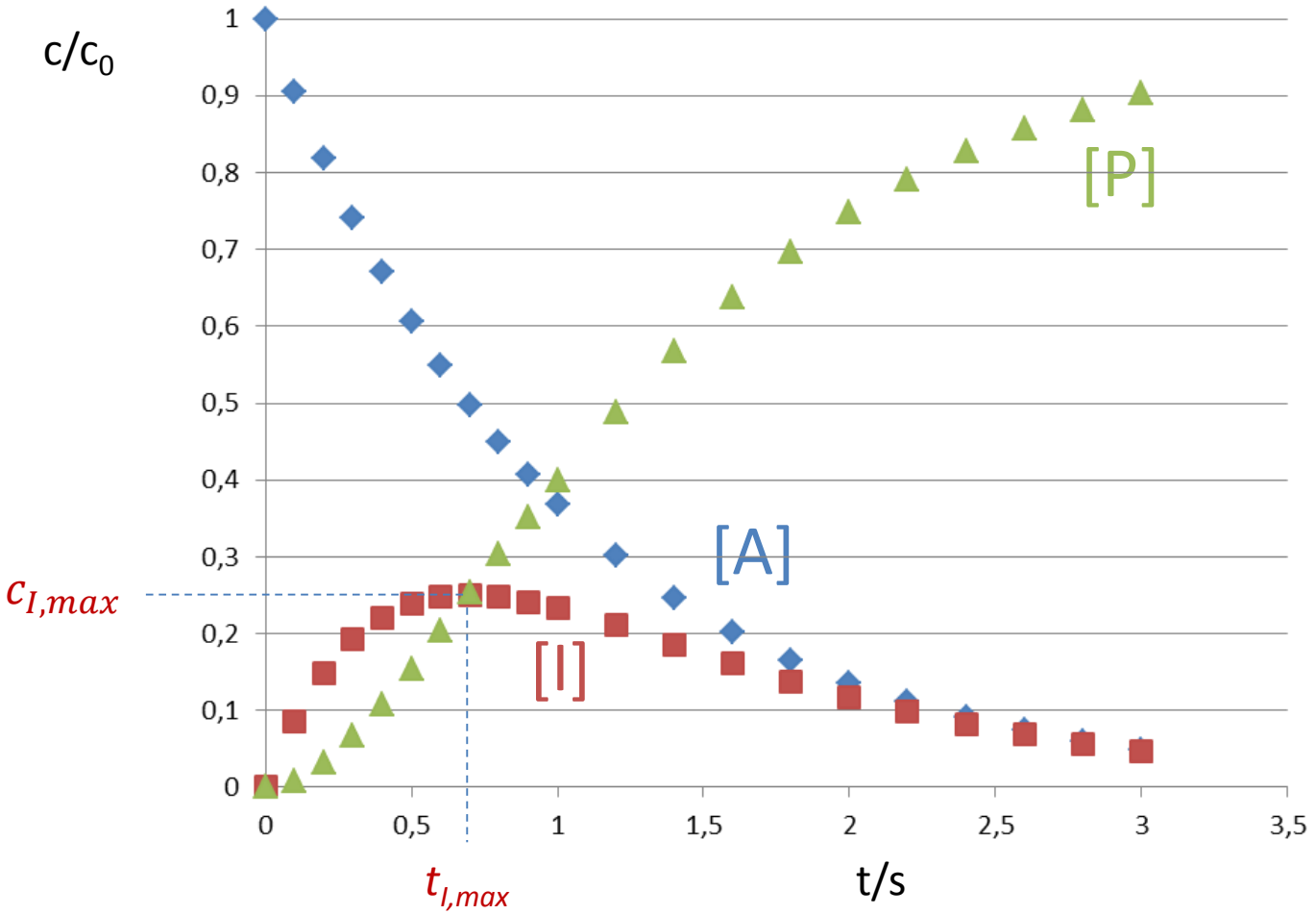
