PQI-3401 – Engenharia de Reações Químicas II

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Kinetics of Nonelementary Reactions (relation between mechanism and kinetics)

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Kinetics = equation for $\Re = f(C_A, C_B, C_C, ..., T)$

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Elementary reaction

direct transformation of reagents into products (no intermediates)
follows power-law type kinetics ("law of mass action")
reaction order for each reagent = |stoichiometric coeff.|

$$aA + bB \rightarrow cC \qquad \frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{+c} = \Re = k(C_A)^a (C_B)^b$$

Non-elementary reaction

conversion of reagents into products is not "direct"
there are intermediates ($\therefore$ there is a reaction mechanism)
rate equation is empirical (determined from experiments)

$$aA + bB \rightarrow cC \qquad \Re = k(C_A)^\alpha (C_B)^\beta$$

$$\alpha = \text{order de A (not necessarily} = \text{a)}$$

$$\beta = \text{order de B (not necessarily} = \text{b)}$$

$$\Re = \frac{k_1 (C_A)^n (C_B)^m}{1 + k_2 C_A + k_3 C_B}$$

KINETICS OF NONELEMENTARY REACTIONS

Mechanism $\Rightarrow$ Rate equation

Nonelementary reactions - Examples

$$\underbrace{CH_3CHO}_{A} \rightarrow CH_4 + \mathrm{CO} \qquad \Re = (-r_A) = k(C_A)^{3/2}$$

$$\underbrace{H_2}_{A} + \underbrace{I_2}_{B} \rightarrow 2\underbrace{HI}_{C} \qquad \Re = (-r_A) = (-r_B) = \frac{r_c}{2} = \frac{k_1 C_A C_B}{k_2 + k_{31} C_B}$$

$$\underbrace{H_2}_{A} + \underbrace{Br_2}_{B} \rightarrow 2\underbrace{HBr}_{C} \qquad \Re = (-r_A) = (-r_B) = \frac{r_c}{2} = \frac{k_1 C_A C_B{}^{1/2}}{k_2 + (C_C / C_B)}$$

$$\underbrace{N_2}_{A} + 3\underbrace{H_2}_{B} \rightarrow 2\underbrace{NH_3}_{C} \qquad \Re = \frac{r_A}{-1} = \frac{r_B}{-3} = \frac{r_c}{+2} = k_1 C_A$$

$$\underbrace{(CH_3)_2 N_2}_{A} \rightarrow C_2H_6 + N_2 \qquad \begin{cases} \text{at high P} & (-r_A) = k_1 C_A \\ \text{at low P} & (-r_A) = k_1 C_A^2 \end{cases}$$

Reaction Mechanism

Reaction Mechanism is a **set of elementary reaction steps** that **explains how the reactants are converted into the products**.

Besides the reactants and products, the reaction mechanism includes formation and consumption of **active intermediates**

Typical characteristics of an active intermediate:

- **Highly reactive**
- **Very short lifetime (e.g. ~10^{-9} s)**
- **Difficult to measure, very low concentrations**

Examples:

- activated complex
- transition state
- free radicals
- enzyme-substrate complex
- ions

Pseudo-Steady-State Hypothesis (PSSH)

Active intermediate has high reactivity/short lifetime/very low concentration

PSSH Pseudo-Steady-State Hypothesis

QSSH Quasi-Steady-State Hypothesis

HEPE: Hipótese de Estado Pseudo-Estacionário

PSSH: the net rate of formation of an active intermediate is zero.

Consequences:

(1) For each active intermediate, we have an equation : $\mathbf{r_{intermediate,i} = 0}$

(2) We can solve this system of equations to obtain the concentrations of the intermediates as a function of the non-intermediate species (reactants and products) $\mathbf{r_{intermediate,i} = 0 \Rightarrow C_{intermediate,i} = f(C_{reactants} \text{ and } C_{products})}$

(3) We can then substitute the concentrations of the intermediate and eliminate them from the final expression for the rate equation of the reaction (**the final rate equation for the overall reaction must be a function of the concentrations of reactants and products, but not intermediates**)

$$\mathfrak{R}_{global} = f(C_{reactants}, C_{products}, \text{but NOT } C_{intermediates})$$

