1.3.1 Aufstellen von Geschwindigkeitsgesetzen - Allgemeines Rezept

1) Reaktionsschema identifizieren / Elementarreaktionen auflisten

Bsp: $H_2 + I_2 \rightleftharpoons 2HI$

Reaktion 2. Ordnung mit RR

Schema

$$H_2 + I_2 \xrightarrow{k_1} HI + HI$$

$$HI + HI \xrightarrow{k_2} H_2 + I_2$$

2) Ratengleichungen aufstellen für alle Spezies

Annahme unimolek. Schritt – Ordnung 1
bimolek. Schritt Ordnung 2 usw.

$$\frac{d[H_2]}{dt} = -k_1[H_2]\cdot[I_2] + k_2[HI]^2$$

$$\frac{d[I_2]}{dt} = -k_1[H_2]\cdot[I_2] + k_2[HI]^2$$

$$\frac{d[HI]}{2dt} = k_1[H_2]\cdot[I_2] - k_2[HI]^2$$

3) Überprüfen der Stöchiometrie

$$r = \frac{d[A_i]}{\upsilon_i dt} = \frac{d[HI]}{2dt} = \frac{d[H_2]}{-dt} = \frac{d[I_2]}{-dt}$$

4) Integrieren

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

$$\frac{d[A]}{dt} = -k_1 \cdot [A] \quad \Rightarrow \quad [A] = [A]_0 \cdot e^{-k_1 \cdot t}$$

$$\frac{d[B]}{dt} = -k_2 \cdot [B] + k_1 \cdot [A]$$

/ [A] einsetzen

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

$/ \; * \; e^{k_2 \cdot t}$

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

/ Differenzieren, Produktregel

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

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

/ Variablen trennen

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

/ Integrieren

$$\int_{[B]_0=0}^{[B]} d\left([B]e^{k_2 \cdot t}\right) = k_1 \cdot [A]_0 \cdot \int_0^t e^{(k_2 - k_1)\cdot t} dt$$

Anfangsbedingung $[B]_0 = 0$

$$\int dx = x \qquad \int e^{ax} dx = \frac{1}{a} e^{ax}$$

$$[B]e^{k_2 \cdot t} - 0 = \frac{k_1}{k_2 - k_1} \cdot [A]_0 \cdot \left(e^{(k_2 - k_1)\cdot t} - e^0\right)$$

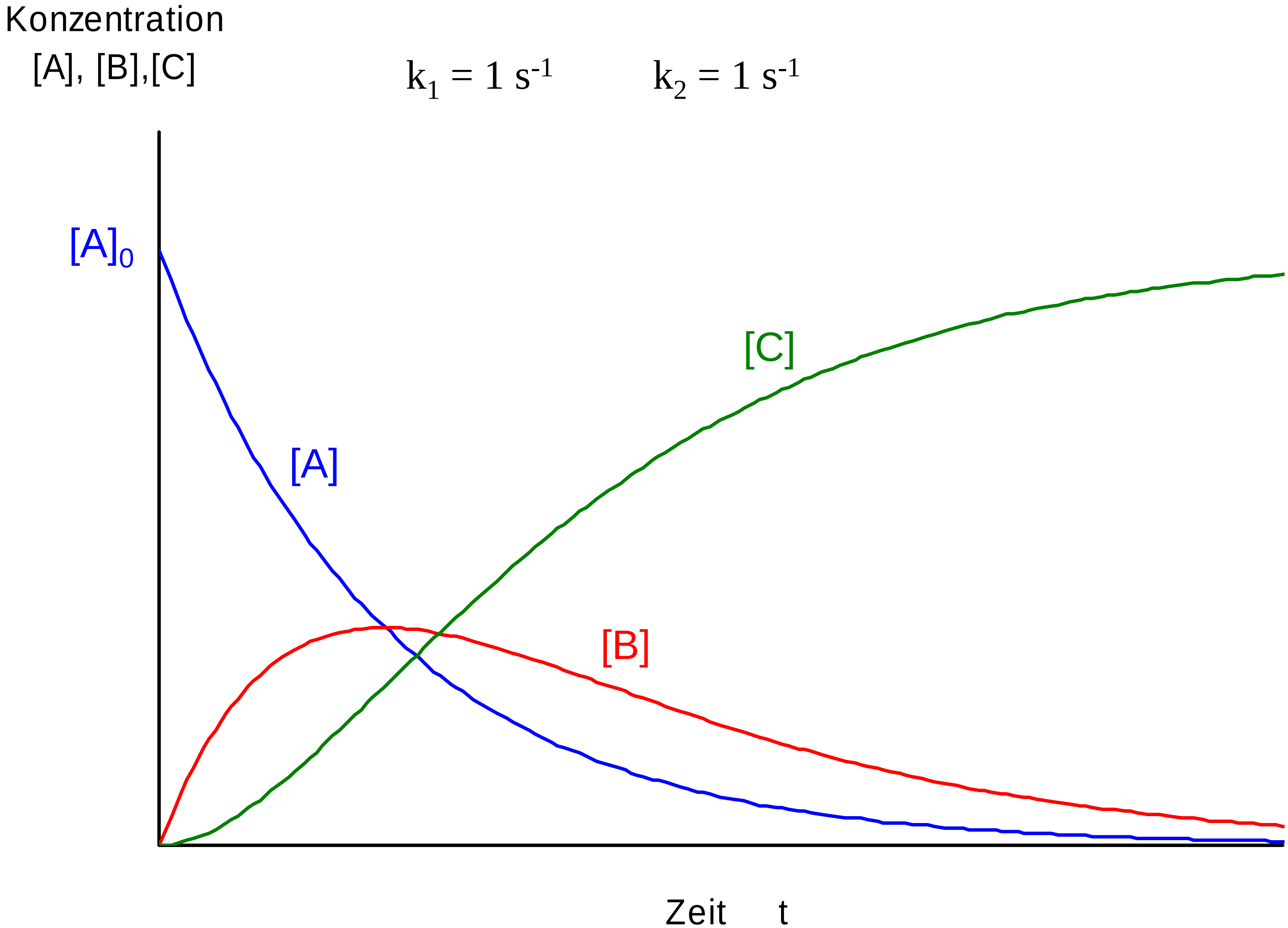
$$[B]e^{k_2 \cdot t} = \frac{k_1}{k_2 - k_1} \cdot [A]_0 \cdot \left(e^{(k_2 - k_1)\cdot t} - 1\right)$$

$/ \; * \; e^{-k_2 \cdot t}$

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

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

$k_1 = 1\ s^{-1}$ $\qquad$ $k_2 = 1\ s^{-1}$

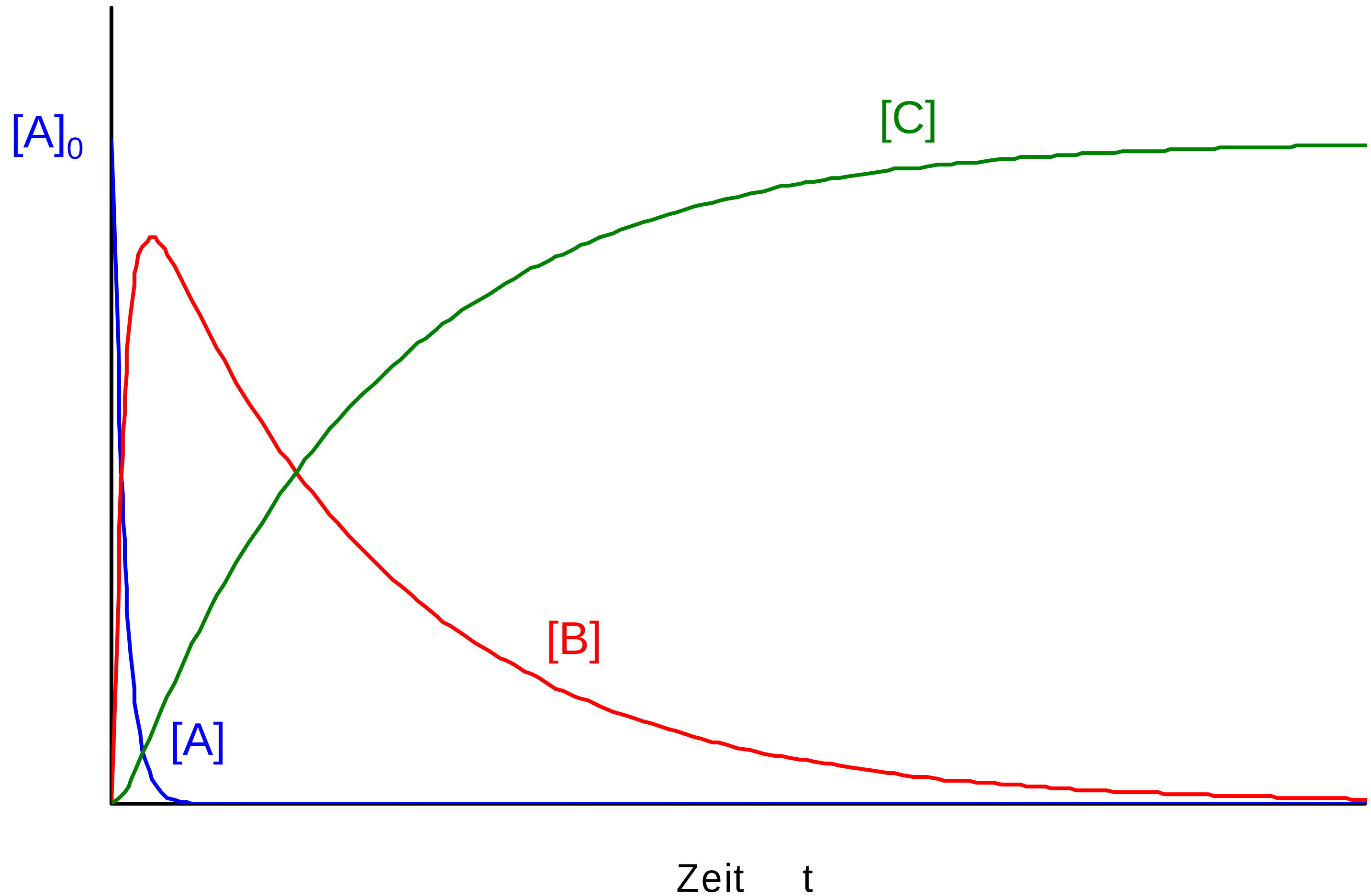


$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Konzentration
[A], [B],[C]

