Приближенные методы кинетики

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Олимпиадный сезон 2020-21

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Последовательные реакции

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

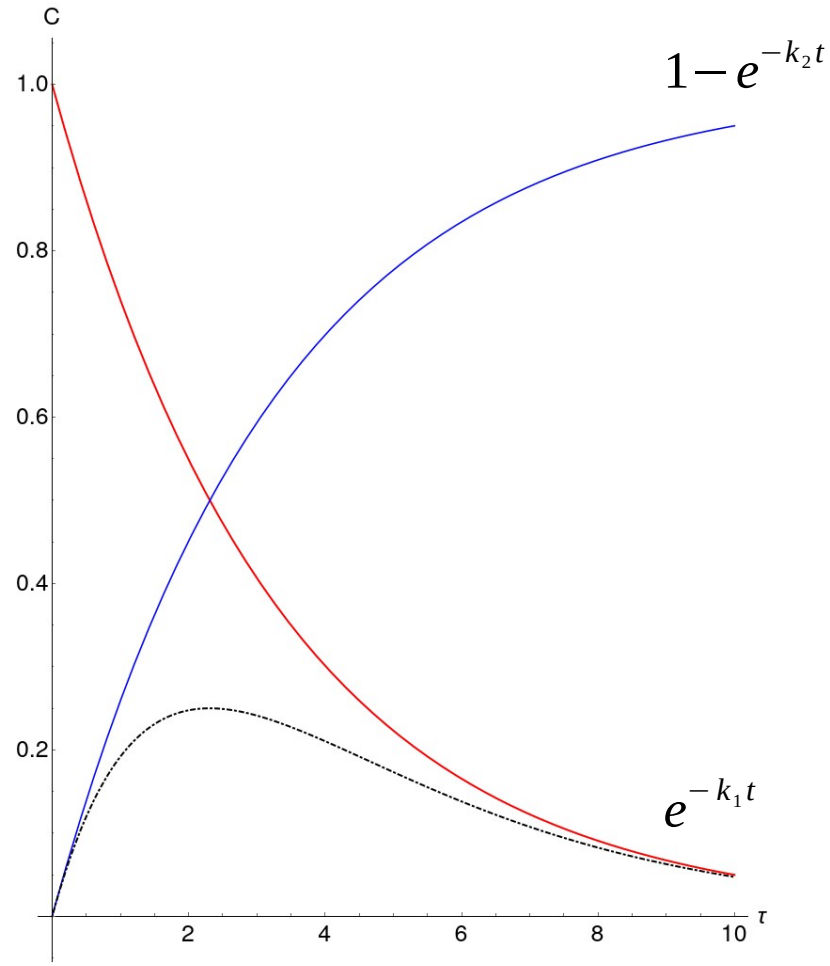
$$\begin{cases} \dfrac{d[A]}{dt} = -k_1[A] \\ \dfrac{d[B]}{dt} = k_1[A] - k_2[B] \\ \dfrac{d[C]}{dt} = k_2[B] \end{cases} \Longrightarrow \begin{cases} [A] = [A]_0 e^{-k_1 t} \\ \dfrac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B] \\ [C] = [A]_0 - [A] - [B] \end{cases}$$

$$[B](t) = ?$$

Последовательные реакции

Предположим...

$$[B](t) = K\left(e^{-k_1 t} - e^{-k_2 t}\right), K = const$$



Последовательные реакции

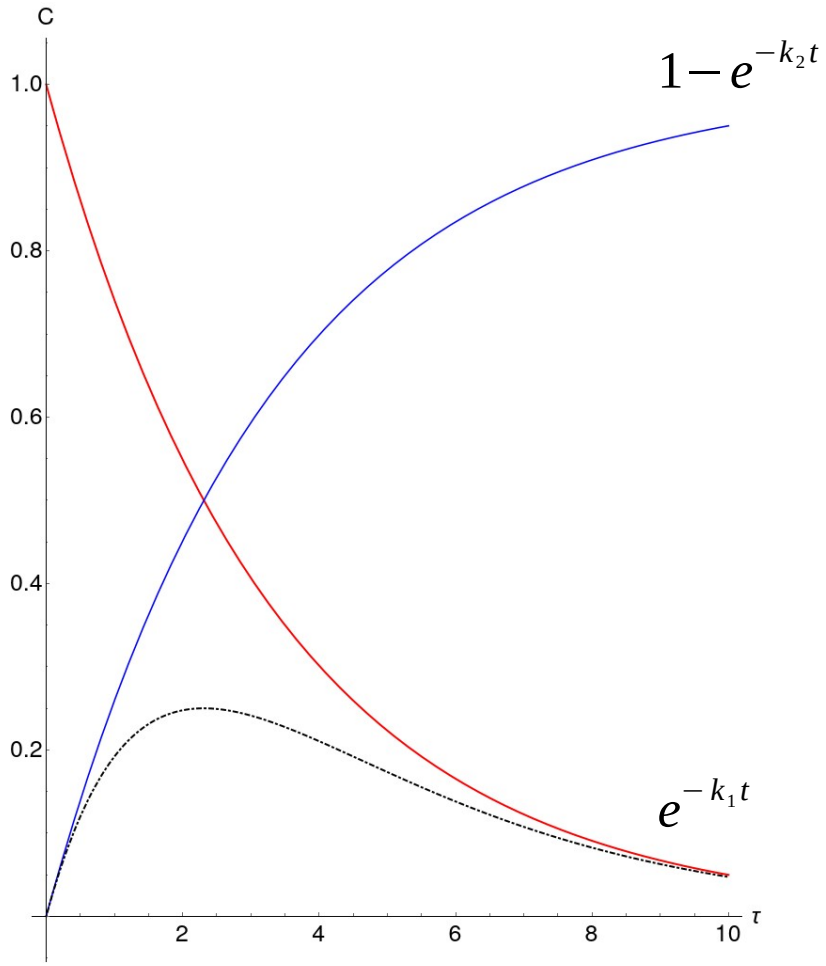
Предположим...

$$[B](t) = K\left(e^{-k_1 t} - e^{-k_2 t}\right), K = const$$

... и проверим

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

$$\frac{d[B]}{dt} = K\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right)$$