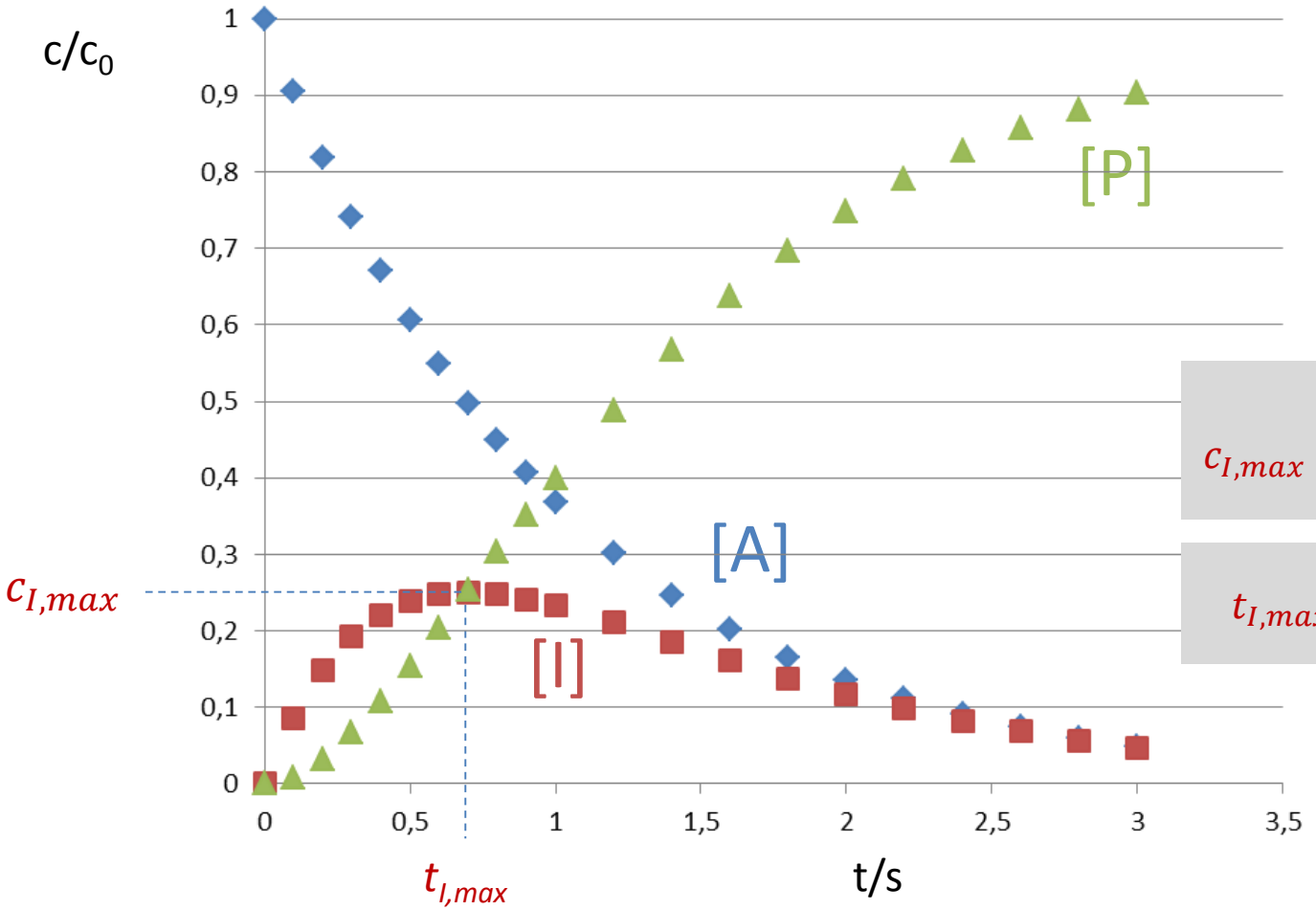
Folgereaktionen

