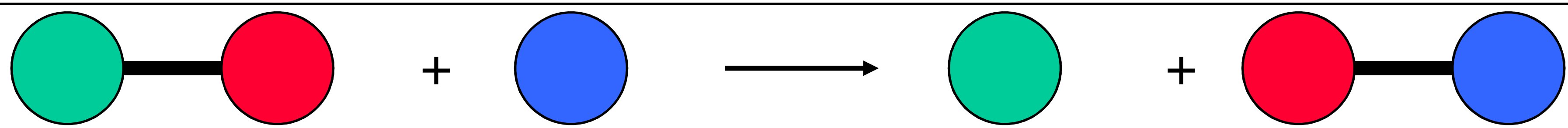
chemical reactions - two basic questions:



1) What is the driving force behind a chemical reaction?

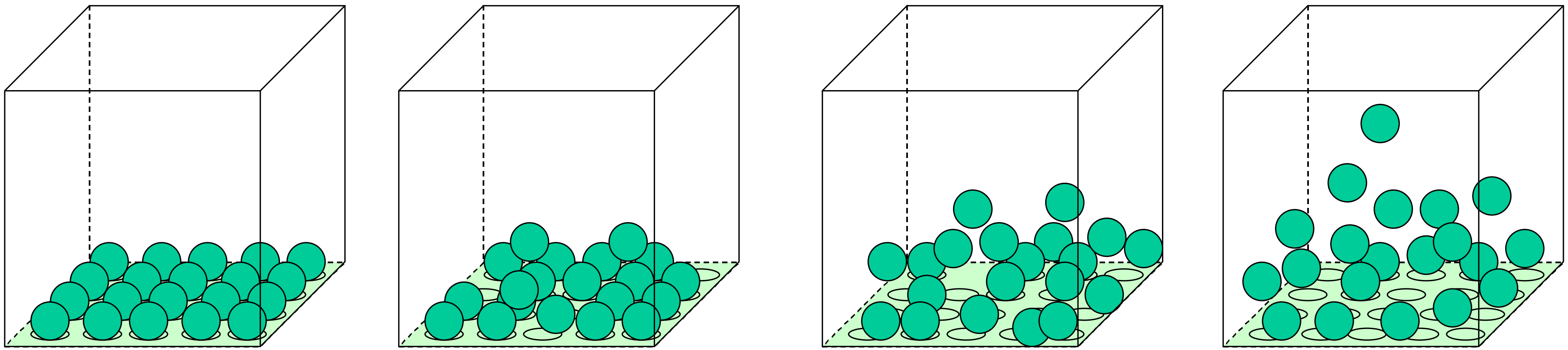
2) How fast does a chemical reaction proceed?

Chemical thermodynamics - What drives a chemical reaction?

