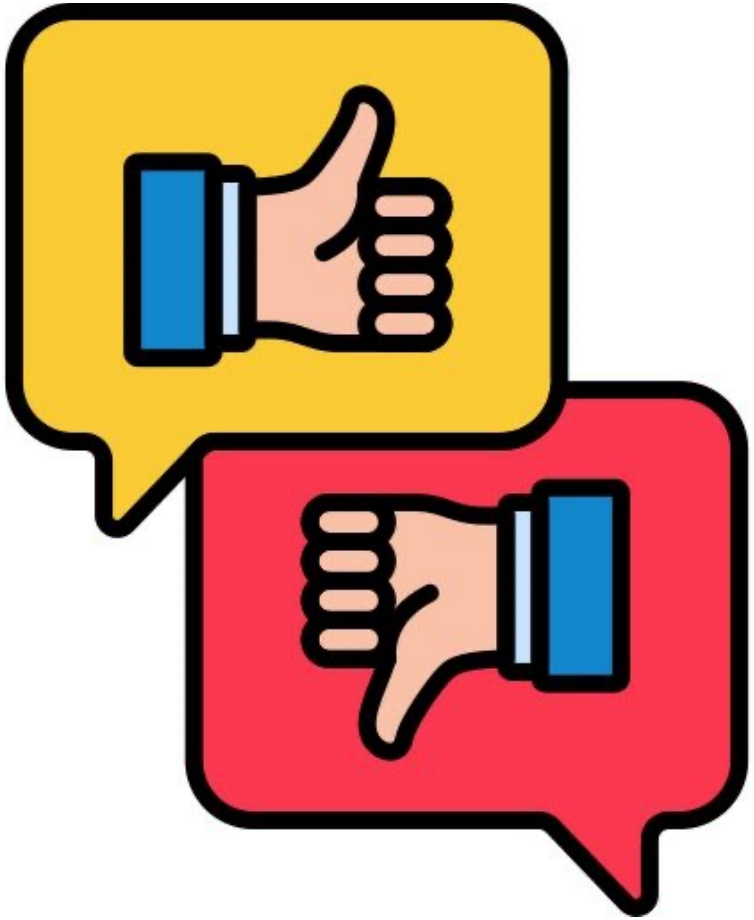
# Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

# Evaluation time!

- I am super grateful for any feedback you may have!
- Please be honest, so I can improve further ☺
- Thank you for still being here so close to the winter break
- Have some brownies and treat yourself



# About this Revision Session

- The following summary is by no means exhaustive
- it is meant for us to recapitulate together about what we have learned this semester
- all materials (script and slides) discussed in our lectures are examinable, with the exception of Sascha’s research talk in the end of the previous session (hence no slides for that part)
- grey parts in the script table of contents will not be examined

# Course Contents

# Chapter 1

## Basic Concepts of Kinetics

# Definitions

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

- 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]

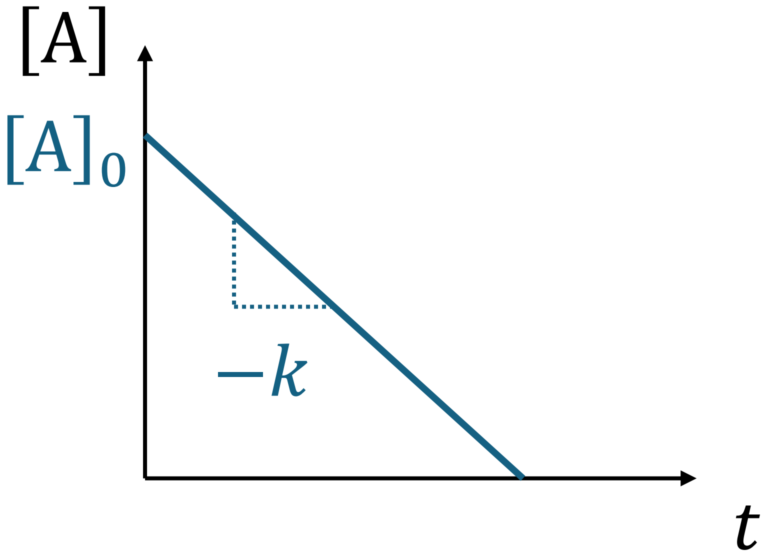
- *Elementary* vs *complex* reactions
- *Molecularity* & *order* of reactions

# Zero-order reactions

(e.g. heterogeneous catalysis)

$$R = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^0 = k$$

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

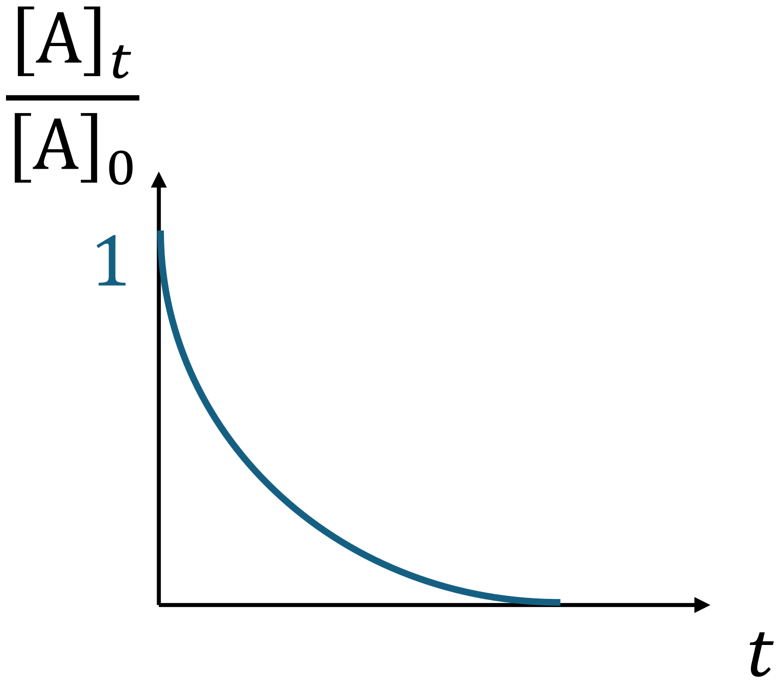


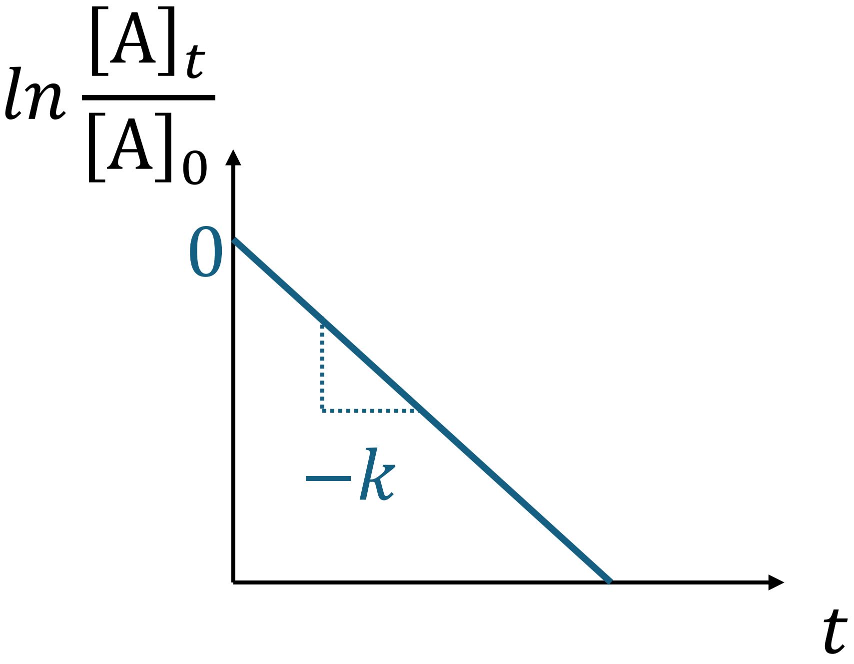
## First-order reactions

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

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

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



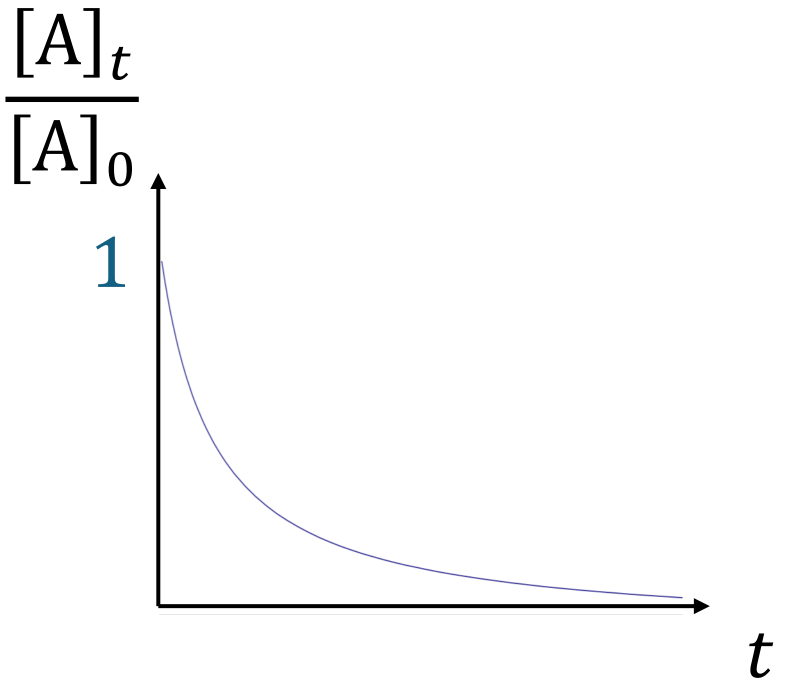


# Second-order reactions

**First case:** $2\text{A} \rightarrow \text{products}$

- Rate equation: $R = -\frac{1}{2}\frac{d[\text{A}]}{dt} = k[\text{A}]^2$

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



**Second case:** A + B → products

reminder:
$x$ = extent of reaction
in units of concentration

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

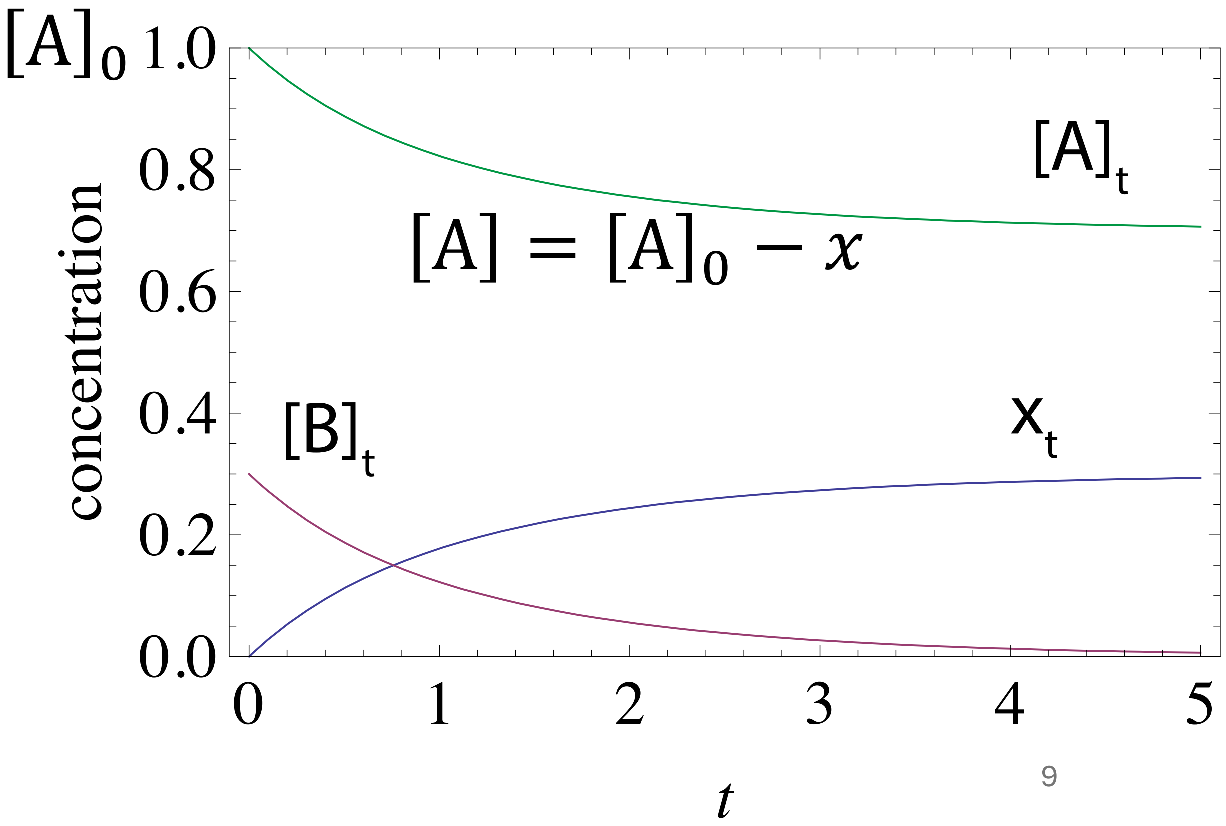
- $-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]\,[\mathrm{B}]$ … problematic

