# General Chemistry
# Winter Term 2023/24

Dr. Lars Birlenbach
Physikalische Chemie 1 (PC1)
AR-F0102
Tel.: 0271 740 2817
eMail: birlenbach@chemie.uni-siegen.de

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

Login Data for slides:
User: Ludwig
Password: Boltzmann

---

# Reactions of 0th order

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

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

$$c(\mathrm{A}) = -kt + C$$

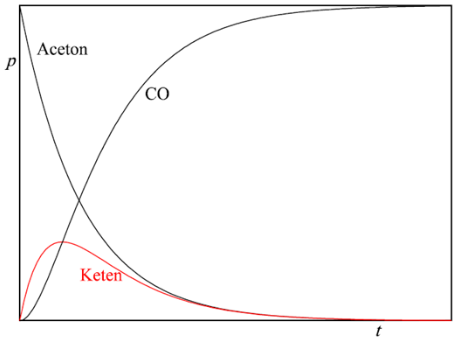
$$c(\mathrm{A}) = c_0(\mathrm{A}) \text{ at } t = 0! \quad \text{so: } C = c_0(\mathrm{A})$$

Reaction rate does not depend on educt concentration!

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

## Reaction mechanismn

- describes how reaction takes place
- often more complex than A + B → AB
- Example: $2CH_3COCH_3 \rightarrow 2CH_4 + 2CO + C_2H_4$



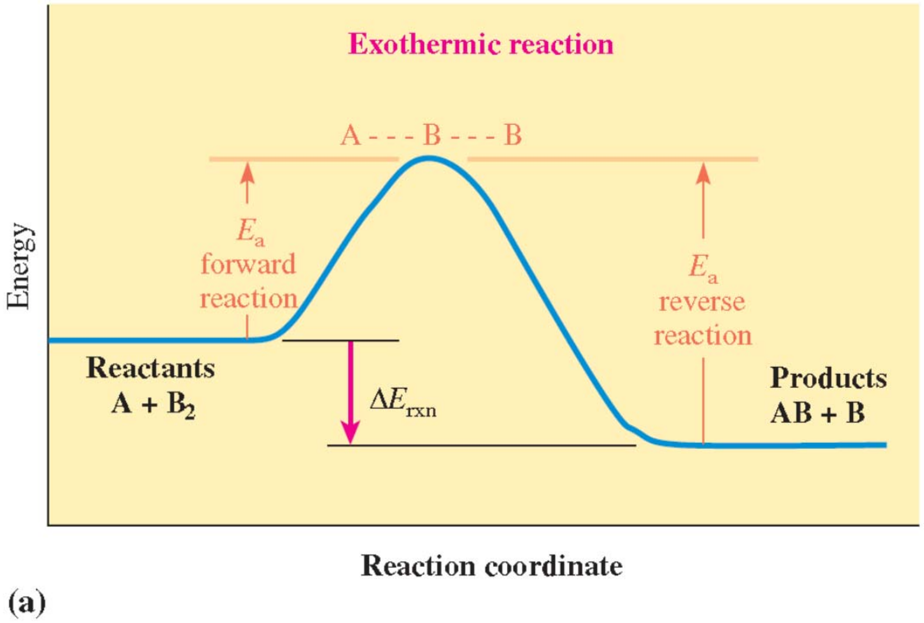
1st step:

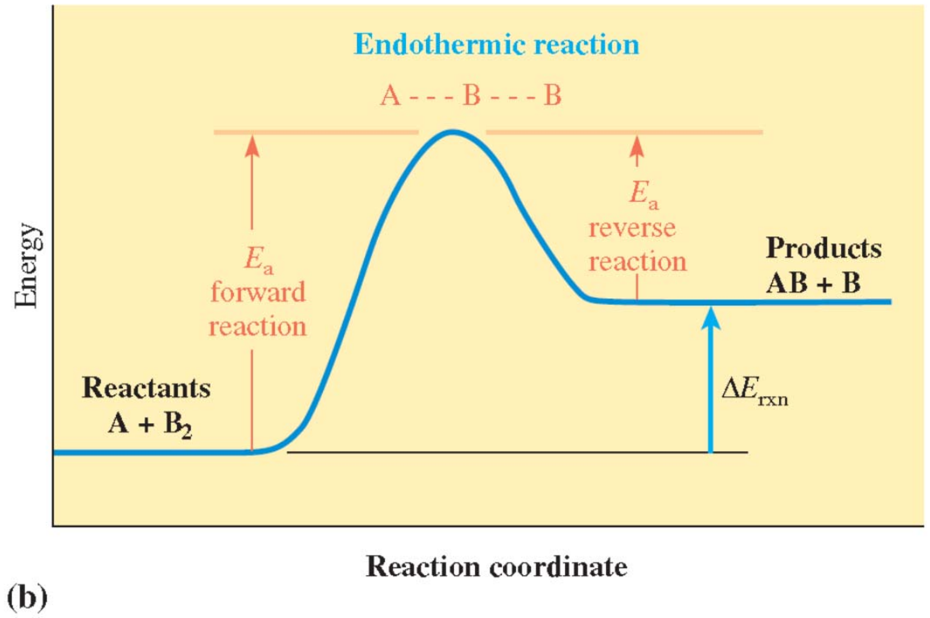
$CH_3COCH_3 \rightarrow CH_2{=}C{=}O + CH_4$

