



Wie beschreiben wir die Kinetik komplexerer Reaktionen? "Reaktionsmechanismen"

Physikalische Chemie by SciFox

PHYSICAL CHEMISTRY BASICS

PART 10: REACTION MECHANISM

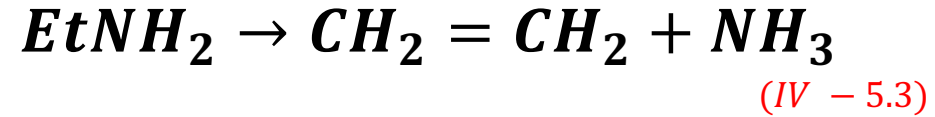
How does reaction mechanism affect reaction rate?



${}^{226}\text{Ra}$ -Activity: 30 Bq

$[Rn] = ?$

What are the kinetic parameters of the simple reaction $A \rightarrow B$?



$$r = 0.14 \frac{1}{h} \cdot [EtNH_2]^1$$

$$[EtNH_2] = [EtNH_2]_0 e^{-0.14 \frac{1}{h} \cdot t}$$

$$k = 8.12 \cdot 10^{10} \frac{1}{s} \cdot e^{-\frac{176.4 \frac{kJ}{mol}}{RT}} \quad (IV - 5.7)$$

#Ordnung

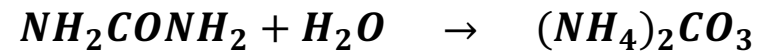
#Aktivierungsenergie

#Frequenzfaktor

How do chemical reactions work at an **atomic level**?

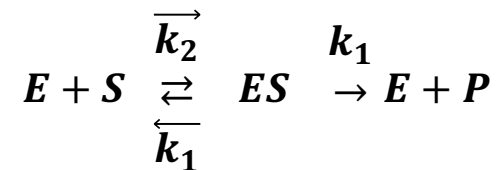
Enzyme E

Urease



Substrate S

Product P



#ElementaryReaction

#Mechanism

What is an elementary reaction in chemical kinetics?



$$r = \left(\frac{d[ES]}{dt} \right) = \overrightarrow{k_2} \cdot [S] \cdot [E]$$



$$-r' = \left(\frac{d[ES]}{dt} \right)' = \overleftarrow{k_1} \cdot [ES]$$

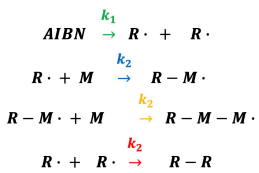


$$-r'' = \left(\frac{d[ES]}{dt} \right)'' = k_1 \cdot [ES]$$

#Molecularity

#ReactionOrder

(IV - S.27)



True or False?

The dimerization of two polymer chain radicals proceeds as an elementary step of radical polymerization according to a ...

A:
2th order
kinetics.

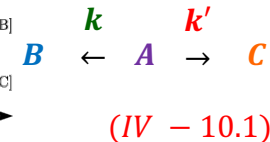
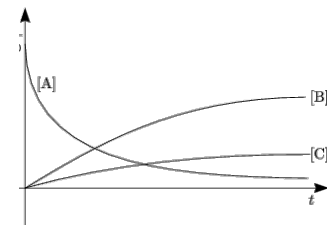
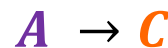
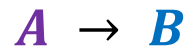
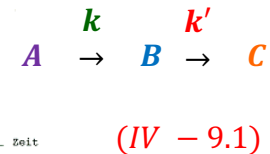
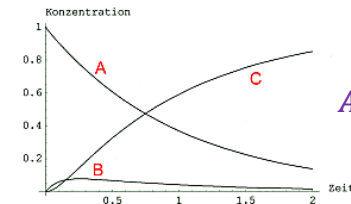
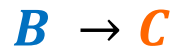
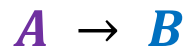
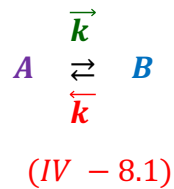
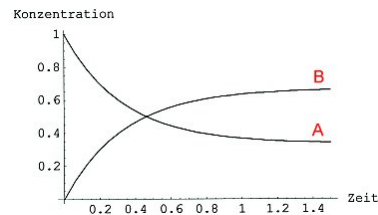
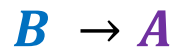
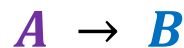
B:
1st order
kinetics

C:
1.5nd order
kinetics

D:
2nd order
kinetics



Which mechanisms can we combine from **2 elementary reactions**?



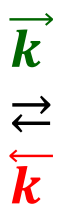
#ReversibleReaction

#ConsecutiveReaction

#ParallelReaction

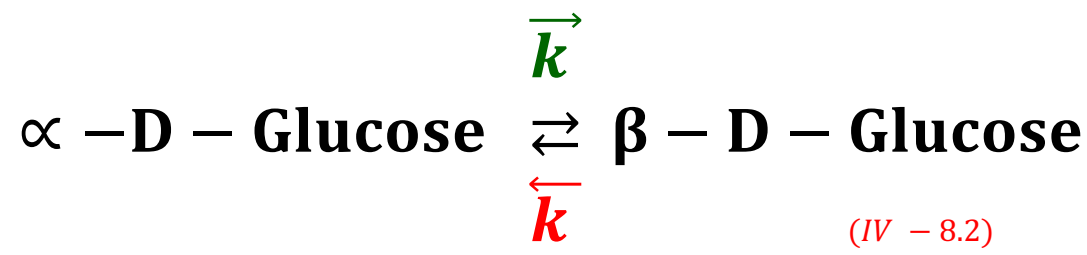


A



B

What is the mechanism of a reversible reaction?



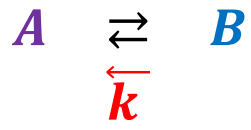
$$\vec{r} = - \left(\frac{d[\alpha]}{dt} \right)_{\rightarrow} \quad \vec{r} = \vec{k} \cdot [\alpha] \quad (IV - 8.3)$$



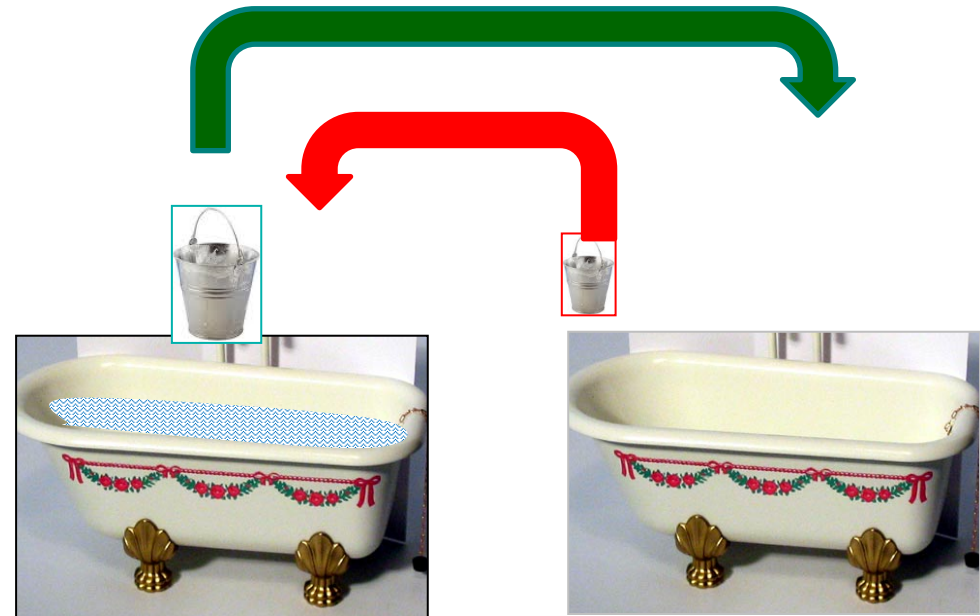
$$\vec{r} = \left(\frac{d[\alpha]}{dt} \right)_{\leftarrow} \quad \vec{r} = \overleftarrow{k} [\beta] \quad (IV - 8.4)$$