$k_1 = 20\ s^{-1}$ $\qquad$ $k_2 = 1\ s^{-1}$

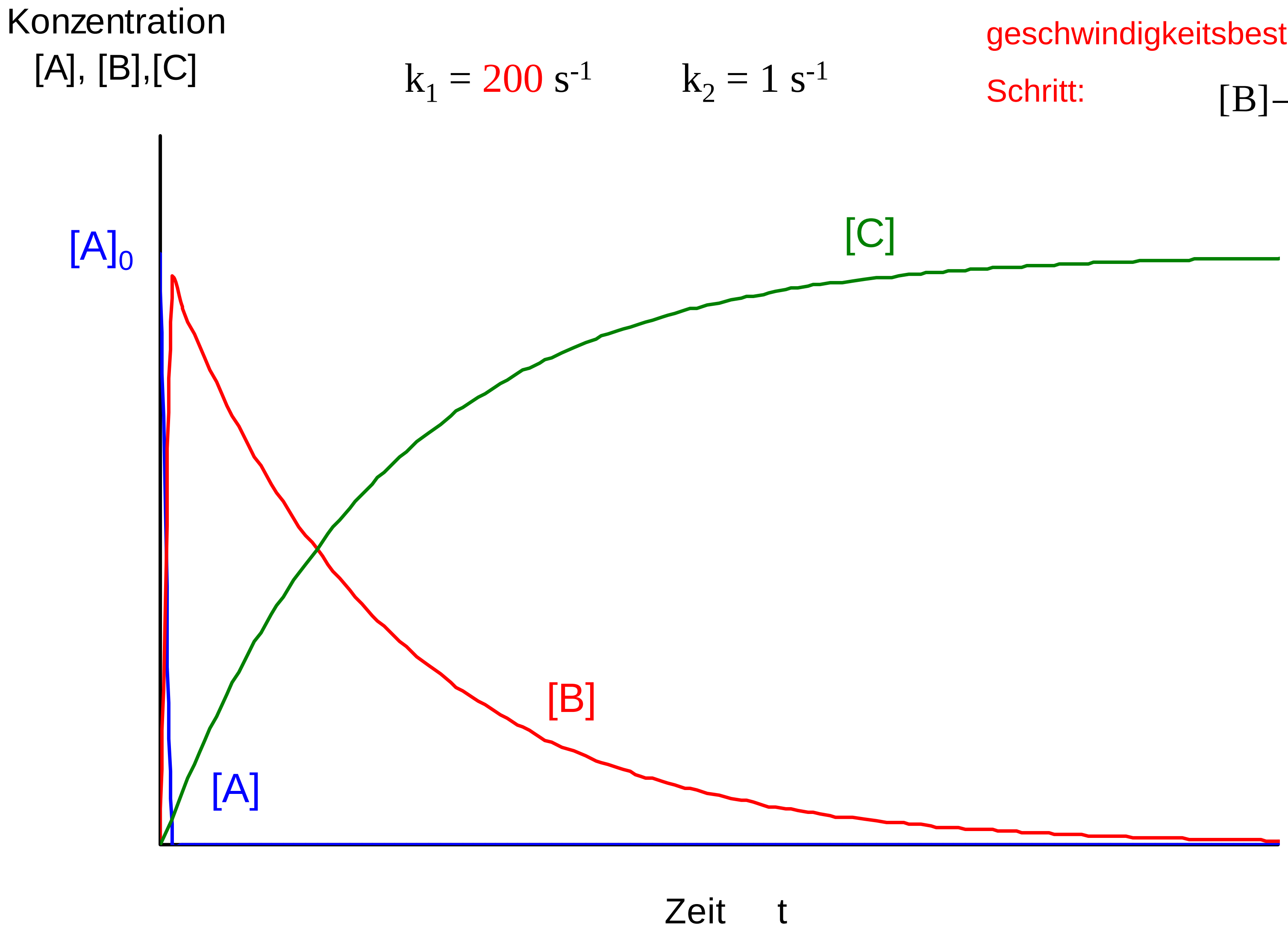
geschwindigkeitsbestimmender Schritt: $[B] \xrightarrow{k_2} [C]$



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

$k_1 = 200\ s^{-1}$ $\quad k_2 = 1\ s^{-1}$

geschwindigkeitsbestimmender Schritt: $[B] \xrightarrow{k_2} [C]$

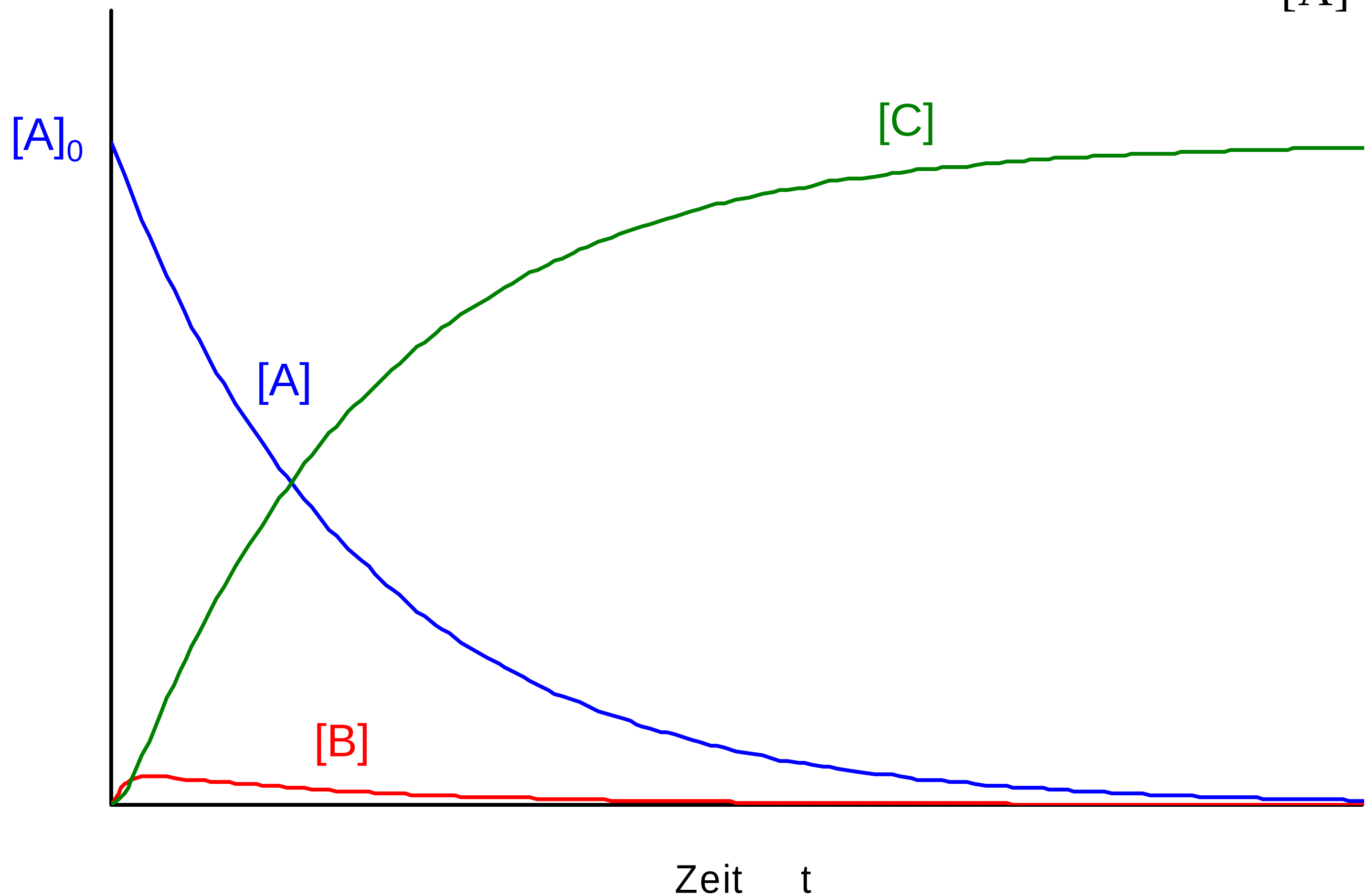


$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$k_1 = 1\ s^{-1}$ $\qquad$ $k_2 = 20\ s^{-1}$

geschwindigkeitsbestimmender Schritt: $[A] \xrightarrow{k_1} [B]$

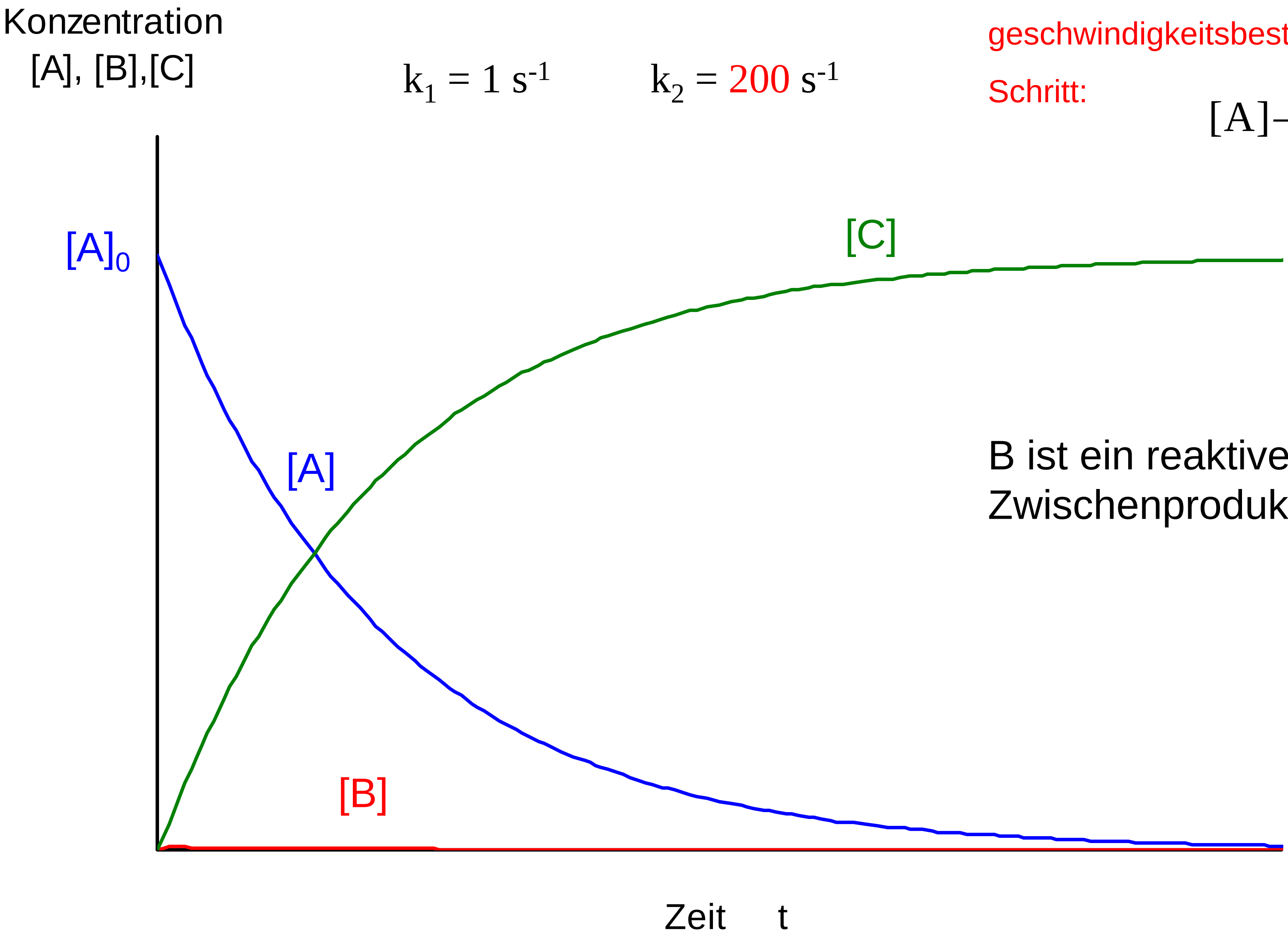
Konzentration
[A], [B],[C]