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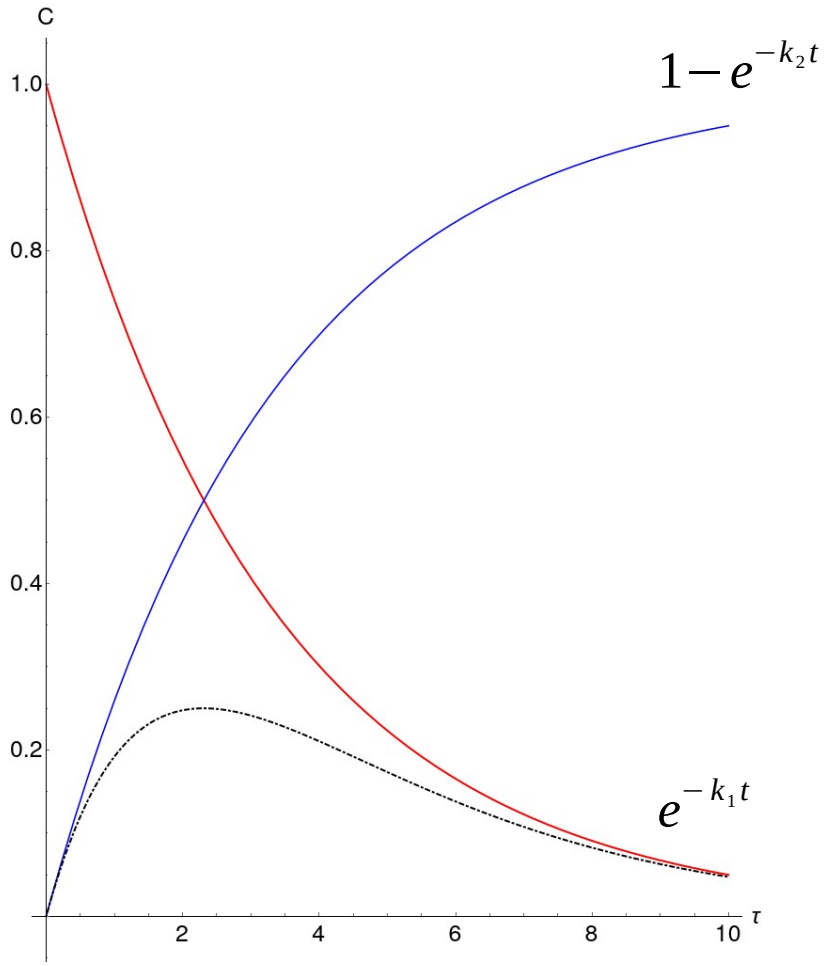
$$K\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right) = k_1[A]_0 e^{-kt} - k_2 K\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$-k_1 K e^{-k_1 t} = k_1[A]_0 e^{-k_1 t} - k_2 K e^{-k_1 t}$$

$$K = \frac{k_1[A]_0}{k_2 - k_1}$$

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



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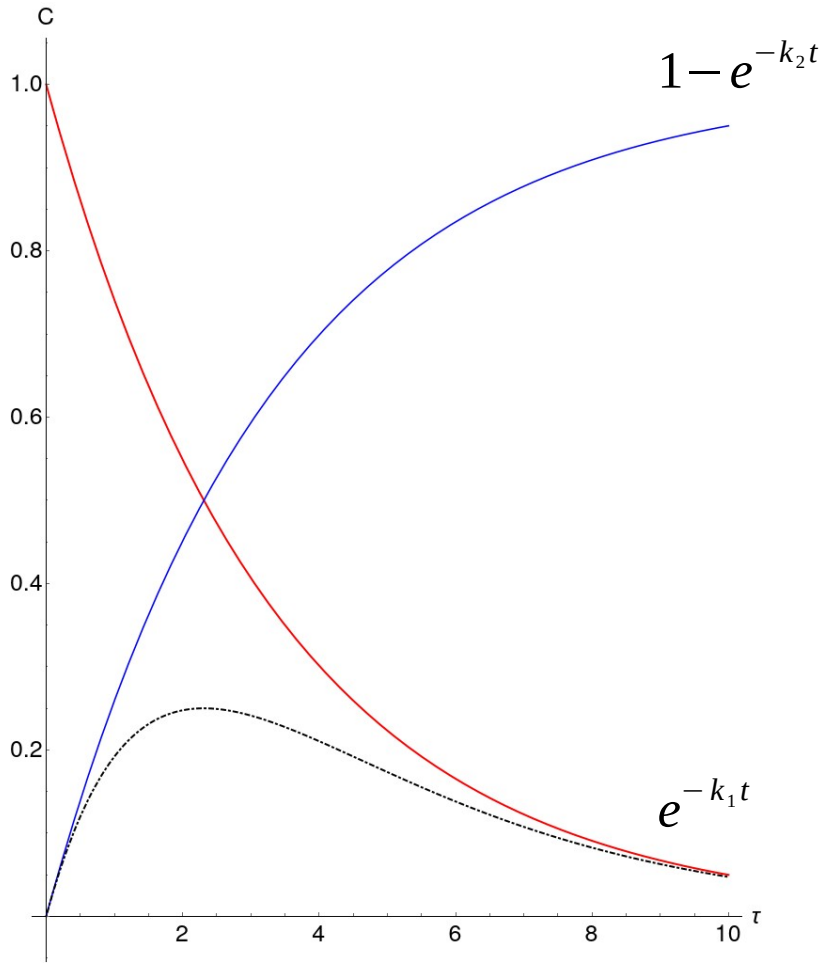