The key parameter is the change of the Free Enthalpy

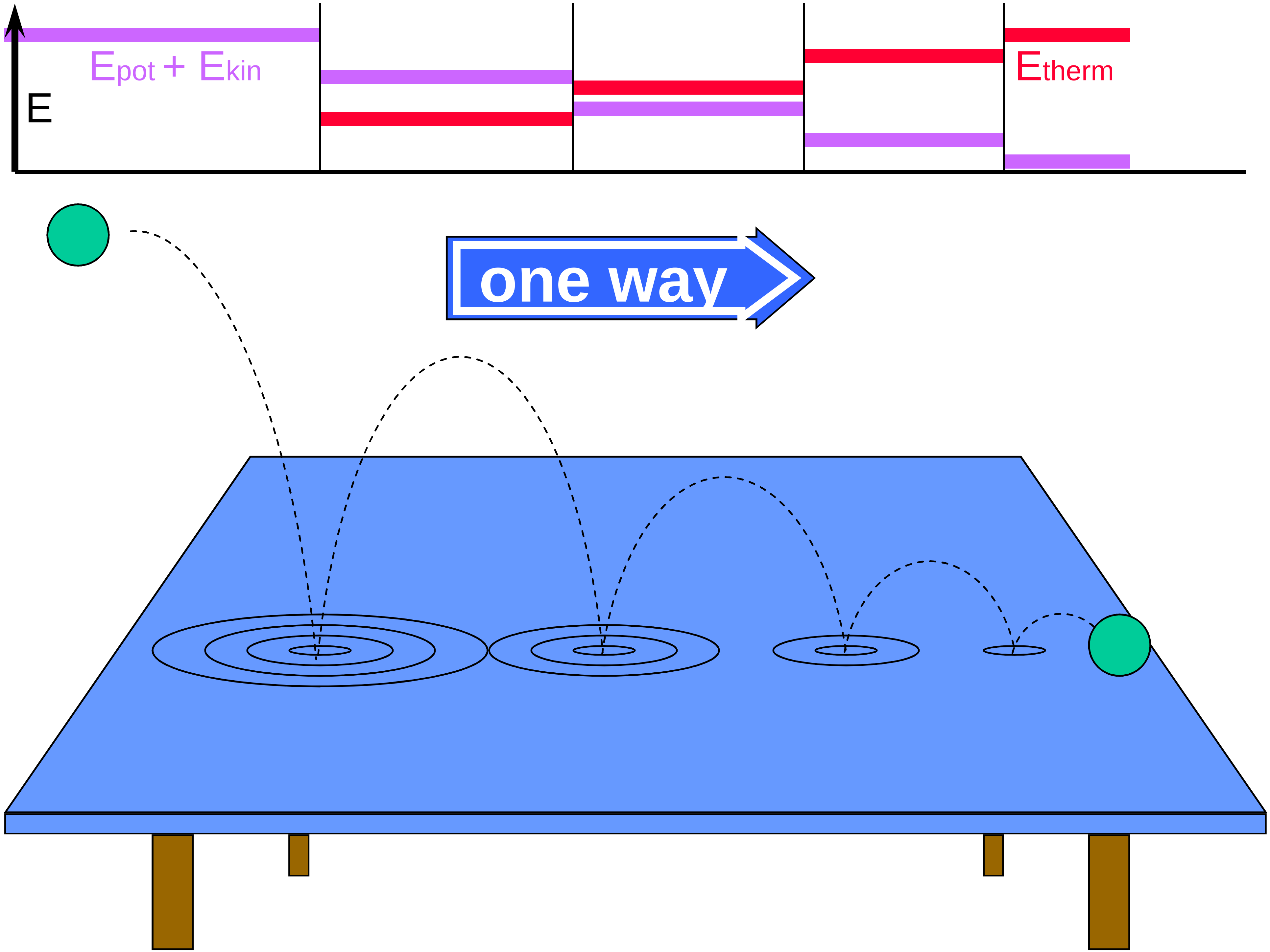
$$\Delta G$$

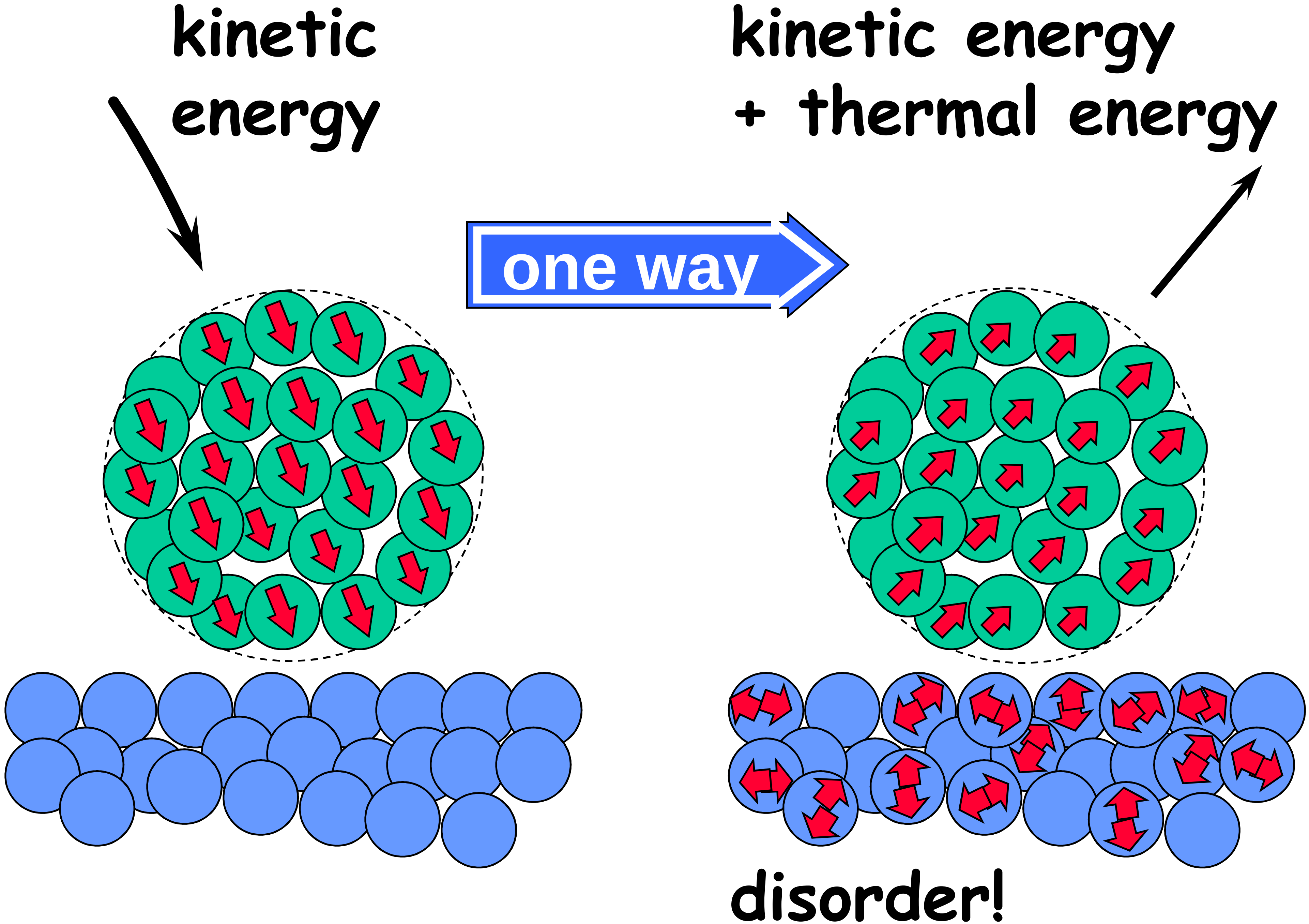
general driving force for all spontaneous processes: the decrease of order, the decrease of free enthalpy ΔG



