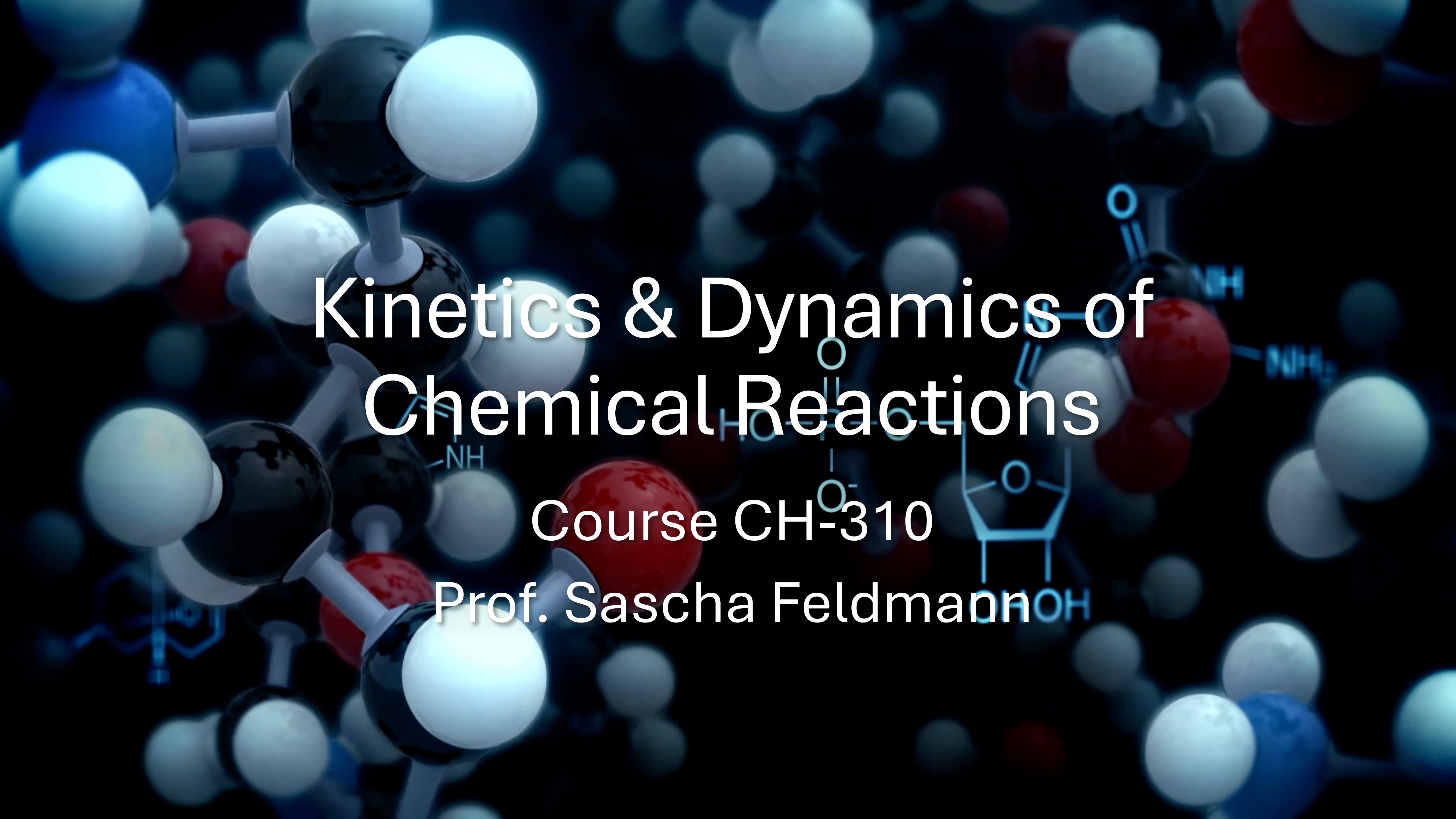


Kinetics & Dynamics of Chemical Reactions

Course CH-310

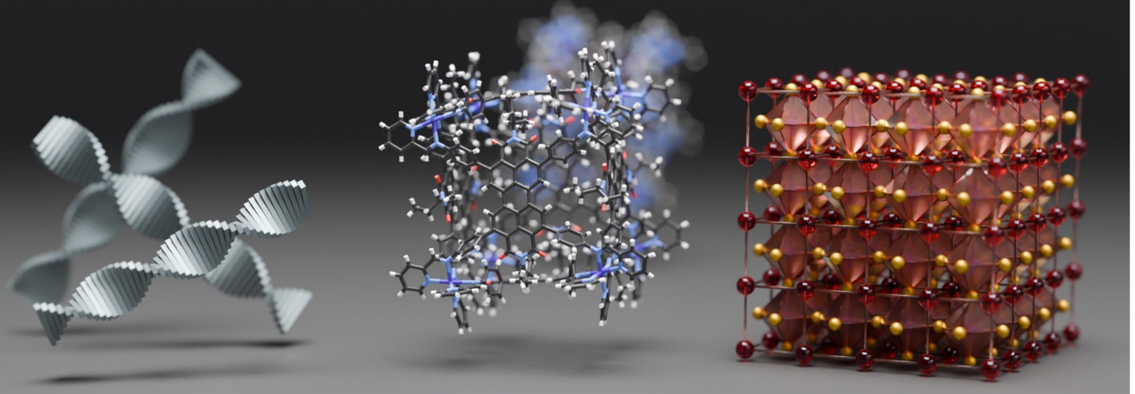
Prof. Sascha Feldmann

MATERIALS

CHIRAL STRUCTURES

SUPRAMOLECULAR ASSEMBLIES

HALIDE PEROVSKITES



ULTRAFAST MAGNETO-CHIROPTICAL SPECTROSCOPY

APPLICATIONS

SOLAR CELLS

DISPLAYS

QUANTUM INFORMATION

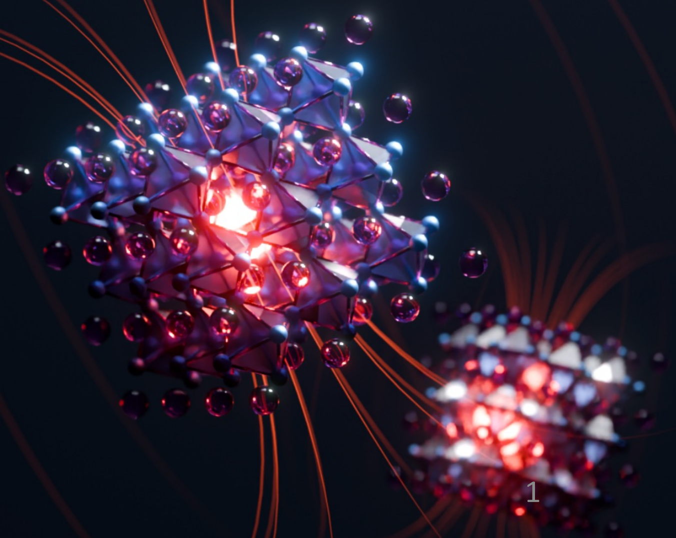
ENGINEERING

DOPING

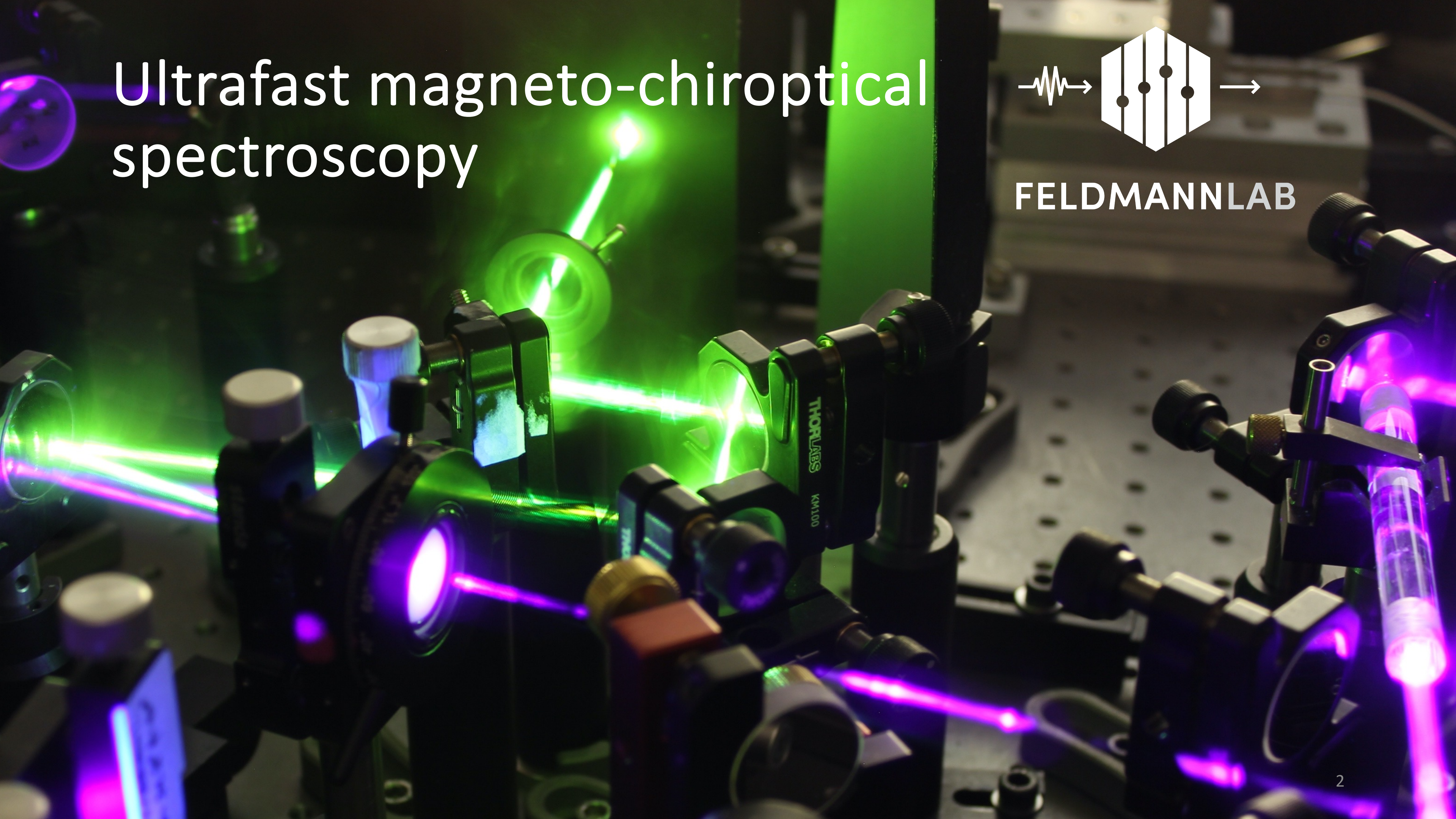
MAGNETISM

DESIGNED CHIRALITY

QUANTUM CONFINEMENT



Ultrafast magneto-chiroptical spectroscopy



FELDMANNLAB

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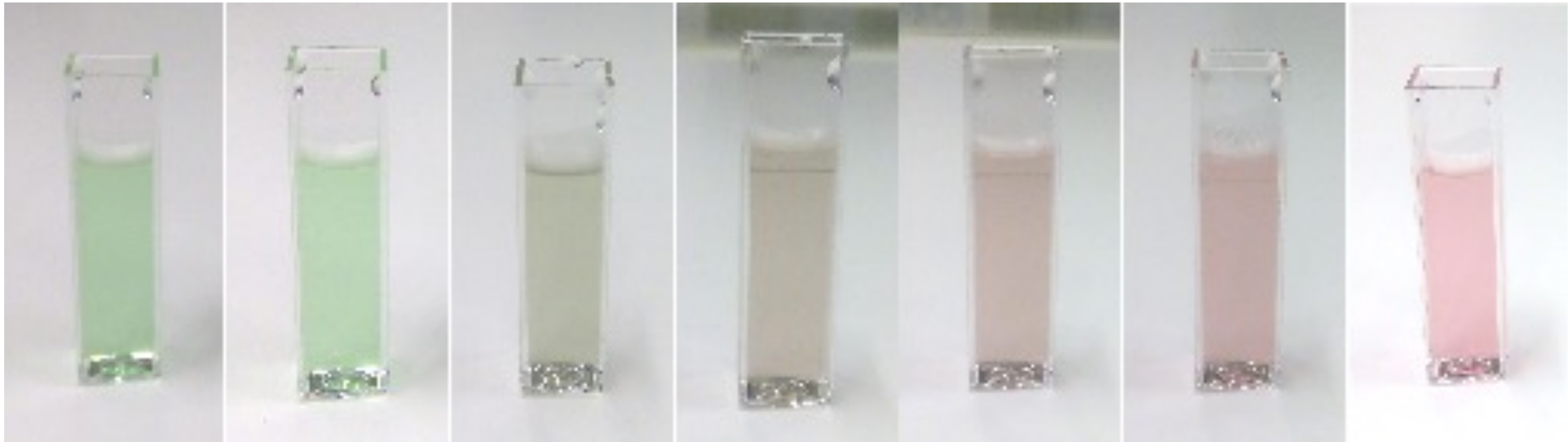
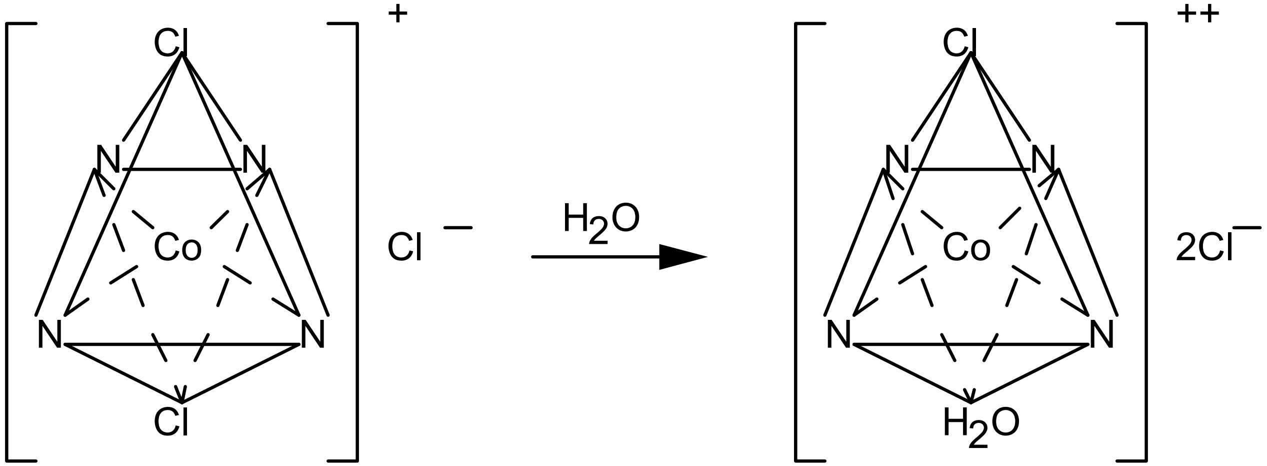
What is “chemical kinetics”?





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	**Time-dependent Schrödinger equation**
$H\Psi = E\Psi$	$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$

Course Contents

Chapter 1

Basic Concepts of Kinetics