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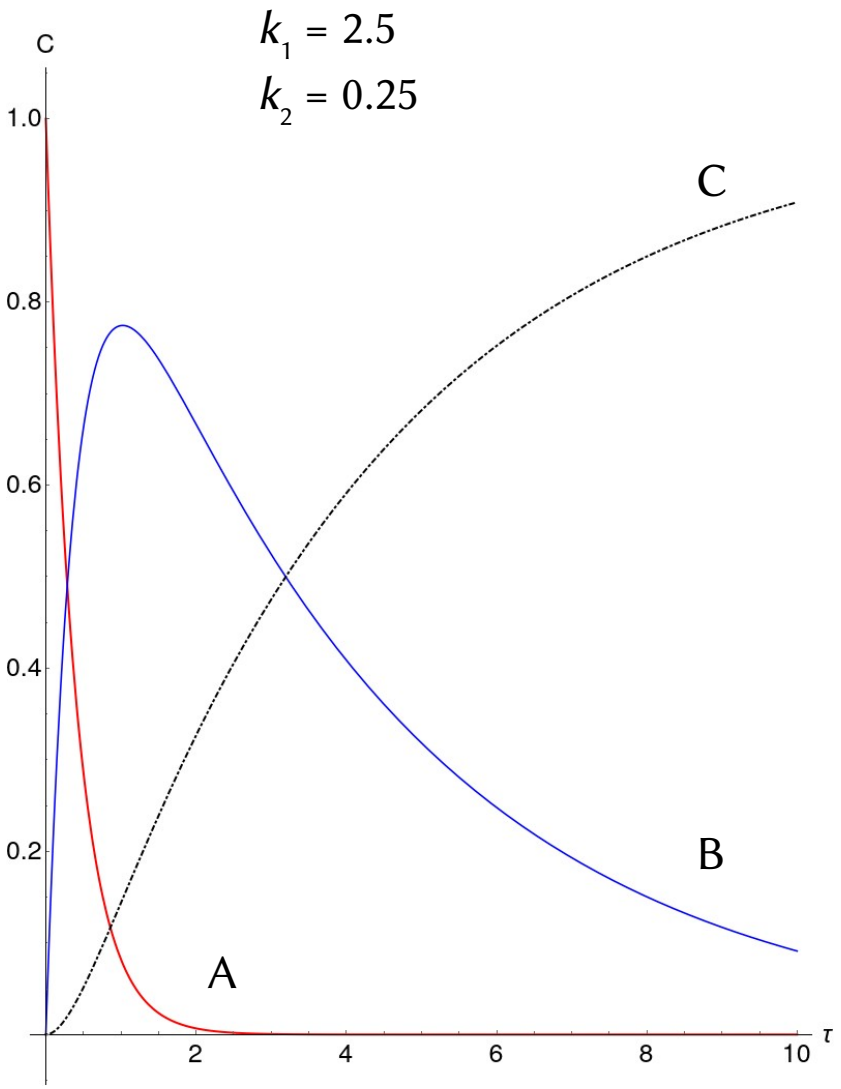

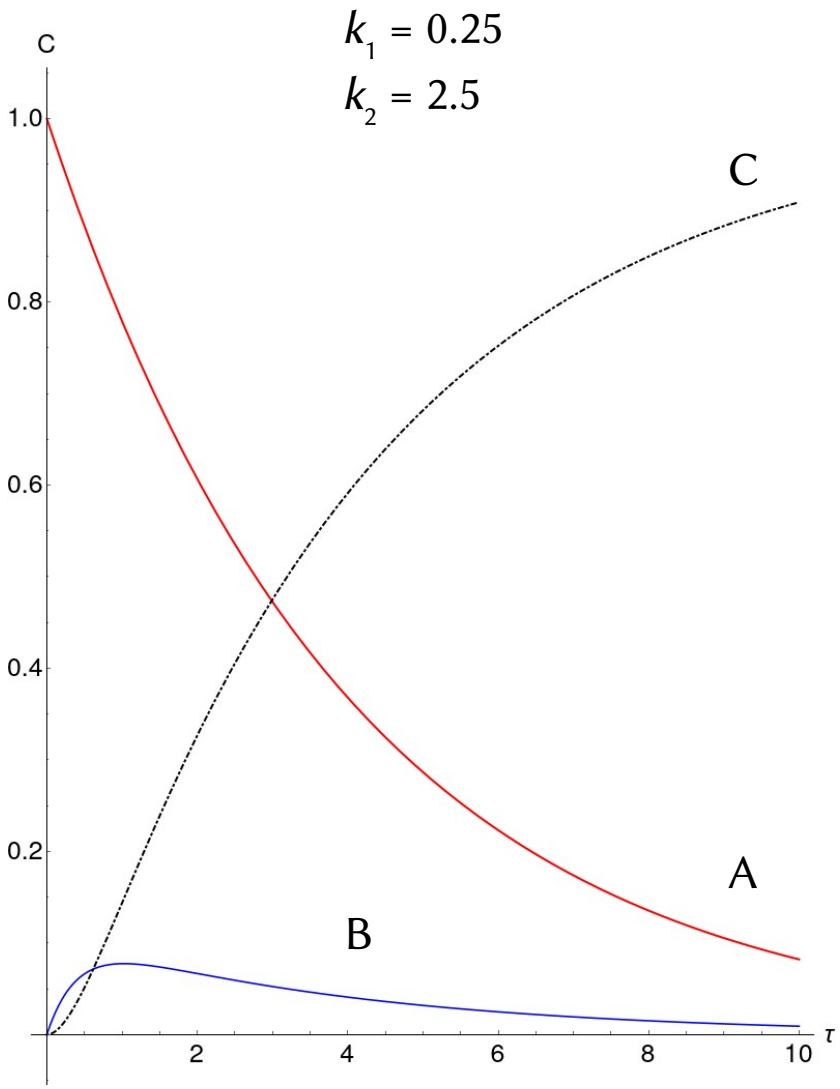

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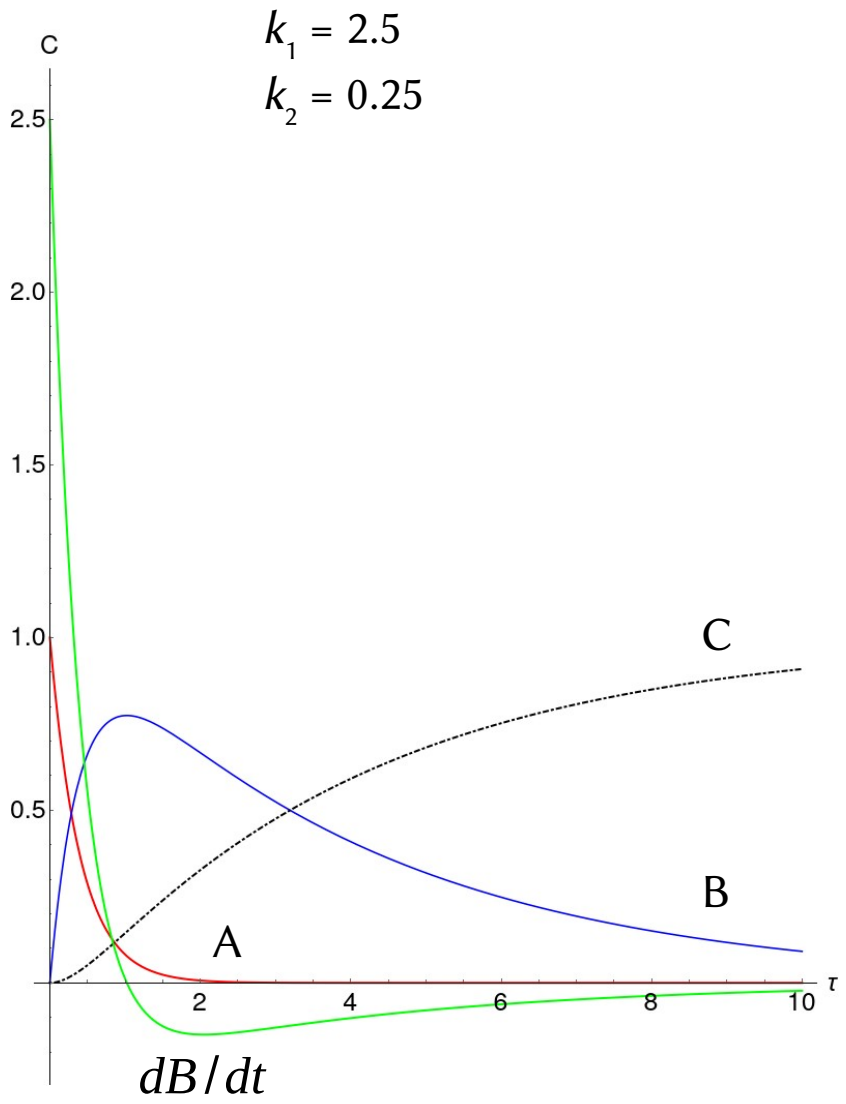