#ForwardReaction

#ReverseReaction

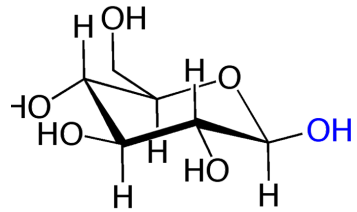
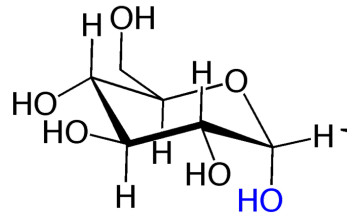


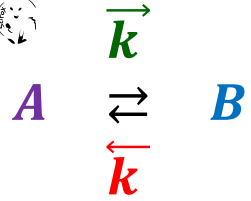
How to model a reversible reaction?



#Rate

#RateConstant





How do we determine the **rate law** for a reversible reaction?

$$\overleftarrow{r} = \left(\frac{d[A]}{dt} \right)_{\leftarrow} \quad \overleftarrow{r} = \overleftarrow{k} [B]$$



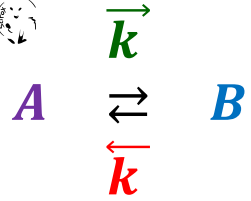
$$\frac{d[A]}{dt} = \overleftarrow{k} [B] - \overrightarrow{k} \cdot [A] \quad (IV - 8.5)$$



$$\overrightarrow{r} = - \left(\frac{d[A]}{dt} \right)_{\rightarrow} \quad \overrightarrow{r} = \overrightarrow{k} \cdot [A]$$

#Source

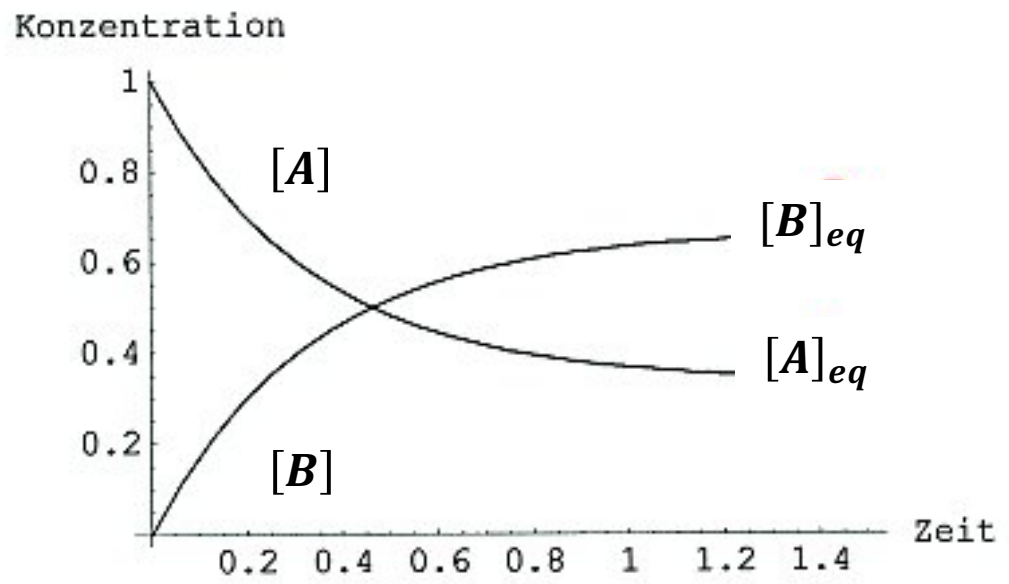
#Sink



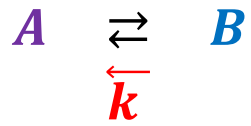
How do concentrations change over time?

$$[A] = \frac{[A]_0}{k_{-1} + k_1} \left(k_{-1} + k_1 \cdot e^{-(k_{-1} + k_1)t} \right) \quad (IV - 8.21)$$

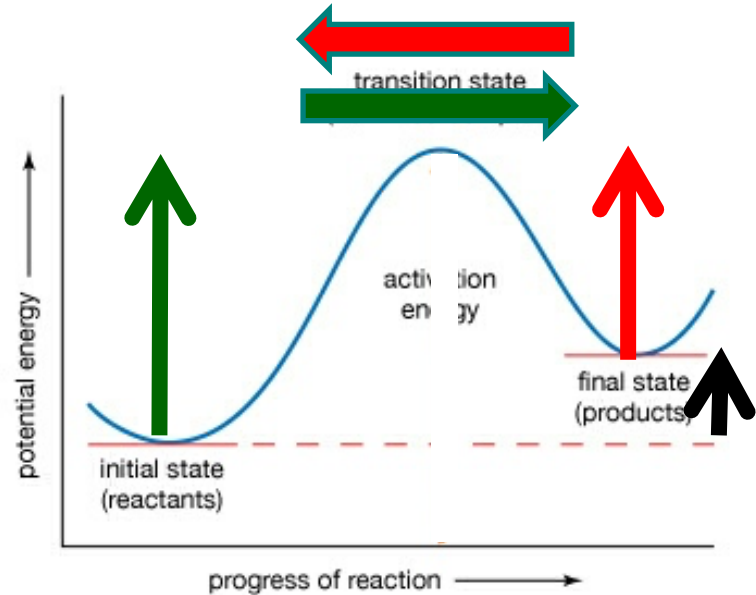
$$[B] = [A]_0 - [A]$$



#IntegratedRateLaw



Thermodynamics and kinetics of a reversible reaction



$$\overrightarrow{E_A} - \overleftarrow{E_A} = \Delta_R H \quad (IV - 8.28)$$

$$\overleftarrow{k} [B]_{eq} = \overrightarrow{k} \cdot [A]_{eq}$$

(IV - 8.26)

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{\overrightarrow{k}}{\overleftarrow{k}}$$

(IV - 8.27)

#DynamicEquilibrium

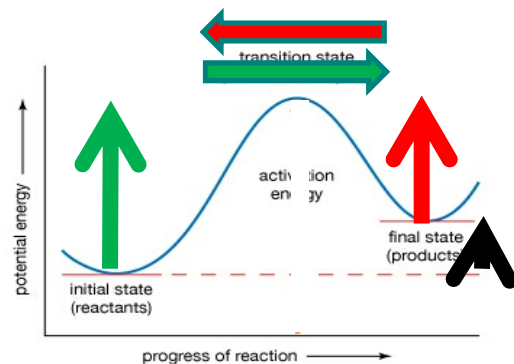
True or False?

