

Cinètica Química i Dinàmica Molecular

Chemical Kinetics and Reaction Dynamics

Sergei Vyboishchikov

CLASSES and EVALUATION

Classes: 2 classes every week (Monday and Wednesday/Friday at 8:40 a.m.);

Lectures and recitations when needed.

Attendance is not obligatory.

For the recitation class you have to bring the problems booklet.

Exams: 80% theory + 20% problems. A problem only counts if fully solved!

Recuperation: the partial exams are recoverable.

Tutoring: with prior appointment (sergey.vyboishchikov@udg.edu) in-office or online

Exams:

Exam	Percentage of the total grade	Date
1st partial exam (formal kinetics)	40%	November 8
2nd (reaction dynamics)	40%	January 7, 9:30 AM
Numerical simulation (<i>Python</i>) written report	20%	November 18, 7:00 AM
Recuperation exam	40% + 40%	January 22

Language of lectures: English

recitation classes: English

exam tasks: English

exam answers: whatever

ATKINS P., DE PAULA J., 2006, *Atkins' Physical Chemistry* (8th Ed.), Oxford University press, Oxford.

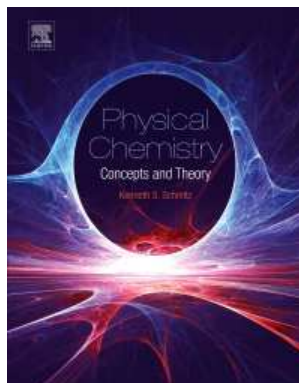
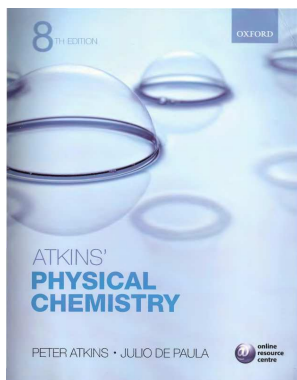
Not available on the internet; ask your professor how to get it if interested.

ARNAUT L., FORMOSINHO S., BURROWS H., Chemical Kinetics. From Molecular Structure to Chemical Reactivity, 2006, Elsevier.

Available at <http://www.sciencedirect.com/science/book/9780444521866>

SCHMITZ K.S., Physical Chemistry, 2017, Chapter 15: *Reaction Rates and Mechanisms* Elsevier.

No longer available on the internet; ask you professor how to get it if interested.



- **Why chemical kinetics?**

Thermodynamics does not tell us how fast a reaction is.

- ▶ Phenomenological (“formal”) *Chemical Kinetics* studies *reaction rates* (= **velocitats de reacció**);

Rate prediction using molecular data only is *not* possible ($\Delta_r H^\circ$, $\Delta_r G^\circ$ are of no help);

Determination of *reaction mechanism* is possible in principle (not always in practice).

- ▶ *Reaction dynamics* (= **dinàmica molecular**) studies what exactly happens in an elementary process: changes in geometric configuration, energy redistribution etc.

Intents to *predict* reaction rates for elementary reactions.

- **Elementary reactions:**

- ▶ Those in which the reactants transform into products directly:



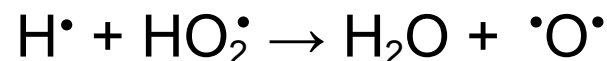
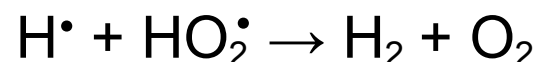
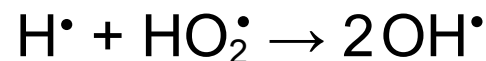
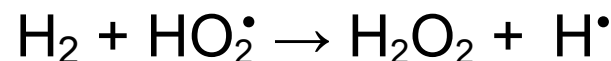
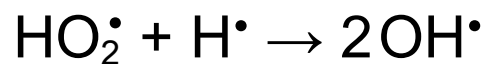
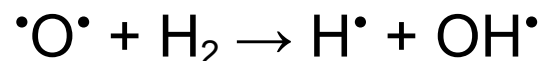
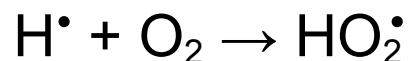
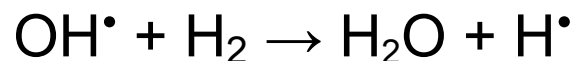
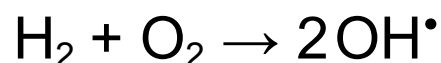
- **Most observed chemical reactions are complex (*not* elementary)**

- ▶ A reaction is usually a succession of several elementary reactions (*steps = etapes*);

- ▶ A product of one of the steps that serves as reactant for a subsequent step is referred to as **intermediate**.

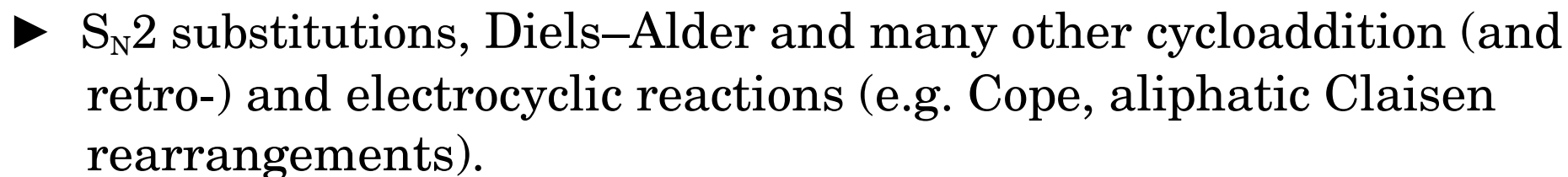
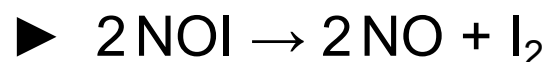
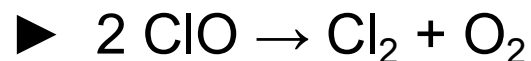
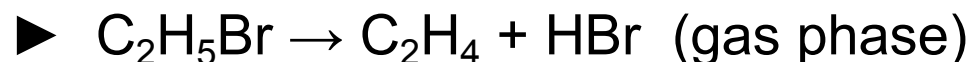
- ▶ The **mechanism** is the succession of all the elementary steps leading from the reactants to the products.

- **Example:** $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$



and much more steps.

- **Examples** of elementary reactions:



They are considered elementary (= *reacciones sencillas*); the contrary was not proven.

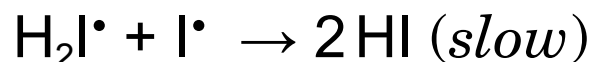
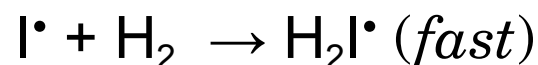
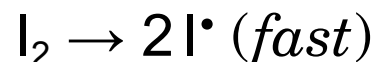
- If a reaction is elementary, the *inverse* reaction is also elementary.

- **Example of a non-elementary process:** $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$

- ▶ The kinetics is first order with respect to each component:

$$v = k[\text{H}_2][\text{I}_2]$$

- ▶ Nevertheless, the mechanism accepted now is as follows:



- *Formal (phenomenological) kinetics* studies *reaction rates* in a descriptive way.
 - ▶ Given a *mechanism* and the rate constants, **find** the evolution of concentrations of species (reactants, products, and intermediates A_i) $[A_i]_t$ at any moment of time t .
 In general, there is at least a *numerical* solution to this problem. An *analytical* solution exists only in simple cases.
 - **deduce** a *rate law* for a non-elementary reaction from a mechanism. For instance, deduce the rate law $v = k[\text{H}_2][\text{I}_2]$ for the $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ reaction. In general, a *rate law* is an analytic expression for the *reaction rate* v as a function of *reactant concentrations*. Sometimes *product* or *catalyst* concentrations can also enter a rate law. *Integrated rate law* is an expression for the *reactant concentration* as a function of *time*.
 - ▶ An opposite task: from the concentration evolution of *some* species $[A_i]_t$, **find out** the *mechanism* and the rate constants. There is **no** general solution to this. Typically, we have to conjecture a mechanism, solve the kinetic problem for that mechanism, and compare the resulting $[A_i]_t$ with experimental observations. Sometimes, various mechanism are compatible with the same experimental rate law.

Reaction rates (for elementary reactions)

- *Reaction rate* (= **velocitat de reacció**) is the number of elementary events (elementary acts) per unit time and unit volume (usually divided by N_A).
 - ▶ The reaction rate is always *positive* by definition.
 - ▶ *Average reaction rate* (= **velocitat de reacció mitjana**) in the interval of time $[t, t + \Delta t]$ (if *one* reactant molecule disappears in one elementary event: $A \rightarrow C$ or $A + B \rightarrow C$): $-(N_{\text{reactant}}(t + \Delta t) - N_{\text{reactant}}(t)) = N_{\text{el-act}}$

$$\begin{aligned} v[t, t + \Delta t] &= \frac{1}{N_A} \cdot \frac{N_{\text{el-act}}}{V \cdot \Delta t} = - \frac{1}{N_A} \cdot \frac{N_{\text{reactant}}(t + \Delta t) - N_{\text{reactant}}(t)}{V \cdot \Delta t} = \\ &= - \frac{[\text{reactant}]_{t+\Delta t} - [\text{reactant}]_t}{\Delta t} \end{aligned}$$

since the molar concentration $[x] = \frac{n}{V} = \frac{N_x}{N_A V}$

- ▶ *Instantaneous reaction rate* at time t :

$$v(t) = \lim_{\Delta t \rightarrow 0} \left(- \frac{[\text{reactant}]_{t+\Delta t} - [\text{reactant}]_t}{\Delta t} \right) = - \frac{d[\text{reactant}]}{dt}$$

- ▶ $v > 0$ always!
- ▶ *Units*: [concentration]/[time] $\Rightarrow \text{M} \cdot \text{s}^{-1}$

Reaction rates (elementary and complex reactions)

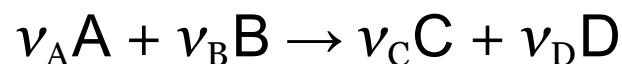
► Watch the stoichiometric coefficients!

- If *two* reactant molecules disappear in one elementary event ($2A \rightarrow C$):

$$N_{\text{reactant}}(t+\Delta t) - N_{\text{reactant}}(t) = -2 N_{\text{el-act}}$$

$$\frac{d[\text{reactant}]}{dt} = -2v(t) \Rightarrow v(t) = -\frac{1}{2} \frac{d[\text{reactant}]}{dt}$$

- In general:



$$v(t) = -\frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{\nu_B} \frac{d[B]}{dt} = +\frac{1}{\nu_C} \frac{d[C]}{dt} = +\frac{1}{\nu_D} \frac{d[D]}{dt}$$

$$\frac{d[A]}{dt} = -\nu_A v; \quad \frac{d[B]}{dt} = -\nu_B v; \quad \frac{d[C]}{dt} = \nu_C v; \quad \frac{d[D]}{dt} = \nu_D v.$$

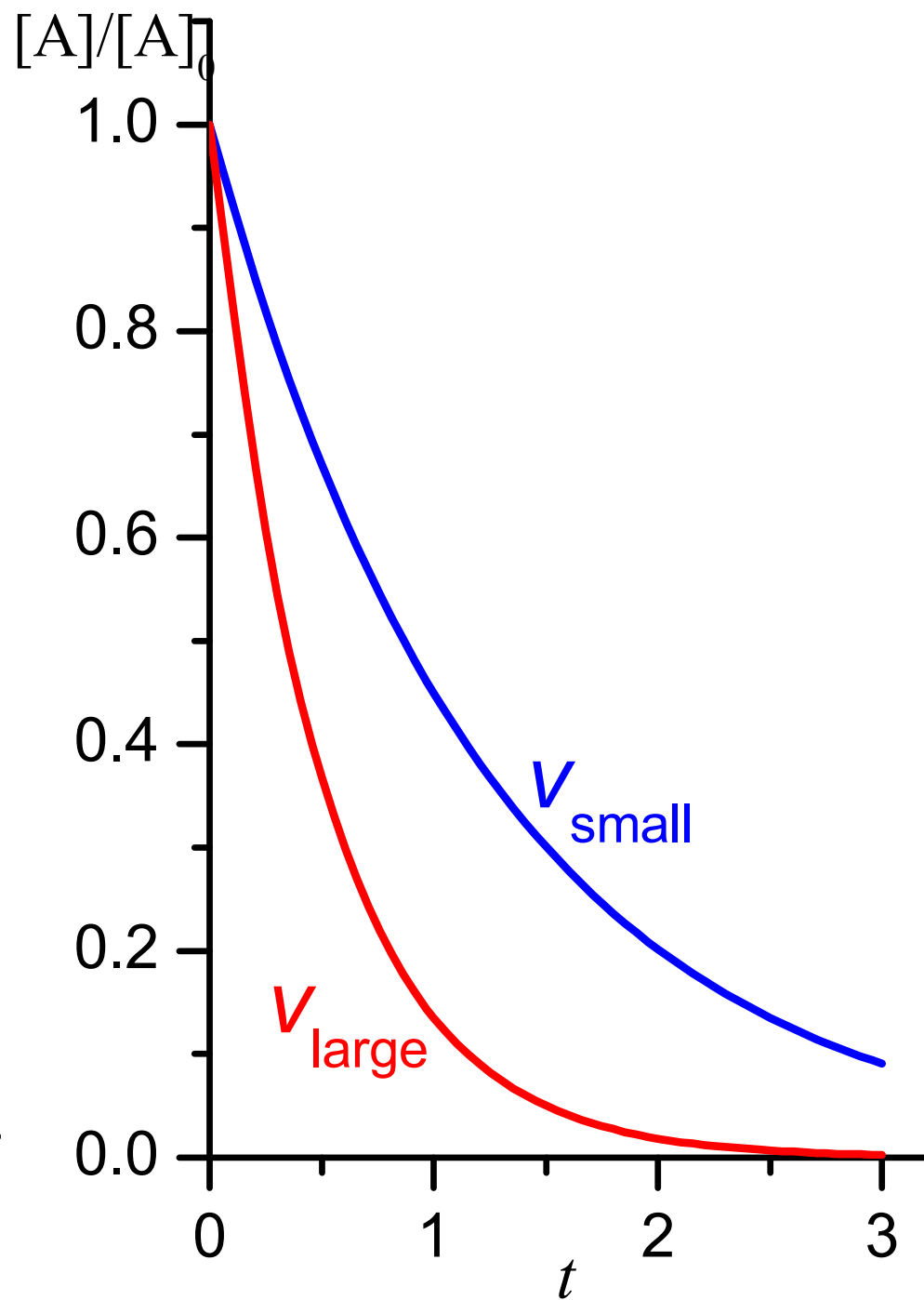
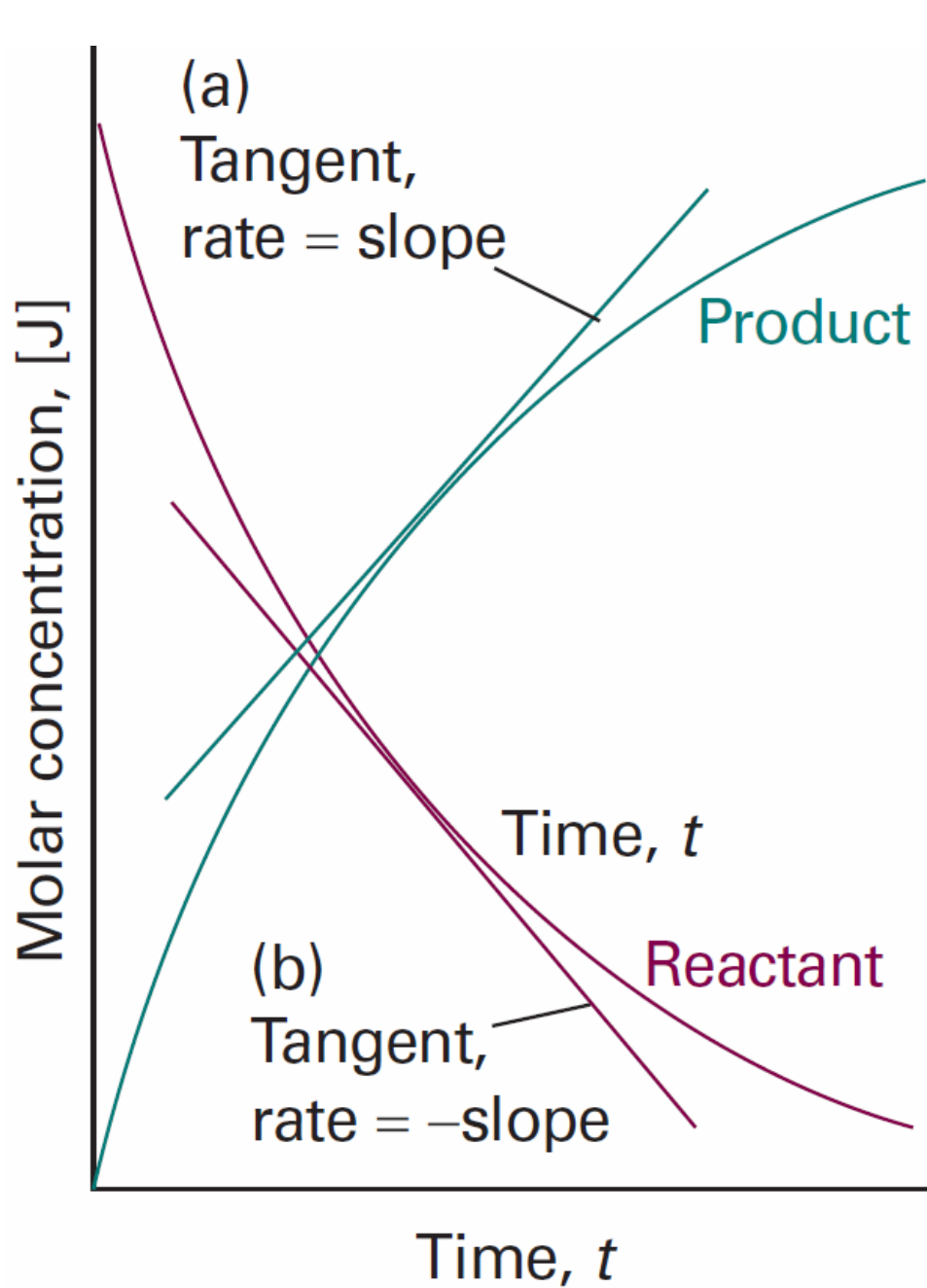
► Reaction rate through the *extent* of the reaction (=advancement = *grau d'avenç*): $\xi(t) = V \cdot ([A]_0 - [A]_t) / \nu_A = V([B]_0 - [B]_t) / \nu_B = -V \cdot ([C]_0 - [C]_t) / \nu_C$

$$v = \frac{1}{V} \frac{d\xi}{dt}$$

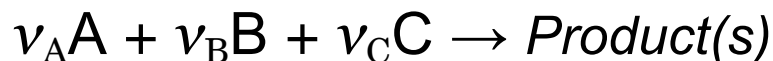
► Reaction rate *with respect to* a certain component:

$$v_A = -\frac{d[A]}{dt}; \quad v_B = -\frac{d[B]}{dt}; \quad v_C = +\frac{d[C]}{dt}; \quad v_D = +\frac{d[D]}{dt}$$

$$v_A \neq v_B \neq v_C \neq v_D; \quad v = \frac{v_A}{\nu_A} = \frac{v_B}{\nu_B} = \frac{v_C}{\nu_C} = \frac{v_D}{\nu_D}$$



- **Molecularity** is a number of molecules participating in an **elementary event**. This notion only applies to *elementary* reactions.



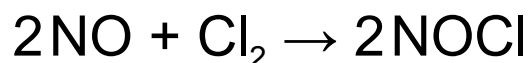
$\nu_A + \nu_B + \nu_C$ is the **molecularity** (≤ 3)

- ▶ Unimolecular reactions: $A \rightarrow \text{Product(s)}$
- ▶ Bimolecular reactions: $2A \rightarrow \text{Product(s)}$; $A + B \rightarrow \text{Product(s)}$

- ▶ Trimolecular (termolecular) reactions:



Trimolecular reactions are rare (but not too rare) for molecules, more common for atomic and ionic gas-phase processes:



— Understanding trimolecular reactions:

- trimolecular reactions usually do *not* occur through simultaneous collision of 3 molecules. Rather, 2 molecules collide to form a short-living species, which a very short time later collides with the third molecule.
- very often, the third molecule serves to absorb an extra energy that the reacting atoms have: $\text{F}^\cdot + \text{F}^\cdot + \text{M} \rightarrow \text{F}_2 + \text{M}$

Kinetic law of mass action (elementary reactions)

- For an elementary reaction (*Attention!* for an elementary reaction only!)



the rate v is given by the equation (the *Law of mass action* – Guldberg and Waage 1867):

$$v = k[A]^{\nu_A} [B]^{\nu_B} [C]^{\nu_C}$$

- Recalling that

$$v = -\frac{1}{\nu_A} \frac{d[A]}{dt}$$

A *rate law* (rate equation) is obtained:

$$-\frac{1}{\nu_A} \frac{d[A]}{dt} = k[A]^{\nu_A} [B]^{\nu_B} [C]^{\nu_C}$$

Attention: a differential equation!

- ▶ k is referred to as *rate constant*. Note: $k > 0$ always!
- ▶ *Units of k* : $[\text{concentration}]^{1-(\nu_A+\nu_B+\nu_C)}/[\text{time}] \Rightarrow \text{M}^{1-(\nu_A+\nu_B+\nu_C)} \cdot \text{s}^{-1}$

depend on the reaction order:

s^{-1} for first-order reactions

$\text{M}^{-1} \cdot \text{s}^{-1}$ for second-order reactions

$\text{M}^{-2} \cdot \text{s}^{-1}$ for third-order reactions

Hr. Cand. Guldberg holdt et Foredrag om Lovene for Affiniteten, specielt Tidens Indflydelse paa de kemiske Processer.

lem den i en uendelig kort Tid omvandlede Mængde og denne Tid, saa er $v = \frac{dx}{dt} = k (p-x)^a (q-x)^b$. (1)



Guldberg and Waage

Kinetic law of mass action (elementary reactions) – various cases

- Unimolecular reaction: $A \rightarrow B$

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

$$\begin{cases} \frac{d[A]}{dt} = -v = -k[A] \\ \frac{d[B]}{dt} = v = k[A] \end{cases}$$

Unimolecular reaction: $A \rightarrow 2B$

$$v = -\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt} = k[A]$$

$$\begin{cases} \frac{d[A]}{dt} = -v = -k[A] \\ \frac{d[B]}{dt} = 2v = 2k[A] \end{cases}$$

- Bimolecular reactions:



$$v = -\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A]^2$$

$$\begin{cases} \frac{d[A]}{dt} = -2v = -2k[A]^2 \\ \frac{d[B]}{dt} = v = k[A]^2 \end{cases}$$

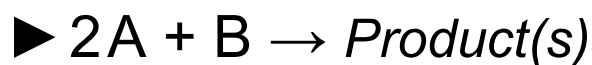


$$v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B] \quad \left\{ \begin{array}{l} \frac{d[A]}{dt} = -v = -k[A][B] \\ \frac{d[B]}{dt} = -v = -k[A][B] \\ \frac{d[C]}{dt} = v = k[A][B] \end{array} \right.$$

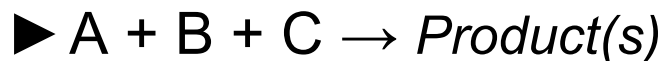
- Termolecular reactions:



$$v = -\frac{1}{3} \frac{d[A]}{dt} = k[A]^3 \quad \frac{d[A]}{dt} = -3k[A]^3$$



$$v = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^2[B] \quad \frac{d[A]}{dt} = -2k[A]^2[B]$$

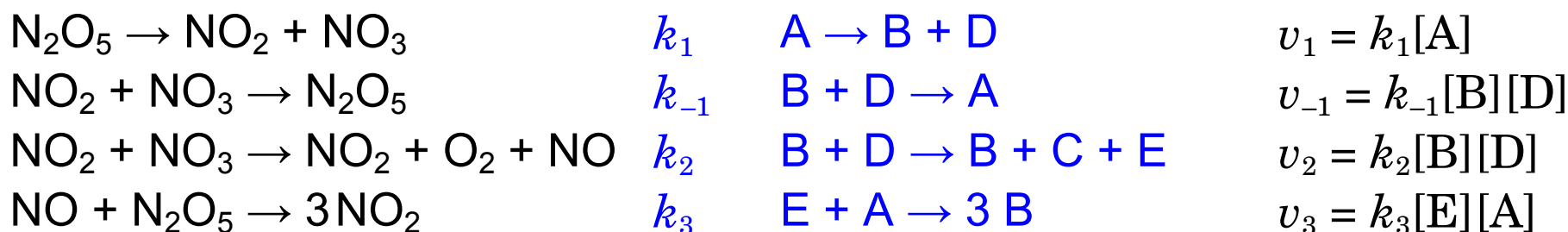


$$v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{d[C]}{dt} = k[A][B][C]$$

Rates for complex reactions

- For a non-elementary (*complex*) reaction, the law of mass action must be applied to each reaction step individually. Each step has its own rate. The variations of concentrations with time are linear combinations of the individual rates resulting in a system of differential equations. For example,
 - $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. Overall reaction: $2\text{A} \rightarrow 4\text{B} + \text{C}$

Ogg's mechanism:



$$\frac{d[\text{A}]}{dt} = -v_1 + v_{-1} - v_3 = -k_1[\text{A}] + k_{-1}[\text{B}][\text{D}] - k_3[\text{E}][\text{A}]$$

$$\frac{d[\text{B}]}{dt} = v_1 - v_{-1} + 3v_3 = k_1[\text{A}] - k_{-1}[\text{B}][\text{D}] + 3k_3[\text{E}][\text{A}]$$

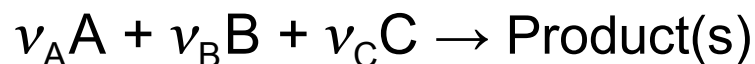
$$\frac{d[\text{C}]}{dt} = v_2 = k_2[\text{B}][\text{D}]$$

$$\frac{d[\text{D}]}{dt} = v_1 - v_{-1} - v_2 = k_1[\text{A}] - k_{-1}[\text{B}][\text{D}] - k_2[\text{B}][\text{D}]$$

$$\frac{d[\text{E}]}{dt} = v_2 - v_3 = k_2[\text{B}][\text{D}] - k_3[\text{E}][\text{A}]$$

Effective rate “law” for complex reactions

- For a total complex reaction:



no fundamental rate law exists! The effective rate law (e.g., the product formation rate $v = f([A],[B],[C]...)$ depends on a particular mechanism. May include reactant and/or catalyst concentrations.

- ▶ In many cases (but not always) the rate law of a complex reaction is expressed by an empirical equation:

$$v = k[A]^{n_A}[B]^{n_B}[C]^{n_C}$$

where the powers n_A, n_B, n_C are, in general, **not** equal to the stoichiometric coefficients ν_A, ν_B, ν_C .

n_A, n_B, n_C are **orders** with respect to reactants A, B, C.

$(n_A + n_B + n_C)$ is the total **order** of the reaction.

n_A, n_B, n_C are often positive integer (1 or 2) or half-integer ($1/2, 3/2$) numbers, but may be zero, non-integer or even negative. Example:



- ▶ In some cases other rate laws were found. Example: $\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}$

$$v = \frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''[\text{HBr}] / [\text{Br}_2]}$$

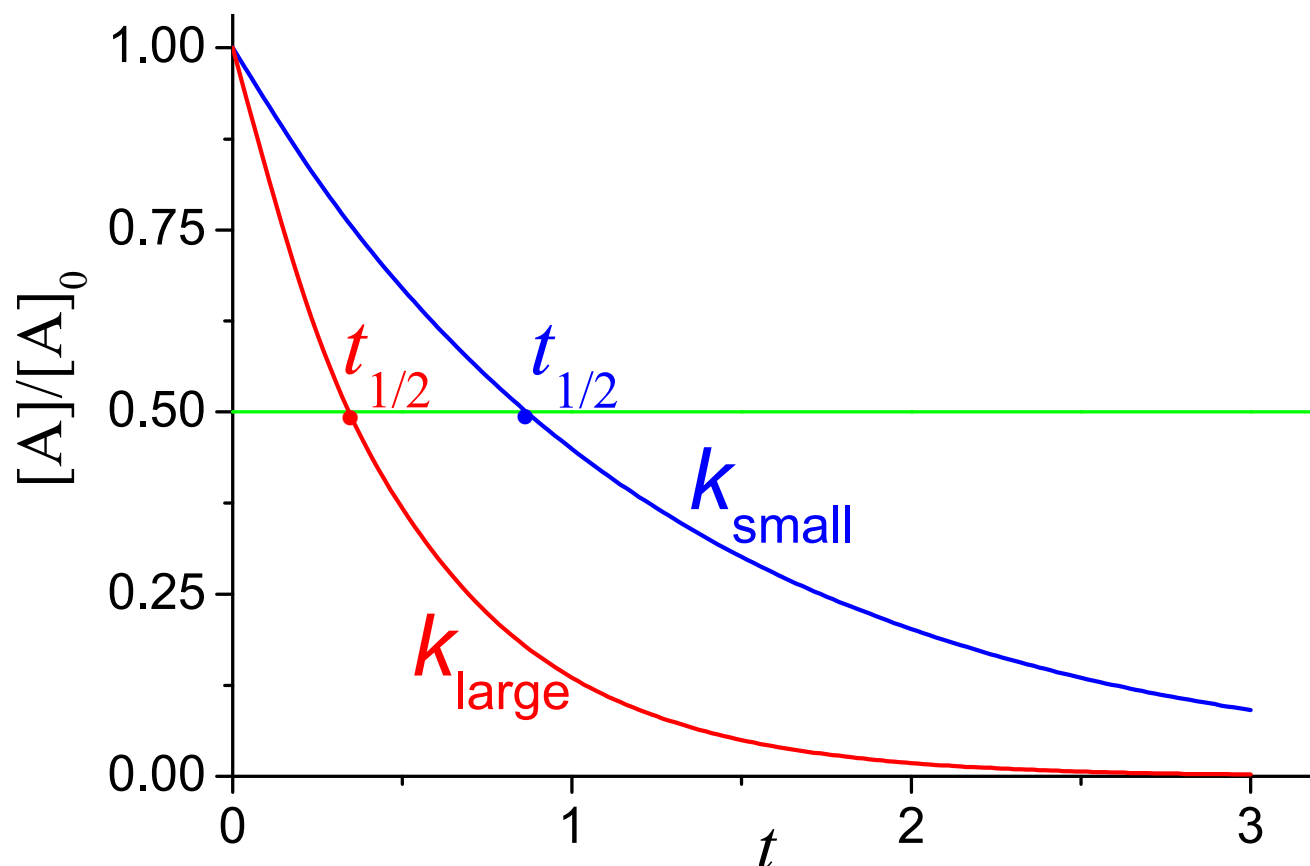
Non-elementary (complex) reactions

- In general, it is very difficult (nearly impossible) to prove that a reaction *is* elementary.
- On the contrary, it is sometimes very easy to show that a reaction is *not* elementary. Typical cases when we can be sure that our reaction is *not* elementary even if the exact mechanism is unknown:
 - when the sum of *left-hand stoichiometric coefficients* is greater than 3:
$$\text{C}_{12}\text{H}_{22}\text{O}_{11} + 12 \text{O}_2 \rightarrow 12 \text{CO}_2 + 11 \text{H}_2\text{O}$$
 - when there are great *structural changes* in the course of reaction (many bonds are broken and/or formed);
 - when the *experimental rate* law does not correspond to the law of mass action. See examples on the previous page 17.

Half-life

- **Halflife** (= *temps de la semivida*; not exactly the same as the *mean life-time*) $t_{1/2}$ ($\tau_{1/2}$) is the period of time when the concentration of the reactant is a half of its initial value:

$$[A]_{t_{1/2}} = \frac{1}{2}[A]_0$$



- Other **characteristic times** can be also defined. E.g., $t_{3/4}$, $t_{1/10}$:

$$[A]_{t_{3/4}} = \frac{1}{4}[A]_0; \quad [A]_{t_{1/10}} = \frac{9}{10}[A]_0$$

First- and second-order reactions – examples

Kinetic data for first-order reactions*

	Phase	$T, ^\circ\text{C}$	k, s^{-1}	$t_{1/2}$
$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$	gas	25	$3.38 \cdot 10^{-5}$	5.7 h
	HNO_3 (liq.)	25	$1.47 \cdot 10^{-6}$	131 h
	Br_2 (liq.)	25	$4.27 \cdot 10^{-5}$	4.5 h
$\text{C}_2\text{H}_6 \rightarrow 2 \text{CH}_3^\bullet$	gas	700	$5.36 \cdot 10^{-4}$	21.6 min
$\triangle \rightarrow \diagup$	gas	500	$6.71 \cdot 10^{-4}$	17.2 min
$\text{CH}_3\text{N}_2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{N}_2$	gas	327	$3.4 \cdot 10^{-4}$	34 min
saccharose \rightarrow glucose + fructose	aqueous (H^+)	25	$6.0 \cdot 10^{-5}$	3.2 h

Kinetic data for second-order reactions*

	Phase	$T, ^\circ\text{C}$	$k, \text{M}^{-1} \cdot \text{s}^{-1}$
$2\text{NOBr} \rightarrow 2\text{NO} + \text{Br}_2$	gas	10	0.80
$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	gas	300	0.54
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	gas	400	$2.42 \cdot 10^{-2}$
$2\text{I} \rightarrow \text{I}_2$	gas	23	$7 \cdot 10^9$
$\text{CH}_3^\bullet + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}^\bullet$	gas	2000	$8.1 \cdot 10^8$
$\text{CH}_3\text{Cl} + \text{CH}_3\text{O}^- \rightarrow \text{CH}_3\text{OCH}_3 + \text{Cl}^-$	methanol	25	$2.3 \cdot 10^{-6}$
$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	water	25	$1.25 \cdot 10^{11}$
	ice	-10	$8.6 \cdot 10^{12}$

- The rate constant for a given elementary reaction under given conditions is a constant! It does not depend on other reactions occurring in the same time.

*Data from Laidler K. J., Chemical Kinetics (3rd Ed.), Harper and Row, New York, 1987.