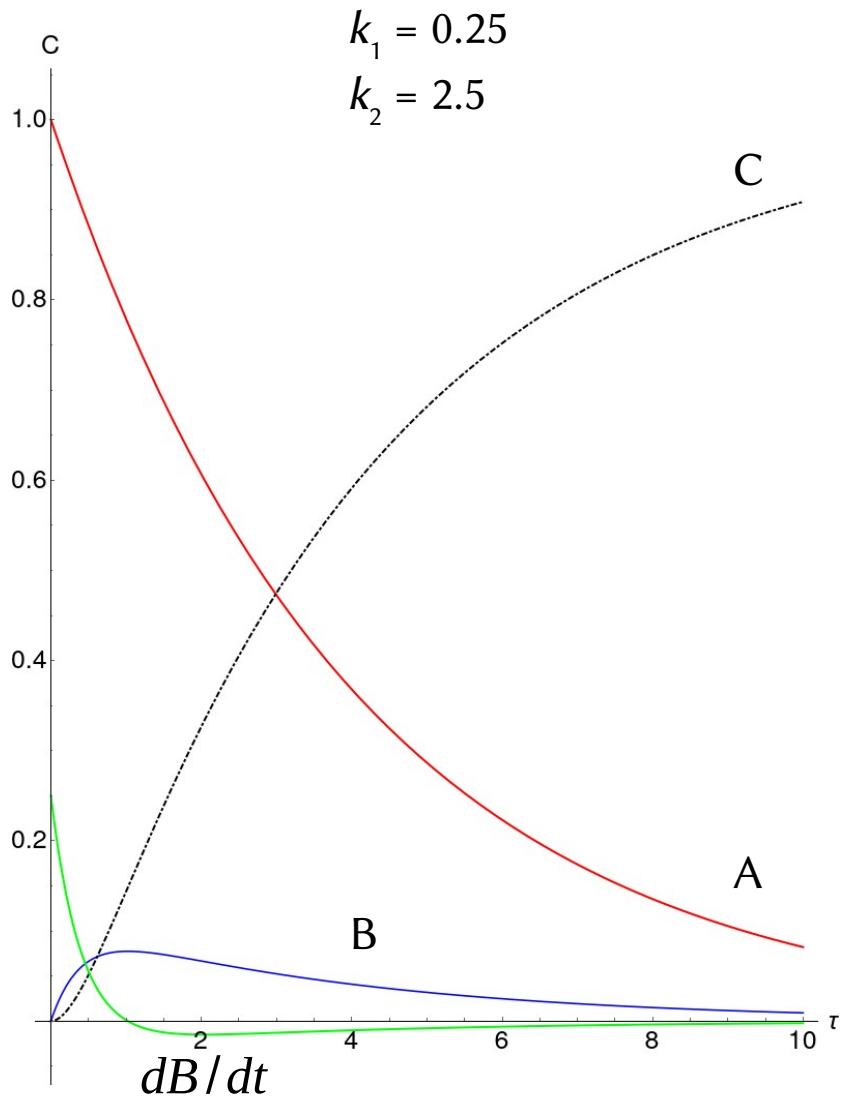

Квазистационарное приближение

$$\frac{d[B]}{dt} \approx 0$$

$$\begin{cases} \frac{d[A]}{dt} = -k_1[A] \\ \frac{d[B]}{dt} = k_1[A] - k_2[B] \\ \frac{d[C]}{dt} = k_2[B] \end{cases} \Longrightarrow \begin{cases} [A] = [A]_0 e^{-k_1 t} \\ [B] = \frac{k_1}{k_2}[A] = \frac{k_1}{k_2}[A]_0 e^{-k_1 t} \\ [C] = [A]_0 - [A] - [B] \end{cases}$$

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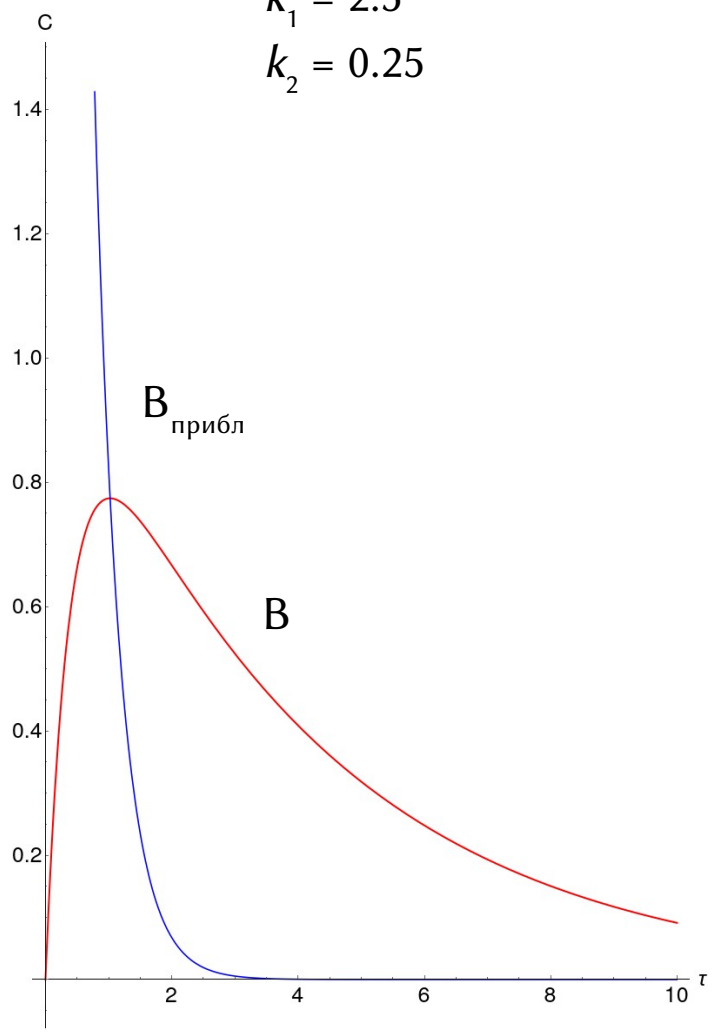
Аналогично можно упростить точное решение

$$[B](t) = \frac{k_1[A]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \Rightarrow [B](t) = \frac{k_1[A]_0}{k_2} e^{-k_1 t}$$