At dynamic chemical equilibrium...

A: ...the rate of the forward reaction is equal to the rate of the reverse reaction

B: ...the rate constant of the forward reaction is equal to the rate constant of the reverse reaction

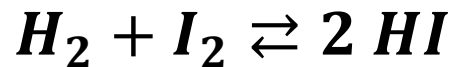
C: ...the activation energy of the forward reaction is equal to the activation energy of the reverse reaction





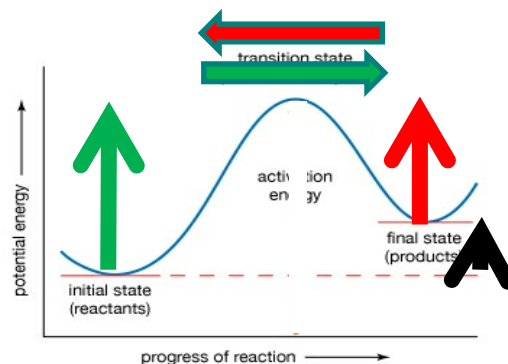
Max Bodenstein
1871 - 1942

How does temperature affect a reversible reaction?



	\xrightarrow{k}	\xleftarrow{k}	K_{eq}
T_1	$2.14 \cdot 10^{-10} \frac{m^3}{mol s}$	$1.66 \cdot 10^{-12} \frac{m^3}{mol s}$	129
T_2	$2.14 \cdot 10^{-7} \frac{m^3}{mol s}$	$2.75 \cdot 10^{-9} \frac{m^3}{mol s}$	77.8
T_3	$3.02 \cdot 10^{-5} \frac{m^3}{mol s}$	$5.5 \cdot 10^{-7} \frac{m^3}{mol s}$	54.9

(IV – Tab.8.1)



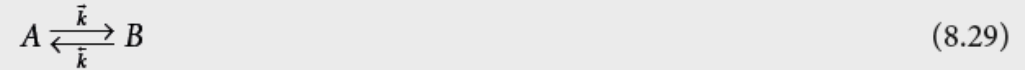
#ArrheniusEquation

#van'tHoff'sReactionIsobar

How does temperature affect **rate constants** and **equilibrium constant**?

Fragen

7. Gegeben ist eine Gleichgewichtsreaktion:



Hinreaktion : $k(298 \text{ K}) = 3,7 \text{ 1/h}$; $E_A = 9.86 \text{ kJ/mol}$;

Rückreaktion: $k(298 \text{ K}) = 2,7 \text{ 1/h}$; $E_A = 19.7 \text{ kJ/mol}$;

- Berechnen Sie die Geschwindigkeitskonstanten \bar{k}' und \bar{k}'' bei 398 K
- Berechnen Sie die Gleichgewichtskonstanten K_{eq} bei 298 K und 398 K.

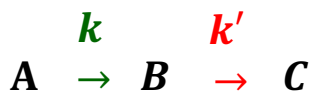
(IV – 11.43) – (IV – 11.51)

PCÜ38 Einfluss der Temperatur auf Thermodynamik und Kinetik einer Gleichgewichtsreaktion

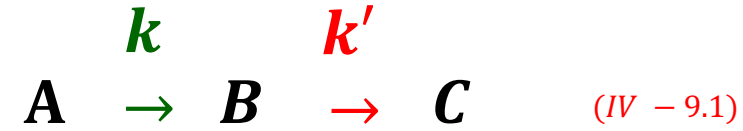
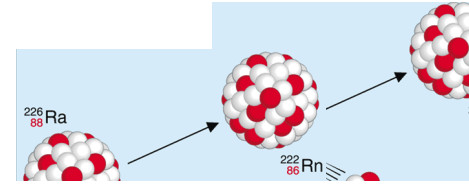
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2:21





What is the mechanism of a **consecutive reaction**?



$$r = \left(\frac{d[B]}{dt} \right)_I \quad r = k \cdot [A] \quad (IV - 9.2)$$

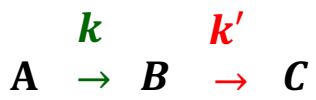


$$r = - \left(\frac{d[B]}{dt} \right)_{II} \quad r = k' [B] \quad (IV - 9.3)$$

#Intermediate

#RateOfFormation

#RateOfDecay



How to **model** a consecutive reaction?



Ra



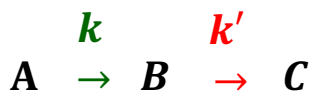
Rn



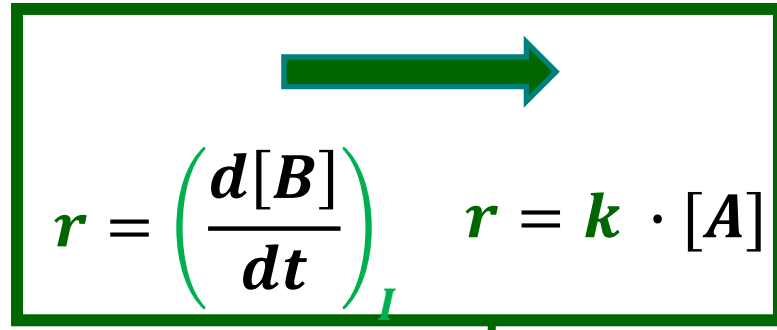
Po

#Rate

#RateConstant



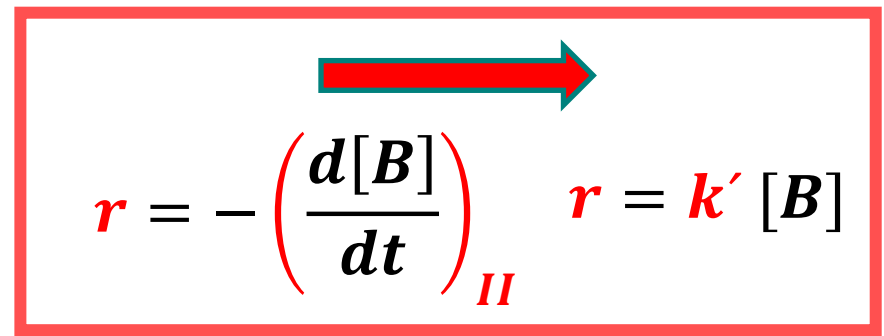
How do we determine the **rate law** for a consecutive reaction?