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



Folgereaktionen

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



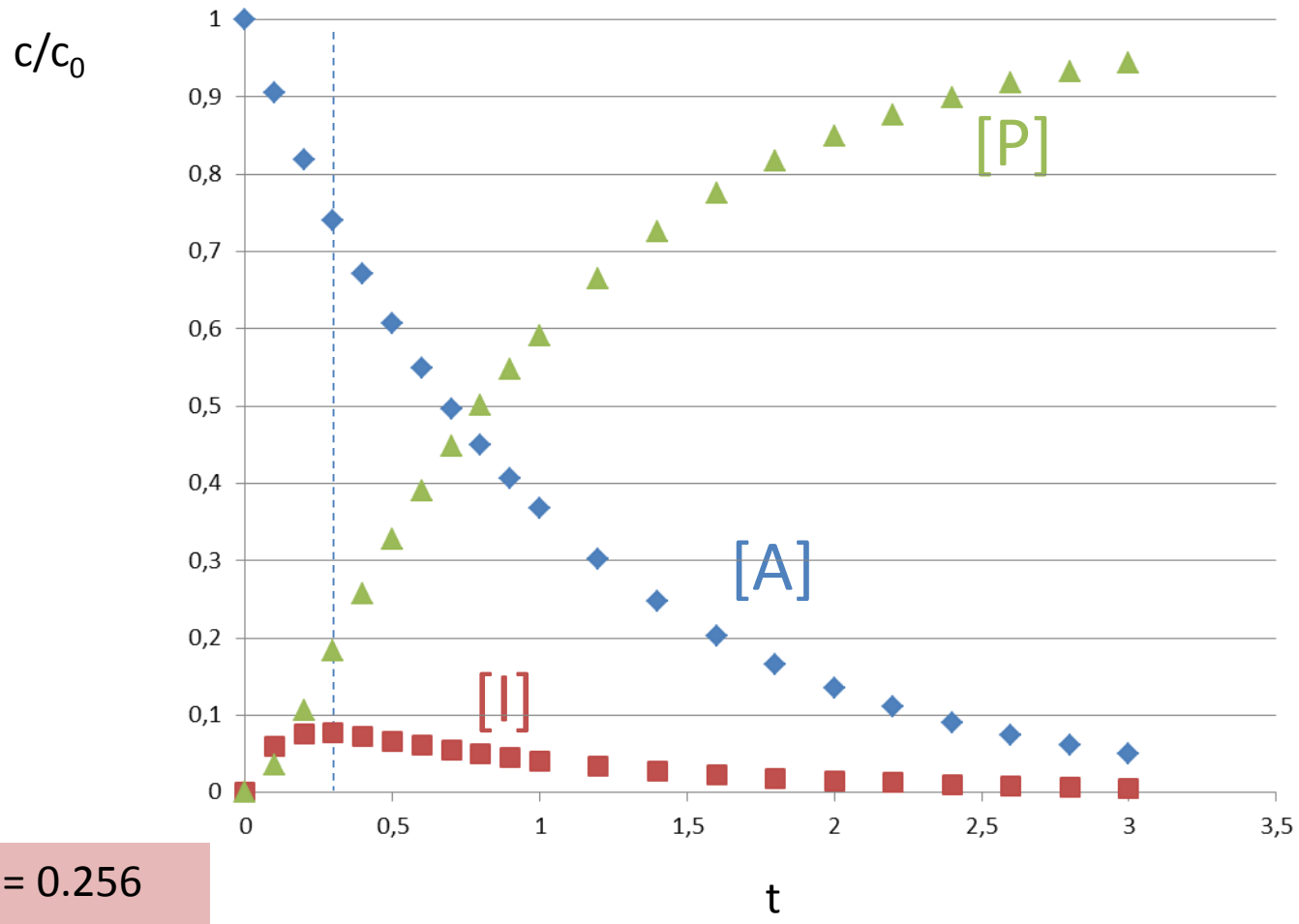
$$k_1 = 1/s$$

$$k_2 = 2/s$$

$$c_{I,max} = c_{A,0}\left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2-k_1}\right)}$$

$$t_{I,max} = \frac{1}{k_2 - k_1} ln \frac{k_2}{k_1}$$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