Квазистационарное приближение

$k_1 = 2.5$

$k_2 = 0.25$



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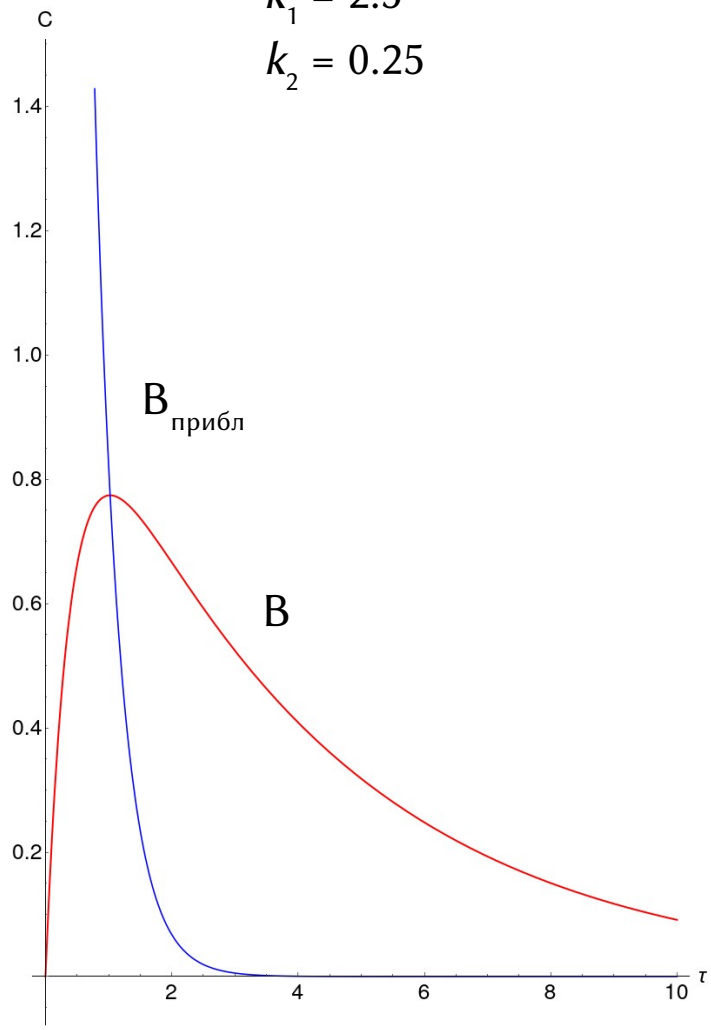
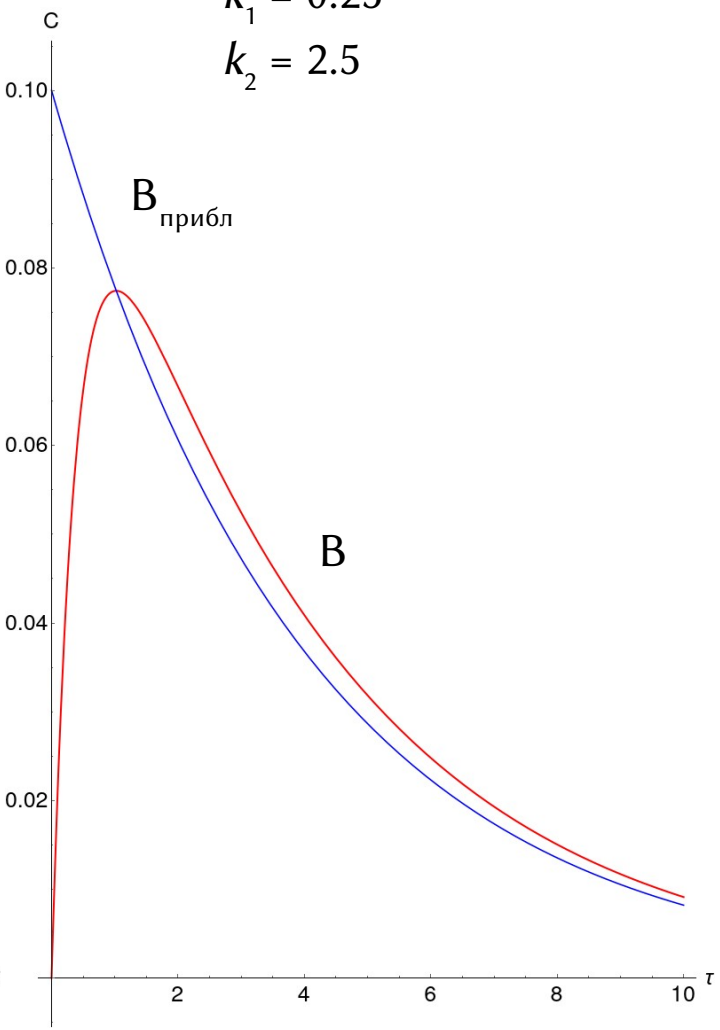