$$r = \left(\frac{d[B]}{dt} \right)_I = k \cdot [A]$$

$$\frac{d[B]}{dt} = k [A] - k' \cdot [B]$$

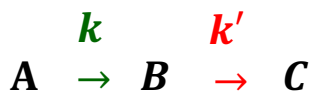
(IV - 9.5)



$$r = - \left(\frac{d[B]}{dt} \right)_{II} = k' [B]$$

#Source

#Sink

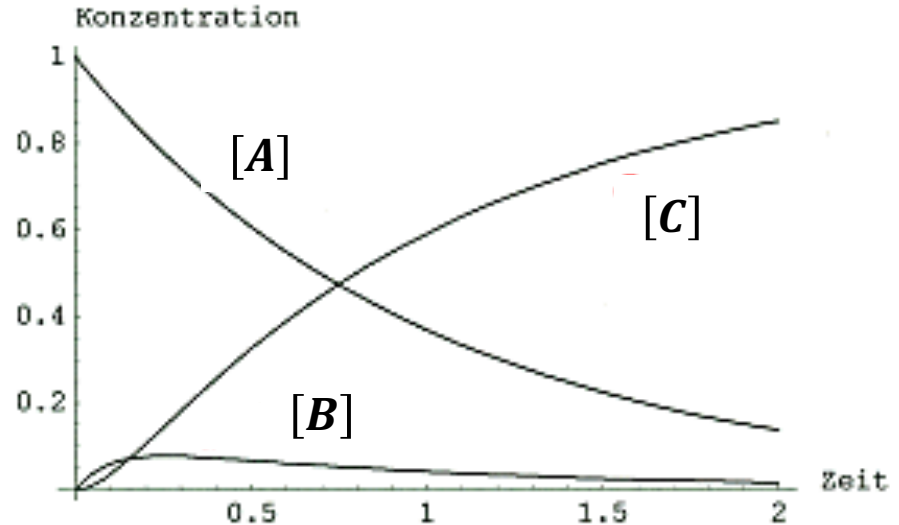


How do **concentrations** change over time?

$$[A] = [A]_0 e^{-k t} \quad (IV - 9.10)$$

$$[B] = \frac{k}{k' - k} \cdot [A]_0 (e^{-k t} - e^{-k' t}) \quad (IV - 9.19)$$

$$[C] = [A]_0 \left(1 - \frac{k'}{k' - k} e^{-k t} + \frac{k}{k' - k} e^{-k' t} \right) \quad (IV - 9.21)$$

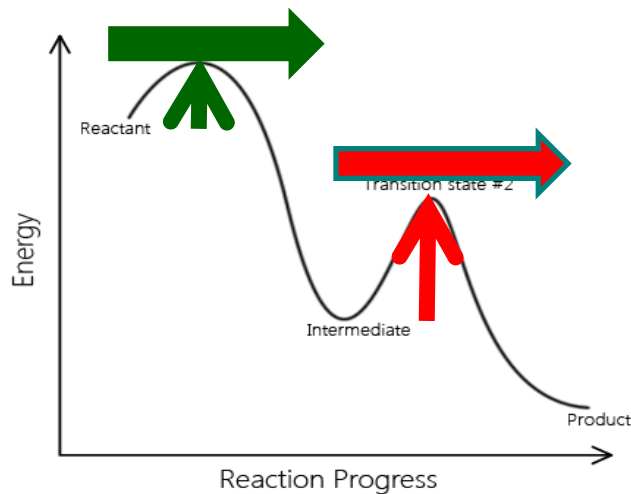


#IntegratedRateLaw



Max Bodenstein
1871 - 1942

How **reactive** is the intermediate?



#SteadyStateApproximation

#RateDeterminingStep

$$\frac{d[B]}{dt} = k[A] - k'[B]$$

(IV - 9.24)

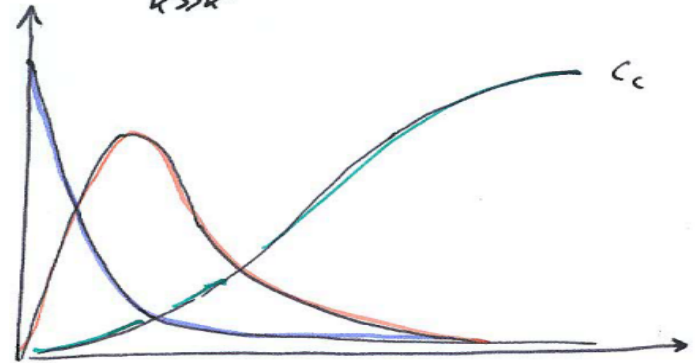
$$[B] \approx 0$$

(IV - 9.25)

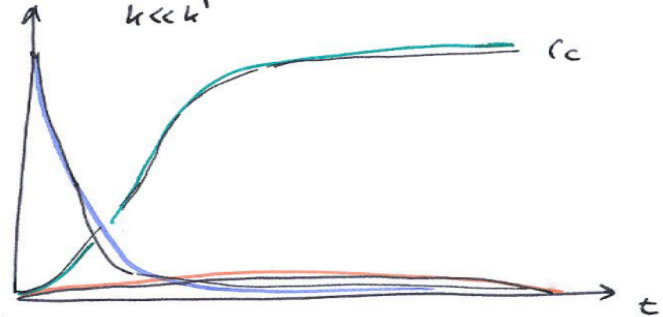
Which is **rate-limiting step** in a consecutive reaction?

$$[B] = \frac{k}{k' - k} \cdot [A]_0 (e^{-k t} - e^{-k' t})$$

$$k \gg k'$$



$$k \ll k'$$



#non – reactiveIntermediate

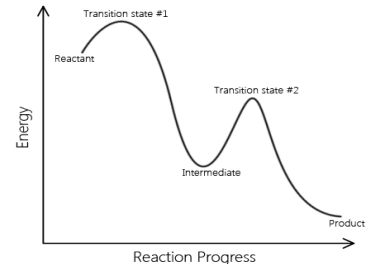
#ReactiveIntermediate



True or False?

A: The rate determining step is the **slowest step** in a consecutive reaction mechanism

B: The rate determining step is the **fastest step** in a consecutive reaction mechanism



#Bottleneck



True or False?

Steady state approximation means:

A: The concentration of a reactive intermediate is very low.

C: The rate of formation of a reactive intermediate is equal to its rate of decay.

B: The concentration of a reactive intermediate does not change with time.

E: The rate of formation of a reactive intermediate is slower than its rate of decay.