1.1 Definitions

- Homogeneous vs heterogeneous catalysis
- Irreversible reaction: $2\ H_2 + O_2 \rightarrow 2\ H_2O$
- Reversible reaction: $H_2 + I_2 \rightleftharpoons 2\ HI$
- Elementary reaction: $O. + H_2 \rightarrow OH. + H.$ *vs* Complex reactions

- $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$
- Rate of consumption of A: $v_{\mathrm{A}} = -\frac{d[\mathrm{A}]}{dt}$
- Rate of formation of C: $v_{\mathrm{C}} = \frac{d[\mathrm{C}]}{dt}$
- Rate of reaction: $R = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{c}\frac{d[\mathrm{C}]}{dt} = \frac{1}{d}\frac{d[\mathrm{D}]}{dt} = \frac{dx}{dt}$
- x: extent of reaction per unit volume
- Unit of R: [concentration/time]
- Unit of x: [concentration]
- ξ (”xi”): extent of reaction $\xi = xV$
- Or: $\xi = -\frac{1}{a}\left(n_{\mathrm{A}}(t) - n_{\mathrm{A}}(t=0)\right) = \frac{1}{c}\left(n_{\mathrm{C}}(t) - n_{\mathrm{C}}(t=0)\right) = \cdots$

1.2 Order and Molecularity of a Reaction

- Unimolecular reaction: $\mathrm{N_2O_4 \rightarrow 2NO_2}$
- Bimolecular reaction: $\mathrm{O + H_2 \rightarrow OH + H}$
- Termolecular reaction: $\mathrm{A + B + M \rightarrow AB + M}$
- What is the *rate equation* for $\mathrm{A + B} \rightarrow Products$? (elementary r.)

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

$$= k[\mathrm{A}][\mathrm{B}]$$

… but such molecularity only applies directly to elementary reactions.

– Otherwise?

- For *complex* reactions: $R = k[\mathrm{A}]^m[\mathrm{B}]^n$
- This reaction is of *order* m in A and of *order* n in B
- The *overall order* of this reaction is: $\mathrm{p} = m + n$
- In general: $R = k \prod_i c_i^{n_i}$ and $p = \sum_i n_i$
- Example: For $\mathrm{H_2} + \mathrm{Br_2} \rightarrow 2\mathrm{HBr}$ it is found that $\frac{d[\mathrm{HBr}]}{dt} = k[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}$

  (already shows you this is a complex r.)

