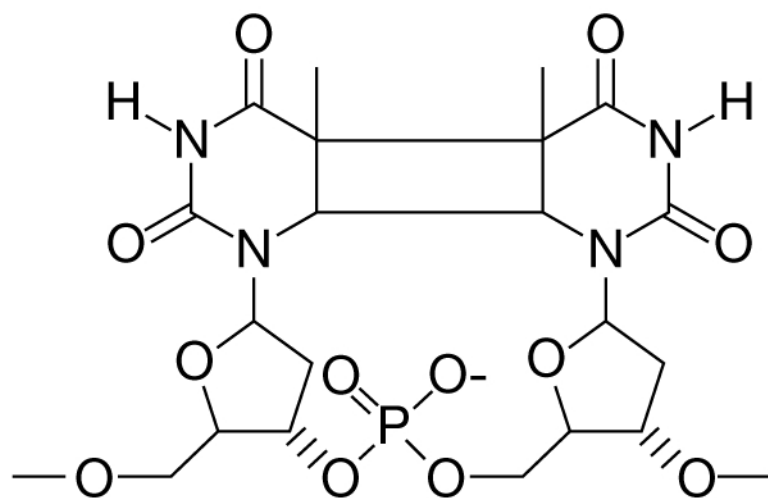
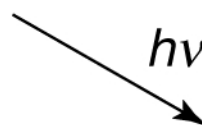
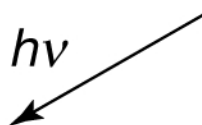
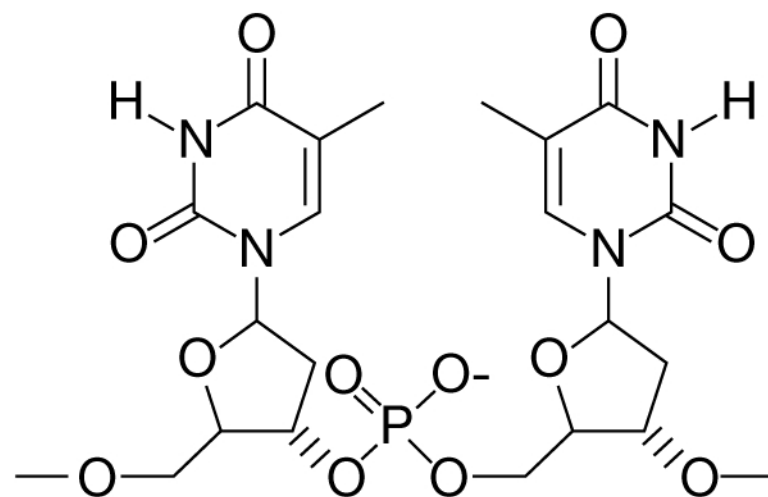