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

$k_1 = 1\ s^{-1}$ $\qquad$ $k_2 = 200\ s^{-1}$

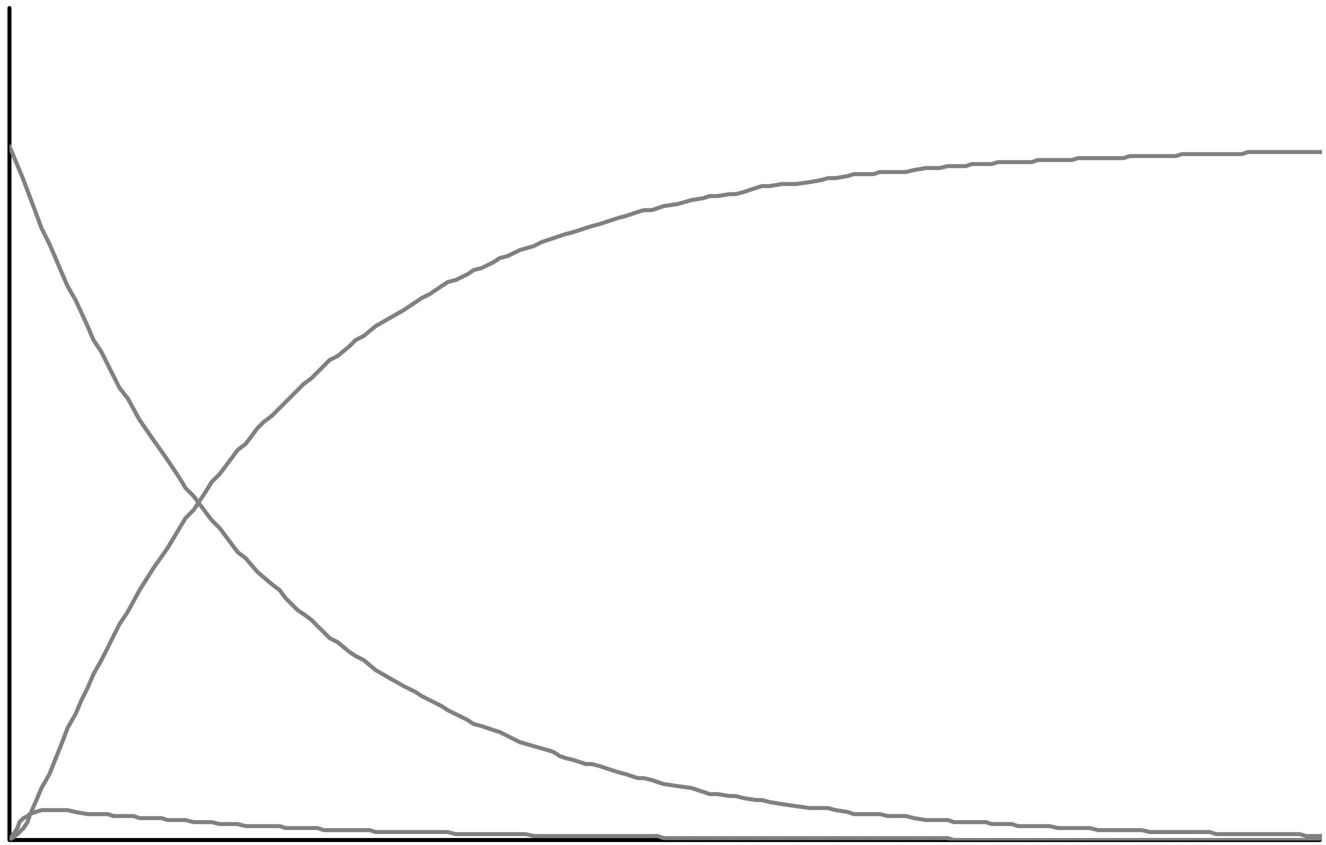
geschwindigkeitsbestimmender Schritt: $[A] \xrightarrow{k_1} [B]$



B ist ein reaktives Zwischenprodukt

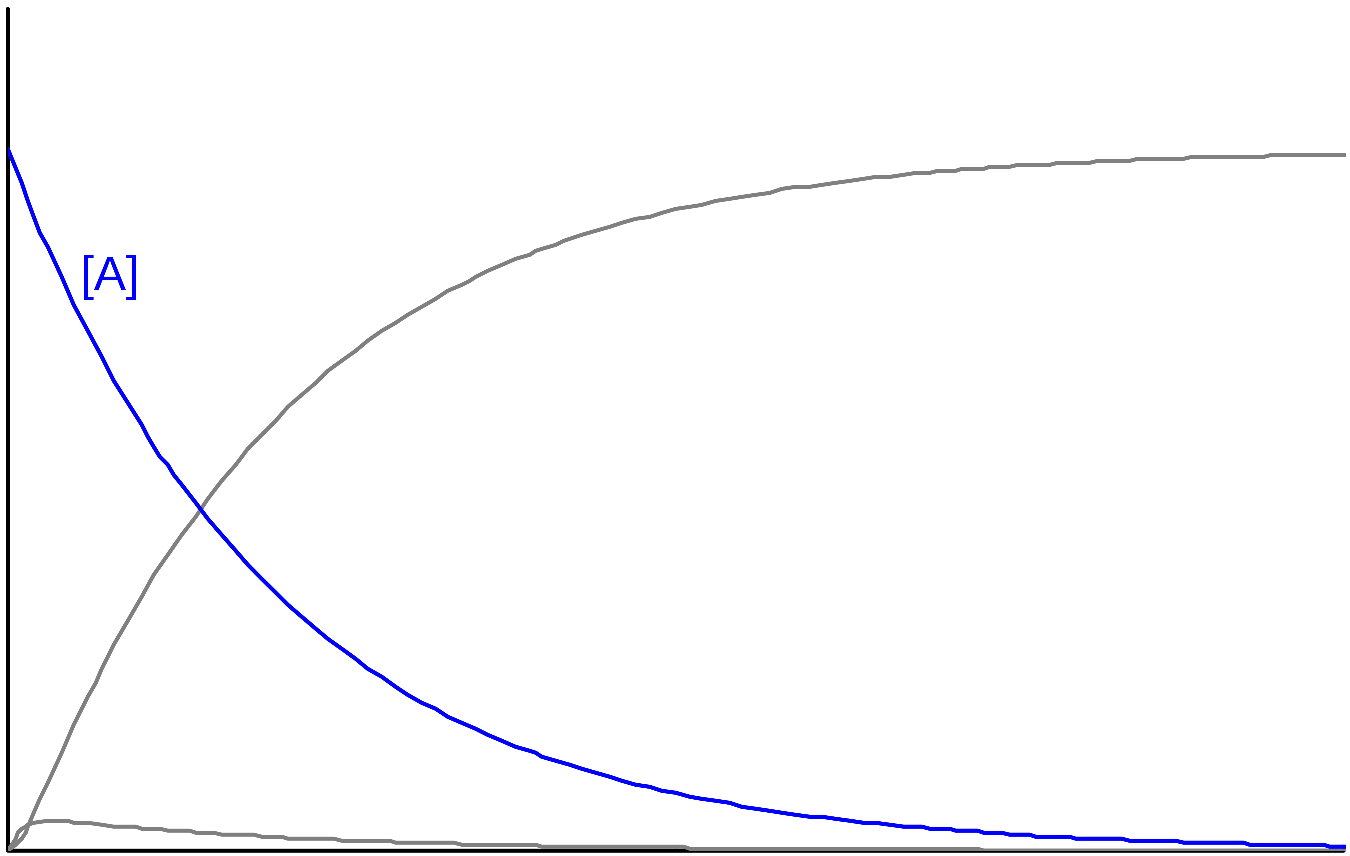
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$k_1 = 1\ s^{-1}$ $\qquad$ $k_2 = 20\ s^{-1}$



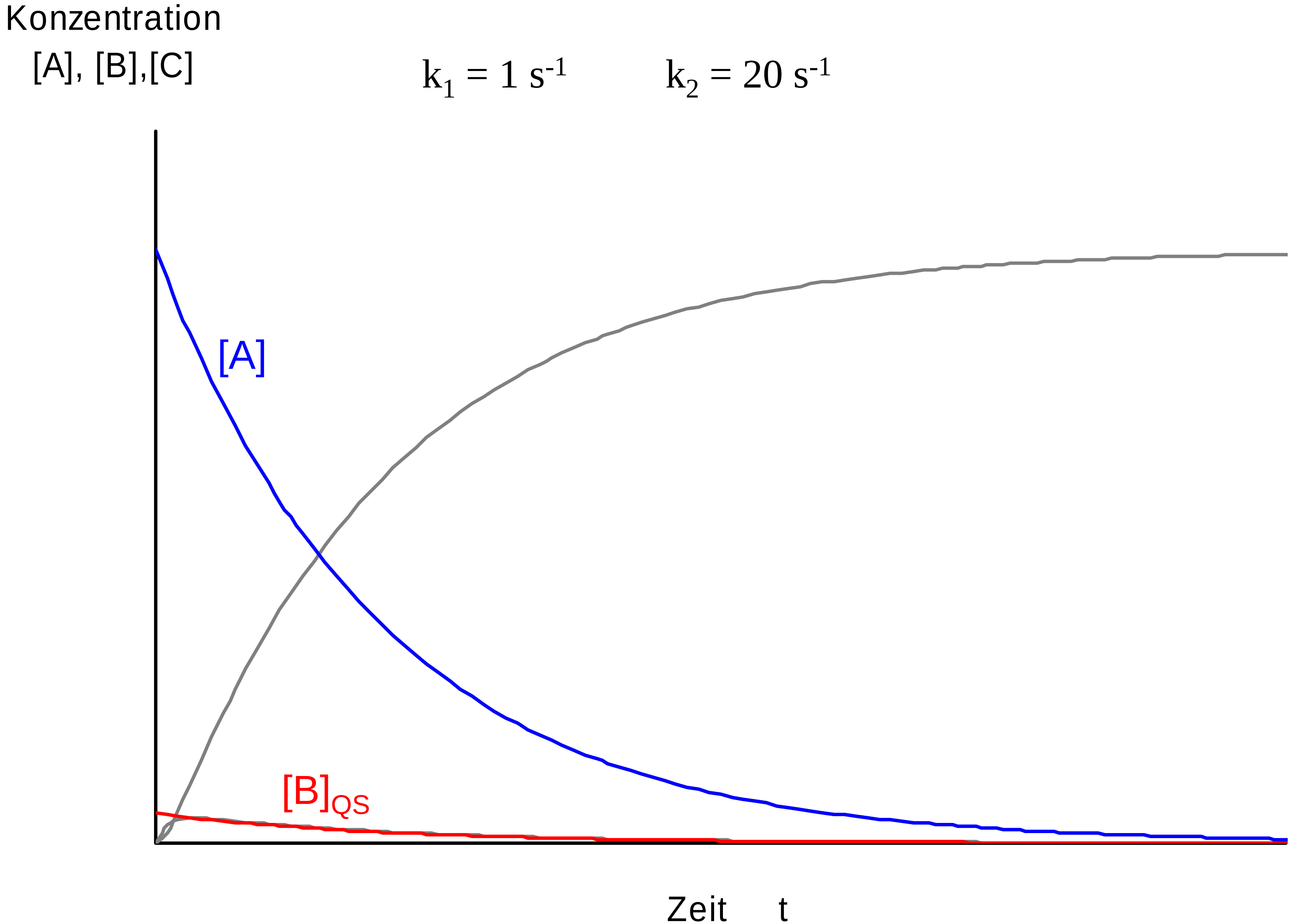
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$k_1 = 1\ s^{-1} \qquad k_2 = 20\ s^{-1}$$



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

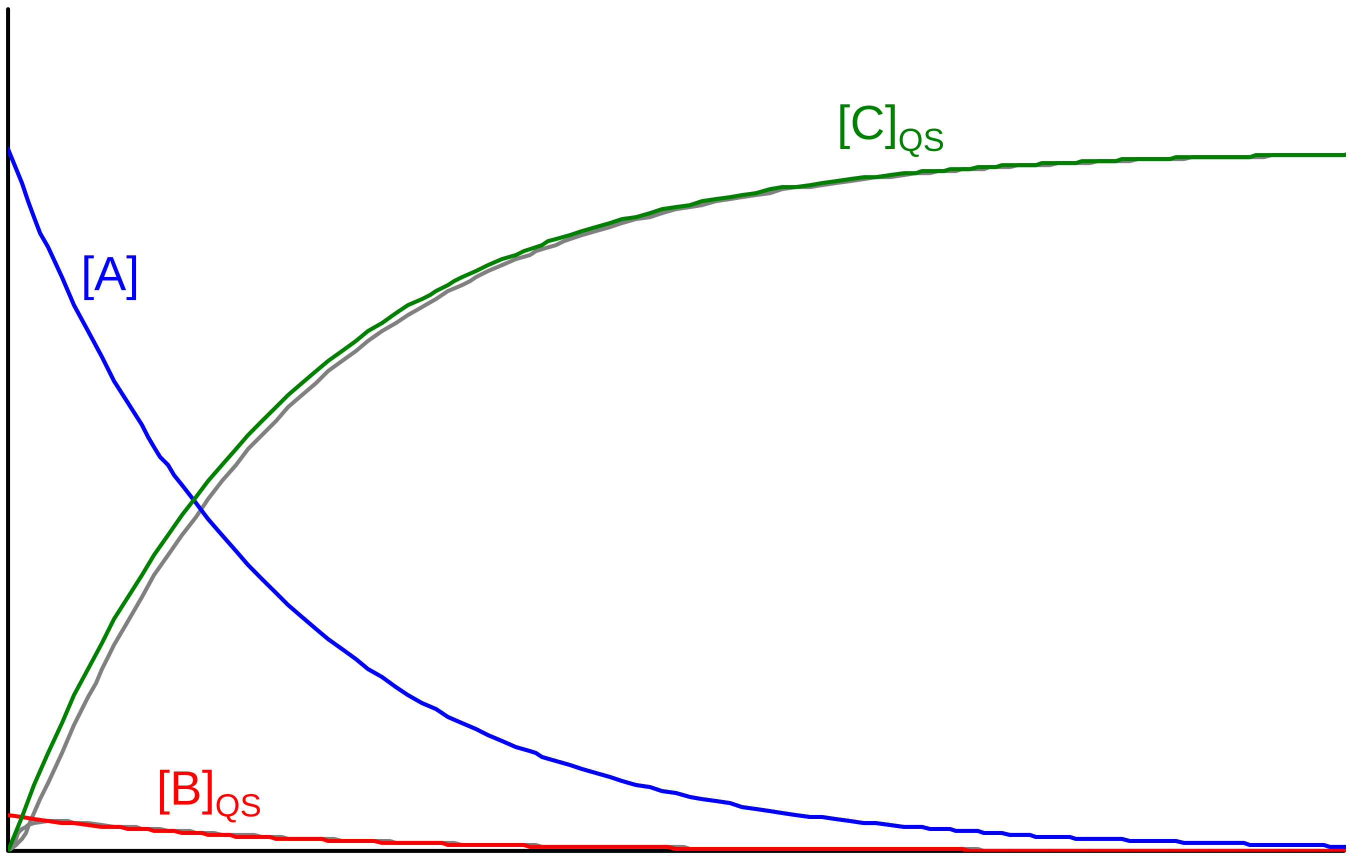
$k_1 = 1\ s^{-1}$ $k_2 = 20\ s^{-1}$



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

Konzentration
[A], [B],[C]