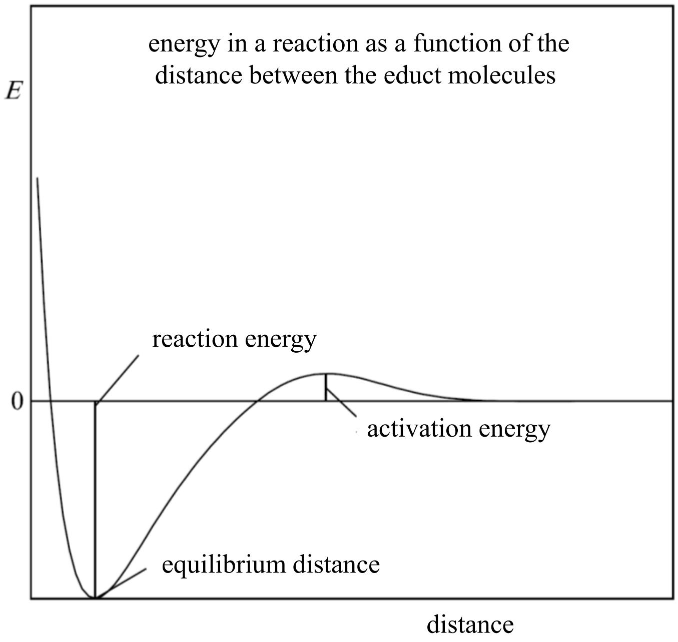
2nd step:

$2CH_2{=}C{=}O \rightarrow CH_2{=}CH_2 + 2CO$

---




Endothermic reaction
A - - - B - - - B
Energy
$E_a$ forward reaction
$E_a$ reverse reaction
Products AB + B
Reactants A + $B_2$
$\Delta E_{rxn}$
Reaction coordinate
(b)


energy in a reaction as a function of the distance between the educt molecules
E
0
reaction energy
activation energy
equilibrium distance
distance

# 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

---

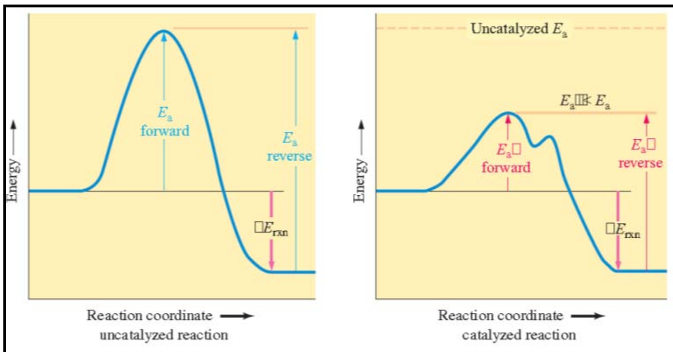


**Figure 16-15** Potential energy diagrams showing the effect of a catalyst. The catalyst provides a different mechanism, corresponding to a lower-energy pathway, for the formation of the products. A catalyzed reaction typically occurs in several steps, each with its own barrier, but the overall energy barrier for the net reaction, $E_a'$, is lower than that for the uncatalyzed reaction, $E_a$. The value of $\Delta E_{rxn}$ depends only on the states of the reactants and products (thermodynamics), so it is the same for either path.

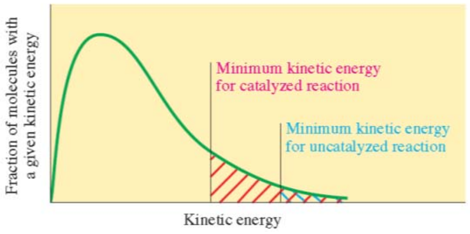


**Figure 16-16** When a catalyst is present, the energy barrier is lowered. Thus, more molecules possess the minimum kinetic energy necessary for reaction. This is analogous to allowing more students to pass a course by lowering the requirements.