→introduce extent of reaction

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

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

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



# Reactions of General Order

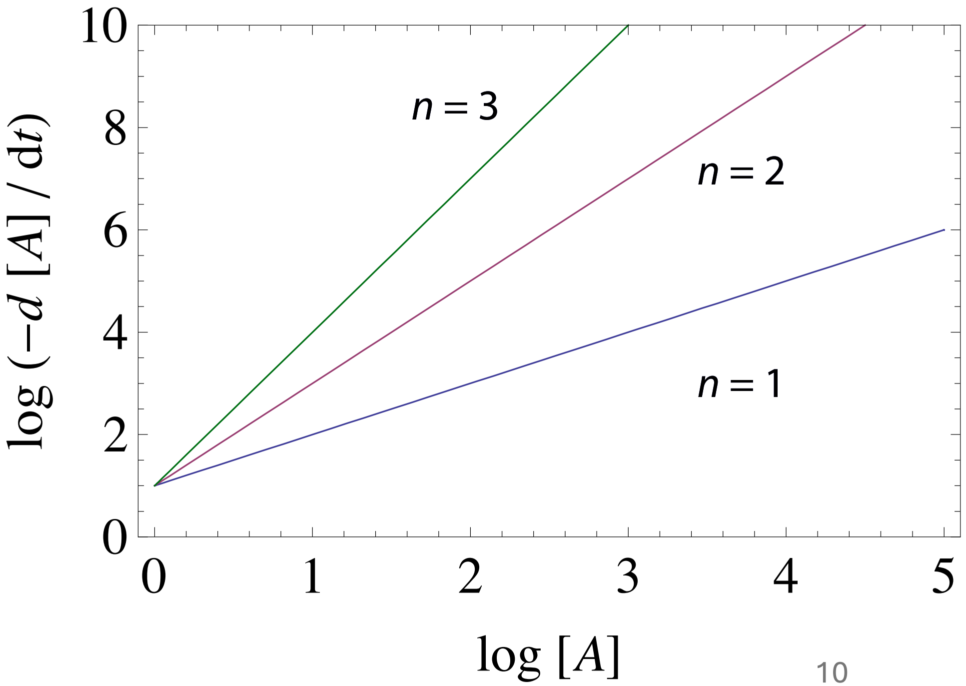
$$aA \rightarrow Products$$

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

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

- *van't Hoff plot* to find out order of reaction:

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



# Arrhenius Equation:

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

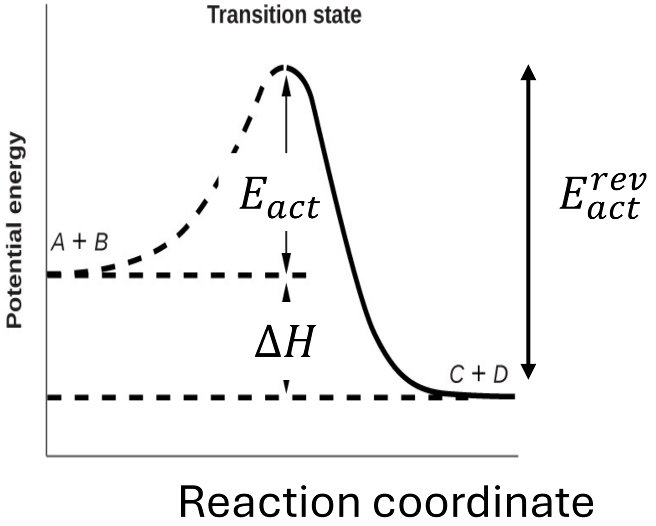
- to obtain $A$ and $E_{act}$ , plot in logarithmic form:

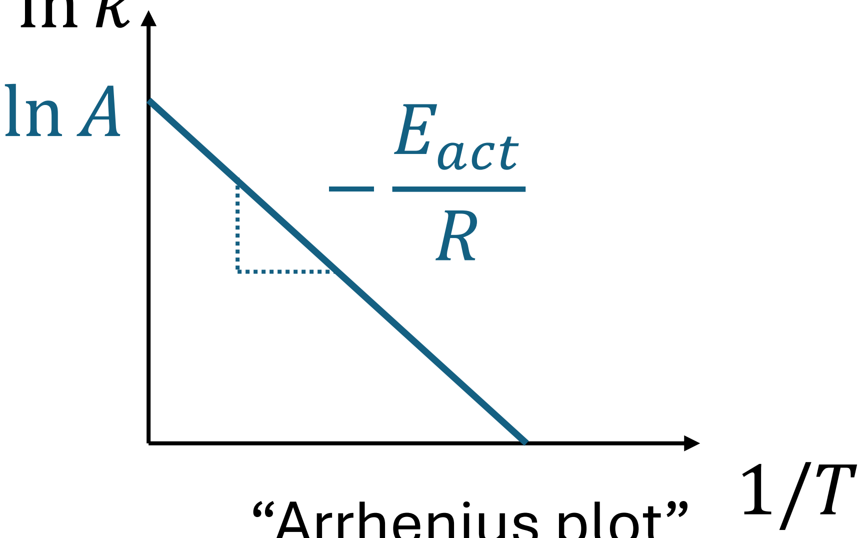
$$\ln k = \ln A - \frac{E_{act}}{RT}$$

- For reversible reactions (equilibrium):

$$\mathrm{A} + \mathrm{B} \underset{k_{\text{reverse}}}{\overset{k_{\text{forward}}}{\rightleftarrows}} \mathrm{C} + \mathrm{D}$$

- $K_{\text{eq}} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{A_{\text{forward}}}{A_{\text{reverse}}} e^{-\frac{\Delta H^0}{RT}}$





“Arrhenius plot”

# Chapter 2

## Complex Reactions

# Reversible Reactions

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

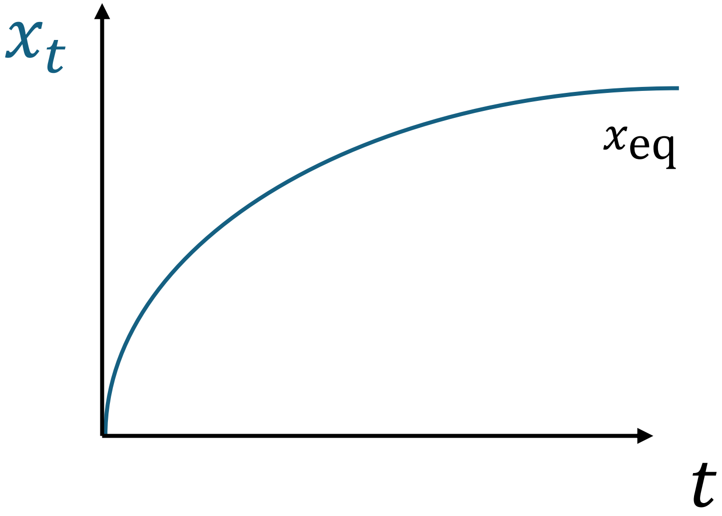
$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}]$$

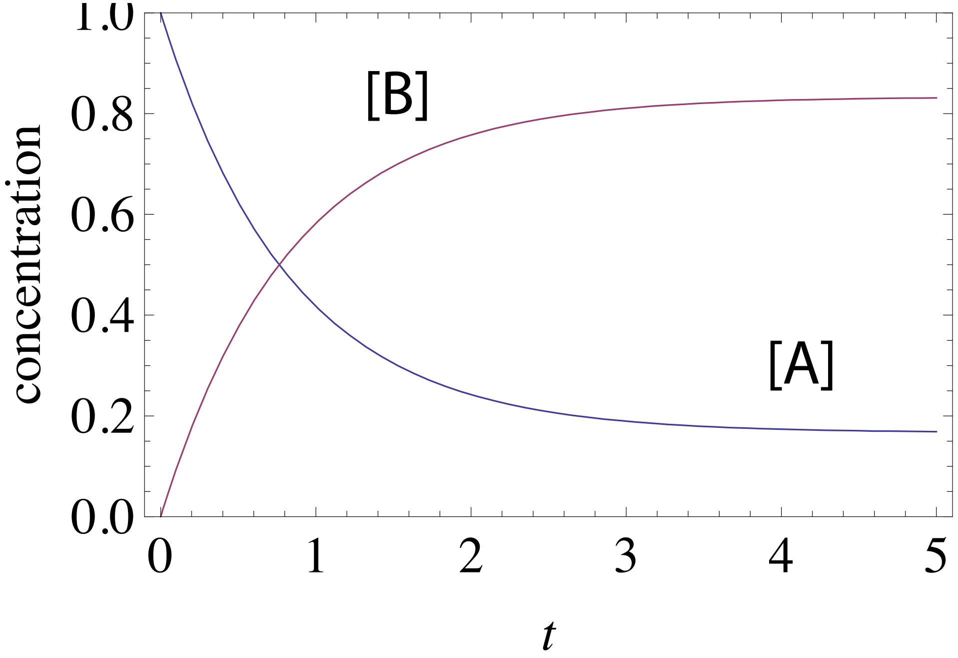
$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}]$$

- we found for extent of reaction

$x_t = \frac{c}{k}\left(1 - e^{-kt}\right)$ and

$$x_{\mathrm{eq}} = \lim_{t\to\infty} x_t = \frac{k_1[\mathrm{A}]_0 - k_{-1}[\mathrm{B}]_0}{(k_1 + k_{-1})}$$





# Consecutive Reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$ (e.g. radioactive decay)

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$$

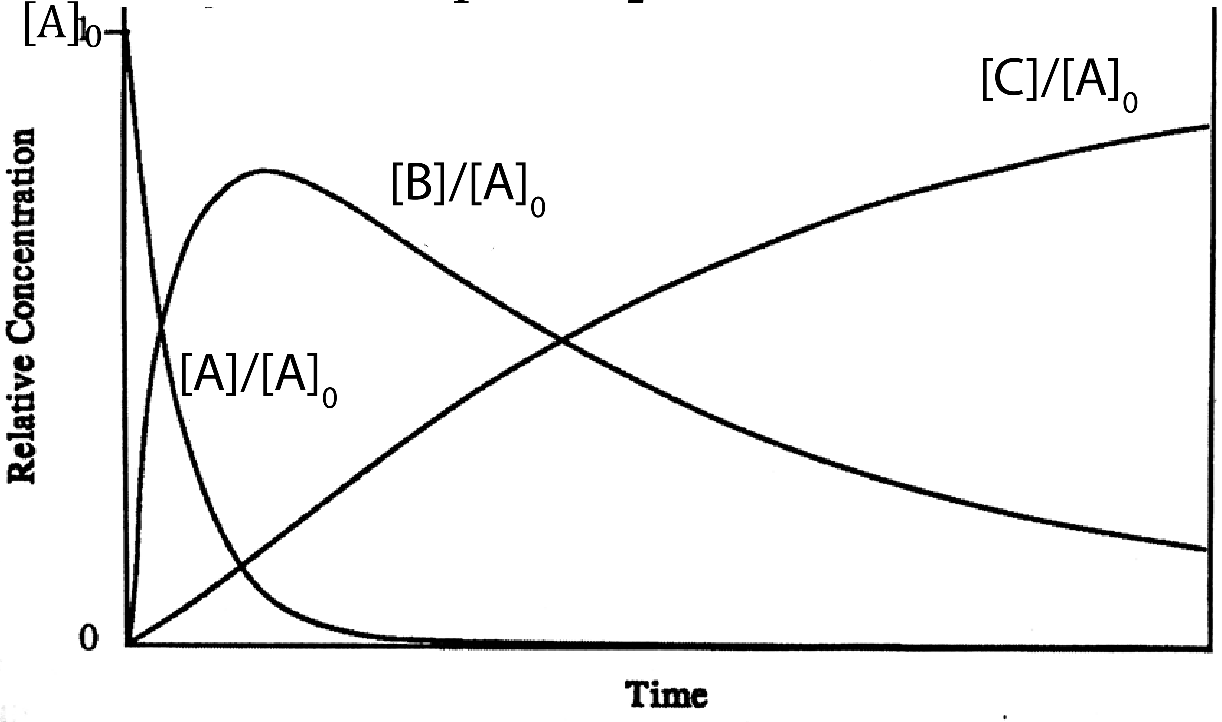
$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[\mathrm{C}] = [\mathrm{A}]_0\left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right)$$

**two cases:**

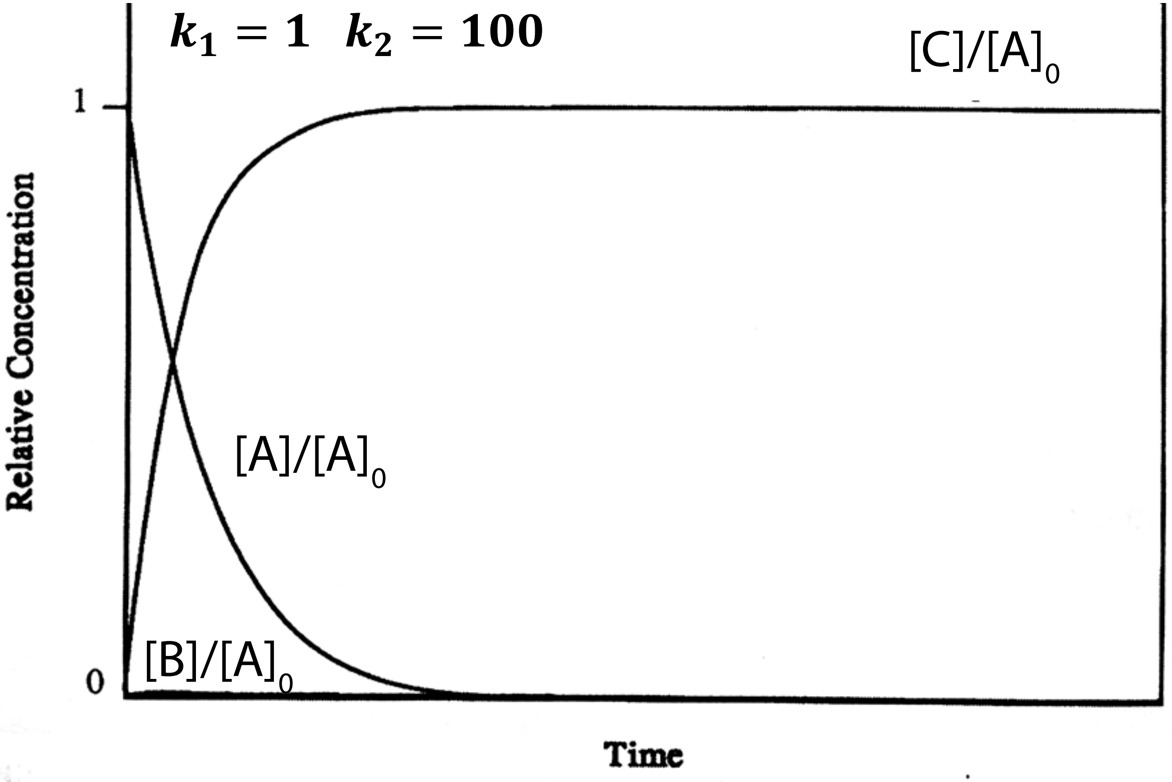
**for $k_1 \gg k_2$**

$k_1 = 1 \quad k_2 = 0.1$



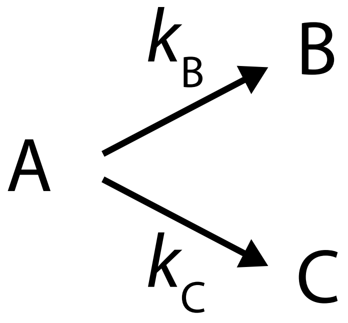
**for $k_2 \gg k_1$** $[\mathrm{C}] \approx [A]_0(1 - e^{-k_1 t})$