First-order irreversible reaction kinetics

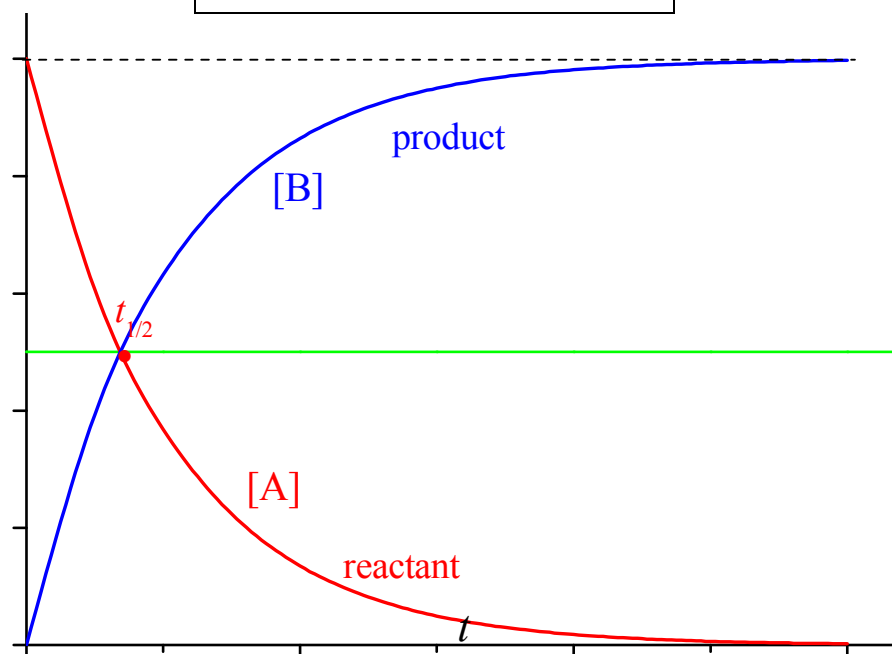
- $A \rightarrow B$. k in s^{-1} :

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

$$\begin{cases} \frac{d[A]}{dt} = -k[A] \\ \frac{d[B]}{dt} = k[A] \end{cases}$$

- Integrated rate equation (solution see Appendix 1 on page 169 or <https://tinyurl.com/1storderkinetics>)

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



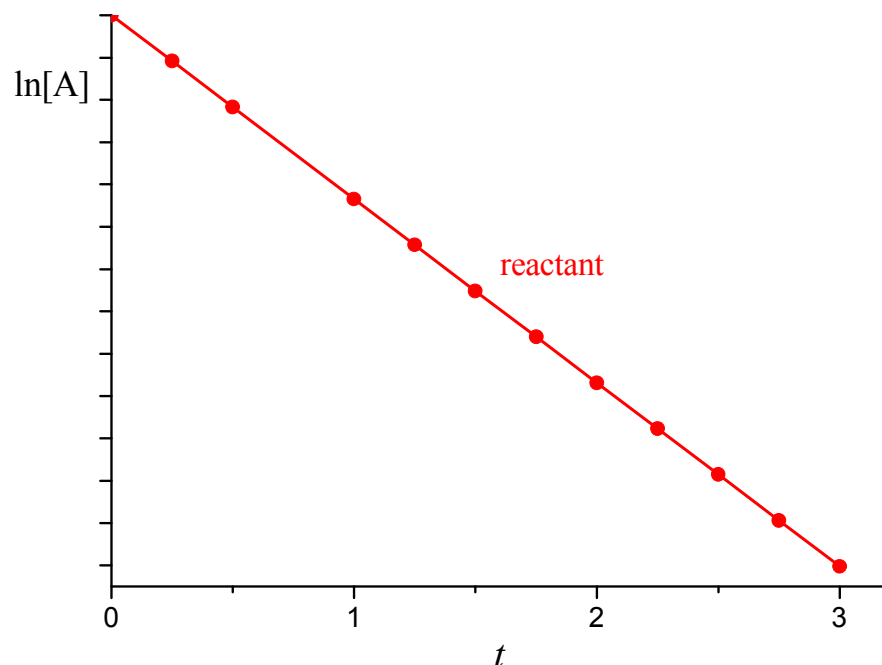
- Product concentration:

$$[B]_t = [A]_0 - [A]_t = [A]_0(1 - e^{-kt})$$

First-order reaction kinetics

- Linearized form suitable for linear regression (only for reactant):

$$\ln[A] = \ln[A]_0 - kt$$



- Halflife:

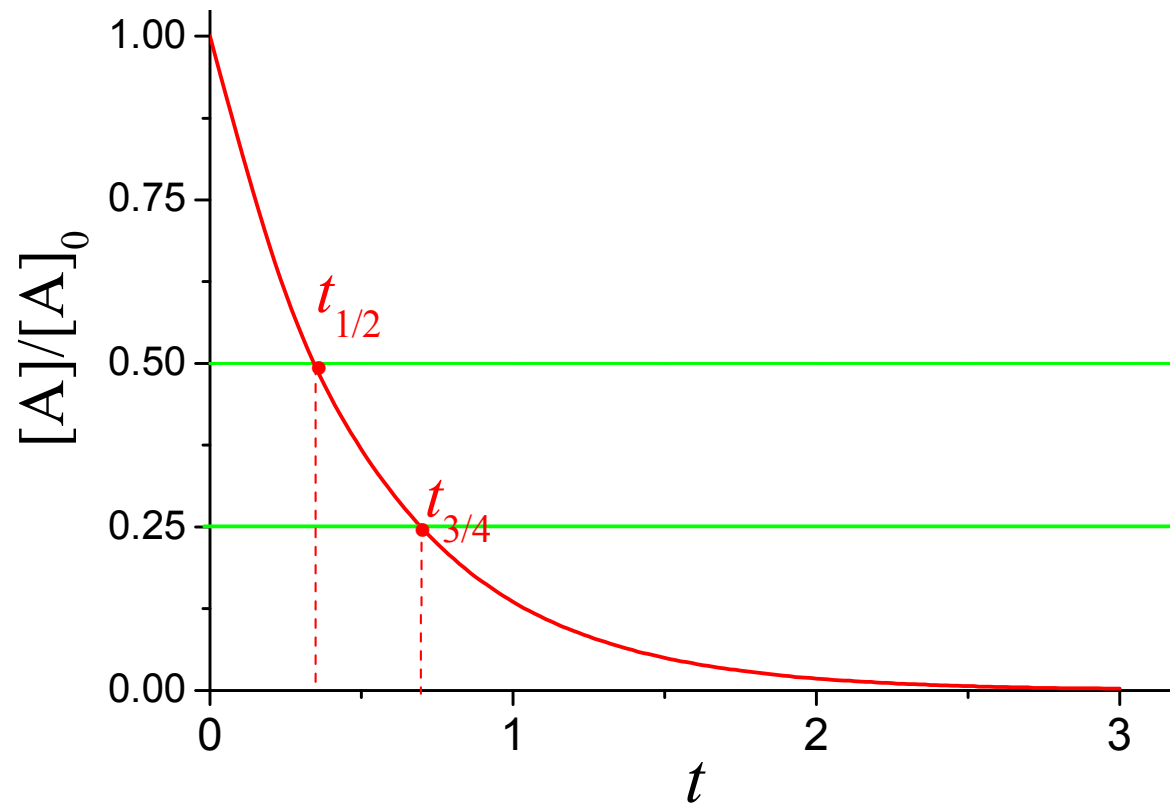
$$[A]_t = [A]_0 e^{-kt} \quad \frac{[A]_0}{2} = [A]_0 e^{-kt_{1/2}} \Rightarrow \frac{1}{2} = e^{-kt_{1/2}} \Rightarrow -\ln 2 = -kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

- $t_{1/2}$, $t_{3/4}$... do not depend on $[A]_0$ (for first-order reactions only!).

$$[A]_t = [A]_0 2^{-t/t_{1/2}}$$

- Other characteristic times:



► $t_{3/4} = 2 t_{1/2}$ (for first-order reactions only!)

- One-substrate n -th order reaction $nA \rightarrow P$:

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

$$\int_{[A]_0}^{[A]_t} [A]^{-n} d[A] = -kn \int_0^t dt$$

$$\frac{[A]_t^{1-n}}{1-n} - \frac{[A]_0^{1-n}}{1-n} = -knt$$

$$[A]_t^{1-n} - [A]_0^{1-n} = (n-1)knt$$

$$[A]_t^{1-n} = (n-1)knt + [A]_0^{1-n}$$

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

$$[A]_t = \frac{1}{\sqrt[n-1]{(n-1)knt + \frac{1}{[A]_0^{n-1}}}} = \frac{[A]_0}{\sqrt[n-1]{(n-1)kn[A]_0^{n-1}t + 1}}$$

► Be prepared to perform independently a similar derivation for any particular n .

► Half-life $t_{1/2}$:

$$[A]_{t_{1/2}} = \frac{[A]_0}{2} = \frac{[A]_0}{n\sqrt[n-1]{(n-1)nk[A]_0^{n-1}t_{1/2} + 1}} \Rightarrow n\sqrt[n-1]{(n-1)nk[A]_0^{n-1}t_{1/2} + 1} = 2$$

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)nk[A]_0^{n-1}}$$

but it may be easier to derive it from the linearized form:

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

$$\frac{1}{\left(\frac{[A]_0}{2}\right)^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)knt_{1/2} \Rightarrow \frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)knt_{1/2}$$

$$\Rightarrow \frac{2^{n-1} - 1}{[A]_0^{n-1}} = (n-1)knt_{1/2} \Rightarrow t_{1/2} = \frac{2^{n-1} - 1}{(n-1)nk[A]_0^{n-1}}$$

- $t_{1/2}$ is always inversely proportional to k .
- $t_{1/2}$ decreases with increasing $[A]_0$ for $n > 1$ (second-order reactions etc.)
- $t_{1/2}$ decreases with increasing $[A]_0$ for $n > 1$ (second-order reactions etc.)
- $t_{1/2}$ increases with increasing $[A]_0$ for $n < 1$ (zeroth-order reactions etc., order $1/2$...)
- $t_{1/2}$ does not depend on $[A]_0$ for $n = 1$ (first-order reactions)

A similar derivation is valid also for *any* characteristic time ($t_{3/4}$, $t_{1/10}$...)

$$t_{3/4} = \frac{4^{n-1} - 1}{(n-1)nk[A]_0^{n-1}}$$

► Be prepared to perform independently a similar derivation for any particular n .

Second-order reaction kinetics – one substrate

- $2A \rightarrow B$: (k in $M^{-1} \cdot s^{-1}$):

$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A]^2 \quad \left\{ \begin{array}{l} \frac{d[A]}{dt} = -2k[A]^2 \\ \frac{d[B]}{dt} = k[A]^2 \end{array} \right.$$

- Integrated rate equation (see Appendix 2 on page 171 or <https://tinyurl.com/2ndorderkinetics>)

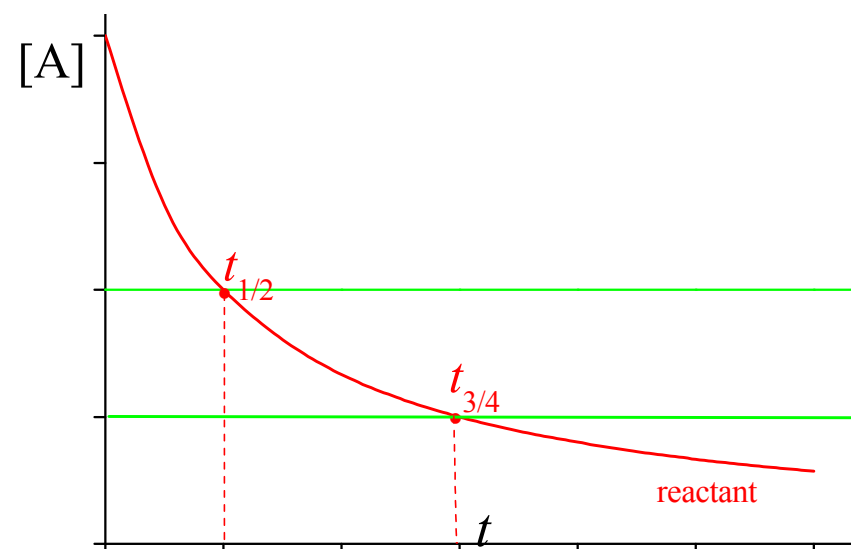
$$\boxed{\frac{1}{[A]} = 2kt + \frac{1}{[A]_0}}$$

$$[A] = \frac{[A]_0}{1 + 2k[A]_0 t}$$

- $t_{3/4} = 3 t_{1/2}$ (for second-order reactions only!)

► *Half-life:*

$$t_{1/2} = \frac{1}{2k[A]_0}$$



Second-order reaction kinetics – two substrates ($[A]_0 = [B]_0$)

- For a *two*-substrate reaction: $A + B \rightarrow C$:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B] \quad \left\{ \begin{array}{l} \frac{d[A]}{dt} = -k[A][B] \\ \frac{d[B]}{dt} = -k[A][B] \\ \frac{d[C]}{dt} = k[A][B] \end{array} \right.$$

- If the initial concentrations are *equal* ($[A]_0 = [B]_0$):

$$-\frac{d[A]}{dt} = k[A]^2$$

The same equation as for one substrate, except that there is no factor “2”.

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

$$[A] = [B] = \frac{[A]_0}{1 + k[A]_0 t}$$

- *Half-life*:

$$t_{1/2} = \frac{1}{k[A]_0}$$

Second-order reaction kinetics – two substrates ($[A]_0 \neq [B]_0$)

► $A + B \rightarrow C$ when the initial concentrations are *not equal* ($[A]_0 \neq [B]_0$):

$$-\frac{d[A]}{dt} = k[A][B] \Rightarrow \frac{1}{[A]} \frac{d[A]}{dt} = -k[B]$$

$$-\frac{d[B]}{dt} = k[A][B] \Rightarrow \frac{1}{[B]} \frac{d[B]}{dt} = -k[A]$$

Let's subtract:

$$\frac{1}{[A]} \frac{d[A]}{dt} - \frac{1}{[B]} \frac{d[B]}{dt} = k([A] - [B])$$

$$\frac{d}{dt}(\ln[A]) - \frac{d}{dt}(\ln[B]) = k([A] - [B])$$

$$\frac{d}{dt}(\ln[A] - \ln[B]) = k([A] - [B])$$

$$\frac{d}{dt} \ln \frac{[A]}{[B]} = k([A] - [B])$$

Note that due to stoichiometry: $[A]_0 - [A] = [B]_0 - [B] \Rightarrow [A] - [B] = [A]_0 - [B]_0$.

Thus, the right-hand side is a constant $k([A]_0 - [B]_0)$. Upon integration we get:

$$\ln \frac{[A]}{[B]} = k([A]_0 - [B]_0)t + \ln \frac{[A]_0}{[B]_0} \Rightarrow [A] = \frac{[A]_0([A]_0 - [B]_0)}{[A]_0 - [B]_0 \exp(-k([A]_0 - [B]_0)t)}$$

- Linearization in the second-order kinetics:

- ▶ *One-substrate* reaction:

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

t is used as abscissa and $1/[A]$ as ordinate. The slope will be $2k$ and the intercept $1/[A]_0$.

- ▶ *Two-substrate* reaction, *equal* initial concentrations ($[A]_0 = [B]_0$):

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

t is used as abscissa and $1/[A]$ as ordinate. The slope will be k (not $2k$) and the intercept $1/[A]_0$.

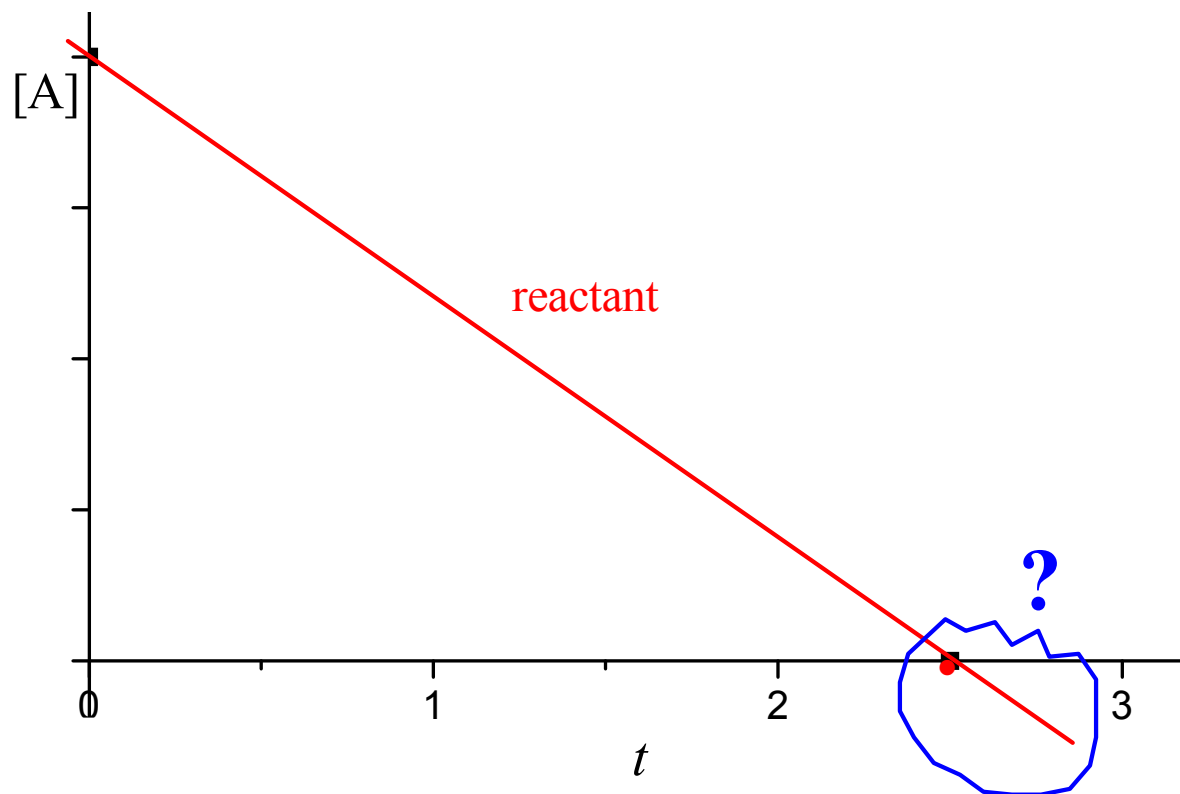
- ▶ *Two-substrate* reaction, *different* initial concentrations ($[A]_0 \neq [B]_0$):

$$\ln \frac{[A]}{[B]} = k([A]_0 - [B]_0)t + \ln \frac{[A]_0}{[B]_0}$$

t is used as abscissa and $\ln([A]/[B])$ as ordinate. The slope will be $k([A]_0 - [B]_0)$ and the intercept $\ln([A]_0/[B]_0)$.

Zeroth-order reaction kinetics

- $$-\frac{d[A]}{dt} = k \Rightarrow [A] = [A]_0 - kt$$



► Zeroth-order kinetics:

- never takes place for elementary reactions;
- quite typical of catalytic reactions, when a reactant is in excess;
- also often observed in other complex reaction, when a reactant not involved in a rate-determining step is in excess;
- never holds for low reactant concentrations; it becomes first or second order when a low concentration of the reactant remains.

Summary on rate laws (kinetic equations) – (orders 0–1–2)

Order	Explicit equation	Linearized form
0	$[A] = [A]_0 - kt$	
1	$[A] = [A]_0 \exp(-kt)$	$\ln [A] = \ln [A]_0 - kt$
2 (one substrate)	$[A] = \frac{[A]_0}{1 + 2k[A]_0 t}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
2 (two substrates, $[A]_0 = [B]_0$)	$[A] = \frac{[A]_0}{1 + k[A]_0 t}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
2 (two substrates, $[A]_0 > [B]_0$)	$[A] = \frac{[A]_0 ([A]_0 - [B]_0)}{[A]_0 - [B]_0 \exp(-k([A]_0 - [B]_0)t)}$	$\ln \frac{[A]}{[B]} = k([A]_0 - [B]_0)t + \ln \frac{[A]_0}{[B]_0}$

- **Warning:** you should be able to *derive* not only the above equations (except for the last case), but also similar ones. For instance, you should do it for a one-substrate reaction of *any* order.

Treatment of experimental data – explicit use of concentration – regression

- When the **order** is *known* or *assumed*: the rate constant from *least-squares fitting (regression)* using the integrated rate law.
- Non-linear regression (more and more dominating approach nowadays):
 - can provide more accurate rate constants.
 - An iterative optimization procedure with an initial approximation ("initial guess") is needed: e.g. `scipy.optimize.curve_fit` or `scipy.optimize.least_squares` in Python.
 - Minimizing the Mean Squared Error (MSE) as a function of the parameters to be fitted.

Example for a first-order reaction: $[A]_t = A_0 e^{-kt}$

N experimental points, A_0 and k are the parameters to be fitted:

$$\min_{A_0, k} MSE(A_0, k) = \min_{A_0, k} \sum_{i=1}^N \left([A]_{t_i} - [A]_{t_i}^{\text{predicted}} \right)^2 = \min_{A_0, k} \sum_{i=1}^N \left([A]_{t_i} - A_0 e^{-kt_i} \right)^2$$

where $[A]_{t_i}$ is the experimental reactant concentration at time t_i .

- Linear regression:
 - Requires a *linearized* form of the integrated rate law.
 - Simple non-iterative calculation \Rightarrow computationally easy \Rightarrow always used in the past; still often used nowadays; available in pocket calculators, online, in Excel, Python (e.g. `scipy.stats.linregress`).
 - A unique solution.

Treatment of experimental data – explicit use of concentration – linear regression

- Linearized form of the integrated rate law:

Order	Linearized integrated rate law
0	$[A] = [A]_0 - kt$
1	$\ln [A] = \ln [A]_0 - kt$
2 (one substrate)	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
2 (two substrates, $[A]_0 = [B]_0$)	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
2 (two substrates, $[A]_0 \neq [B]_0$)	$\ln \frac{[A]}{[B]} = k([A]_0 - [B]_0)t + \ln \frac{[A]_0}{[B]_0}$

! We must use the concentration of a reactant (not product!)

Treatment of experimental data – Guggenheim method

- The Guggenheim relation links any measurable quantity (“signal”) Y with the reactant concentration $[A]$:

$$\boxed{\frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty}}$$

Condition: Y must be a *linear function* of the concentrations:

$$Y = Y_M + \sum_i \lambda_i [A_i]$$

Examples of Y : optical absorbance, electrical conductivity, total pressure of a gas mixture, angle of rotation of polarized light, volume of titrant, a product concentration, amount, volume (for gases), or weight...

But *not* optical transmittance, electrical resistance, pH..., as they are not linear functions of the concentrations.

Derivation: Pages 22–23 of the *Problem Booklet*.

The Guggenheim relation expresses laws of stoichiometry, not of kinetics. It must be combined with an integrated kinetic rate law.

- 1st-order reaction;
- 2nd-order reaction with $[A]_0 = [B]_0$

Treatment of experimental data – Guggenheim method – 1st order

- **First-order reaction – Guggenheim I method** (not actually due to E.A.Guggenheim)

Rate law:

Guggenheim relation (taking into account that $[A]_{\infty} = 0$):

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

$$\frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}} = \frac{[A]_t - [A]_{\infty}}{[A]_0 - [A]_{\infty}} = \frac{[A]_t}{[A]_0}$$

If $Y_t > Y_{\infty}$:

$$\frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}} = e^{-kt} \Rightarrow Y_t - Y_{\infty} = (Y_0 - Y_{\infty})e^{-kt} \Rightarrow \ln(Y_t - Y_{\infty}) = \ln(Y_0 - Y_{\infty}) - kt$$

If $Y_t < Y_{\infty}$: $\ln(Y_{\infty} - Y_t) = \ln(Y_{\infty} - Y_0) - kt$

In general: $\boxed{\ln |Y_t - Y_{\infty}| = \ln |Y_0 - Y_{\infty}| - kt}$ – Guggenheim I method (requires Y_{∞})

Linear regression $\ln |Y_t - Y_{\infty}|$ vs. time. The slope is k .

- **First-order reaction – Guggenheim II method** (Guggenheim 1926, Y_{∞} not required):

Equidistant data in terms of time are required: $Y_t, Y_{t+\Delta t}, Y_{t+2\Delta t}, Y_{t+3\Delta t}, Y_{t+4\Delta t}, \dots$ ($\Delta t = \text{const}$)

$\ln |Y_{t+\Delta t} - Y_t| = \ln(|Y_{\infty} - Y_0|(1 - e^{-k\Delta t})) - kt$: Guggenheim II method (requires equidistant data)

$\boxed{\ln |Y_{t+\Delta t} - Y_t| = \vartheta - kt}$ *Linear regression* $\ln |Y_{t+\Delta t} - Y_t|$ vs. time. The slope is k .

- **First-order reaction – KMS method** (Kezdy–Mangelsdorf–Swinbourne, Y_{∞} not required):

$Y_{t+\Delta t} = Y_{\infty}(1 - e^{-k\Delta t}) + e^{-k\Delta t}Y_t$: the KMS method (also requires equidistant data)

$\boxed{Y_{t+\Delta t} = \vartheta + e^{-k\Delta t}Y_t}$ *Linear regression* $Y_{t+\Delta t}$ vs. Y_t . The slope will be $e^{-k\Delta t}$, from which we can get k .

- **R/R method** for a first-order reaction – using the signal derivative $R(t) = dY/dt$:

$$\boxed{k = \frac{\ln(R_{t+\Delta t} / R_t)}{\Delta t}}$$

Treatment of experimental data – Guggenheim method – 2nd order

- **2nd-order reaction, equal initial concentrations** ($[A]_0 = [B]_0$):

Rate law:

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

Guggenheim relation:

$$\frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty} = \frac{[A]_t}{[A]_0}$$

Y_∞ not required, but $[A]_0$ is needed:

$$Y_t = \frac{1}{k[A]_0} \left(\frac{Y_0 - Y_t}{t} \right) + Y_\infty$$

Linear regression: Y_t vs. $(Y_0 - Y_t)/t$. The slope is $1/k[A]_0 = t_{1/2}$.

- **2nd-order reaction, equal initial concentrations** ($[A]_0 = [B]_0$), alternative. Both Y_∞ and $[A]_0$ are required:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \Rightarrow \frac{[A]_0}{[A]_t} = 1 + k[A]_0 t \Rightarrow \frac{Y_0 - Y_\infty}{Y_t - Y_\infty} = 1 + k[A]_0 t$$

Linear regression: $(Y_0 - Y_\infty)/(Y_t - Y_\infty)$ vs. time. The slope is $k[A]_0$

- **Zeroth-order reaction:**

Rate law:

$$[A]_t = [A]_0 - kt$$

Guggenheim relation:

$$\frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty} = \frac{[A]_t}{[A]_0} \Rightarrow [A]_t = [A]_0 \frac{Y_t - Y_\infty}{Y_0 - Y_\infty}$$

$$Y_t = Y_0 + \frac{k(Y_\infty - Y_0)}{[A]_0} t$$

Linear regression: Y_t vs. time.

Treatment of experimental data – Guggenheim method – summary

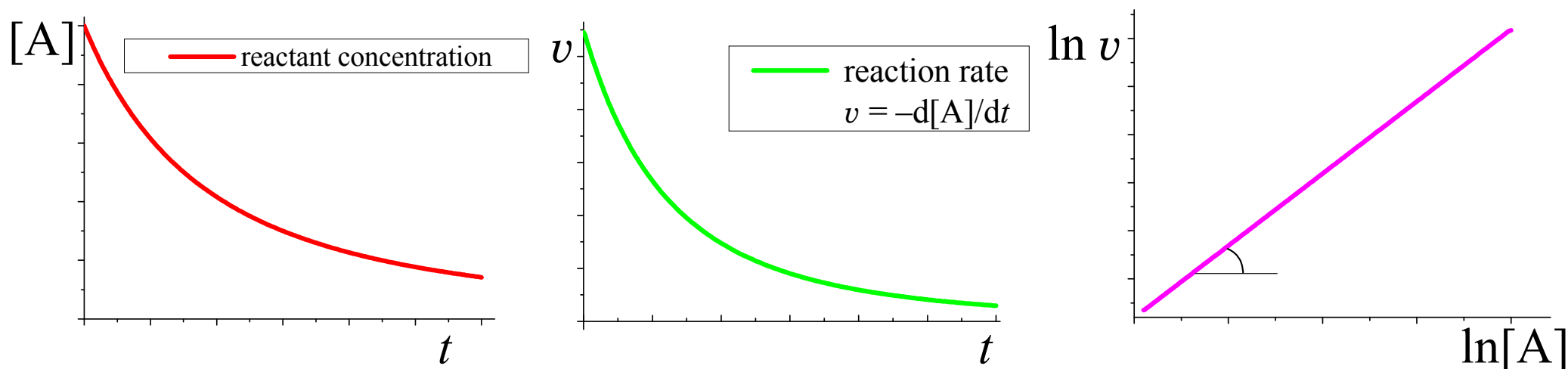
Summary:

Method	Equation	Requirement
1st order – Guggenheim I	$\ln Y_t - Y_\infty = \wp - kt$	Y_∞ is needed
1st order – Guggenheim II	$\ln Y_{t+\Delta t} - Y_t = \wp - kt$	equidistant data ($\Delta t = \text{const}$) are needed
1st order – KMS	$Y_{t+\Delta t} = \wp + e^{-k\Delta t} Y_t$	
2nd order – Guggenheim I	$Y_t = \wp + (1/(k[A]_0))((Y_0 - Y_t)/t)$	Y_∞ is <i>not</i> needed
2nd order – Guggenheim II	$(Y_0 - Y_\infty)/(Y_t - Y_\infty) = 1 + k[A]_0 t$	Y_∞ is needed
0th order – Guggenheim	$Y_t = \wp + k((Y_\infty - Y_0)/[A]_0)t$	

The rate constant in all these methods is eventually obtained from the *slope*. The Georgian letter \wp (“tsil”) means here an intercept, which is not used and the exact form of which is unimportant.

Methods of determination of reaction order – one substrate

- From a single kinetic experiment $[A](t)$ through numerical differentiation:



- ▶ The order n is obtained from the slope of the $\ln v (\ln [A])$ line, since
$$v = k[A]^n \Rightarrow \ln v = \ln k + n \ln [A]$$
- ▶ an entire high-quality smooth curve is required for a reliable numerical differentiation (a table is not enough) \Rightarrow continuous (or at least very frequent) concentration monitoring.
- From a single kinetic experiment $[A](t)$ from characteristic times $t_{1/2}$ and $t_{3/4}$:
 - ▶ Quite approximate; for details see page 41 below.
- From a series of kinetic experiments – From dependence of v_0 upon $[A]_0$ – Method of initial rates (*mètode de velocitats inicials*); for details see page 39.
- From a series of kinetic experiments – From dependence of $t_{1/2}$ upon $[A]_0$: for details see page 41 below.
- ▶ All the methods are applicable both to *one*- and *two*-substrate reactions.

- Method of **initial rates** (*mètode de velocitats inicials*)

One-substrate:

$$v_0 = k[A]_0^n$$

$$\ln v_0 = \ln k + n \ln [A]_0$$

$$Y = A + nX$$

Two-substrate:

$$v_0 = k[A]_0^n[B]_0^m$$

$$\ln v_0 = \ln k + n \ln [A]_0 + m \ln [B]_0$$

$$Y = A + nX_1 + mX_2$$

► The initial rates are obtained from *finite differences*:

$$v_0 = -\left. \frac{d[A]}{dt} \right|_{t=0} \approx \frac{[A]_0 - [A]_{\Delta t}}{\Delta t}$$

► *Multilinear fit* (multiple linear regression, least-squares method) in coordinates $\ln v_0(\ln[A]_0, \ln[B]_0)$ (*adjust multilinear, regressió multilinear, mètode dels mínims quadrats lineal*)

[https://stats.blue/Stats Suite/multiple linear regression calculator.html](https://stats.blue/Stats_Suite/multiple_linear_regression_calculator.html) or the [Python code](#) on Moodle or [online](#) or Excel with LINEST (TENDENCIA) function.

► Alternatively, if multilinear fit is not available (obsolete):

- Fixing a certain $[B]_0$, then doing linear fit (least-squares method) in coordinates $\ln v_0(\ln[A]_0)$

- Fixing a certain $[A]_0$, then doing linear fit (least-squares method) in coordinates $\ln v_0(\ln[B]_0)$

- Half-life for a one-substrate n -th order reaction $nA \rightarrow P$ (see page 24):

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)nk[A]_0^{n-1}}$$

$$\ln t_{1/2} = \ln \frac{2^{n-1} - 1}{(n-1)nk} - (n-1) \ln [A]_0$$

Linear regression in coordinates $\ln t_{1/2}$ vs. $\ln [A]_0$:

$$\ln t_{1/2} = \ln \frac{2^{n-1} - 1}{(n-1)nk} - (n-1) \ln [A]_0$$

The latter equation is valid even for $n=1$

Methods of determination of reaction order – one substrate

- Reaction order from $t_{1/2}$ and $t_{3/4}$:

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)nk[A]_0^{n-1}}$$

► Analogously,

$$t_{3/4} = \frac{4^{n-1} - 1}{(n-1)nk[A]_0^{n-1}}$$

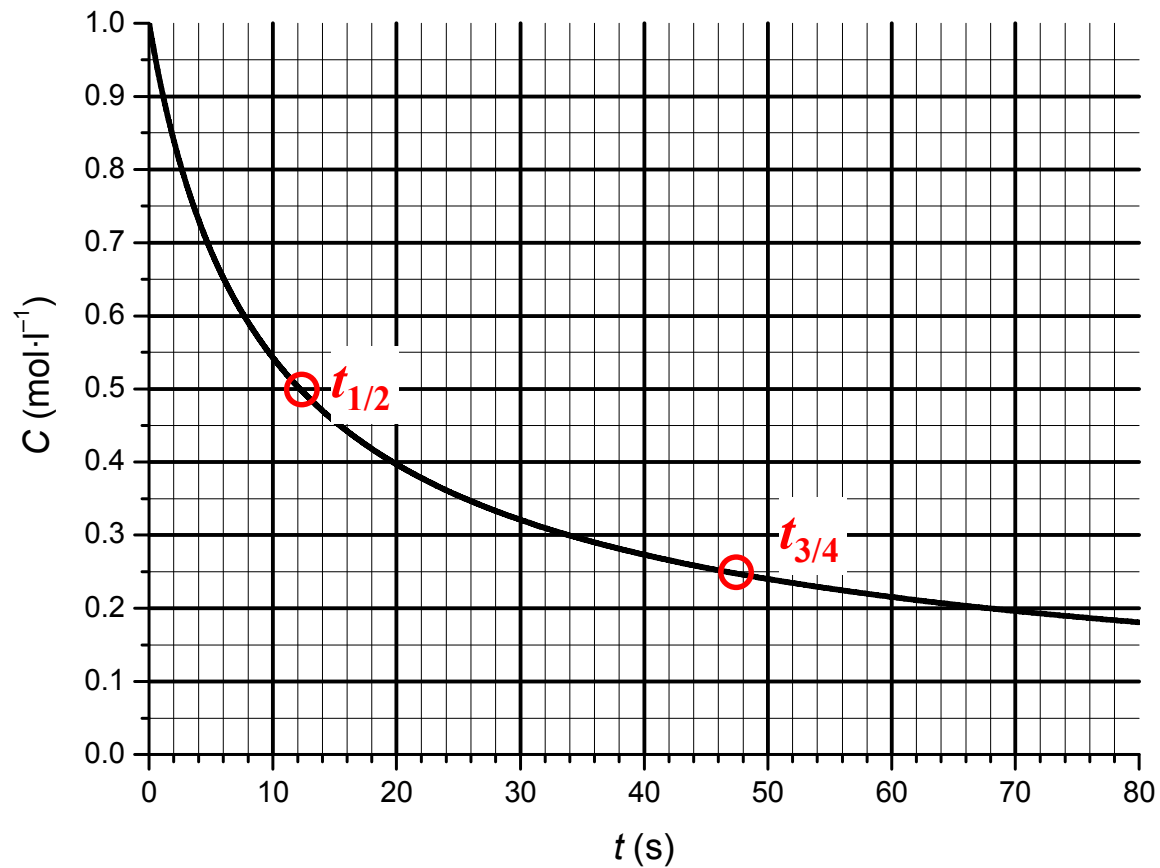
Dividing the expressions:

$$\frac{t_{3/4}}{t_{1/2}} = \frac{4^{n-1} - 1}{2^{n-1} - 1} = \frac{(2^{n-1})^2 - 1}{2^{n-1} - 1} = 2^{n-1} + 1$$

$$n = \log_2 \left(\frac{t_{3/4}}{t_{1/2}} + 1 \right)$$

This formula is helpful for a quick estimation of n from $t_{1/2}$ and $t_{3/4}$; the accuracy of this method is not very high.

n	0	0.5	1	1.5	2
$t_{3/4}/t_{1/2}$	1.5	$1+1/\sqrt{2}$	2	$1+\sqrt{2}$	3



- How to reduce a problem of a *two-substrate* reaction to *one substrate*:
Ostwald's isolation method (cf. problem 1-23 from the *Problem Booklet*):

$$v_0 = k[A]^n[B]^m$$

Three key steps:

- 1) Maintaining a large excess of reactant A: $[A]_0 \gg [B]_0$. In this case, *relative* change in $[A]$ during the reaction is small ($[A] \approx \text{const}$) and we can follow the kinetics with respect to $[B]$. Eventually, we can find the order m with respect to B and an effective rate constant $k' = k[A]_0^n$.
- 2) Maintaining a large excess of reactant B: $[A]_0 \ll [B]_0$. Now, the *relative* change in $[B]$ during the reaction is small ($[B] \approx \text{const}$); we now follow the kinetics with respect to $[A]$. Finally, we find the order n with respect to A and the effective rate constant $k'' = k[B]_0^m$.
- 3) From the the effective rate constants k' and k'' and orders n and m obtained in two previous experiments:

$$k' = k[A]_0^n$$

$$k'' = k[B]_0^m$$

we obtain the real rate constant k .