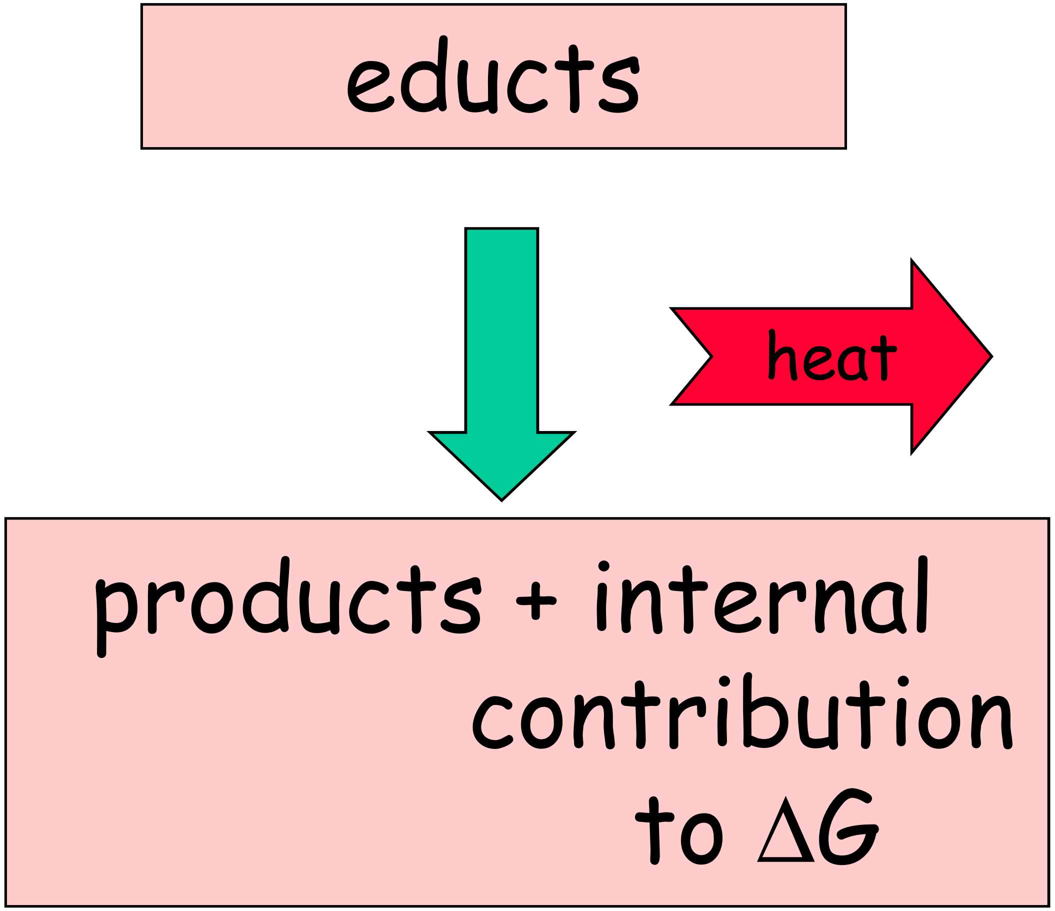
$\Delta G < 0$

decrease of order
decrease of free enthalpy


E
Epot + Ekin
Etherm
one way


kinetic energy
one way
kinetic energy + thermal energy
disorder!

the decrease of free enthalpy connected to chemical reactions - internal and external contributions:



ΔH, leads to external contribution to ΔG

Chemical reactions primarily driven by the emission of heat:

$$2Cu + O_2 \longrightarrow 2CuO$$
$$2Na + Cl_2 \longrightarrow 2NaCl$$

Chemical reactions primarily driven by the generation of internal disorder:

$$H_2CO_3 \longrightarrow H_2O + CO_2$$
$$NH_4Cl \longrightarrow HCl + NH_3$$

Summary

The key criterium is the decrease of the free enthalpy (or $\Delta G < 0$).

Two contributions to a negative enthalpy change are important:

- the emission of heat

- the generation of internal disorder

Chemical kinetics -
how fast are chemical reactions?

v = velocity of a chemical reaction

The velocity of a given chemical reaction generally depends on three parameters:

- the concentration of the educts
- the temperature
- the presence or the absence of a catalyst

time frame of important chemical reactions

slow — fast

10^{3} | 10^{0} | 10^{-3} | 10^{-6} | 10^{-9} | 10^{-12} | 10^{-15} s

typical reactions in organic chemistry: substitutions, additions...

enzymatically catalyzed reactions

typical reactions in inorganic chemistry: dissociations, reductions, oxidations

diffusion controlled elementary reactions

molecular rotation

molecular vibration

electronic excitation

Chemical kinetics - dependence of v on concentrations

v generally depends on the concentration of the reaction educts A, B, C, ... (with concentrations c_A c_B c_C ...) according to the equation:

$$v \quad = \quad k\, c_A^a\, c_B^b\, c_C^c \ldots$$

with k being the rate constant of the reaction.
The exponents a, b, c, ... characterize the individual dependencies of v on the concentrations of A, B, C, ...
The sum $s = a+b+c+\ldots$ is called the <u>order of the reaction.</u>

interpretation of the rate „constant" k:

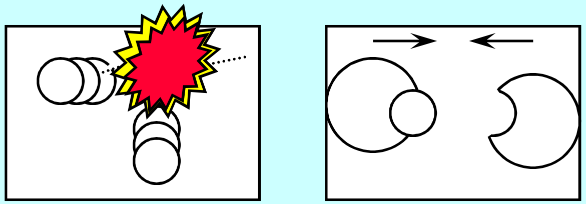
$$k$$

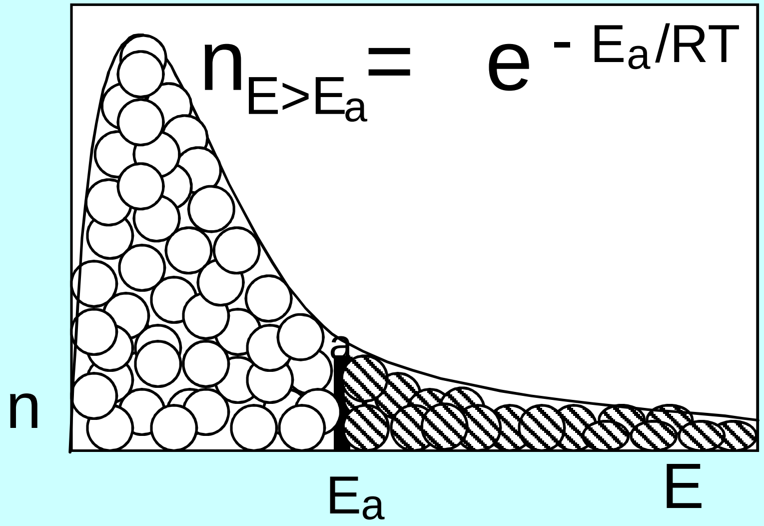
$$k \quad = \quad A \quad * \quad e^{-E_a/RT}$$

frequency factor:
The fraction of molecules that fulfill sterical conditions

Boltzmann-factor:
The fraction of molecules with an energy higher than E_a

- collision frequency
- sterical factors (conformation, molecular orientation)





