

The background features a dark blue field filled with various molecular models. On the left, a large ball-and-stick model shows a complex organic structure with black, white, and blue spheres. On the right, a skeletal chemical structure of a five-membered ring with an oxygen atom and a hydroxyl group is visible. Other smaller molecular models and structures are scattered throughout the background.

Kinetics & Dynamics of Chemical Reactions

Course CH-310

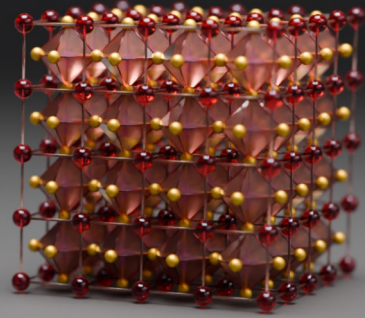
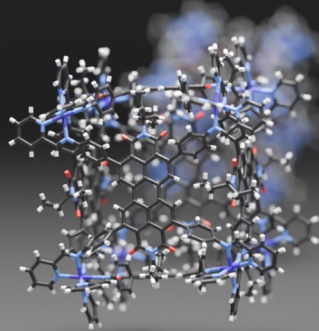
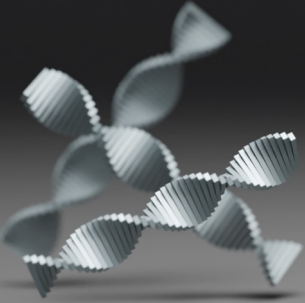
Prof. Sascha Feldmann