$k_1 = 1 \quad k_2 = 100$



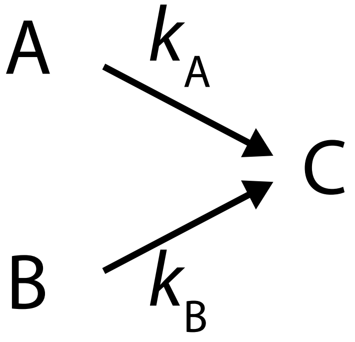
# Parallel Reactions

## Case 1: First-order decay to different products



- $[A] = [A]_0\, e^{-(k_B+k_C)t}$
- $[\mathrm{B}]_\mathrm{t} = \frac{k_B}{(k_B+k_C)}[A]_0\,(1-e^{-(k_B+k_C)t})$
- $[\mathrm{C}]_\mathrm{t} = \frac{k_C}{(k_B+k_C)}[A]_0\,(1-e^{-(k_B+k_C)t})$

## Case 2: First-order decay to the same product



## The Steady-State Approximation (SSA)

- valid, if conc. of intermediate small. Then can set: $\frac{d[\mathrm{A}_i]}{dt} \approx 0$
- applied it to simple 2-step consecutive reaction with $k_2 \gg k_1$
- applied it to 2-step consecutive reaction with reversible first step;
  with cases of 1st or 2nd step rate-limiting got different results

## The Pseudo-First-Order Method

- e.g. for $\mathrm{A}_1 + \mathrm{A}_2 \xrightarrow{k_1}$ products & $\mathrm{A}_1 + \mathrm{A}_3 \xrightarrow{k_2}$ products

- trick: supply $[\mathrm{A}_1]$ in large excess in your reaction
- $[\mathrm{A}_1] \approx \text{const.}$ over time

# Chapter 3

## Catalysis & Polymerization

# Michaelis-Menten Enzyme Kinetics

$$\mathrm{E} + \mathrm{S} \rightleftarrows \mathrm{ES} \rightleftarrows \mathrm{EZ} \rightleftarrows \mathrm{EP} \rightleftarrows \mathrm{E} + \mathrm{P}$$

- we simplify this for MMM to

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P}$$

**MMM assumptions:**

- **1**): only 2 steps
- **2**): no reverse reaction (or restrict to initial stage of reaction where back-reaction neglectable)
- **3**): steady-state approximation for intermediate ES
- **4**): [E] << [S]

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P}$$

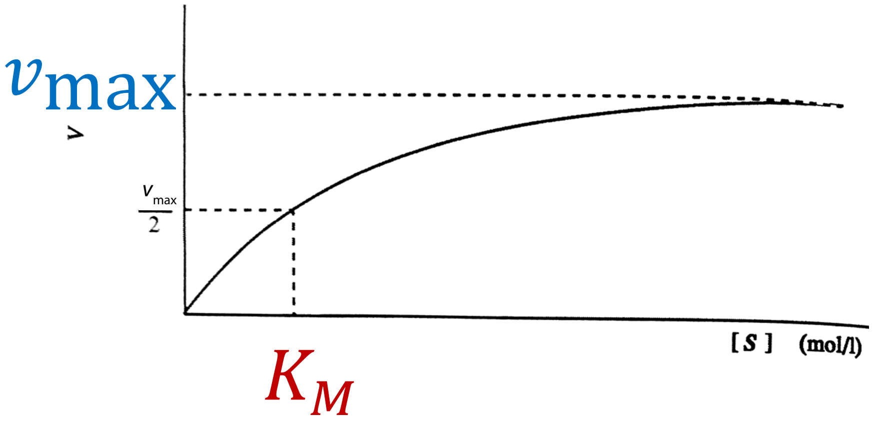
maximum rate $v_{\max}$

***MMEq.***:

$$v = \frac{\overbrace{k_2[\mathrm{E}]_0}}{1 + \underbrace{\frac{k_{-1}+k_2}{k_1[\mathrm{S}]}}} = \frac{v_{\max}}{1 + \frac{K_M}{[\mathrm{S}]}}$$

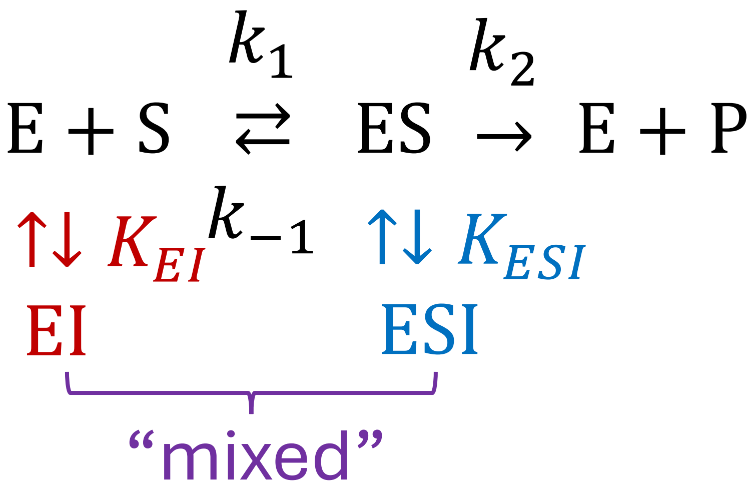
Michaelis constant $K_M = (k_{-1} + k_2)/k_1$

(units of concentration)



## Inhibition mechanisms in enzyme kinetics

- competitive
- uncompetitive
- mixed (non-competitive)



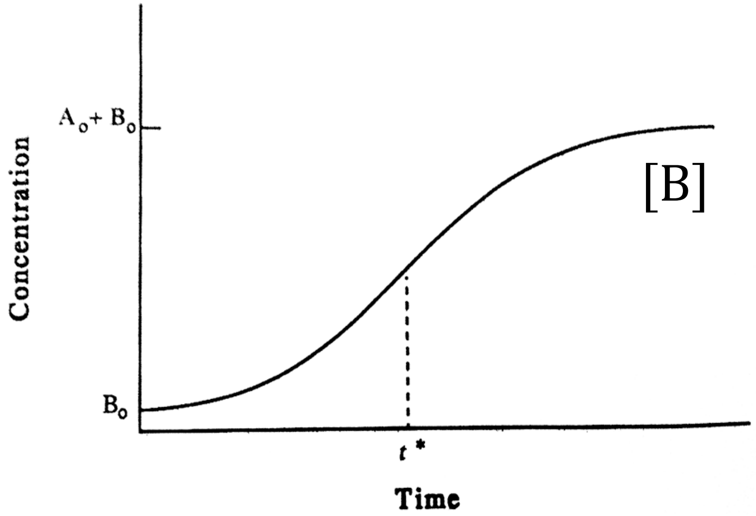
$$\begin{tikzcd} E + S \arrow[r, shift left, "k_1"] \arrow[d, shift left] & ES \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, shift left] & E + P \\ EI \arrow[u, shift left, "K_{EI}"'] & ESI \arrow[u, shift left, "K_{ESI}"'] & \end{tikzcd}$$

$$\underbrace{\text{EI} \qquad\qquad \text{ESI}}_{\text{“mixed”}}$$

## **Autocatalysis** (follows an “S curve”)

$$A + B \xrightarrow{k} 2B$$

$$[B]_t = \frac{[A]_0 + [B]_0}{1 + \frac{[A]_0}{[B]_0} \, e^{-\left([A]_0 + [B]_0\right)kt}}$$



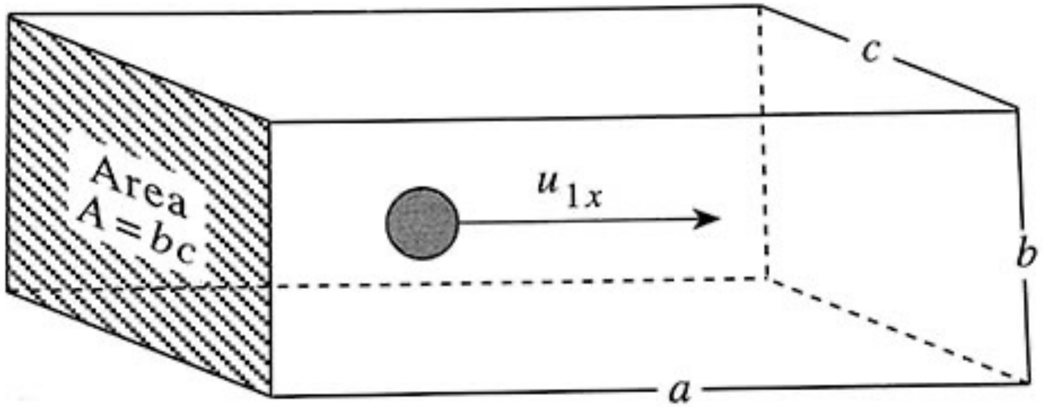
## Polymerization

- Stepwise: linear growth
  - average chain length $\langle N \rangle = \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = \frac{1}{1-p} = 1 + kt[\mathrm{A}]_0$
- chain type: 3 steps
  - initiation
  - propagation
  - Termination
  - $\langle N \rangle = 2\lambda = \frac{k_p}{(f k_i k_t)^{\frac{1}{2}}} [\mathrm{In}]^{-\frac{1}{2}} [\mathrm{M}]$
- kinetic chain length $\lambda$ and degree of polym. $\langle N \rangle$

# Chapter 4

## Kinetic Theory of Gases

# Kinetic theory of gases



- Ideal gas law: $\boldsymbol{PV = Nk_BT = nRT}$

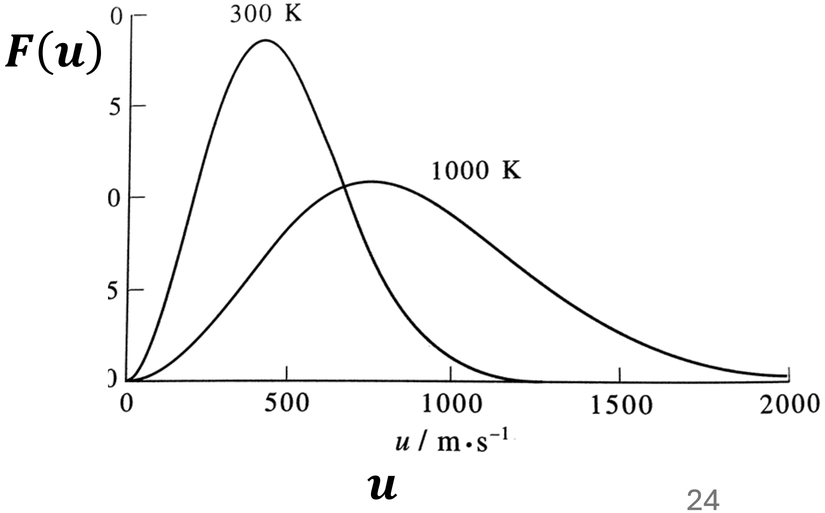
- only kinetic energy, collisions elastic

$$u_{rms} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_BT}{m}}$$

# Maxwell-Boltzmann distribution

- in 1D: $f(u_j)du_i = \sqrt{\frac{m}{2\pi k_B T}} \; e^{-\frac{mu_j^2}{2k_B T}} du_i$
- in 3D: $F(u)du = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_B T}} du$
- and how curve changes with composition
  & with temperature
- and how to measure speed distributions experimentally:

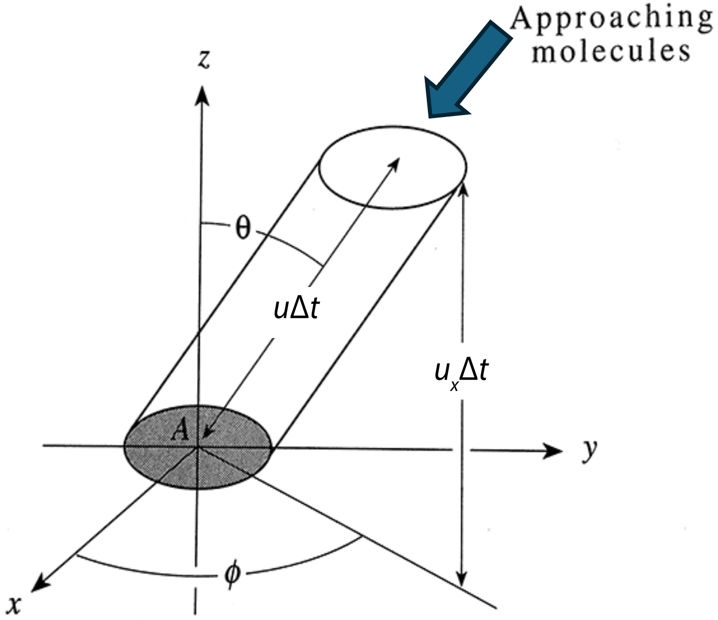
Doppler effect vs rotating discs slit machine



# Chapter 5

## Collisions

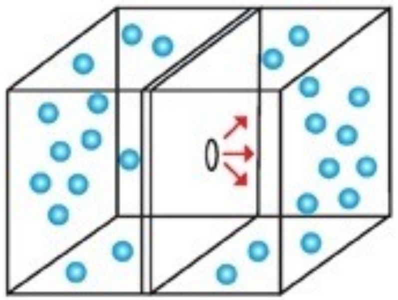
# Hard Spheres – Collisions with a wall



**Collision flux:** $z_{\text{coll}} = \frac{\rho}{4}\langle u \rangle = \sqrt{\frac{k_B T}{2\pi\, m}}\rho$ [s$^{-1}$m$^{-2}$]

