

# Lecture General Chemistry

## Winter Term 2022/23

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- Website (Slides, Exercises):
- <http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/>

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## Reaktion kinetics

- Basics, describing quantities
- Definition of reaction rates
- Order of a reaction
- influence of temperature

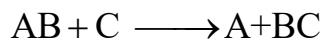
## Some quantities

- molar amount  $n$ : number of particles, [mol]  
 $1 \text{ Mol} = 6,022 \cdot 10^{23} \text{ particles}$ 
  - Def.: 1 Mol contains as many particles as 12 g of  $^{12}_6\text{C}$
- molar mass  $M$ : Mass of 1 Mol of particles [g/mol]
- molar concentration  $c$ : particles per volume, [mol/L] (molarity)
  - another: molality, [mol/kg]
    - does not change with temperature

## More quantities

- molar fraction  $x$ : 
$$x_a = \frac{n_a}{n_{\text{total}}} \quad \left( = \frac{n_a}{\sum_{i=1}^j n_i} \right)$$
- partial pressure  $p$ : 
$$p_a = x_a \cdot p$$
- mass fraction  $w$ : 
$$w_a = \frac{m_a}{m_{\text{gesamt}}} \quad \left( = \frac{m_a}{\sum_{i=1}^j m_i} \right)$$

### reaction rate $v$



- The higher the educt concentration, the faster the product is formed

$$v_f \propto c(\text{AB}) \text{ and: } v_f \propto c(\text{C})$$

$$v_f \propto c(\text{AB}) \cdot c(\text{C})$$

- Reactions can proceed in both directions

$$v_r \propto c(\text{A}) \text{ and: } v_r \propto c(\text{BC})$$

$$v_r \propto c(\text{A}) \cdot c(\text{BC})$$

### reaction rate $v$

- Proportionality is not enough for accurate calculations, so a constant is introduced:

$$v_f = k_f \cdot c(\text{AB}) \cdot c(\text{C})$$

- for  $2\text{A} \rightarrow \text{B}$

$$v_f = k_f \cdot c(\text{A}) \cdot c(\text{A}) = k_f \cdot c(\text{A})^2$$

- Stoichiometric coefficients appear as exponents in the rate expression

## reaction rate $v$

Definition of  $v$ , example reaction:  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$

$$\left. \begin{aligned} v &= -\frac{dp(\text{H}_2)}{dt} \\ v &= -\frac{dp(\text{I}_2)}{dt} \\ v &= \frac{1}{2} \frac{dp(\text{HI})}{dt} \end{aligned} \right\} v = \frac{1}{\nu_A} \frac{dp_A}{dt}$$

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## Definition of the order of a reaction

- The reaction order is the sum of the exponents of the concentrations in the rate law
- $v = k \cdot c(\text{A}) \cdot c(\text{B})$  2<sup>nd</sup> Order
- $v = k \cdot c(\text{A}) \cdot c(\text{A}) = k \cdot c^2(\text{A})$  2<sup>nd</sup> Order
- $v = -\frac{dc(\text{A})}{dt} = k \cdot c(\text{A})$  1<sup>st</sup> Order
- $v = -\frac{dc(\text{A})}{dt} = k$  0<sup>th</sup> Order

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## Reaction 1<sup>st</sup> Order: $A \rightarrow \text{Product(s)}$