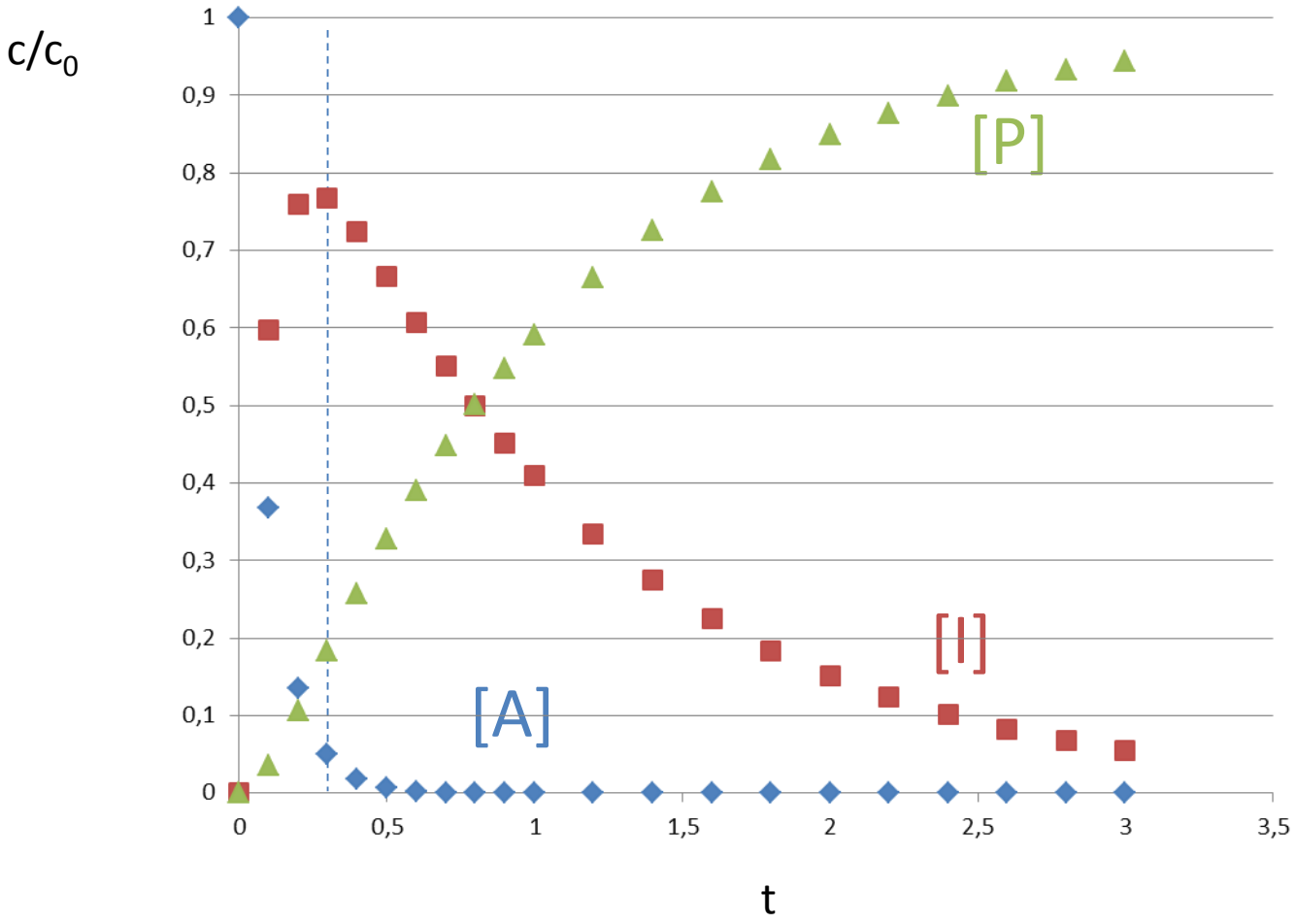
$k_1 = 1/s$

$k_2 = 10/s$

$t_{I,max} = 0.256$

$c_{I,max} = c_{A,0} \cdot (0.08)$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