$k_1 = 0.25$
$k_2 = 2.5$



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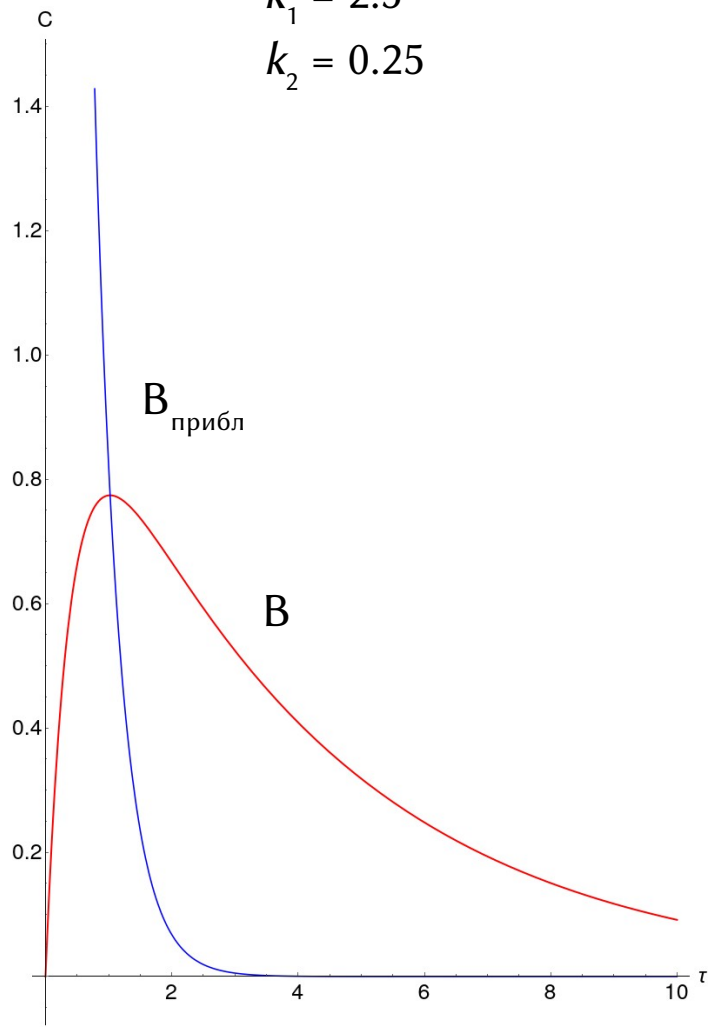

$k_1 = 0.25$
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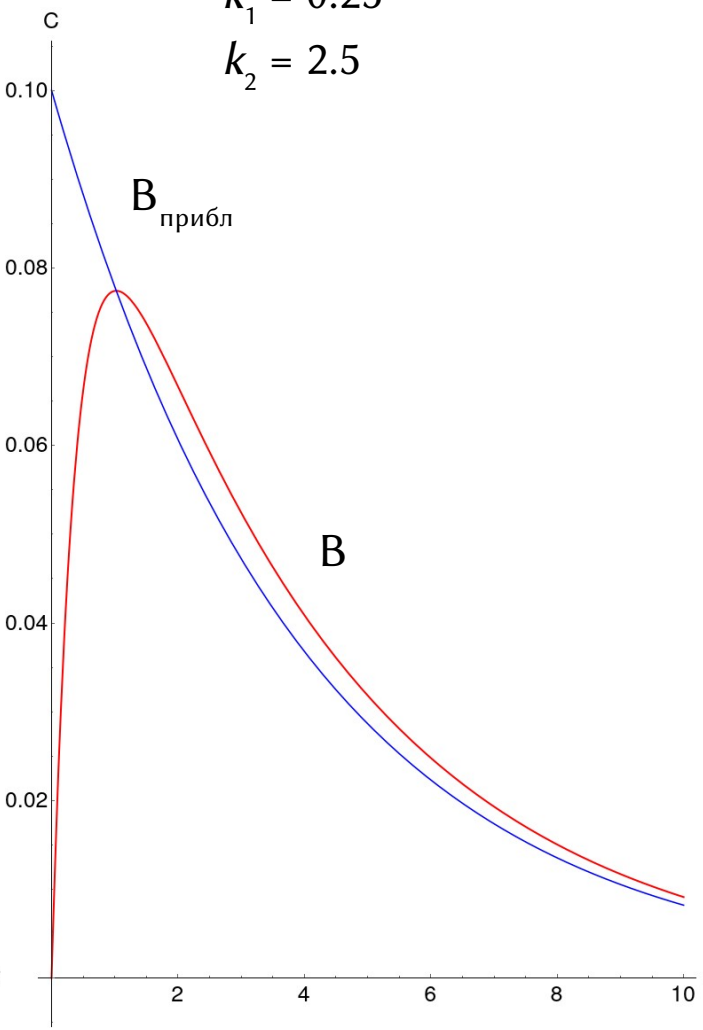
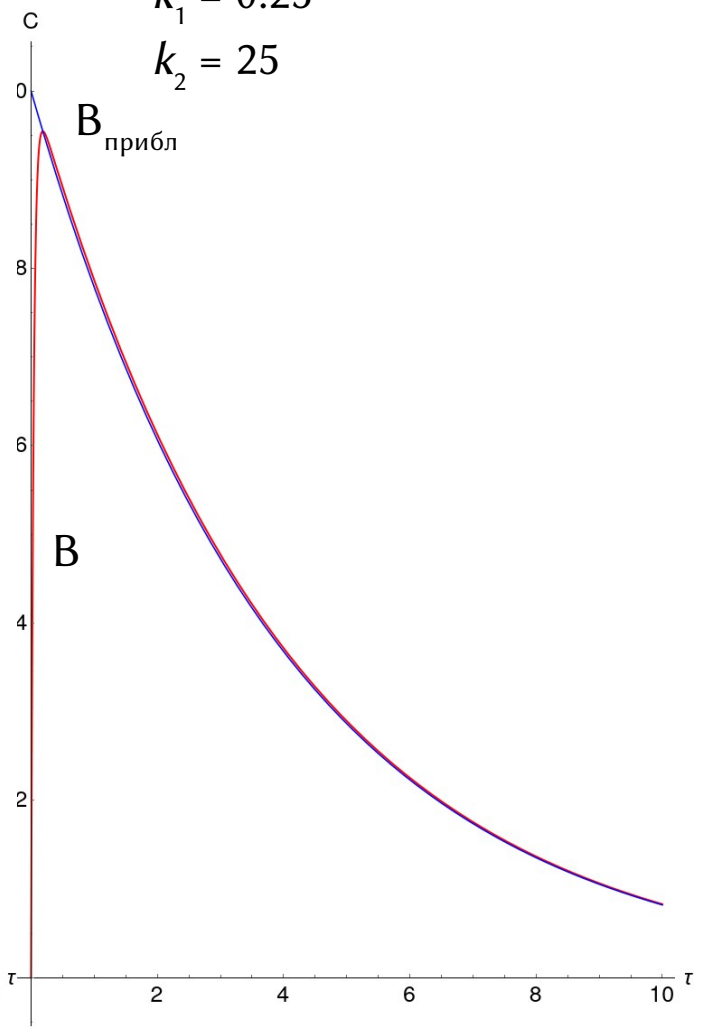