MATERIALS

CHIRAL
STRUCTURES

SUPRAMOLECULAR
ASSEMBLIES

HALIDE
PEROVSKITES



ULTRAFAST MAGNETO- CHIROPTICAL SPECTROSCOPY

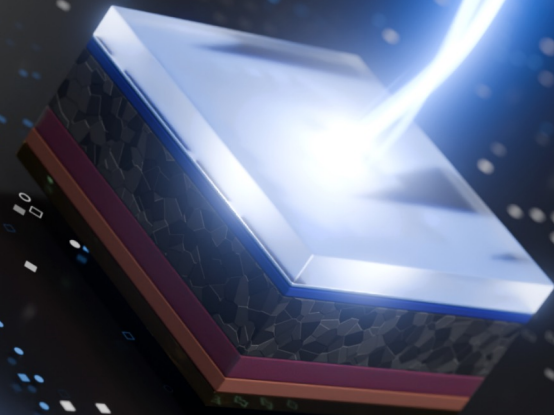


APPLICATIONS

SOLAR CELLS

DISPLAYS

QUANTUM
INFORMATION



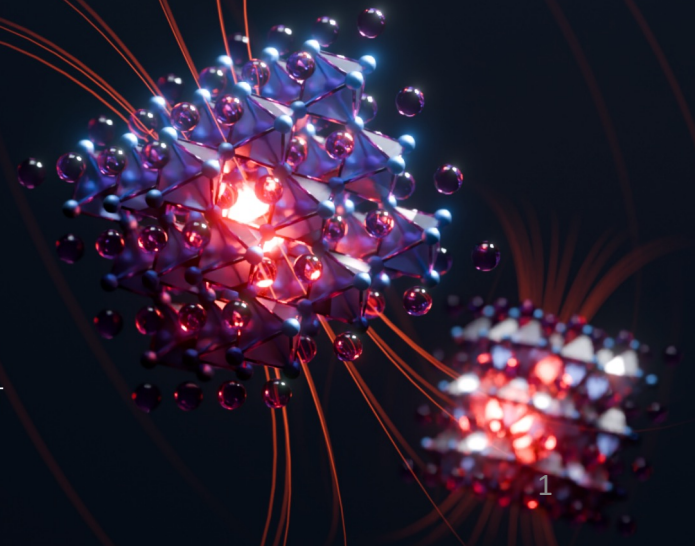
ENGINEERING

DOPING

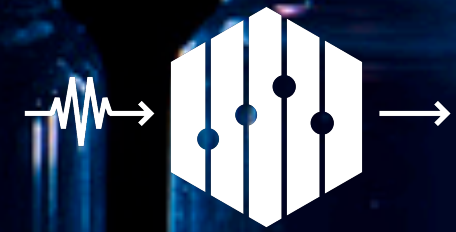
MAGNETISM

DESIGNED
CHIRALITY

QUANTUM
CONFINEMENT



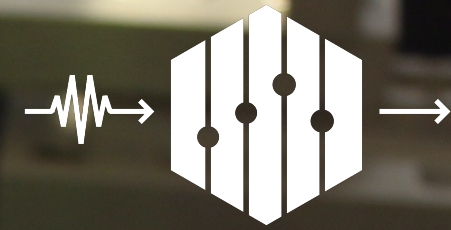
Printable Semiconductor Quantum Dots



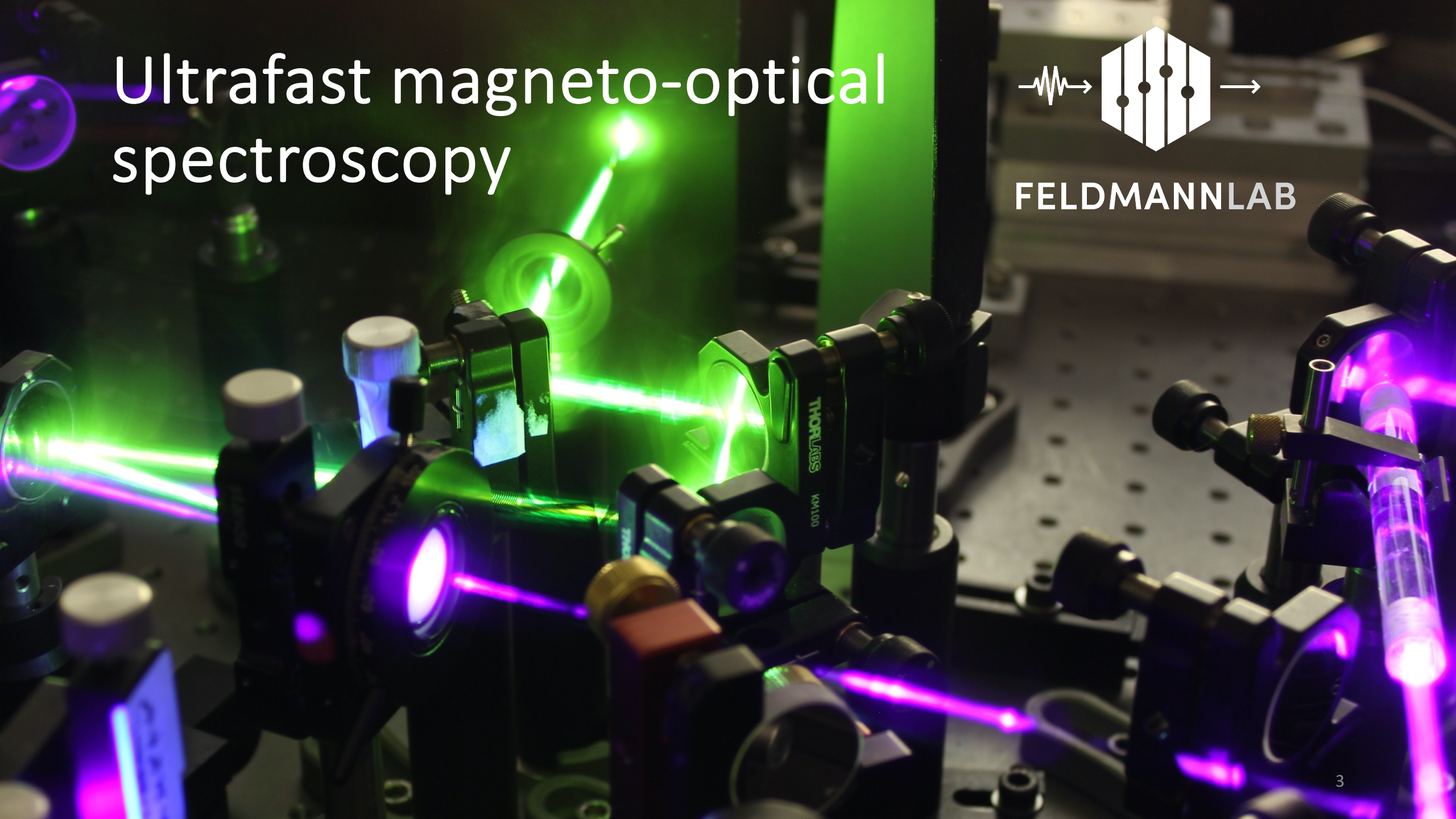
FELDMANNLAB



Ultrafast magneto-optical spectroscopy



FELDMANLAB

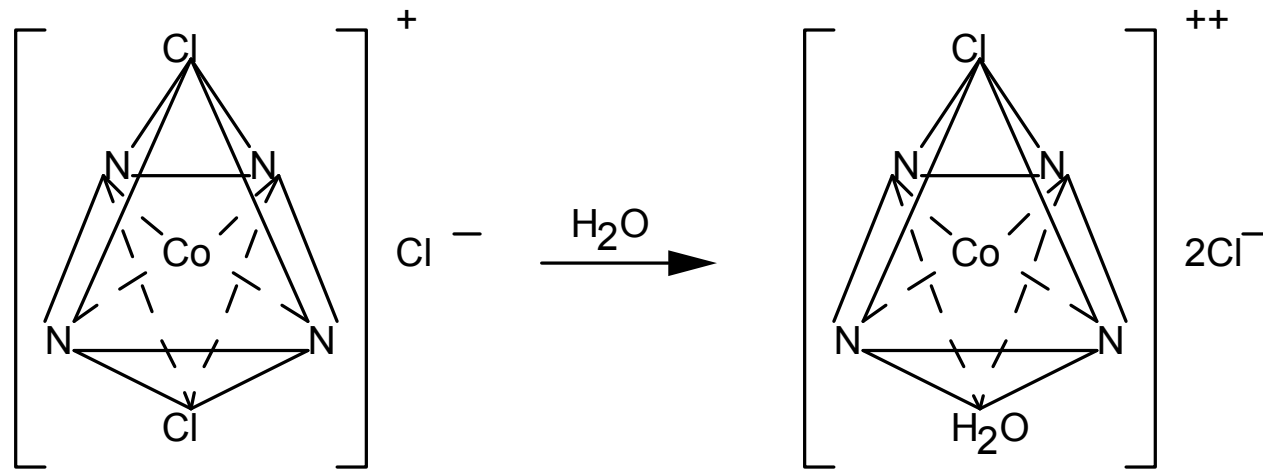
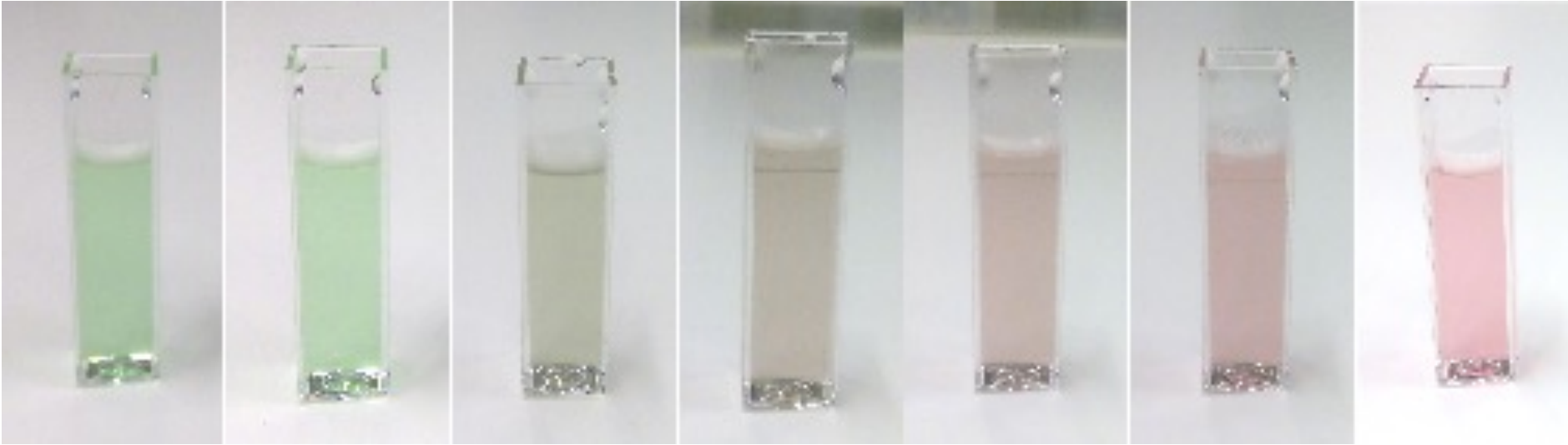


Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

What is “chemical kinetics”?