## Effusion

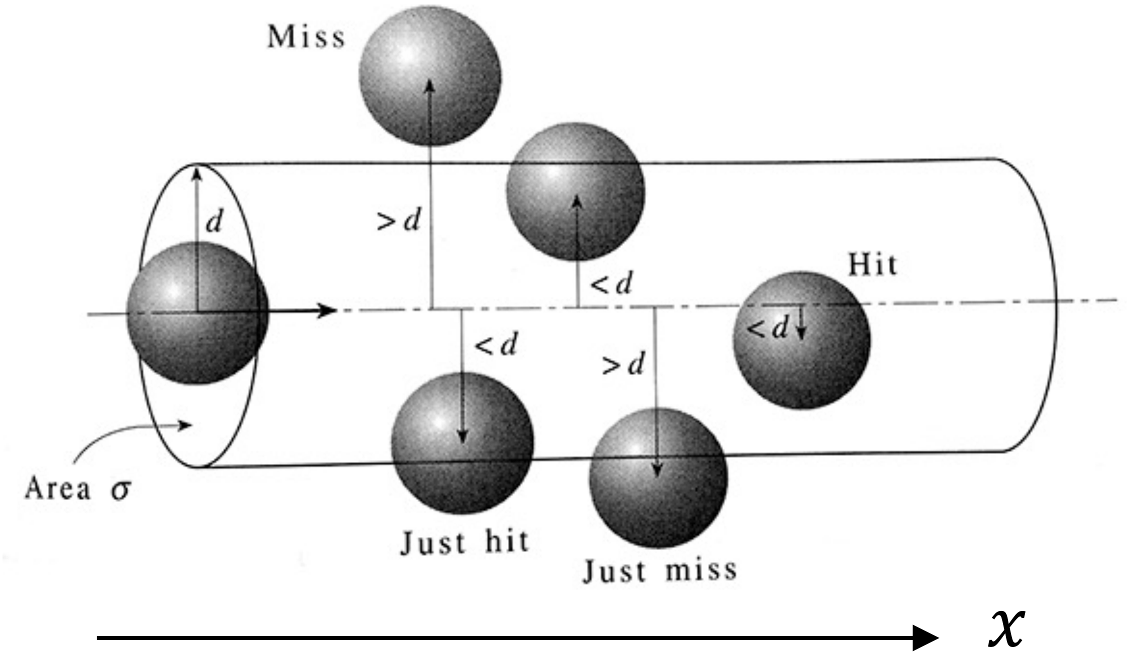
- low pressure, small hole vs. large mean free path
- **effusion rate** $k_{\text{effusion}} = z_{\text{coll}}\, A = \frac{pA}{\sqrt{2\pi m k_B T}}$ [s$^{-1}$]
- Knudsen method to measure vapor pressure of liquids



**Collision rate:**

$$z_A = \rho\sigma\langle u_{AB}\rangle = \rho\sigma\sqrt{2}\langle u\rangle$$

$$= \sqrt{2}\rho\sigma\sqrt{\frac{8k_BT}{\pi m}} = \rho\sigma\sqrt{\frac{8k_BT}{\pi\mu}}$$



**Mean free path:** $l = \dfrac{\langle u\rangle}{z_A} = \dfrac{1}{\sqrt{2}\rho\sigma}$ [m]

- number of unscattered molecules as they pass through the volume of other particles and scatter decays as:

$$n(x) = n_0 e^{-\sigma\rho x} = n_0 e^{-\frac{x}{l}}$$

# Center-of-mass coordinates

- $(\boldsymbol{v}_A, \boldsymbol{v}_B) \rightarrow (\boldsymbol{v}_{cm}, \boldsymbol{w}_{AB})$

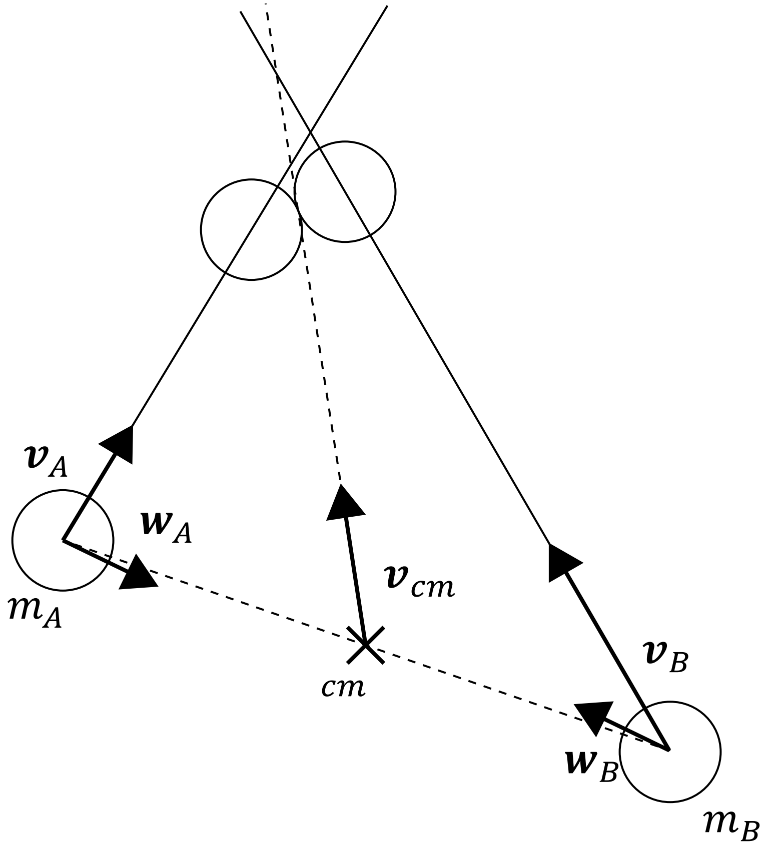
$$\boldsymbol{v}_A = \boldsymbol{v}_{cm} + \mu \boldsymbol{w}_{AB}/m_A$$

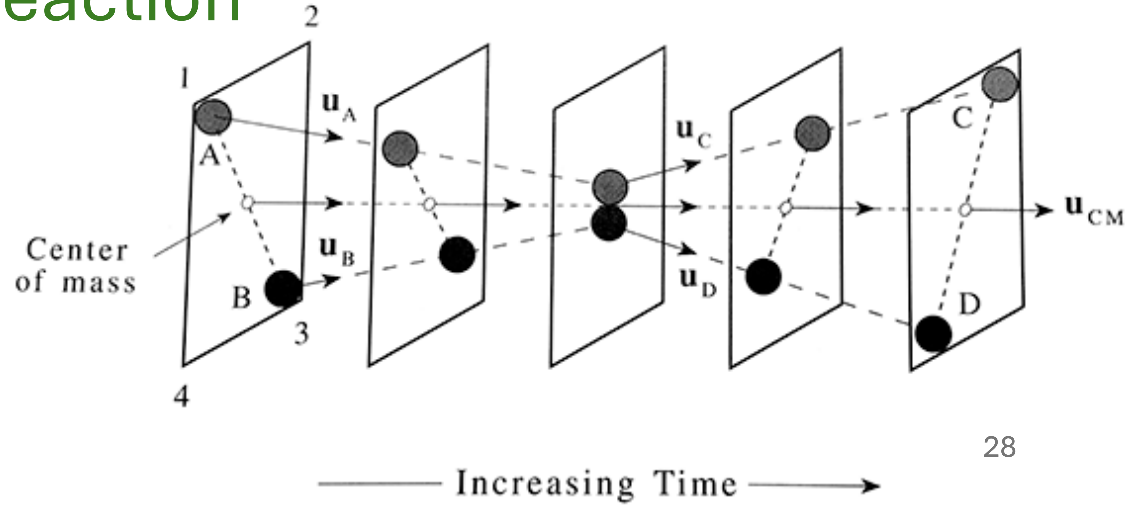
$$\boldsymbol{v}_B = \boldsymbol{v}_{cm} - \mu \boldsymbol{w}_{AB}/m_B$$

- $\mathrm{E_{kin}} = \frac{1}{2}(m_A + m_B)v_{cm}^2 + \frac{1}{2}\mu v_{AB}^2$

$$= \quad E_{\text{kin, cm}} \quad + \quad E_{\text{kin, AB}}$$

conserved! available for reaction





# distribution of relative velocities:

$$f\left(v_{Ax}, v_{Ay}, v_{Az}, v_{Bx}, v_{By}, v_{Bz}\right) dv_{Ax} dv_{Ay} dv_{Az} dv_{Bx} dv_{By} dv_{Bz}$$

- transformed to c.m. system
- integrated out c.m. part

$$f\left(\ v_{ABx}, v_{ABy}, v_{ABz}\right) dv_{AB,x} dv_{AB,y} dv_{AB,z}$$

- transformed to spherical coordinates
- integrated out spherical part (isotropic)

$$f(v_{AB}) dv_{AB} = 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v_{AB}^2 \quad e^{-\frac{\mu v_{AB}^2}{2k_B T}} \ dv_{AB}$$

**a M.B. distribution for particles of mass $\boldsymbol{\mu}$**

# Bimolecular collisions

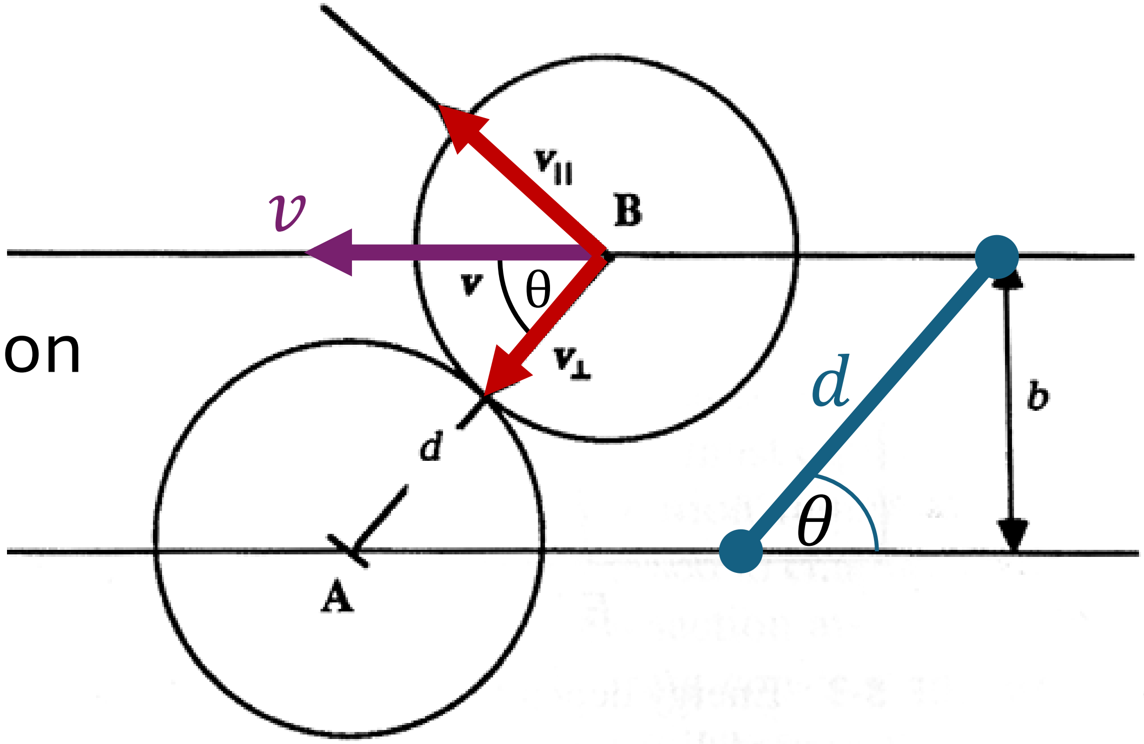
**Reactive hard spheres** ($A + B \rightarrow Products$)

- If *all* collisions were reactive: $-\frac{\rho_A}{dt} = -\frac{\rho_B}{dt} = z_{AB} = \underbrace{\sigma_{AB}\langle u_{AB}\rangle}_{k(T)}\ \underset{[A][B]}{\rho_A\rho_B}$
- rate would be much too high
- temp. dependence wrong: $k(T) \propto \sqrt{T}$ *vs* Arrhenius: $k(T) \propto e^{-E_{act}/k_BT}$

→ Idea: $k(T) = \sigma_{AB}\langle u_{AB}\rangle \quad \rightarrow \quad k(T) = \langle \sigma_R(E)\, u_{AB}\rangle$

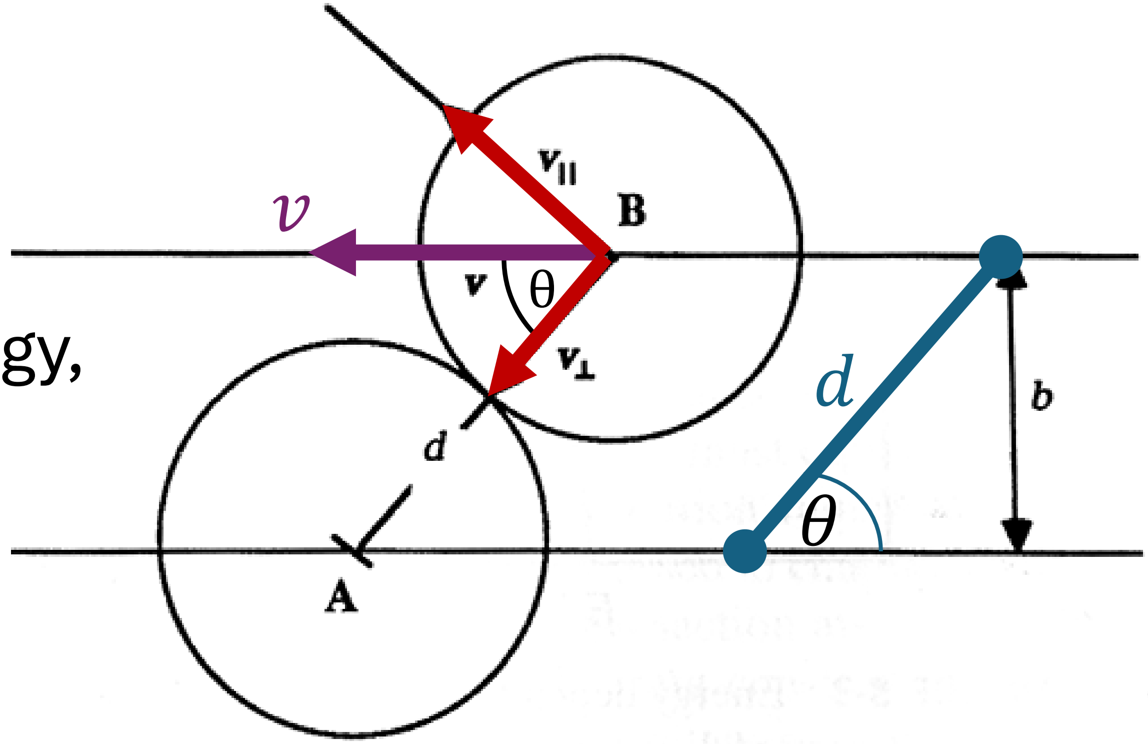
# Reactive hard spheres model

- the closer the **impact parameter *b*** gets to 0, the more heads-on is a collision