Nonelementary reactions – An example

Gas-phase decomposition of azomethane. The observed kinetics is:

$$\underbrace{(CH_3)_2N_2}_{A} \rightarrow \underbrace{C_2H_6}_{B} + \underbrace{N_2}_{C} \qquad \begin{cases} \text{at high P} & (-r_A) = kC_A \\ \text{at low P} & (-r_A) = kC_A^2 \end{cases}$$

Let us postulate the following mechanism (series of elementary steps):

$$\begin{cases} \text{(step 1)} & A + A \xrightarrow{k_1} A + A^* \\ \text{(step 2)} & A^* + A \xrightarrow{k_2} A + A \\ \text{(step 3)} & A^* \xrightarrow{k_3} B + C \end{cases}$$

$$\begin{cases} \text{(step } 1 \leftrightarrow 2\text{)} & A + A \underset{k_2}{\overset{k_1}{\rightleftarrows}} A + A^* \\ \text{(step 3)} & A^* \xrightarrow{k_3} B + C \end{cases}$$

Gas-phase decomposition of azomethane $A \rightarrow B + C$

$$\text{(step 1)} \quad A + A \xrightarrow{k_1} A + A^* \qquad R_1 = k_1 C_A^2$$

$$\text{(step 2)} \quad A^* + A \xrightarrow{k_2} A + A \qquad R_2 = k_2 C_A C_{A^*}$$

$$\text{(step 3)} \quad A^* \xrightarrow{k_3} B + C \qquad R_3 = k_3 C_{A^*}$$

$$r_A = \sum_{j=1}^{3} \nu_{A,j} R_j = -2R_1 + R_1 - R_2 + 2R_2 + 0R_3 = -R_1 + R_2 = -k_1 C_A^2 + k_2 C_A C_{A^*}$$

$$r_{A^*} = \sum_{j=1}^{3} \nu_{A^*,j} R_j = +R_1 - R_2 - R_3 = +k_1 C_A^2 - k_2 C_A C_{A^*} - k_3 C_{A^*}$$

$$r_B = \sum_{j=1}^{3} \nu_{B,j} R_j = +0R_1 + 0R_2 + R_3 = R_3 = k_3 C_{A^*}$$

$$r_C = \sum_{j=1}^{3} \nu_{C,j} R_j = +0R_1 + 0R_2 + R_3 = R_3 = k_3 C_{A^*}$$

Gas-phase decomposition of azomethane $A \rightarrow B + C$

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(step 1) $A + A \xrightarrow{k_1} A + A^*$ $\quad R_1 = k_1 C_A^2$

(step 2) $A^* + A \xrightarrow{k_2} A + A$ $\quad R_2 = k_1 C_A C_{A^*}$

(step 3) $A^* \xrightarrow{k_3} B + C$ $\quad R_3 = k_3 C_{A^*}$

$$r_A = \sum_{j=1}^{3} \nu_{A,j} R_j = \overbrace{-2R_1 + R_1}^{-R_1} \overbrace{- R_2 + 2R_2}^{+R_2} + 0R_3 = -R_1 + R_2 = -k_1 C_A^2 + k_2 C_A C_{A^*}$$

A* is an intermediate

$$r_{A^*} = \sum_{j=1}^{3} \nu_{A^*,j} R_j = +R_1 - R_2 + R_3 = +k_1 C_A^2 - k_2 C_A C_{A^*} - k_3 C_{A^*} \overbrace{=}^{PSSH} 0$$

$$r_B = \sum_{j=1}^{3} \nu_{B,j} R_j = +0R_1 + 0R_2 + R_3 = R_3 = k_3 C_{A^*}$$

$$r_C = \sum_{j=1}^{3} \nu_{C,j} R_j = +0R_1 + 0R_2 + R_3 = R_3 = k_3 C_{A^*}$$

$$C_{A^*} = \frac{k_1 C_A^2}{k_3 + k_2 C_A}$$

Gas-phase decomposition of azomethane $A \rightarrow B + C$

$$\text{(step 1)} \quad A + A \xrightarrow{k_1} A + A^* \qquad R_1 = k_1 C_A^2$$

$$\text{(step 2)} \quad A^* + A \xrightarrow{k_2} A + A \qquad R_2 = k_1 C_A C_{A^*}$$

$$\text{(step 3)} \quad A^* \xrightarrow{k_3} B + C \qquad R_3 = k_3 C_{A^*}$$

$$r_A = \sum_{j=1}^{3} \nu_{A,j} R_j = -2R_1 + R_1 - R_2 + 2R_2 + 0R_3 = -R_1 + R_2 = -k_1 C_A^2 + k_2 C_A C_{A^*}$$