Chemistry – the science of the transformation of atoms & compounds

Phenomenological Thermodynamics

- equilibrium properties of matter
- concepts: Free Energy G , equilibrium constant K , ...
- ensemble averaged properties

Macroscopic or Phenomenological Kinetics

- chemical transformations
- concepts: rate constant k , molecularity and order of a reaction
- ensemble averaged picture of reactions

Statistical Thermodynamics

- thermodynamics derived from an atomic/molecular picture

Microscopic Kinetics or Reaction Dynamics

- molecular origins of chemical reactions, reaction mechanisms

The chemical bond

Dynamics of the chemical bond

Quantum Mechanics

Time-independent Schrödinger equation

$$H\Psi = E\Psi$$

Time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

Course Contents

- 1 Basic Concepts of Kinetics**
- 2 Complex Reactions**
- 3 Catalysis and Polymerization**
- 4 The Kinetic Theory of Gases**
- 5 Collisions**
- 6 Unimolecular Reaction Dynamics**
- 7 Basic Concepts of Statistical Thermodynamics**
- 8 Transition State Theory**

Appendix A – The Gamma Function

Appendix B – The Translational, Rotational, and Vibrational Partition Functions

About the final exam

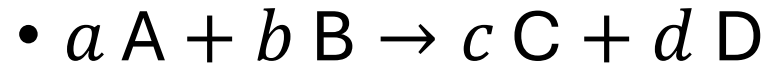
- The written exam will take place in the exam period of January 2026 with a duration of 3 hours.
- All contents of the hand-out, of all slides, and of all exercises will be directly examinable, unless marked otherwise.
- You are allowed to bring a simple, non-programmable calculator and an A5-sized, hand-written and single-sided formula sheet.
- Strong advice: **ATTEND THE EXERCISE SESSIONS!**
- Practice makes perfect: You have to *keep practicing* how to calculate a given quantity or how to set up and solve a differential equation.
- Don't wait until the exam period for this ("just memorizing" is insufficient to pass this course).
- Try and solve past exam questions without help first, for good practice

Chapter 1

Basic Concepts of Kinetics

1.1 Definitions

- Homogeneous vs heterogeneous catalysis
- Irreversible reaction: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$
- Reversible reaction: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$
- Elementary reaction: $\text{O} \cdot + \text{H}_2 \rightarrow \text{OH} \cdot + \text{H} \cdot$ vs Complex reactions



- Rate of consumption of A: $v_A = -\frac{d[A]}{dt}$

- Rate of formation of C: $v_C = \frac{d[C]}{dt}$

- Rate of reaction: $R = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = \frac{dx}{dt}$

- x : extent of reaction per unit volume

- unit of R : [concentration/time]

- unit of x : [concentration]

- ξ ("xi"): extent of reaction $\xi = xV$

- or: $\xi = -\frac{1}{a} \left(n_A(t) - n_A(t=0) \right) = \frac{1}{c} \left(n_C(t) - n_C(t=0) \right) = \dots$

1.2 Order and Molecularity of a Reaction

- Unimolecular reaction: $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$
- Bimolecular reaction: $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$
- Termolecular reaction: $\text{A} + \text{B} + \text{M} \rightarrow \text{AB} + \text{M}$
- What is the *rate equation* for $\text{A} + \text{B} \rightarrow \text{Products}$? (elementary r.)

$$R = -\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = \frac{d[\text{Products}]}{dt}$$
$$= k[\text{A}][\text{B}]$$

... but such molecularity only applies directly to elementary reactions.
– Otherwise?

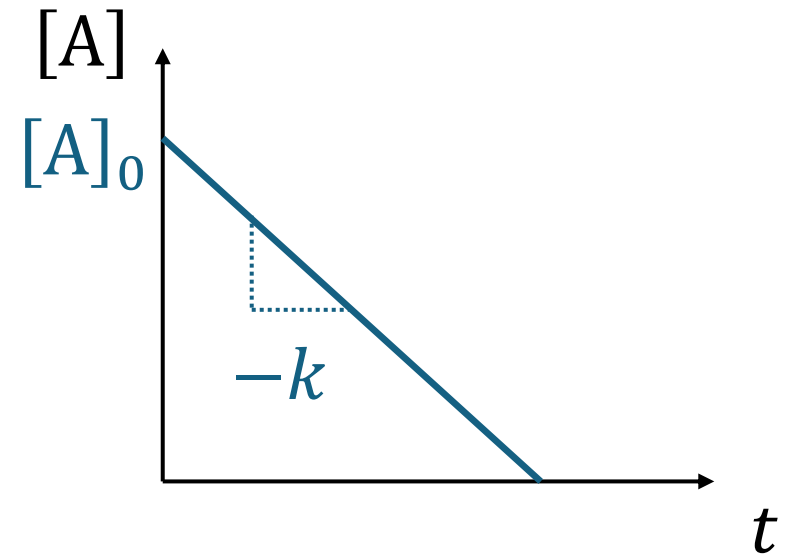
- For *complex* reactions: $R = k[A]^m[B]^n$
- This reaction is of *order m* in *A* and of *order n* in *B*
- The *overall order* of this reaction is: $p = m + n$
- In general: $R = k \prod_i c_i^{n_i}$ and $p = \sum_i n_i$
- Example: For $H_2 + Br_2 \rightarrow 2HBr$ it is found that $\frac{d[HBr]}{dt} = k[H_2][Br_2]^{\frac{1}{2}}$
(already shows you this is a complex r.)
- But under other reaction conditions might find: $\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{\frac{1}{2}}}{1+k'[HBr]}$
- ...for complex reactions everything goes ...even negative exponents
– inhibition
- Note that k is now only a mere phenomenological coefficient, not a rate constant (like it is in elementary r.)