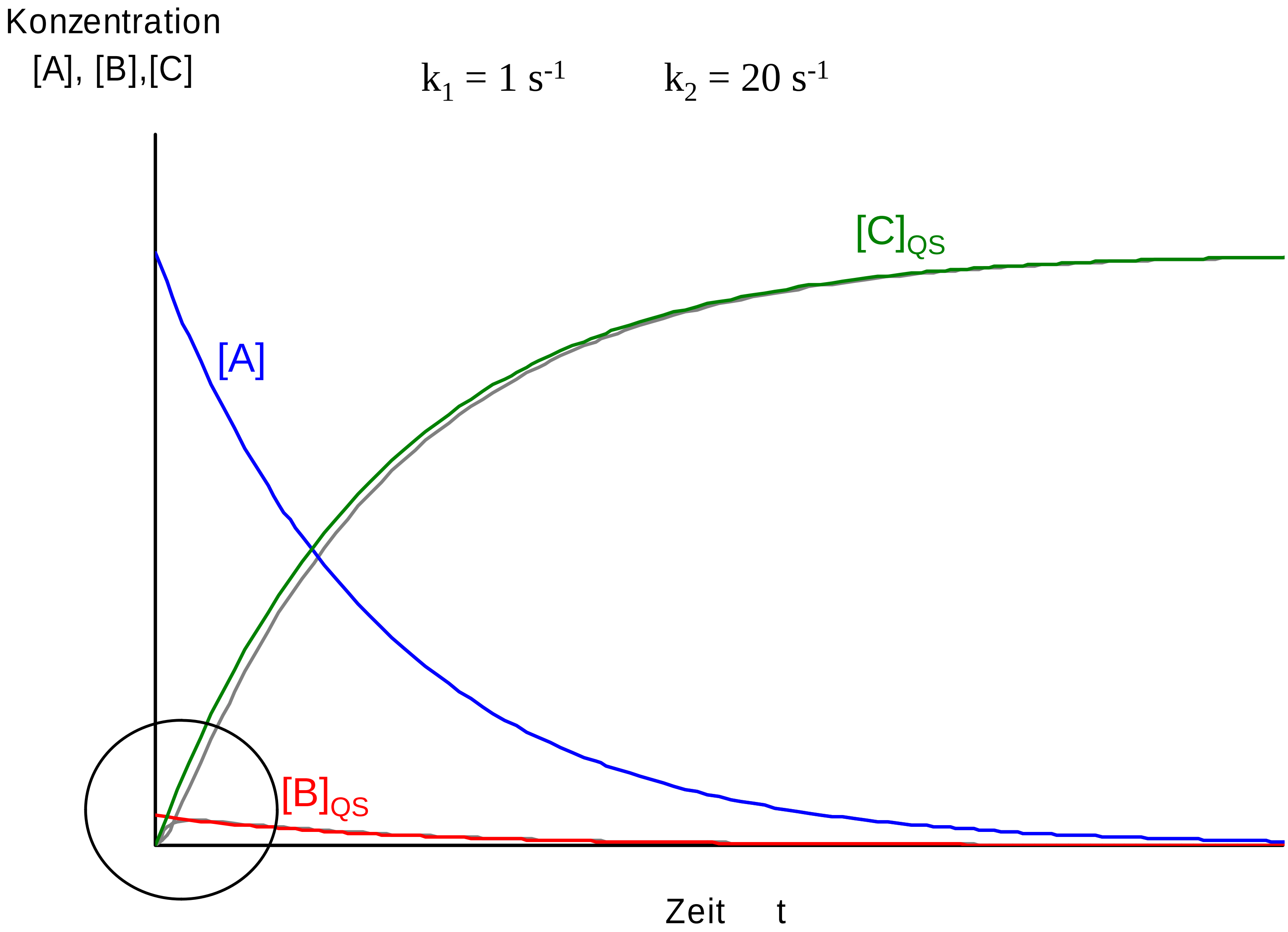
$k_1 = 1\ s^{-1}$ $k_2 = 20\ s^{-1}$



Zeit t

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

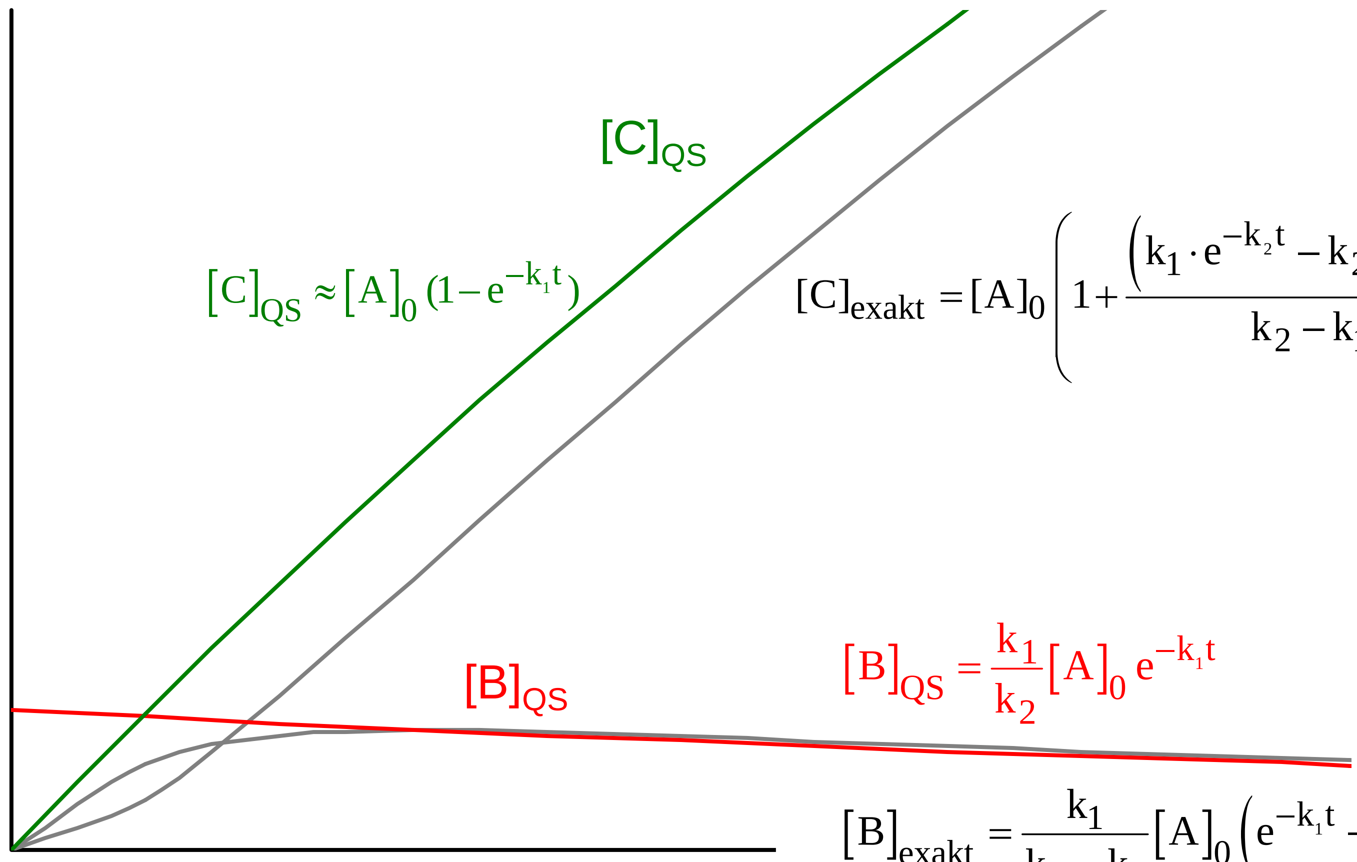
$k_1 = 1\ s^{-1}$ $\qquad$ $k_2 = 20\ s^{-1}$



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

$$k_1 = 1\ s^{-1} \qquad k_2 = 20\ s^{-1}$$

Konzentration
[A], [B],[C]



$$[C]_{QS} \approx [A]_0\,(1 - e^{-k_1 t})$$

$$[C]_{exakt} = [A]_0 \left(1 + \frac{\left(k_1 \cdot e^{-k_2 t} - k_2 \cdot e^{-k_1 t}\right)}{k_2 - k_1} \right)$$

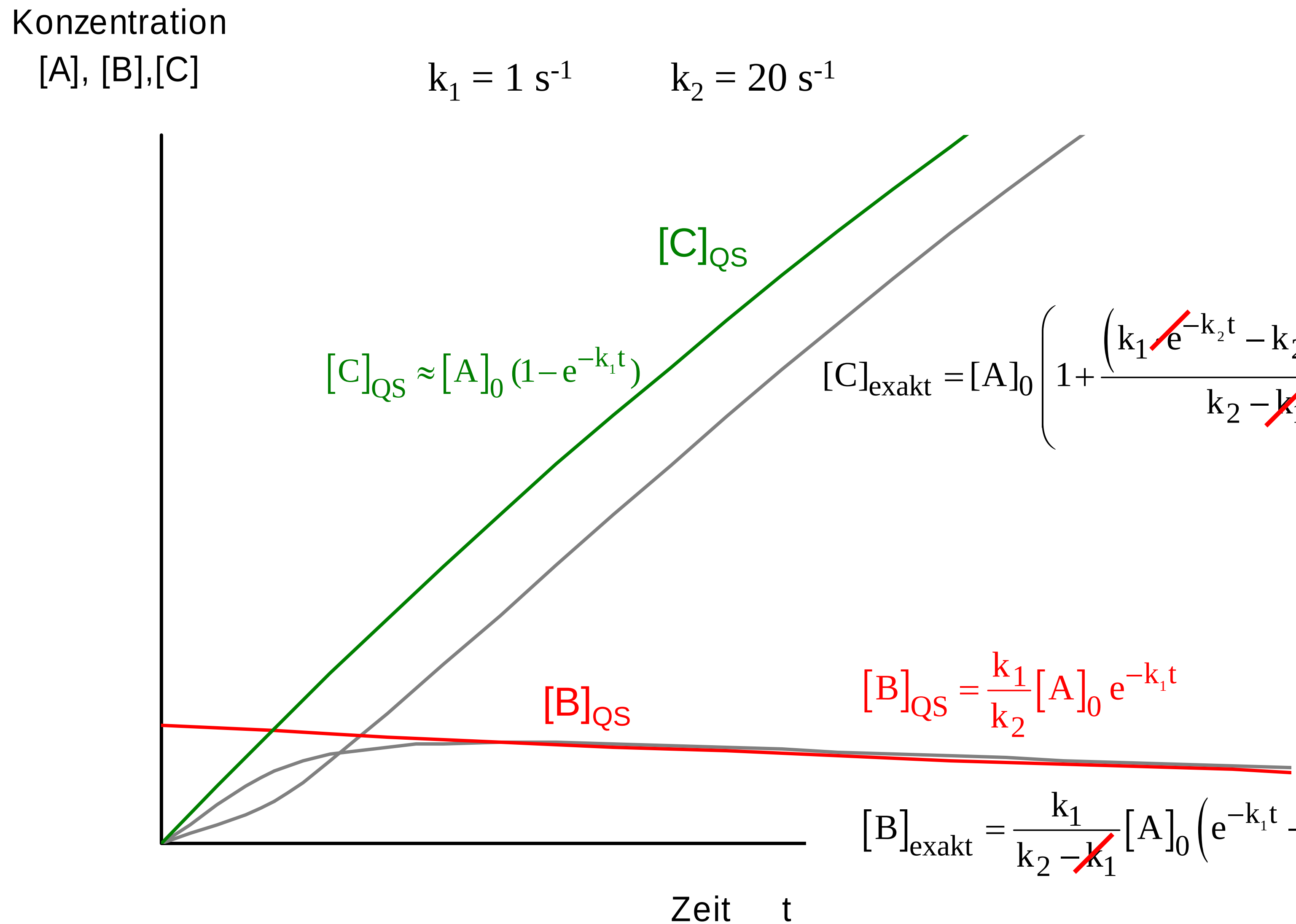
$$[B]_{QS} = \frac{k_1}{k_2} [A]_0\, e^{-k_1 t}$$