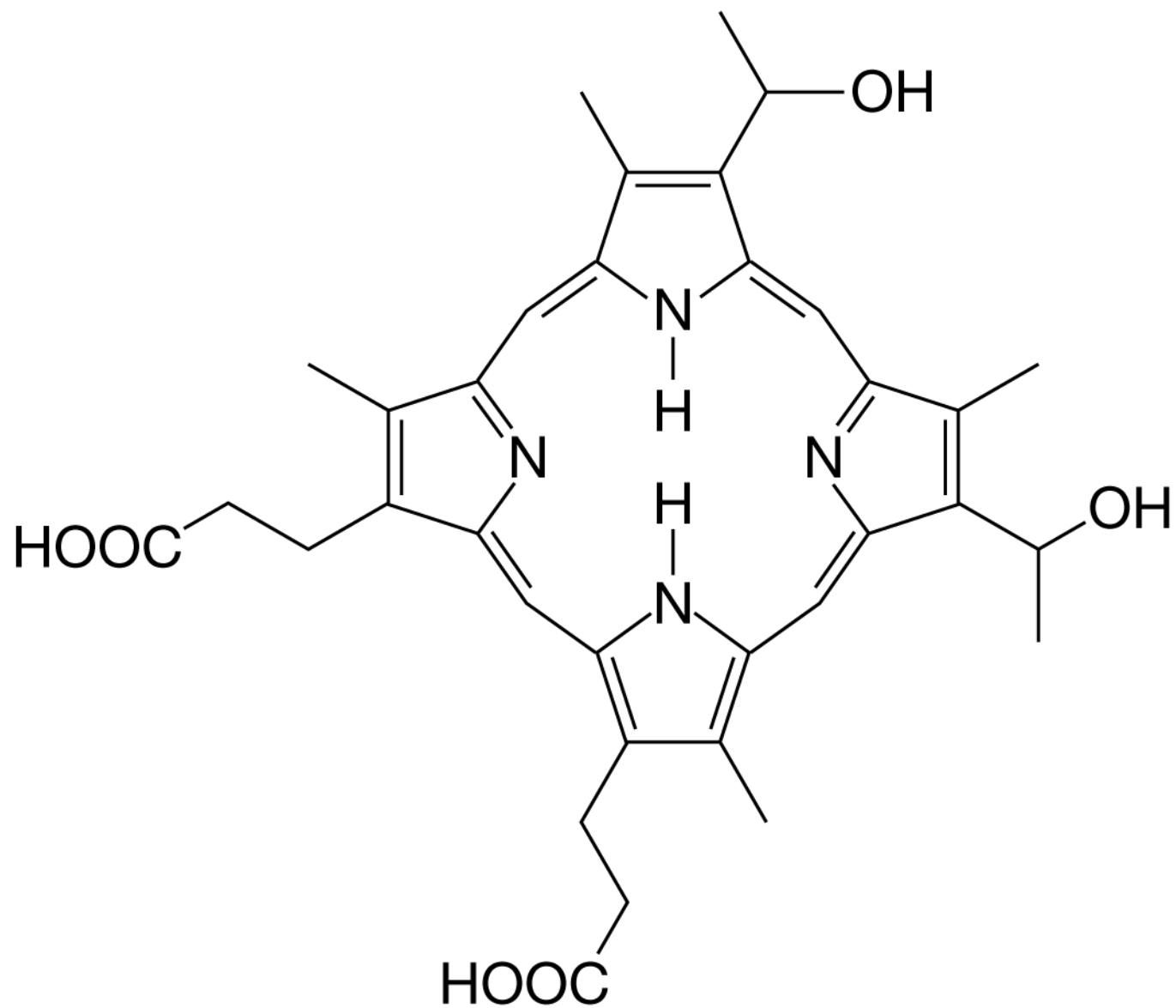


1 Chlorophylls a ($R = CH_3$) and b ($R = CHO$)