The Chemical Equilibrium

example:

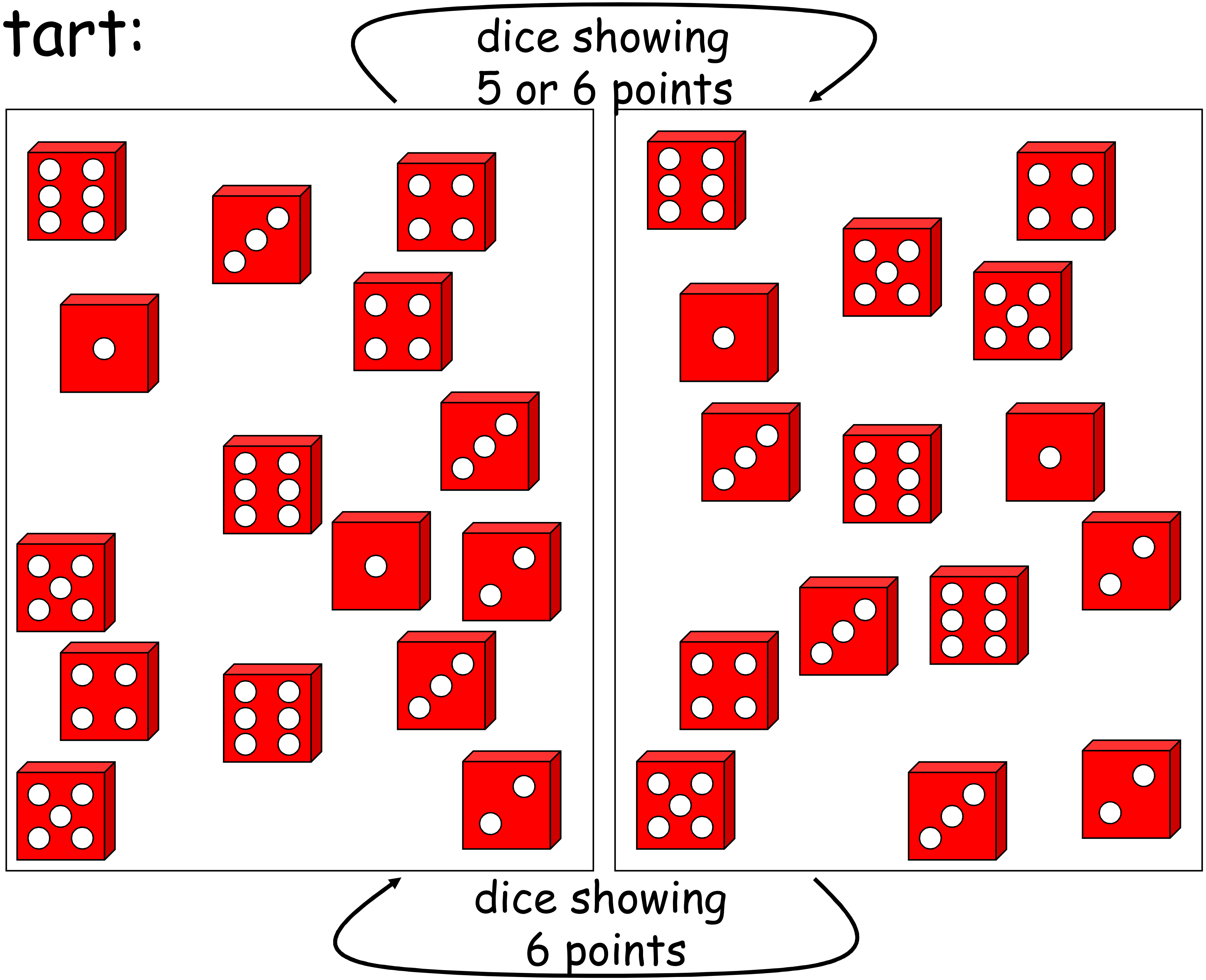
$$2A + B \underset{v_2}{\overset{v_1}{\rightleftharpoons}} 2C + 3D$$

An equilibrium is reached, when both reaction rates are equal ($v_1 = v_2$). In this case, an equilibrium constant is defined as:

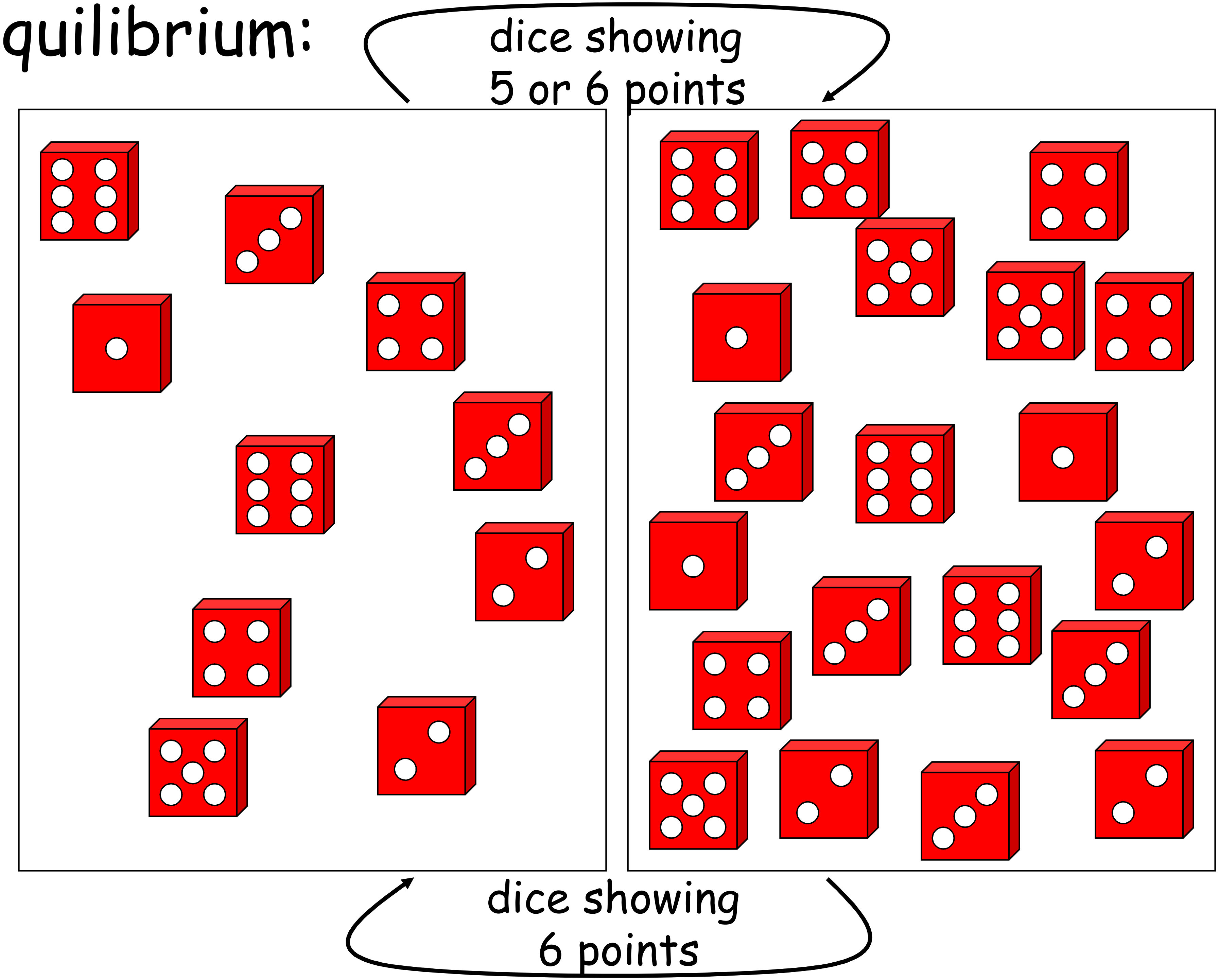
$$K_c = \frac{c_C^{\,2} \cdot c_D^{\,3}}{c_A^{\,2} \cdot c_B}$$

K_c is constant at a given temperature.

start:



equilibrium:



Summary

The velocity v of a given chemical reaction generally depends on:

- the concentration of the educts:
  according to $v = k\, c_A^a\, c_B^b\, c_C^c \ldots$
- the temperature:
  according to $k = A \exp(-E_a/RT)$
- the presence or the absence of a catalyst:
  a catalyst lowers the activation energy E_a

The chemical equilibrium is reached when forward and backward reaction velocities are equal. In this case, an equilibrium constant K_c is given which is constant for a given temperature.