$k_1 = 0.25$
$k_2 = 25$

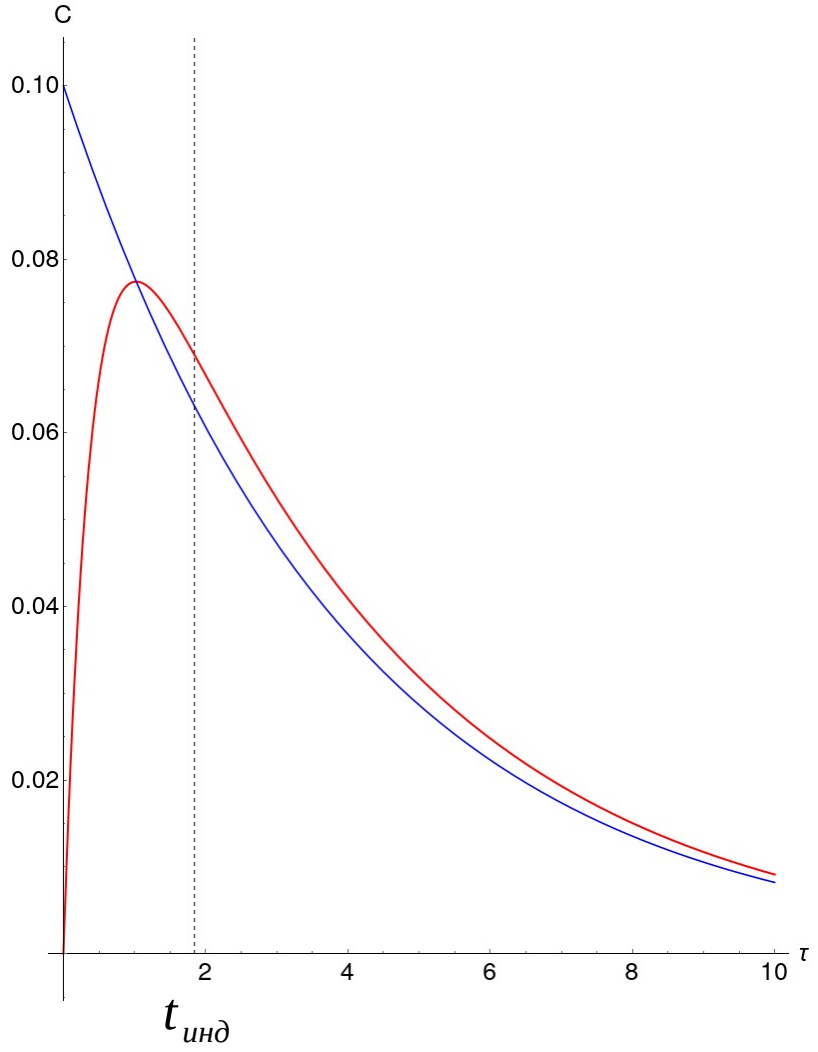


Индукционный период

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

$$\frac{e^{-k_1 t_{инд}}}{e^{-k_2 t_{инд}}}>10^2 \Rightarrow \left(k_2-k_1\right) t_{инд}>2\ln 10$$

$$t_{инд}>\frac{2\ln 10}{k_2-k_1}\approx\frac{2\ln 10}{k_2}$$

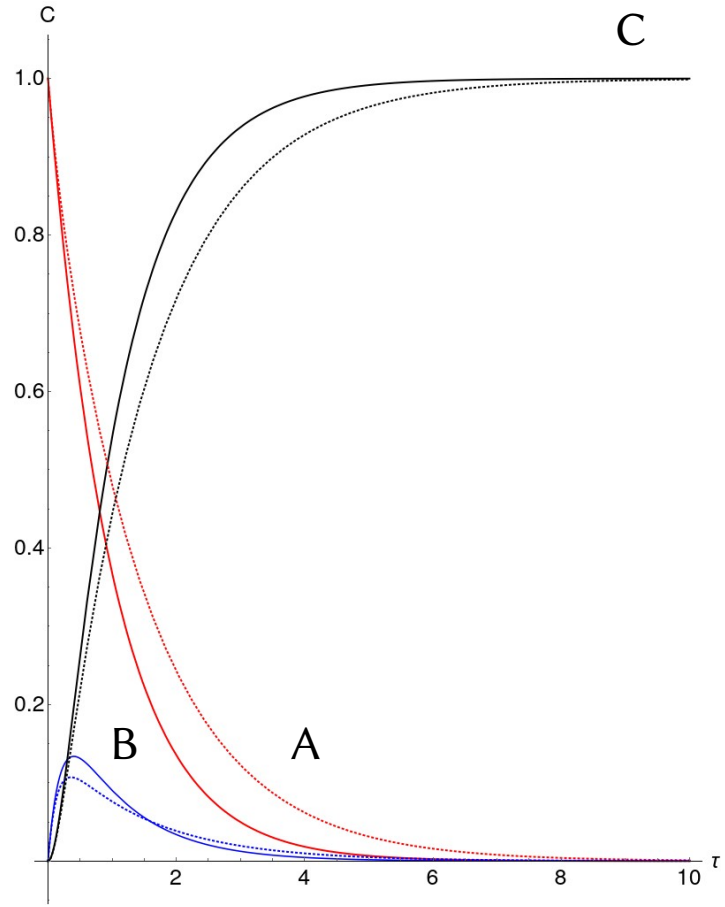


Простые модели

$$\mathbf{A} \leftrightarrow \mathbf{B} \rightarrow \mathbf{C}$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B] = 0$$