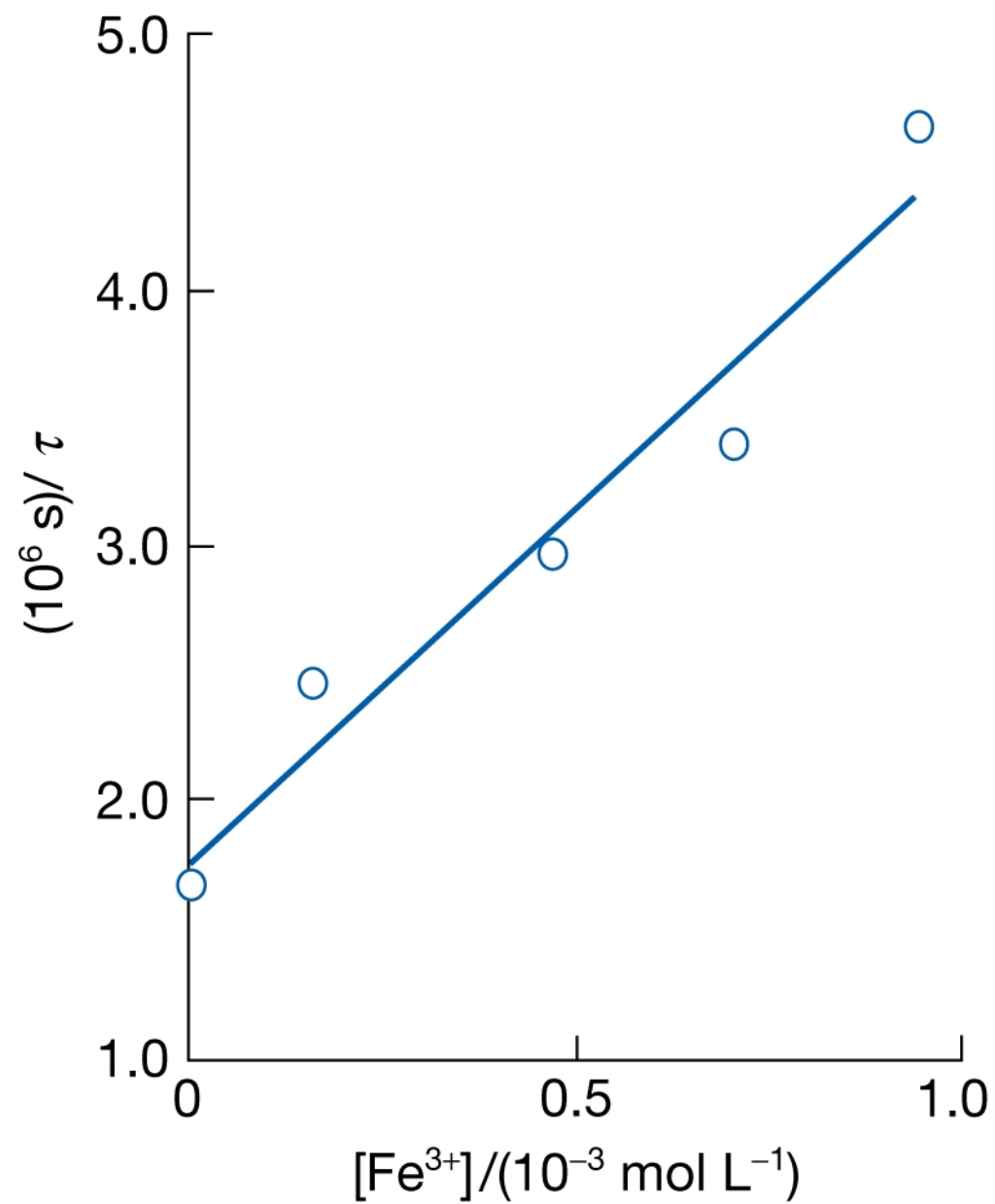


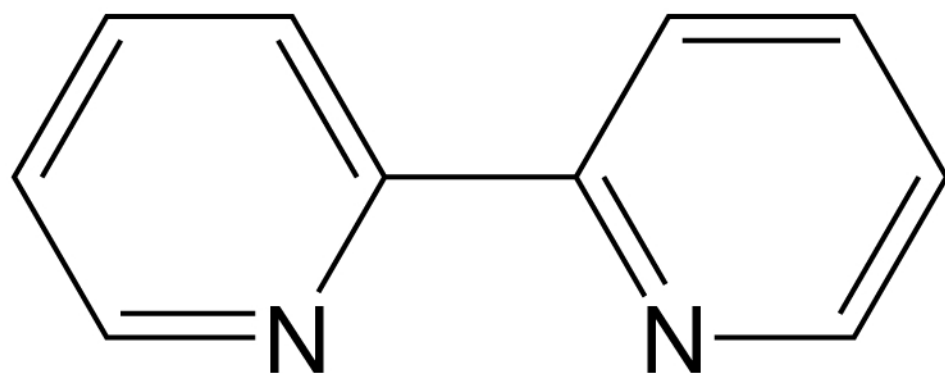
2 β -Carotene





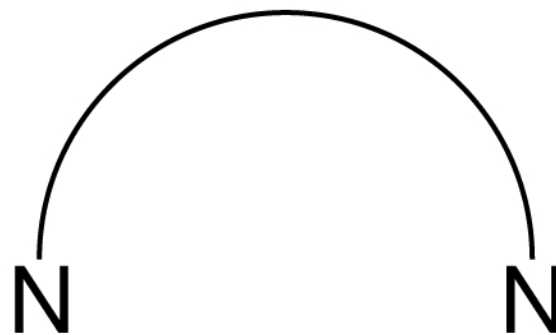