How much **radon gas** is emitted from concrete? (^{226}Ra -Activity: 30 Bq)



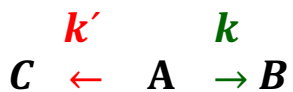
$$r = k [Ra] = k' [Rn]$$

$$k = \frac{\ln(2)}{1620 \cdot 365} = 1.17 \cdot 10^{-6} \frac{1}{d}$$

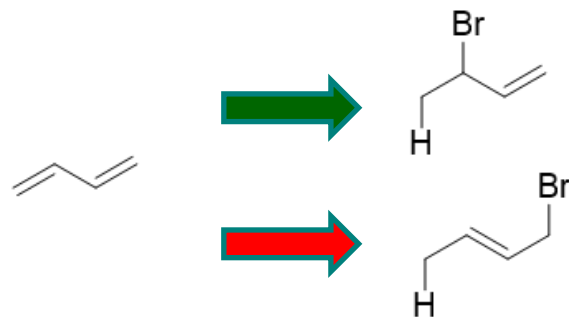
$$k' = \frac{\ln(2)}{3.82} = 1.81 \cdot 10^{-1} \frac{1}{d}$$

$$[Rn] = \frac{r}{k'} = \frac{2.59 \cdot 10^6 \frac{1}{d}}{1.81 \cdot 10^{-1} \frac{1}{d}} = 1.43 \cdot 10^7$$

#DecayChain



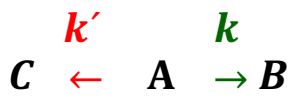
What is the mechanism of a **parallel reaction**?



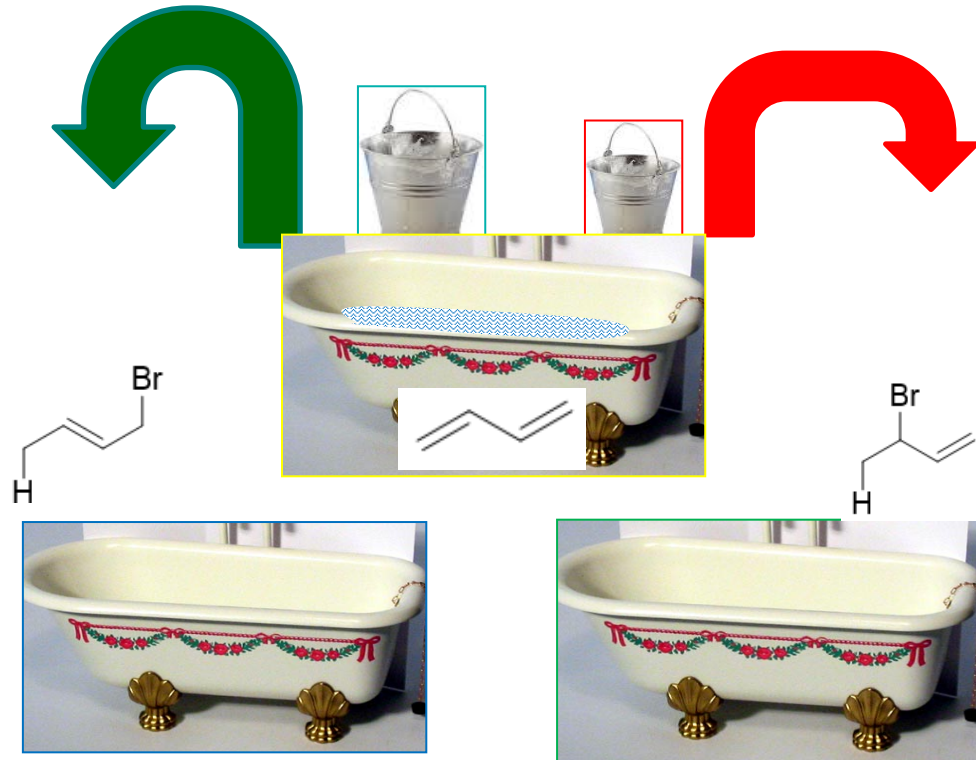
$$r = - \left(\frac{d[A]}{dt} \right)_I \quad r = k \cdot [A]$$

$$r = - \left(\frac{d[A]}{dt} \right)_{II} \quad r = k' [A]$$

#CompetingReactions

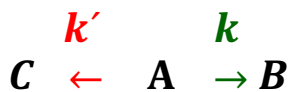


How to **model** a parallel reaction?

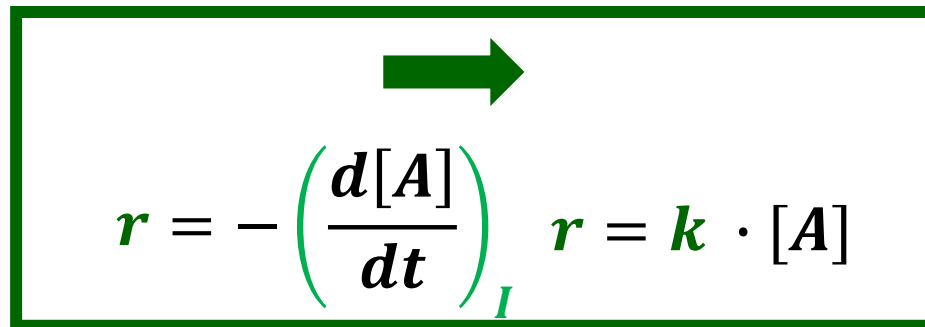


#Rate

#RateConstant

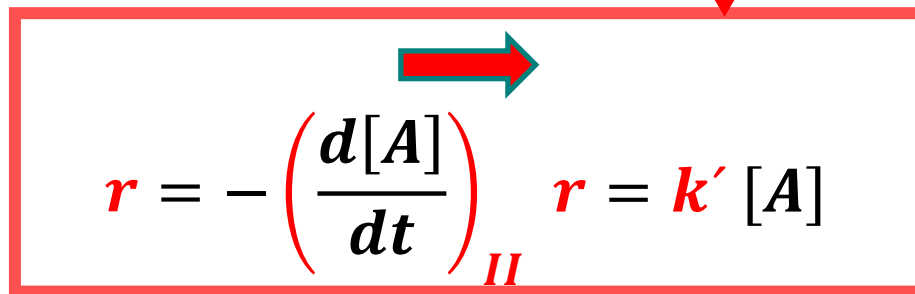


How do we determine the **rate law** for a parallel reaction?



$$r = - \left(\frac{d[A]}{dt} \right)_I \quad r = k \cdot [A]$$

$$\frac{d[A]}{dt} = -k[A] - k'[A] \quad (IV - 10.3)$$



$$r = - \left(\frac{d[A]}{dt} \right)_{II} \quad r = k' [A]$$

#Source

#Sink



Rudolf Wegscheider
1859 -1935

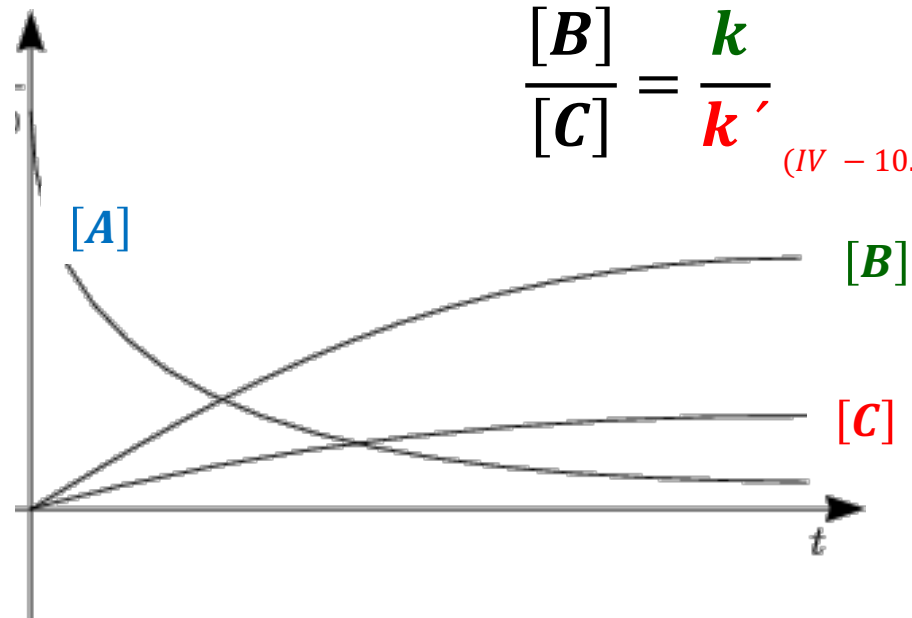
How do concentrations change over time?