- But under other reaction conditions might find: $\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}}{1+k\prime[\mathrm{HBr}]}$
- …for complex reactions everything goes …even negative exponents

– inhibition

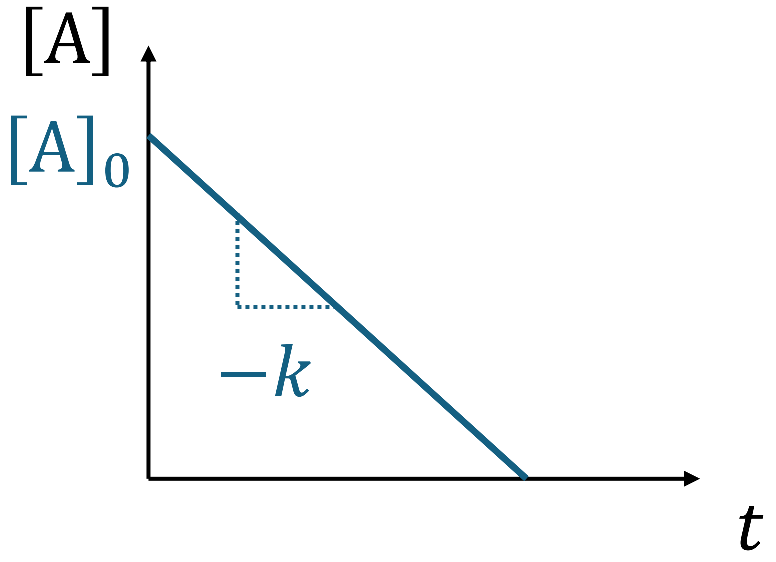
- Note that k is now only a mere phenomenological coefficient, not a rate constant (like it is in elementary r.)

1.3 Integrated Reaction Rate Laws

1.3.1 Zero-order reactions

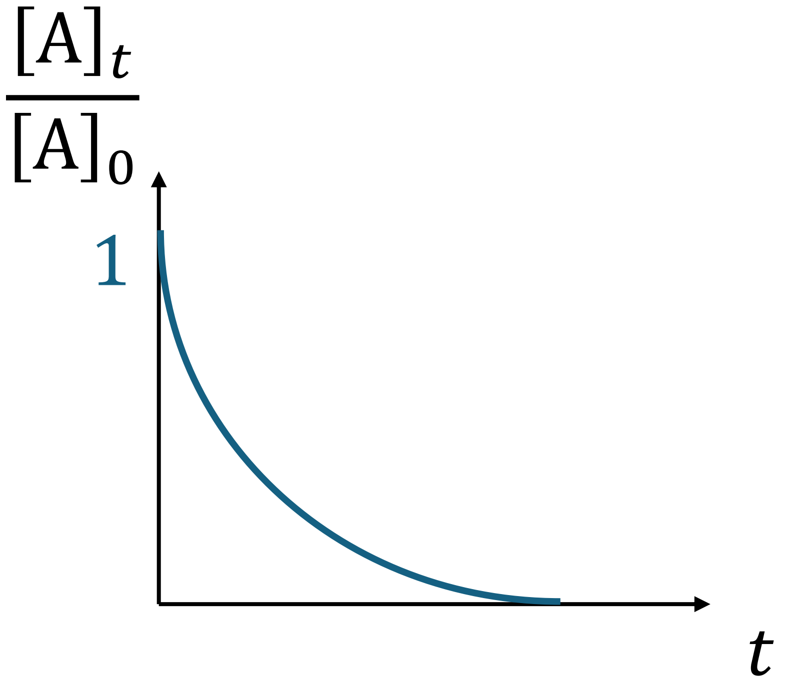
(e.g. heterogeneous catalysis)

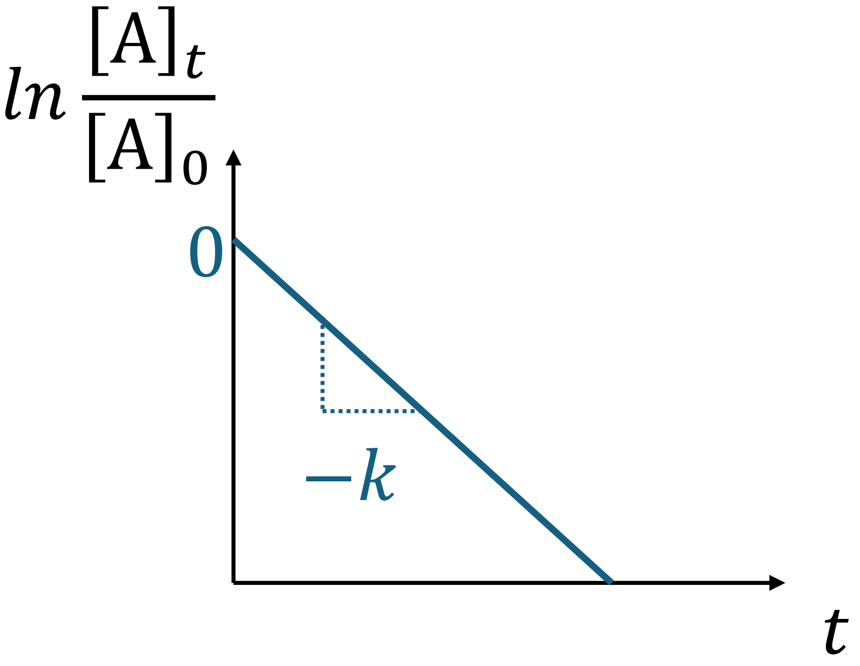
- $R = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^0 = k$
- $d[\mathrm{A}] = -kdt$
- $\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = -k\int_{t_0=0}^{t} dt$
- $[\mathrm{A}]_t = [\mathrm{A}]_0 - kt$