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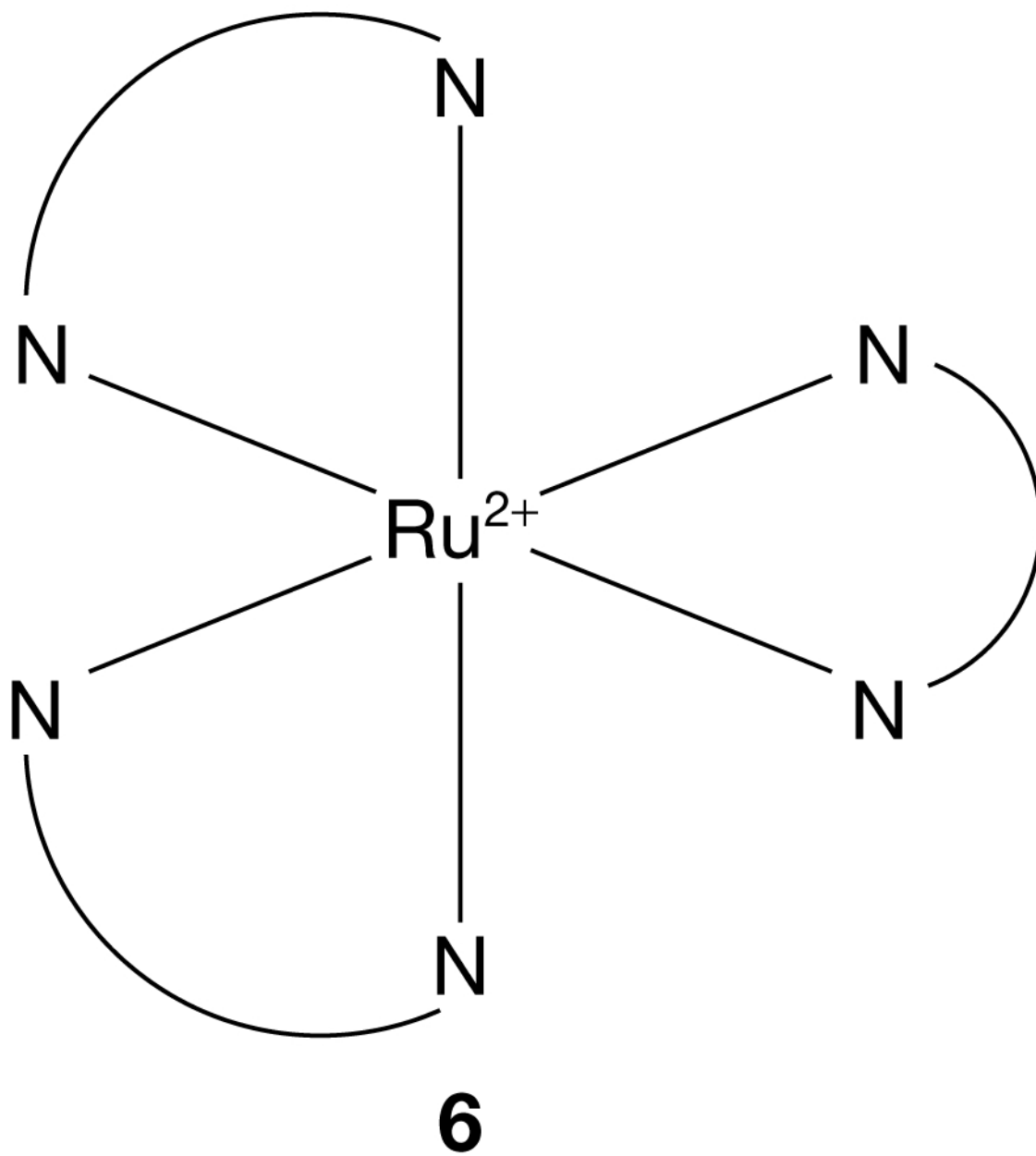