Note: steps 1 and 2 can be repeated several times at various $[B]_0$ and $[A]_0$, respectively.

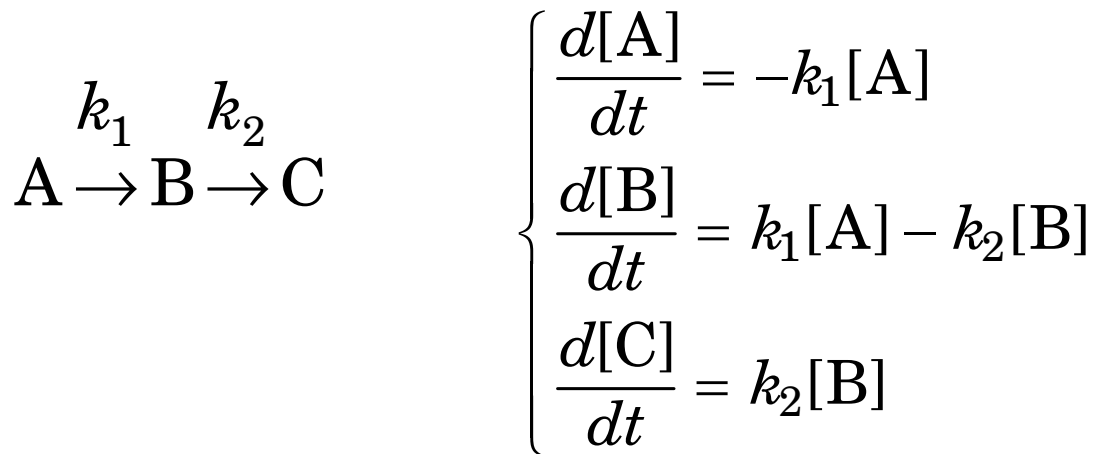
Complex reactions

- Main types (model examples, first-order):

Reversible:	$ \begin{array}{c} k_1 \\ A \rightleftharpoons B \\ k_{-1} \\ A \rightarrow B \quad k_1 \\ B \rightarrow A \quad k_{-1} \end{array} $	$ \begin{cases} \frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] \\ \frac{d[B]}{dt} = k_1[A] - k_{-1}[B] \end{cases} $
Parallel:	$ \begin{array}{c} k_1 \\ A \rightarrow B \\ k_2 \\ A \rightarrow C \end{array} $	$ \begin{cases} \frac{d[A]}{dt} = -(k_1 + k_2)[A] \\ \frac{d[B]}{dt} = k_1[A] \\ \frac{d[C]}{dt} = k_2[A] \end{cases} $
Consecutive:	$ \begin{array}{c} k_1 \quad k_2 \\ A \rightarrow B \rightarrow C \end{array} $	$ \begin{cases} \frac{d[A]}{dt} = -k_1[A] \\ \frac{d[B]}{dt} = k_1[A] - k_2[B] \\ \frac{d[C]}{dt} = k_2[B] \end{cases} $

First-order complex reactions – matrix approach

- Here we consider complex reactions in which all elementary steps are unimolecular (first-order). Example (consecutive reactions):



$$\left\{
 \begin{array}{l}
 \frac{d[\text{A}]}{dt} = -k_1[\text{A}] + 0 \cdot [\text{B}] + 0 \cdot [\text{C}] \\
 \frac{d[\text{B}]}{dt} = k_1[\text{A}] - k_2[\text{B}] + 0 \cdot [\text{C}] \\
 \frac{d[\text{C}]}{dt} = 0 \cdot [\text{A}] + k_2[\text{B}] + 0 \cdot [\text{C}]
 \end{array}
 \right.
 \quad
 \begin{array}{l}
 \text{In matrix form: } \frac{d\mathbf{y}}{dt} = \mathbf{K}\mathbf{y} \\
 \mathbf{y} \text{ is the concentration vector} \\
 \mathbf{K} \text{ is the rate matrix} \\
 \text{The system is coupled: } d[\text{B}]/dt \text{ depends} \\
 \text{not only on } [\text{B}], \text{ but also on } [\text{A}].
 \end{array}$$

$$\mathbf{K} = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} \quad \mathbf{y} = \begin{pmatrix} [\text{A}] \\ [\text{B}] \\ [\text{C}] \end{pmatrix} \quad \mathbf{y}_0 = \begin{pmatrix} [\text{A}]_0 \\ [\text{B}]_0 \\ [\text{C}]_0 \end{pmatrix} \quad \frac{d\mathbf{y}}{dt} = \begin{pmatrix} d[\text{A}]/dt \\ d[\text{B}]/dt \\ d[\text{C}]/dt \end{pmatrix}$$

\mathbf{y}_0 is the initial-concentration vector

First-order complex reactions – matrix method – general

- System of first-order (homogeneous) differential equations in general form:

$$\frac{d\mathbf{y}}{dt} = \mathbf{K}\mathbf{y}$$

- Let's find the eigenvalues (*valors propis*) $\lambda_1, \lambda_2, \dots, \lambda_N$, and corresponding eigenvectors (*vectors propis*) $\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_N$ of \mathbf{K} :

$$\mathbf{K}\mathbf{s}_i = \lambda_i\mathbf{s}_i$$

- Then we can express \mathbf{K} through its eigenvalues and eigenvectors (“eigen-decomposition of matrix \mathbf{K} ”). *Note* that matrix multiplication is not commutative:

$$\mathbf{K} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1} = \mathbf{S} \begin{pmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & \dots & \lambda_N \end{pmatrix} \mathbf{S}^{-1}$$

where $\mathbf{\Lambda}$ is the diagonal matrix of eigenvalues and \mathbf{S} is the square matrix of all the eigenvectors \mathbf{s}_i put columnwise. \mathbf{S}^{-1} is the inverse matrix.

- Insert the eigendecomposition of \mathbf{K} into the system of equations and then left-multiply by \mathbf{S}^{-1} :

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}\mathbf{y} \Rightarrow \mathbf{S}^{-1}\frac{d\mathbf{y}}{dt} = \mathbf{\Lambda}\mathbf{S}^{-1}\mathbf{y} \Rightarrow \frac{d(\mathbf{S}^{-1}\mathbf{y})}{dt} = \mathbf{\Lambda}\mathbf{S}^{-1}\mathbf{y}$$

First-order complex reactions – matrix method – general

- Then making a substitution $\mathbf{S}^{-1}\mathbf{y} = \tilde{\mathbf{y}}$, we obtain: $d\tilde{\mathbf{y}}/dt = \Lambda\tilde{\mathbf{y}}$

$$\frac{d\tilde{\mathbf{y}}}{dt} = \begin{pmatrix} d\tilde{y}_1/dt \\ d\tilde{y}_2/dt \\ \dots \\ \tilde{y}_N/dt \end{pmatrix}; \quad \Lambda\tilde{\mathbf{y}} = \begin{pmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & \dots & \lambda_N \end{pmatrix} \begin{pmatrix} \tilde{y}_1 \\ \tilde{y}_2 \\ \dots \\ \tilde{y}_N \end{pmatrix} = \begin{pmatrix} \lambda_1\tilde{y}_1 \\ \lambda_2\tilde{y}_1 \\ \dots \\ \lambda_N\tilde{y}_N \end{pmatrix}$$

$d\tilde{\mathbf{y}}/dt = \Lambda\tilde{\mathbf{y}}$, written element by element, reads as follows: $d\tilde{y}_i/dt = \lambda_i\tilde{y}_i$. Thus, the system of equations is now *decoupled* and we can easily solve each of the equations $d\tilde{y}_i/dt = \lambda_i\tilde{y}_i$ separately. The solution is well known:

$$\tilde{y}_i(t) = e^{\lambda_i t} \tilde{y}_i(0)$$

Now let's rewrite the above solution in vector-matrix notations: $\tilde{\mathbf{y}} = e^{\Lambda t} \tilde{\mathbf{y}}_0$, where $e^{\Lambda t}$ means the *matrix exponential* of the diagonal matrix Λt :

$$e^{\Lambda t} = \begin{pmatrix} e^{\lambda_1 t} & 0 & \dots & 0 \\ 0 & e^{\lambda_2 t} & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & \dots & e^{\lambda_N t} \end{pmatrix}$$

In order to recover the original \mathbf{y} , recall that $\tilde{\mathbf{y}} = \mathbf{S}^{-1}\mathbf{y}$ and $\tilde{\mathbf{y}}_0 = \mathbf{S}^{-1}\mathbf{y}_0$:

$$\mathbf{S}^{-1}\mathbf{y} = e^{\Lambda t} \mathbf{S}^{-1}\mathbf{y}_0 \Rightarrow \mathbf{y} = \mathbf{S} e^{\Lambda t} \mathbf{S}^{-1} \mathbf{y}_0$$

Matrix $\mathbf{S}e^{\mathbf{A}t}\mathbf{S}^{-1}$, which is not diagonal, is considered the *matrix exponential* of matrix $\mathbf{K}t$: $\mathbf{S}e^{\mathbf{A}t}\mathbf{S}^{-1} = e^{\mathbf{K}t}$. It has the same eigenvectors as \mathbf{K} and $\mathbf{K}t$, but different eigenvalues. Both $\mathbf{K}t$ and $e^{\mathbf{K}t}$ are square matrices of the same size as \mathbf{K} . Thus, we finally have the solution:

$$\mathbf{y}(t) = e^{\mathbf{K}t} \mathbf{y}_0$$

In this context, the matrix exponential $e^{\mathbf{K}t}$ is called *evolution operator*.

- Technically, the matrix exponential can be calculated:
 - Analytically: WolframAlpha ([MatrixExp\[\]](#)), Python ([sympy.exp\(\)](#))
 - Numerically: e.g. Python ([scipy.linalg.expm\(\)](#) function);

► *Note:* For most matrices the eigendecomposition $\mathbf{K} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}$ exists (in which case the matrix is called *diagonalizable*), but not for all matrices. For example, a non-diagonalizable matrix appears for the $A \rightarrow B \rightarrow C$ reaction system if the two rate constants are identical ($k_1 = k_2$, cf. problem 2a-2 from the *Problem Booklet*). So, in the case of a non-diagonalizable matrix, the above method of calculating the matrix exponential must be modified: the so-called *Jordan normal form* is used instead of the diagonal matrix. This advanced matrix calculus goes beyond our course. Ask your professor if interested. Anyway, the calculation of the matrix exponential is always possible for *all* square matrices.

First-order complex reactions – matrix method – example

- For the above example of the $A \rightarrow B \rightarrow C$ *consecutive reactions*:

$$\mathbf{K}t = \begin{pmatrix} -k_1t & 0 & 0 \\ k_1t & -k_2t & 0 \\ 0 & k_2t & 0 \end{pmatrix} \quad e^{\mathbf{K}t} = \begin{pmatrix} e^{-k_1t} & 0 & 0 \\ \frac{k_1(e^{-k_2t} - e^{-k_1t})}{k_1 - k_2} & e^{-k_2t} & 0 \\ \frac{k_1(1 - e^{-k_2t}) - k_2(1 - e^{-k_1t})}{k_1 - k_2} & 1 - e^{-k_2t} & 1 \end{pmatrix}$$

The final step (for the case $[B]_0 = [C]_0 = 0$):

$$\mathbf{y}(t) = \begin{pmatrix} [A]_t \\ [B]_t \\ [C]_t \end{pmatrix} = e^{\mathbf{K}t} \cdot \mathbf{y}_0 = \begin{pmatrix} e^{-k_1t} & 0 & 0 \\ \frac{k_1(e^{-k_2t} - e^{-k_1t})}{k_1 - k_2} & e^{-k_2t} & 0 \\ \frac{k_1(1 - e^{-k_2t}) - k_2(1 - e^{-k_1t})}{k_1 - k_2} & 1 - e^{-k_2t} & 1 \end{pmatrix} \cdot \begin{pmatrix} [A]_0 \\ 0 \\ 0 \end{pmatrix} =$$

$$= \begin{pmatrix} [A]_0 e^{-k_1t} \\ \frac{k_1(e^{-k_2t} - e^{-k_1t})}{k_1 - k_2} [A]_0 \\ \frac{k_1(1 - e^{-k_2t}) - k_2(1 - e^{-k_1t})}{k_1 - k_2} [A]_0 \end{pmatrix}$$

<https://www.wolframalpha.com/input?i=MatrixExp%5B%7B%7B-k1%C2%B7t%2C+0%2C+0%7D%2C+%7Bk1%C2%B7t%2C+-k2%C2%B7t%2C0%7D%2C+%7B0%2C+k2%C2%B7t%2C0%7D%7D%2C%7BA%2C0%2C0%7D%5D&assumption=%7B%22FunClash%22%2C+%22MatrixExp%22%7D+-+%3E+%7B%22MatrixExp%22%7D>

See also the problems 2a on page 7 of the *Problem Booklet*.

- Properties of the **K** matrix in kinetics:
 - Diagonal elements are negative (*think why!*).
 - Diagonal elements are equal to the minus sum of the off-diagonal ones in the same column (true if material balance is fulfilled – *think why!*):
$$K_{ii} = - \sum_{j(\neq i)} K_{ji}$$
 - The eigenvalues of **K** are functions of the rate constants.
 - The eigenvalues of **K** are real: $\{\lambda_i\} \subset \mathbb{R}$.
 - The eigenvalues of **K** are non-positive: $\lambda_i \leq 0$ (true if material balance is fulfilled). At least one eigenvalue of **K** is zero: $\lambda_1 = 0$.
- Implications for kinetics:
 - First-order systems have analytical solutions, as long as we can find the eigenvalues of **K**.
 - Solutions $[A_i]_t$ are linear combinations of decreasing exponentials $e^{\lambda_i t}$. (increasing exponentials may appear when material balance is not fulfilled).
 - Oscillations are impossible in first-order systems. This is because the eigenvalues are real. If there were complex eigenvalues, the solution would be oscillating, but this is not the case. *Note*: oscillating chemical processes do exist (cf. page 90), but not in first-order systems.

- $A \rightleftharpoons B$ **reversible reaction** (elementary derivation see App.4 page 180)

$$\begin{cases} \frac{d[A]}{dt} = -v_1 + v_{-1} = -k_1[A] + k_{-1}[B] \\ \frac{d[B]}{dt} = v_1 - v_{-1} = k_1[A] - k_{-1}[B] \end{cases}$$

$$\mathbf{K} = \begin{pmatrix} -k_1 & k_{-1} \\ k_1 & k_{-1} \end{pmatrix} \quad \mathbf{K}t = \begin{pmatrix} -k_1 t & k_{-1} t \\ k_1 t & k_{-1} t \end{pmatrix}$$

Using WolframAlpha:

$$e^{\mathbf{K}t} = \frac{1}{k_1 + k_{-1}} \begin{pmatrix} k_1 e^{-(k_1+k_{-1})t} + k_{-1} & k_{-1} (1 - e^{-(k_1+k_{-1})t}) \\ k_1 (1 - e^{-(k_1+k_{-1})t}) & k_1 + k_{-1} e^{-(k_1+k_{-1})t} \end{pmatrix}$$

when $[B]_0 = 0$:

$$\begin{aligned} \begin{pmatrix} [A]_t \\ [B]_t \end{pmatrix} &= e^{\mathbf{K}t} \begin{pmatrix} [A]_0 \\ 0 \end{pmatrix} = \frac{1}{k_1 + k_{-1}} \begin{pmatrix} k_1 e^{-(k_1+k_{-1})t} + k_{-1} & k_{-1} (1 - e^{-(k_1+k_{-1})t}) \\ k_1 (1 - e^{-(k_1+k_{-1})t}) & k_1 + k_{-1} e^{-(k_1+k_{-1})t} \end{pmatrix} \begin{pmatrix} [A]_0 \\ 0 \end{pmatrix} = \\ &= \begin{pmatrix} \frac{k_1 e^{-(k_1+k_{-1})t} + k_{-1}}{k_1 + k_{-1}} [A]_0 \\ \frac{k_1 (1 - e^{-(k_1+k_{-1})t})}{k_1 + k_{-1}} [A]_0 \end{pmatrix} = \begin{pmatrix} \frac{k_{-1}[A]_0}{k_1 + k_{-1}} + \frac{k_1[A]_0}{k_1 + k_{-1}} e^{-(k_1+k_{-1})t} \\ \frac{k_1[A]_0}{k_1 + k_{-1}} - \frac{k_{-1}[A]_0}{k_1 + k_{-1}} e^{-(k_1+k_{-1})t} \end{pmatrix} \end{aligned}$$

$$[A]_t = \frac{k_{-1}[A]_0}{k_1 + k_{-1}} + \frac{k_1[A]_0}{k_1 + k_{-1}} e^{-(k_1 + k_{-1})t}$$

$$[B]_t = \frac{k_1[A]_0}{k_1 + k_{-1}} - \frac{k_1[A]_0}{k_1 + k_{-1}} e^{-(k_1 + k_{-1})t}$$

- Behavior at infinite time:

$$[A]_\infty = \frac{k_{-1}[A]_0}{k_1 + k_{-1}}$$

$$[B]_\infty = \frac{k_1[A]_0}{k_1 + k_{-1}}$$

$$\frac{[B]_\infty}{[A]_\infty} = \frac{k_1}{k_{-1}} = K_{\text{eq}}$$

$$[A] = [A]_\infty + [B]_\infty e^{-(k_1 + k_{-1})t} = [A]_\infty + ([A]_0 - [A]_\infty) e^{-(k_1 + k_{-1})t}$$

- ▶ !!! The rates of the forward and reverse reactions at equilibrium ($t = \infty$) are equal!!!:

$$k_1[A]_\infty = k_{-1}[B]_\infty ; v_1 = v_{-1}$$

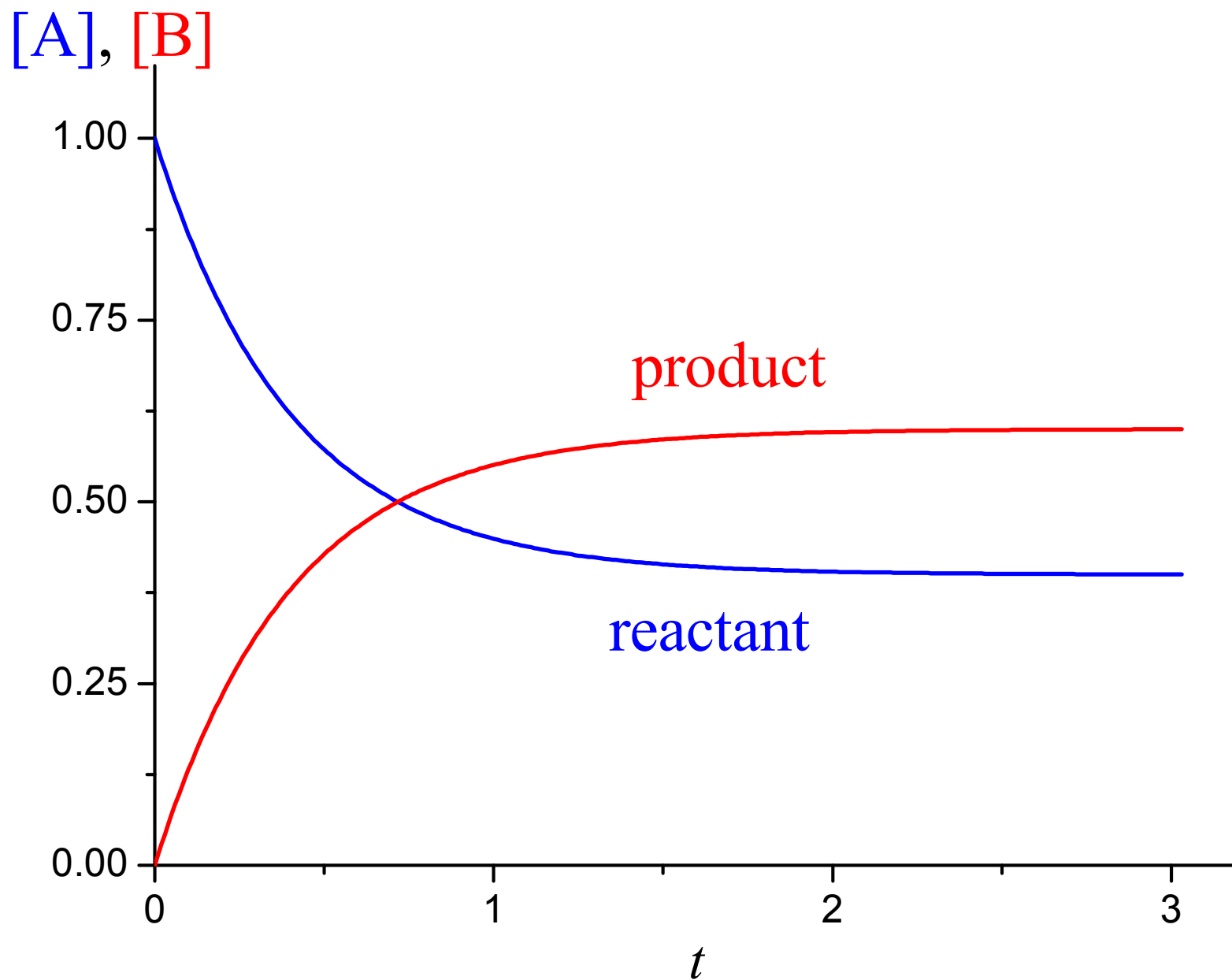
- ▶ Linearization allows us to determine $k_1 + k_{-1}$:

$$\ln([A] - [A]_\infty) = \ln([A]_0 - [A]_\infty) - (k_1 + k_{-1})t$$

To find the individual constants k_1 , k_{-1} , $K_{\text{eq}} = k_1/k_{-1} = [B]_\infty/[A]_\infty$ is needed. *Note*: Guggenheim etc. are also applicable.

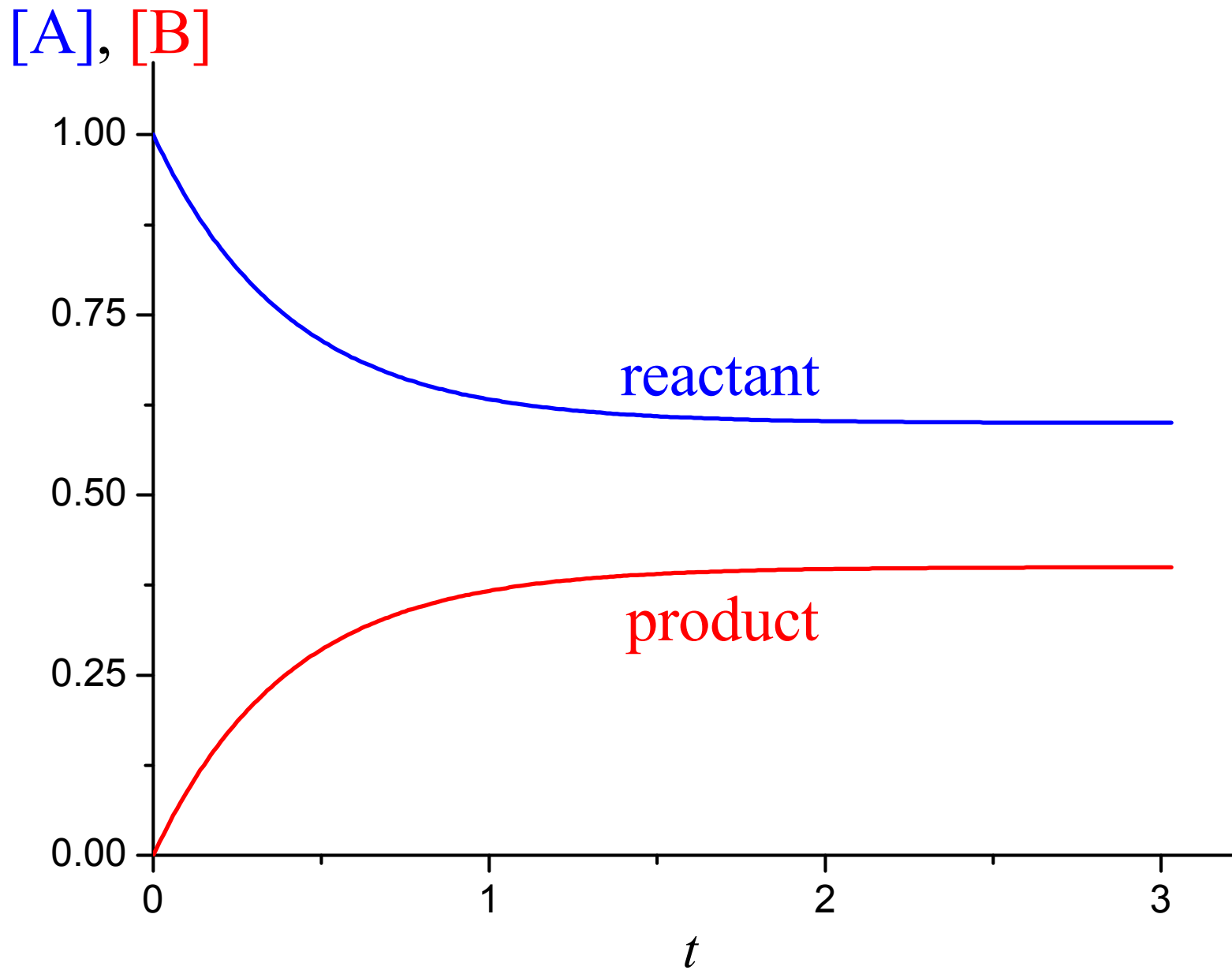
Reversible reactions

► $k_1 > k_{-1}$:



Reversible reactions

► $k_1 < k_{-1}$:



Parallel (competitive) reactions

- $A \rightarrow B, A \rightarrow C$ **parallel reaction** (elem. derivation in App. 5 p. 182):

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A]; \quad \frac{d[B]}{dt} = k_1[A]; \quad \frac{d[C]}{dt} = k_2[A]$$

$$\mathbf{K} = \begin{pmatrix} -k_1 - k_2 & 0 & 0 \\ k_1 & 0 & 0 \\ k_2 & 0 & 0 \end{pmatrix} \quad \mathbf{K}t = \begin{pmatrix} -(k_1 + k_2)t & 0 & 0 \\ k_1 t & 0 & 0 \\ k_2 t & 0 & 0 \end{pmatrix}$$

Using WolframAlpha:

$$e^{\mathbf{K}t} = \begin{pmatrix} e^{-(k_1+k_2)t} & 0 & 0 \\ \frac{k_1(1 - e^{-(k_1+k_2)t})}{k_1 + k_2} & 1 & 0 \\ \frac{k_2(1 - e^{-(k_1+k_2)t})}{k_1 + k_2} & 0 & 1 \end{pmatrix}$$

when $[B]_0 = [C]_0 = 0$:

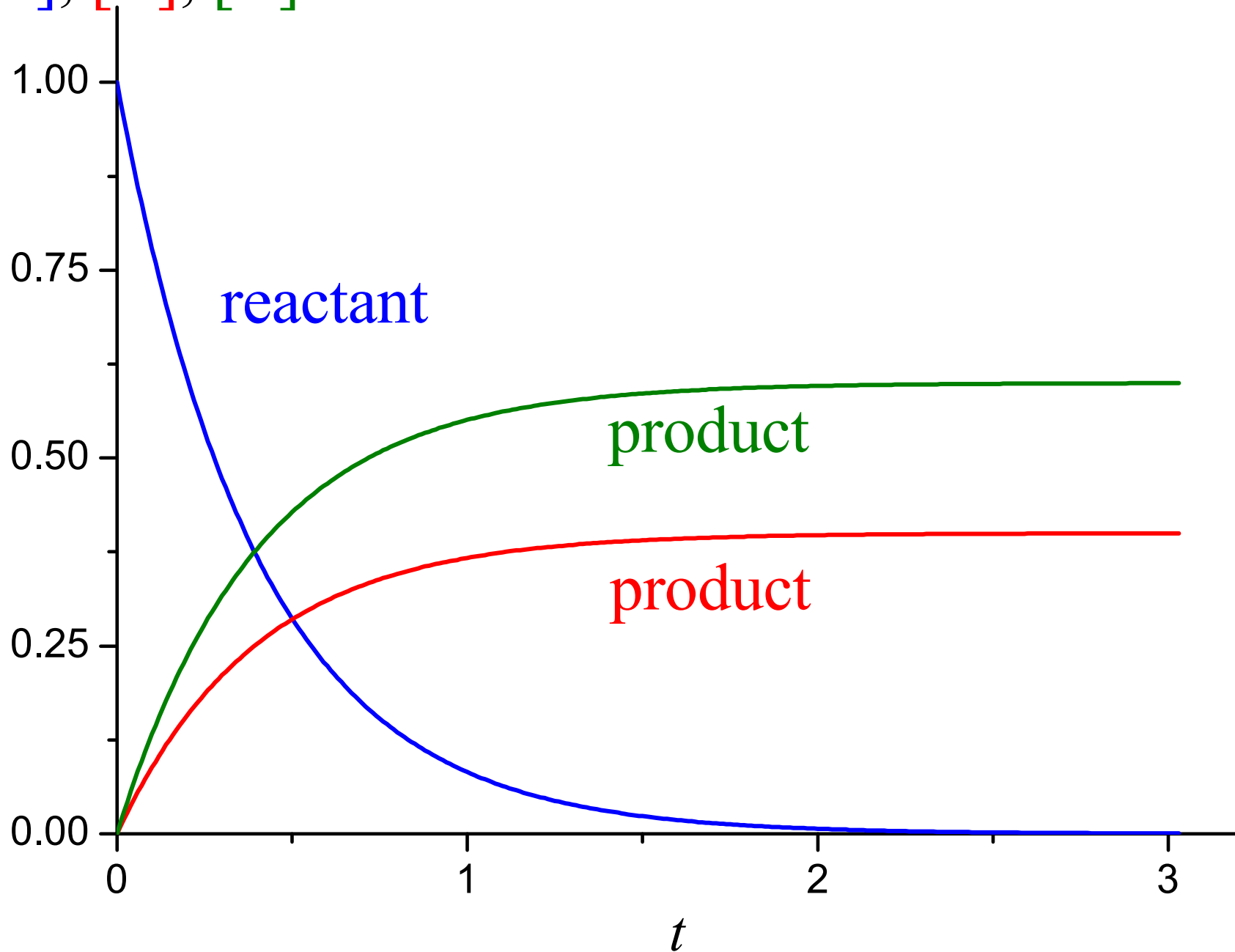
$$\begin{pmatrix} [A]_t \\ [B]_t \\ [C]_t \end{pmatrix} = e^{\mathbf{K}t} \begin{pmatrix} [A]_0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} [A]_0 e^{-(k_1+k_2)t} \\ \frac{[A]_0 k_1}{k_1 + k_2} (1 - e^{-(k_1+k_2)t}) \\ \frac{[A]_0 k_2}{k_1 + k_2} (1 - e^{-(k_1+k_2)t}) \end{pmatrix} \Rightarrow \frac{[B]_t}{[C]_t} = \frac{k_1}{k_2} \text{ at any moment of time}$$

– for same-order reactions only!

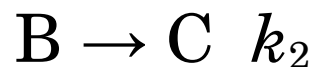
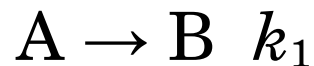
► Linearization: $\ln[A] = \ln[A]_0 - (k_1 + k_2)t$

Parallel (competitive) reactions

$[A]$, $[B]$, $[C]$



Consecutive reactions



$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

- **K**-matrix derivation see page 44. Elementary derivation see Appendix 6 page 183.