## 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)

---

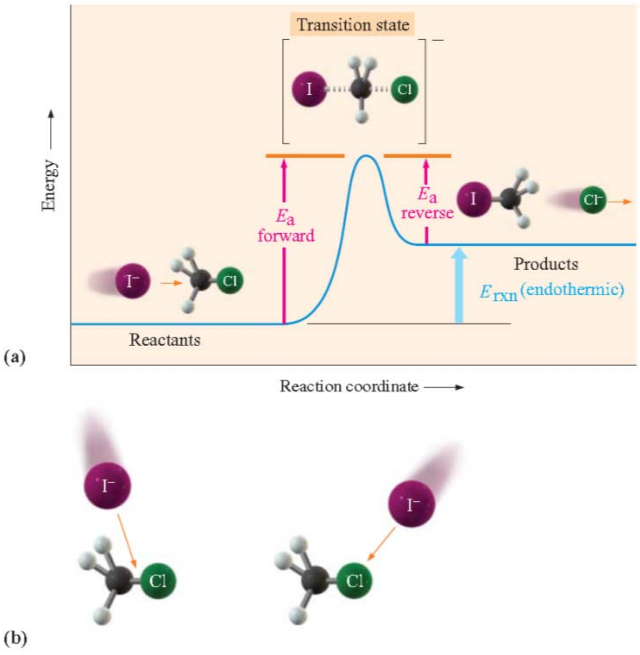
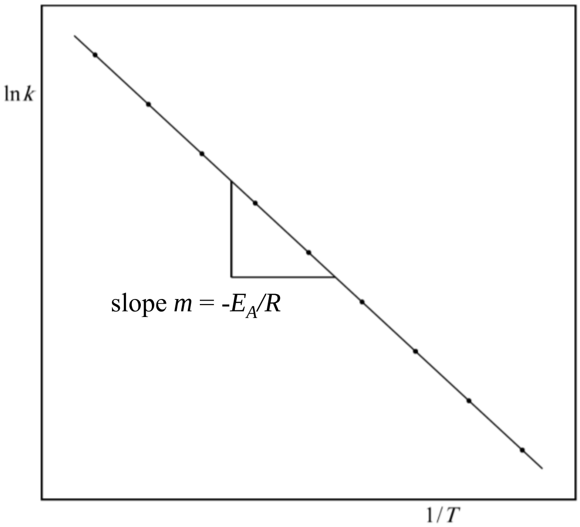


**Figure 16-11** (a) A collision that could lead to reaction of $I^-$ + $CH_3Cl$ to give $CH_3I$ + $Cl^-$. The $I^-$ must approach along the "back side" of the C — Cl bond. (b) Two collisions that are not in the "correct" orientation to cause a reaction.

# Arrhenius-diagram



---

# *k* is a function of temperature

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

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

## dynamic equilibrium

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

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

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

$$v_f = v_r$$

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

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

## Law of mass action

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

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

- stochiometric coefficients become exponents

## Experiment in lab course: ferric thiocyanate

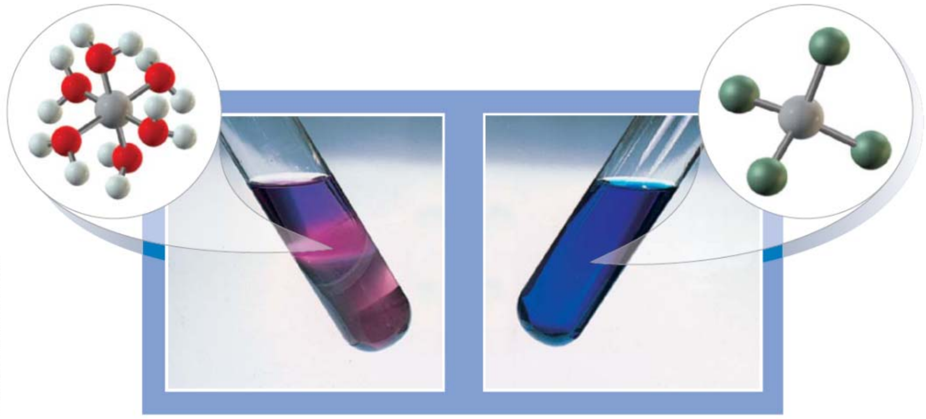
$$\underbrace{\mathrm{Fe}^{3+}}_{\text{yellowish}} + \underbrace{3\,\mathrm{SCN}^{-}}_{\text{colourless}} \rightleftarrows \underbrace{\mathrm{Fe(SCN)}_3}_{\text{red}}$$

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

---

## principle of LeChatelier

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



© Cengage Learning/Charles Steele

Effects of changes in concentration on the equilibrium

$$[Co(OH_2)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

A solution of $CoCl_2 \cdot 6H_2O$ in isopropyl alcohol and water is purple (not shown) due to the mixture of $[Co(OH_2)_6]^{2+}$ (*pink*) and $[CoCl_4]^{2-}$ (*blue*). When we add concentrated HCl, the excess $Cl^-$ shifts the reaction to the right (*blue, right photo*). Adding $AgNO_3(aq)$ removes some $Cl^-$ by precipitation of $AgCl(s)$ and favors the reaction to the left (produces more $[Co(OH_2)_6]^{2+}$); 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.