$$k_1 = 10/s$$

$$k_2 = 1/s$$

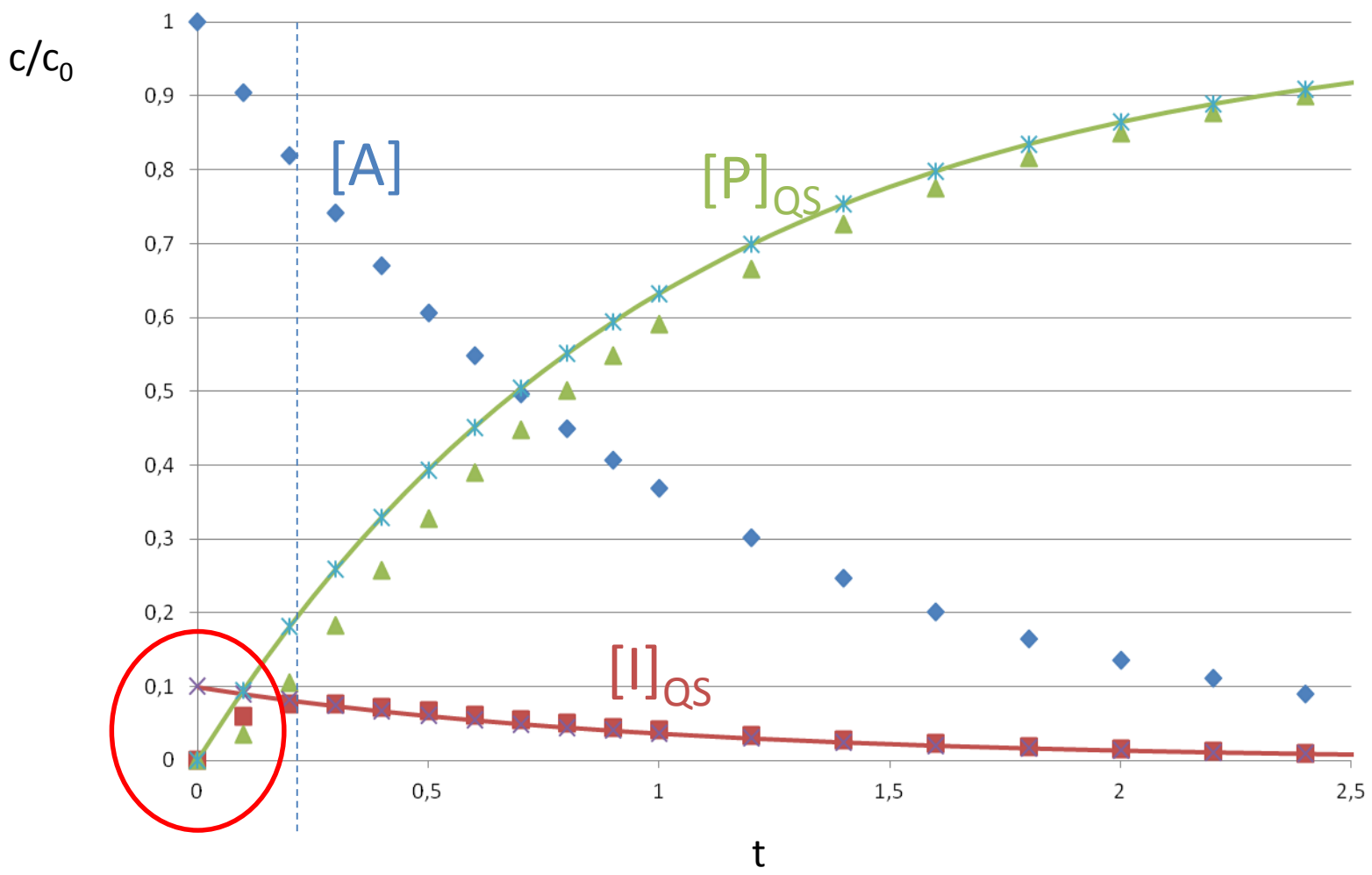
Quasistationaritätsprinzip

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

$$[I] \approx const \quad \Longrightarrow \quad \frac{d[I]}{dt} \approx 0$$

Max Bodenstein (1871-1942)