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

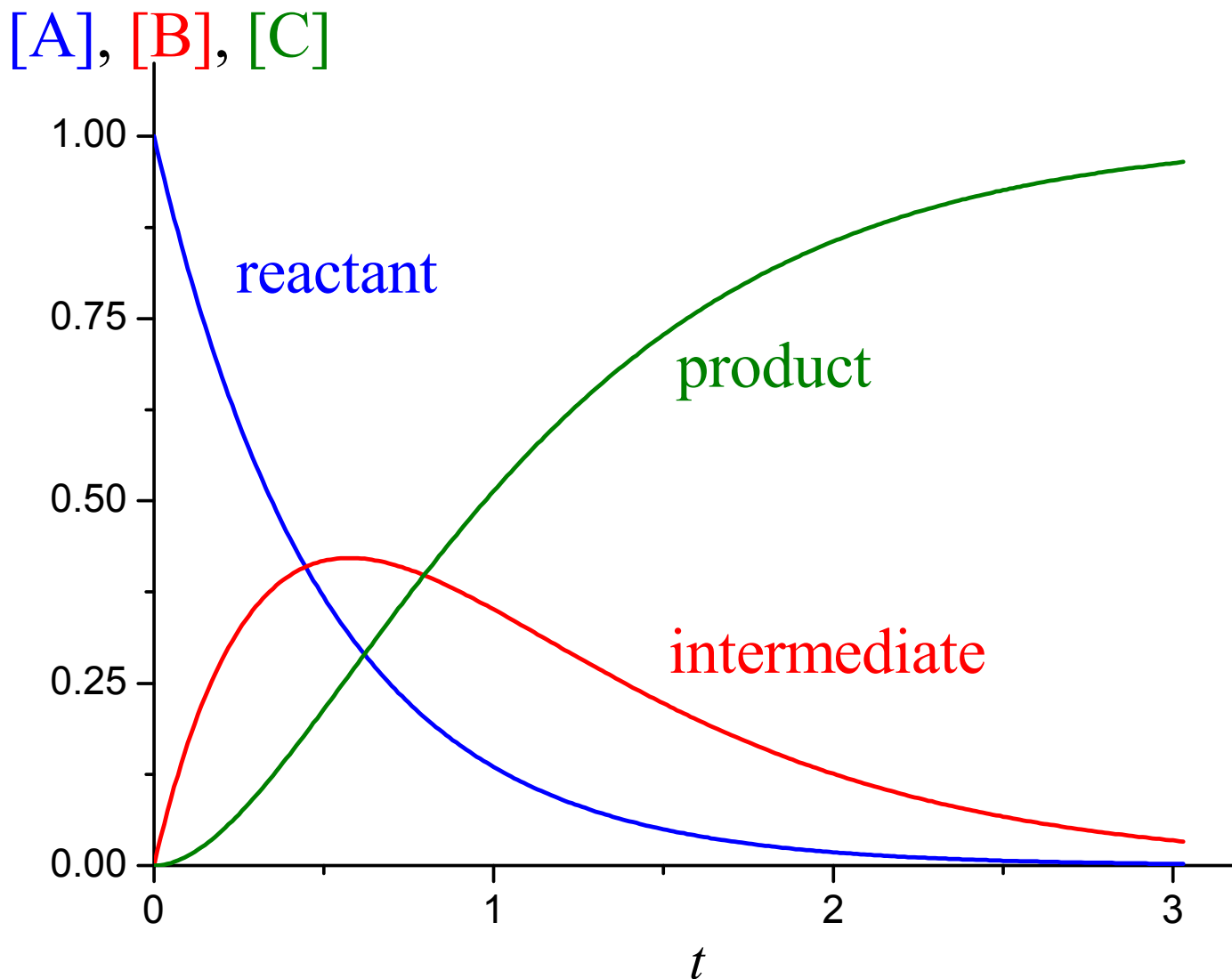
$$[B] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t});$$

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

Not valid for $k_1 = k_2$ (cf. problem 2a-2 from the *Problem Booklet*)

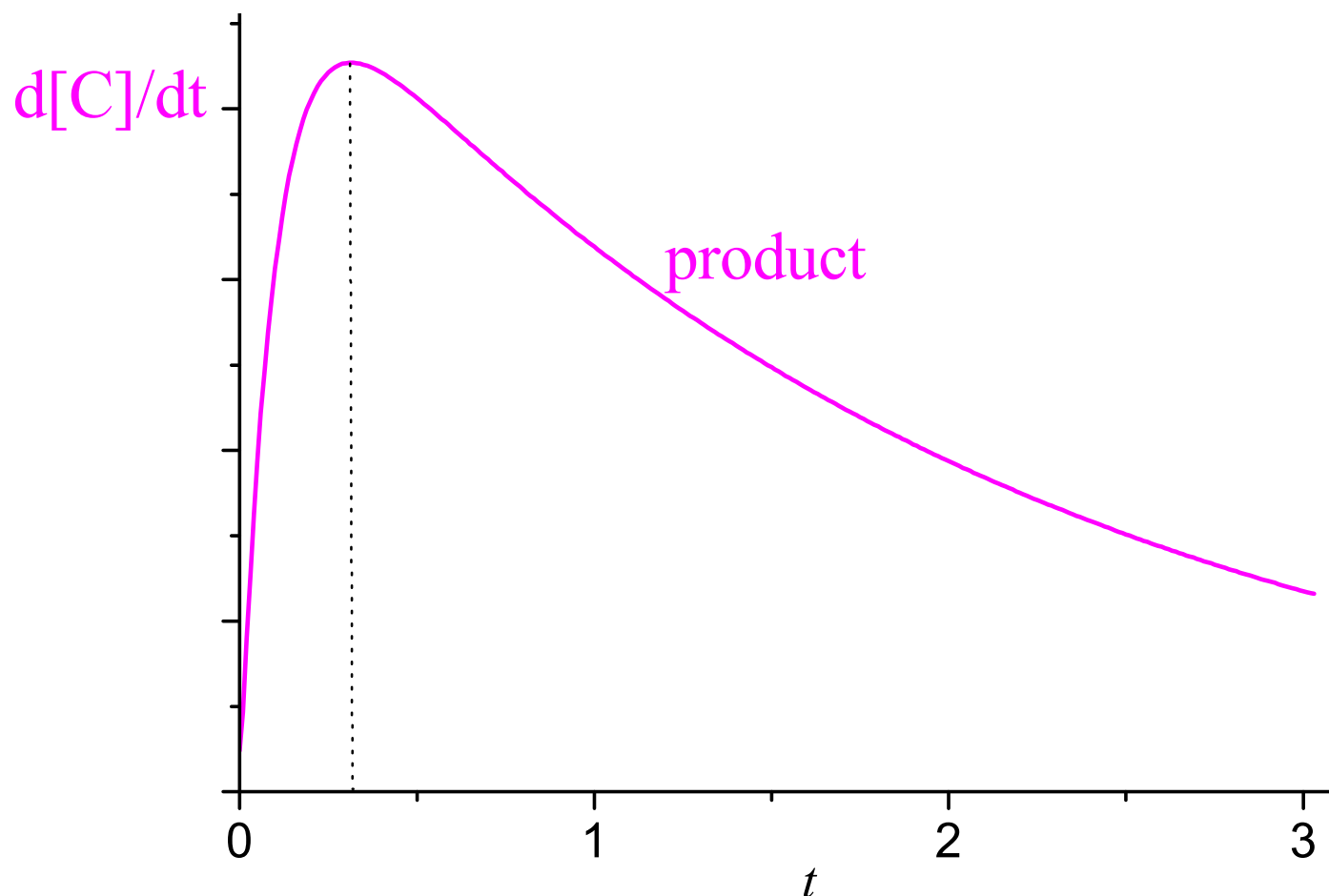
Consecutive reactions

- Comparable k_1 and k_2 :



Consecutive reactions – induction time

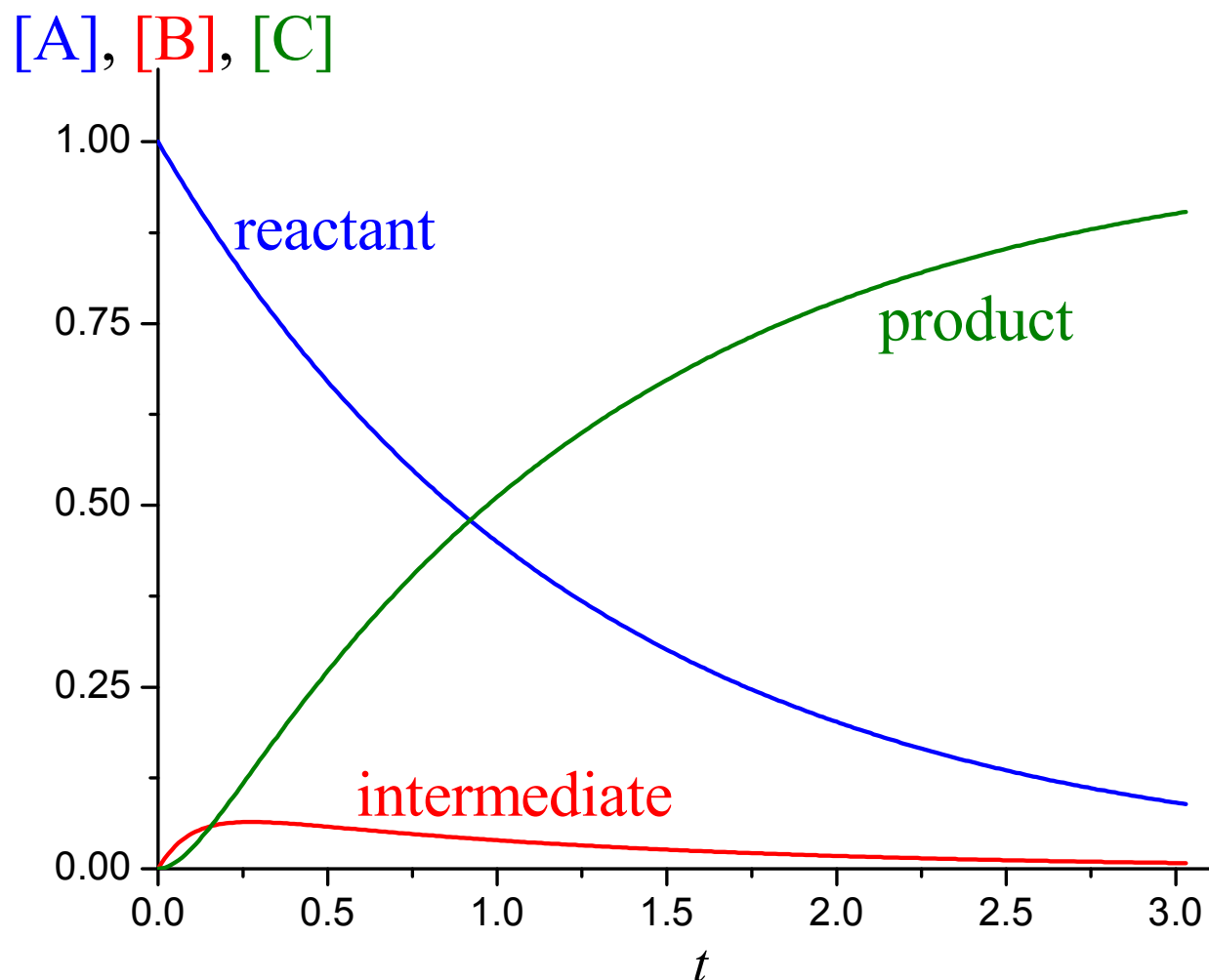
- Product formation rate $d[C]/dt = k_2[B]$



- *Induction time* (= *induction period* = *període d'inducció*); maximum product formation rate, maximum concentration of the intermediate.

Consecutive reactions

► $k_1 \ll k_2$:

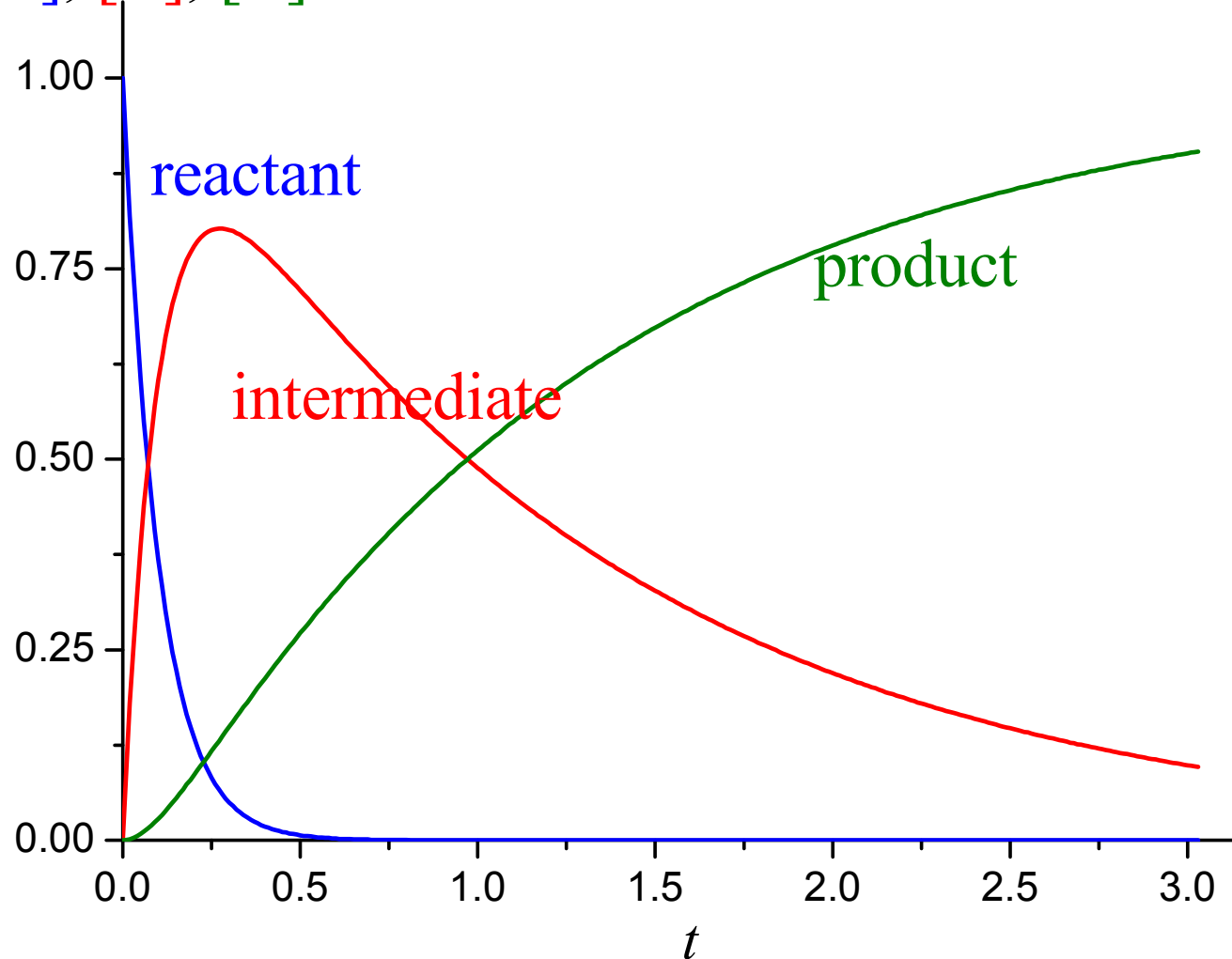


$$[C] = \frac{k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t})}{k_2 - k_1} [A]_0 \approx \frac{k_2 (1 - e^{-k_1 t})}{k_2} [A]_0 = (1 - e^{-k_1 t}) [A]_0$$

- The product formation rate is determined by $k_1 \Rightarrow A \rightarrow B$ is the **rate-determining step** (= *rate-limiting step* = *etapa limitant de velocitat*).
A slowly yields B, then B quickly yields C.

Consecutive reactions – rate-limiting step

► $k_1 \gg k_2$: [A], [B], [C]

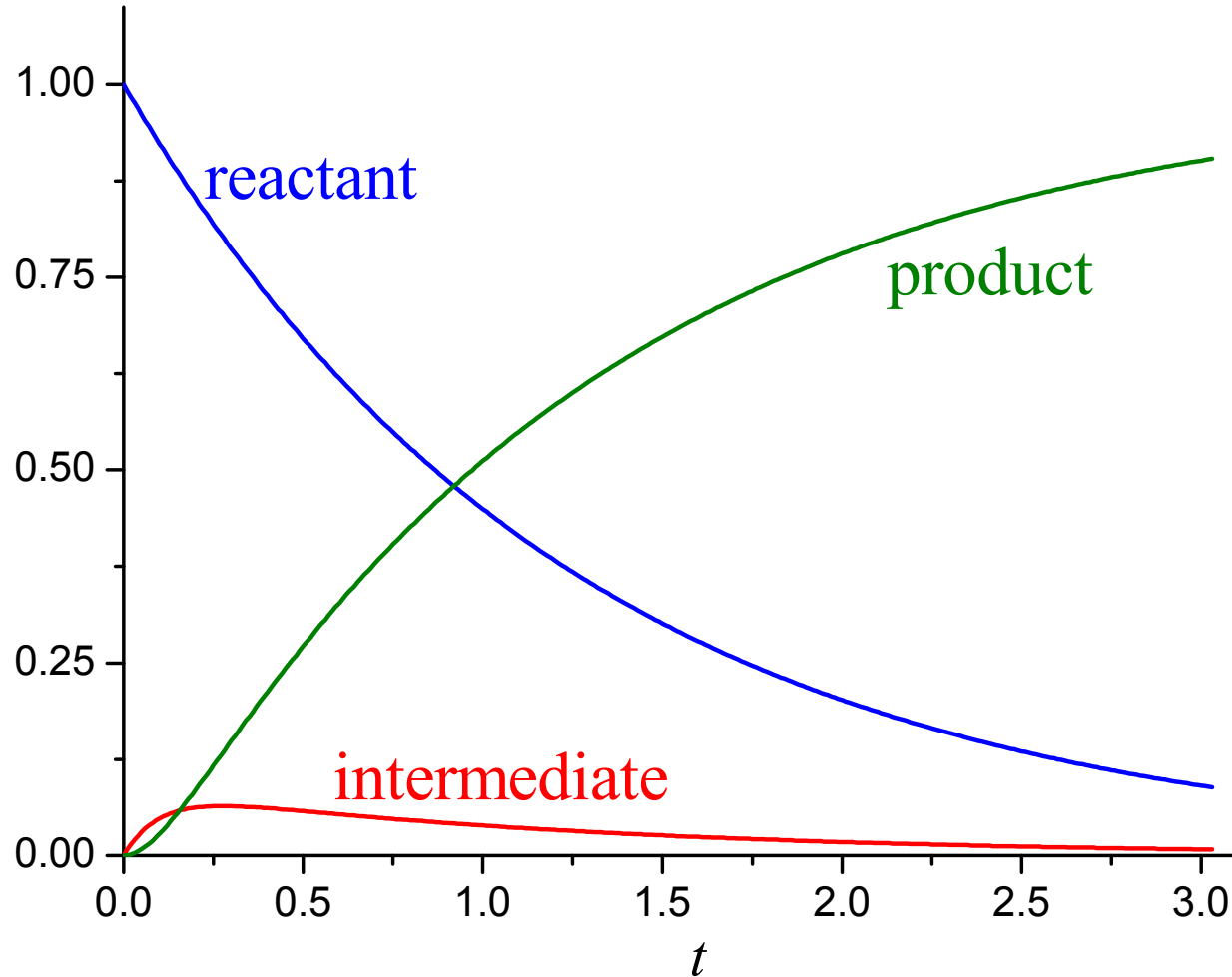


$$[C] = \frac{k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})}{k_2 - k_1} [A]_0 \approx \frac{-k_1(1 - e^{-k_2 t})}{-k_1} [A]_0 = (1 - e^{-k_2 t}) [A]_0$$

► The product formation rate is determined by $k_2 \Rightarrow \text{B} \rightarrow \text{C}$ is the **rate-determining step**. A quickly yields B, then B slowly yields C.

Steady-state approximation

► $k_1 \ll k_2$: [A], [B], [C]



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

This is equivalent to $k_1[A] - k_2[B] \approx 0$. Since $k_1[A] - k_2[B] = d[B]/dt$ this is in turn equivalent to $d[B]/dt \approx 0$: *(quasi-)steady-state approximation* (*aproximació de l'estat (quasi)estacionari*).

Steady-state approximation

- Using the steady-state approximation

► $[B] \ll [A]$; $d[B]/dt \approx 0$.

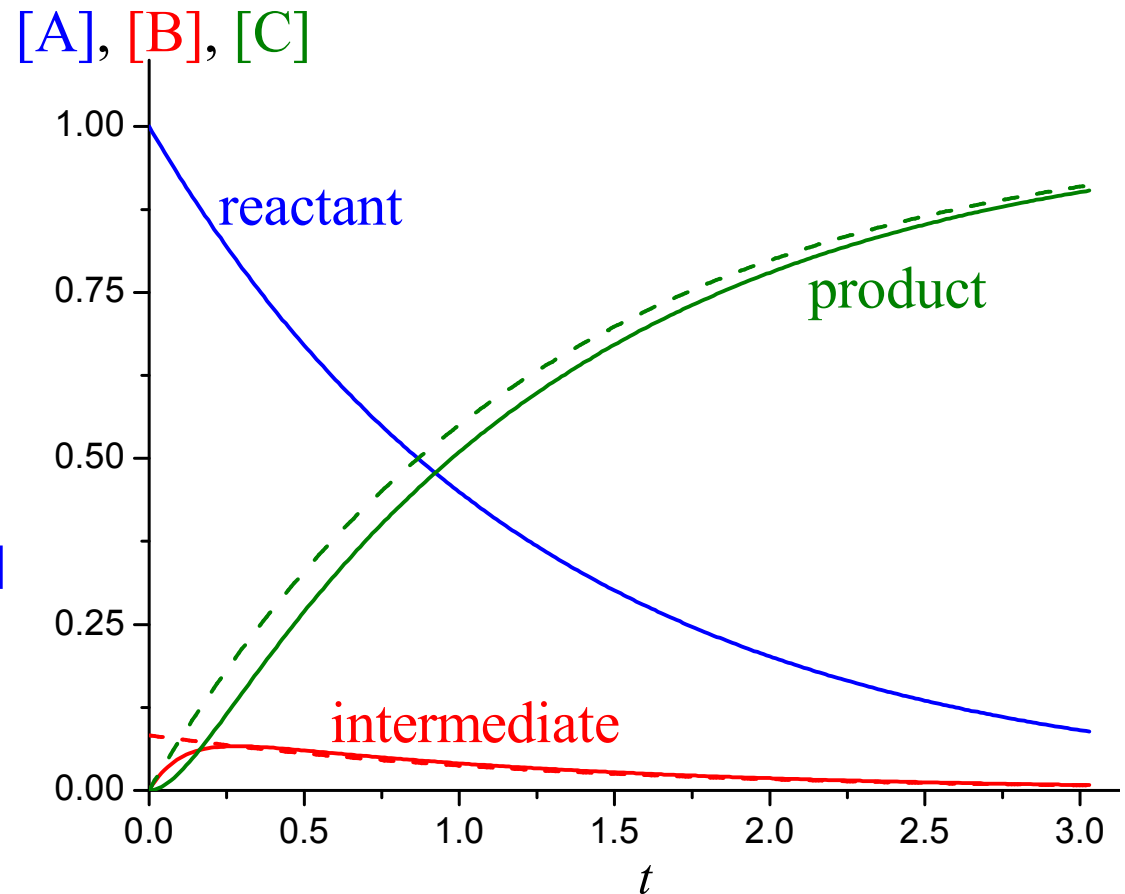
$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \approx 0$$

$$\Rightarrow [B] \approx \frac{k_1[A]}{k_2}$$

$$\frac{d[C]}{dt} = k_2[B] \approx k_2 \frac{k_1[A]}{k_2} = k_1[A]$$

$$\boxed{\frac{d[C]}{dt} \approx k_1[A]}$$



In this example: $k_2/k_1 = 12$

$$\frac{d[C]}{dt} \approx k_1[A]_0 e^{-k_1 t} \Rightarrow [C] = [A]_0 (1 - e^{-k_1 t})$$

Steady-state approximation

- Key point: **rates** of change for **intermediates** are assumed to be **zero**.
 - ▶ This allows algebraically deducing the rate law.
 - ▶ Effective, because intermediates are often highly reactive and short-living.
- Step-by-step procedure (Bodenstein 1913):
 - ▶ Write the reaction mechanism.
 - ▶ Formulate rate equations: derive the system of differential kinetic equations (rate laws) for *all* intermediates and *at least* one product or reactant.
 - ▶ Identify short-living intermediates and equate their rates of change to zero.
You should do it for all intermediates, otherwise it will not work!
You should never equate the rates for products or reactants to zero!
 - ▶ From the equations obtained, express the concentration of intermediates in terms of the concentrations of reactants (and maybe products).
 - ▶ Substitute intermediate concentrations into the rate equation for the product or reactant to get the overall rate law.

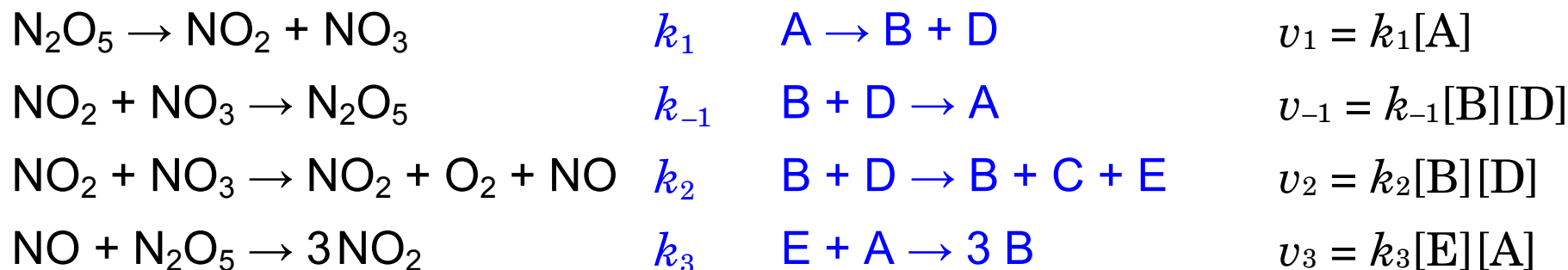


Max Bodenstein (1871–1942)

Steady-state approximation – example

- $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$: overall reaction: $2A \rightarrow 4B + C$

Ogg's mechanism (cf. page 16):



- Product B formation rate:

$$\frac{d[B]}{dt} = v_1 - v_{-1} + 3v_3 = k_1[A] - k_{-1}[B][D] + 3k_3[E][A]$$

- Formation rates for intermediates **D** and **E**:

$$\frac{d[\text{D}]}{dt} = v_1 - v_{-1} - v_2 = k_1[A] - k_{-1}[B][\text{D}] - k_2[B][\text{D}] = 0$$

$$\frac{d[\text{E}]}{dt} = v_2 - v_3 = k_2[B][\text{D}] - k_3[\text{E}][A] = 0$$

Steady-state approximation – example

- Solving the system of equations with respect to $[D]$ and $[E]$:

$$\begin{cases} k_1[A] - (k_{-1} + k_2)[B][D] = 0 \\ k_2[B][D] - k_3[E][A] = 0 \end{cases}$$

$$[D] = \frac{k_1[A]}{(k_{-1} + k_2)[B]}$$

$$[E] = \frac{k_2[B][D]}{k_3[A]} = \frac{k_2[B]}{k_3[A]} \frac{k_1[A]}{(k_{-1} + k_2)[B]} = \frac{k_2}{k_3} \frac{k_1}{(k_{-1} + k_2)} = \frac{k_1 k_2}{k_3(k_{-1} + k_2)}$$

- Product B formation rate

$$\begin{aligned} \frac{d[B]}{dt} &= k_1[A] - k_{-1}[B][D] + 3k_3[E][A] \\ &= k_1[A] - k_{-1}[B] \frac{k_1[A]}{(k_{-1} + k_2)[B]} + 3k_3 \frac{k_1 k_2}{k_3(k_{-1} + k_2)} [A] = \frac{4k_1 k_2}{k_{-1} + k_2} [A] \end{aligned}$$

- Product C formation rate:

$$\frac{d[C]}{dt} = v_2 = k_2[B][D]$$

- Reactant A consumption rate:

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B][D] - k_3[E][A] = -k_1[A] + k_{-1} \frac{k_1[A]}{k_{-1} + k_2} - k_3 \frac{k_1 k_2 [A]}{k_3(k_{-1} + k_2)} = -\frac{2k_1 k_2}{k_{-1} + k_2} [A]$$

Steady-state approximation – a shortcut

- Sometimes a more compact solution is possible. Note that the $d[B]/dt$ rate depends on the $[B][D]$ and $[E][A]$ products:

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B][D] + 3k_3[E][A]$$

The steady-state equation also contain the same $[B][D]$ and $[E][A]$ products:

$$\begin{cases} k_1[A] - (k_{-1} + k_2)[B][D] = 0 \\ k_2[B][D] - k_3[E][A] = 0 \end{cases}$$

From the first equation we get $[B][D]$:

$$[B][D] = \frac{k_1}{k_{-1} + k_2}[A]$$

From the second equation we get $k_3[E][A]$:

$$k_3[E][A] = k_2[B][D].$$

Finally we obtain by substitution:

$$\begin{aligned} \frac{d[B]}{dt} &= k_1[A] - k_{-1}[B][D] + 3k_3[E][A] = \\ &= k_1[A] - k_{-1}[B][D] + 3k_2[B][D] = \\ &= k_1[A] + (3k_2 - k_{-1})[B][D] = k_1[A] + (3k_2 - k_{-1})\frac{k_1}{k_{-1} + k_2}[A] = \frac{4k_1k_2}{k_{-1} + k_2}[A] \end{aligned}$$

A solution for $d[C]/dt$ will be even easier, since we need $[B][D]$ only!

- A situation that the same blocks appear in several equations is very common (*think why!*). You should make use of it as much as possible.

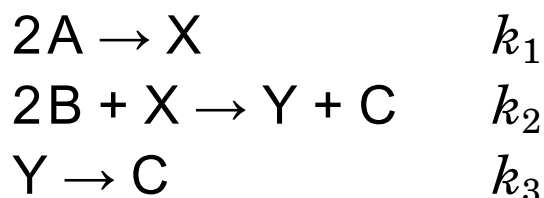
Steady-state approximation – useful property

- In the previous example, we derived $d[A]/dt$, $d[B]/dt$, and $d[C]/dt$ independently and observed that for the reaction $2A \rightarrow 4B + C$:

$$\frac{d[C]}{dt} = -\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$$

This is a general property of the quasi-steady-state approximation:

- The rate laws for any reactant or product obtained within the quasi-steady-state approximation are identical, differing only by a constant factor equal to the ratio of their stoichiometric coefficients of the *overall* reaction.
 - Thus, we can first derive the rate law for the most convenient component and subsequently obtain it for the desired one by applying stoichiometric coefficients from the *overall* reaction.
 - This is *not true* for the exact solution.
 - Consider, for example, the following reaction: $A + B \rightarrow C$ with the following mechanism (exam 30/10/2017):

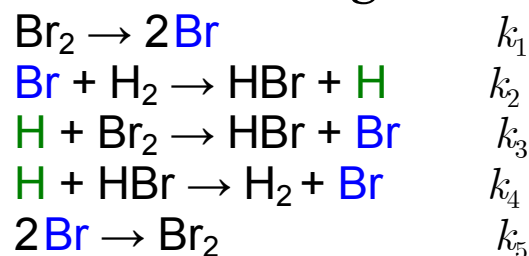


The derivation of $d[A]/dt$ is very simple, because A occurs only in the first equation: $d[A]/dt = -2k_1[A]^2$. Then, from stoichiometry we know that $d[C]/dt = -d[A]/dt$. Therefore, $d[C]/dt = 2k_1[A]^2$. That's it.

An independent derivation of $d[C]/dt$ would be much more sophisticated, since expressions for intermediates [X] and [Y] would be needed first.

$\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}$ reaction

- Bodenstein's original example ($\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}$):



► Product formation rate:

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

- Steady-state equations for active intermediates **Br** and **H**:

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \approx 0 \Rightarrow k_2[\text{Br}][\text{H}_2] - k_4[\text{H}][\text{HBr}] = k_3[\text{H}][\text{Br}_2]$$

$$\frac{d[\text{HBr}]}{dt} = 2k_3[\text{H}][\text{Br}_2]$$

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - \underbrace{k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2}_{=0}$$

$$2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2 = 0 \Rightarrow [\text{Br}] = \left(k_1 / k_5\right)^{1/2} [\text{Br}_2]^{1/2}$$

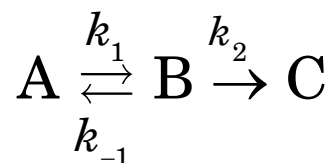
$$[\text{H}] = \frac{k_2[\text{Br}][\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} = \frac{k_2 \left(k_1 / k_5\right)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}$$

$$\frac{d[\text{HBr}]}{dt} = 2k_3[\text{H}][\text{Br}_2] = 2k_3 \frac{k_2 \left(k_1 / k_5\right)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} [\text{Br}_2]$$

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_3k_2 \left(k_1 / k_5\right)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_3 + k_4[\text{HBr}] / [\text{Br}_2]}$$

Experimental equation:
$$v = \frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''[\text{HBr}] / [\text{Br}_2]}$$

- Consider a complex reaction:



in which $k_{-1} \gg k_2$. Let us apply the steady-state approximation to this system:

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B] \approx 0 \Rightarrow \frac{[B]}{[A]} = \frac{k_1}{k_{-1} + k_2}$$

Neglecting k_2 in the denominator, we get

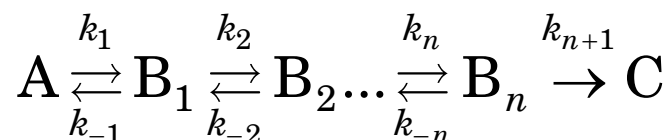
$$\frac{[B]}{[A]} \approx \frac{k_1}{k_{-1}} = K_{\text{eq}}$$

This means that $[B]$ can be obtained simply from the equilibrium constant of the $A \rightleftharpoons B$ process without writing down a full equation for the steady state: $[B] = K_{\text{eq}}[A]$.

- Product formation rate:

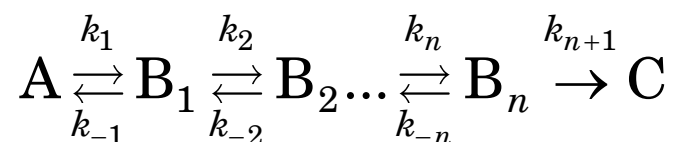
$$\frac{d[C]}{dt} = k_2[B] = k_2 \frac{k_1}{k_{-1}} [A] = k_2 K_{\text{eq}} [A]$$

- The *pre-equilibrium* (*prior equilibrium*, *quasi-equilibrium*) approximation can be used for more complex reactions:



Pre-equilibrium approximation

- *Pre-equilibrium (prior equilibrium, quasi-equilibrium)* for complex reactions:



Assuming the equilibrium in each step:

$$A \xrightleftharpoons[k_{-1}]{k_1} B_1 \quad K_{eq1} = \frac{[B_1]}{[A]} = \frac{k_1}{k_{-1}} \quad B_1 \xrightleftharpoons[k_{-2}]{k_2} B_2 \quad K_{eq2} = \frac{[B_2]}{[B_1]} = \frac{k_2}{k_{-2}}$$

$$B_{n-1} \xrightleftharpoons[k_{-n}]{k_n} B_n \quad K_{eqn} = \frac{[B_n]}{[B_{n-1}]} = \frac{k_n}{k_{-n}}$$

$$K_{eq1} K_{eq2} \dots K_{eqn} = \frac{[B_1]}{[A]} \cdot \frac{[B_2]}{[B_1]} \dots \frac{[B_n]}{[B_{n-1}]} = \frac{[B_n]}{[A]} = \frac{k_1}{k_{-1}} \cdot \frac{k_2}{k_{-2}} \dots \frac{k_n}{k_{-n}} = K_{eq}$$

If $k_{-n} \gg k_{n+1}$, $[B_n]$ and $d[C]/dt$ are as follows:

$$\frac{d[C]}{dt} = k_{n+1}[B_n] = k_{n+1} \frac{k_1 k_2 \dots k_n}{k_{-1} k_{-2} \dots k_{-n}} [A] = k_{n+1} K_{eq} [A]$$

- *Pre-equilibrium (prior equilibrium, quasi-equilibrium)* approximation can be justified without invoking the steady-state approximation.
- Pre-equilibrium approximation can be used *not* in all cases with a reversible reaction step. The condition $k_{-n} \gg k_{n+1}$ must be fulfilled.
- It is *not* required that $k_{n+1} \gg k_n$.
- Pre-equilibrium approximation is often applied to reactions including dissociations or association (coordination).

- It is always possible to formulate a system of kinetic equations for a given reaction.
- By far not always it is possible to solve it *analytically*.
- A *numerical* solution is usually (in principle, always) possible.
 - ▶ It is always approximate, but any desired level of accuracy can be achieved in principle.
 - ▶ It always corresponds to specific initial concentrations, yielding *particular* solutions rather than general ones.
 - ▶ *Discrete* representation of the results; no analytical form is obtained.
- Example – first-order kinetics $A \rightarrow B$:

$$\begin{cases} \frac{d[A]}{dt} = -k[A] \\ \frac{d[B]}{dt} = k[A] \end{cases}$$

$$[A]_t = [A]_0 e^{-kt}; \quad [B]_t = [B]_0 + [A]_0(1 - e^{-kt})$$

This *analytical* solution is a general one; it is valid for any initial concentrations $[A]_0$, $[B]_0$ and any rate constant k .

A *numerical* solution $[A]_0, [A]_1, [A]_2, \dots [B]_0, [B]_1, [B]_2, \dots$ is obtained on a discrete set of time points t_0, t_1, t_2, \dots for *given* initial concentrations $[A]_0, [B]_0$.

- A system of kinetic differential equations always has the following form:

$$\begin{cases} \frac{d[A]}{dt} = f_1([A],[B],...) \\ \frac{d[B]}{dt} = f_2([A],[B],...) \\ \dots \end{cases}$$

For example, for first-order kinetics:

$$\begin{cases} \frac{d[A]}{dt} = -k[A] & f_1([A],[B]) = -k[A] \\ \frac{d[B]}{dt} = k[A] & f_2([A],[B]) = k[A] \end{cases}$$

► Changing to vector notations:

$$\mathbf{y} = [A], [B], \dots \quad d\mathbf{y}/dt = d[A]/dt, d[B]/dt, \dots \quad \mathbf{f} = f_1, f_2, \dots$$

For example, for the first-order kinetics $\mathbf{f}(\mathbf{y}) = \mathbf{K}\mathbf{y}$.

- $\frac{d\mathbf{y}}{dt} = \mathbf{f}(t, \mathbf{y})$

although in chemical kinetics f does not actually depend on time t .