1.3 Integrated Reaction Rate Laws

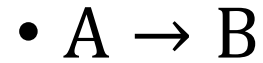
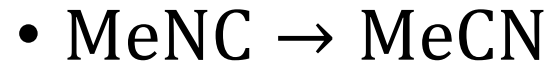
1.3.1 Zero-order reactions

(e.g. heterogeneous catalysis)

- $R = -\frac{d[A]}{dt} = k[A]^0 = k$
- $d[A] = -kdt$
- $\int_{[A]_0}^{[A]_t} d[A] = -k \int_{t_0=0}^t dt$
- $[A]_t = [A]_0 - kt$



1.3.2 First-order reactions



- $R = -\frac{d[A]}{dt} = k[A]^1$

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

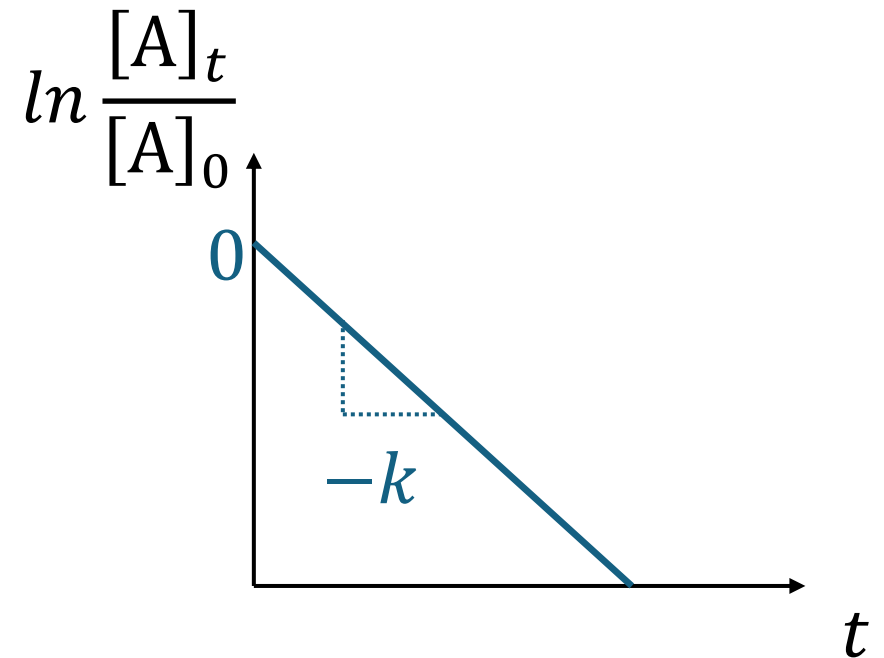
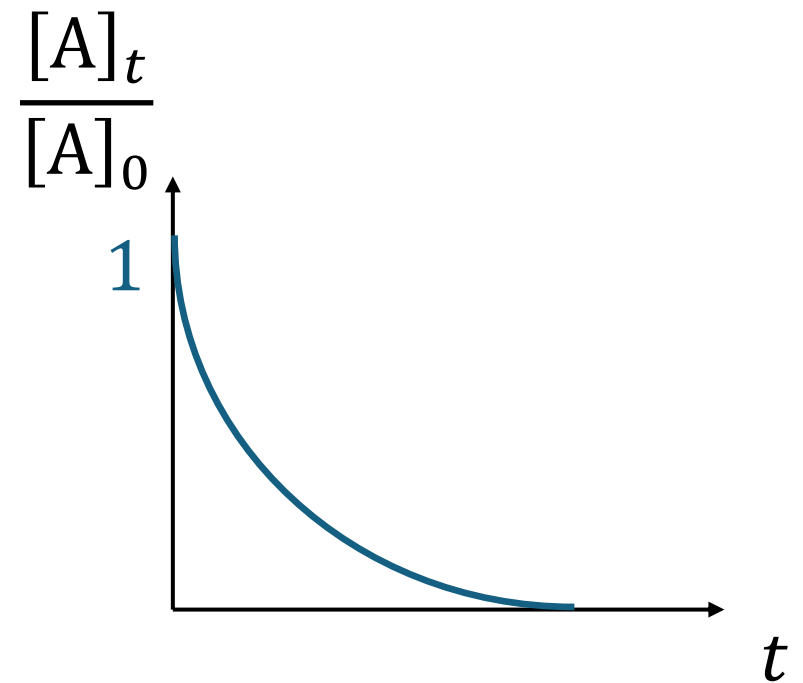
- $\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_{t_0=0}^t dt$

- $\ln \frac{[A]_t}{[A]_0} = -kt$

- $[A]_t = [A]_0 e^{-kt}$

- characteristic decay time: $\tau = \frac{1}{k}$

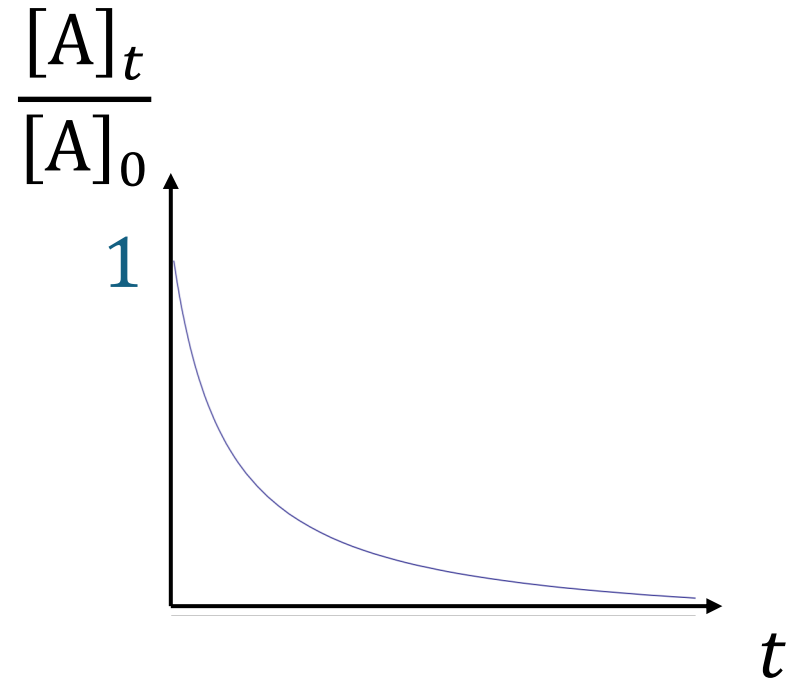
- half-life: $t_{\frac{1}{2}} = \frac{\ln 2}{k}$