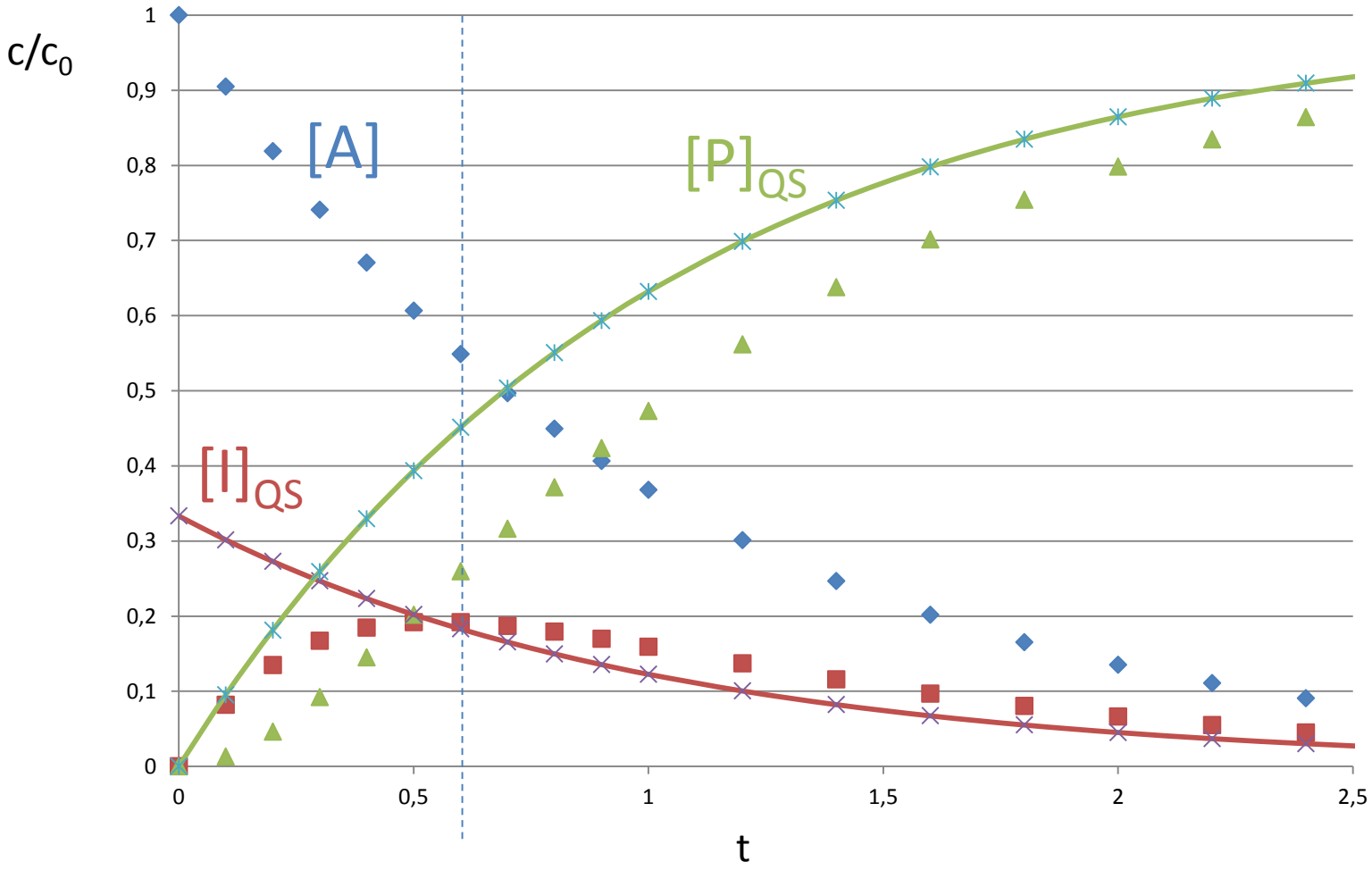
$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



$k_1 = 1/s$

$k_2 = 10/s$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



$k_1 = 1/s$

$k_2 = 3/s$

Iodwasserstoffreaktion

$$H_2 + I_2 \rightarrow 2HI$$

$$\frac{d[HI]}{dt} = 2k'[I_2][H_2]$$

Bodenstein, 1899

Max Bodenstein (1871-1942)

$I_2 \rightleftharpoons I + I$

$I + H_2 \rightleftharpoons IH_2$

$I + IH_2 \longrightarrow HI + HI$

J. Sullivan, *Journal of Chemical Physics* **1967,** *46*, 73-78

Iodwasserstoffreaktion

$$[IH_2] = \frac{k_2[H_2]\sqrt{k_1[I_2]}}{k_{-2}\sqrt{k_{-1}} + k_3\sqrt{k_1[I_2]}} \qquad [I] = \sqrt{\frac{k_1}{k_{-1}}[I_2]}$$

$$\frac{d[HI]}{dt} = 2k_3[I][IH_2] = 2k_3\sqrt{\frac{k_1}{k_{-1}}[I_2]}\left(\frac{k_2[H_2]\sqrt{k_1[I_2]}}{k_{-2}\sqrt{k_{-1}} + k_3\sqrt{k_1[I_2]}}\right)$$

(exakte Lösung)

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I + I$$

$$I + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} IH_2$$

$$I + IH_2 \xrightarrow{k_3} HI + HI$$

J. Sullivan, *Journal of Chemical Physics* **1967,** *46*, 73-78

Iodwasserstoffreaktion

Bodenstein: $$\frac{d[HI]}{dt} = k'[I_2][H_2]$$

Sullivan: $$\frac{d[HI]}{dt} = 2k_3\sqrt{\frac{k_1}{k_{-1}}[I_2]}\left(\frac{k_2[H_2]\sqrt{k_1[I_2]}}{k_{-2}\sqrt{k_{-1}} + k_3\sqrt{k_1[I_2]}}\right)$$