Numerical solution of differential equations – Euler method – two versions

- In all methods, the initial-concentration vector $\mathbf{y}_0 = \mathbf{y}(t=0)$ must be set.
- **Euler method:** $d\mathbf{y}/dt$ is substituted by the finite-difference ratio:

$$\frac{d\mathbf{y}}{dt} \approx \frac{\Delta \mathbf{y}}{\Delta t} = \frac{\mathbf{y}_{n+1} - \mathbf{y}_n}{\Delta t}$$

$$\frac{\mathbf{y}_{n+1} - \mathbf{y}_n}{\Delta t} = \mathbf{f}(t_n, \mathbf{y}_n)$$

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \mathbf{f}(t_n, \mathbf{y}_n) \Delta t \quad t_{n+1} = t_n + \Delta t$$

or, in a more stepwise way:

$$\mathbf{k}_1 = \mathbf{f}(t_n, \mathbf{y}_n) \cdot \Delta t$$

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \mathbf{k}_1$$

- The “**predictor-corrector**” version of the Euler method:
 - 1) Calculate the initial approximation (“prediction”) by the usual Euler method:

$$\tilde{\mathbf{y}}_{n+1} = \mathbf{y}_n + \mathbf{f}(t_n, \mathbf{y}_n) \cdot \Delta t$$

- 2) Correct the initial approximation:

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \frac{\mathbf{f}(t_n, \mathbf{y}_n) + \mathbf{f}(t_{n+1}, \tilde{\mathbf{y}}_{n+1})}{2} \cdot \Delta t$$

$\tilde{\mathbf{y}}_{n+1}$ is then discarded; \mathbf{y}_{n+1} is used as the result for t_{n+1} .

The same algorithm presented stepwise:

$$\mathbf{k}_1 = \mathbf{f}(t_n, \mathbf{y}_n) \cdot \Delta t$$

$$\mathbf{k}_2 = \mathbf{f}(t_{n+1}, \mathbf{y}_n + \mathbf{k}_1) \cdot \Delta t$$

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \frac{1}{2} (\mathbf{k}_1 + \mathbf{k}_2)$$

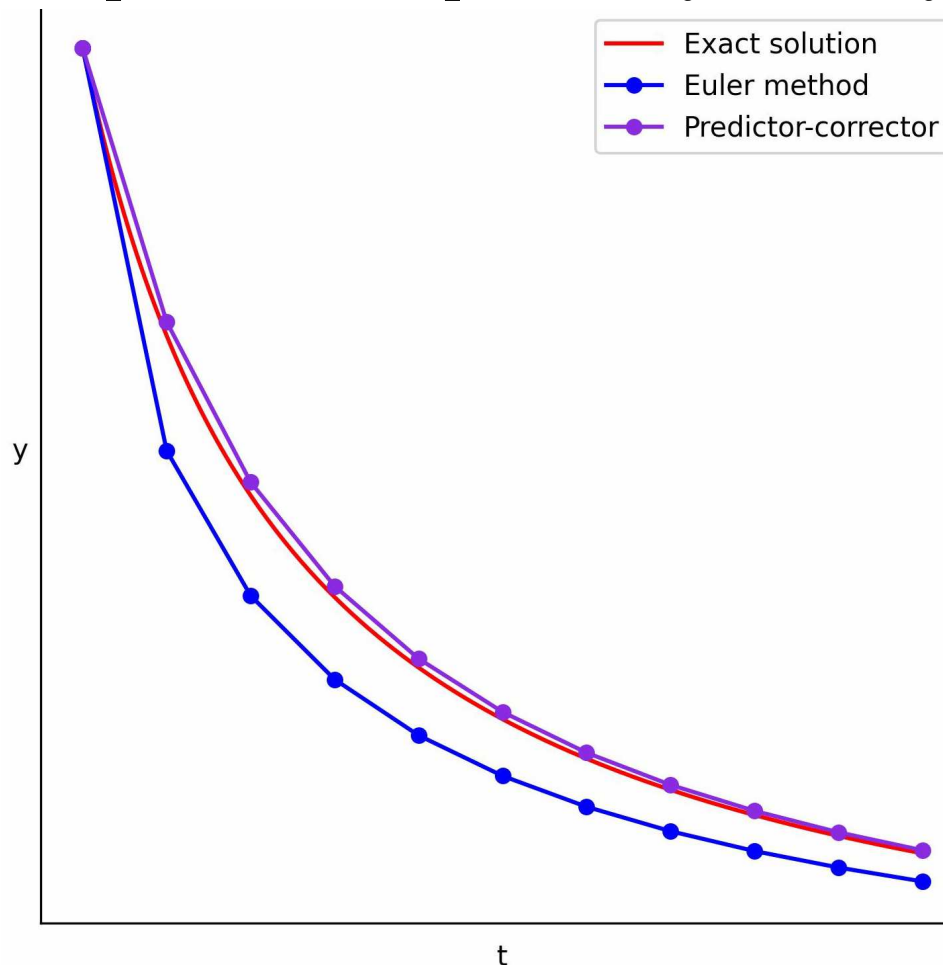
Numerical solution of differential equations – Euler method – inaccuracy

- The Euler method is simple but not very accurate (error accumulation, sometimes wrong solutions of kinetics); the “predictor-corrector” version is better.



Leonhard Euler (1707–1783)

Example for the equation $dy/dt = -2y^2$:



$\Delta t = 0.2$

- The **midpoint** method – another improvement over the Euler method:
First doing an Euler half-step ($\Delta t/2$):

$$\tilde{\mathbf{y}} = \mathbf{y} + \mathbf{f}(t, \mathbf{y}(t)) \cdot \frac{\Delta t}{2}$$

Then calculate the derivatives there and do a full step with these derivatives:

$$\mathbf{y}(t + \Delta t) \approx \mathbf{y} + \mathbf{f}\left(t + \frac{\Delta t}{2}, \tilde{\mathbf{y}}\right) \cdot \Delta t$$

Stepwise algorithm:

$$\mathbf{k}_1 = \mathbf{f}(t_n, \mathbf{y}_n) \cdot \Delta t$$

$$\mathbf{k}_2 = \mathbf{f}\left(t_n + \frac{\Delta t}{2}, \mathbf{y}_n + \frac{\mathbf{k}_1}{2}\right) \cdot \Delta t$$

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \mathbf{k}_2$$

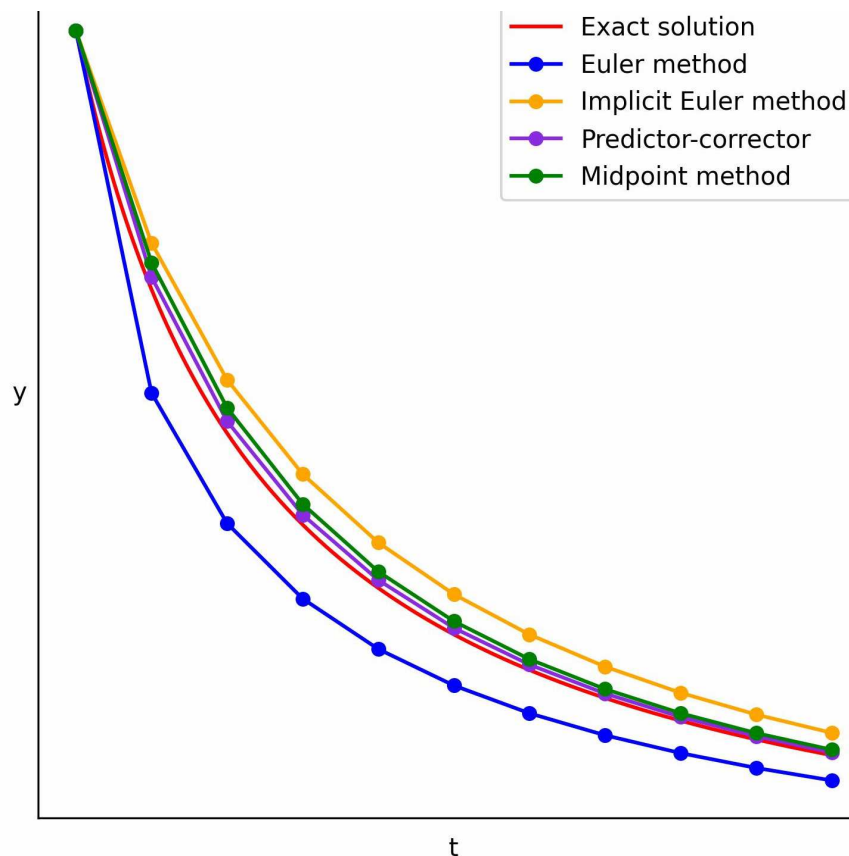
The midpoint method has a comparable accuracy to the Euler predictor-corrector method.

- **Implicit Euler method:** The same as Euler, but \mathbf{y}_{n+1} instead of \mathbf{y}_n :

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \mathbf{f}(t_{n+1}, \mathbf{y}_{n+1})\Delta t$$

instead of $\mathbf{y}_{n+1} = \mathbf{y}_n + \mathbf{f}(t_n, \mathbf{y})\Delta t$

Since \mathbf{y}_{n+1} is now both in the left- and right-hand sides, an algebraic equation must be solved each time to find $\mathbf{y}_{n+1} \Rightarrow$ more complicated and expensive, but the solution is more accurate and stable. Not generally better than predictor-corrector and midpoint.



Numerical solution of differential equations – 4th-order Runge–Kutta method

- The 4th-order **Runge–Kutta** method:

$$\mathbf{k}_1 = \mathbf{f}(t_n, \mathbf{y}_n) \Delta t$$

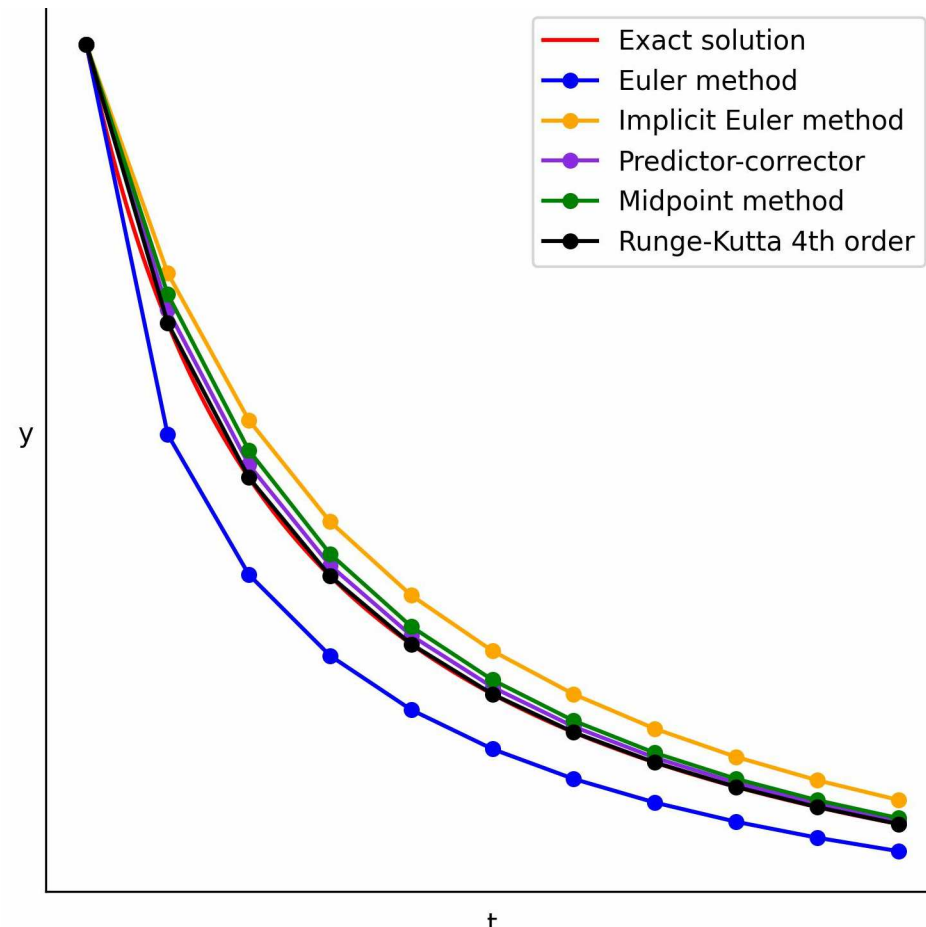
$$\mathbf{k}_2 = \mathbf{f}\left(t_n + \frac{\Delta t}{2}, \mathbf{y}_n + \frac{\mathbf{k}_1}{2}\right) \cdot \Delta t$$

$$\mathbf{k}_3 = \mathbf{f}\left(t_n + \frac{\Delta t}{2}, \mathbf{y}_n + \frac{\mathbf{k}_2}{2}\right) \cdot \Delta t$$

$$\mathbf{k}_4 = \mathbf{f}(t_n + \Delta t, \mathbf{y}_n + \mathbf{k}_3) \cdot \Delta t$$

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \frac{1}{6}(\mathbf{k}_1 + 2\mathbf{k}_2 + 2\mathbf{k}_3 + \mathbf{k}_4)$$

no need to learn it by heart



The Euler and midpoints methods can be considered as a lower-order (1st and 2nd, respectively) of the Runge–Kutta family.

- Other methods (very useful in kinetics):
 - implicit Runge–Kutta, Radau,...
 - multistep methods that rely on information from several previous points to calculate the next one (e.g. Adams–Bashforth–Moulton).
 - algorithms with automatic method and timestep choice (“LSODA”...)

- **Catalysis** is the phenomenon of increasing reaction rate due to a presence of a substance (*catalyst*) that is *not* consumed in the reaction (Ostwald's definition)
Concept coined by Berzelius in 1836.
Conversion of starch to sugars by acids, combustion of hydrogen over platinum, decomposition of hydrogen peroxide by metals are early examples.
 - ▶ A catalyst *cannot* alter the equilibrium constant (or the reaction free energy $\Delta_r G^\circ$) – this would be against the 1st law of thermodynamics (*think why!*).
 - ▶ Catalytic reactions are *complex* reactions. The catalyst forms intermediates with reactants. The catalyst concentration enters the rate law.
 - ▶ A catalyst alters the reaction mechanism. Thus, the catalyst does *participate* in the reaction by forming intermediates. Heterogeneous catalysis always includes *adsorption* (*chemisorption* or *physisorption*) of a reactant on the catalyst surface.
 - ▶ A catalyst *decreases* the activation energy E_a and the activation free energy $\Delta^\ddagger G^\circ$ – to be discussed later.



Jöns Jacob Berzelius
(1779–1848)

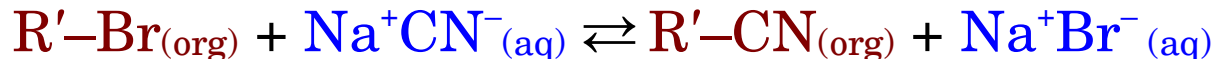


Wilhelm Ostwald
(1853–1932)

- **Classification by phase:**

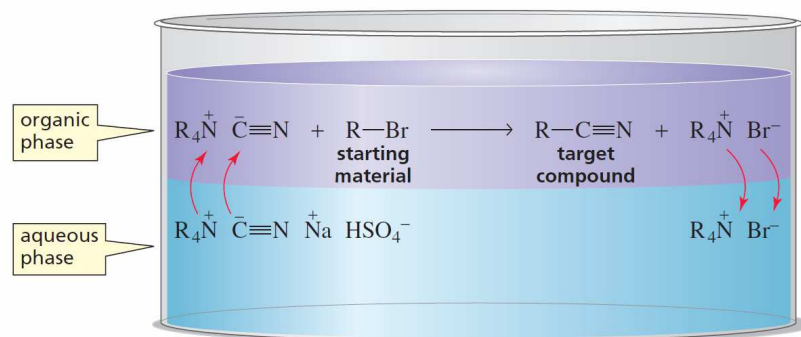
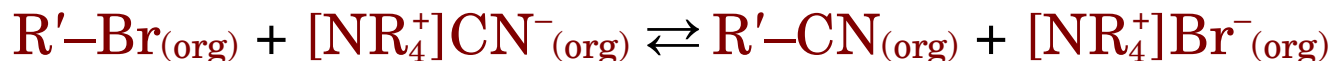
- **Homogeneous** catalysis: both the catalyst and the reactants (“substrates”) are in the same phase (usually liquid or gas);
- **Heterogeneous** catalysis: the catalysts and the reactants are in different phases (usually solid catalyst and liquid or gaseous reactants); occurs through adsorption of reactant(s) on the catalyst surface.
- **Phase-transfer** catalysis (Makosza 1965): an active intermediate is formed in one phase (aqueous), then migrates to react in the other, immiscible phase (organic). Example:

Overall reaction:



Catalyst: $[\text{NR}_4^+]\text{Br}^-_{(\text{org})}$ (R is a bulky alkyl substituent (^tBu or similar))

Mechanism:



- *Classification by catalyst:*

- **Acid-base** catalysis: H^+ or OH^- or a Lewis acid or base as a catalyst; often includes a protonated or deprotonated active intermediates.
- **Coordination complex** catalysis;
- **Organometallic** catalysis: an organometallic complex as a catalyst;
- **Redox** catalysis: changing catalyst oxidation state;
- **Organocatalysis** (2021 Nobel prize) an organic molecule as a catalyst; often a special case of acid-base catalysis; typically stereoselective.
- **Enzymatic** catalysis: a protein (enzyme) as a catalyst;
- **Nanocatalysis**: nanoparticle as a catalyst or catalyst support; often indistinguishable from heterogeneous catalysis.
- **Others**

Think about examples of each kind!

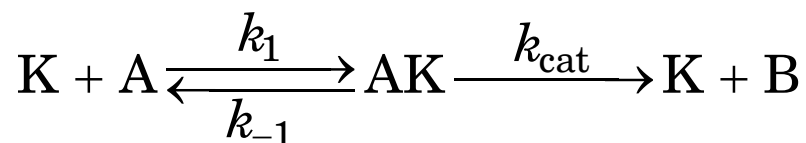
► Most important industrial heterogenous catalytic processes:

Reaction	Catalyst
Catalytic cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co–Mo, Ni–Mo, Ni–W (sulfidic form)
Reforming of naphtha (to gasoline)	Pt, Pt–Re, Pt–Ir
Alkylation	H ₂ SO ₄ , HF, solid acids
Polymerization of ethylene, propylene, a.o.	Cr, TiCl _x /MgCl ₂
Ethylene epoxidation to ethylene oxide	Ag
Vinyl chloride (ethylene + Cl ₂)	Cu (as chloride)
Steam reforming of methane to CO + H ₂	Ni
Water-gas shift reaction	Fe (oxide), Cu–ZnO
Methanation	Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO ₃	Pt–Rh
Acrylonitrile from propylene and ammonia	Bi–Mo, Fe–Sb (oxides)
Hydrogenation of vegetable oils	Ni
Sulfuric acid	V (oxide)
Oxidation of CO & hydrocarbons (car exhaust)	Pt, Pd
Reduction of NO _x (in exhaust)	Rh, vanadium oxide

Chorkendorff, Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics*, Wiley-VCH, 2003

Catalysis – simple model

- A *simple model* of a one-substrate process $A \rightarrow B$ in the presence of catalyst K:



Applying the steady-state approximation to the [AK] intermediate, we eventually obtain:

$$v = \frac{d[B]}{dt} = \frac{k_{\text{cat}}[K]_0[A]}{\frac{k_{-1} + k_{\text{cat}}}{k_1} + [A]} = \frac{v_{\text{max}}[A]}{K_M + [A]}$$

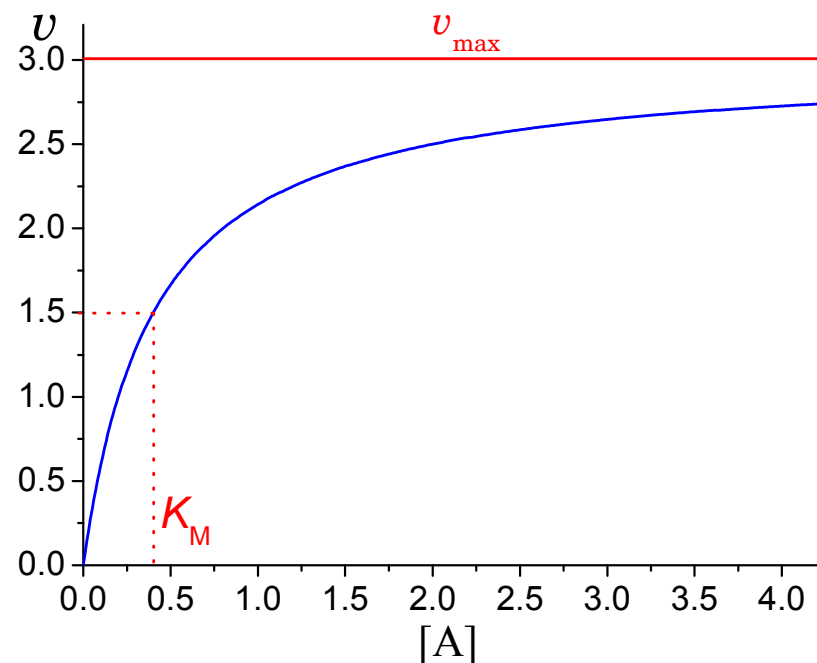
Analogous to Michaelis–Menten equation in *enzymatic catalysis* (not a part of our course).

Different use of the steady-state: $d[B]/dt$ is expressed through $[K]_0$, not $[K]$!

$$[K]_0 = [K] + [AK]$$

Note saturation effect and nearly 0th order with respect to [A] at large [A].

- k_{cat} (in s^{-1}) is called **turnover frequency** (TOF) (or *turnover number* (TON) in enzymatic catalysis). *Meaning*: one molecule of the catalyst can convert a maximum of k_{cat} molecules of the substrate within 1 second.
- Note a different meaning of the *turnover number* (TON) in organo-metallic catalysis: the number of substrate molecules that one catalyst molecule can convert before becoming *inactivated* (*desactivated*).



- **Heterogeneous catalysis:**

► A simple model for a one-substrate reaction (Z stands for the catalyst surface)



Let us apply the steady-state approximation, but expressing the result through $[Z]_0$:

$$d[AZ]/dt = k_1[A][Z] - k_{-1}[AZ] - k_2[AZ] = k_1[A][Z] - (k_{-1} + k_2)[AZ]$$

$$[Z] = [Z]_0 - [AZ]$$

$$d[AZ]/dt = k_1[A][Z] - (k_{-1} + k_2)[AZ] = k_1[A]([Z]_0 - [AZ]) - (k_{-1} + k_2)[AZ] =$$

$$= k_1[A][Z]_0 - (k_1[A] + k_{-1} + k_2)[AZ] = 0 \quad \Rightarrow [AZ] = \frac{k_1[A][Z]_0}{k_{-1} + k_2 + k_1[A]}$$

$$\frac{d[P]}{dt} = k_2[AZ] = \frac{k_2[A][Z]_0}{[A] + \frac{k_{-1} + k_2}{k_1}}$$

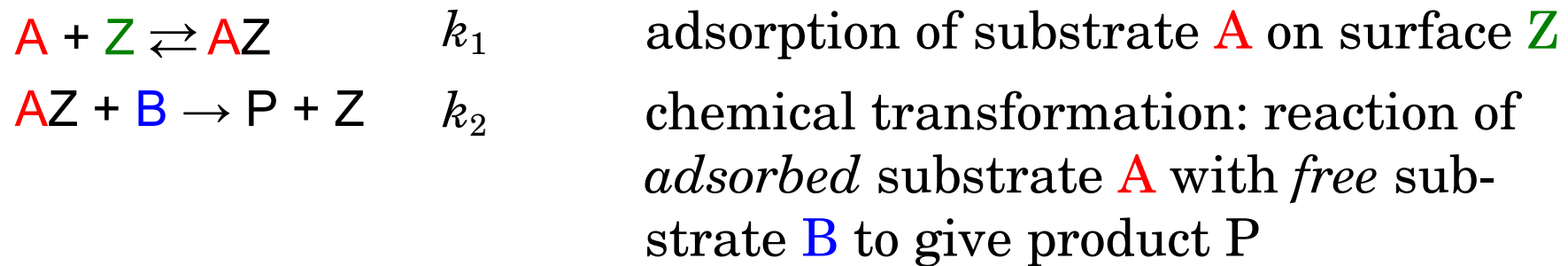
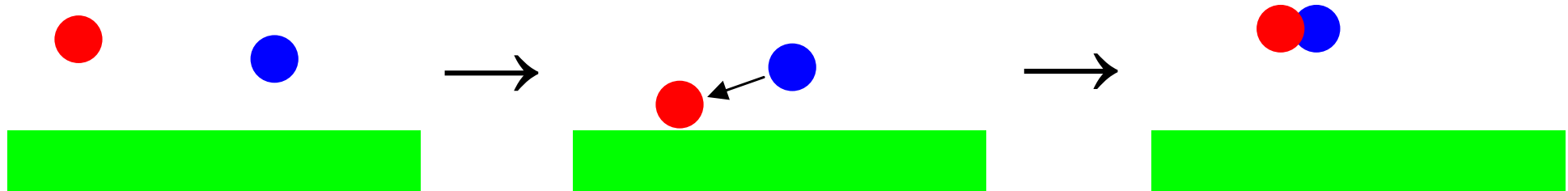
– analogous to the Michaelis–Menten equation

The resulting equation for $d[P]/dt$ is analogous to the Michaelis–Menten equation. But let us now recall that Z is actually a *solid* catalyst; it does not have a *concentration*. Then $[Z]_0$ should be replaced by the *total active surface area* S . In heterogeneous catalysis the reaction rate is measured per unit catalyst surface, i.e., in $\text{M} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$: $v = d[P]/dt / S$

$$v = \frac{d[P]/dt}{S} = \frac{k_2[A]}{[A] + (k_{-1} + k_2)/k_1}$$

- Heterogeneous catalysis:**

► A simple model for a *two-substrate* reaction $A + B \rightarrow P$ (Eley–Rideal 1938):



$$v = \frac{k_1 k_2 [A][B]}{k_1 [A] + k_2 [B] + k_{-1}}$$

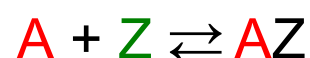
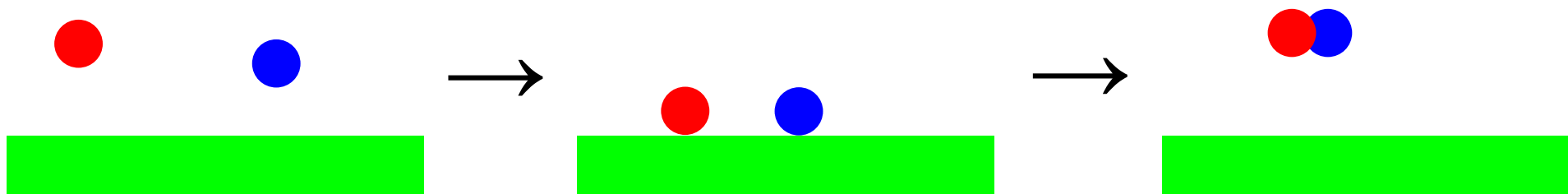
Derivation see in Appendix 9 Page 189.

At large $[B]$: zeroth order with respect to $[B]$ (saturation):

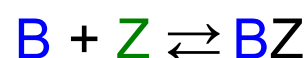
$$v \approx \frac{k_1 k_2 [A][B]}{k_2 [B]} = k_1 [A] = k_1 [A][B]^0$$

- Heterogeneous catalysis:**

► Another model for a *two-substrate* reaction $A + B \rightarrow P$ (Langmuir–Hinshelwood 1926):



adsorption of substrate **A** on surface **Z**



adsorption of substrate **B** on surface **Z**



chemical transformation: reaction of adsorbed substrate **A** with adsorbed substrate **B** to give product **P**

$$v = \frac{k'k''[A][B]}{(1 + k'[A] + k''[B])^2}$$

derivation omitted

At large $[B]$ – negative order(!) with respect to $[B]$ – *autoinhibition*:

$$v \approx \frac{k'k''[A][B]}{(k''[B])^2} = \frac{k'[A]}{k''[B]} = (k'/k'')[A][B]^{-1}$$

- **Heterogeneous catalysis** – more comments:

- ▶ Rate laws in heterogeneous catalysis are often written with *partial pressures* instead of concentrations, if the reactants are in gas phase. The units of rates and of rate constants are adjusted accordingly.
- ▶ In the literature on heterogeneous catalysis, one often operates with *coverage* θ . Notation we have used here ($[AZ]$, $[BZ]$...) are not typical of heterogeneous catalysis.

Coverage θ_A is the number of adsorbed molecules A per the total number of active centers on the surface; or the surface covered by molecules A per the total active surface; thus, θ_A is used instead of our $[AZ]$:

$$\theta_A = [AZ]/[Z]_0$$

For instance, if there are two adsorbed substances A and B, the coverage of *vacant* sites on the surface is $1-\theta_A-\theta_B$; it is used instead of our $[Z]$:

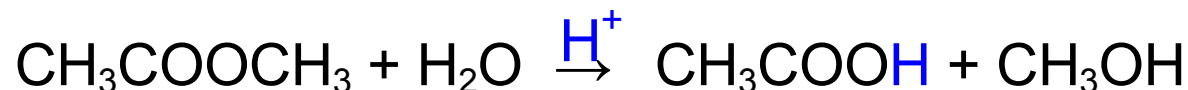
$$1-\theta_A-\theta_B = [Z]/[Z]_0$$

Coverage is dimensionless and is between 0 and 1.

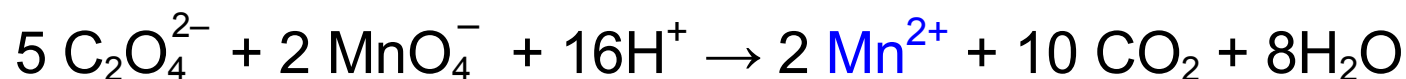
- **Autocatalysis** (Ostwald 1890): a product is the catalyst.

- ▶ Examples:

- Acid-catalyzed reactions in which an acid is formed:



- Some redox reactions:



- Formose reaction (Butlerov 1861):



- ▶ Biochemical examples:

- Formation of **trypsin** from trypsinogen;
- Glycolysis (two ATP molecules are consumed in one phase, but four are produced in a subsequent phase).

- ▶ Non-chemical examples:

- Human or animal reproduction;
- Infectious disease proliferation;
- Economic growth.

- Autocatalytic reactions are usually complex reactions.
 - ▶ Nevertheless, it is possible to describe them using simple models, e.g.:

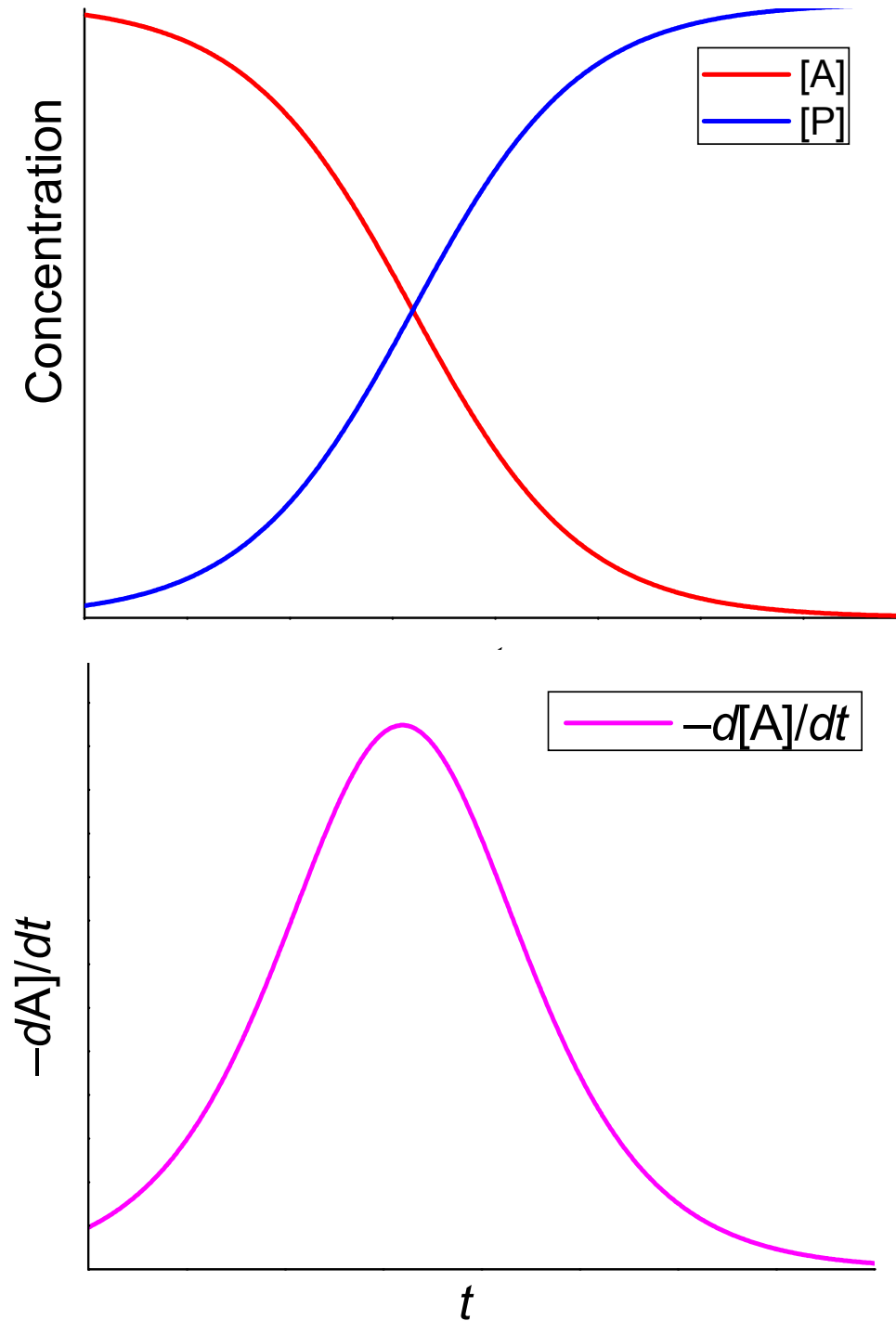


- Analytically solvable (solution is similar to that on page 28. See also *Problem Booklet* problems 2.2–2.4):

$$[A]_t = [A]_0 \frac{[A]_0 + [P]_0}{[A]_0 + [P]_0 e^{k([A]_0 + [P]_0)t}}$$

$$[P]_t = [P]_0 \frac{([A]_0 + [P]_0)e^{k([A]_0 + [P]_0)t}}{[A]_0 + [P]_0 e^{k([A]_0 + [P]_0)t}}$$

Autocatalysis – model

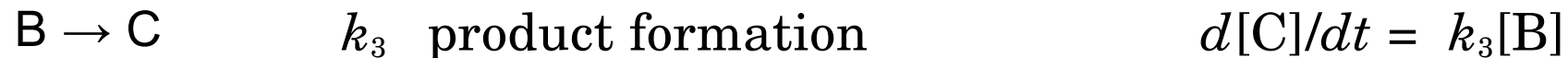


Reaction first accelerates, then decelerates. Maximum rate is achieved when $[A] = [P]$.