$$[A] = [A]_0 e^{-(k' + k)t} \quad (IV - 10.7)$$

$$[B] = \frac{k}{k' + k} \cdot [A]_0 (1 - e^{-(k' + k)t}) \quad (IV - 10.13)$$

$$[C] = \frac{k'}{k' + k} \cdot [A]_0 (1 - e^{-(k' + k)t}) \quad (IV - 10.17)$$

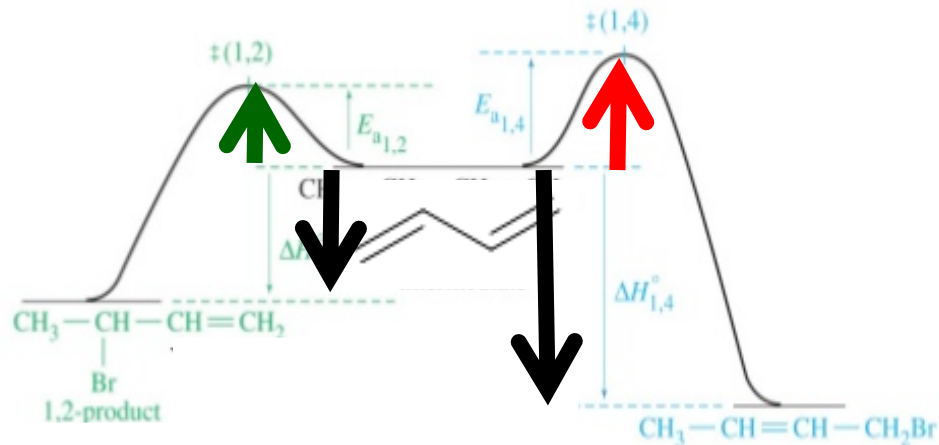
$$\frac{[B]}{[C]} = \frac{k}{k'} \quad (IV - 10.18)$$



#Selectivity

#IntegratedRateLaw

Which **product dominates** in a parallel reaction?



$$\frac{[B]}{[C]} = \frac{k}{k'}$$

$$\frac{[B]}{[C]} = \frac{K_{eq}}{K'_{eq}}$$

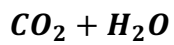
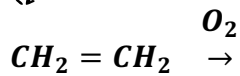
#KineticReactionControl

$T \downarrow; t \downarrow; K_{at}$

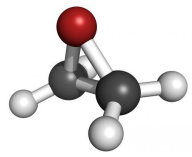
$T \uparrow; t \uparrow$

#ThermodynamicReactionControl

#RateDeterminingStep



(IV - S.39)

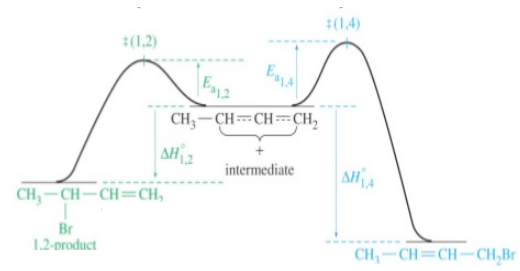


True or False?

To get the kinetic product...

A: ...use higher temperatures. **B:** ...lengthen the reaction time.

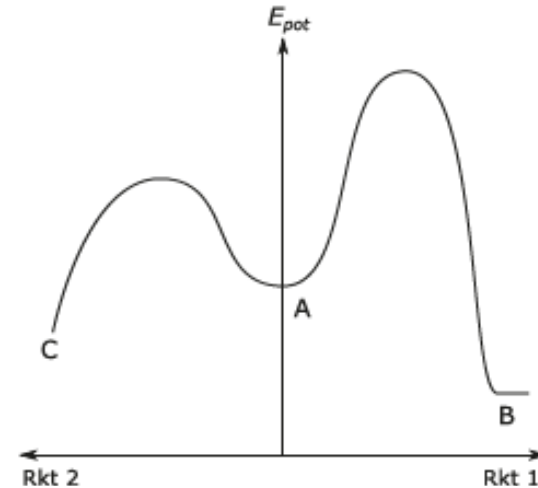
C: ...use a catalyst.



Which **product dominates** in a parallel reaction?

10. Eine Konkurrenzreaktion besitzt ein Reaktionsprofil wie in \circ Abb. 10.2.
- Unter welchen Bedingungen entsteht aus dem Ausgangsstoff das Produkt B?
 - Unter welchen Bedingungen entsteht aus dem Ausgangsstoff das Produkt C?

(IV – 11.74) – (IV – 11.75)



(IV – Fig.10.2)

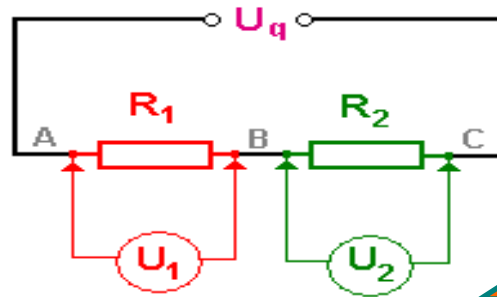
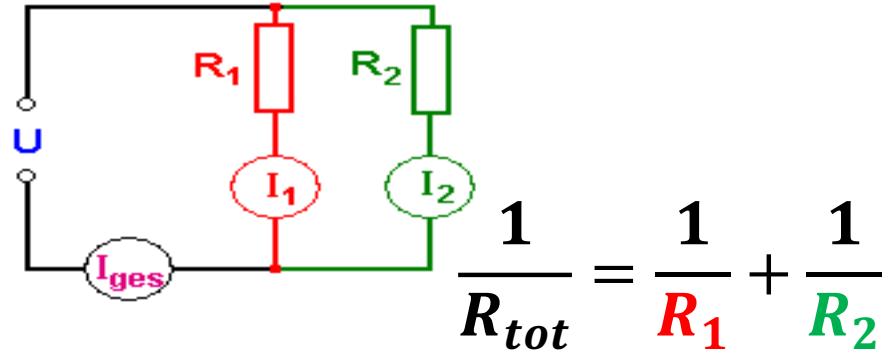


PCÜ41 Wann liefert die Reaktion das thermodynamische bzw. das kinetische Produkt?