1.3.3 Second-order reactions

- First case: $2 A \rightarrow \text{products}$
- Rate equation: $R = -\frac{1}{2} \frac{d[A]}{dt} = k[A]^2$
- $\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -2k \int_{t_0=0}^t dt$
- $\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$
- $[A]_t = \frac{[A]_0}{1+2[A]_0 kt}$
- rearranged to some useful form:

$$\frac{[A]_t}{[A]_0} = \frac{1}{1+2[A]_0 kt}$$



• Second case: $A + B \rightarrow \text{products}$

• $R = k[A][B]$

• $-\frac{d[A]}{dt} = k[A][B]$... problematic, why?

$$= -\frac{d[B]}{dt} = \frac{dx}{dt}$$

$[A]_0 - x$

$[B]_0 - x$

→ Let's use
 $x = \text{extent of reaction}$
[in units of concentration]

• $\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x)$

• $\frac{dx}{([A]_0 - x)([B]_0 - x)} = k dt$

• $\int_0^{x_t} \frac{dx}{([A]_0 - x)([B]_0 - x)} = k \int_{t_0=0}^t dt$

- $$\int_0^{x_t} \frac{dX}{([A]_0 - x)([B]_0 - x)} = k \int_{t_0=0}^t dt$$

- Apply method of *Partial Fractions*:

- $$\frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{\alpha}{[A]_0 - x} + \frac{\beta}{[B]_0 - x}$$

- $$\alpha([B]_0 - x) + \beta([A]_0 - x) = 1$$

- Try to look for the zeros! Set: $x = [B]_0 \rightarrow \beta = \frac{1}{([A]_0 - [B]_0)}$

- Or, set $x = [A]_0 \rightarrow \alpha = \frac{1}{([B]_0 - [A]_0)}$

- $$\int_0^{x_t} \frac{dX}{([A]_0 - x)([B]_0 - x)} = \frac{1}{[A]_0 - [B]_0} \left\{ \int_0^{x_t} \frac{dX}{x - [A]_0} - \int_0^{x_t} \frac{dX}{x - [B]_0} \right\}$$

$$\bullet \int_0^{x_t} \frac{dX}{([A]_0 - x)([B]_0 - x)} = \frac{1}{[A]_0 - [B]_0} \left\{ \int_0^{x_t} \frac{dX}{x - [A]_0} - \int_0^{x_t} \frac{dX}{x - [B]_0} \right\}$$

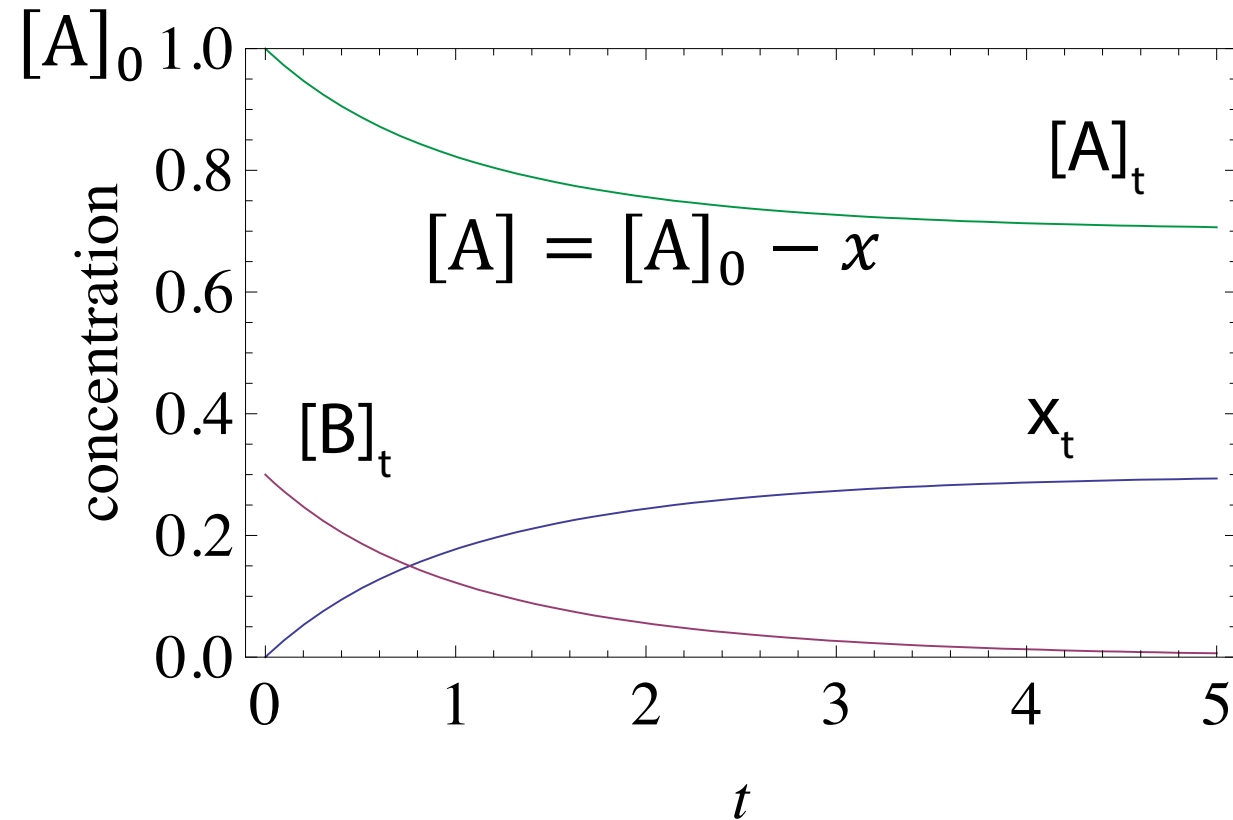
$\ln|x - [A]_0|_0^{x_t}$
 $-\ln|x - [B]_0|_0^{x_t}$

$$\bullet = \frac{1}{[A]_0 - [B]_0} \ln \frac{([A]_0 - x_t)[B]_0}{([B]_0 - x_t)[A]_0} = kt$$

$$\bullet \text{ and } x_t = \frac{[A]_0[B]_0 (e^{[A]_0 kt} - e^{[B]_0 kt})}{[A]_0 e^{[A]_0 kt} - [B]_0 e^{[B]_0 kt}}$$

-let's plot the last expressions

$$\bullet \frac{1}{[A]_0 - [B]_0} \ln \frac{([A]_0 - x_t)[B]_0}{([B]_0 - x_t)[A]_0} = kt \quad \text{and} \quad x_t = \frac{[A]_0[B]_0 (e^{[A]_0 kt} - e^{[B]_0 kt})}{[A]_0 e^{[A]_0 kt} - [B]_0 e^{[B]_0 kt}}$$



But what happens, if $[A]_0 = [B]_0$?!