$$[B] = \frac{k_1}{k_{-1} + k_2}[A]$$

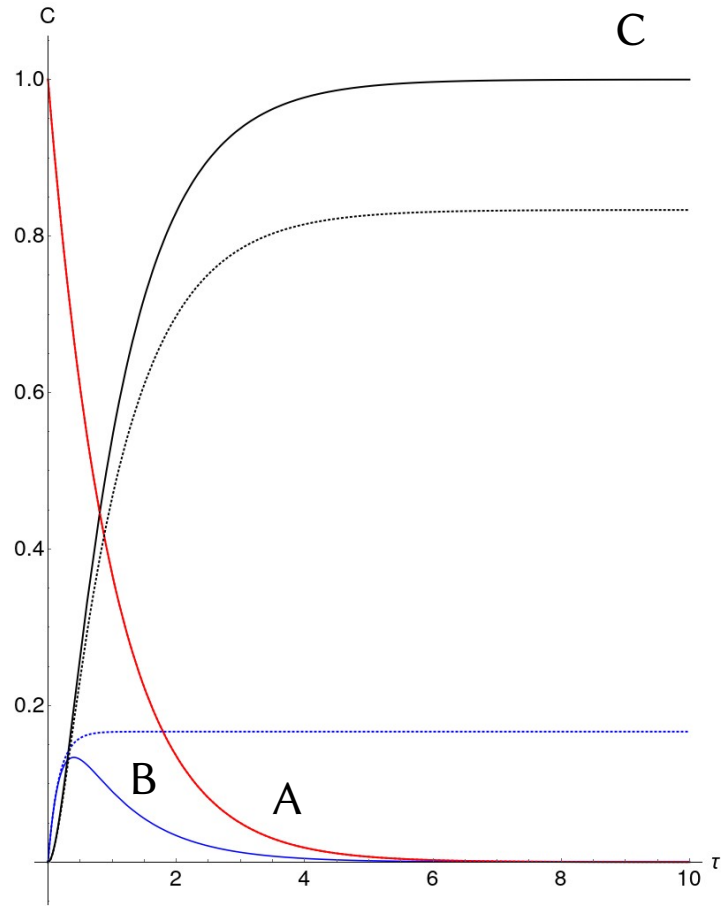


Простые модели

$$\mathbf{A} \rightarrow \mathbf{B} \leftrightarrow \mathbf{C}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] + k_{-2}[C] = 0$$

$$[B] = \frac{k_1[A] + k_{-2}[C]}{k_2}$$



Простые модели

$$\mathbf{A \rightarrow B \leftrightarrow C}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] + k_{-2}[C] = 0$$

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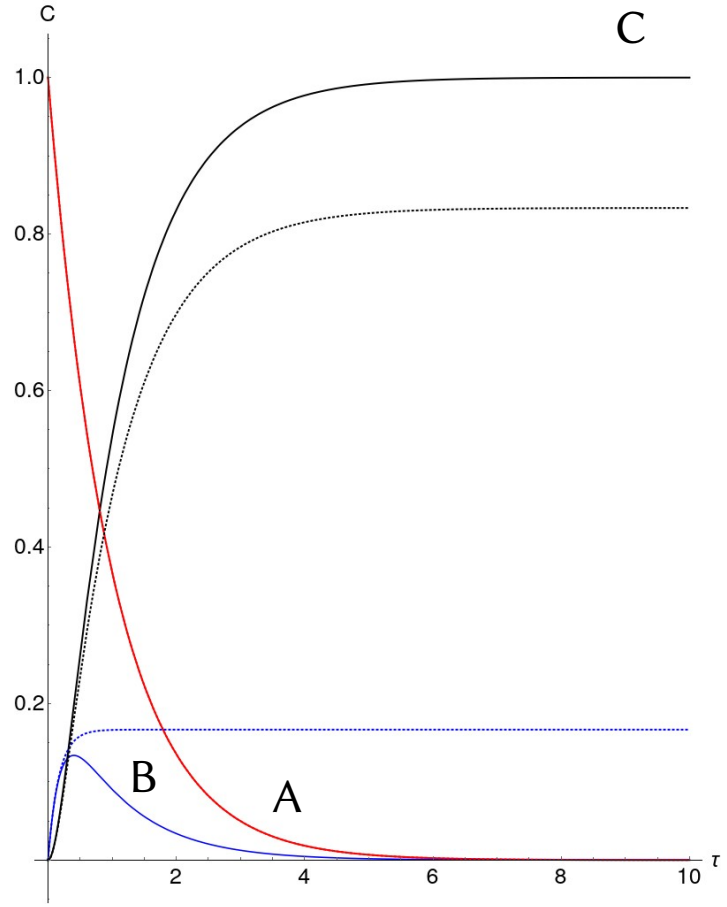

Подумайте самостоятельно, как будут выглядеть кинетические кривые для схемы A ↔ B ↔ C

$H_2 + Br_2$

$Br_2 \longrightarrow 2Br$	k_1
$Br + H_2 \longrightarrow HBr + H$	k_2
$H + Br_2 \longrightarrow HBr + Br$	k_3
$H + HBr \longrightarrow H_2 + Br$	k_4
$2Br \longrightarrow Br_2$	k_5

$$\frac{d[\mathrm{HBr}]}{dt} = ?$$

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$$\frac{d[\mathrm{HBr}]}{dt} = ?$$

$$\frac{d[\mathrm{HBr}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{HBr}][\mathrm{H}]$$

$$\frac{d[\mathrm{Br}]}{dt} = 2\,k_1[\mathrm{Br_2}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{HBr}][\mathrm{H}] - 2\,k_5[\mathrm{Br}]^2 = 0$$

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{HBr}] = 0$$

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$$\frac{d[\mathrm{Br}]}{dt} = 2k_1[\mathrm{Br_2}] - 2k_5[\mathrm{Br}]^2 = 0 \Rightarrow [\mathrm{Br}] = \left(k_1/k_5\right)^{1/2}[\mathrm{Br_2}]^{1/2}$$

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{HBr}][\mathrm{H}] = 0 \Rightarrow [\mathrm{H}] = \frac{k_2\left(k_1/k_5\right)^{1/2}[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]}$$

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$$\frac{d[\mathrm{HBr}]}{dt} = k_2\left(k_1/k_5\right)^{1/2}[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}] + \left(k_3[\mathrm{Br_2}] - k_4[\mathrm{HBr}]\right)\frac{k_2\left(k_1/k_5\right)^{1/2}[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]}$$

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k_2 k_3\left(k_1/k_5\right)^{1/2}[\mathrm{Br_2}]^{3/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]}$$

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В начале реакции $[Br_2] \gg [HBr]$

$$\frac{d[\mathrm{HBr}]}{dt} = k_2 \left(k_1/k_5\right)^{1/2} [\mathrm{Br_2}]^{1/2} [\mathrm{H_2}]$$

В конце реакции $[Br_2] \ll [HBr]$

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k_2 k_3 \left(k_1/k_5\right)^{1/2} [\mathrm{Br_2}]^{3/2} [\mathrm{H_2}]}{k_4[\mathrm{HBr}]}$$

Квазиравновесное приближение

$HA \longrightarrow H^+ + A^-$ k_1

$H^+ + A^- \longrightarrow HA$ k_{-1}

$A^- + B \longrightarrow P$ k_2

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{A}^-][\mathrm{B}]$$

$$K = \frac{k_1}{k_{-1}} = \frac{[\mathrm{H}^+][A^-]}{[\mathrm{HA}]} \Rightarrow [A^-] = \frac{k_1}{k_{-1}} \frac{[\mathrm{HA}]}{[\mathrm{H}^+]}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2 \frac{k_1}{k_{-1}} \frac{[\mathrm{HA}]}{[\mathrm{H}^+]}[\mathrm{B}]$$