$$r_{A^*} = \sum_{j=1}^{3} \nu_{A^*,j} R_j = +R_1 - R_2 + R_3 = +k_1 C_A^2 - k_2 C_A C_{A^*} - k_3 C_{A^*} \overbrace{=}^{PSSH} 0$$

$$C_{A^*} = \frac{k_1 C_A^2}{k_3 + k_2 C_A}$$

$$r_B = \sum_{j=1}^{3} \nu_{B,j} R_j = +0R_1 + 0R_2 + R_3 = R_3 = k_3 C_{A^*}$$

$$r_C = \sum_{j=1}^{3} \nu_{C,j} R_j = +0R_1 + 0R_2 + R_3 = R_3 = k_3 C_{A^*}$$

Gas-phase decomposition of azomethane $A \rightarrow B + C$

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$$\text{(step 1)} \quad A + A \xrightarrow{k_1} A + A^* \qquad R_1 = k_1 C_A^2$$

$$\text{(step 2)} \quad A^* + A \xrightarrow{k_2} A + A \qquad R_2 = k_1 C_A C_{A^*}$$

$$\text{(step 3)} \quad A^* \xrightarrow{k_3} B + C \qquad R_3 = k_3 C_{A^*}$$

$$r_{A^*} = +k_1 C_A^2 - k_2 C_A C_{A^*} - k_3 C_{A^*} \overbrace{=}^{PSSH} 0 \Rightarrow C_{A^*} = \frac{k_1 C_A^2}{k_3 + k_2 C_A}$$

$$r_A = -k_1 C_A^2 + k_2 C_A C_{A^*} \Rightarrow r_A = \frac{-k_3 k_1 C_A^2}{k_3 + k_2 C_A}$$

$$r_B = k_3 C_{A^*} \Rightarrow r_B = \frac{k_3 k_1 C_A^2}{k_3 + k_2 C_A}$$

$$r_C = k_3 C_{A^*} \Rightarrow r_C = \frac{k_3 k_1 C_A^2}{k_3 + k_2 C_A}$$

$$(-r_A) = +r_B = +r_C = \frac{k_3 k_1 C_A^2}{k_3 + k_2 C_A}$$

Gas-phase decomposition of azomethane $A \rightarrow B + C$

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$$\left.\begin{array}{ll}
\text{(step 1)} & A + A \xrightarrow{k_1} A + A^* \\
\text{(step 2)} & A^* + A \xrightarrow{k_2} A + A \\
\text{(step 3)} & A^* \xrightarrow{k_3} B + C
\end{array}\right\} \quad (-r_A) = +r_B = +r_C = \frac{k_3 k_1 C_A^2}{k_3 + k_2 C_A}$$

$$\text{high P} \Rightarrow \text{high } C_A \Rightarrow k_2 C_A >> k_3 \Rightarrow$$

$$\Rightarrow (-r_A) = \frac{k_3 k_1 C_A^2}{\cancel{k_3} + k_2 C_A} \cong \frac{k_3 k_1 C_A^2}{k_2 C_A} = \left(\frac{k_3 k_1}{k_2}\right) C_A \Rightarrow \text{1st order}$$

$$\text{low P} \Rightarrow \text{low } C_A \Rightarrow k_2 C_A << k_3 \Rightarrow$$

$$\Rightarrow (-r_A) = \frac{k_3 k_1 C_A^2}{k_3 + \cancel{k_2 C_A}} \cong \frac{k_3 k_1 C_A^2}{k_3} = k_1 C_A^2 \qquad \Rightarrow \text{2nd order}$$

$$C_A = \frac{y_A P}{RT} \qquad (P\uparrow \Rightarrow C_A \uparrow)$$

Kinetics of Nonelementary Reactions

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MECHANISM $\Rightarrow$ RATE LAW

but

Rate Law $\not\Rightarrow$ Mechanism

rate law may help to propose a mechanism or to discard a mechanism (but it is not enough to confirm a given mechanism)

if the rate law derived from the mechanism is able to explain the experimental data, this is an evidence (not a confirmation) that the mechanism is true

PSSH, QSSH for all active intermediates

$$R_{intermediate,i} = 0 \Rightarrow C_{intermediate,i} = f_i(C_{reactants}, C_{products})$$

Other possible hypotheses:

- *rate-limiting step*
- *steps at quasi-equilibrium*

Kinetics of Nonelementary Reactions (Fogler, Chapter 7)

Recommended exercises:

P-7.4

P-7.5

P-7.3

P-7.7

P-7.8 (** COVID)

P-7.5 (Fogler) Oxidation of NO. The observed kinetics is:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (-r_{NO}) = kC_{NO}^2 C_{O2} \qquad \underbrace{k\downarrow \text{ when } T\uparrow}_{\text{anomalous behavior(??)}}$$

Let us postulate the following mechanism (series of elementary steps):

$$\begin{cases} \text{(step 1)} & NO + O_2 \xrightarrow{k_1} NO_3 \\ \text{(step 2)} & NO_3 \xrightarrow{k_2} NO + O_2 \\ \text{(step 3)} & NO + NO_3 \xrightarrow{k_3} 2NO_2 \end{cases}$$

Verify whether the above proposed mechanism can explain the experimental observations.

P-7.5 (Fogler) Oxidation of NO. The observed kinetics is:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (-r_{NO}) = kC_{NO}^2 C_{O2}$$

$\underbrace{\text{k}\downarrow \text{ when } \text{T}\uparrow}_{\text{anomalous behavior (??)}}$

Let us postulate the following mechanism (series of elementary steps):

$$\begin{cases} \text{(step 1)} & NO + O_2 \xrightarrow{k_1} NO_3 & R_1 = k_1 C_{NO} C_{O2} \\ \text{(step 2)} & NO_3 \xrightarrow{k_2} NO + O_2 & R_2 = k_2 C_{NO3} \\ \text{(step 3)} & NO + NO_3 \xrightarrow{k_3} 2NO_2 & R_3 = k_3 C_{NO} C_{NO3} \end{cases}$$

$$r_{NO3} = +R_1 - R_2 - R_3 = +k_1 C_{NO} C_{O2} - k_2 C_{NO3} - k_3 C_{NO} C_{NO3} \overbrace{= 0}^{PSSH}$$

$$r_{NO} = -R_1 + R_2 - R_3 = -k_1 C_{NO} C_{O2} + k_2 C_{NO3} - k_3 C_{NO} C_{NO3}$$

$$r_{O2} = -R_1 + R_2 = -k_1 C_{NO} C_{O2} + k_2 C_{NO3}$$

$$r_{NO2} = +2R_3 = +2k_3 C_{NO} C_{NO3}$$

P-7.5 (Fogler) Oxidation of NO. The observed kinetics is:

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$$2NO + O_2 \rightarrow 2NO_2 \qquad (-r_{NO}) = kC_{NO}^2 C_{O2}$$

$\underbrace{k \downarrow \text{ when } T \uparrow}_{\text{anomalous behavior (??)}}$

Let us postulate the following mechanism (series of elementary steps):

$$\begin{cases} \text{(step 1)} & NO + O_2 \xrightarrow{k_1} NO_3 & R_1 = k_1 C_{NO} C_{O2} \\ \text{(step 2)} & NO_3 \xrightarrow{k_2} NO + O_2 & R_2 = k_2 C_{NO3} \\ \text{(step 3)} & NO + NO_3 \xrightarrow{k_3} 2NO_2 & R_3 = k_3 C_{NO} C_{NO3} \end{cases}$$

$$r_{NO3} = +R_1 - R_2 - R_3 = +k_1 C_{NO} C_{O2} - k_2 C_{NO3} - k_3 C_{NO} C_{NO3} \overbrace{=}^{PSSH} 0$$

$$r_{NO} = -R_1 + R_2 - R_3 = -k_1 C_{NO} C_{O2} + k_2 C_{NO3} - k_3 C_{NO} C_{NO3}$$

$$r_{O2} = -R_1 + R_2 = -k_1 C_{NO} C_{O2} + k_2 C_{NO3}$$

$$r_{NO2} = +2R_3 = +2k_3 C_{NO} C_{NO3}$$

Solve this PSSH equation for C_{NO3} and substitute the result in the other equations to eliminate C_{NO3}

Oxidation of NO. The observed kinetics is:

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$$2NO + O_2 \rightarrow 2NO_2 \qquad (-r_{NO}) = kC_{NO}^2 C_{O2} \qquad \underbrace{k\downarrow \quad \text{when} \quad T\uparrow}_{\text{anomalous behavior(??)}}$$

mechanism

$$\left.\begin{array}{ll} \text{(step 1)} & NO + O_2 \xrightarrow{k_1} NO_3 \\ \text{(step 2)} & NO_3 \xrightarrow{k_2} NO + O_2 \\ \text{(step 3)} & NO + NO_3 \xrightarrow{k_3} 2NO_2 \end{array}\right\} \Re = \frac{r_{NO}}{-2} = \frac{r_{O2}}{-1} = \frac{r_{NO2}}{+2} = \frac{k_3 k_1 C_{NO}^2 C_{O2}}{k_2 + k_3 C_{NO}}$$

$$\Re = \frac{k_3 k_1 C_{NO}^2 C_{O2}}{k_2 + k_3 C_{NO}} \xrightarrow{\text{if } k_2 >> k_3 C_{NO}} \Re = \frac{k_3 k_1 C_{NO}^2 C_{O2}}{k_2}$$

$$k_{app} = \frac{k_3 k_1}{k_2} = \frac{k_{30}\exp\left(\frac{-E_3}{RT}\right) k_{10}\exp\left(\frac{-E_1}{RT}\right)}{k_{20}\exp\left(\frac{-E_2}{RT}\right)} = \frac{k_{30}k_{10}}{k_{20}}\exp\left(\frac{-(E_3 + E_1 - E_2)}{RT}\right)$$

$$E_{app} = E_3 + E_1 - E_2 \quad \Rightarrow \quad \text{if } \boxed{E_3 + E_1 < E_2} \text{ then } E_{app} < 0 \Rightarrow \boxed{\text{if } T\uparrow \text{ then } k_{app}\downarrow}$$

Understanding the meaning of the PSSH

Pseudo-Steady-State Hypothesis (PSSH)

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

$x=C_A/C_{Ao}$, $y=C_B/C_{Ao}$, $w=C_C/C_{Ao}$

$$\frac{dx}{dt} = -k_1 x$$

$$\frac{dy}{dt} = k_1 x - k_2 y$$

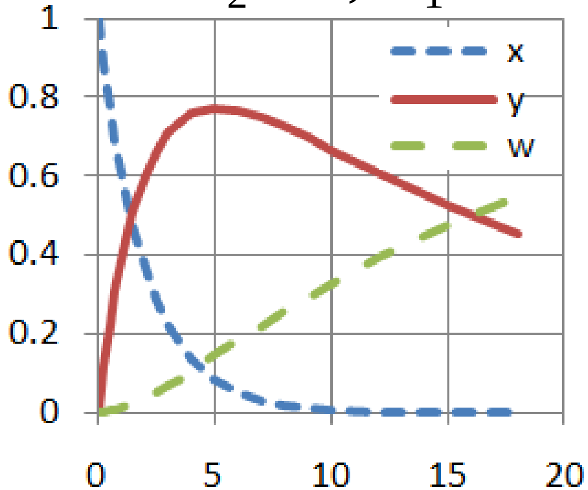
$$\frac{dw}{dt} = k_2 y$$

$$x = \exp(-k_1 t)$$

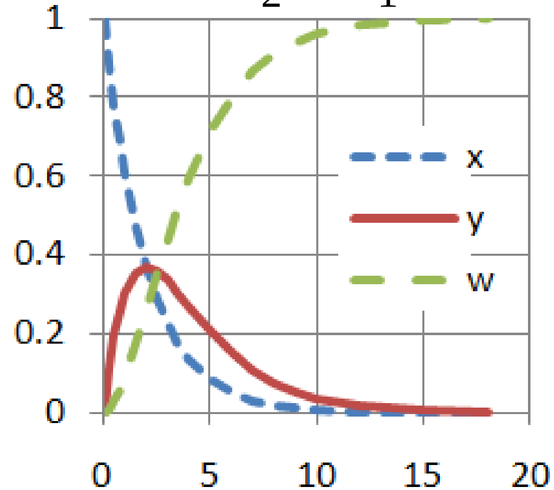
$$y = \frac{k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right]$$

$$w = 1 - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) + \frac{k_1}{k_2 - k_1}\exp(-k_2 t)$$