- only orthogonal component can drive reaction
- probability: $P_R(E_\perp) = \begin{cases} 0 & \text{if } E_\perp < E^* \\ p & \text{if } E_\perp \geq E^* \end{cases}$
- hard sphere collision cross section: $\sigma_{AB} = \pi d^2$
- reaction cross section: $\sigma_R(E) = \begin{cases} 0 & \text{if } E < E^* \\ \pi d^2 p (1 - \frac{E^*}{E}) & \text{if } E \geq E^* \end{cases}$

# Reactive hard spheres model



reaction cross section depends on energy, so we calculated the thermal average using the M.B. distribution and got:

$$k(T) = \underline{\pi d^2 \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}} \; p} \; e^{-\frac{E^*}{k_BT}}$$

hard-sphere cross section × mean velocity × Arrhenius eq.

Arrhenius pre-factor $A$

# 2-body classical scattering

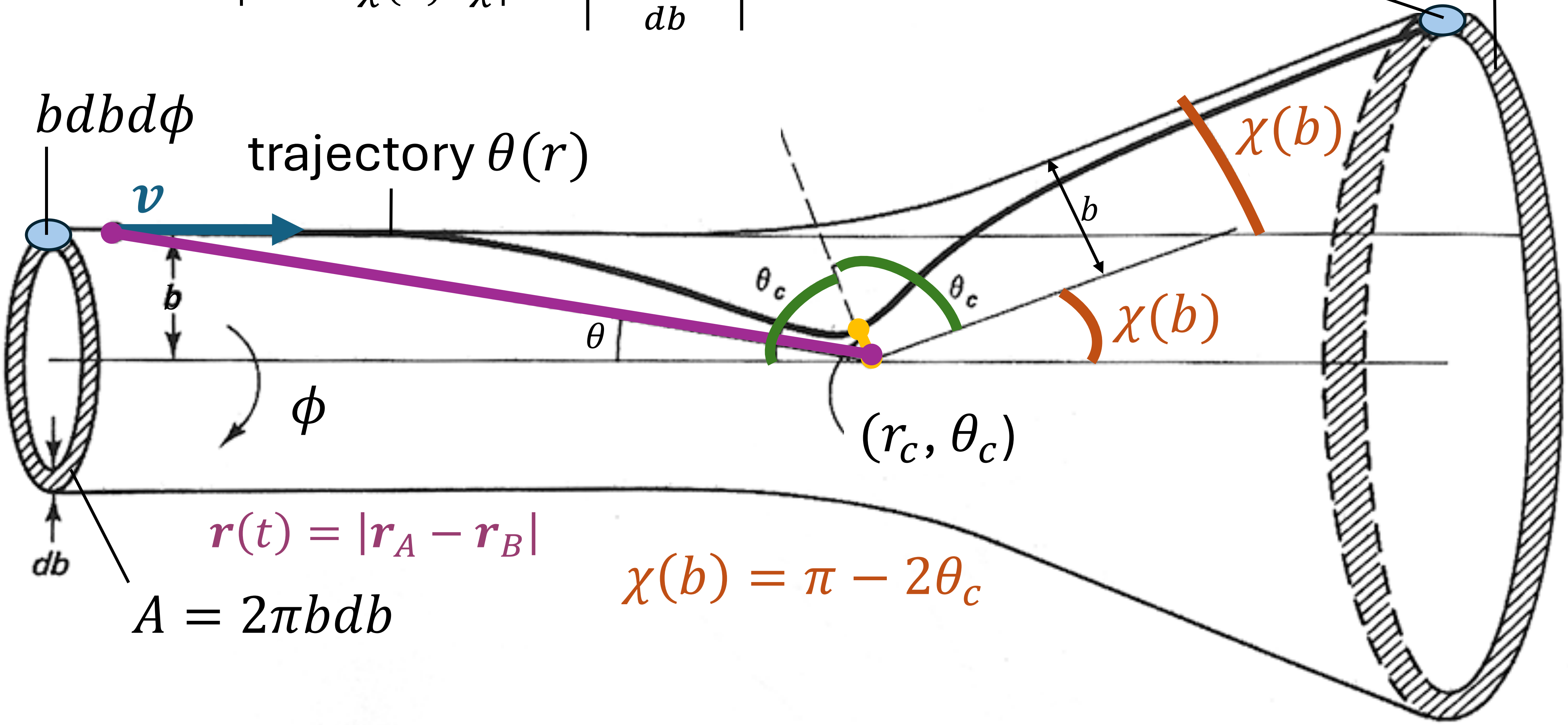
- angular dependence and *differential* reaction cross section $I_R$
- to learn more details about reaction mechanisms
- central interaction potential $U(r)$ (at least works for spherical rare gas atoms)
- the symmetrical nature of such a potential will make our life easier
- again, treat all in center of mass framework

- Ask: What fraction of particles (a part of the total reaction cross section $\sigma_R$) scatters into a specific solid angle (a small element $d\Omega$ of the total solid angle $\Omega$)?

# 2-body classical scattering

Differential scattering cross-section:

$$I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi b d b}{|2\pi sin\chi(b) d\chi|} = \frac{b}{\left|\frac{d(\cos\chi)}{db}\right|}$$



$$A' = 2\pi sin\chi d\chi$$

$$d\Omega = sin\chi d\chi d\phi$$

$$bdbd\phi$$

trajectory $\theta(r)$

$$\boldsymbol{r}(t) = |\boldsymbol{r}_A - \boldsymbol{r}_B|$$

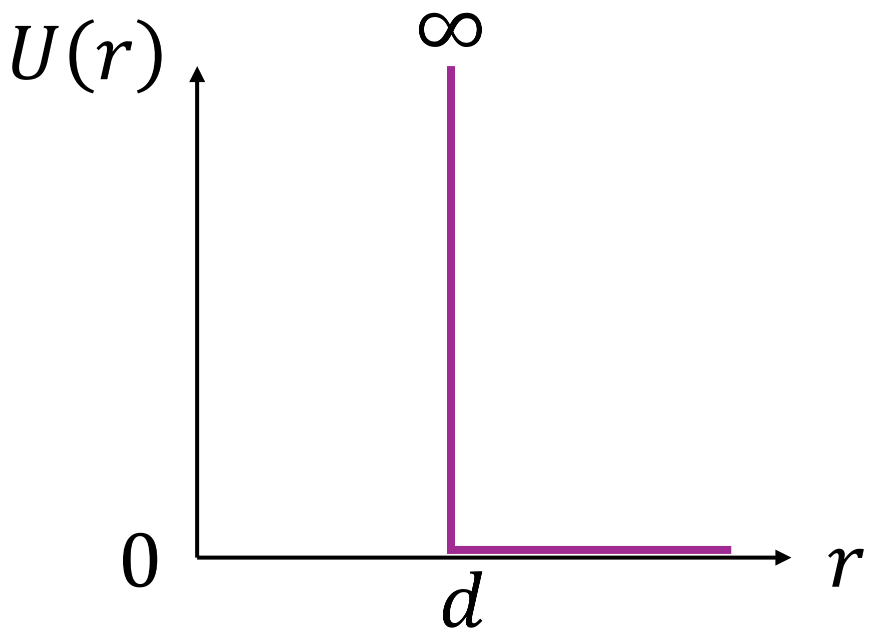
$$\chi(b) = \pi - 2\theta_c$$

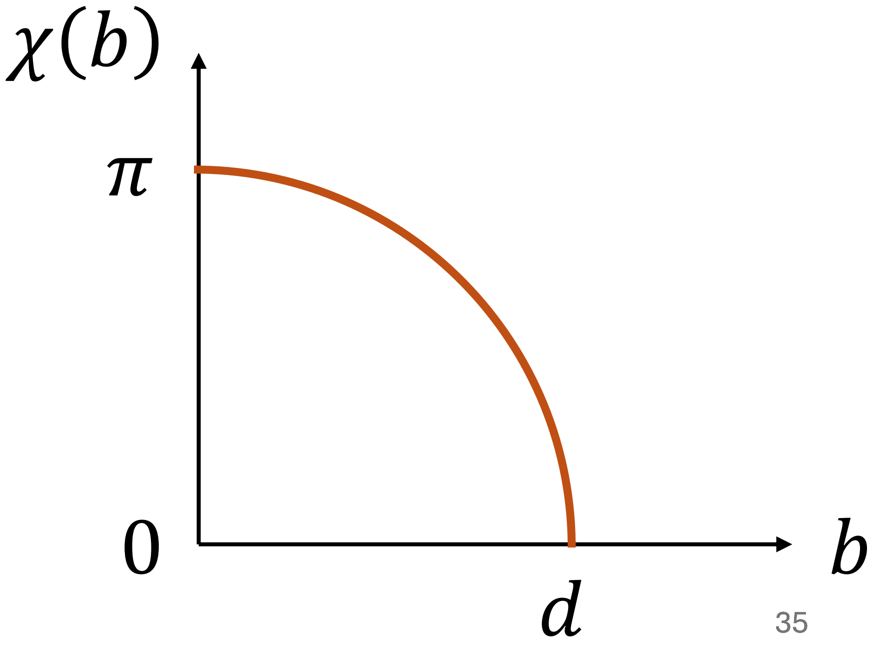
$$A = 2\pi b d b$$

# 2-body classical scattering

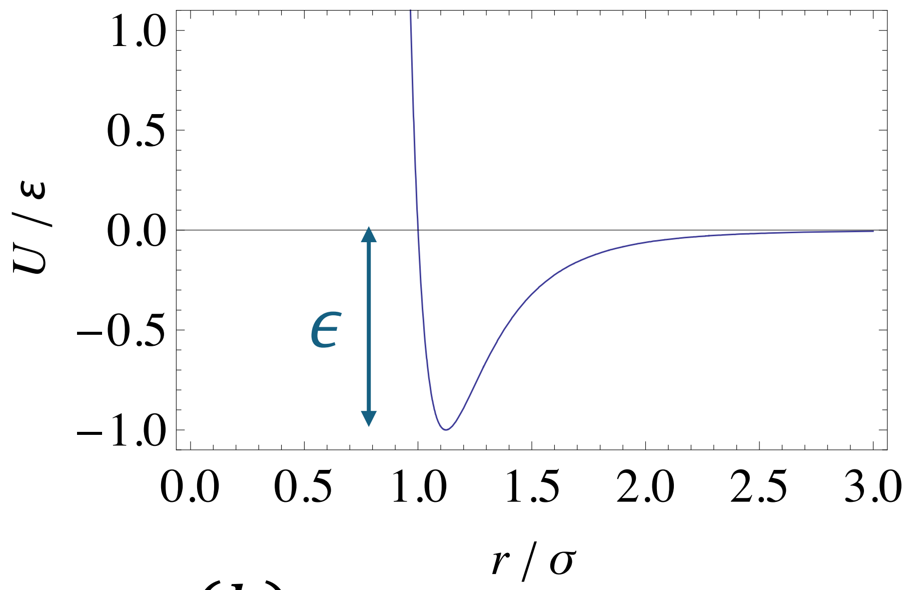
$$I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi b db}{|2\pi sin\chi(b)d\chi|} = \frac{b}{\left|\frac{d(\cos\chi)}{db}\right|}$$

- for hard spheres: $U(r) = \begin{cases} 0 & (r > d) \\ \infty & (r \leq d) \end{cases}$
  - $\chi(E, b) = 2\arccos\frac{b}{d}$
  - $I_R(E, \chi) = \frac{d^2}{4}$