- rate law: 
$$v = -\frac{dc(A)}{dt} = k \cdot c(A)$$

Integration by separation of the variables

$$\frac{dc(A)}{c(A)} = -k dt$$

$$\ln c(A) = -kt + C$$

Determination of the integration constant C  
from initial conditions

initial condition:  $c(A) = c_0(A)$  at  $t = 0$

$$\ln c(A) = -kt + \ln c_0(A)$$

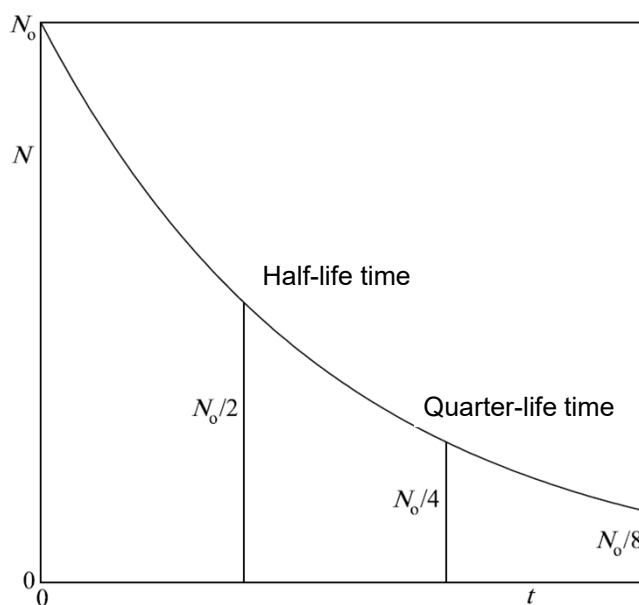
$$c(A) = c_0(A) \cdot e^{-kt}$$

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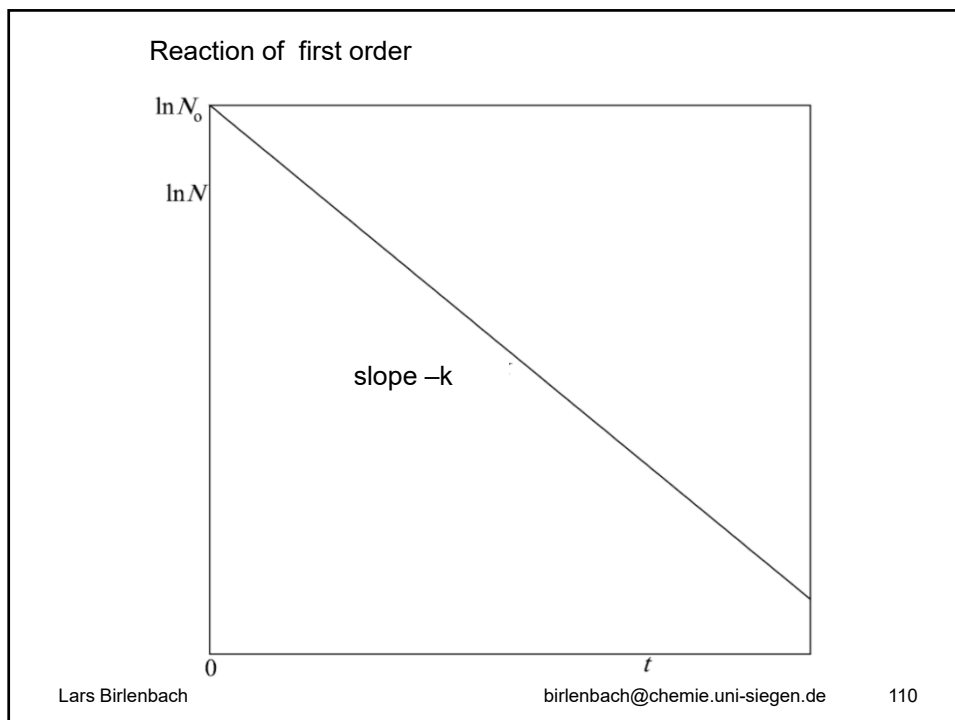
Reaction of first order



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**Reaction of second order:**  
**A + B → Products**

- rate law: 
$$v = -\frac{dc(A)}{dt} = -\frac{dc(B)}{dt} = k \cdot c(A) \cdot c(B)$$

$$-\frac{dc(A)}{dt} = k \cdot c(A) \cdot c(B) \quad \text{one more variable! simplify!}$$

$$c(A) = c_0(A) - x \qquad c_0(A) = c_0(B)$$

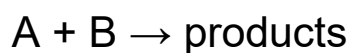
$$c(B) = c_0(B) - x$$

$$c(A) \cdot c(B) = (c_0(B) - x) \cdot (c_0(A) - x)$$

$$c(A) \cdot c(B) = (c_0(A) - x)^2 \qquad \frac{dx}{dt} = -k(c_0(A) - x)^2$$

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## Reaction of second order:



$$\frac{dx}{dt} = -k(c_0(A) - x)^2 \quad \frac{dx}{(c_0(A) - x)^2} = -k dt$$

Integrate:  $\frac{1}{c_0(A) - x} = \frac{1}{c(A)} = kt + C$

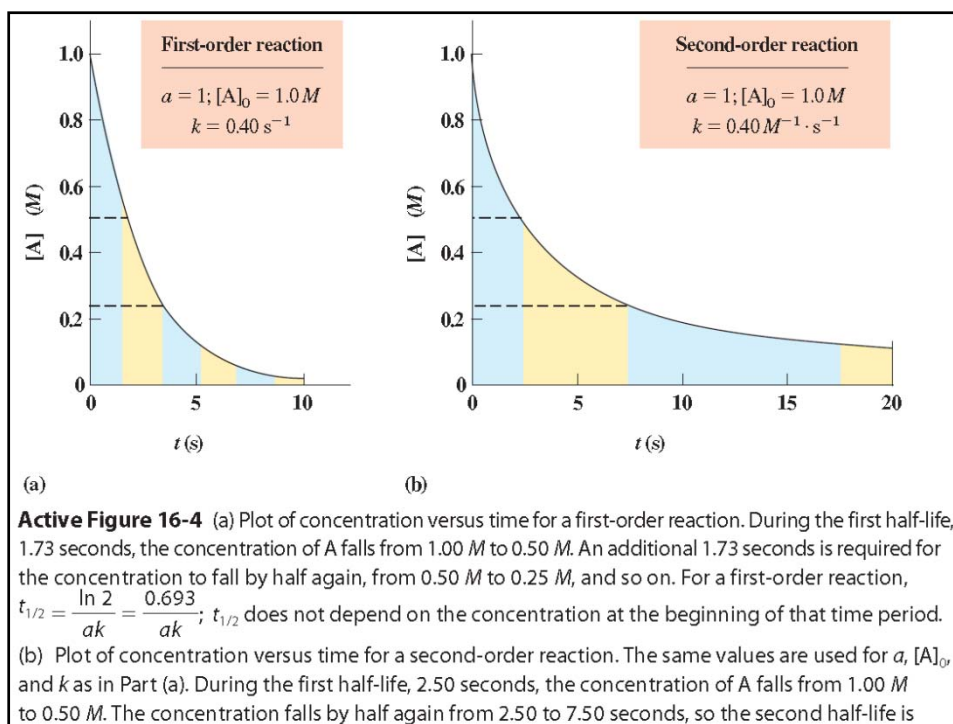
boundary condition:  $t = 0 : C = \frac{1}{c_0(A)}$

$$\frac{1}{c(A)} = \frac{1}{c_0(A)} + kt$$

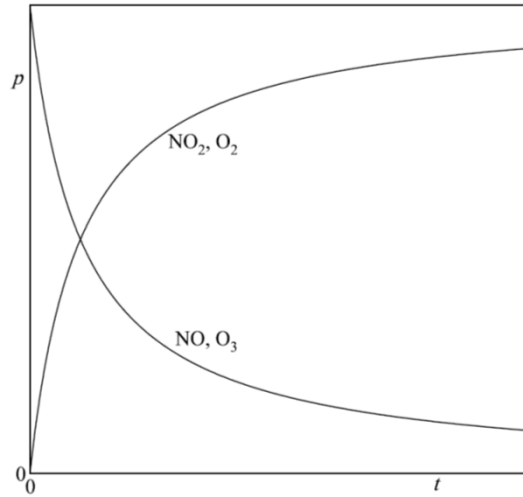
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example:  $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$