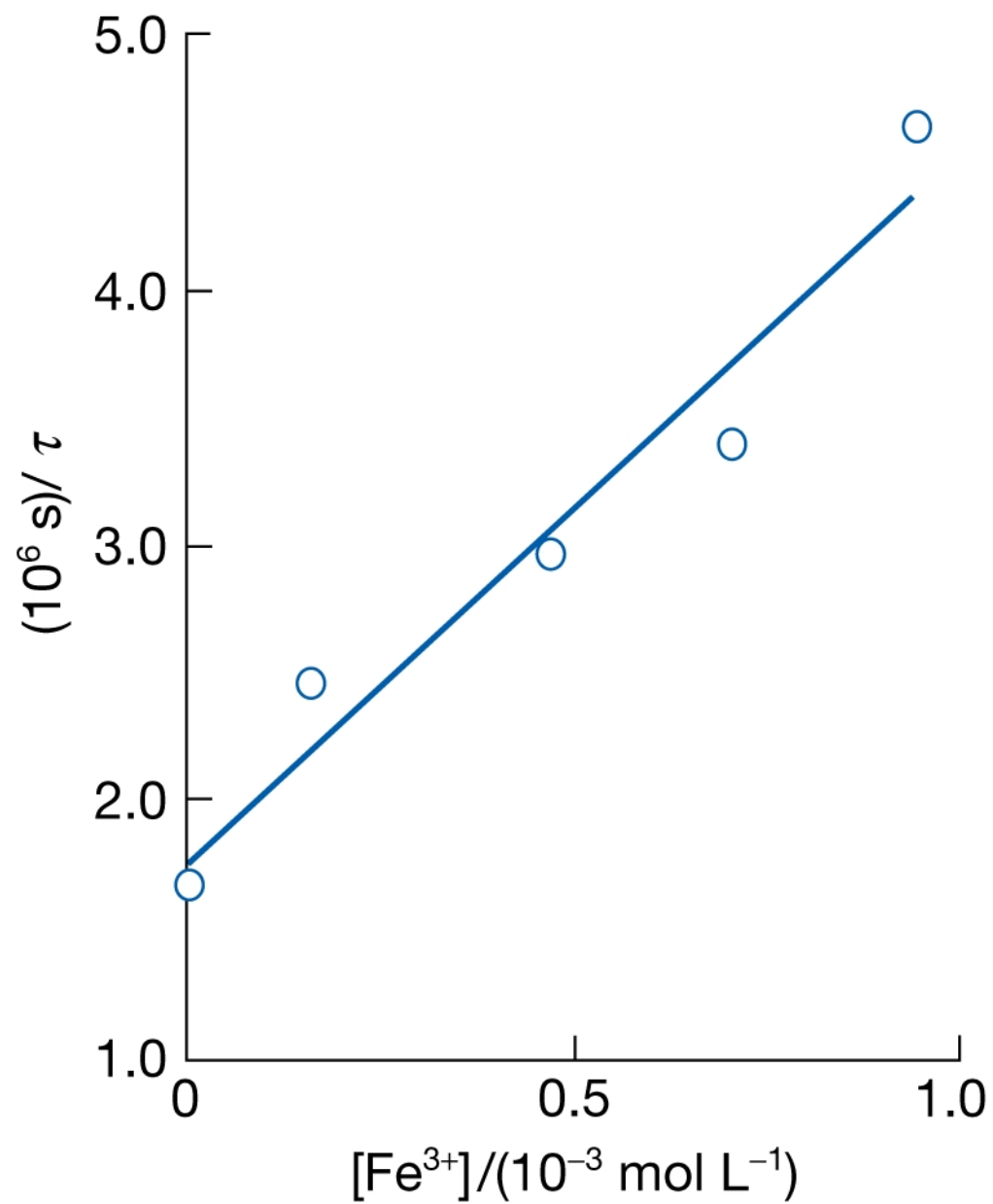


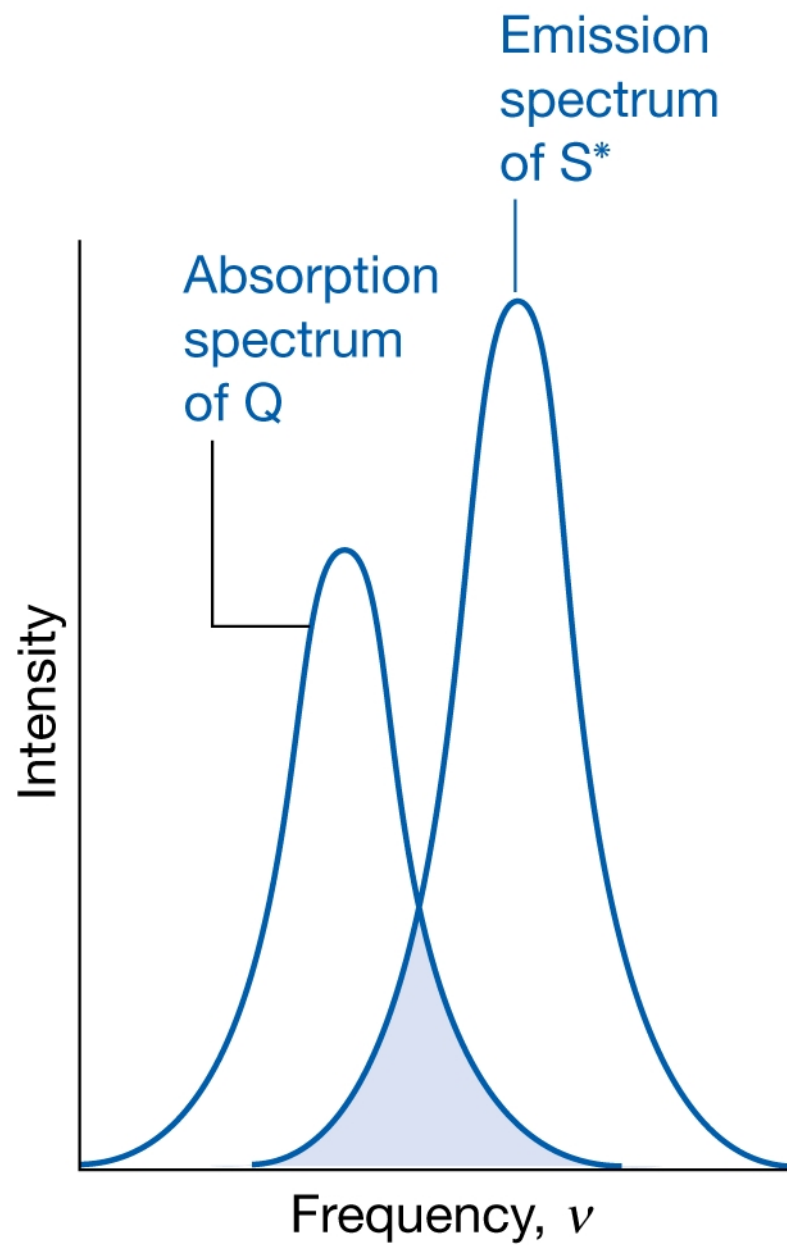
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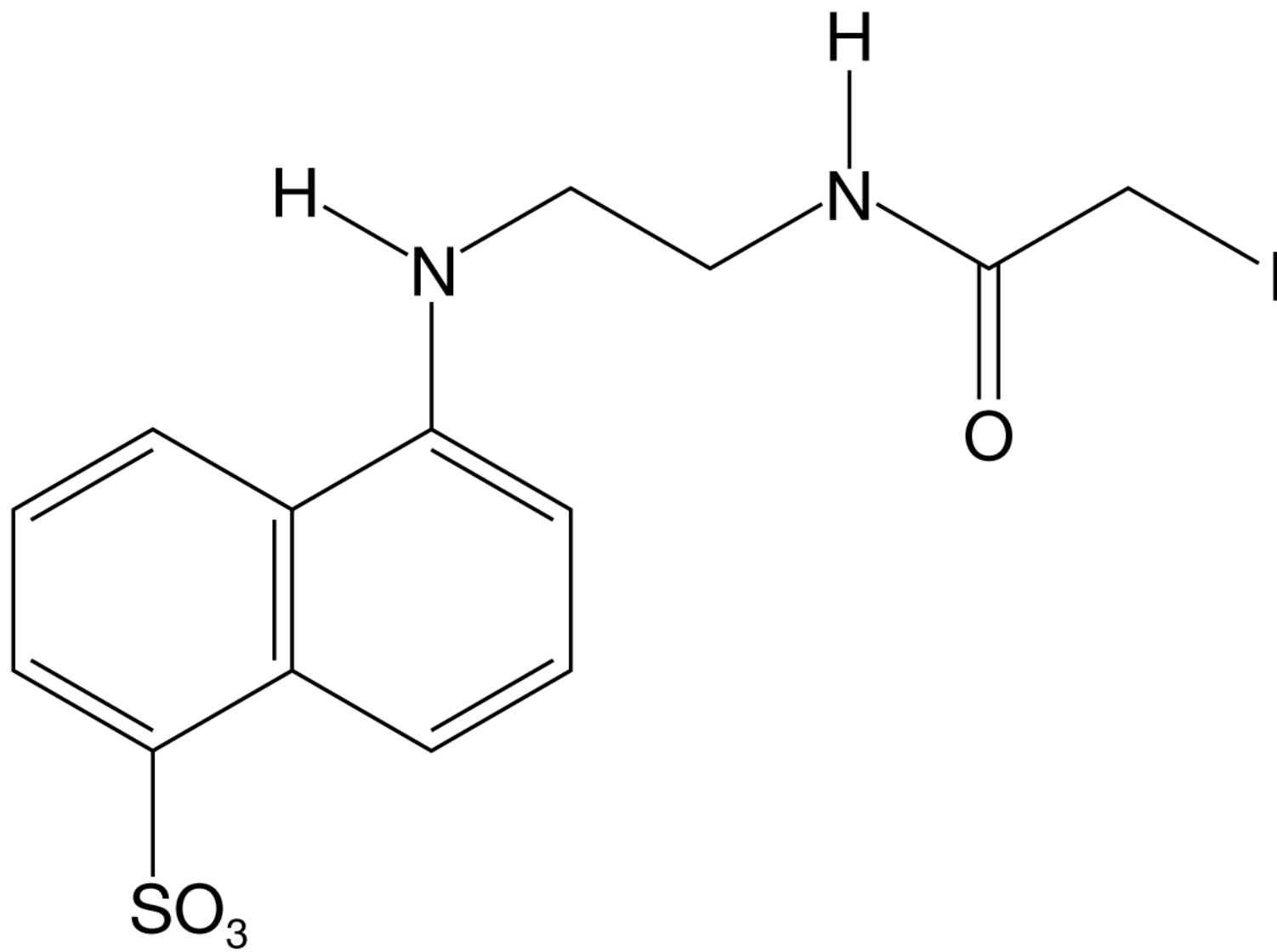
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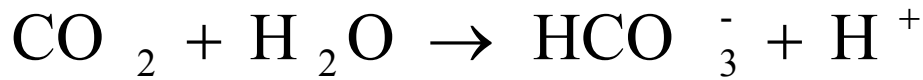




7

$$k_{\text{cat}} = k_{\text{b}} = \frac{v_{\text{máx}}}{[\text{E}]_0}$$

$$\varepsilon = \frac{k_{\text{cat}}}{K_{\text{M}}} = \frac{k_{\text{a}} k_{\text{b}}}{k'_{\text{a}} + k_{\text{b}}}$$



$$v_{\text{máx}} = \frac{1}{4,0 \times 10^{-3} \text{ Lmol}^{-1} \text{ s}} = 2,5 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}$$

$$K_{\text{M}} = (2,5 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}) \times (40 \text{ s}) = 1,0 \times 10^{-2} \text{ molL}^{-1}$$

$$k_{\text{cat}} = \frac{2,5 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}}{2,3 \times 10^{-9} \text{ molL}^{-1}} = 1,1 \times 10^5 \text{ s}^{-1}$$

$$\varepsilon = \frac{k_{\text{cat}}}{K_{\text{M}}} = \frac{1,1 \times 10^5 \text{ s}^{-1}}{1,0 \times 10^{-2} \text{ molL}^{-1}} = 1,1 \times 10^7 \text{ Lmol}^{-1} \text{ s}^{-1}$$