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

Zeit t

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

$k_1 = 1\ s^{-1}$ $\qquad$ $k_2 = 20\ s^{-1}$



$$[C]_{QS} \approx [A]_0 \left(1 - e^{-k_1 t}\right)$$

$$[C]_{exakt} = [A]_0 \left(1 + \frac{\left(k_1 \cancel{\cdot e^{-k_2 t}} - k_2 \cdot e^{-k_1 t}\right)}{k_2 - \cancel{k_1}}\right)$$

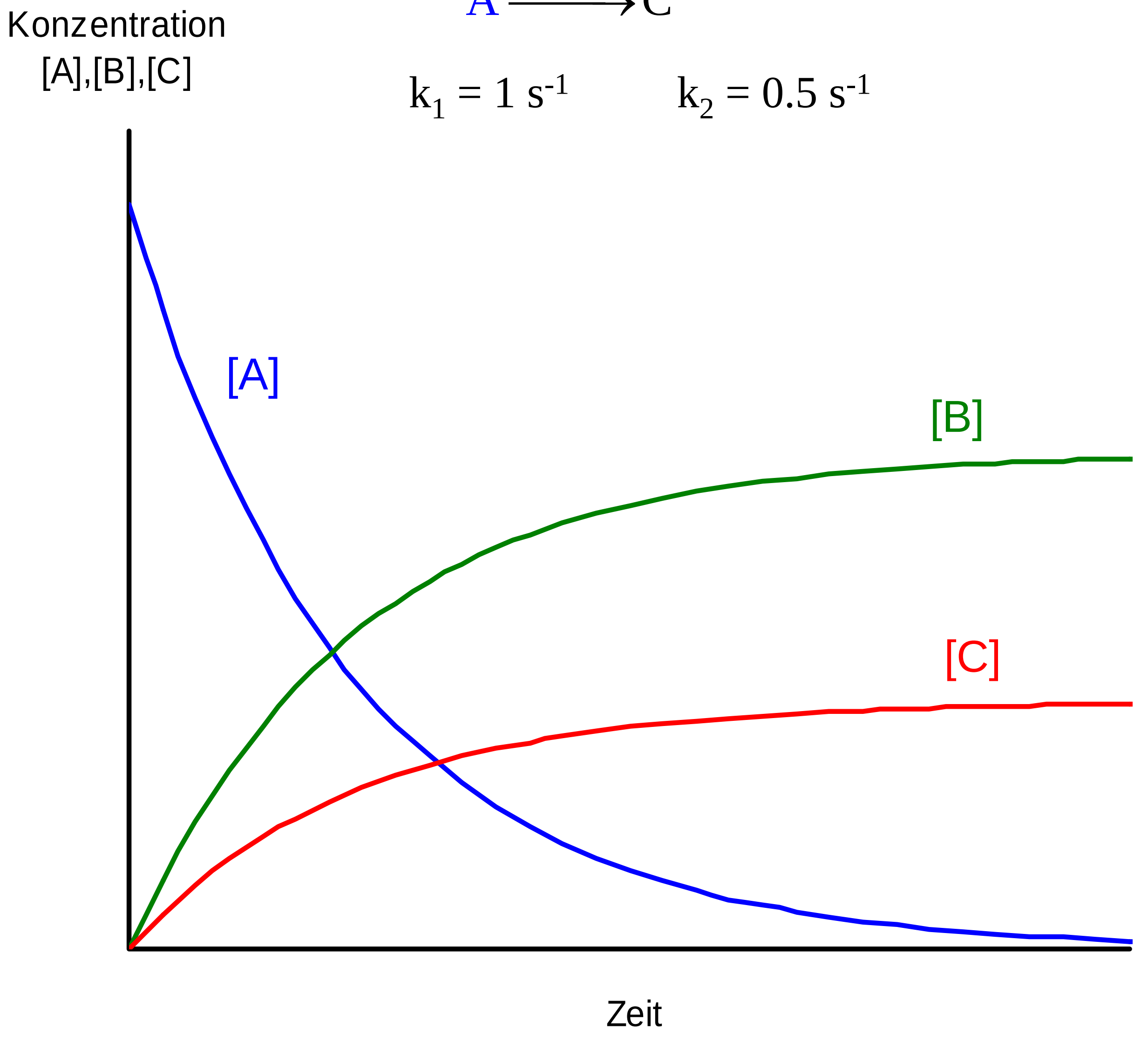
$$[B]_{QS} = \frac{k_1}{k_2} [A]_0\, e^{-k_1 t}$$

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

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

$k_1 = 1\ s^{-1}$ $k_2 = 0.5\ s^{-1}$



$$C \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

konkretes Beispiel:

$k_1 = 1 s^{-1}$ $\quad$ $k_{-1} = 0.01\ s^{-1}$

$k_2 = 0.1\ s^{-1}$ $\quad$ $k_{-2} = 0.0001\ s^{-1}$

<u>kurze Zeiten (Rückreaktion vernachlässigbar)</u>

$$C \underset{k_2}{\overset{k_{-2}}{\leftrightarrows}} A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

konkretes Beispiel:

$k_1 = 1 s^{-1}$ $\quad$ $k_{-1} = 0.01\ s^{-1}$

$k_2 = 0.1\ s^{-1}$ $\quad$ $k_{-2} = 0.0001\ s^{-1}$

<u>kurze Zeiten (Rückreaktion vernachlässigbar)</u>

$$\boxed{\frac{[B]_{früh}}{[C]_{früh}} = \frac{k_1}{k_2} = 10}$$

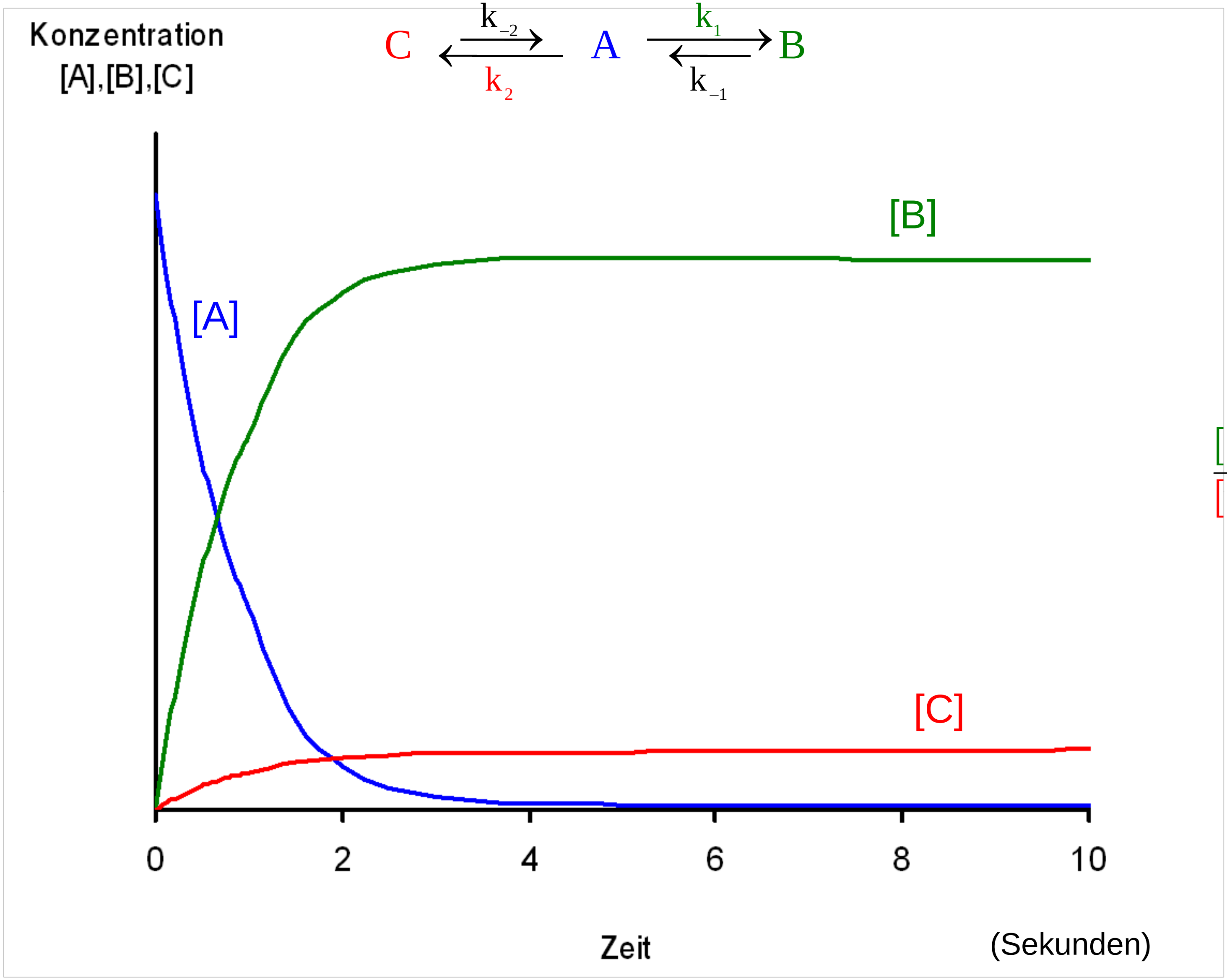
„kinetische Kontrolle“

$$[A]_{früh} = [A]_0 \cdot e^{-(k_1+k_2)t}$$

$$[B]_{früh} = \frac{k_1}{k_1+k_2} \cdot [A]_0 \cdot \left(1 - e^{-(k_1+k_2)t}\right)$$

$$[C]_{früh} = \frac{k_2}{k_1+k_2} \cdot [A]_0 \cdot \left(1 - e^{-(k_1+k_2)t}\right)$$

s. 1.3.3



$$\frac{[B]_{\text{früh}}}{[C]_{\text{früh}}} = \frac{k_1}{k_2} = 10$$

$$C \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

konkretes Beispiel:

$k_1 = 1 s^{-1}$ $\qquad$ $k_{-1} = 0.01\ s^{-1}$

$k_2 = 0.1\ s^{-1}$ $\qquad$ $k_{-2} = 0.0001\ s^{-1}$

kurze Zeiten

$$\boxed{\frac{[B]_{früh}}{[C]_{früh}} = \frac{k_1}{k_2} = 10}$$

„kinetische Kontrolle“

lange Zeiten (Gleichgewicht)

$$K_1^e = \frac{k_1}{k_{-1}} = 100 \qquad K_2^e = \frac{k_2}{k_{-2}} = 1000$$

$$\boxed{\frac{[B]_\infty}{[C]_\infty} = \frac{K_1^e}{K_2^e} = 0.1}$$

„thermodynamische Kontrolle“

$$[A]_\infty = \frac{[A]_0}{1101} \approx 0.1\%[A]_0$$

$$[B]_\infty = \frac{100[A]_0}{1101} \approx 9.1\%[A]_0$$

$$[C]_\infty = \frac{1000[A]_0}{1101} \approx 90.8\%[A]_0$$

$$C \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

konkretes Beispiel:

$k_1 = 1 s^{-1}$ $\qquad$ $k_{-1} = 0.01\ s^{-1}$

$k_2 = 0.1\ s^{-1}$ $\qquad$ $k_{-2} = 0.0001\ s^{-1}$

kurze Zeiten

$$\boxed{\frac{[B]_{früh}}{[C]_{früh}} = \frac{k_1}{k_2} = 10}$$

„kinetische Kontrolle“

lange Zeiten (Gleichgewicht)

$$K_1^e = \frac{k_1}{k_{-1}} = 100 \qquad K_2^e = \frac{k_2}{k_{-2}} = 1000$$

$$\boxed{\frac{[B]_\infty}{[C]_\infty} = \frac{K_1^e}{K_2^e} = 0.1}$$

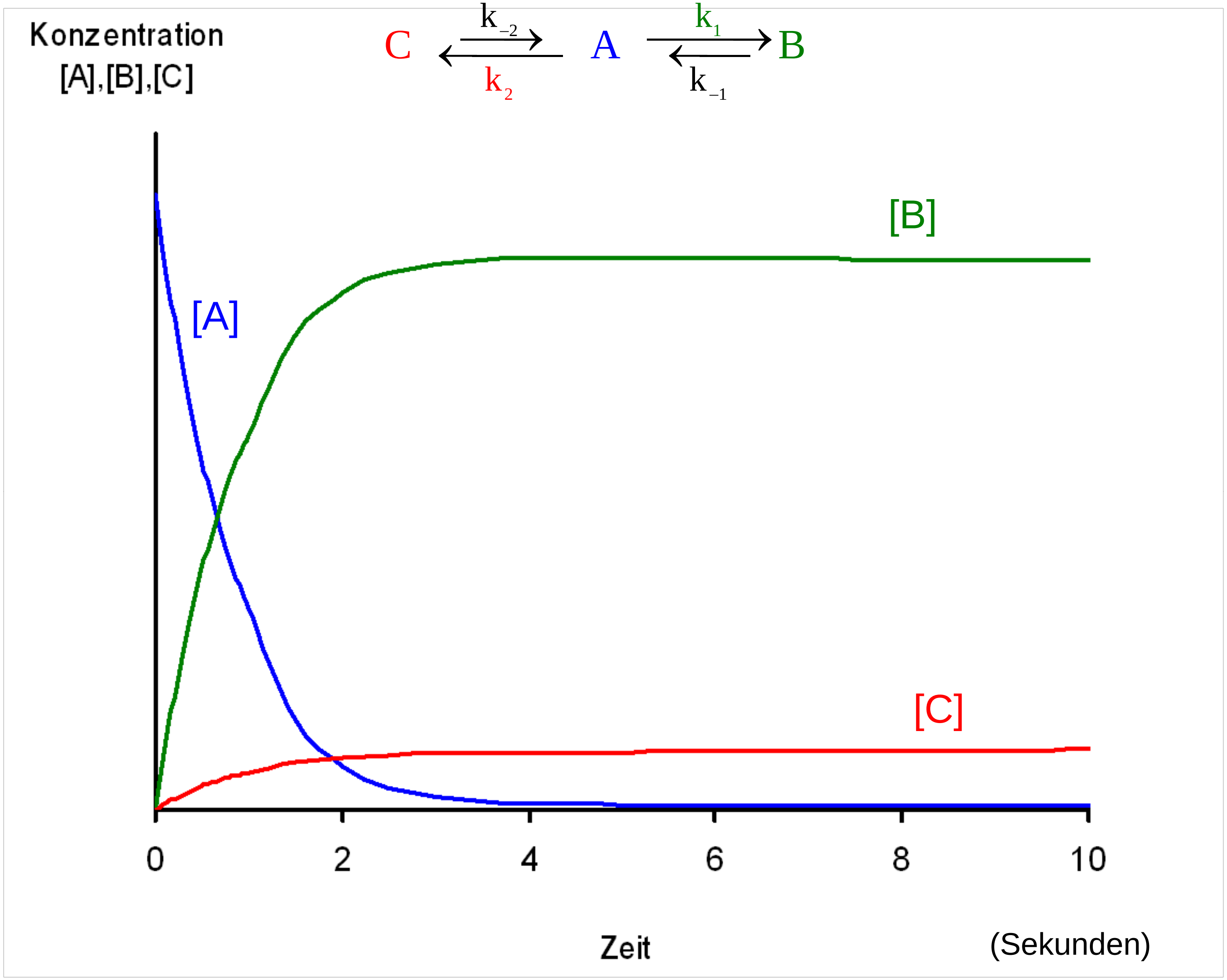
„thermodynamische Kontrolle“

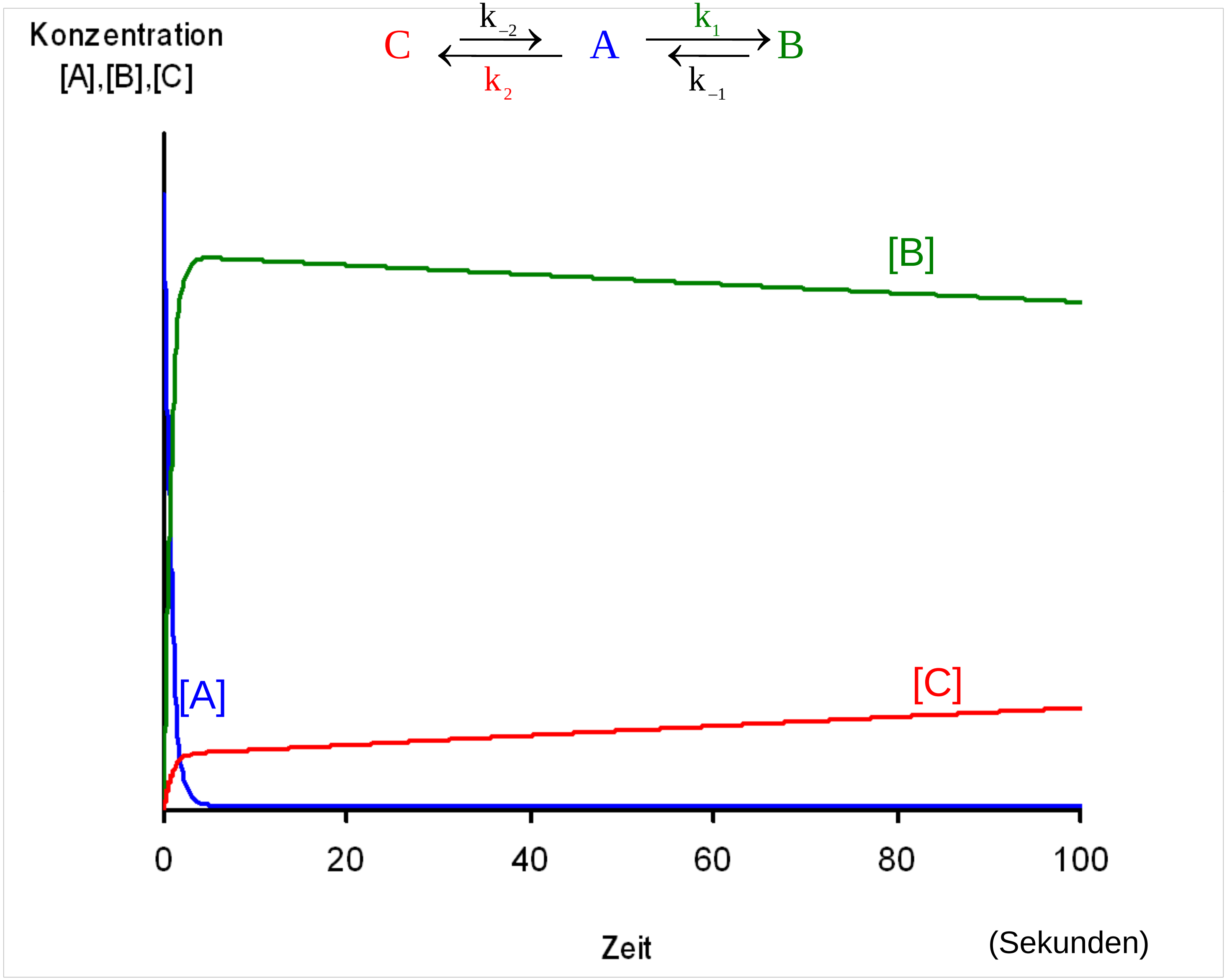
$$[A]_\infty = \frac{[A]_0}{1101} \approx 0.1\%[A]_0$$

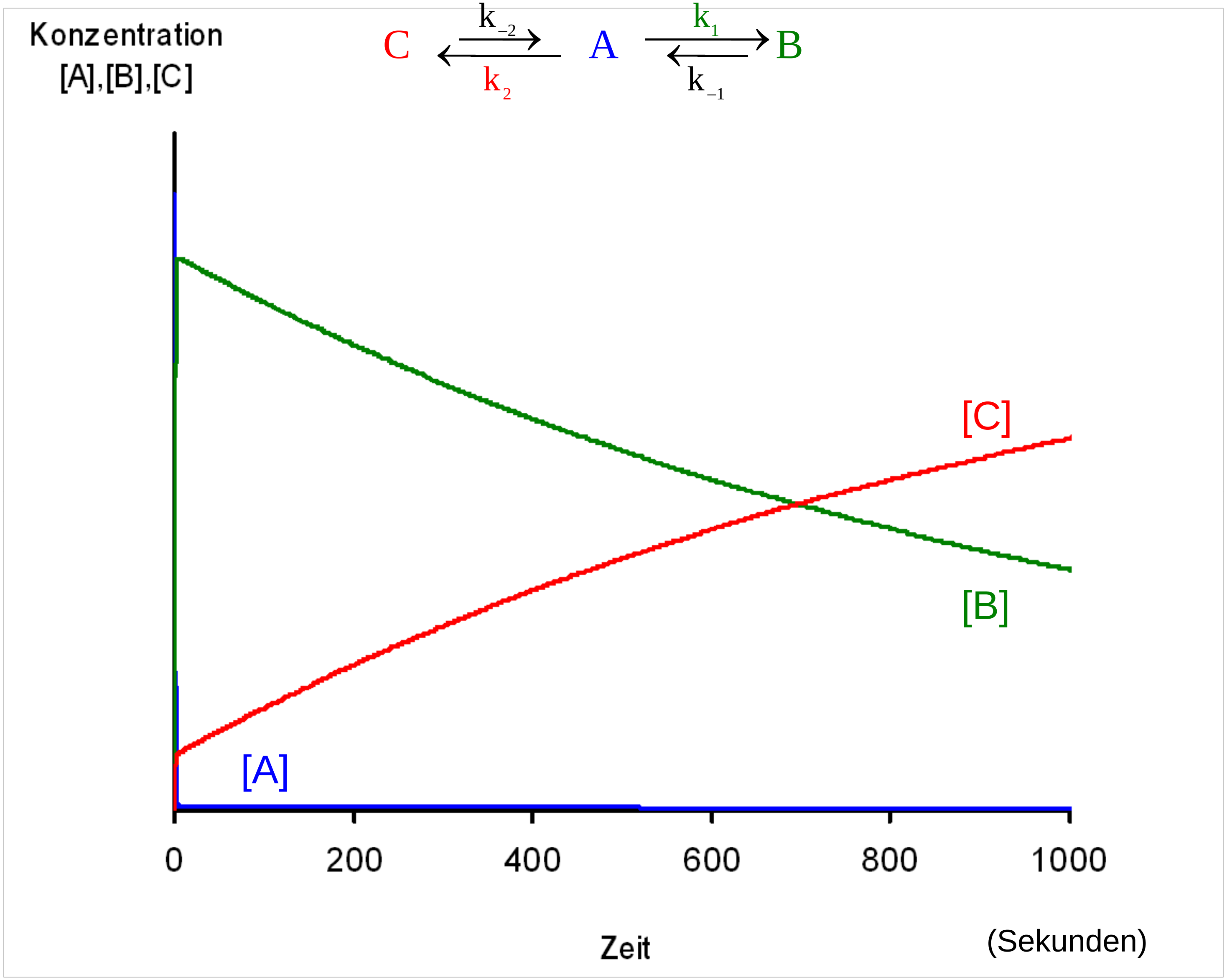
$$[B]_\infty = \frac{100[A]_0}{1101} \approx 9.1\%[A]_0$$