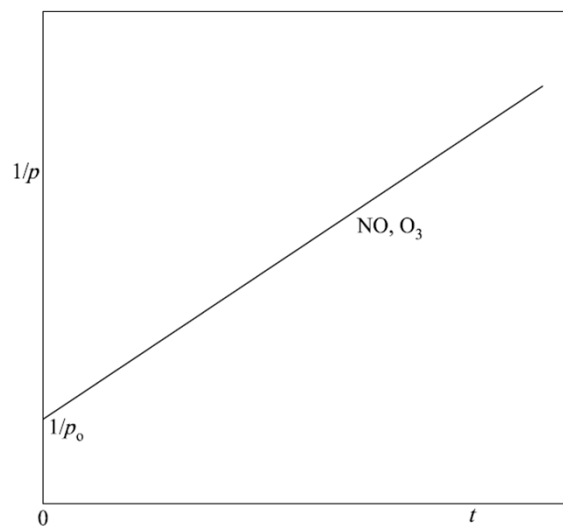


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Reaction 2<sup>nd</sup> Order: plot  $1/p$  against time



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## Reactions of 0<sup>th</sup> order

$$v = -\frac{dc(A)}{dt} = k$$

$$-\frac{dc(A)}{dt} = k \quad ; \quad dc(A) = -kdt$$

$$c(A) = -kt + C$$

$$c(A) = c_0(A) \text{ at } t = 0! \text{ so: } C = c_0(A)$$

Reaction rate does not depend on educt concentration!

Example: Reaction at catalyst surface.  
Size of the surface determines rate

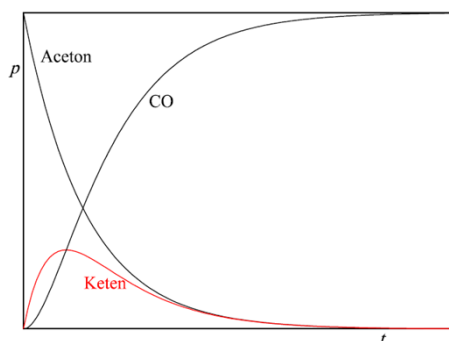
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## Reaction mechanism

- describes how reaction takes place
- often more complex than  $A + B \rightarrow AB$
- Example:  $2\text{CH}_3\text{COCH}_3 \rightarrow 2\text{CH}_4 + 2\text{CO} + \text{C}_2\text{H}_4$



1<sup>st</sup> step:



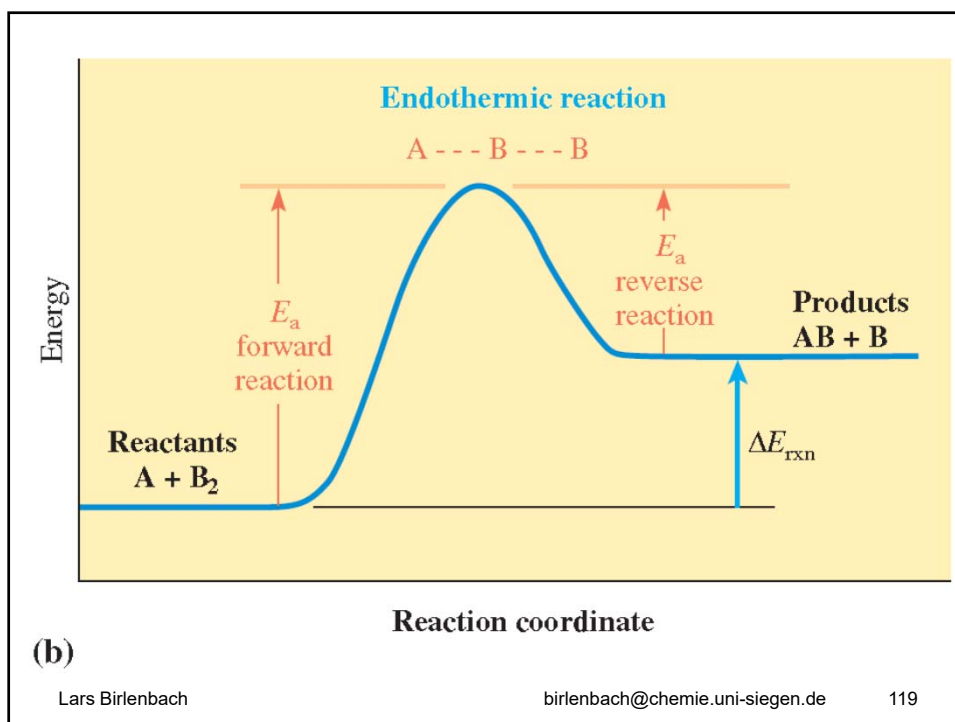
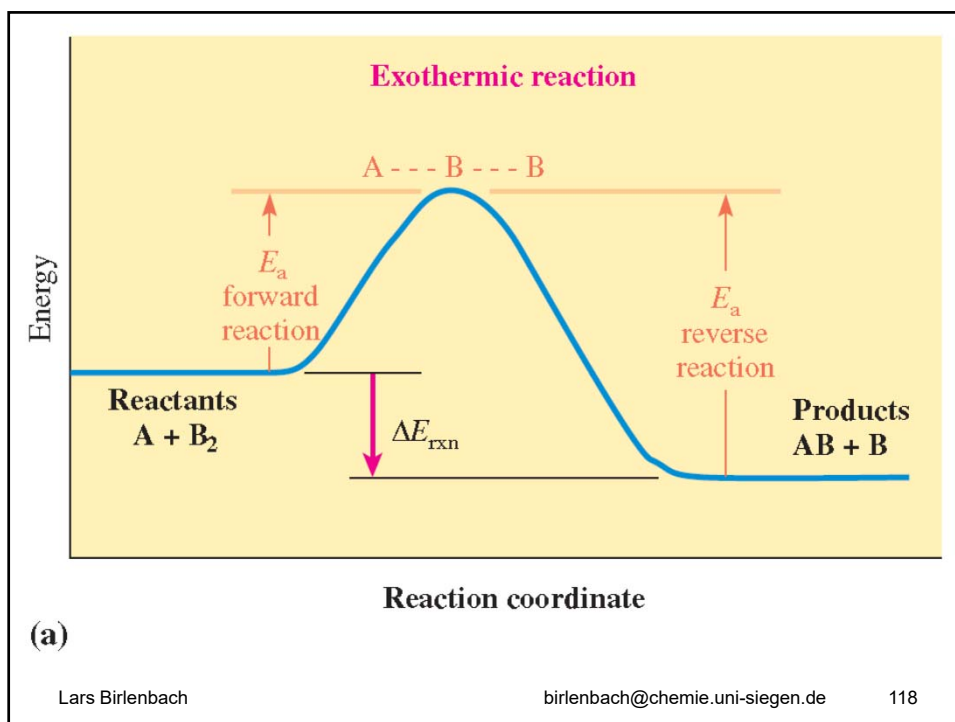
2<sup>nd</sup> step:

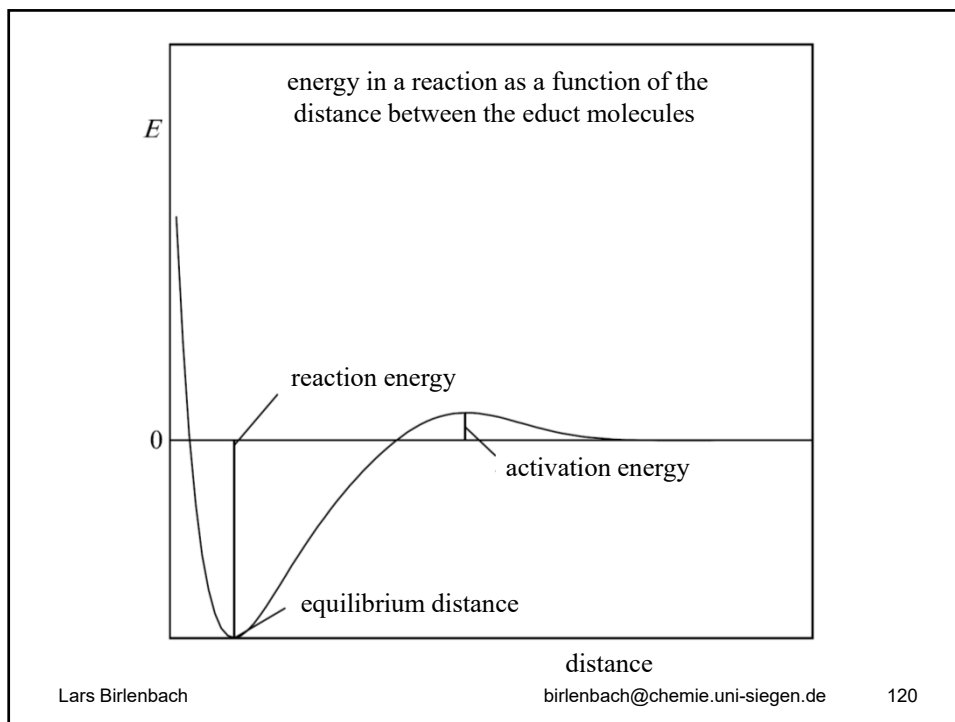


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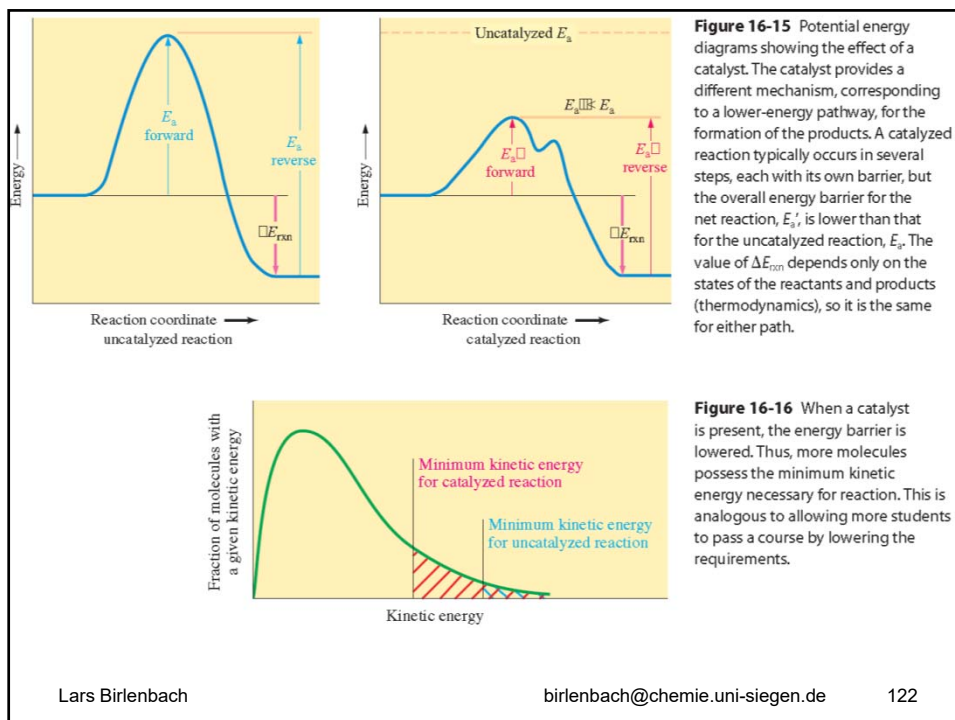
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## catalysts

- lower activation energy
- increase reaction rate
- chemical equilibrium is reached faster
- do not influence the composition in chemical equilibrium
- important, used very much in lab and industry