1:45

Physikalische Chemie by SciFox

How is the **total resistance** related to the individual resistances?



$$R_{tot} = R_1 + R_2$$

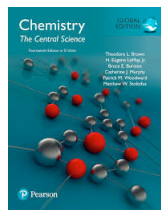
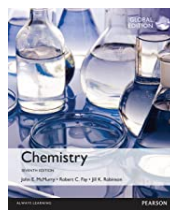
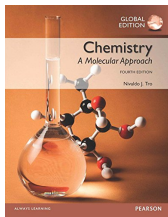
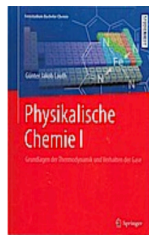
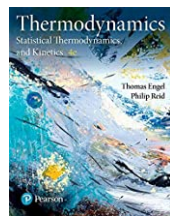


#SeriesCircuit

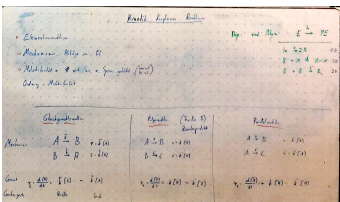
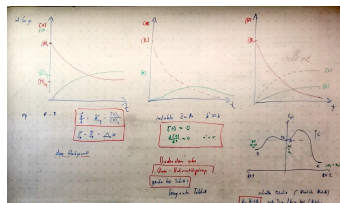
#ParallelCircuit



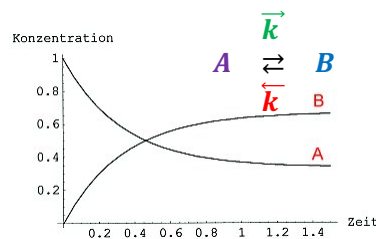
REFERENCES:



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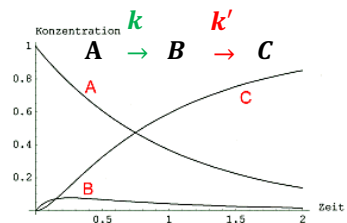


PHYSICAL CHEMISTRY BASICS PART 10: REACTION MECHANISM

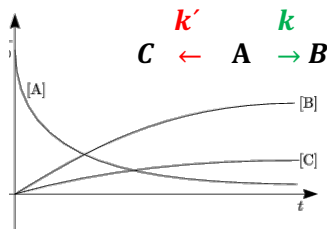


$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{\overrightarrow{k_1}}{\overleftarrow{k_1}}$$

$$\overrightarrow{E_A} - \overleftarrow{E_A} = \Delta_R H$$

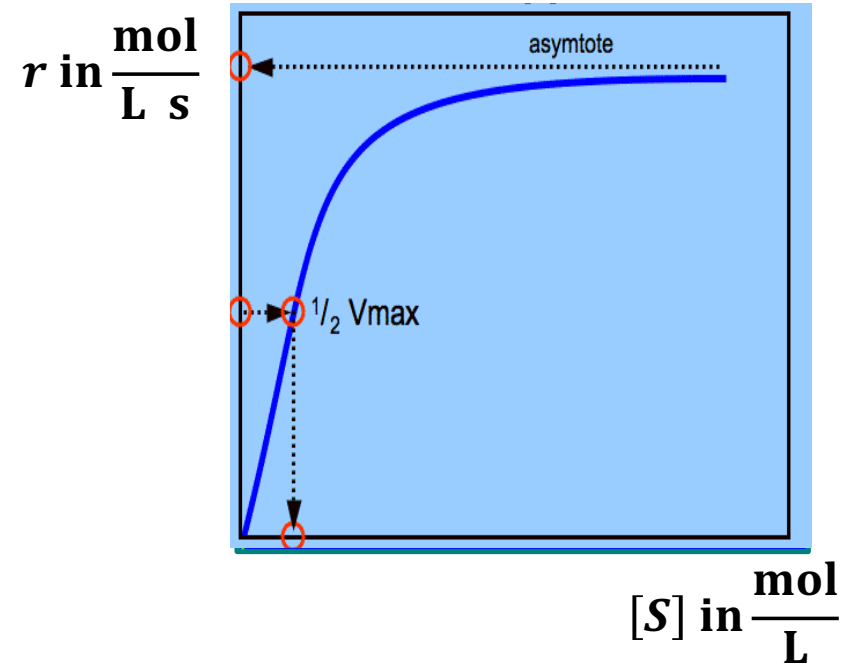


$$\frac{d[B]}{dt} = k_1[A] - k'_1 \cdot [B] \approx 0$$



$$\frac{[B]}{[C]} = \frac{k_1}{k'_1}$$

Why does kinetics **change** from 0th order to 1st order?



What **elementary reactions** are involved in enzyme catalysis?



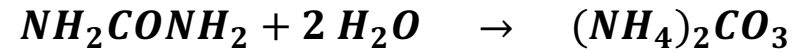
Maud Menten (1879 – 1960)



Leonor Michaelis (1875 – 1949)

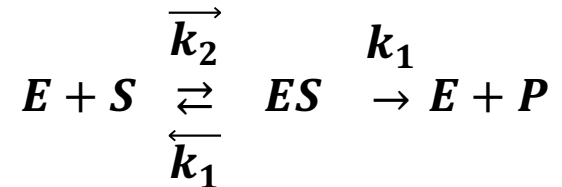
Enzyme E

Urease

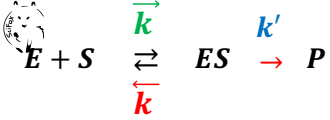


Substrate S

Product P



#MichaelisMentenMechanism



What are the **elementary reactions** in enzyme kinetics?



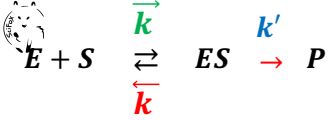
$$r = \left(\frac{d[ES]}{dt} \right) = \overrightarrow{k_2} \cdot [S] \cdot [E]$$