1.3.2 First-order reactions

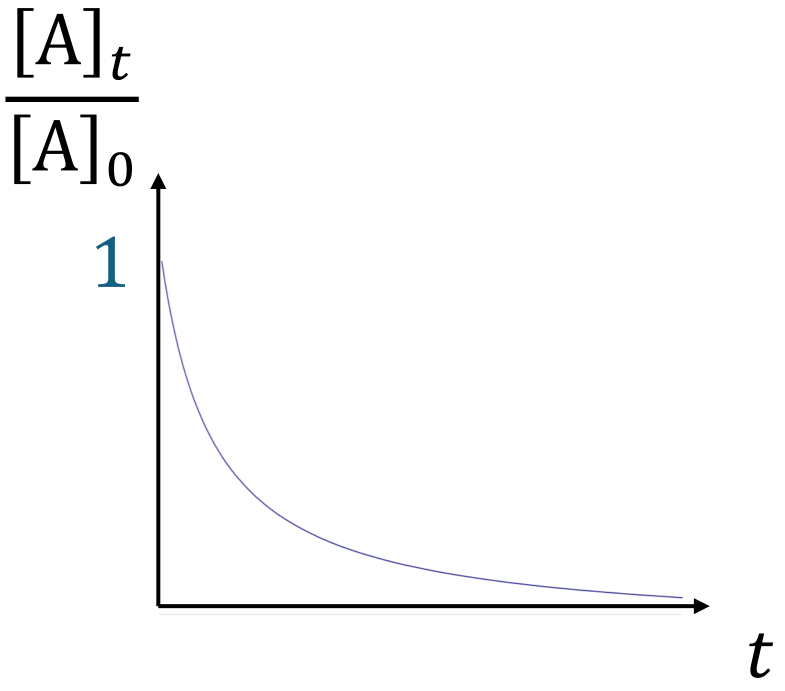
- $\mathrm{MeNC} \rightarrow \mathrm{MeCN}$
- $\mathrm{A} \rightarrow \mathrm{B}$
- $R = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^1$
- $\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]$
- $\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k\int_{t_0=0}^{t} dt$
- $\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt$
- $[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt}$
- Characteristic decay time: $\tau = \frac{1}{k}$
- Half-life: $t_{\frac{1}{2}} = \frac{\ln 2}{k}$





1.3.3 Second-order reactions

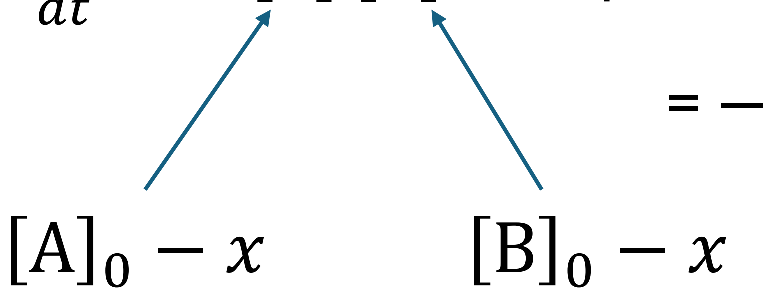
- First case: $2\mathrm{A} \rightarrow \text{products}$
- Rate equation: $R = -\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2$
- $\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -2k\int_{t_0=0}^{t} dt$
- $\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + 2kt$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



- Second case: A + B → products

- $R = k[\mathrm{A}][\mathrm{B}]$
- $-\dfrac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]\,[\mathrm{B}]$ … problematic

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



$[\mathrm{A}]_0 - x$ $[\mathrm{B}]_0 - x$

- $\dfrac{dx}{dt} = k([\mathrm{A}]_0 - x)\,([\mathrm{B}]_0 - x)$
- $\dfrac{dx}{\left([\mathrm{A}]_0 - x\right)\left([\mathrm{B}]_0 - x\right)} = k\,dt$
- $\displaystyle\int_0^{x_t} \frac{dx}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)} = k\int_{t_0=0}^{t} dt$

Reminder:
x = extent of reaction
in units of concentration

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

- Apply method of *Partial Fractions:*
- $\frac{1}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)} = \frac{\alpha}{[\mathrm{A}]_0 - x} + \frac{\beta}{[\mathrm{B}]_0 - x}$
- $\alpha([\mathrm{B}]_0 - x) + \beta([\mathrm{A}]_0 - x) = 1$
- Try to look for the zeros! Set: $x = [\mathrm{B}]_0$ → $\beta = \frac{1}{([\mathrm{A}]_0 - [\mathrm{B}]_0)}$
- Or, set $x = [\mathrm{A}]_0$ → $\alpha = \frac{1}{([\mathrm{B}]_0 - [\mathrm{A}]_0)}$
- $\int_0^{x_t} \frac{dX}{\left([\mathrm{A}]_0 - x\right)\left([\mathrm{B}]_0 - x\right)} = \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \left\{ \int_0^{x_t} \frac{dX}{x - [\mathrm{A}]_0} - \int_0^{x_t} \frac{dX}{x - [\mathrm{B}]_0} \right\}$