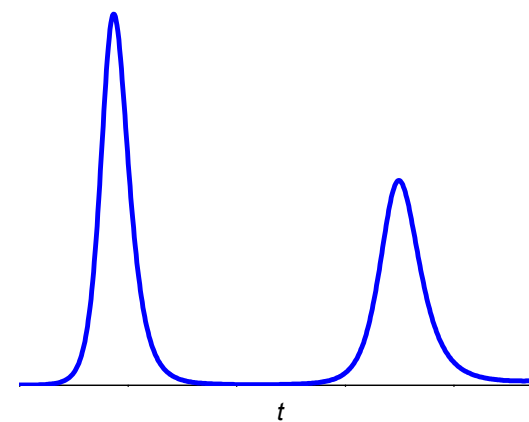
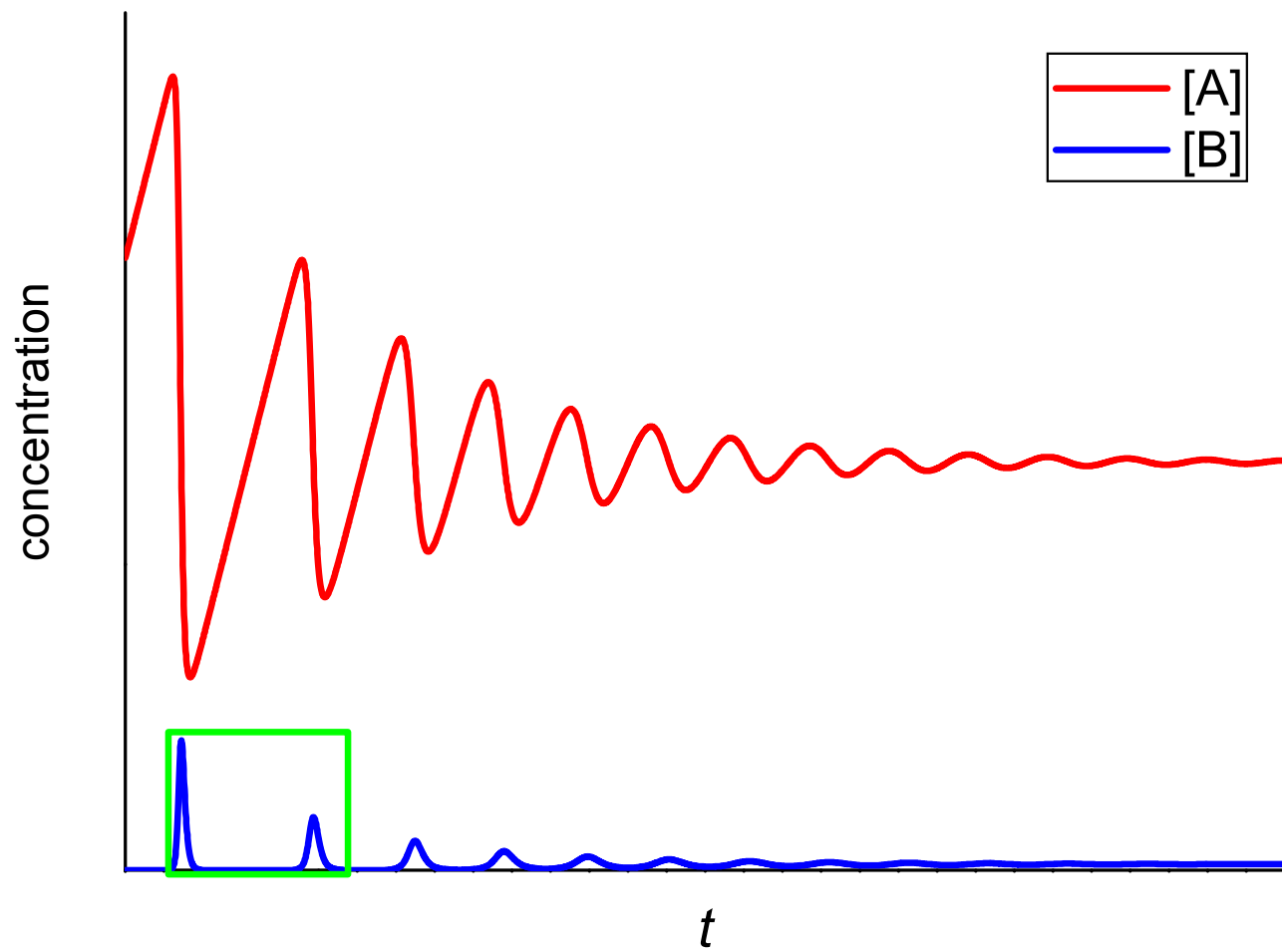
Oscillating reactions

- Oscillating reactions – concentration oscillates with time!

► Simplest model – first Lotka model (*damped* (*cat. esmorteïdes*) oscillations):



Some $[B] > 0$ is needed to start the autocatalytic process. Let's start with a very small $[B]$, such that $k_1 \gg k_2[A][B]$. Also, as long as $[A]$ and $[B]$ are small, $k_3 > k_2[B] \Rightarrow d[B]/dt < 0$ and $[B]$ further decreases. In the beginning $k_1 - k_2[A][B]$ remains almost constant, and $[A]$ increases almost linearly. But with A accumulating, $k_1 - k_2[A][B]$ switches to negative $\Rightarrow [A]$ starts decrease. At this moment still $k_2[A] > k_3$, so $d[B]/dt > 0$ and $[B]$ is increasing. At some moment, when $[A]$ is small enough, $d[B]/dt$ becomes negative again and B start to decrease again. The $[B]$ oscillations are shifted with respect to $[A]$ oscillations.



Oscillating reactions

- Oscillating reactions

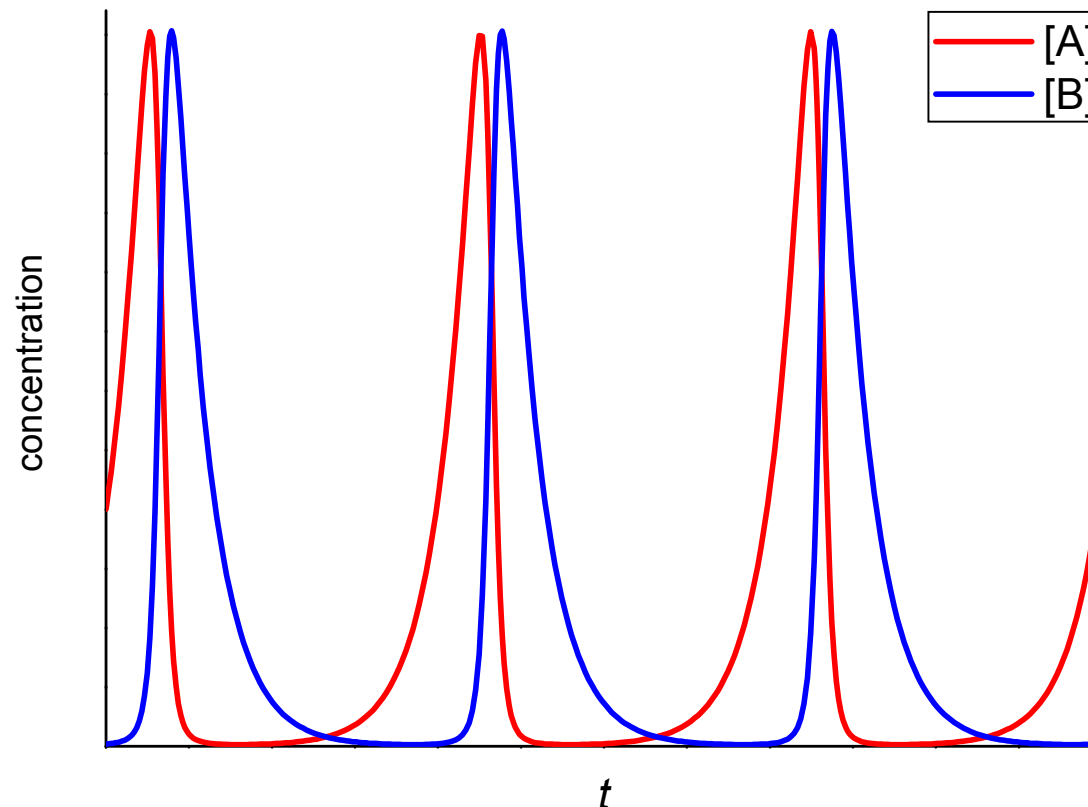
► Another simple model – Lotka–Volterra (undamped oscillations):

$A \rightarrow 2A$ autocatalytic step: rabbit reproduction

$A + B \rightarrow 2B$ inhibition (or predation) step: foxes eat rabbits and reproduce

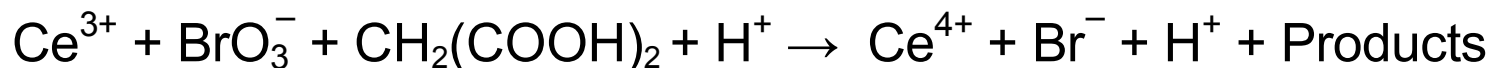
$B \rightarrow C$ foxes die

Does not exist in chemistry, but corresponds to prey-predator dynamics in biology.



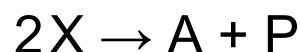
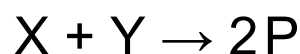
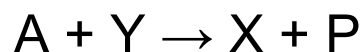
Oscillating reactions – real examples

- Oscillating reactions are real (Belousov–Zhabotinsky, Briggs–Rauscher...)
 - Real chemical example – the Belousov–Zhabotinsky reaction:



Oscillations of $[\text{Ce}^{3+}]$ and $[\text{Ce}^{4+}]$.

Simplified mechanism (“Oregonator” model):



where $\text{A} = \text{BrO}_3^-$; $\text{B} = \text{CH}_2(\text{COOH})_2$; $\text{X} = \text{HBrO}_2$; $\text{Y} = \text{Br}^-$; $\text{Z} = \text{Ce}^{4+}$; $\text{P} = \text{HOBr}$.



Boris Belousov
(1893–1970)



Anatoly Zhabotinsky
(1938–2008)

Dependence of rate constants on temperature

- A simple rule of thumb:
Increase in temperature by 10 K typically results in a reaction rate increase by a factor of 2 to 4:
 $k(T) = a\gamma^{T/10K} \quad (2 < \gamma < 4).$

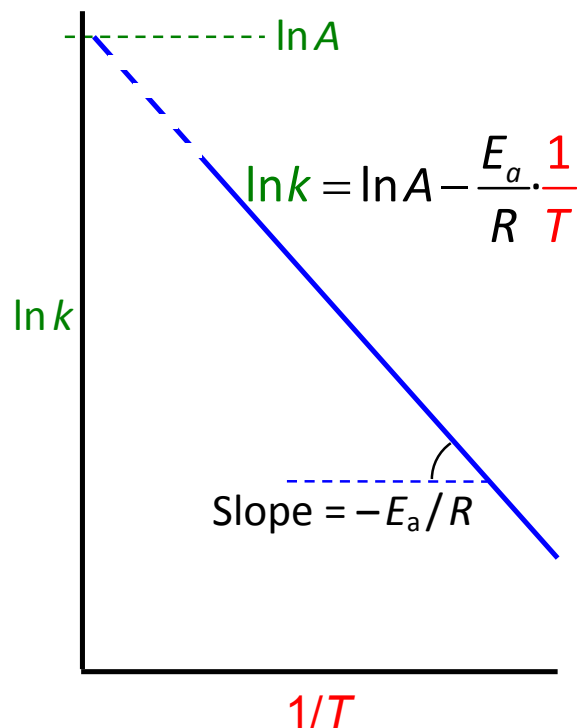
- Arrhenius equation (1889) – originally due to

Hood and van't Hoff (1884)): $k = Ae^{-\frac{E_a}{RT}}$

E_a is referred to as **activation energy**.

A is the **pre-exponential** or **frequency** factor.

► Linearized form:



Jacobus Henricus van't Hoff
(1852–1911)



Svante Arrhenius
(1859–1927)

Arrhenius equation – interpretation

- ▶ The activation energy E_a is almost always positive, but can be *slightly* negative in exceptional cases, when k decreases with T .
- ▶ For a reaction to be observable at room temperature, E_a should be $\leq \sim 25$ kcal/mol (~ 100 kJ/mol)
- Not all the molecules A are able to react; only those “active” molecules A^* with energy higher than a certain threshold (*llindar*) E_a will do.
- ▶ Arrhenius’ idea: “active” and “non-active” molecules are in equilibrium $A \rightleftharpoons A^*$:

$$\frac{[A^*]}{[A]} = e^{-\frac{E_a}{RT}}$$

where $\exp(-E_a/RT)$ gives a share of molecules that have an energy greater than E_a .

- ▶ For bimolecular reactions, $\exp(-E_a/RT)$ is a share of reactive collisions, while A is the collision frequency (approximately). That's why the term *frequency factor* for A .
- ▶ The Arrhenius equation is enormously helpful and very widely used. However, it is approximate rather than fundamental.

Activation energies – examples

- Arrhenius parameters:

First-order reactions	A, s^{-1}	$E_a, \text{kJ/mol}$
$\triangle \rightarrow \diagup$	$1.58 \cdot 10^{15}$	272
$\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$	$3.98 \cdot 10^{13}$	160
$\text{cis-CHD=CHD} \rightarrow \text{trans-CHD=CHD}$	$3.16 \cdot 10^{12}$	256
Cyclobutane $\rightarrow 2\text{C}_2\text{H}_4$	$3.98 \cdot 10^{15}$	261
$\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$	$2.51 \cdot 10^{13}$	209
$\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3^\bullet$	$2.51 \cdot 10^{17}$	384
$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$	$4.94 \cdot 10^{13}$	103
$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$	$7.94 \cdot 10^{11}$	250
$\text{C}_2\text{H}_5^\bullet \rightarrow \text{C}_2\text{H}_4 + \text{H}^\bullet$	$1.0 \cdot 10^{13}$	167

Second-order reactions	$A / (\text{L mol}^{-1} \text{s}^{-1})$		$E_a / (\text{kJ mol}^{-1})$	P
	Experiment	Theory		
$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$	9.4×10^9	5.9×10^{10}	102.0	0.16
$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	2.0×10^9	4.0×10^{10}	111.0	5.0×10^{-2}
$2\text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	6.3×10^7	2.5×10^{10}	0.0	2.5×10^{-3}
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	1.24×10^6	7.3×10^{11}	180	1.7×10^{-6}
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	1.0×10^{12}	2.1×10^{11}	0.0	4.8

Modified Arrhenius equation

- More accurate is the *modified* Arrhenius equation (Kooij, van't Hoff 1893):

$$k = k(T) = aT^m e^{-E'/RT}$$

- ▶ Linearized form:

$$\ln\left(\frac{k}{T^m}\right) = \ln a - \frac{E'}{R} \cdot \frac{1}{T}$$

- ▶ m is usually predicted from theoretical considerations rather than a fully empirical parameter.

- ▶ The collision theory for elementary bimolecular reactions predicts $m = 1/2$:

- The mean *translational* kinetic energy is proportional to T :

$$\bar{E}_{\text{tr.kin}} = \frac{3}{2} k_B T$$

- On the other hand, $\bar{E}_{\text{tr.kin.}}$ is proportional to the *square* of the mean molecular velocity: $\bar{E}_{\text{tr.kin.}} = m\bar{v}^2/2 \Rightarrow \bar{v} = \sqrt{3k_B T / m}$

- The *collision frequency* is proportional to \bar{v} and thus to \sqrt{T} .

\Rightarrow The rate of a bimolecular reaction is proportional to $\sqrt{T} \exp(-E'/RT)$, where E' is some *threshold* energy (the energy necessary to react)

- ▶ Reaction rate increases with temperature mainly because at a higher temperature *more molecules have energies* $>E'$. The increase of the *collision frequency* is a *minor* effect.

- ▶ More elaborate theories (such as the Transition-State Theory) predict various integer or half-integer m values ($m = 1/2, 1, 3/2$, or $-1/2, -1..$) depending on the molecular structure.

- Relation to the Arrhenius equation is as follows:

$$k = aT^m e^{-\frac{E'}{RT}} \Rightarrow \ln k = \ln a + m \ln T - \frac{E'}{RT}$$

$$k = Ae^{-\frac{E_a}{RT}} \Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

Differentiating both equations yields the following:

$$\frac{d \ln k}{dT} = \frac{m}{T} + \frac{E'}{RT^2} = \frac{mRT + E'}{RT^2}$$

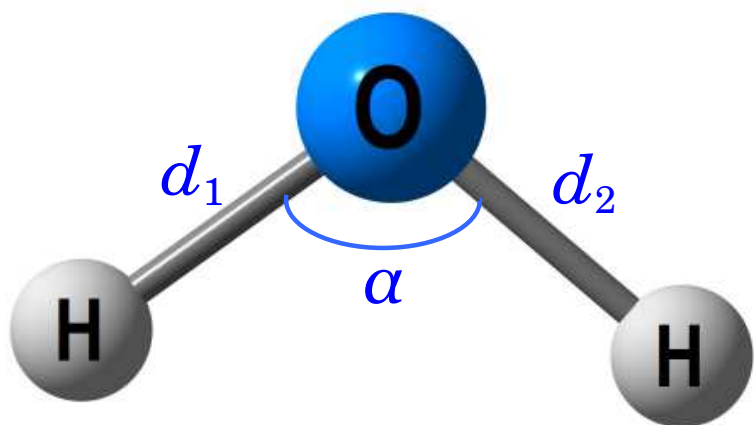
$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

Comparing these two equations we conclude that $E_a = E' + mRT$.

- Usually this relation is used to obtain the E' energy from the Arrhenius activation energy as follows: $E' = E_a - mRT$

- The ultimate purpose of all the *theories of the elementary event of reaction* (= reaction dynamics) is to calculate the *rate constant* from some *molecular data*.
- In other words, *Reaction Dynamics* is the study of the mechanism of an elementary chemical reaction at molecular level.
- Kinetics theory:
 - ▶ ~~Collision theory~~
 - ▶ Potential energy surface
 - ▶ Transition state theory
 - ▶ Solvent effect
 - ▶ Kinetic salt effect
 - ▶ Kinetic isotope effect
 - ▶ Tunnel effect
 - ▶ ~~Unimolecular reactions (Lindemann-Hinshelwood, RRK, RRKM theories)~~
 - ▶ Dynamics of the elementary act
 - ▶ ~~Electron-transfer processes; Marcus theory~~

- Consider water molecule



We can characterize its structure (“geometry”) by two O–H distances (d_1 , d_2) and one H–O–H angle (α).

At equilibrium, $d_1 = d_2 = 0.9584 \text{ \AA}$; $\alpha = 104.45^\circ$. Each combination (d_1 , d_2 , α) corresponds to a different *geometry* and has a different *energy*.

- ▶ Thus, the *energy* depends on the parameters d_1 , d_2 , α : $E = E(d_1, d_2, \alpha)$
Such a function $E(d_1, d_2, \alpha)$ is referred to as a *potential energy (hyper)-surface* (*PES*) The meaning of the term *surface* will become clear later.
- ▶ The equilibrium geometry corresponds to a *minimum* of $E(d_1, d_2, \alpha)$, since we have to produce a work (= to spend energy) to move an atom away from the equilibrium position.
- Quantum-mechanically, we can solve the electronic Schrödinger equation (e.g. by running the Gaussian program – *the EQF course!*): $\hat{H}_e \Psi_e = \mathbf{E} \Psi_e$. For different geometries \mathbf{E} will be different. Thus, $E(d_1, d_2, \alpha)$ can be calculated by repeatedly running Gaussian.
- Here we have implicitly used the Born–Oppenheimer approximation – s. next page 101.

Potential energy surface – where does it come from?

- In **Quantum Mechanics**, a molecule is a collection of interacting nuclei and electrons that behaves as a **wave** and is described by a wavefunction $\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{r}_1, \dots, \mathbf{r}_n)$

where $\mathbf{R}_i = X_i, Y_i, Z_i$ are coordinates of i th nucleus

$\mathbf{r}_i = x_i, y_i, z_i$ are coordinates of i th electron.

Time-independent Schrödinger equation: $\hat{H}\Psi = E\Psi$

where $\hat{H}(\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{r}_1, \dots, \mathbf{r}_n) = \hat{T}_N(\mathbf{R}_1, \dots, \mathbf{R}_N) + \hat{T}_e(\mathbf{r}_1, \dots, \mathbf{r}_n) + \hat{V}_{NN}(\mathbf{R}_1, \dots, \mathbf{R}_N) + \hat{V}_{eN}(\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{r}_1, \dots, \mathbf{r}_n) + \hat{V}_{ee}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is the molecular **Hamiltonian**

Such a description is exact and universal, but hardly useful.

- It is very common to use the **Born–Oppenheimer approximation**, in which the motion of nuclei and electrons is separated:

$$\hat{H}_e(\mathbf{R}_1, \dots, \mathbf{R}_N | \mathbf{r}_1, \dots, \mathbf{r}_n) \Psi_e(\mathbf{R}_1, \dots, \mathbf{R}_N | \mathbf{r}_1, \dots, \mathbf{r}_n) = E_e(\mathbf{R}_1, \dots, \mathbf{R}_N) \Psi_e(\mathbf{R}_1, \dots, \mathbf{R}_N | \mathbf{r}_1, \dots, \mathbf{r}_n)$$

Now the electronic energy E_e depends on nuclear coordinates as parameters, i.e., every nuclear configuration $\mathbf{R}_1, \dots, \mathbf{R}_N$ corresponds to its own electronic energy $E_e(\mathbf{R}_1, \dots, \mathbf{R}_N)$. This E_e serves as *potential* in the Schrödinger equation for the nuclear motion:

$$\hat{H}_N(\mathbf{R}_1, \dots, \mathbf{R}_N) \Psi_N(\mathbf{R}_1, \dots, \mathbf{R}_N) = E_N \Psi_N(\mathbf{R}_1, \dots, \mathbf{R}_N)$$

$$\text{where } \hat{H}_N(\mathbf{R}_1, \dots, \mathbf{R}_N) = \hat{T}_N(\mathbf{R}_1, \dots, \mathbf{R}_N) + E_e(\mathbf{R}_1, \dots, \mathbf{R}_N)$$

Potential energy surface – where does it come from?

- The function $E_e(\mathbf{R}_1, \dots, \mathbf{R}_N)$ is referred to as the *potential energy surface* (PES, *superfície d'energia potencial*). Its physical meaning is that every nuclear configuration $\mathbf{R}_1, \dots, \mathbf{R}_N$ corresponds to a certain energy E_e .
- In general, the motion of nuclei is described by the nuclear Schrödinger equation (see page 101 above), but sometimes we can consider the nuclear motion as classical (not quantum-mechanical) motion in the same potential.
- The change in the potential energy is minus work made by molecular forces over the trajectory of the molecular motion: $\Delta E = W = -\int \mathbf{F} d\mathbf{s}$. Hence, the force should be minus derivative of the potential energy. More specifically:
- the partial derivative of the PES with respect to each coordinate (with opposite sign) gives the corresponding component of *force* acting on the atoms:

$$F_{x_1} = -\frac{\partial E}{\partial x_1}; \quad F_{y_1} = -\frac{\partial E}{\partial y_1}; \quad F_{z_1} = -\frac{\partial E}{\partial z_1} \quad \text{in Cartesian coordinates}$$

Note: the vector of all the partial derivatives of a function

$f(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N)$ is referred to as *gradient* of f :

$$\begin{aligned} \text{grad } f(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N) &\equiv \nabla f(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N) = \\ &= (\partial f / \partial x_1, \partial f / \partial y_1, \partial f / \partial z_1, \partial f / \partial x_2, \partial f / \partial y_2, \partial f / \partial z_2, \dots, \partial f / \partial x_N, \partial f / \partial y_N, \partial f / \partial z_N) \end{aligned}$$

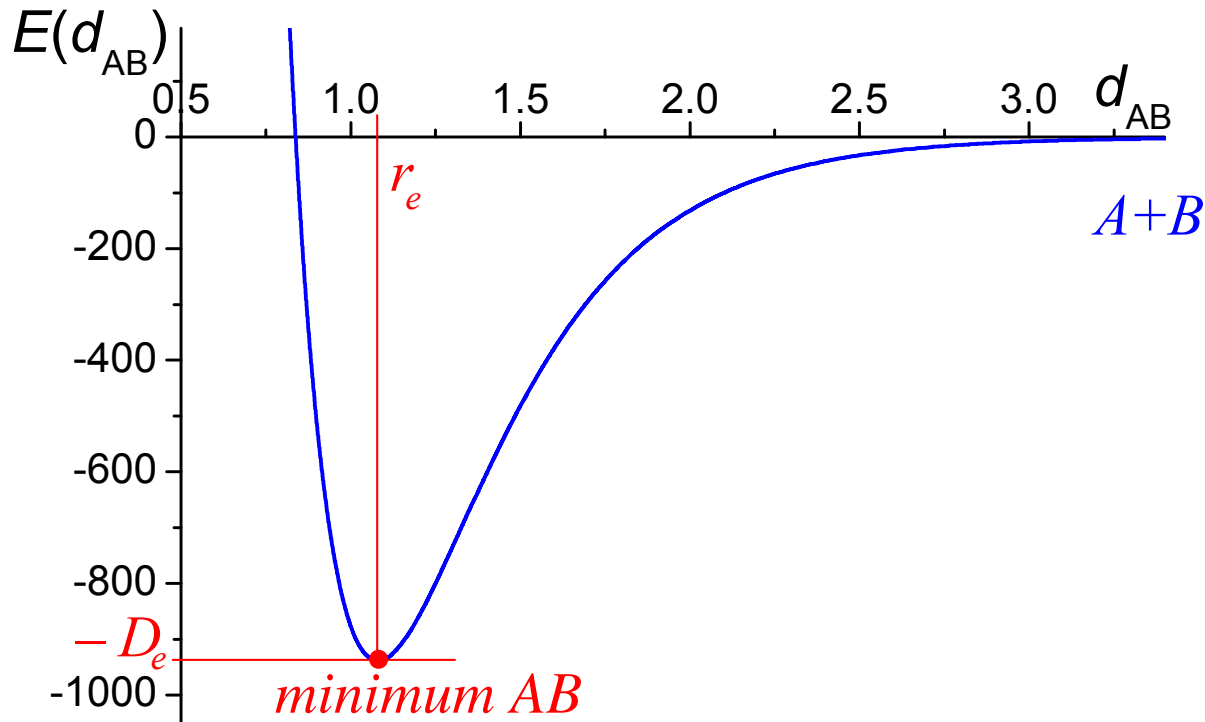
- Typically, in the course of reaction there is some bond formation or bond breaking or both.
 - ▶ Some characteristic distances in the molecule change strongly in the course of reaction since the distance between *bonded* atoms is usually much smaller than between non-bonded ones.
 - ▶ We need some geometric parameters to characterize these changes.
- The PES is usually considered in *internal* coordinates rather than the Cartesians. Internal coordinates characterize relative positions of nuclei. See page 100 for H₂O example.

Potential energy surface – internal coordinates and degrees of freedom

- Consider an entire *reacting molecular system*, consisting of two molecules (for a bimolecular reaction) or of a single molecule (for a unimolecular reaction).
 - ▶ If this system has N atoms, we have $3N$ *degrees of freedom* and need $3N$ Cartesian coordinates $\{x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N\}$ to describe its structure.
 - ▶ Instead, we can separate the *translational* and *rotational* motion and choose:
 - some 3 coordinates (e.g., X, Y, Z of the *center of mass*) to characterize the *translational motion* of the entire system; and
 - some 3 coordinates (e.g., angles φ, θ, ψ) to characterize the rotational motion of the entire system;
 - For a *linear* system (e.g., a diatomic molecule) there are only 2 (not 3) rotational coordinates;
 - some $3N-6$ (or $3N-5$ in the linear case) coordinates are needed to describe vibrations and chemical changes. These (non-linear) combinations of the Cartesian coordinates are called *internal coordinates*; commonly used are:
 - interatomic distances d_{AB} ; angles α_{ABC} ; dihedral angles β_{ABCD} .
- Instead of talking of the motion of N atoms in our usual 3D physical space, we can unite all the $3N$ coordinates (or $3N-6$) and consider them as a coordinates of a single *figurative* point in a $3N$ -dimensional space (or $3N-6$ dimensional).
 - ▶ The motion of the entire molecule or a reacting system is then represented by the motion of that figurative point.

Potential energy surface – diatomic molecule

- For a diatomic molecule AB, upon separation of 3 center-of-mass coordinates and 2 rotational angles, only one internal coordinate d_{AB} remains.



- Minimum position corresponds to the **equilibrium distance** r_e and dissociation energy D_e .
 - ▶ When $d_{AB} > r_e$, $-\partial E / \partial d_{AB} < 0$ and there is a *attraction force* returning the molecule to the equilibrium distance.
 - ▶ When $d_{AB} < r_e$, $-\partial E / \partial d_{AB} > 0$ and there is a *repulsion force* also returning the molecule to the equilibrium distance.

Thus, **vibrations** take place.

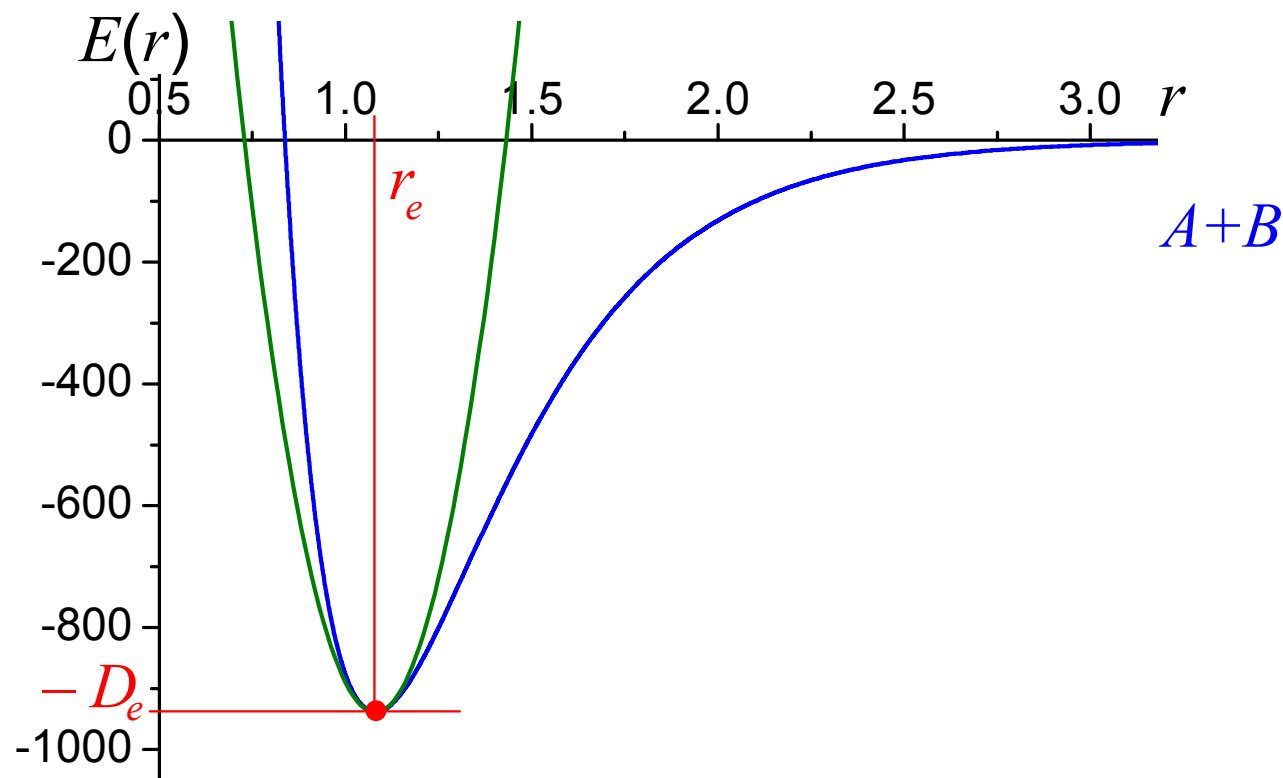
Potential energy surface – diatomic molecule

- Analytic approximations to the PES for a diatomic molecule AB:

- **Harmonic approximation** (quadratic potential suitable to describe small-amplitude vibrations, but not dissociation):

f is the *force constant*, ν is the *vibrational frequency*, μ is the *reduced mass*:

$$f = \frac{d^2 E(r)}{dr^2} \quad E(r) = \frac{f}{2}(r - r_e)^2 \quad \nu = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}}$$

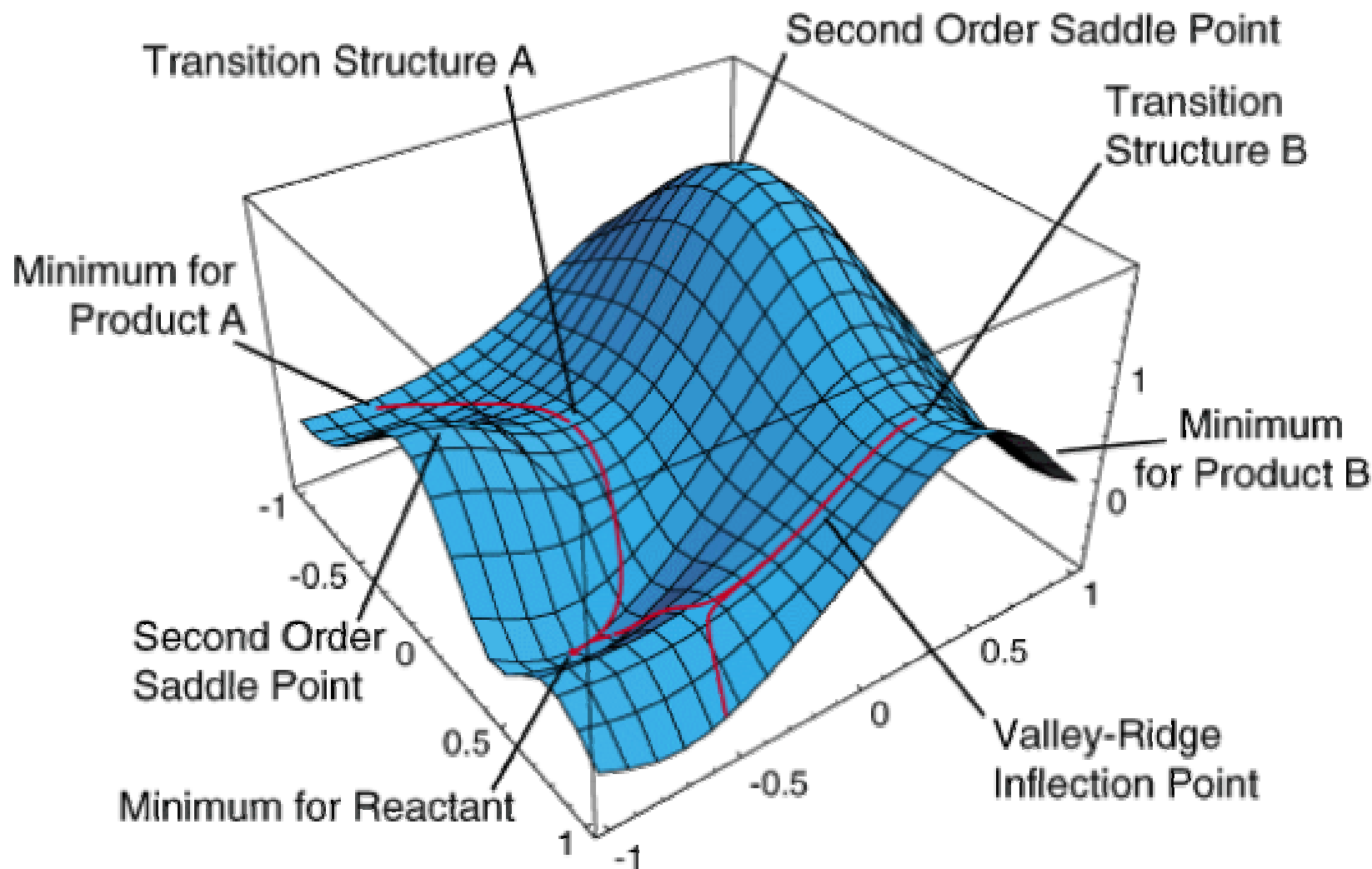


- **Morse potential** (also an approximation, but properly describes dissociation as well as anharmonicity):

$$E(r) = D_e \left(e^{-2\beta(r-r_e)} - 2e^{-\beta(r-r_e)} \right) = D_e \left(1 - e^{-\beta(r-r_e)} \right)^2 - D_e$$

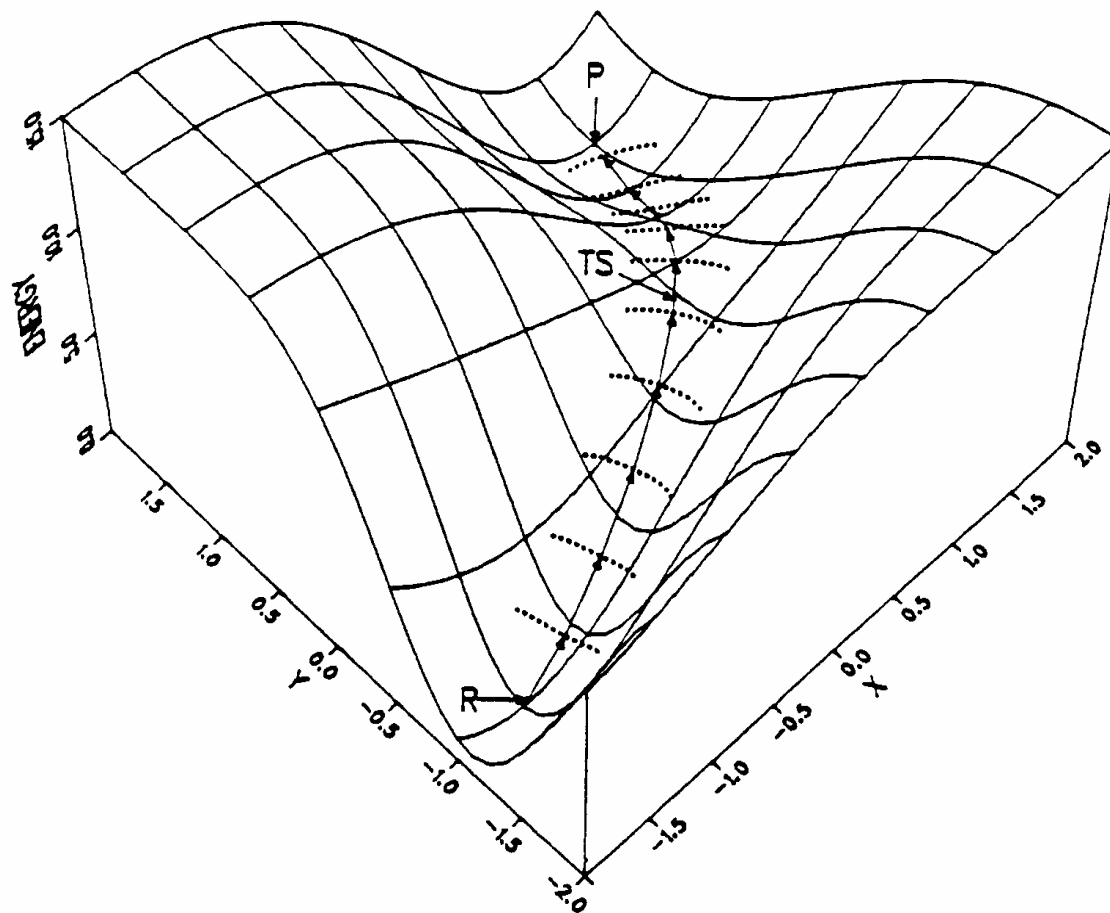
Potential energy surface – polyatomic molecule or reacting system

- In general, the PES is a multidimensional function, represented by a *hypersurface*.