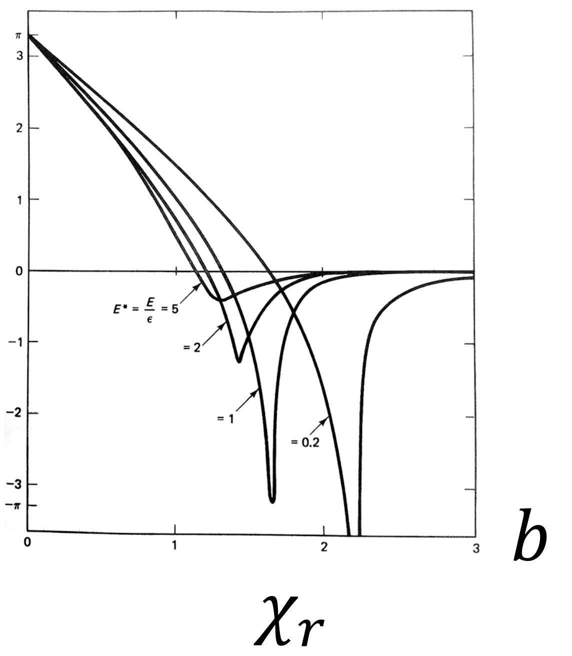


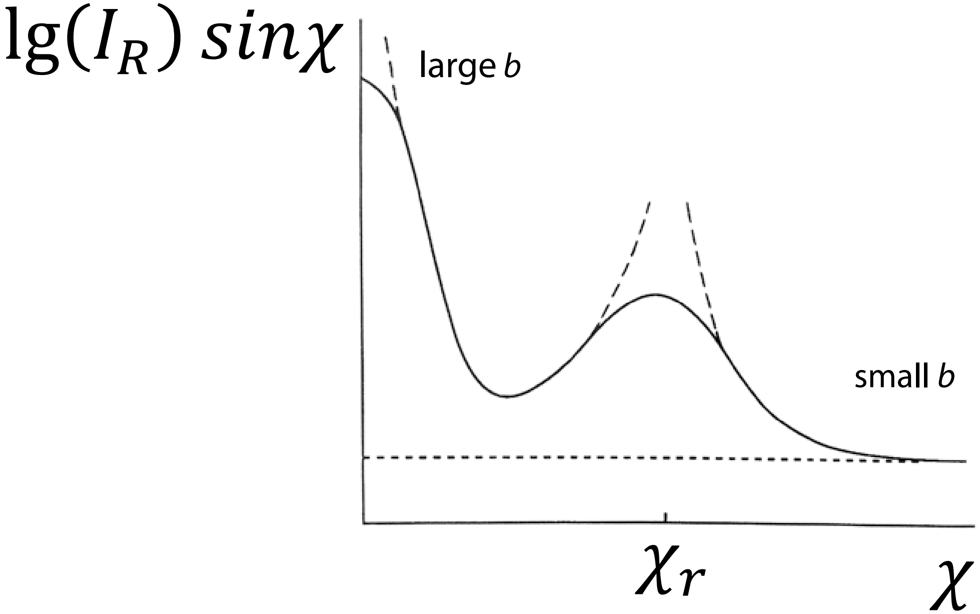
# 2-body classical scattering



$$I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi b db}{|2\pi sin\chi(b) d\chi|} = \frac{b}{\left|\frac{d(\cos\chi)}{db}\right|}$$

- for Lennard-Jones: $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$





- $\chi_r$ rainbow angle

# Chapter 6

## Unimolecular Reaction Dynamics

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{products}$$

- **Lindemann theory** of collision-activated unimolecular reactions
  - strong collision assumption for activation/deactivation

  →gas-kinetic collision rate $z_{\mathrm{AM}}$ for deactivation const. $k_{-1}$:

  $$z_{\mathrm{AM}} = \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle \rho_{\mathrm{A}} \rho_{\mathrm{M}} = k_{-1}\,[\mathrm{A}][\mathrm{M}]$$

  - applied steady-state approximation to $[\mathrm{A}^*]$
  - overall rate: $R = k_{uni}[\mathrm{A}] = k_2[\mathrm{A}^*] = \frac{k_1 k_2[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}]+k_2}$
  - considered high- & low-pressure limits

$$\boxed{\begin{aligned} k_{-1} &= \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle \\ k_{uni} &= \frac{k_1 k_2 [\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} \end{aligned}}$$

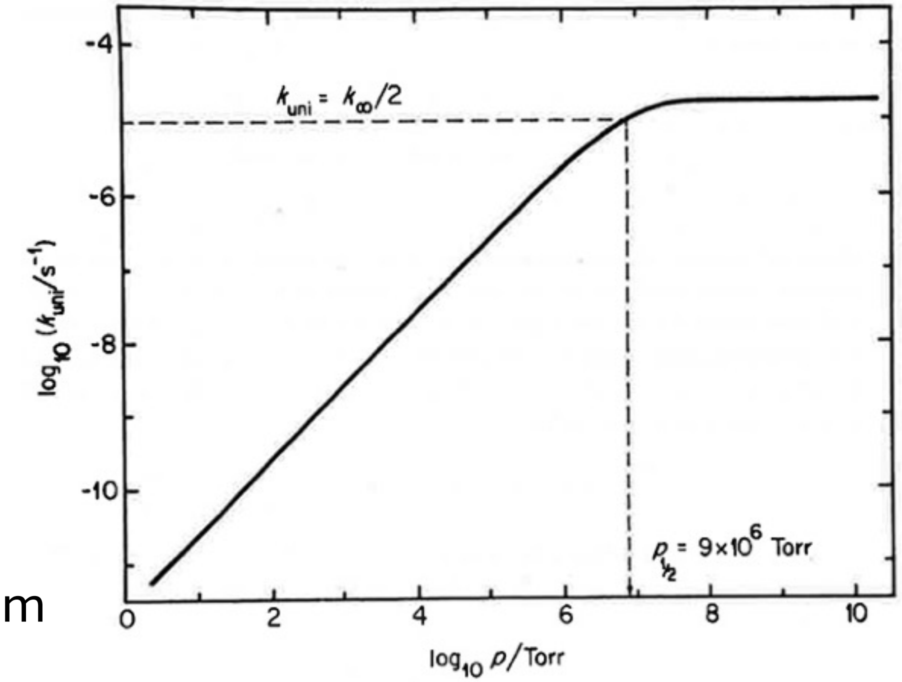
- at <u>low pressure</u> becomes 1st order in collision partner, linear increase of $k_{uni}$ with pressure (activation step is rate-liming)
- at <u>high pressure</u> becomes effectively 0th order, constant with pressure (pre-equilibrium, reaction rate-limiting)

$$\mathrm{A} + \mathrm{M} \overset{k_1}{\rightarrow} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \overset{k_{-1}}{\rightarrow} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \overset{k_2}{\rightarrow} \text{products}$$

$$\boxed{k_{uni} = \frac{k_\infty}{1 + \frac{k_\infty}{k_1[\mathrm{M}]}}}$$



$$k_{-1} = \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle$$

$$k_{uni} = \frac{k_1 k_2 [\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}$$

- ...we realized that using $k_1$ from simply reactive-hard-spheres model underestimated experimental results...

$$\mathrm{A+M} \overset{k_1}{\rightarrow} \mathrm{A^*+M}$$

$$\mathrm{A^*+M} \overset{k_{-1}}{\rightarrow} \mathrm{A+M}$$

$$\mathrm{A^*} \overset{k_2}{\rightarrow} \text{products}$$

# Lindemann-Hinshelwood theory

- to account for ***internal* energy stored in vibrations** that can drive reaction as well, to increase $k_1$ for better agreement with experiment
  - LH theory approximates the ratio

$$\frac{k_1}{k_{-1}} \approx \frac{\left[A_{E>E_0}\right]}{\left[A_{total}\right]}$$

  - only okay for pre-equilibrium approximation, *i.e.*, at *high* pressures (very drastic approximation for low ones!)
  - allowed us to apply statistical thermodynamics to calculate assuming a thermal distribution

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{products}$$

- we derived from first principles:

$$k_1 = \frac{k_{-1}}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$$

- assuming ***s classical* harmonic oscillators**, using stat. TD and density of states
- approximated solution, only valid for small molecules: $s$ small if overall atom number $N$ small, as $s = 3N - 6$ (or 5)
- and for activation energy $E_0$ being relatively large (typical)
- and assuming quasi-equilibrium, *i.e.* high-pressure limit
- then, we could drop all terms in binomial expansion for $j > 0$

*→ compared to just reactive-hard-spheres model, we learned that the reaction rate depends on the internal energy as well, taking into account the vibrational energy stored, which can contribute to successful activation and reaction, accounted for in the equation through the amount of modes s*

# Rice-Ramsperger-Kassel (RRK) Theory

$$\mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M}$$

- assumes $k_2 \rightarrow k(E)$ and $\mathrm{A}^*(E, E + dE)$
- assumes for activated molecules to…

$$\mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

(1) form microcanonical ensemble

(2) dissociate with frequency $\nu$ once reaching $E_0 + E'$ in the **critical mode**

$$\mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}$$

(3) continue to form a microcanonical ensemble because…

(3a) *ergodic hypothesis*, *i.e.*, energy can freely redistribute between all vibrational modes

(3b) *fast IVR* (intramolecular vibrational energy redistribution), *i.e.*, faster than reaction

RRK theory again **assumes equilibrium** (so that we can use statistical TD)
& classical oscillators (no QM)

# Rice-Ramsperger-Kassel (RRK) Theory

$$k(E) = \nu \cdot P(E, E_s \geq E_0)$$

$$k(E) = \nu \cdot \frac{N(E, E_s \geq E_0)}{N(E)}$$

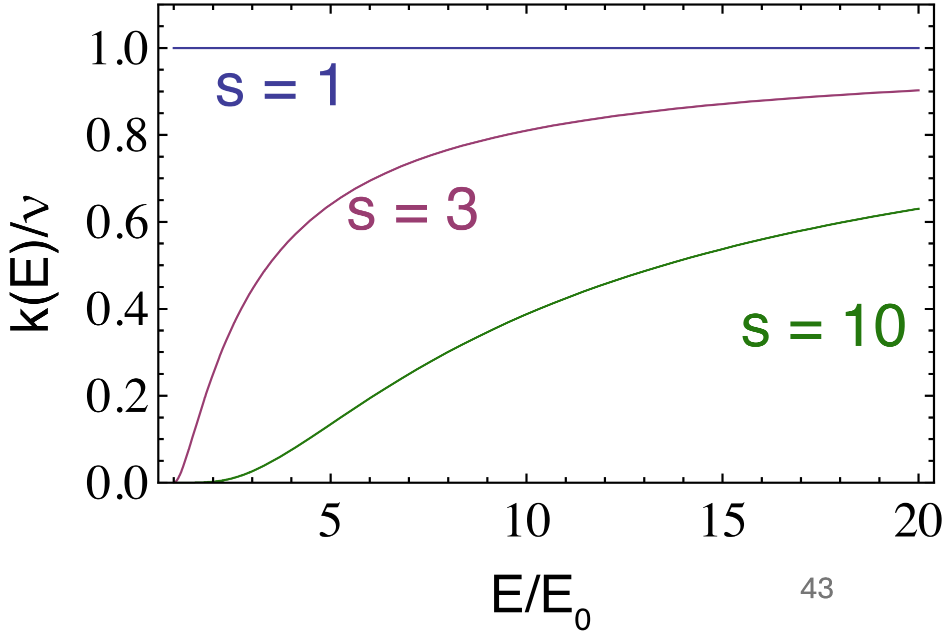
$$\boxed{k(E) = \nu \cdot \left(\frac{E - E_0}{E}\right)^{s-1}}$$

**RRK result for "$k_2$"**

$$\mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M}$$

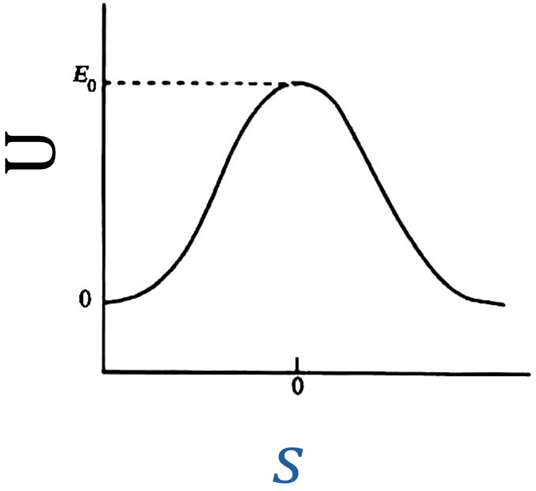
$$\mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

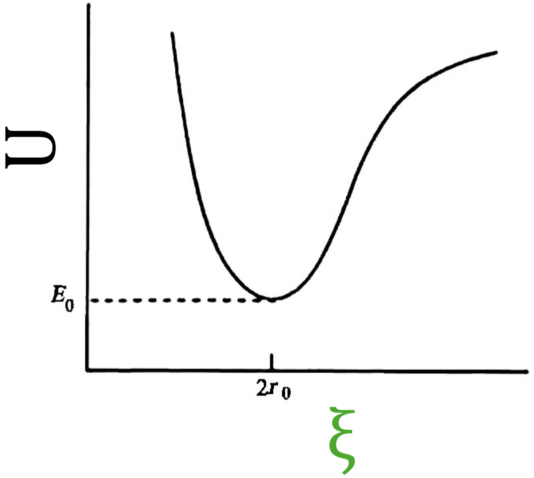
$$\mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}$$