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

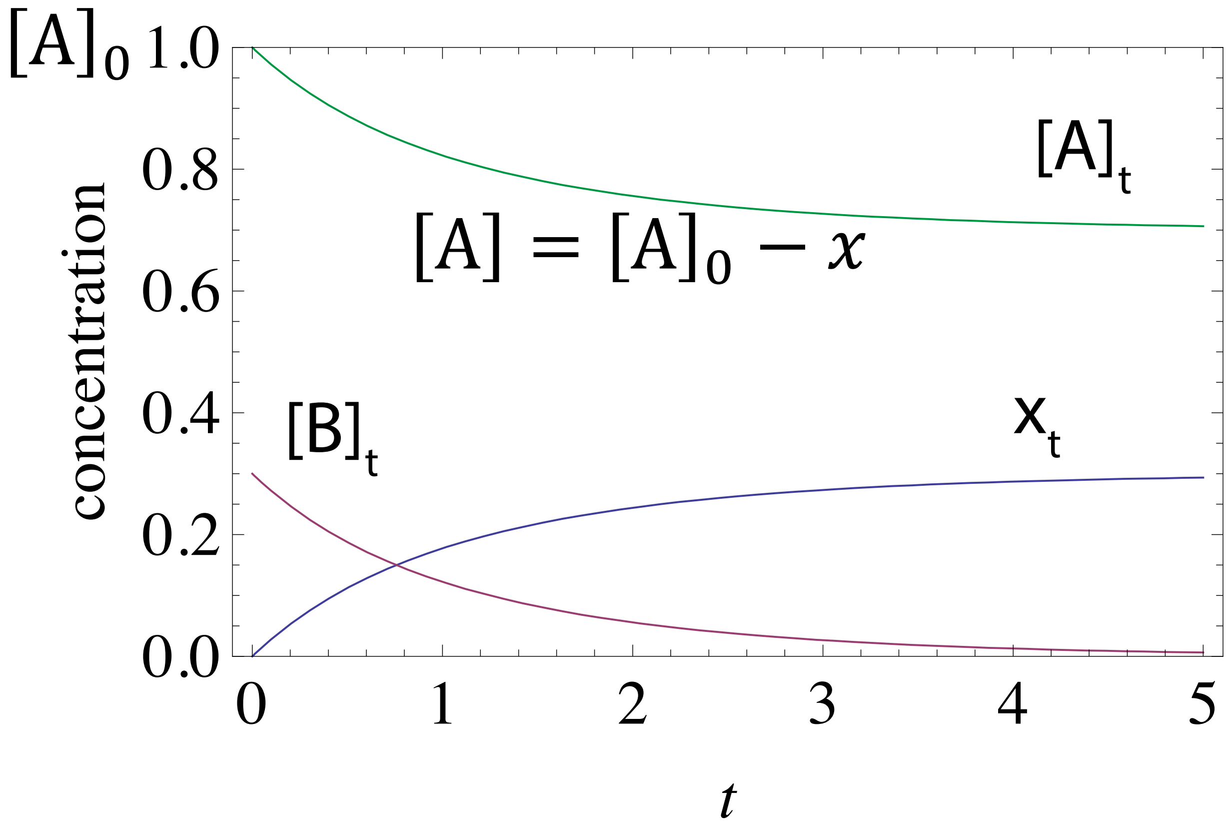
$ln|x - [\mathrm{A}]_0|_0^{x_t}$

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

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

- and $x_t = \frac{[\mathrm{A}]_0[\mathrm{B}]_0\left(e^{[\mathrm{A}]_0 kt} - e^{[\mathrm{B}]_0 kt}\right)}{[\mathrm{A}]_0 e^{[\mathrm{A}]_0 kt} - [\mathrm{B}]_0 e^{[\mathrm{B}]_0 kt}}$ -let’s plot the last expressions

- $\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\ln\frac{([\mathrm{A}]_0-x_t)[\mathrm{B}]_0}{([\mathrm{B}]_0-x_t)[\mathrm{A}]_0}=kt$ and $x_t=\frac{[\mathrm{A}]_0[\mathrm{B}]_0\left(e^{[\mathrm{A}]_0kt}-e^{[\mathrm{B}]_0kt}\right)}{[\mathrm{A}]_0e^{[\mathrm{A}]_0kt}-[\mathrm{B}]_0e^{[\mathrm{B}]_0kt}}$



But what happens, if $[\mathrm{A}]_0 = [\mathrm{B}]_0$?!

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

  But what happens if $[\mathrm{A}]_{\mathbf{0}} = [\mathrm{B}]_{\mathbf{0}}$?!

- → $[\mathrm{A}] = [\mathrm{B}]$ ...we had this case before!

- $R = k[\mathrm{A}]\,[\mathrm{B}] = k[\mathrm{A}]^2$ phew, no more work.

1.3.4 Reactions of General Order

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

$$aA \rightarrow Products$$

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

separation & integration yields

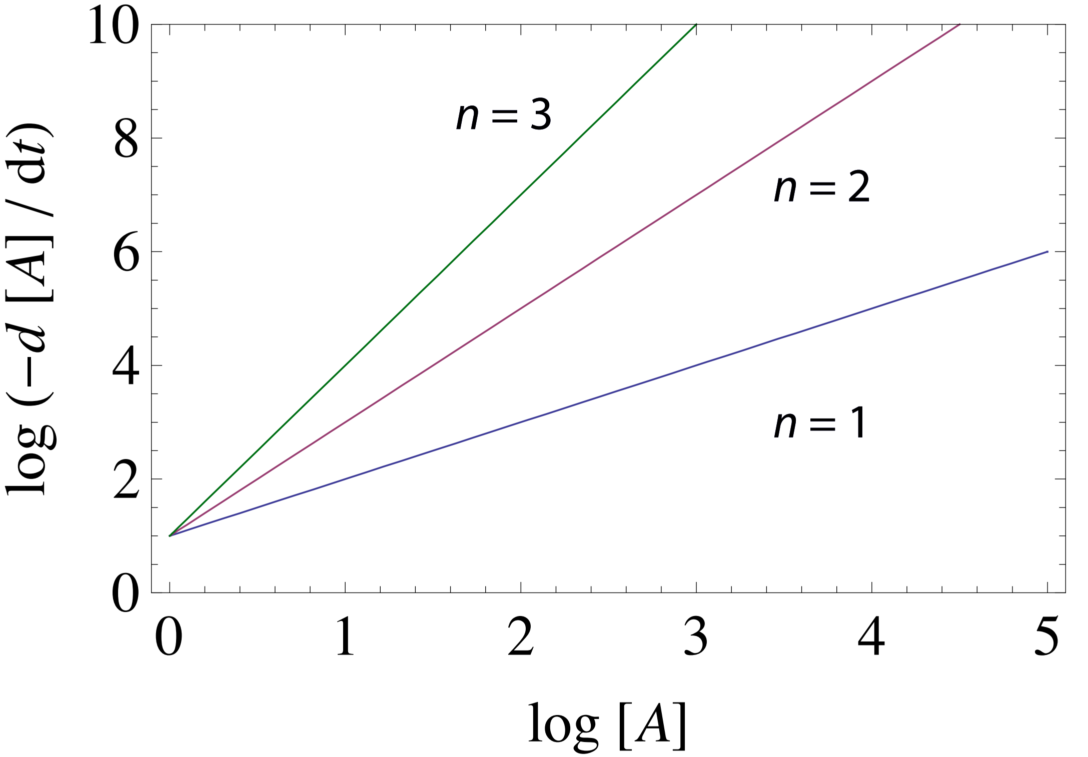
$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = akt\ (n-1)$$

(for $n \neq 1$)

- To figure out the order of a reaction: do a *van’t Hoff plot* by plotting as a log-log plot:

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

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

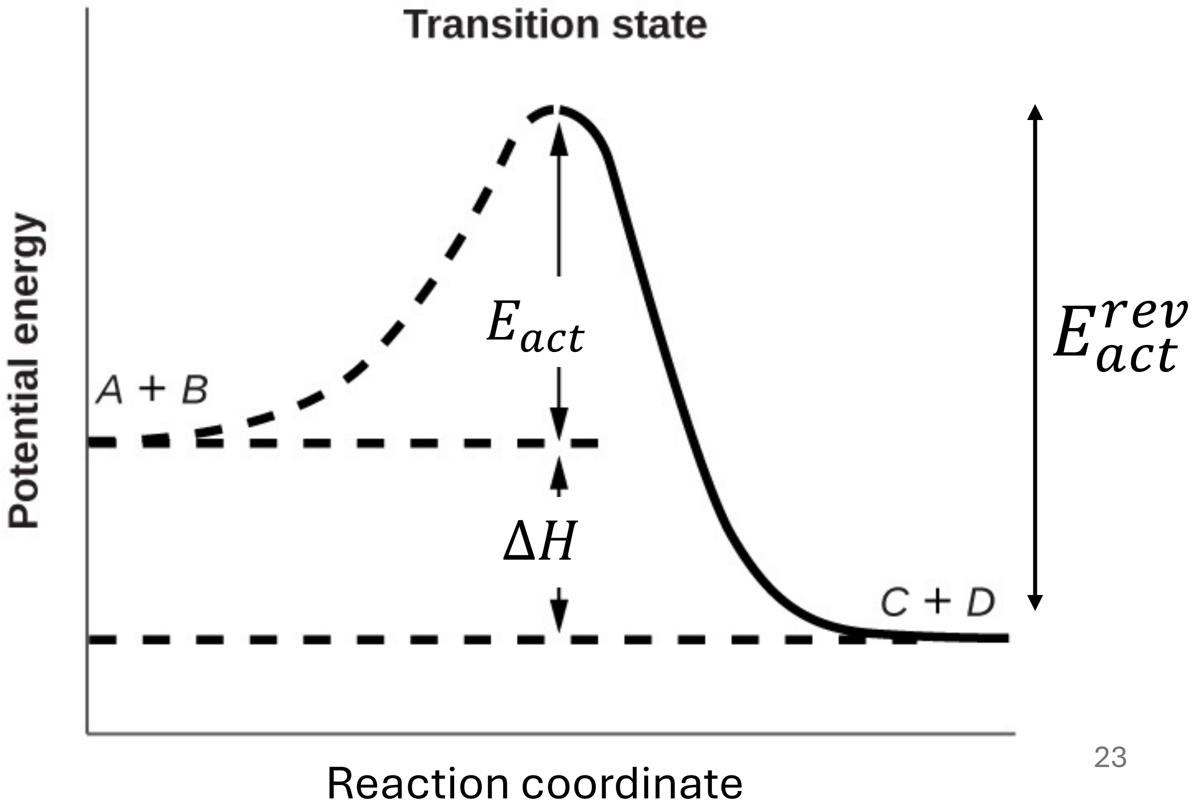


Change of topic (a bit):

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}

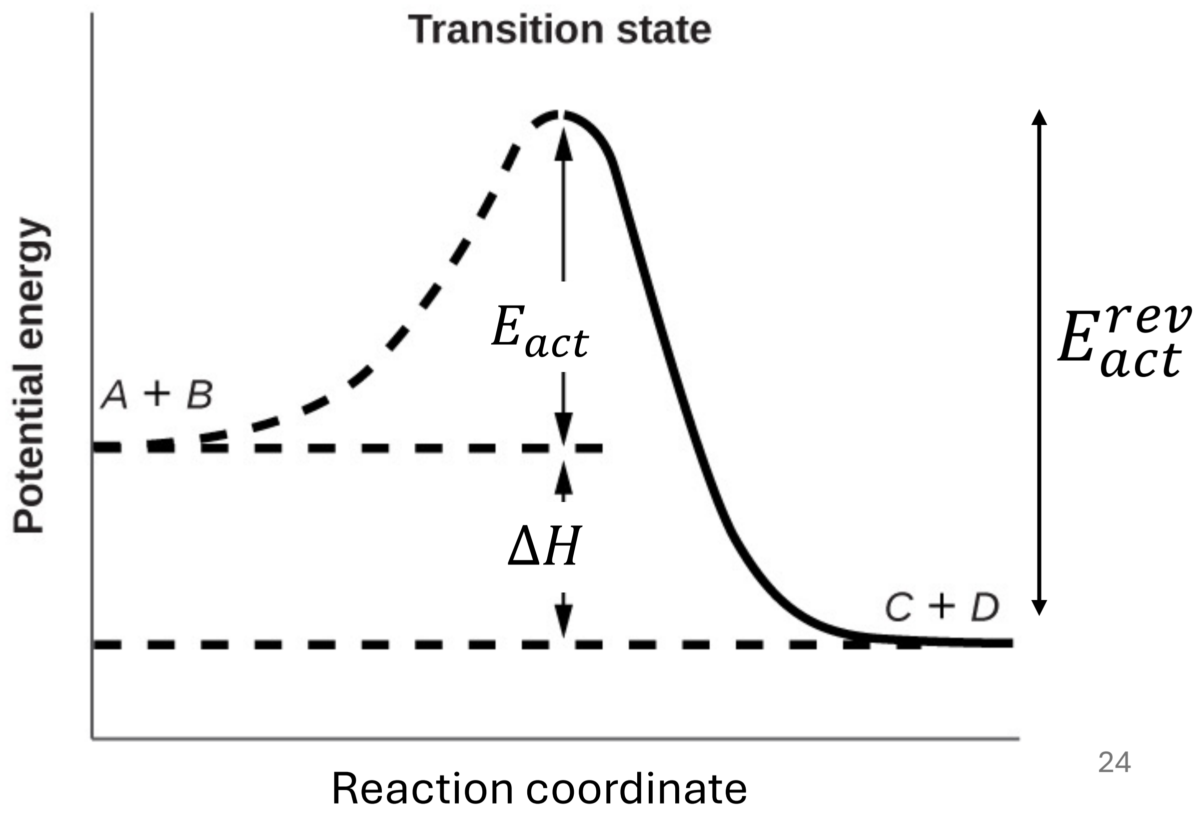


- What is the probability that a molecule has enough energy to react?