- Reactants, products and intermediates are (local) minima on the PES.

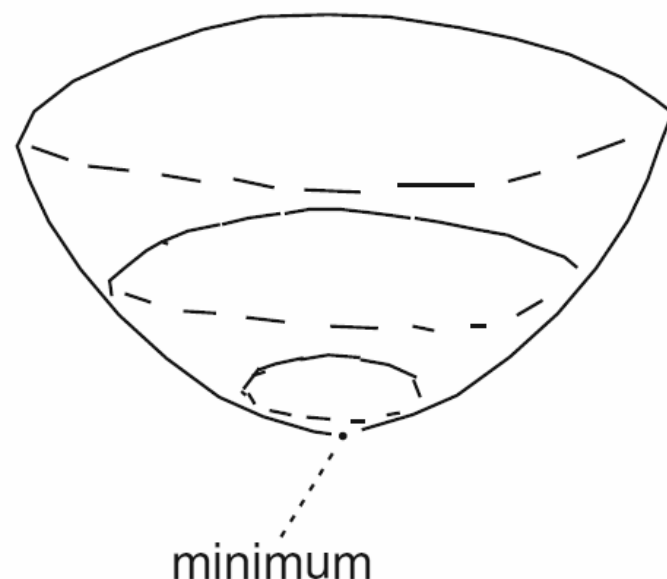
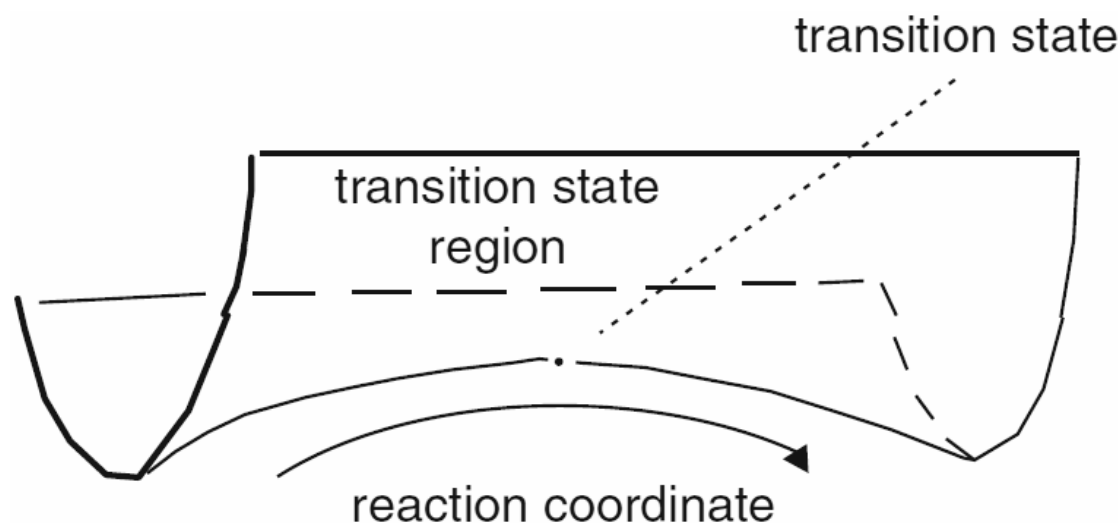
Potential energy surface – various trajectories



- The **reaction coordinate** (reaction path(way)) (= *coordenada de reacció, camí de reacció*) is a path (curve) on the PES along which the energy is a minimum with respect to any *lateral* displacement.
- The **transition state (TS)** (= *estat de transició*) is the highest-energy point on the reaction pathway.
 - Usually, two minima are linked by a single reaction path containing a transition state. However, sometimes, alternative pathways are possible.

Potential energy surface – stationary points

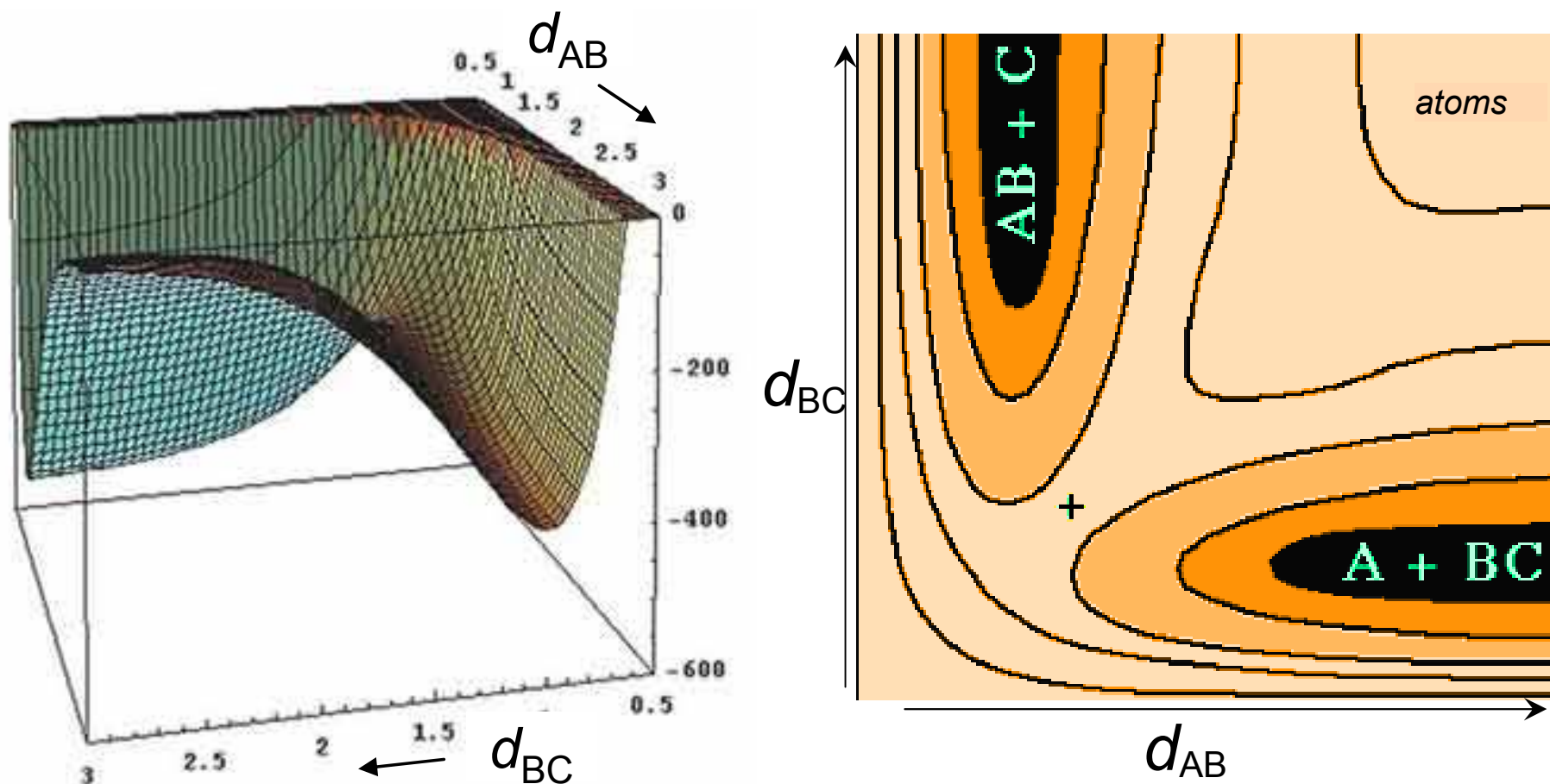
- Equilibrium configurations of molecules correspond to local energy ***minima***:
 - Forces (gradient) vanish in a minimum: $\nabla E = 0$;
 - At small deviation from a minimum, there are forces *returning* the system to the minimum.
- Transition states correspond to ***saddle points*** (*punts de sella*):
 - Forces (gradient) also vanish in a transition state;
 - A transition state is an energy *maximum* with respect to the reaction coordinate, but a *minimum* with respect to all other coordinates:



- All the points on the PES where gradient vanishes ($\nabla E = 0$) are called ***stationary points***. These are *minima*, *transition states*, higher-order saddle points, and maxima. The latter two types play no role in chemistry (see page 118).

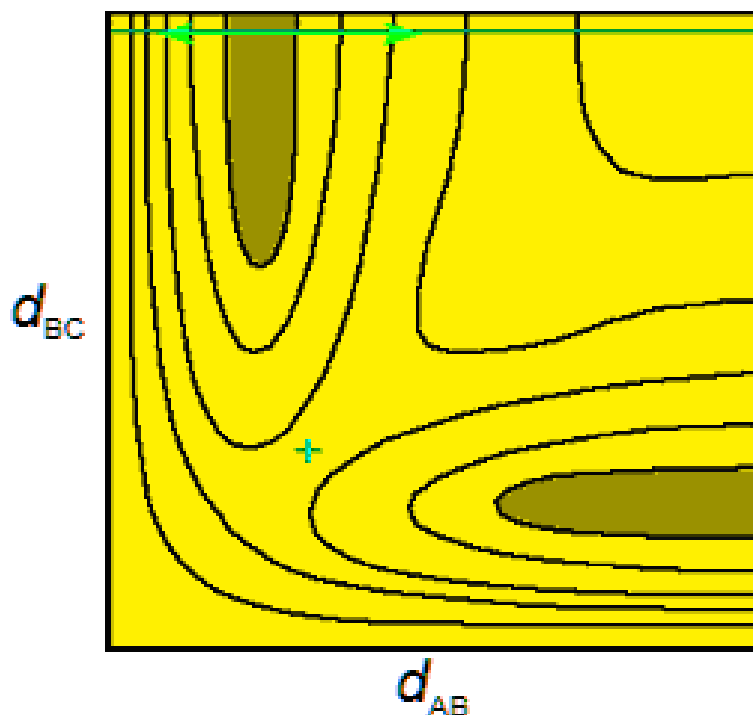
Potential energy surface – triatomic system

- The PES for a triatomic system is a function of $3 \times 3 - 6 = 3$ variables \Rightarrow no graphical representation is possible. In this case we consider a **reduced potential energy surface**, choosing a *subset* of variables (usually interatomic distances, but possibly angles or dihedral angles) whose changes represent the process under study.
- For a chemical process $A + BC \rightarrow AB + C$, it is common to consider the reduced PES in coordinates $E(d_{AB}, d_{BC})$ (bond B–C breaking, bond A–B forming):

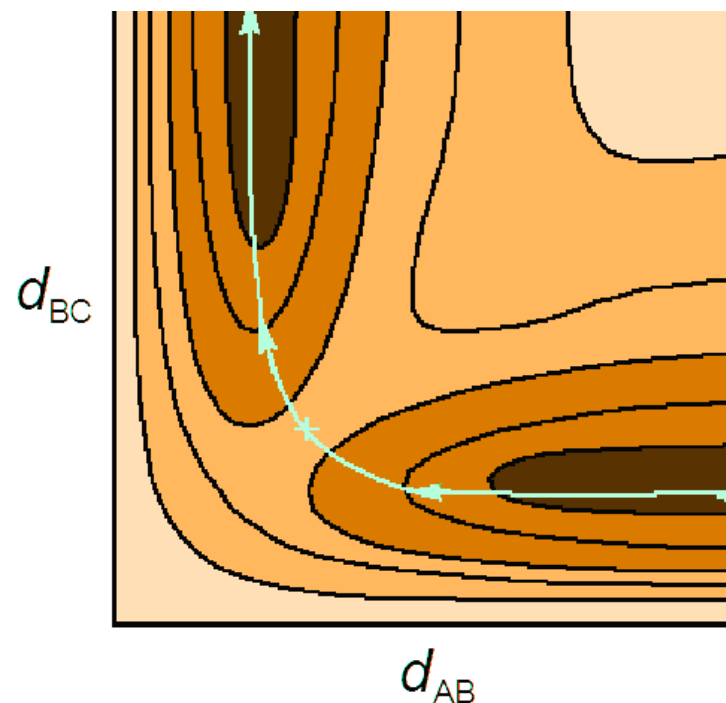


Potential energy surface – various trajectories

- Various trajectories:



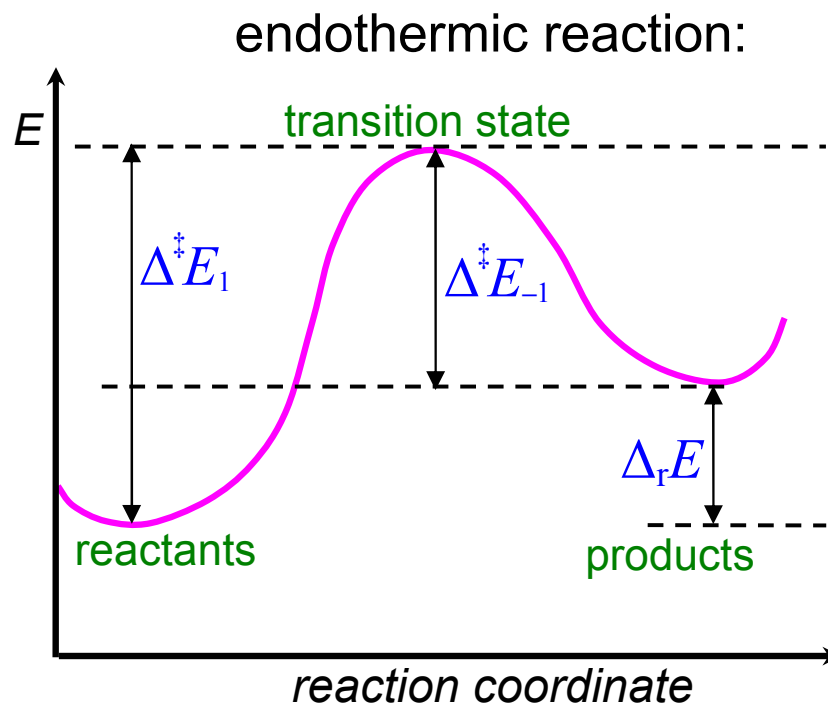
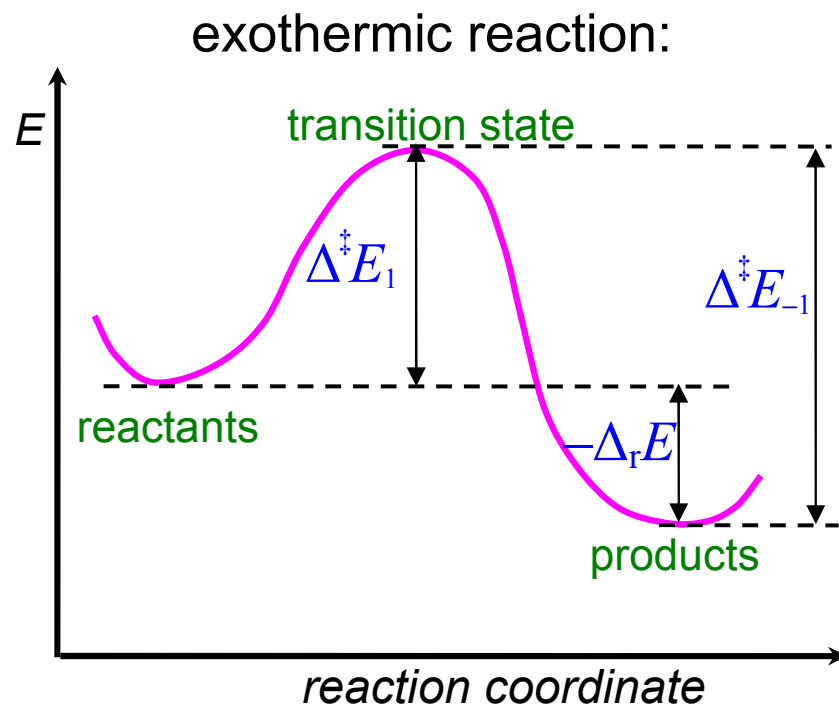
A–B vibrations



$A + BC \rightarrow AB + C$ reaction through TS

- The **reaction coordinate** (*reaction path(way)*) (= *coordenada de reacció, camí de reacció*) is a path (curve) on the PES along which the energy is a minimum with respect to any lateral displacement.
- The **transition state** (= *estat de transició*) is the highest-energy point on the reaction pathway.
 - Usually, two minima are linked by a single reaction path containing a transition state. However, sometimes, alternative pathways are possible.
- A reactive trajectory **does not need** to proceed exactly through the transition state!

Potential energy surface – reaction profile



- $\Delta^\ddagger E$ is referred to as the *reaction energy barrier*. Sometimes it is also called *activation energy* – be careful, this is not correct!
- The reaction energy is related to the energy barriers for the forward and reverse reaction: $\Delta_r E = \Delta^\ddagger E_1 - \Delta^\ddagger E_{-1}$.
- The same philosophy applies to other types of energies: $\Delta^\ddagger G$, $\Delta^\ddagger H$... For instance, $\Delta_r G = \Delta^\ddagger G_1 - \Delta^\ddagger G_{-1}$.

Potential energy surface – search for and characterization of stationary points

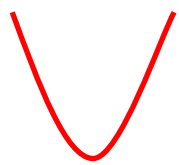
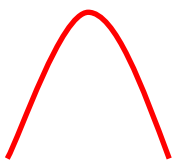

- The criterion of a stationary point is the zero gradient: $\nabla E(q_1, q_2, q_3, \dots, q_N) = 0$, where q_1, q_2, q_3, \dots are *internal* or Cartesian coordinates.

$$\begin{cases} \frac{\partial E}{\partial q_1} = 0 \\ \frac{\partial E}{\partial q_2} = 0 \\ \dots \\ \frac{\partial E}{\partial q_N} = 0 \end{cases}$$

- In one-dimensional case (e.g., for a diatomic molecule), a single equation appears:

$$\frac{dE}{dq} = 0$$

In this case, the **characterization** of the stationary point is based on the second derivative (force constant):

$\frac{d^2 E}{dq^2} > 0$	$\frac{d^2 E}{dq^2} < 0$	$\frac{d^2 E}{dq^2} = 0$
minimum	maximum	inflexion point
		

Potential energy surface – characterization of stationary points

- **Characterization** of a stationary point for a multi-dimensional function $E(q_1, q_2, q_3, \dots, q_N)$ is more sophisticated. It is *not enough* to find the second derivatives (force constants) $\partial^2 E / \partial q_1^2, \partial^2 E / \partial q_2^2, \partial^2 E / \partial q_2^2, \dots, \partial^2 E / \partial q_N^2$.

► To understand this let us first consider a function $f(x, y)$:

$$f(x, y) = x^2 + y^2$$

It has a single minimum $x=0, y=0$:

$$\partial f(0,0) / \partial x = \partial f(0,0) / \partial y = 0$$

$$\partial^2 f(0,0) / \partial x^2 > 0$$

$$\partial^2 f(0,0) / \partial y^2 > 0$$

► Now consider another function $g(x, y)$:

$$g(x, y) = x^2 + y^2 + 6xy$$

It also has a stationary point at $x=0, y=0$.

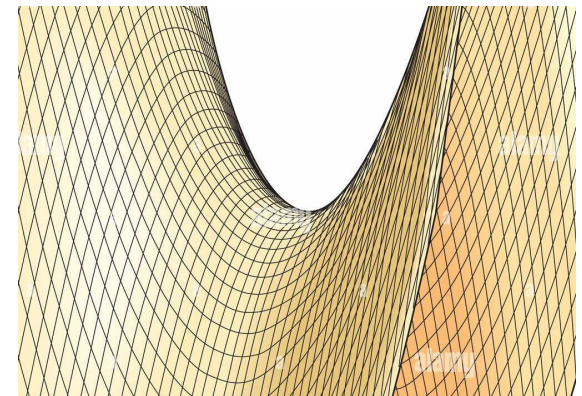
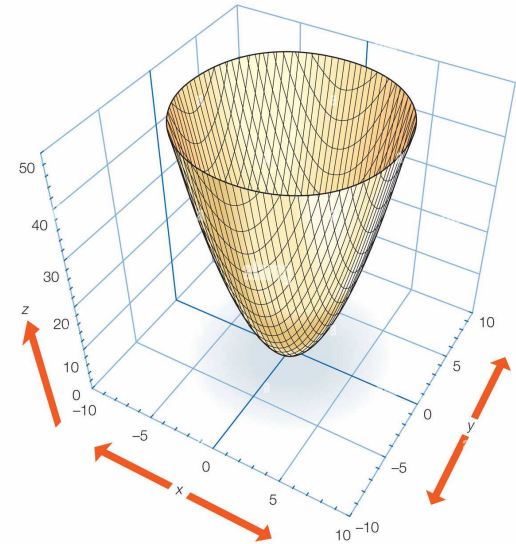
$$\partial g(0,0) / \partial x = \partial g(0,0) / \partial y = 0; \quad \partial^2 g(0,0) / \partial x^2 > 0; \quad \partial^2 g(0,0) / \partial y^2 > 0$$

$$\text{However, } g(x, y) = x^2 + y^2 + 6xy = 2(x+y)^2 - (x-y)^2 = 2X^2 - Y^2$$

where $X = x+y$; $Y = x-y$ are new variables.

If we fix a value of Y , we obtain a *positive* parabola with respect to X . But if we fix a value of X , we have a *negative* parabola with respect to Y .

Thus, it is a *transition state* rather than a minimum!



Potential energy surface –characterization of stationary points

- To *characterize* a stationary point of a multi-dimensional function $E(q_1, q_2, q_3, \dots, q_N)$ we need the entire second-derivative matrix, called **Hessian matrix** or *force-constant matrix*:

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial q_1^2} & \frac{\partial^2 E}{\partial q_1 \partial q_2} & \dots & \frac{\partial^2 E}{\partial q_1 \partial q_N} \\ \frac{\partial^2 E}{\partial q_2 \partial q_1} & \frac{\partial^2 E}{\partial q_2^2} & \dots & \frac{\partial^2 E}{\partial q_2 \partial q_N} \\ \dots & \dots & \dots & \dots \\ \frac{\partial^2 E}{\partial q_N \partial q_1} & \frac{\partial^2 E}{\partial q_N \partial q_2} & \dots & \frac{\partial^2 E}{\partial q_N^2} \end{pmatrix}$$

N is the number of degrees of freedom

This a symmetric $N \times N$ matrix.

- **Eigenvalues** λ_k ($k = 1, \dots, N$) of the Hessian matrix must be calculated. All eigenvalues of a symmetrix matrix are always *real* (not complex), but may be *positive* or *negative*. Then, the following criteria apply:

Number of negative eigenvalues	0	1	2	...	N
Type	minimum	transition state	second-order saddle point	higher-order saddle point	maximum

Potential energy surface –characterization of stationary points – example

- Example of calculation of eigenvalues for a 2×2 matrix through the *characteristic determinant*:

$$g(x,y) = x^2 + y^2 + 6xy$$
$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 g}{\partial x^2} & \frac{\partial^2 g}{\partial x \partial y} \\ \frac{\partial^2 g}{\partial y \partial x} & \frac{\partial^2 g}{\partial y^2} \end{pmatrix} = \begin{pmatrix} 2 & 6 \\ 6 & 2 \end{pmatrix}$$

Characteristic equation:

$$\begin{vmatrix} 2 - \lambda & 6 \\ 6 & 2 - \lambda \end{vmatrix} = 0$$

$$(2 - \lambda)(2 - \lambda) - 6 \cdot 6 = 0$$

$$\lambda^2 - 4\lambda - 32 = 0$$

$$\lambda_1 = 8; \lambda_2 = -4$$

One negative eigenvalue ($\lambda_2 = -4$) indicates that this is a *transition state*.

Potential energy surface – characterization of stationary points

- For larger $N \times N$ matrices, the characteristic equation will be of grade N , and we would need to find all the N roots (solutions) in order to characterize the stationary points.
 - This is never done in practice. Usually, computer programs using efficient methods of linear algebra (such as Jacobi or Householder diagonalization methods) are employed to find the eigenvalues of large matrices.
- Quantum-chemical programs calculate the Hessian (i.e. all the partial second derivatives), its eigenvalues λ_k , and then the harmonic frequencies (wavenumbers) (μ_k are reduced masses – *beyond our course*):

$$\tilde{\nu}_k = \frac{1}{2\pi c} \sqrt{\frac{\lambda_k}{\mu_k}}$$

When all the $\lambda_k > 0$, all the frequencies are *real* and *positive* (e.g. 2000 cm⁻¹)

When some $\lambda_k < 0$, there are *imaginary* frequencies (e.g. 2000*i* cm⁻¹).

Never call them “negative” – it’s a capital mistake!

- The above description of the relation between eigenvalues of the Hesse matrix and the frequencies is a simplification; the full harmonic vibrational theory is beyond our course.

- A second-order (or higher-order) saddle point is a stationary point that is a maximum in two (or more) coordinates, but minimum in all other coordinates. A second-order saddle point has two negative eigenvalues of the Hessian.
- The ***Murrell–Laidler theorem***: On a PES, the minimum-energy path connecting two minima passes through a stationary point that has exactly *one* negative eigenvalue in the Hessian matrix (the transition state).

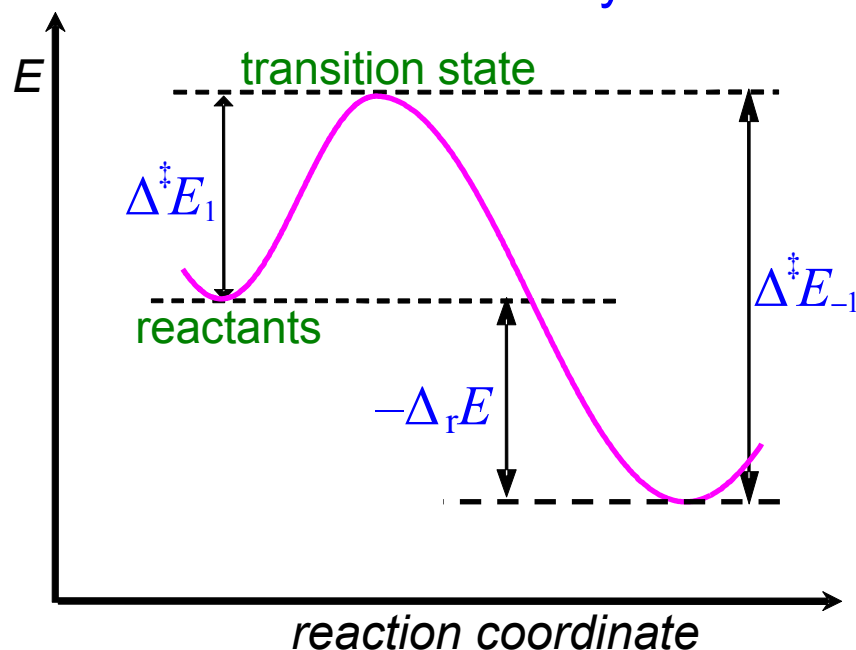
In other words, if two local minima are found to be connected by a path involving a second-order (or higher-order) saddle point, then this is *not* the minimum-energy path. Another lower-energy path must exist that passes through a first-order saddle point (the TS).

- ▶ This *does not* mean that a trajectory through a higher-order saddle point is impossible. It just means that there is a better (=lower-lying) trajectory leading through a transition state (and possible other minima).
- ▶ Limitations of the Murrell–Laidler theorem are known, mainly for highly symmetric potentials.

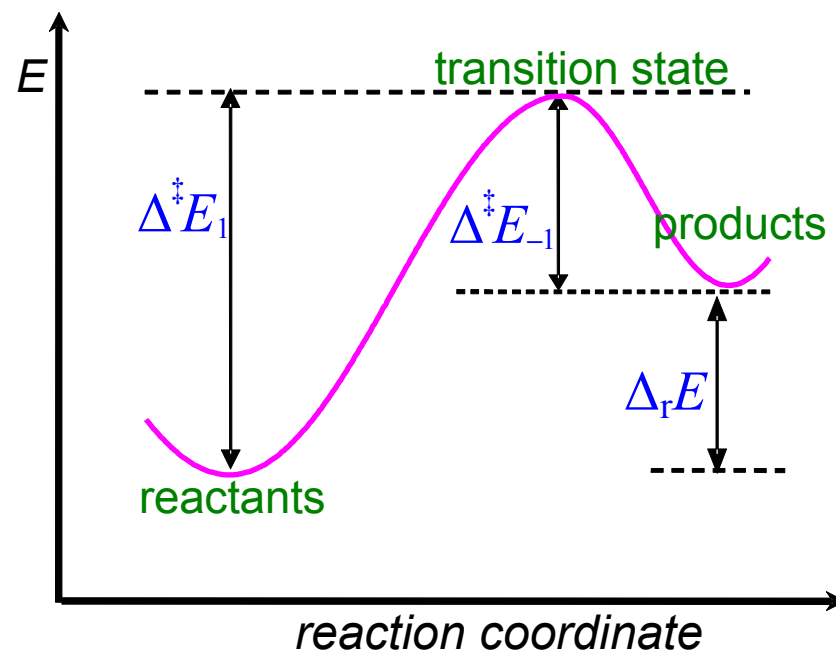
Potential energy surface – Hammond's postulate

- Hammond's postulate (=Hammond's principle = Leffler's assumption):
The transition state bears the greater resemblance (is more similar geometrically) to the *less stable* species (reactant or product):

exothermic reaction – early transition state



endothermic reaction – late transition state



Thus, for an exothermic reaction (see picture above), the transition state resembles more the reactant, and for an endothermic reaction, the product.

► Hammond's postulate is *not* a fundamental law, but is usually fulfilled.

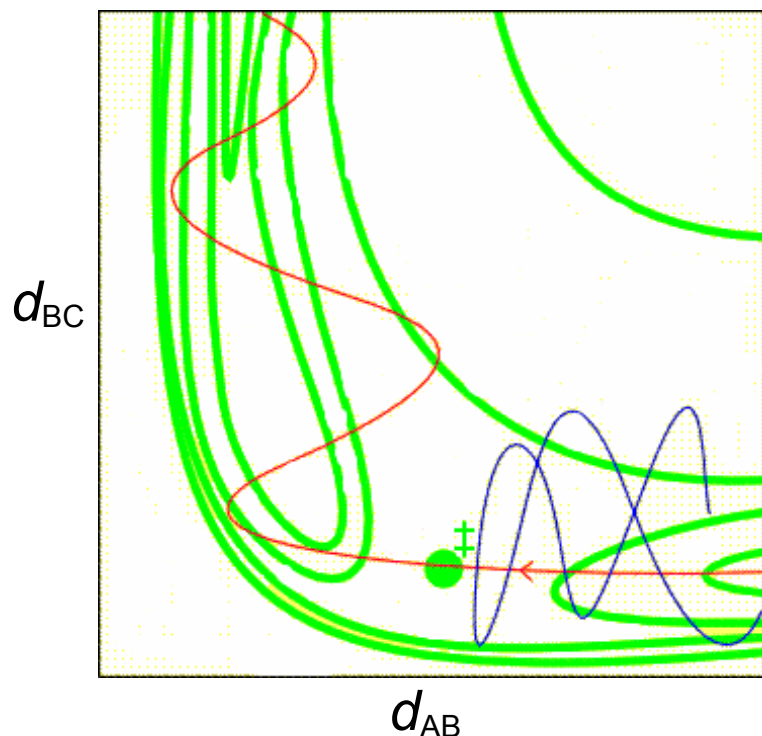
Potential energy surface – various trajectories – reaction dynamics

- Not all the trajectories (even those with sufficient energy) lead to a reaction!



► Various trajectories

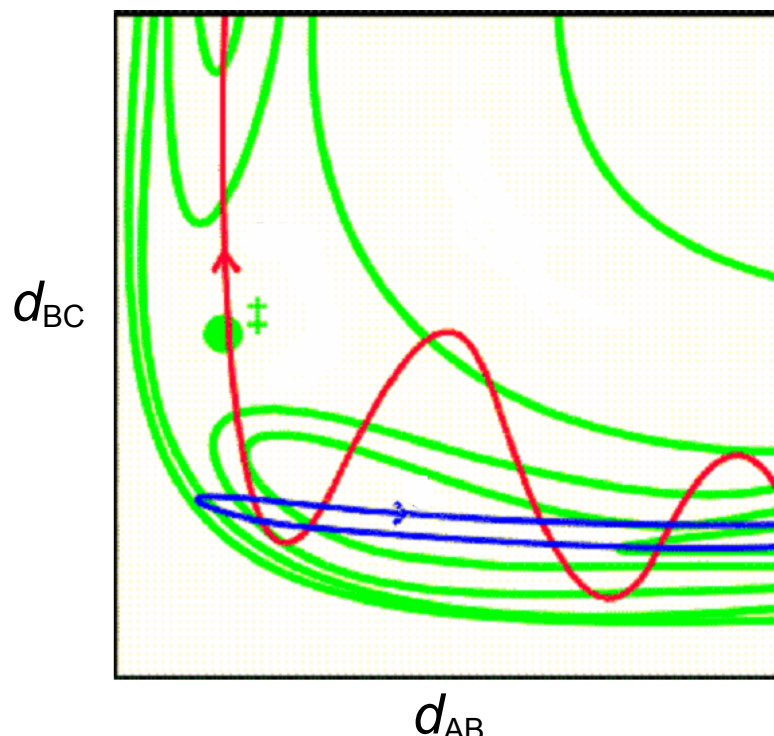
exothermic reaction – early transition state



Large vibrational energy – non-reactive trajectory

Large translational energy – reactive trajectory

endothermic reaction – late transition state



Large translational energy – non-reactive trajectory

Large vibrational energy – reactive trajectory

Partition functions – a reminder

- The partition function is dimensionless and is defined as follows:

$$Q = \sum_i e^{-\frac{\varepsilon_i}{k_B T}}$$

The summation runs over all the quantum states of the molecule; ε_i is the energy of the i -th state.