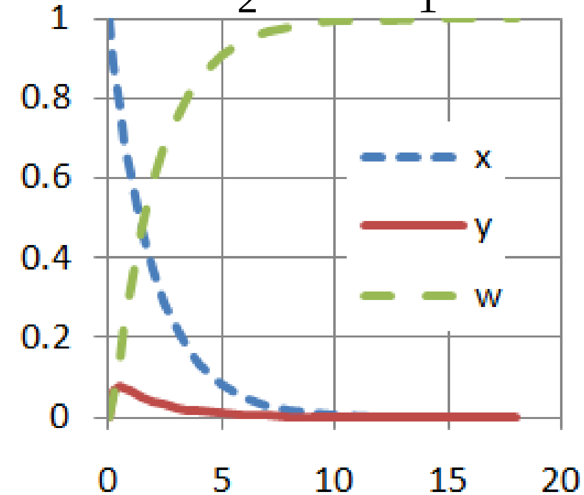
$k_2 = 0{,}1k_1$



$k_2 = k_1$



$k_2 = 10k_1$



Davis & Davis, *Fundamentals of Chemical Reaction Engineering*, McGraw Hill, 1st ed., 2003

Pseudo-Steady-State Hypothesis (PSSH)

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad k_2 >> k_1. \qquad k_1/k_2 \to 0$$

$$x = \exp(-k_1 t)$$

$$y = \frac{k_1}{k_2}\exp(-k_1 t)$$

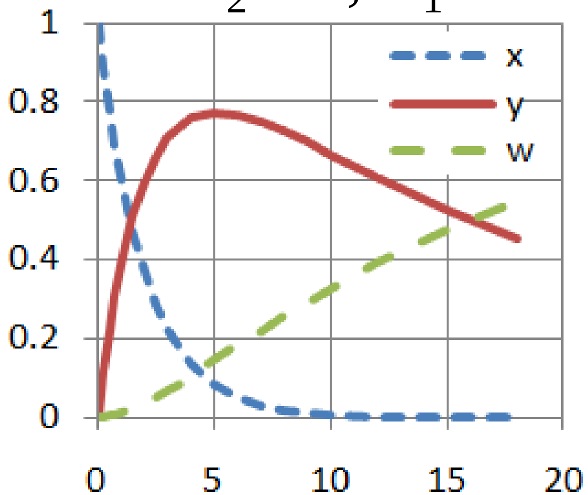
$$w = 1 - \exp(-k_1 t)$$

$$\frac{dx}{dt} = -k_1 x$$

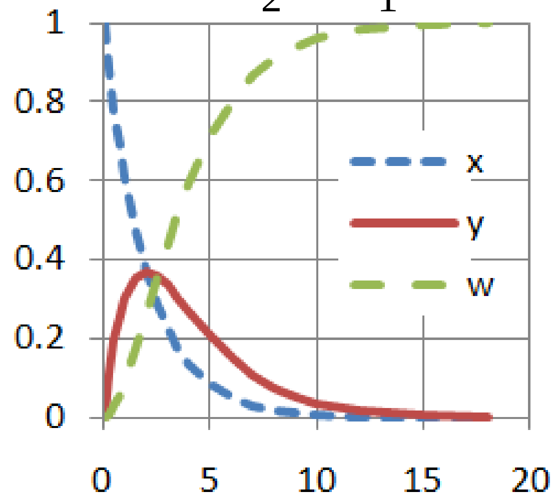
$$0 = k_1 x - k_2 y$$

$$\frac{dw}{dt} = k_2 y$$

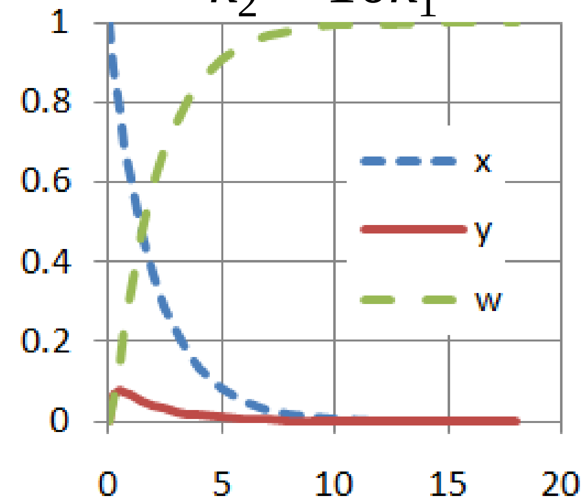
$k_2 = 0{,}1k_1$



$k_2 = k_1$



$k_2 = 10k_1$



Davis & Davis, *Fundamentals of Chemical Reaction Engineering*, McGraw Hill, 1st ed., 2003