- $\frac{1}{[A]_0 - [B]_0} \ln \frac{([A]_0 - x_t)[B]_0}{([B]_0 - x_t)[A]_0} = kt$

But what happens, if $[A]_0 = [B]_0$?!

→ $[A] = [B]$...we had this case before!

- $R = k[A][B] = k[A]^2$ phew, no more work...;)

1.3.4 Reactions of General Order

- for completeness (no known reactions higher than 3rd order):



$$R = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n$$

separation & integration yields

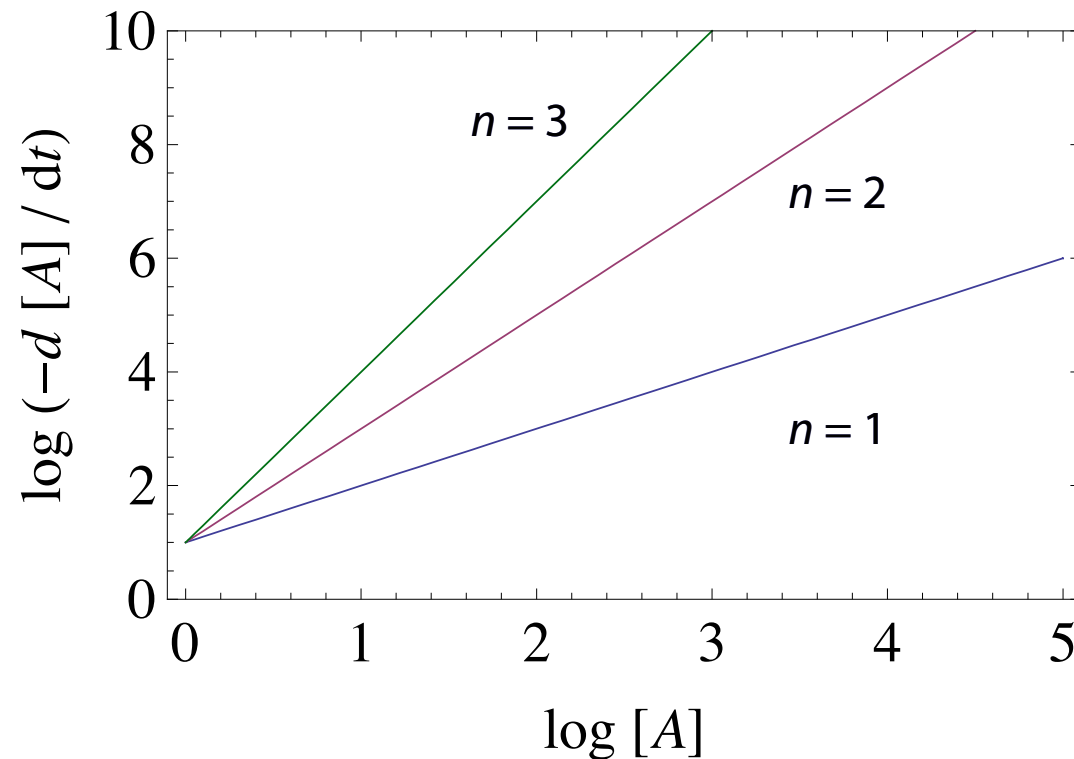
$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = akt (n - 1)$$

(for $n \neq 1$)

- To figure out the order of a reaction: create a van't Hoff plot by plotting as a log-log plot:

$$\ln \left(-\frac{d[A]}{dt} \right) = n \ln[A] + \ln ak$$

- Note: this plots the *rate*, *not* a concentration



Change of topic (a bit):

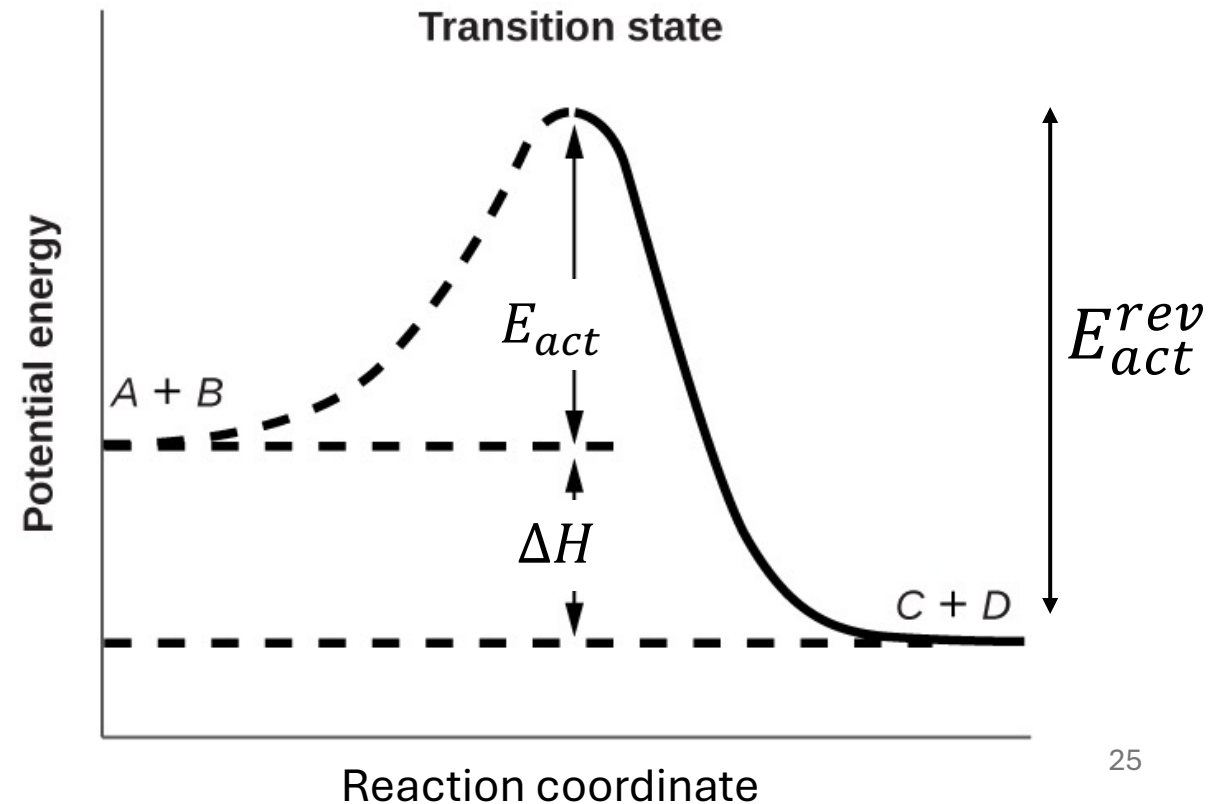
What factors *besides* concentrations determine reaction rates?