Für schnelle GG (K_1, K_2): $$\frac{d[HI]}{dt} =$$

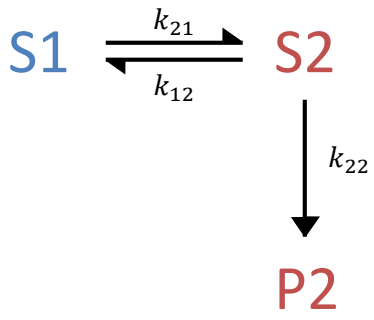
$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I + I$$

$$I + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} IH_2$$

$$I + IH_2 \xrightarrow{k_3} HI + HI$$

J. Sullivan, 1967

Matrizenformulierung für chemische Reaktionen



$$\boldsymbol{T} = \begin{bmatrix} -k_{21} & k_{12} \\ k_{21} & -(k_{12} + k_{22}) \end{bmatrix}$$

$$\overrightarrow{[S]}'(t) = \boldsymbol{T}\overrightarrow{[S]}(t)$$

Lösungsansatz:

$\det(\boldsymbol{T} - \lambda \boldsymbol{E}) = 0$ liefert Eigenwerte λ_i und Eigenvektoren $\overrightarrow{v_i}$

Das DGL-System hat i Lösungen, welche ein Fundamentalsystem bilden: $\overrightarrow{[S]}_i = e^{\lambda_i t}\,\overrightarrow{v_i}$

Matrizenformulierung für chemische Reaktionen

S1 $\underset{b}{\overset{a}{\rightleftharpoons}}$ S2

$$\boldsymbol{T} = \begin{bmatrix} -a & b \\ a & -b \end{bmatrix}$$

P2

$$\overrightarrow{[S]}'(t) = \boldsymbol{T}\overrightarrow{[S]}(t)$$

Lösungsansatz:

$\det(\boldsymbol{T} - \lambda \boldsymbol{E}) = 0$ liefert Eigenwerte $\lambda_1 = 0$ und $\lambda_2 = -a - b$

Eigenvektoren $\overrightarrow{v_1} = \begin{pmatrix} x_1 \\ \frac{a}{b}x_1 \end{pmatrix}$, $\overrightarrow{v_2} = \begin{pmatrix} x_2 \\ -x_2 \end{pmatrix}$

mit $x_1 = x_2 = 1$

$$\begin{pmatrix} [\boldsymbol{S_1}] \\ [\boldsymbol{S_2}] \end{pmatrix} = \boldsymbol{c_1}\begin{pmatrix} \boldsymbol{1} \\ \boldsymbol{\frac{a}{b}} \end{pmatrix}\boldsymbol{e^0} + \boldsymbol{c_2}\begin{pmatrix} \boldsymbol{1} \\ \boldsymbol{-1} \end{pmatrix}\boldsymbol{e^{-(a+b)t}}$$

Matrizenformulierung für chemische Reaktionen

$$S1 \underset{b}{\overset{a}{\rightleftharpoons}} S2 \qquad \boldsymbol{T} = \begin{bmatrix} -a & b \\ a & -b \end{bmatrix}$$

$$\begin{pmatrix} [\boldsymbol{S_1}] \\ [\boldsymbol{S_2}] \end{pmatrix} = \boldsymbol{c_1} \begin{pmatrix} \boldsymbol{1} \\ \boldsymbol{\frac{a}{b}} \end{pmatrix} \boldsymbol{e^0} + \boldsymbol{c_2} \begin{pmatrix} \boldsymbol{1} \\ \boldsymbol{-1} \end{pmatrix} \boldsymbol{e^{-(a+b)t}}$$

$$[S_1] = c_1 + c_2 e^{-(a+b)t}$$

$$[S_2] = c_1 \frac{a}{b} - c_2 e^{-(a+b)t}$$

Randbedingung (t=0) liefert: $c_1 = \frac{b}{a+b}[S_1]_0 \quad , \quad c_2 = \frac{a}{a+b}[S_1]_0$

$$[S_1] = \frac{b}{a+b}[S_1]_0 + \frac{a}{a+b}[S_1]_0 e^{-(a+b)t}$$

Vergleiche mit:

$$[S_1] = \frac{[S_1]_0 k_{-1}}{k_1 + k_{-1}} + \frac{[S_1]_0 k_1 e^{-(k_1+k_{-1})t}}{k_1 + k_{-1}}$$