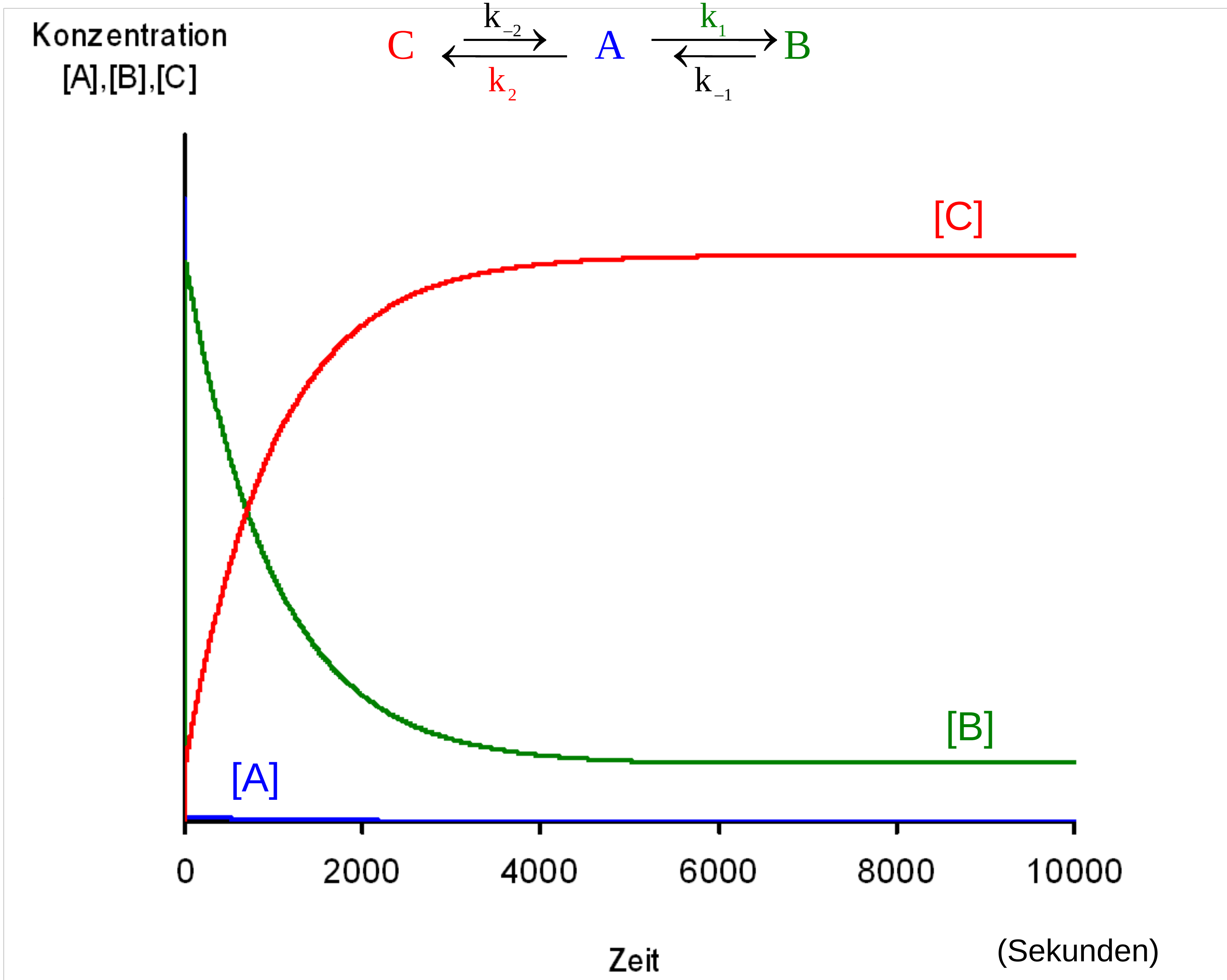
$$[C]_\infty = \frac{1000[A]_0}{1101} \approx 90.8\%[A]_0$$

Wie passt das zusammen ?

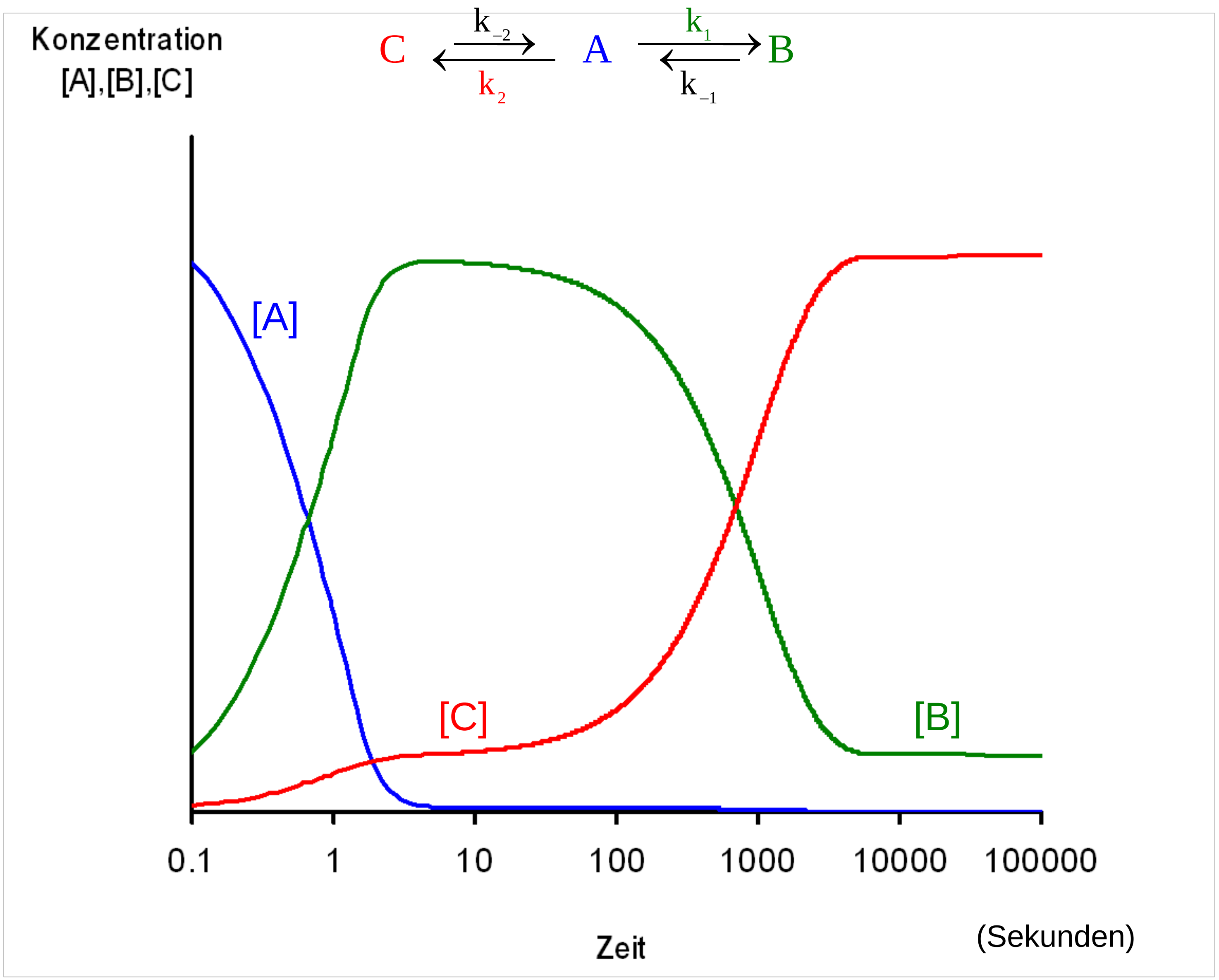

Konzentration
[A],[B],[C]
$C \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$
[B]
[A]
[C]
0
2
4
6
8
10
Zeit
(Sekunden)


Konzentration
[A],[B],[C]
C
k₋₂
k₂
A
k₁
k₋₁
B
[B]
[A]
[C]
0
20
40
60
80
100
Zeit
(Sekunden)

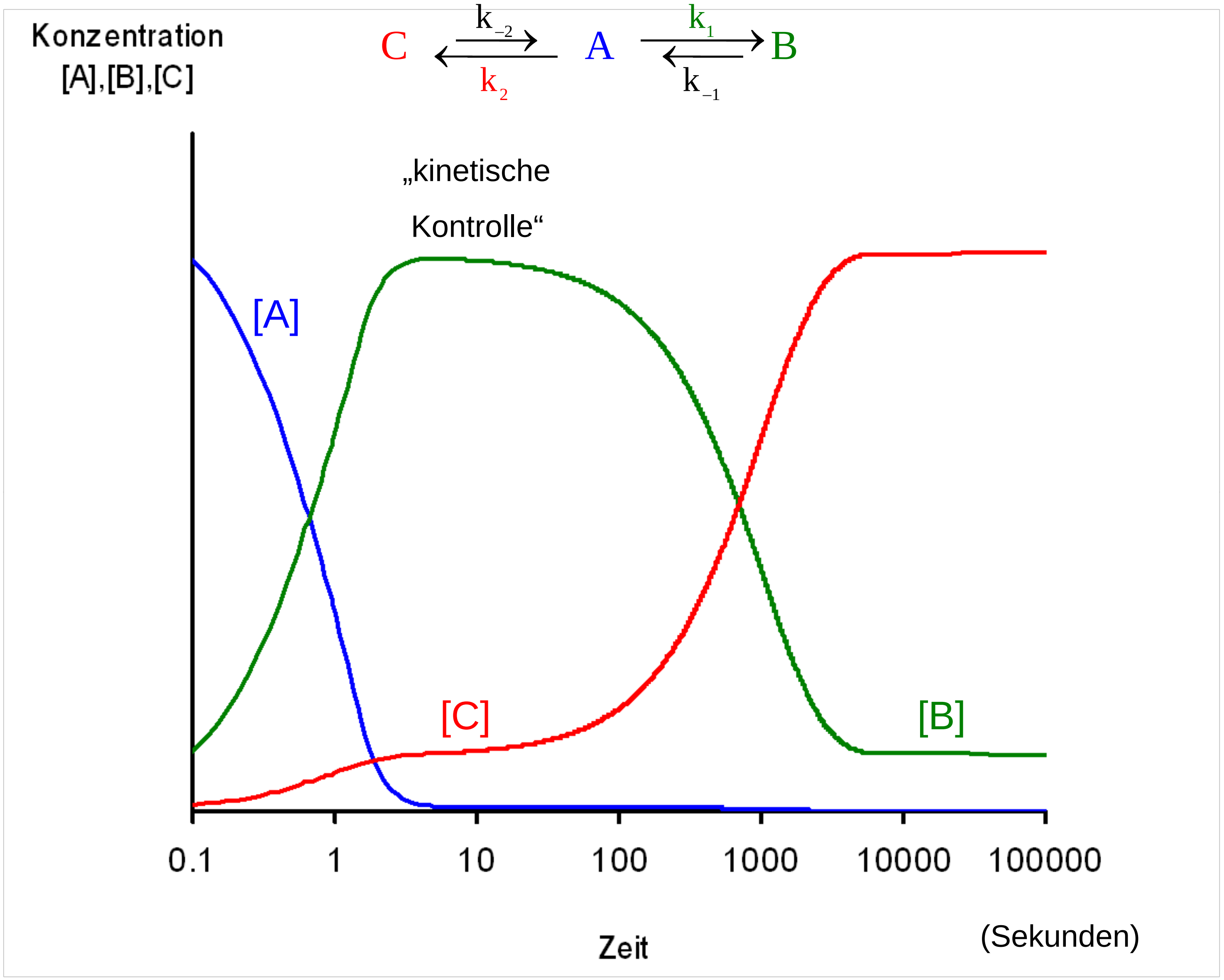

Konzentration
[A],[B],[C]
C
k₋₂
k₂
A
k₁
k₋₁
B
[C]
[B]
[A]
0
200
400
600
800
1000
Zeit
(Sekunden)