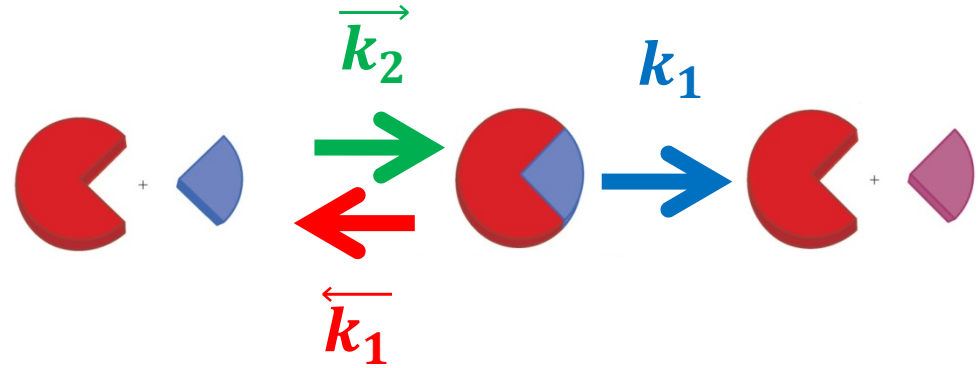
$$-r' = \left(\frac{d[ES]}{dt} \right)' = -\overleftarrow{k_1} \cdot [ES]$$



$$-r'' = \left(\frac{d[ES]}{dt} \right)'' = k_1 \cdot [ES]$$



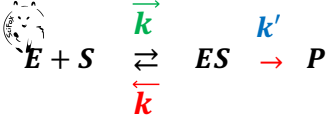
We use **steady state approximation** for the enzyme-substrate intermediate



$$\left(\frac{d[ES]}{dt}\right) = \left(\frac{d[ES]}{dt}\right)_a + \left(\frac{d[ES]}{dt}\right)_b + \left(\frac{d[ES]}{dt}\right)_c$$

$$\left(\frac{d[ES]}{dt}\right) = \vec{k}_2 \cdot [S] \cdot [E] - \overleftarrow{k}_1 \cdot [ES] - k_1 \cdot [ES]$$

$$0 = \vec{k}_2 \cdot [S] \cdot [E] - \overleftarrow{k}_1 \cdot [ES] - k_1 \cdot [ES]$$



How do we calculate the **intermediate concentration**?

$$\left(\frac{d[ES]}{dt}\right) = \bar{k}_2 \cdot [S] \cdot [E] - \bar{k}_1 \cdot [ES] - k_1 \cdot [ES]$$

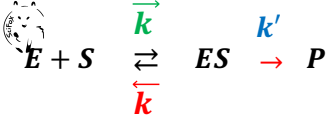
$$[E] = [E]_0 - [ES]$$

$$\left(\frac{d[ES]}{dt}\right) = \bar{k}_2([E]_0 - [ES])[S] - \bar{k}_1[ES] - k_1[ES]$$

$$\frac{d[ES]}{dt} = 0$$

$$[ES] = \frac{[E]_0[S]}{[S] + \frac{\bar{k}_1 + k_1}{\bar{k}_2}}$$

#FreeEnzymeConcentration



What is the **reaction rate** in enzyme kinetics?

$$[ES] = \frac{[E]_0[S]}{[S] + \frac{\overleftarrow{k}_1 + k_1}{\overrightarrow{k}_2}} \quad K_M = \frac{\overleftarrow{k}_1 + k_1}{\overrightarrow{k}_2}$$

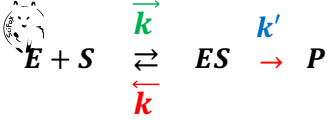
$$[ES] = \frac{[E]_0[S]}{[S] + K_M}$$

$$r = \frac{d[P]}{dt} = k_1 \cdot [ES]$$

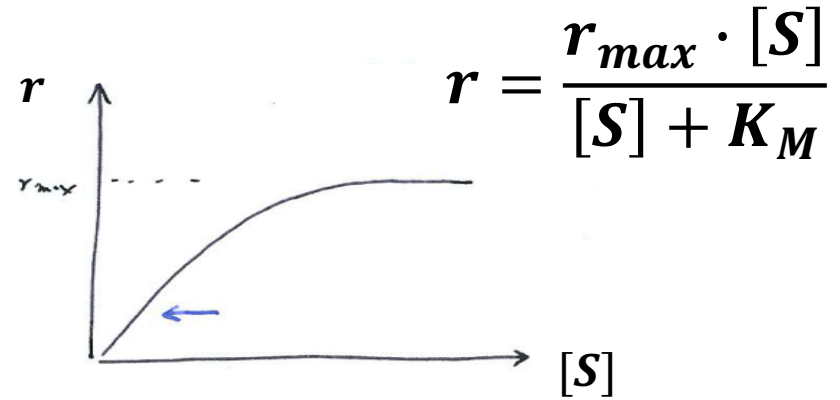
$$r = k_1 \cdot \frac{[E]_0[S]}{[S] + K_M} \quad r_{max} = k_1 \cdot [E]_0$$

$$r = r_{max} \cdot \frac{[S]}{[S] + K_M}$$

#MichaelisMentenEquation



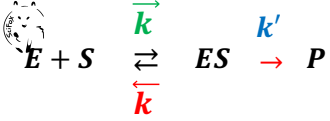
How do we **analyse** the Michaelis-Menten equation to get kinetic parameters?



$$\frac{1}{r} = \frac{K_M}{r_{max}} \cdot \frac{1}{[S]} + \frac{1}{r_{max}}$$

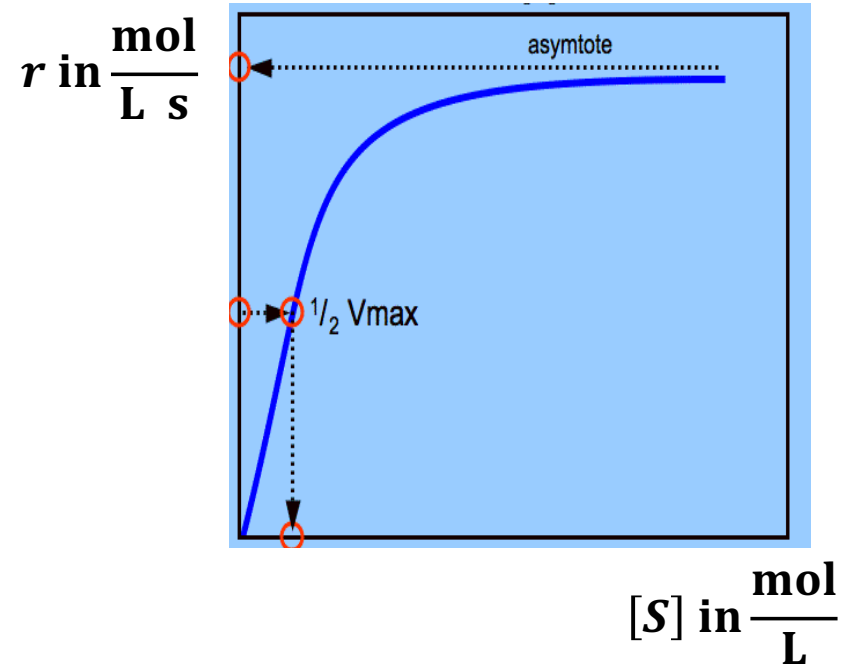


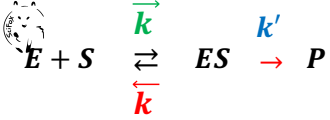
#LINEWEAVER – BURK *Plot*



At what **substrate concentration** has r dropped to half of r_{max} ?

$$r = \frac{r_{max} \cdot [S]}{[S] + K_M}$$





True or False?

ES =
enzyme substrate complex

A: The decay reaction of ES is 1st order

B: The larger the MICHAELIS-MENTEN-constant K_{MM} , the larger is [ES]

C: Steady state approximation applies to ES