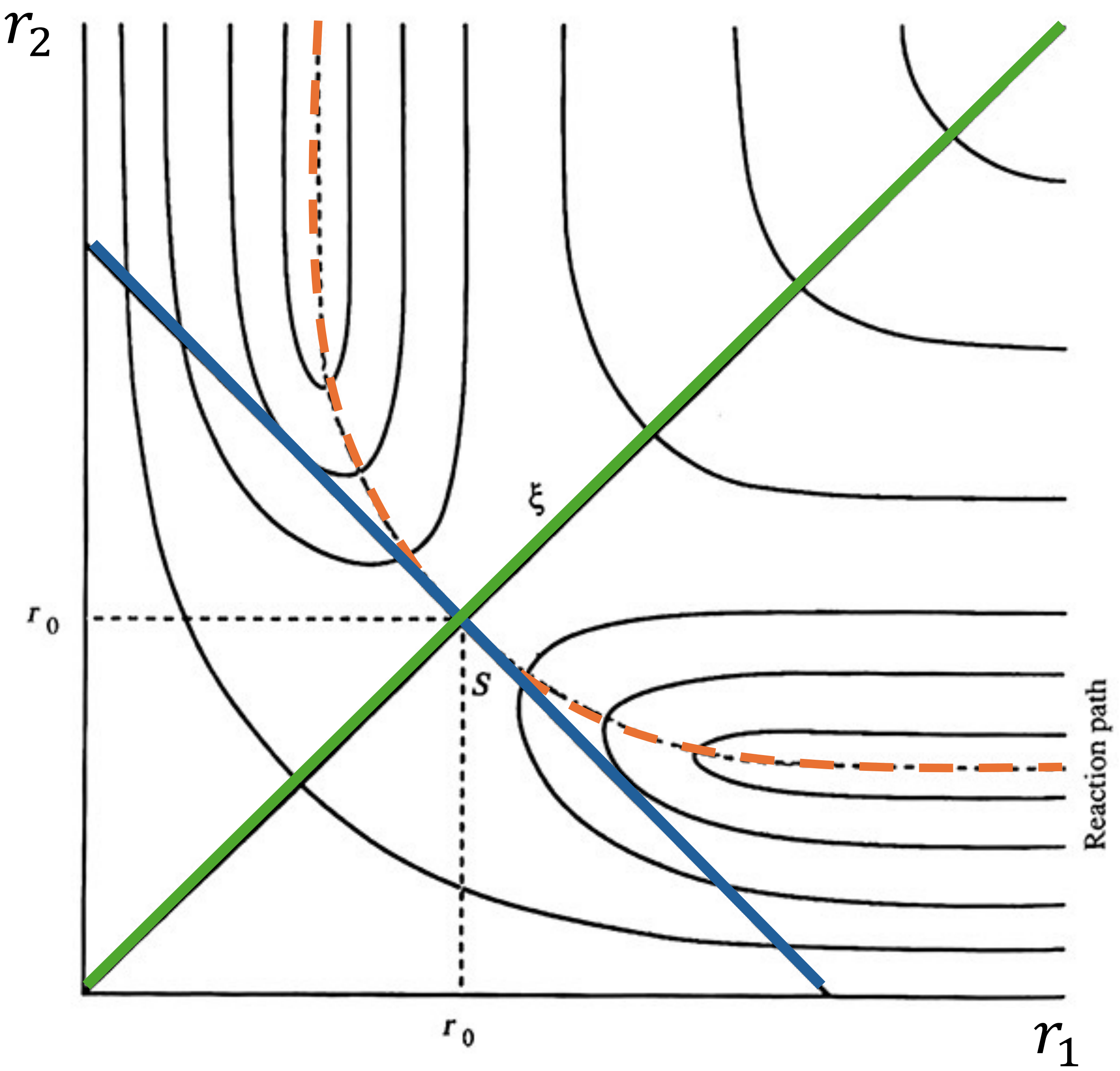
# Chapter 8

## Transition State Theory





- At the TS, minimum energy path mode has *maximum*, while orthogonal path shows *minimum*
- *In general*: ***the transition state is a saddle point, which is a maximum*** **along the reaction coordinate (the minimum energy path) and a minimum along all other normal modes**



# Transition State Theory (TST)

$$A + B \rightarrow N^{\ddagger} \rightarrow \text{Products}$$

- basic assumptions:

(1) Born-Oppenheimer Approximation

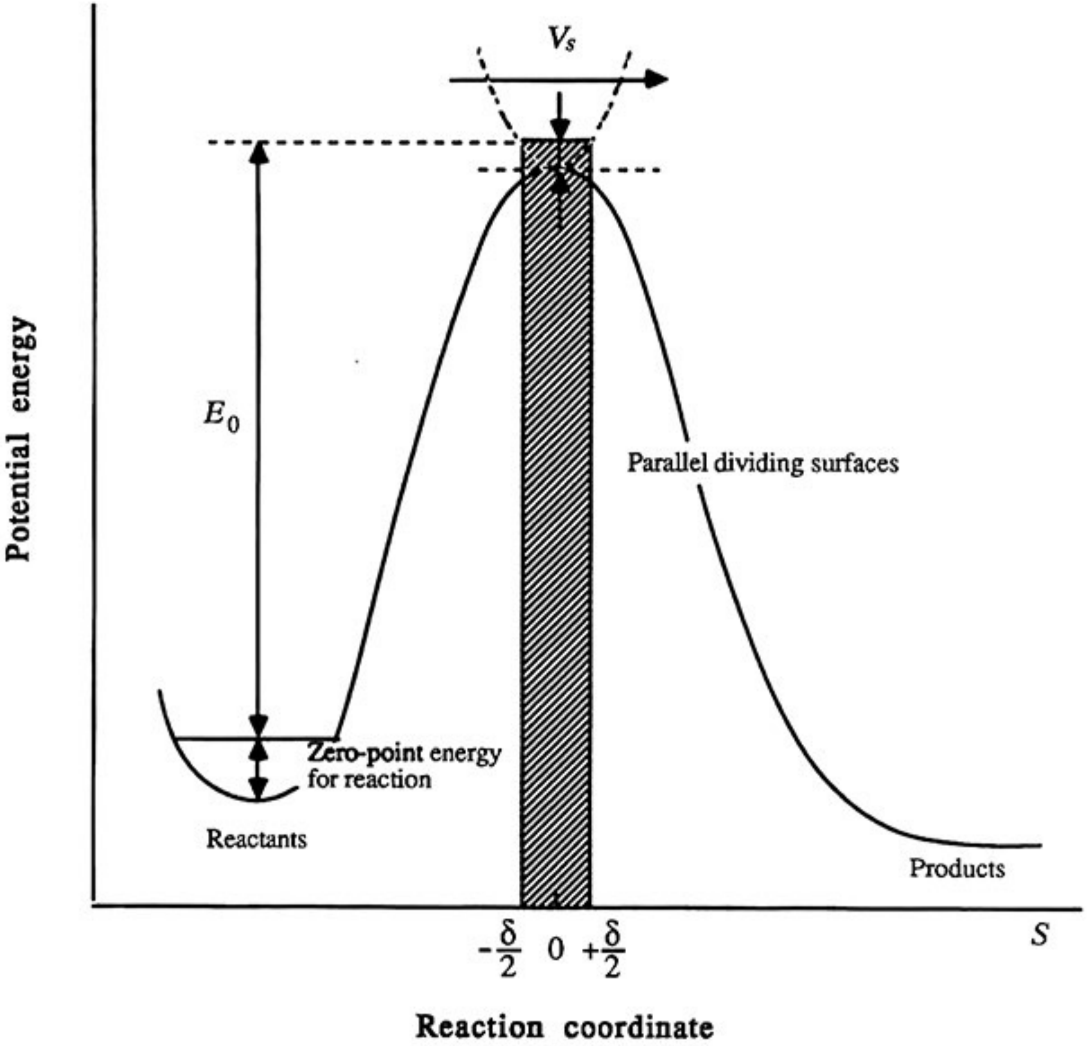
(2) Boltzmann (thermal) distribution

- specific assumptions:

(1) no re-crossing

(2) quasi-equilibrium

(3) classical motion along reaction coordinate (pretending no potential at the top and thus ideal gas behavior)



## Transition State Theory (TST)

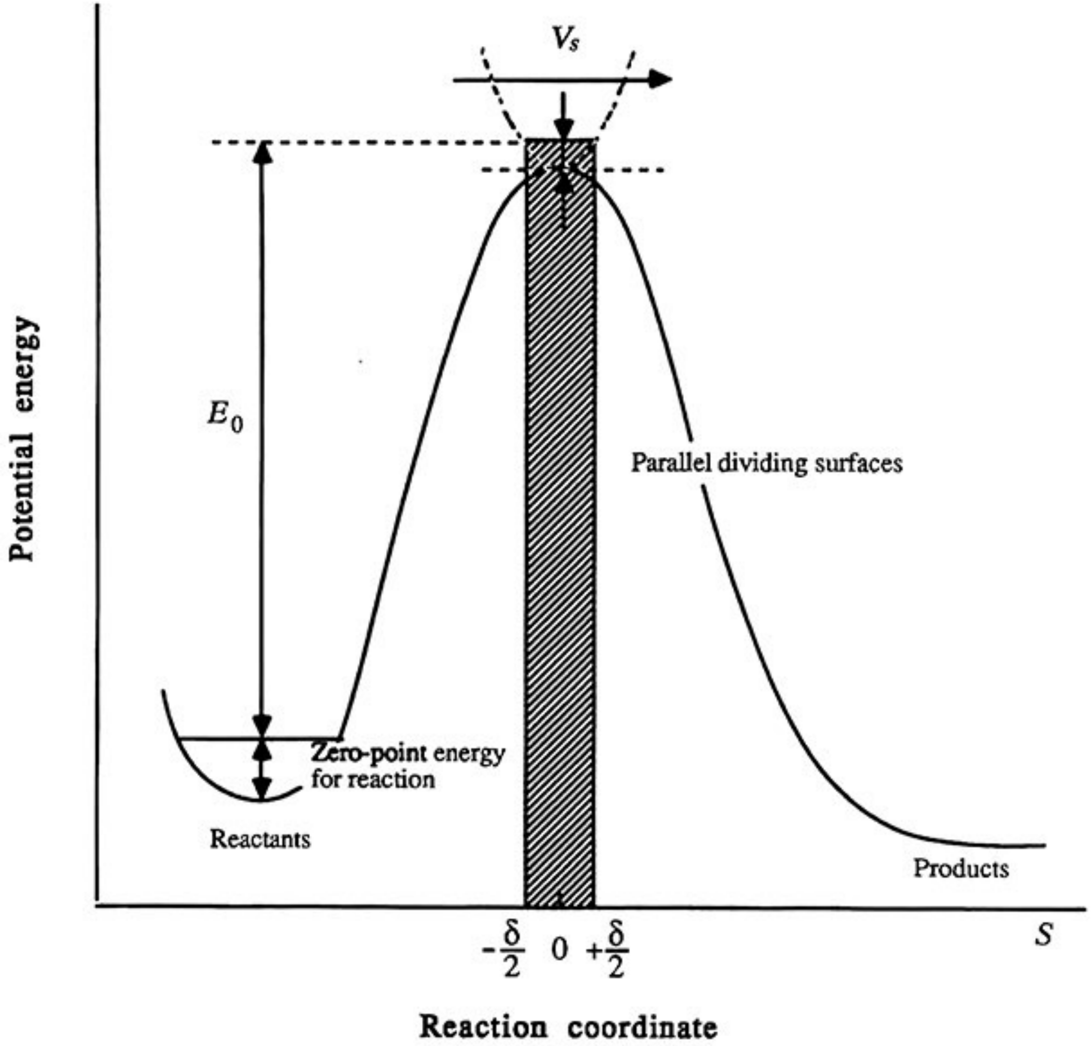
$$k_{TST} = k^{\ddagger}\frac{N_f^{\ddagger}}{[\mathrm{A}][\mathrm{B}]} = \frac{1}{2}k^{\ddagger}K^{\ddagger}$$

$K^{\ddagger} = \frac{Q_s\, Q^{\ddagger}}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$ (stat. thermodynamics)

$Q_s = \frac{\delta}{h}\sqrt{2\pi\mu_s k_B T}$

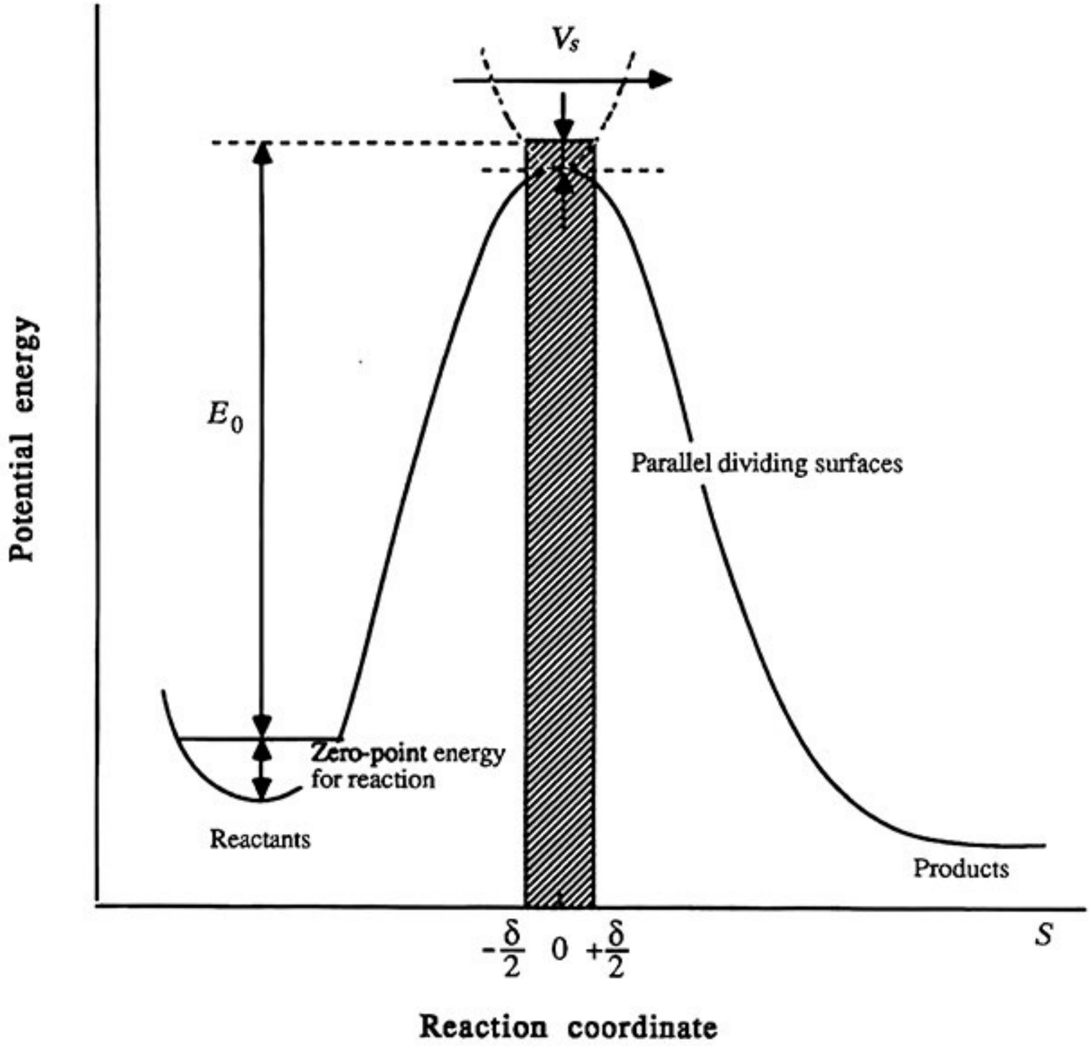
(translation of particle in 1D box)