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

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

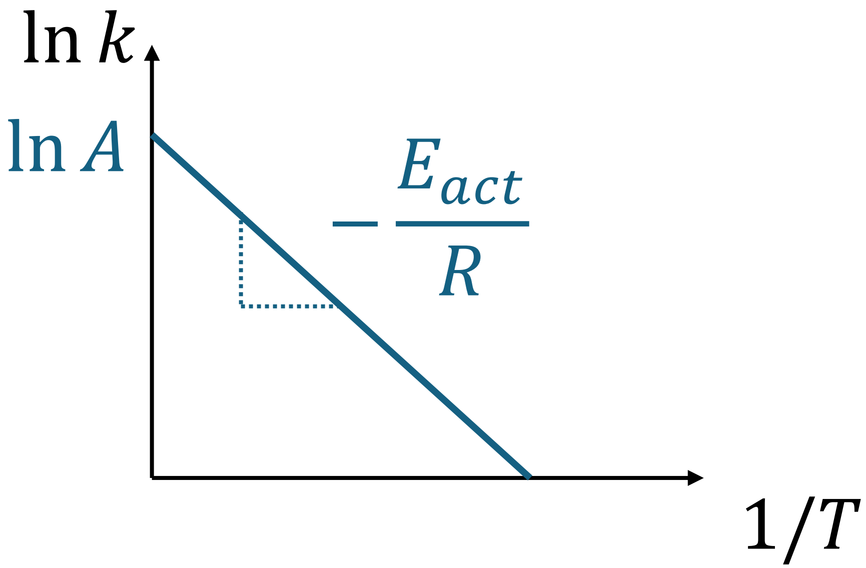
$$\mathrm{I + M \rightarrow IM}$$

$$\mathrm{IM + I \rightarrow I_2 + M}$$

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

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



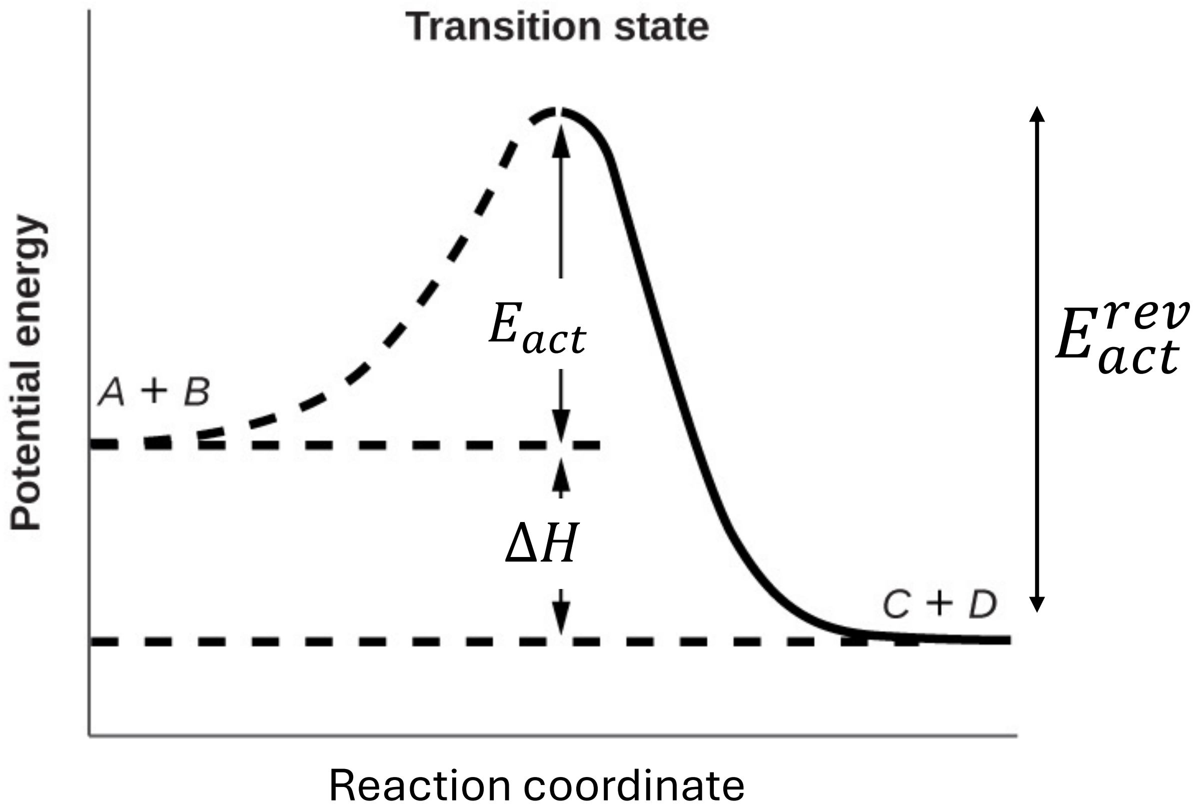
“Arrhenius plot”

- Let's consider a reversible reaction in equilibrium, *e.g.*
- $\mathrm{A} + \mathrm{B} \underset{k_{\text{reverse}}}{\overset{k_{\text{forward}}}{\rightleftarrows}} \mathrm{C} + \mathrm{D}$

- In equilibrium: $k_{\text{forward}}[\mathrm{A}][\mathrm{B}] = k_{\text{reverse}}[\mathrm{C}][\mathrm{D}]$
- Equilibrium constant then is:
- $K_{\text{eq}} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} = \frac{k_{\text{forward}}}{k_{\text{reverse}}}$

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

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



$$= \frac{{}^{A}\text{forward}}{{}^{A}\text{reverse}}\, e^{-\frac{\left({}^{E}\text{act, forward}{}^{-E}\text{act, reverse}\right)}{RT}} = \frac{{}^{A}\text{forward}}{{}^{A}\text{reverse}}\, e^{-\frac{\Delta H^{0}}{RT}}$$

nice! But this only works in equilibrium, don’t forget.