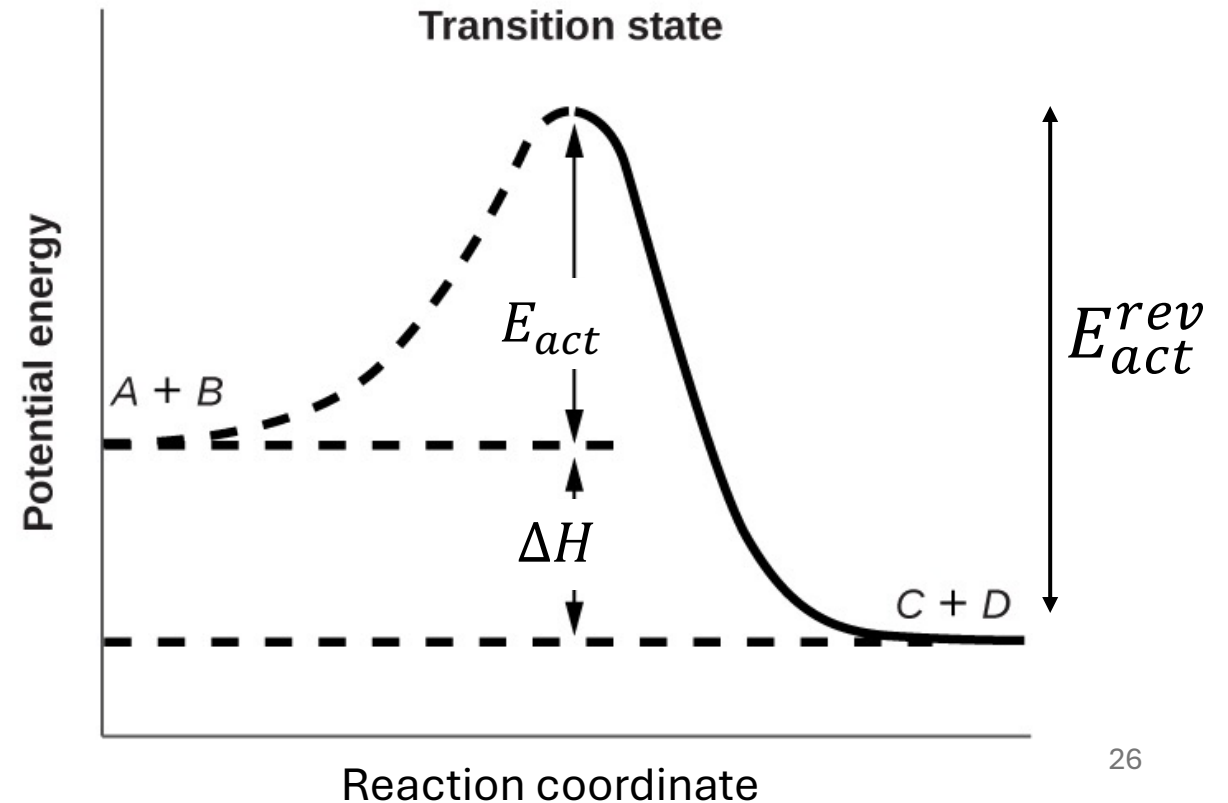
1.4 Temperature Dependence of Rate Constants: The Arrhenius Equation

- Arrhenius found: $k(T) = Ae^{-\frac{E_{act}}{RT}}$
- Prefactor A : different interpretations
- Activation energy E_{act}

- What is the probability that a molecule has enough energy to react?

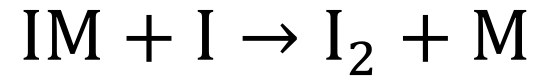
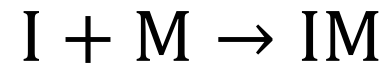


- Arrhenius Equation $k(T) = A e^{-\frac{E_{act}}{RT}}$
 - $p(E \geq E_{act})$? Boltzmann distribution!
 - $p(E \geq E_{act}) \propto \int_{E_{act}}^{\infty} e^{-\frac{E}{RT}} dE \sim e^{-\frac{E_{act}}{RT}}$
- fraction of molecules
with enough energy
to react



Arrhenius Equation $k(T) = A e^{-\frac{E_{act}}{RT}}$

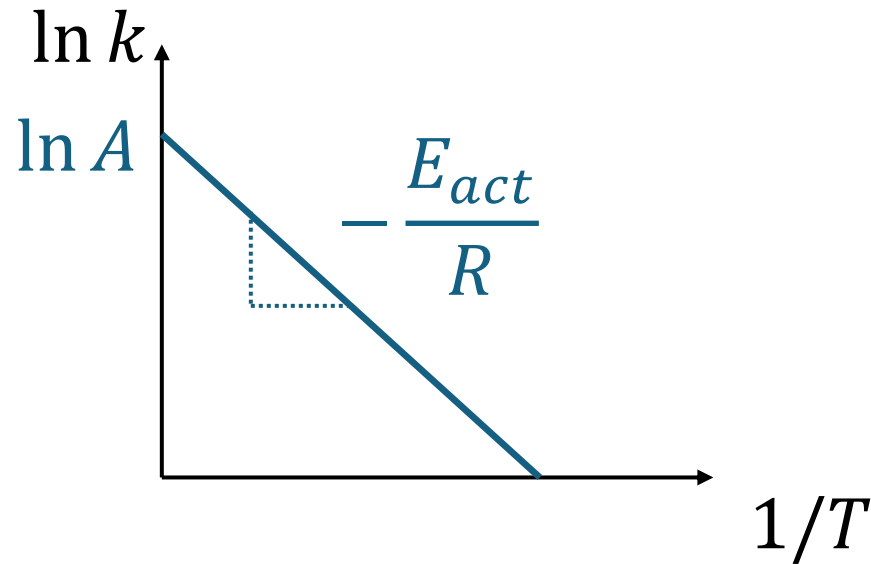
- The activation energy can even be *negative*, e.g., in the following complex reaction, where weakly bound iodine atoms recombine:



- Here, if we heat up, the weakly bound intermediate I-M is actually *less likely* to survive, thus hampering the overall reaction progress

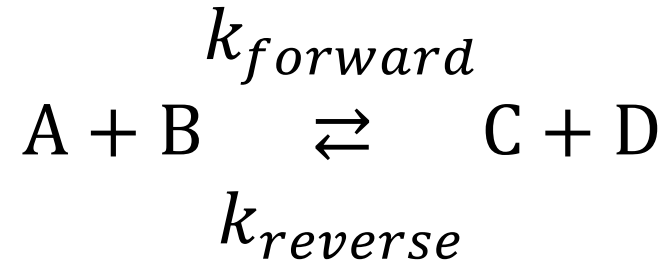
Arrhenius Equation $k(T) = A e^{-\frac{E_{act}}{RT}}$

- To obtain A and E_{act} , plot in logarithmic form: $\ln k = \ln A - \frac{E_{act}}{RT}$



“Arrhenius plot”

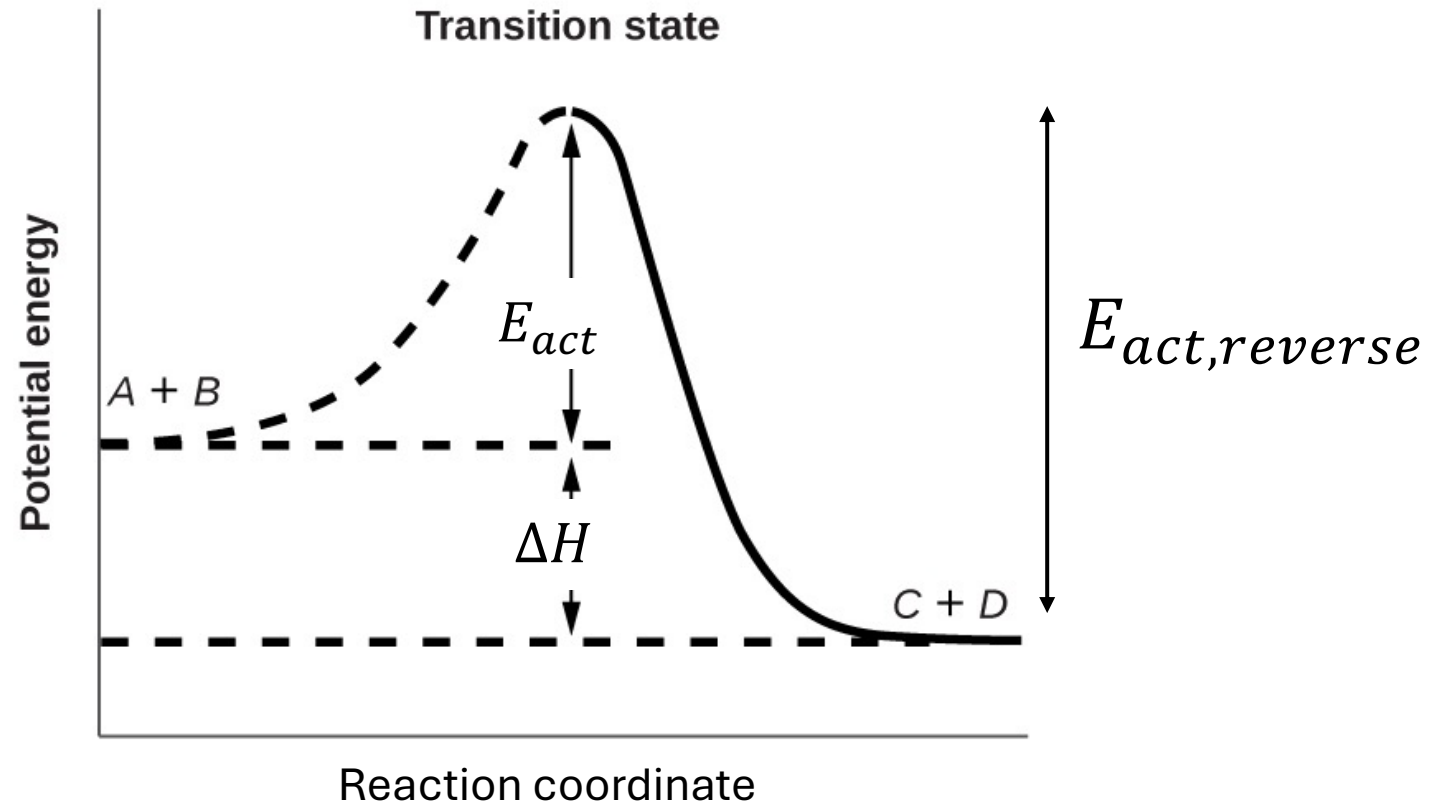
- Let's consider a reversible reaction in equilibrium, e.g.



- In equilibrium: $k_{forward}[A][B] = k_{reverse}[C][D]$
- Equilibrium constant then is:

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{k_{forward}}{k_{reverse}}$$

$$= \frac{A_{forward}}{A_{reverse}} e^{-\frac{E_{act,forward} - E_{act,reverse}}{RT}} = \frac{A_{forward}}{A_{reverse}} e^{-\frac{\Delta H^0}{RT}}$$



$$K_{eq} = \frac{A_{forward}}{A_{reverse}} e^{-\frac{E_{act,forward} - E_{act,reverse}}{RT}} = \frac{A_{forward}}{A_{reverse}} e^{-\frac{\Delta H^0}{RT}}$$

nice! ...but this only works in *equilibrium*, don't forget.