$k^{\ddagger} = \frac{1}{\delta t} = \frac{\langle v_s \rangle}{\delta} = \frac{1}{\delta}\sqrt{\frac{2k_B T}{\pi\mu_s}}$ (classical treatment like kinetic gas theory for $\langle v_s \rangle$)



# Transition State Theory (TST)

$$\boxed{k_{TST} = \frac{k_B T}{h}\frac{Q^{\ddagger}}{Q_A Q_B}\, e^{-\frac{E_0}{k_B T}}}$$



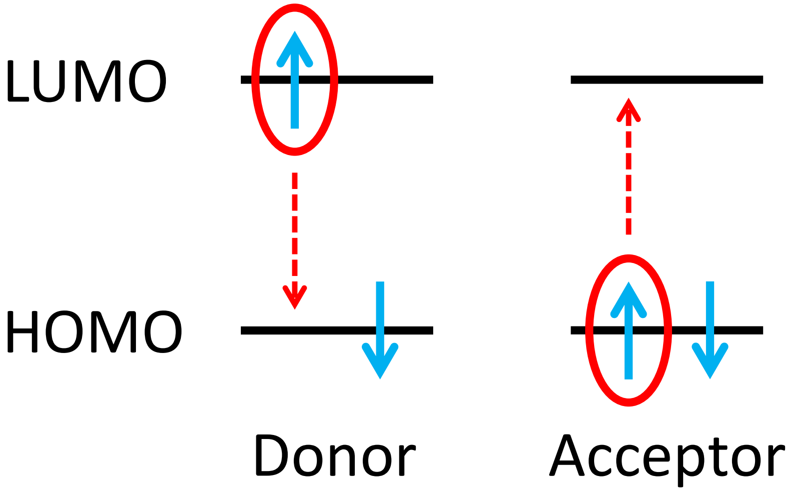
# Chapter X

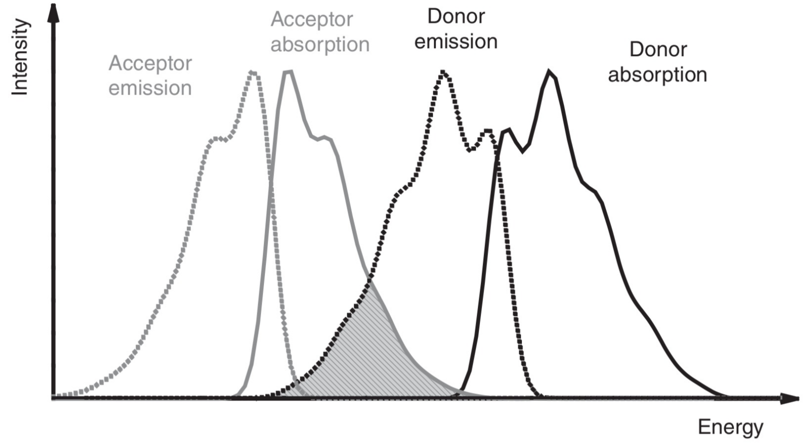
## Kinetics and Energetics in Photosynthesis

# Energy transfer & exciton motion *via* FRET

- exciton motion / energy transfer via Förster resonant energy transfer (FRET) (*vs* Dexter type)
- dipole-dipole coupling
- can be long-range interaction (few nm)
- very fast (sub-ps)

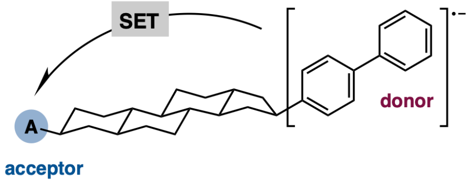
Förster transfer (singlet)

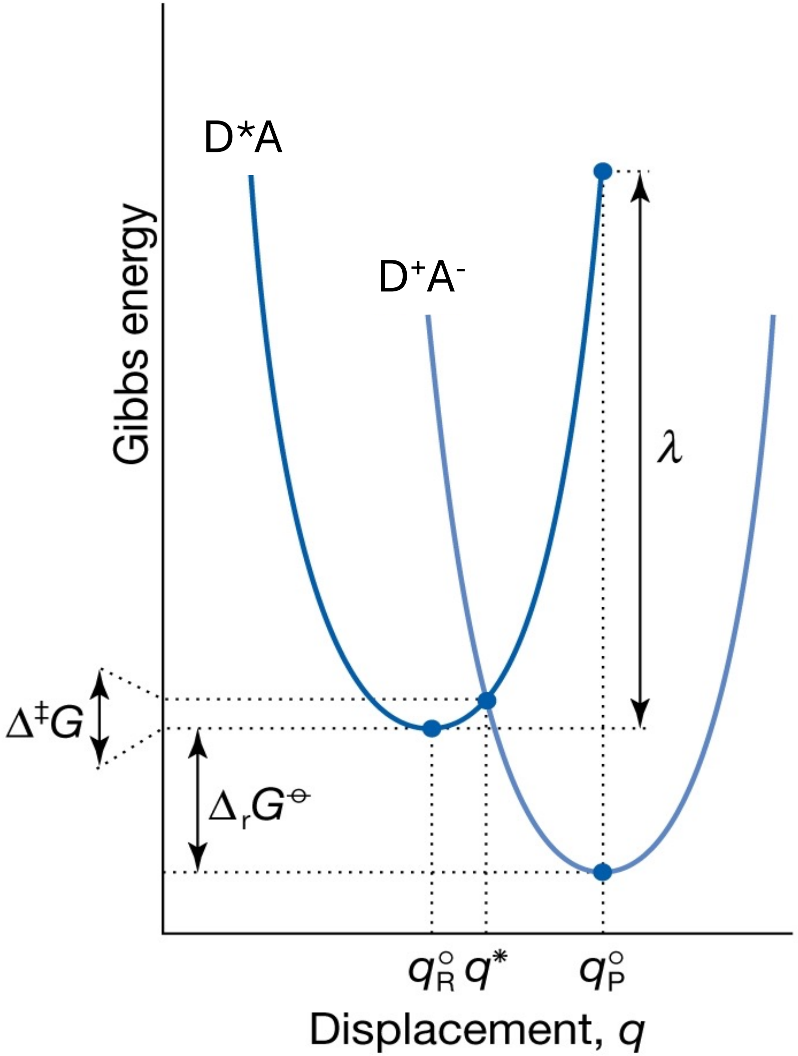


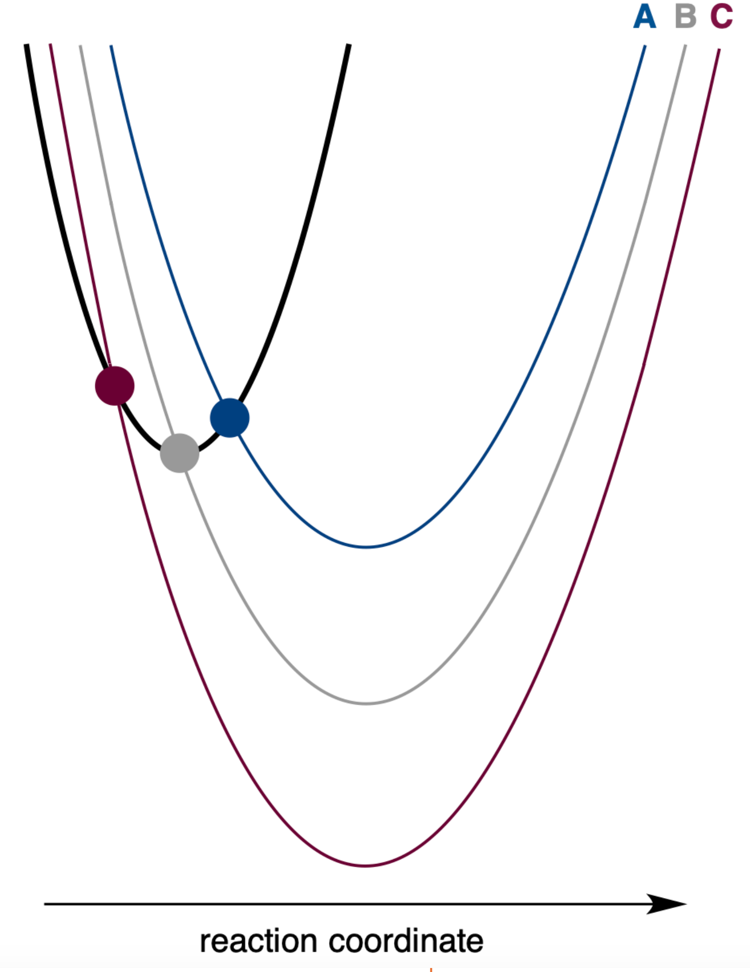


$$k_{DA}(R)=\frac{1}{\tau}\left(\frac{R_F}{R_{DA}}\right)^6$$

# Marcus theory of electron transfer







**A** $\Delta G^\circ < 0$ (somewhat negative)
● $\Delta G^‡ > 0$, rate $k_A$

**B** $\Delta G^\circ = -\lambda$ (quite negative)
● $\Delta G^‡ = 0$, rate $k_B > k_A$

**C** $\Delta G^\circ << 0$ (very negative)
● $\Delta G^‡ > 0$, rate $k_C < k_B$

As $\Delta G^\circ$ approaches $-\lambda$, the rate of reaction *increases*

When $\Delta G^\circ = -\lambda$, the reaction becomes barrierless

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As $\Delta G^\circ$ becomes even more negative ($\Delta G^\circ < -\lambda$), the rate of reaction *decreases* ($\Delta G^‡ > 0$)

***Marcus inverted region***

$$k_{transfer\quad rate} \propto V_{tunnelling}^{2}\, e^{-\left(\frac{\left(\Delta G^{0}+\lambda\right)^{2}}{4\lambda k_{B}T}\right)}$$

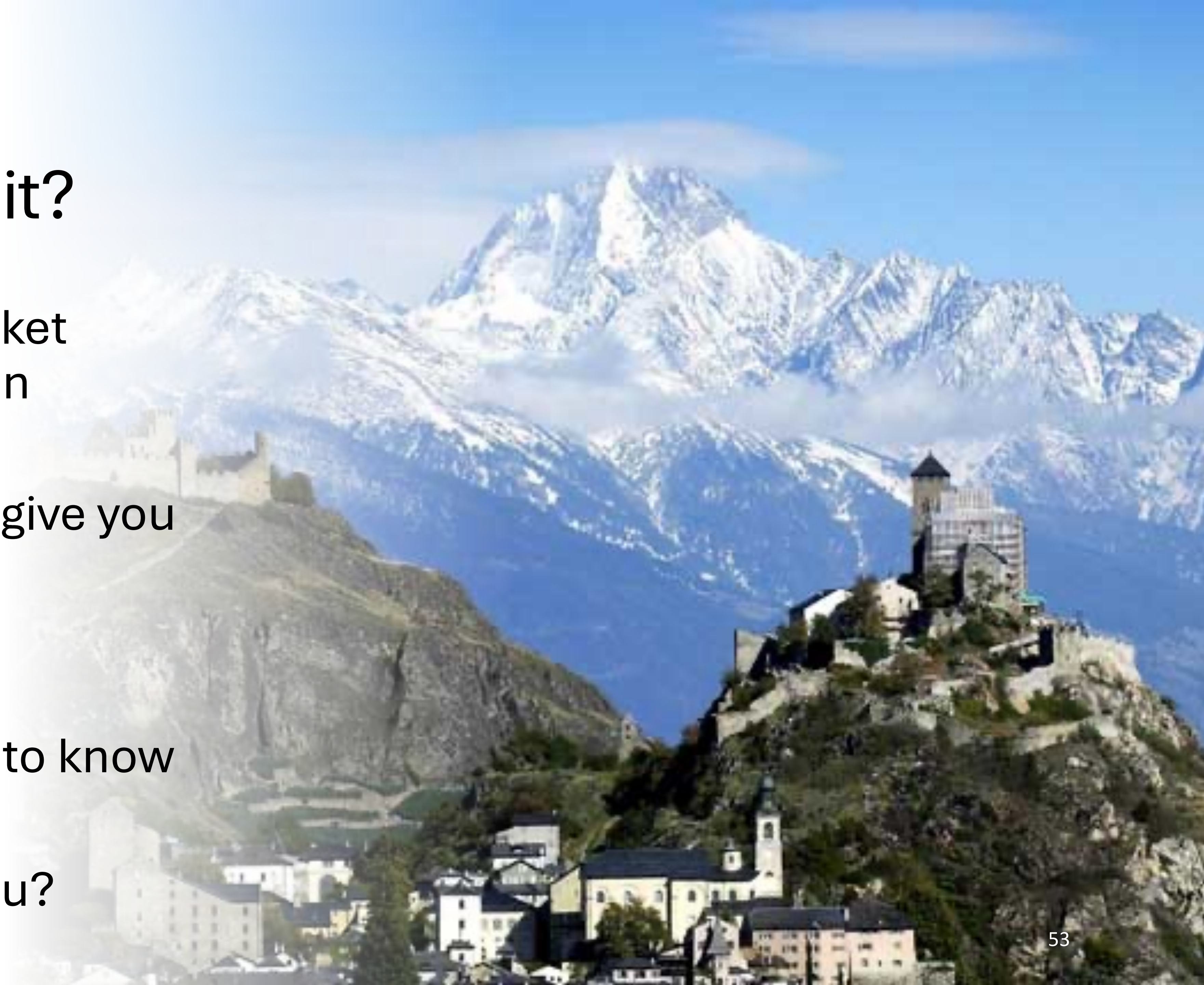
# Information on the Exam

- allowed to bring:
    - 1 hand-written (not print, not digital) A5 single-sided cheat sheet
    - 1 non-programmable calculator
- provided: Exam questions and formula collection

**Friday, 17 January 2025**
**9.15 am - 12.15 pm**
**Room BCH2201**

- time to solve exam: 3hours sharp

- possible types of questions: *all*, for example…
  multiple choice, draw this, read out that, calculate this, explain that, why is this, what are the limitations of that model, in what case is this valid, what happens for early/late times/in excess of X etc.



# Interested in EPFL Valais Visit?

- free return train ticket Lausanne ←→ Sion
- my team and I will give you a lab tour through facilities ☺
- if interested, need to know
  - when?
  - how many of you?