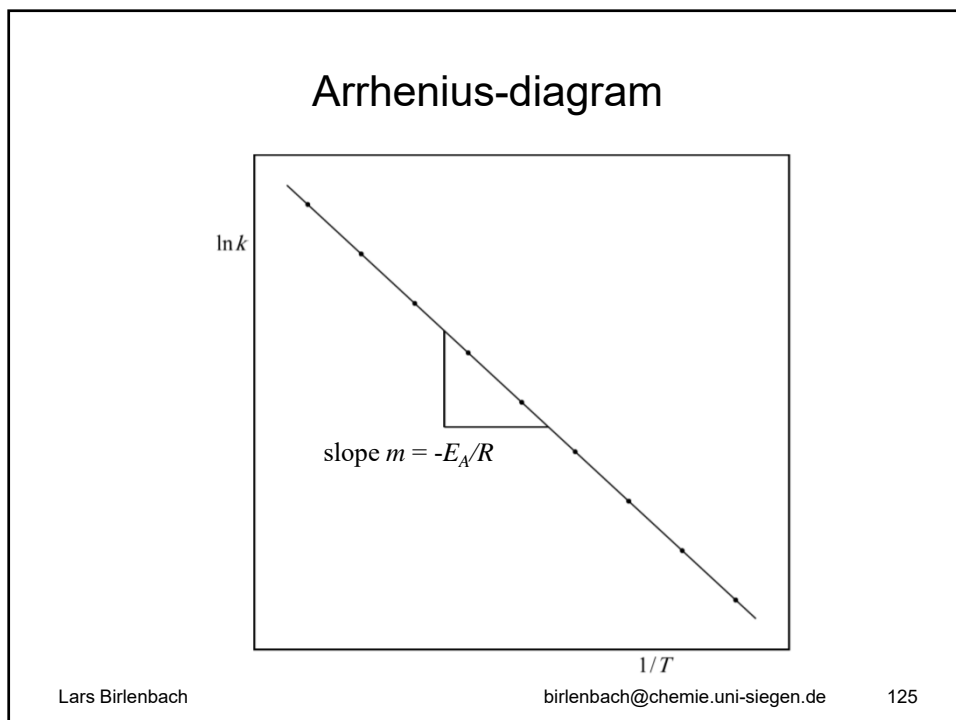
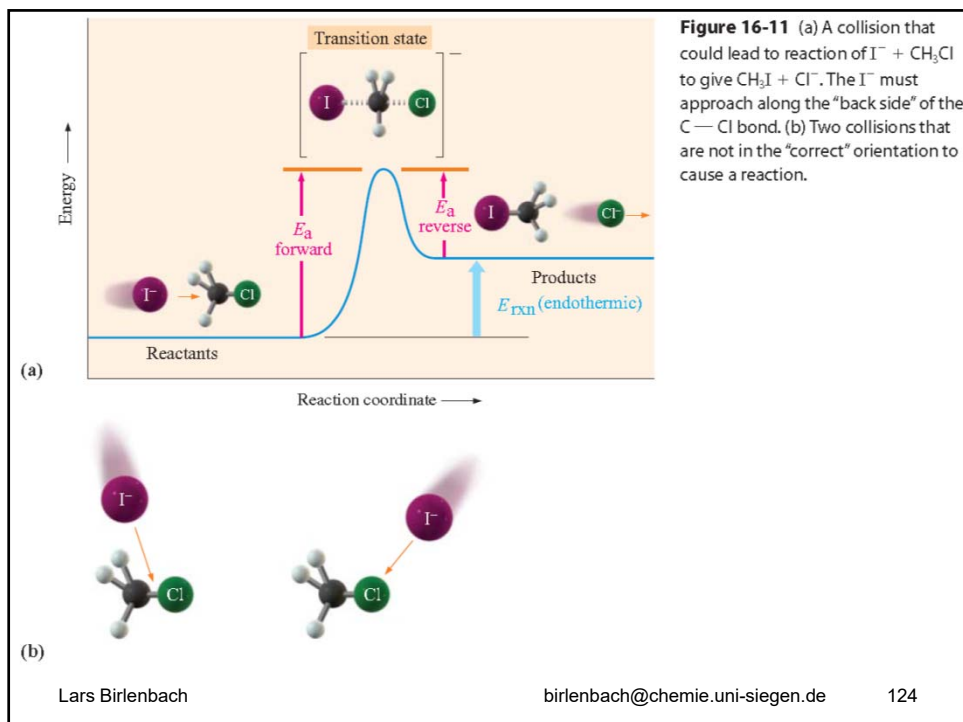


## Arrhenius-Equation

- explains temperature dependence of the rate constant  $k$

$$k = A \cdot e^{\frac{-E_A}{RT}}$$

- $E_A$ : Activation energy
  - Minimal energy necessary for the reaction to happen
  - Molecules have to climb an "activation mountain"
- $A$ : pre-exponential factor (probability of reaction)