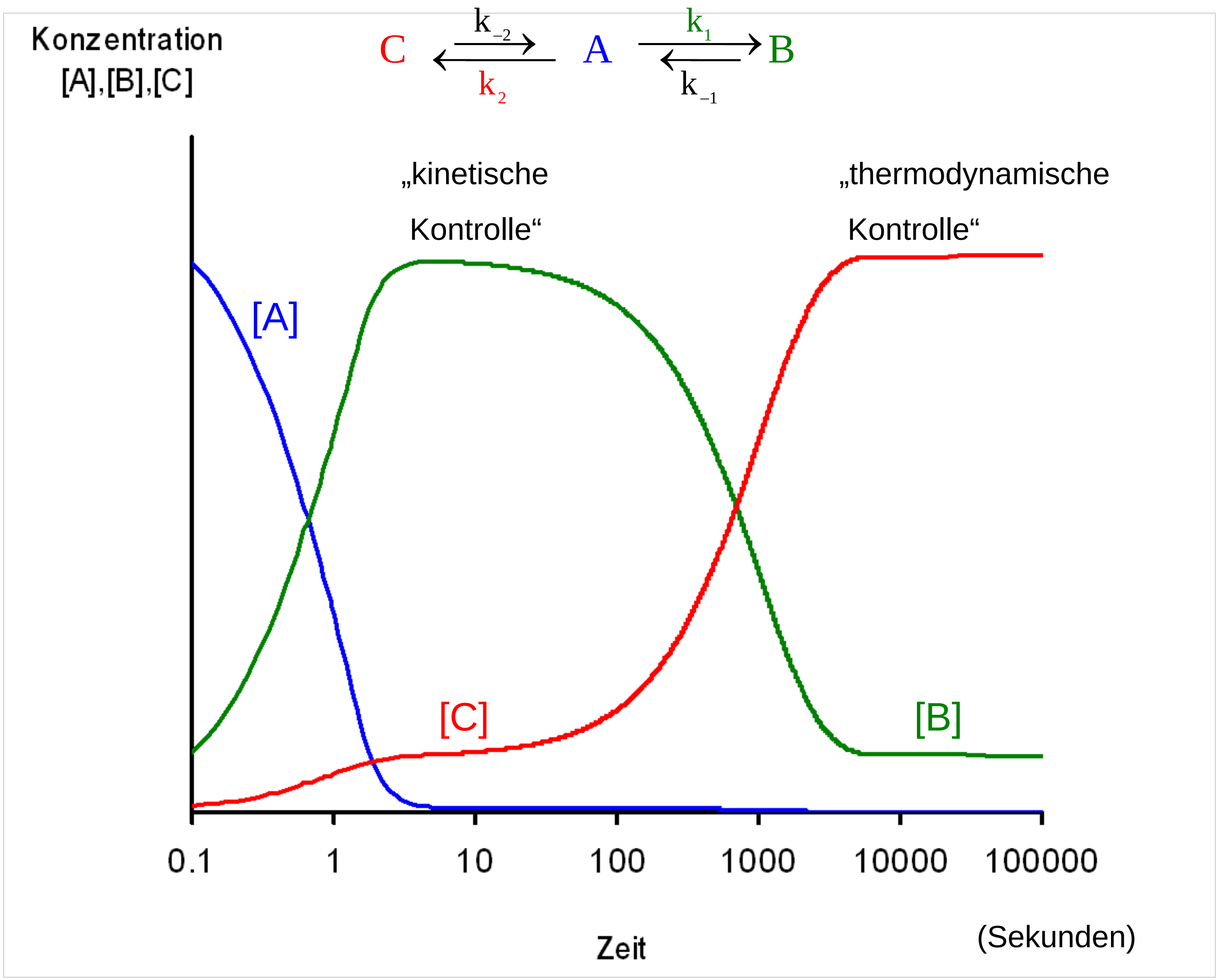
$$\frac{[B]_\infty}{[C]_\infty} = \frac{K_1^e}{K_2^e} = 0.1$$



Konzentration
[A],[B],[C]
C
k₋₂
k₂
A
k₁
k₋₁
B
[A]
[C]
[B]
0.1
1
10
100
1000
10000
100000
Zeit
(Sekunden)

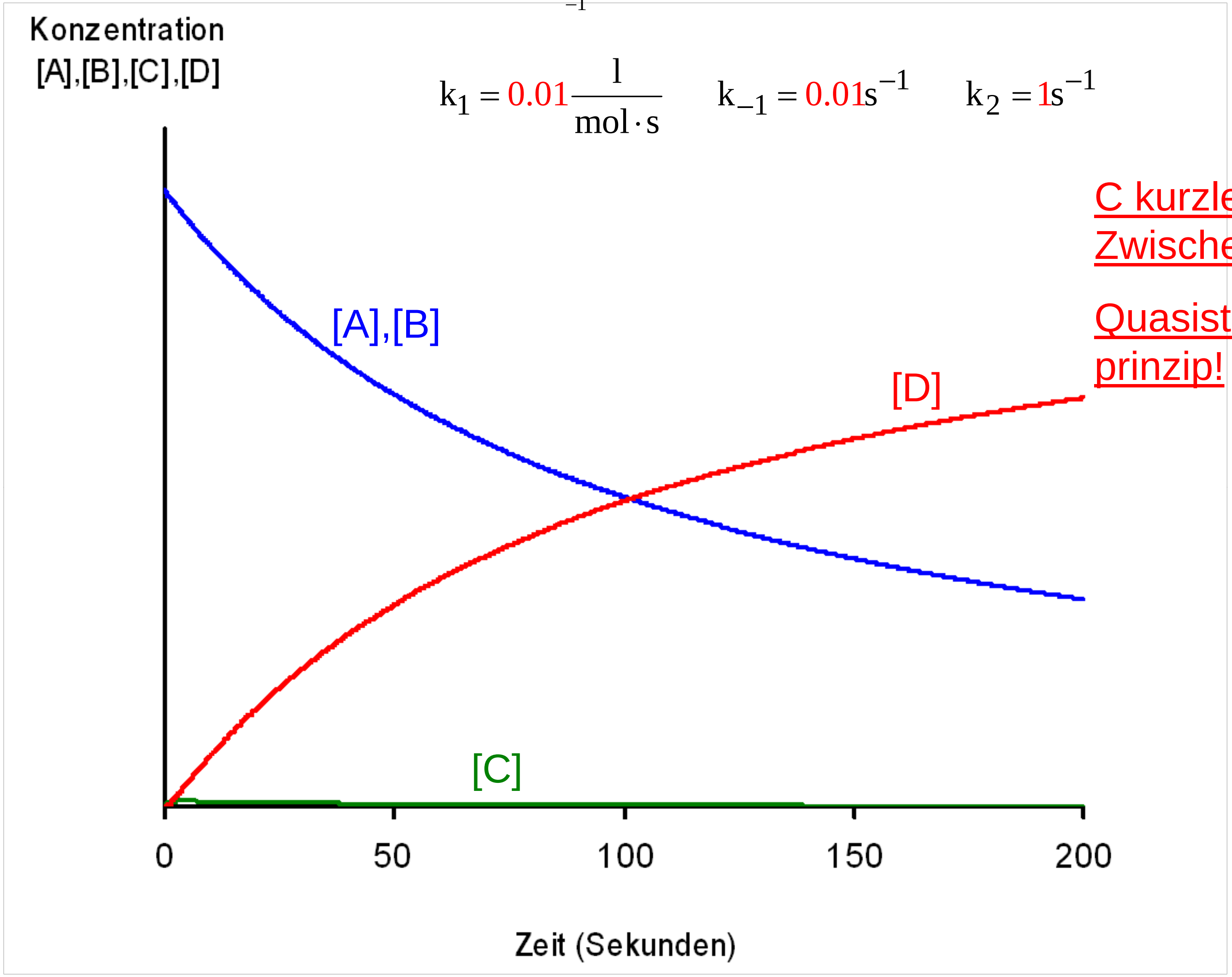


Konzentration
[A],[B],[C]
C
k₋₂
k₂
A
k₁
k₋₁
B
„kinetische
Kontrolle“
[A]
[C]
[B]
0.1
1
10
100
1000
10000
100000
Zeit
(Sekunden)


Konzentration
[A],[B],[C]
C
k_{-2}
k_2
A
k_1
k_{-1}
B
„kinetische Kontrolle“
„thermodynamische Kontrolle“
[A]
[C]
[B]
0.1
1
10
100
1000
10000
100000
Zeit
(Sekunden)

a) $k_1, k_{-1} << k_2$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \xrightarrow{k_2} D$$

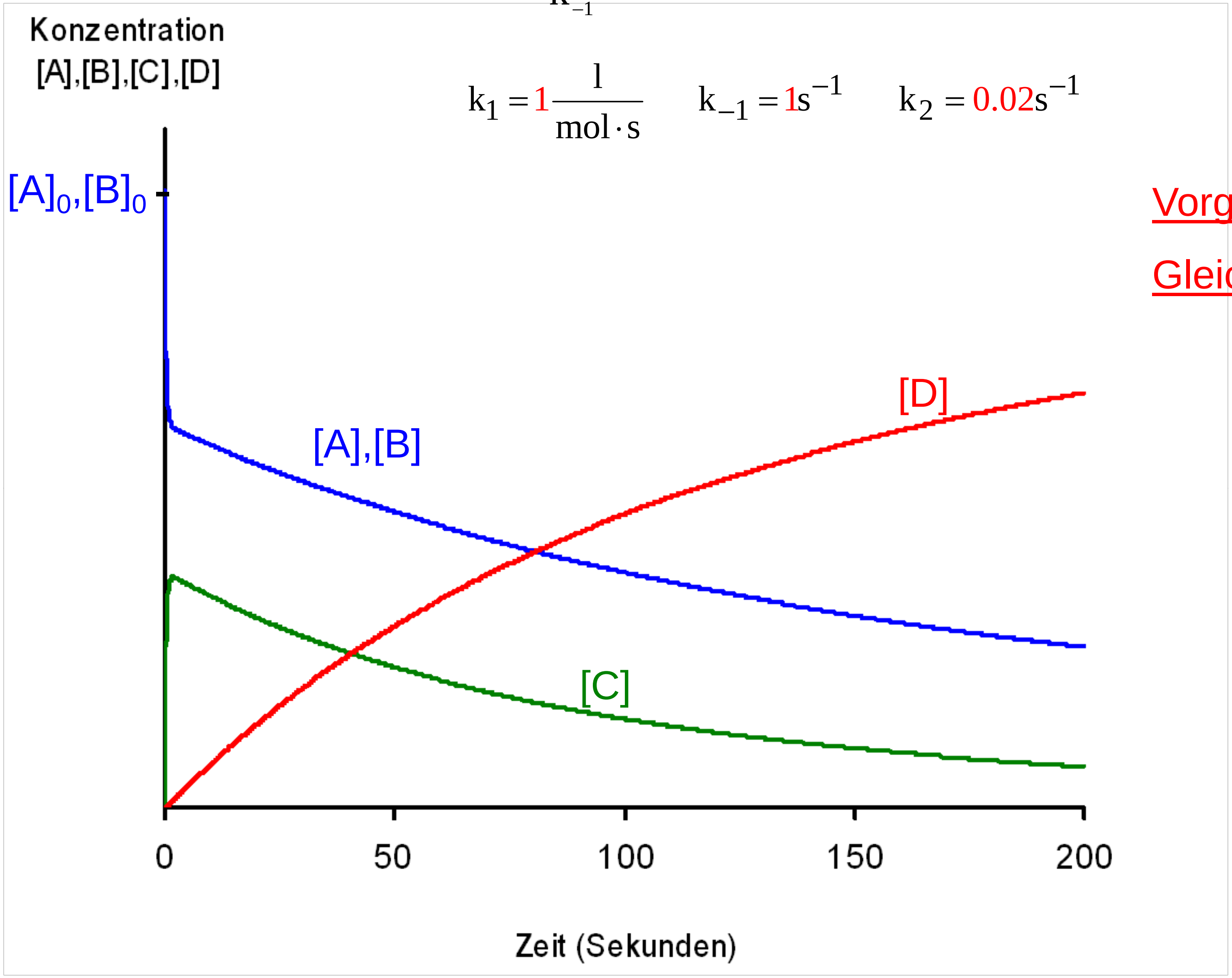


C kurzlebiges Zwischenprodukt

Quasistationaritäts prinzip!

b) $k_1, k_{-1} \gg k_2$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \xrightarrow{k_2} D$$



Vorgelagertes Gleichgewicht