$k$  is a function of temperature

$$\ln k_1 = \ln A - \frac{E_A}{R} \frac{1}{T_1} \quad \ln k_2 = \ln A - \frac{E_A}{R} \frac{1}{T_2}$$

$$E_A = - \frac{R \ln \frac{k_1}{k_2}}{\frac{1}{T_1} - \frac{1}{T_2}} = - \frac{8,314 \ln \frac{1}{2}}{\frac{1}{293,15} - \frac{1}{303,15}} \approx 51 \text{ kJ/mol}$$

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## dynamic equilibrium

- where ends a reaction?
  - Composition does not change anymore if the back and forth reaction rates are equal

$$v_f = k_f \cdot c(\text{AB}) \cdot c(\text{C})$$

$$v_r = k_r \cdot c(\text{BC}) \cdot c(\text{A})$$

$$v_f = v_r$$

$$k_f \cdot c(\text{AB}) \cdot c(\text{C}) = k_r \cdot c(\text{BC}) \cdot c(\text{A})$$

$$\frac{k_f}{k_r} = \frac{c(\text{BC}) \cdot c(\text{A})}{c(\text{AB}) \cdot c(\text{C})}$$

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## Law of mass action

- constants  $k_f$  and  $k_r$  can be combined:

$$\frac{k_f}{k_r} = K_c = \frac{c(\text{BC}) \cdot c(\text{A})}{c(\text{AB}) \cdot c(\text{C})}$$

- stoichiometric coefficients become exponents

## Experiment in lab course: ferric thiocyanate



$$K_c = \frac{c(\text{Fe}(\text{SCN})_3)}{c(\text{Fe}^{3+}) \cdot c^3(\text{SCN}^-)}$$

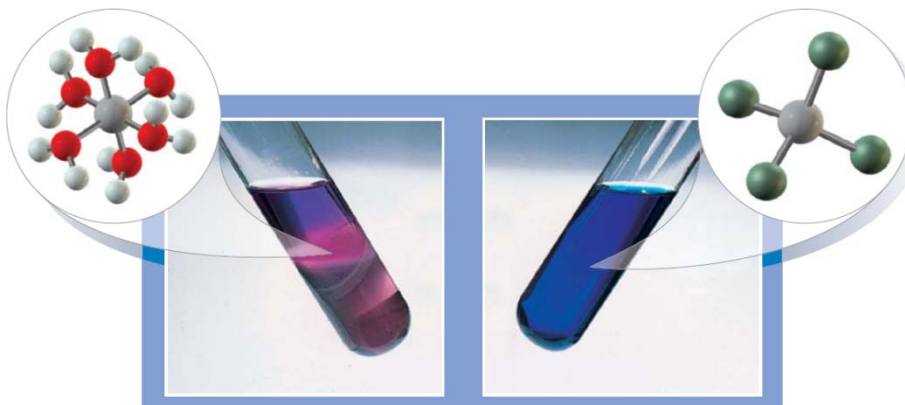
## principle of LeChatelier

- a system (a reaction) evades an external constraint so that  $K$  stays the same
- which constraints?
  - concentration
  - pressure
  - heat

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Effects of changes in concentration on the equilibrium

$$[\text{Co}(\text{OH}_2)_6]^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O}$$

A solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in isopropyl alcohol and water is purple (not shown) due to the mixture of  $[\text{Co}(\text{OH}_2)_6]^{2+}$  (pink) and  $[\text{CoCl}_4]^{2-}$  (blue). When we add concentrated  $\text{HCl}$ , the excess  $\text{Cl}^-$  shifts the reaction to the right (blue, right photo). Adding  $\text{AgNO}_3(\text{aq})$  removes some  $\text{Cl}^-$  by precipitation of  $\text{AgCl}(\text{s})$  and favors the reaction to the left (produces more  $[\text{Co}(\text{OH}_2)_6]^{2+}$ ); the resulting solution is pink (left photo). Each model shows the structure of the cobalt complex species present in higher concentration; other ions and solvent molecules are not shown.

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