- Since $\varepsilon_i = \varepsilon_{i\text{trans}} + \varepsilon_{i\text{rot}} + \varepsilon_{i\text{vib}}$, the partition function can be separated into translational, rotational, and vibrational parts: $Q = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}}$
 - Q_{trans} does not play a role for a *unimolecular* reaction, since $Q_{\text{trans}}^A = Q_{\text{trans}}^B$.
 - Q_{rot} and Q_{vib} may be different for A and B.
 - Q_{rot} and Q_{vib} are normally calculated using the rigid rotor–harmonic oscillator models. This means that the PES is approximated by *paraboloids* around the corresponding A and B minima.
 - Thus, the PES area near the TS is not taken into account. No problem for thermodynamics, since the TS area is high in energy \Rightarrow few molecules are there.
- For a reaction $A+B \rightarrow C$, Q_{trans} and Q_{rot} are very important: usually $Q_{\text{trans}}^A \cdot Q_{\text{trans}}^B \gg Q_{\text{trans}}^C$. $Q_{\text{trans}}^A \cdot Q_{\text{trans}}^B$ and $Q_{\text{rot}}^A \cdot Q_{\text{rot}}^B$ are responsible for all the mutual orientations of the molecules A and B. The equilibrium constant is as follows (c° is the *standard concentration*):

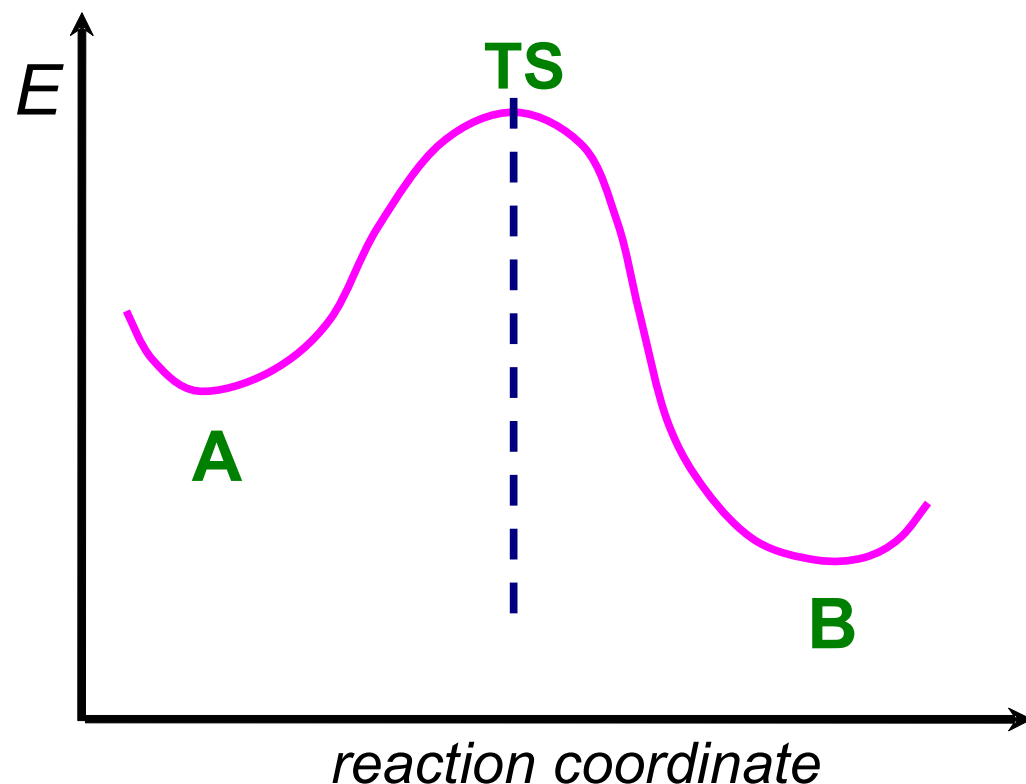
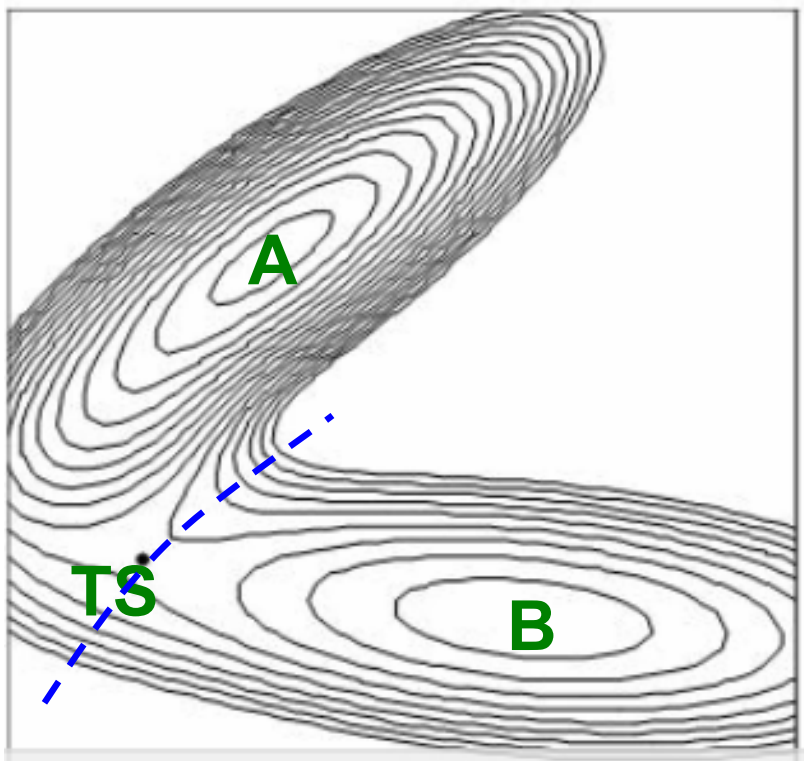
$$K_{\text{eq}} = \frac{[B]/c^\circ}{[A]/c^\circ} = \frac{[B]}{[A]} = \frac{Q^B}{Q^A} e^{-\Delta E/k_B T} \quad K_{\text{eq}} = \frac{[C]/c^\circ}{([A]/c^\circ) \cdot ([B]/c^\circ)} = c^\circ \frac{[C]}{[A][B]} = \frac{Q^C}{Q^A Q^B} e^{-\Delta E/k_B T}$$

unimolecular reaction $A \rightleftharpoons B$

bimolecular reaction $A + B \rightleftharpoons C$

Equilibrium from PES viewpoint

- Consider a two-minimum potential energy surface for a reversible unimolecular reaction:



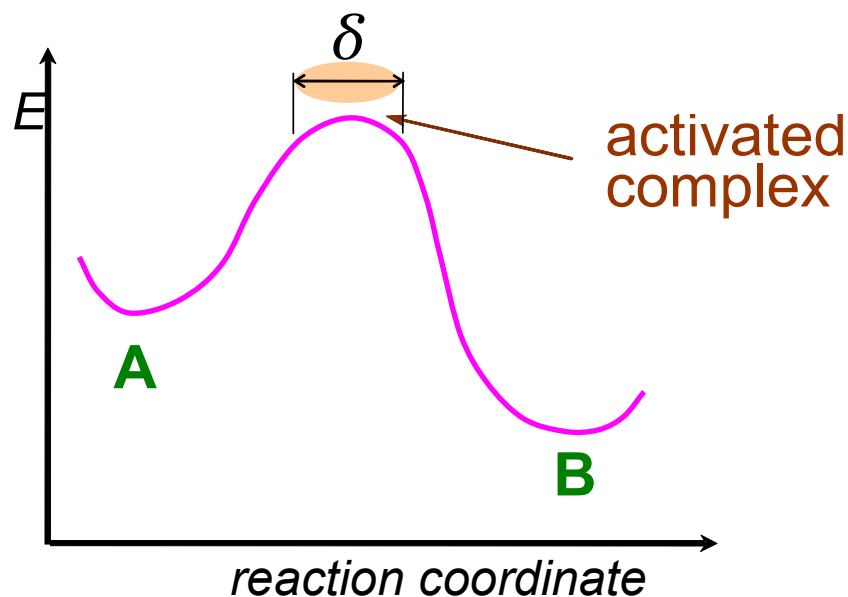
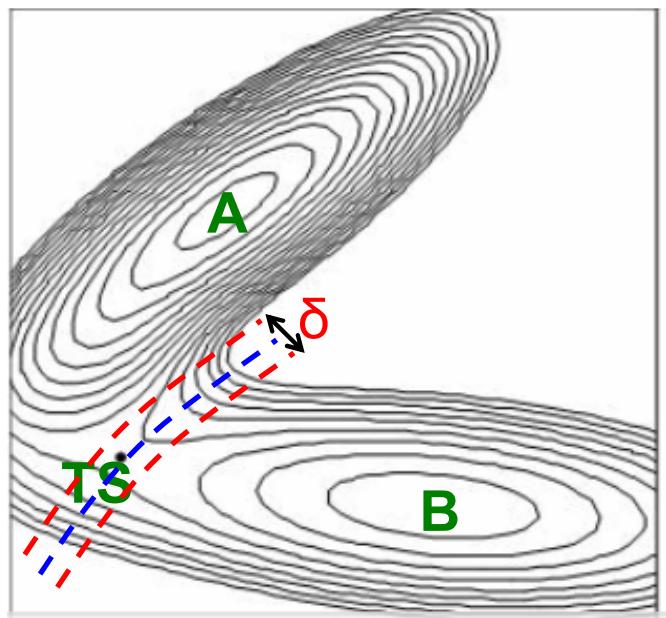
- Normally there are *many* molecules ($\sim 10^{23}$) per unit volume.
- Let's take a *snapshot* in any particular moment of time: each molecule will be in different point of the PES.
- The molecules to the *left* from the TS are counted as “A” molecules; those to the right as “B” molecules. None of them are *exactly* in their minima.

$$[B]/[A] = K_{\text{eq}} = (Q^B/Q^A) \cdot \exp(-\Delta E/k_B T)$$

where Q^A , Q^B are the *partition functions*.

Activated complex vs. transition state

- A **transition state** is a certain stationary point (first-order saddle point) on the potential energy surface (see pages 111–115).
 - It is a single point on the PES, and the reacting system has a *zero probability* of being exactly in this point.
- An **activated complex** is a small area surrounding the transition state.
 - It has some extension in all directions: some *small* extension δ along the reaction coordinate and some *larger* extension perpendicular reaction coordinate. The exact value of δ is not well defined and is arbitrary.



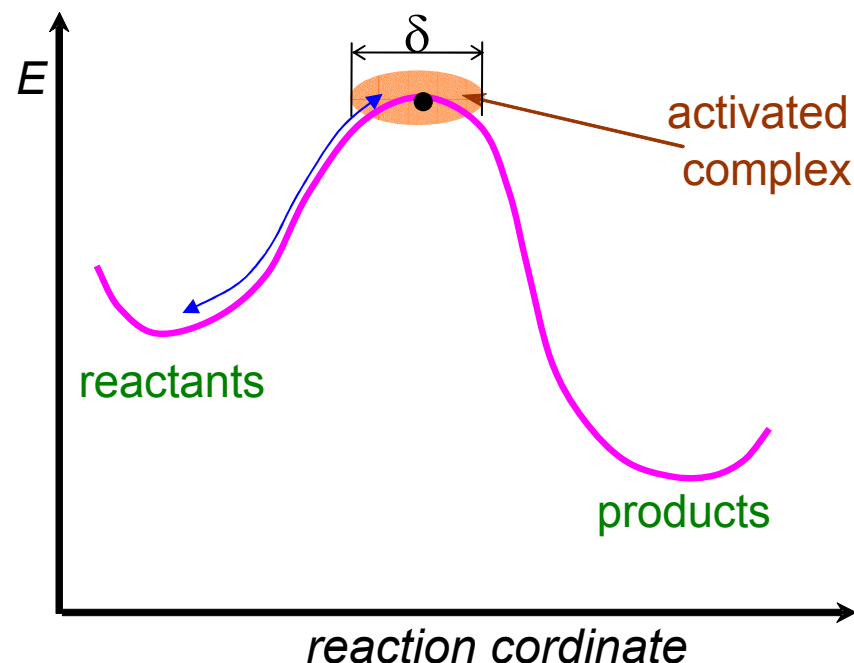
- The molecular system has a *nonzero probability* of being within the activated complex. Hence we can talk about the *concentration* of activated complex at a given moment of time.

- Basic ideas of the TST:

- ▶ The **activated complex** A^\ddagger or $(A\cdots B)^\ddagger$ is in "equilibrium" with the reactant(s) A, B (not with the products!). In other words, the *concentration* of the activated complex $[A^\ddagger]$ or $[(A\cdots B)^\ddagger]$ can be calculated by *statistical mechanics*. $[A^\ddagger]$ or $[(A\cdots B)^\ddagger]$ *depends* on δ : the larger δ , the more molecules it contains in every moment of time and the larger $[A^\ddagger]$ or $[(A\cdots B)^\ddagger]$ is: $[A^\ddagger] \propto \delta$.
- ▶ No *back-crossing (returning)* trajectories: once having reached the activated complex, the reacting system will proceed to the products – it cannot go back to the reactants.
- ▶ The reaction rate v is evaluated as the activated complex concentration *divided* by the time needed to traverse the activated-complex area of width δ : $v = [A^\ddagger]/t_{tr}$ or $v = [(A\cdots B)^\ddagger]/t_{tr}$.
 - $t_{tr} \propto \delta$: the larger δ , the more time is required to pass the activated complex.
 - A particular value of δ is immaterial; it will cancel when dividing $[A^\ddagger]/t_{tr}$.
- ▶ $[A^\ddagger]$ or $[(A\cdots B)^\ddagger]$ is calculated from the partition functions:

$$[A^\ddagger] = (Q^\ddagger/Q^A) \cdot \exp(-\Delta^\ddagger E/k_B T) \cdot [A]$$

$$[(A\cdots B)^\ddagger] = (1/c^\circ) (Q^\ddagger/(Q^A Q^B)) \cdot \exp(-\Delta^\ddagger E/k_B T) [A] [B]$$



• Derivation **Eyring–(Evans)–Polanyi equation**:

Take into account that the *mean relative velocity* \bar{v} of a one-dimensional motion is given by

$$\bar{v} = \sqrt{\frac{k_B T}{2\pi m^\ddagger}}$$

The time necessary to traverse the activated complex of length δ with velocity \bar{v} is:

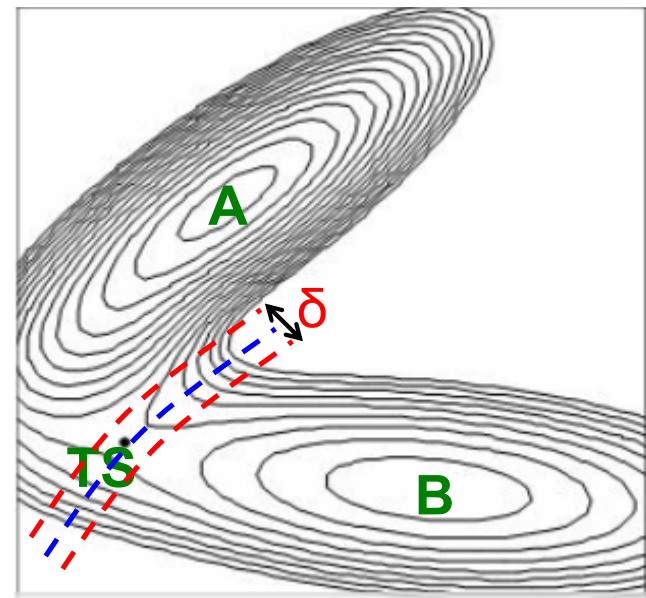
$$t_{\text{tr}} = \frac{\delta}{\bar{v}} = \delta \sqrt{\frac{2\pi m^\ddagger}{k_B T}}$$

Consider again the activated complex concentration $[A^\ddagger]$ for a unimolecular reaction:

$$[A^\ddagger] = \frac{Q^\ddagger}{Q^A} e^{-\Delta^\ddagger E / k_B T} \cdot [A]$$

Let us now detach from the Q^\ddagger a part corresponding to a motion *along the reaction coordinate*. This motion is considered as motion of a *particle in a box*.

$$Q^\ddagger = \frac{\sqrt{2\pi m^\ddagger k_B T}}{h} \delta \cdot \hat{Q}^\ddagger$$



Then the *rate* v of this process (the number of molecules traversing the activated complex per unit time) is:

$$\begin{aligned}
 v &= \frac{[A^\ddagger]}{t_{tr}} = \frac{[A^\ddagger]}{\delta \sqrt{\frac{2\pi m^\ddagger}{k_B T}}} = \frac{\frac{Q^\ddagger}{Q^A} e^{-\Delta^\ddagger E / k_B T} \cdot [A]}{\delta \sqrt{\frac{2\pi m^\ddagger}{k_B T}}} = \frac{\frac{\sqrt{2\pi m^\ddagger k_B T}}{h} \delta \cdot \hat{Q}^\ddagger e^{-\Delta^\ddagger E / k_B T} \cdot [A]}{Q^A \delta \sqrt{\frac{2\pi m^\ddagger}{k_B T}}} = \\
 &= \frac{k_B T}{h} \frac{\hat{Q}^\ddagger}{Q^A} e^{-\Delta^\ddagger E / k_B T} \cdot [A]
 \end{aligned}$$

Thus, the ***Eyring–(Evans)–Polanyi equation*** for a unimolecular reaction expressed through *partition functions*:

$$k = \frac{k_B T}{h} \frac{\hat{Q}^\ddagger}{Q^A} e^{-\Delta^\ddagger E / RT}$$

$$k = \frac{k_{\text{B}}T}{h} \frac{\hat{Q}^{\ddagger}}{Q^{\text{A}}} e^{-\Delta^{\ddagger}E/RT}$$

- Note that \hat{Q}^{\ddagger} in the above equation is the full partition function of the activated complex (transition state) except that it *does not* contain the degree of freedom corresponding to the motion *along* the reaction coordinate (because we already separated it). This degree of freedom is actually an *imaginary vibration* with an *imaginary* frequency and a *negative* Hessian eigenvalue. From now on, we will drop the “hat” over Q^{\ddagger} , but we will always keep in mind that Q^{\ddagger} contains one degree of freedom less (i.e., $3N-1$ degrees of freedom: 3 translational + 3 rotational (or 2 for a linear transition state) + $3N-7$ vibrational (or $3N-6$ for a linear transition state)).

Since $K_{\text{eq}}^{\ddagger} = \frac{Q^{\ddagger}}{Q^{\text{A}}} e^{-\Delta^{\ddagger}E/RT}$ and $K_{\text{eq}}^{\ddagger} = e^{-\Delta^{\ddagger}G^{\circ}/RT}$, we obtain

the **Eyring–Polanyi equation** in two alternative forms:

$$k = \frac{k_{\text{B}}T}{h} e^{-\Delta^{\ddagger}G^{\circ}/RT} = \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q^{\text{A}}} e^{-\Delta^{\ddagger}E/RT}$$

Transition-state theory – bimolecular reactions

- The derivation of the Eyring–Polanyi equation for bimolecular reactions is mathematically identical to the unimolecular case, except that:

$$K_{\text{eq}}^{\ddagger} = \frac{Q^{\ddagger}}{Q^{\text{A}}Q^{\text{B}}} e^{-\Delta^{\ddagger}E/RT} = \frac{[(\text{A}\cdots\text{B})^{\ddagger}]/c^{\circ}}{([\text{A}]/c^{\circ})([\text{B}]/c^{\circ})}$$

where c° is the *standard concentration*. Therefore,

$$[(\text{A}\cdots\text{B})^{\ddagger}] = \frac{1}{c^{\circ}} \frac{Q^{\ddagger}}{Q^{\text{A}}Q^{\text{B}}} e^{-\Delta^{\ddagger}E/RT} [\text{A}][\text{B}]$$

- The ***Eyring–(Evans)–Polanyi equation***:

unimolecular	bimolecular	termolecular
$k = \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q^{\text{A}}} e^{-\frac{\Delta^{\ddagger}E}{RT}}$	$k = \frac{1}{c^{\circ}} \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q^{\text{A}}Q^{\text{B}}} e^{-\frac{\Delta^{\ddagger}E}{RT}}$	$k = \frac{1}{c^{\circ 2}} \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q^{\text{A}}Q^{\text{B}}Q^{\text{C}}} e^{-\frac{\Delta^{\ddagger}E}{RT}}$
$k = \frac{k_{\text{B}}T}{h} e^{-\frac{\Delta^{\ddagger}G^{\circ}}{RT}}$	$k = \frac{1}{c^{\circ}} \frac{k_{\text{B}}T}{h} e^{-\frac{\Delta^{\ddagger}G^{\circ}}{RT}}$	$k = \frac{1}{c^{\circ 2}} \frac{k_{\text{B}}T}{h} e^{-\frac{\Delta^{\ddagger}G^{\circ}}{RT}}$

- The *Eyring–Polanyi equation* for a bimolecular reaction:

$$k = \frac{1}{c^\circ} \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A Q^B} e^{-\frac{\Delta^\ddagger E}{RT}} = \frac{1}{c^\circ} \frac{k_B T}{h} e^{-\frac{\Delta^\ddagger G^\circ}{RT}}$$

- The above equations depend on the standard concentration c° . However, physically k cannot depend on c° (which is arbitrary). The paradox is explained by the fact that *translational* Q also depends on c° through the *standard volume* V° : $Q_{\text{trans}} = (2\pi m k_B T / h^2)^{3/2} \cdot V^\circ$, where V° is the volume available to a single molecule at the standard concentration:

$$\begin{aligned} V^\circ &= \frac{1}{N_A c^\circ} \quad \Leftrightarrow \quad c^\circ = \frac{1}{N_A V^\circ} \\ k &= \frac{1}{c^\circ} \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A Q^B} e^{-\frac{\Delta^\ddagger E}{RT}} = N_A V^\circ \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A Q^B} e^{-\frac{\Delta^\ddagger E}{RT}} = \\ &= N_A \frac{k_B T}{h} \frac{(Q^\ddagger / V^\circ)}{(Q^A / V^\circ)(Q^B / V^\circ)} e^{-\frac{\Delta^\ddagger E}{RT}} \end{aligned}$$

All the quantities Q/V° are volume-independent, since Q is proportional to V° through the Q_{trans} .

- In the Eyring equation $\Delta^\ddagger G^\circ = G^\circ(\text{TS}) - G^\circ(\text{reactants})$ is the **standard activation free energy**, i.e., calculated at a standard concentration c° (normally 1 M for solutions, 1 atm = 101325 Pa for gases). G° is calculated from Q .
- Units:
 - For **uni**molecular reactions, $k_B T/h$ gives s^{-1} automatically.
 - For **bi**molecular reactions, the correct units ($\text{M}^{-1} \cdot \text{s}^{-1}$) comes from the $1/c^\circ$ factor.
 - If $c^\circ = 1 \text{ M}$ (standard for solutions), $\Delta^\ddagger G^\circ$ has to be calculated at 1 M.
 - If $\Delta^\ddagger G^\circ$ has been calculated by the GaussianTM program, the standard pressure $P^\circ = 1 \text{ atm} = 101325 \text{ Pa} \Rightarrow c^\circ = P^\circ/(1000RT) = 0.0409 \text{ M}$ (at 298.15 K). The factor 1000 originates from the conversion of m^3 to liters. P° is *not* the pressure under which the reaction occurs!

Alternatively, for **bi**molecular reactions we can include the factor $c^\circ = P^\circ/(1000RT)$ into the exponent:

$$k = \frac{1}{c^\circ} \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ/RT} = e^{-\ln c^\circ} \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ/RT} = \frac{k_B T}{h} e^{-(\Delta^\ddagger G^\circ + RT \ln c^\circ)/RT}$$

Thus, passing from 1 atm to 1 M for a bimolecular reaction is equivalent to decreasing $\Delta^\ddagger G^\circ$ by $RT \ln(1000RT/P^\circ)$. At 298 K this corresponds to a $\Delta^\ddagger G^\circ$ **decrease** of $1.89 \text{ kcal} \cdot \text{mol}^{-1}$.

This idea can be represented differently: changing a standard state from c° to $c^{\circ'}$ corresponds to a ΔG change of $RT \ln(c^{\circ'}/c^\circ)$. Setting $c^{\circ'} = 0.0409 \text{ M}$ and $c^\circ = 1 \text{ M}$, we obtain the same $\Delta^\ddagger G^\circ$ correction of $-1.89 \text{ kcal} \cdot \text{mol}^{-1}$ for a bimolecular reaction.

Transition-state theory – various forms of the equation

- To take into account *back-crossing trajectories* (that not all molecules that have reached the transition state pass to the products), the *transmission coefficient* κ can be included:

$$k = \kappa \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$$

but we will not use κ in further equations.

- Since $\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$, we obtain:

unimolecular	bimolecular
$k = \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT}$	$k = \frac{1}{c^\circ} \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT}$

⇒ both activation **enthalpy** $\Delta^\ddagger H^\circ$ and activation **entropy** $\Delta^\ddagger S^\circ$ affect the reaction rate: k increases with decreasing $\Delta^\ddagger H^\circ$ or increasing $\Delta^\ddagger S^\circ$.

- Linearized form (“**Eyring plot**”) for temperature dependence $k(T)$:

unimolecular	bimolecular
$\ln\left(\frac{k}{T}\right) = \left(\ln \frac{k_B}{h} + \frac{\Delta^\ddagger S^\circ}{R}\right) - \frac{\Delta^\ddagger H^\circ}{R} \cdot \frac{1}{T}$	$\ln\left(\frac{kc^\circ}{T}\right) = \left(\ln \frac{k_B}{h} + \frac{\Delta^\ddagger S^\circ}{R}\right) - \frac{\Delta^\ddagger H^\circ}{R} \cdot \frac{1}{T}$

For a bimolecular reaction, $c^\circ = 1 \text{ M}$ and does not numerically affect the calculation. This means that $\Delta^\ddagger S^\circ$ and $\Delta^\ddagger G^\circ$ obtained correspond to $c^\circ = 1 \text{ M}$. The use of the SI units is important; k or kc° should be in s^{-1} ! $\ln(k_B/h) \approx 23.76$.

- In the Eyring equation:

$$k = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S^\circ}{R}} e^{-\frac{\Delta^\ddagger H^\circ}{RT}}$$

$\Delta^\ddagger H^\circ$ and $\Delta^\ddagger S^\circ$ are *activation enthalpy* and *entropy*, correspondingly.

$\Delta^\ddagger H^\circ$ is related to the energy barrier, while $\Delta^\ddagger S^\circ$ can be considered as a measure of change of *disorder*.

- For a bimolecular reaction:

The entropy of the activated complex (one particle = transition state) is *lower* than that of the reactants (two reacting molecules, less ordered).

Therefore, $\Delta^\ddagger S^\circ < 0$ (typically about $-40 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at room temperature) mostly due to *translational* contributions (6 translational degrees of freedom in reactants, 3 ones in the activated complex). The effect is less pronounced in solution than in the gas phase.

- For a unimolecular reaction:

The activation entropy is usually relatively small, since the translational contribution in the activated complex and the reactant is the same, and rotational is usually *almost* the same. The small non-zero $\Delta^\ddagger S^\circ$ originates mostly from the vibrational contributions. However, there are some exceptions from this: $\Delta^\ddagger S^\circ < 0$ e.g. for cyclization reactions; $\Delta^\ddagger S^\circ > 0$ e.g. for dissociations. This information can be useful for finding out the rate-determining step in a complex reaction.

- The ***Eyring–(Evans)–Polanyi equation***:

unimolecular	bimolecular
$k = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$	$k = \frac{1}{c^\circ} \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$
$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A} e^{-\Delta^\ddagger E / RT}$	$k = \frac{1}{c^\circ} \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A Q^B} e^{-\Delta^\ddagger E / RT}$

- The transition-state theory allows predicting the rate constant from molecular data (cf. the original name “absolute rate constant theory”).
- Unlike $\Delta_r G^\circ$, $\Delta^\ddagger G^\circ$ is not available from any kind of thermochemical data.
- The *partition functions* Q of the reactants and the transition state can be calculated by statistical thermodynamics (see pages 121 and 135).
- G° can be calculated from Q when needed – this is done e.g. by GaussianTM.

Transition-state theory – calculation of k from Q

- The partition function can be separated into translations, rotational, and vibrational parts (see next page 135): $Q = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}}$
There is also an electronic partition function Q_{el} , but it is usually neglected. *Exception:* for spin-degenerate states, $Q_{\text{el}} = \text{spin multiplicity}$ (2 for doublets (free radicals), 3 for triplets, etc.)
- Molecular data for both the reactant(s) and the transition state are needed for the k calculation:
 - Molecular energies: for $\Delta^\ddagger E$.
 - Atomic masses: for Q_{trans} and Q_{rot} .
 - Molecular geometries: moment of inertia for Q_{rot} (see next page 135).
 - Vibrational frequencies: for Q_{vib} (see next page 135).
- Rate constant for a unimolecular reaction ($Q_{\text{trans}}^\ddagger = Q_{\text{trans}}^A$ since $m^\ddagger = m^A$):

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A} e^{-\frac{\Delta^\ddagger E}{RT}} = \frac{k_B T}{h} \frac{Q_{\text{rot}}^\ddagger Q_{\text{vib}}^\ddagger}{Q_{\text{rot}}^A Q_{\text{vib}}^A} e^{-\frac{\Delta^\ddagger E}{RT}}$$

- Rate constant for a bimolecular reaction:

$$k = N_A \frac{k_B T}{h} \frac{(Q^\ddagger / V^\circ)}{(Q^A / V^\circ)(Q^B / V^\circ)} e^{-\frac{\Delta^\ddagger E}{RT}} = \frac{RT}{h} \frac{(Q^\ddagger / V^\circ)}{(Q^A / V^\circ)(Q^B / V^\circ)} e^{-\frac{\Delta^\ddagger E}{RT}}$$

Q / V° is actually V° -independent (see page 129).

Partition functions:

- From each *translational* coordinate (L is the length of the potential box):

$$q_{\text{trans}} = \frac{\sqrt{2\pi m k_B T}}{h} L \quad Q_{\text{trans}} = \frac{(2\pi m k_B T)^{3/2}}{h^3} V^\circ$$

from one tr. coordinate total translational

- Rotational *partition* function – depends on the molecule's mass and size:

► For linear molecules:

$$Q_{\text{rot}} = \frac{1}{\sigma} \frac{8\pi^2 I}{h^2} k_B T$$

► For non-linear molecules:

$$Q_{\text{rot}} = \frac{1}{\sigma} \frac{16\pi^3 \sqrt{2\pi I_A I_B I_C}}{h^3} (k_B T)^{3/2}$$

I is the *moment of inertia* I_A, I_B, I_C are *principal moments of inertia*

For the “symmetry numbers” σ ask your professor or consult E.Besalú's book vol. 2 page 132 or Atkins pages 595 and 619 if interested.

- Vibrational partition function – depends on individual vibrational frequencies:

► From each vibrational coordinate:

$$q_{\text{vib},m} = \frac{e^{-h\nu_m/2k_B T}}{1 - e^{-h\nu_m/k_B T}}, \quad m = 1, \dots, 3N - 6(5)$$

► The total vibrational:

$$Q_{\text{vib}} = \prod_{m=1}^{3N-6(5)} q_{\text{vib},m}$$

reactant

$$Q_{\text{vib}} = \prod_{m=1}^{3N-7(6)} q_{\text{vib},m}$$

transition state

Transition-state theory – temperature dependence of k

- Temperature dependence of the *pre-exponential factor* can be analyzed based on partition functions:

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A} e^{-\Delta^\ddagger E / RT} \qquad k = \frac{1}{c^\circ} \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A Q^B} e^{-\Delta^\ddagger E / RT}$$

- Each *translational* and *rotational* degree of freedom contribute $\propto T^{1/2}$ to each partition function. Therefore:

Species	Degrees of freedom		Q
	translational	rotational	
Single atom	3	0	$\propto T^{3/2}$
Linear molecule	3	2	$\propto T^{5/2}$
Non-linear molecule	3	3	$\propto T^{6/2} = T^3$

- A *vibrational* degrees of freedom:

– does *not* contribute significantly if $T \ll \Theta_{\text{vib}} = h\nu/k_B$;

– contributes $\propto T$ if $T \gg \Theta_{\text{vib}}$.

- Example: a reaction of two atoms A and B (for an exact calculation see page 202):

$$Q^A \propto T^{3/2}$$

$$Q^B \propto T^{3/2}$$

$$Q^\ddagger = Q^{(A \cdots B)} \propto T^{5/2}$$

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A Q^B} e^{-\frac{\Delta^\ddagger E}{RT}} \propto T \frac{T^{5/2}}{T^{3/2} T^{3/2}} e^{-\frac{\Delta^\ddagger E}{RT}} = T^{1/2} e^{-\frac{\Delta^\ddagger E}{RT}}$$

- See also problems 4.8–4.10 of the *Problem Booklet*.

Transition-state theory – “negative activation energy” possible

- Usually rate constant strongly increases with increasing temperature due to the $\exp(-\Delta^\ddagger E/RT)$ factor in the Eyring equation ($\Delta^\ddagger E > 0$ always):

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A} e^{-\Delta^\ddagger E/RT} \qquad k = \frac{1}{c^\circ} \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A Q^B} e^{-\Delta^\ddagger E/RT}$$

- However, if $\Delta^\ddagger E$ is *very small*, the behavior of Q^\ddagger/Q^A or $Q^\ddagger/(Q^A Q^B)$ becomes dominant and determines the overall temperature dependence of k (see previous page 136).

► Low-barrier **bimolecular** reaction of *two non-linear molecules*:

In certain cases, if $TQ^\ddagger/(Q^A Q^B)$ follows a *negative* power of T , k will *decrease* with increasing temperature, since $TQ^\ddagger/(Q^A Q^B) \propto T \cdot T^3/(T^3 \cdot T^3) = T^{-2}$. The physical explanation of this effect lies in a stronger increase of $Q_{\text{rot}}^A \cdot Q_{\text{rot}}^B$ compared to Q_{rot}^\ddagger , as the number of mutual orientations of the reactant molecules increases, leading to a reduced probability of successful collisions that result in reaction.

Note: this is different for reactions of two atoms. In such cases, the temperature dependence follows the total $T^{+1/2}$ effect (see previous page 136).

► Low-barrier **unimolecular** reaction:

Consider a cyclization reaction involving a long, flexible reactant such as a biradical $\cdot\text{CH}_2-(\text{CH}_2)_n-\text{CH}_2\cdot$. The reactant has a lot of conformational degrees of

freedom. However, the TS is much more rigid, because a new C–C bond has already formed. A similar phenomenon occurs in the gas-phase decomposition of ethyl acetate ($E_a = -0.2$ kcal/mol): $\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_4$: here the flexible, non-cyclic reactant transitions to a rigid, cyclic TS. As temperature increases, the reactant gains access to more and more conformations, most of which are not suitable for the reaction. This increase of non-reactive conformations reduces the likelihood of the reactant adopting the suitable conformation and the reaction slows down. Mathematically, this phenomenon is partly covered by the analysis like that on page 136 if we take into account low-frequency *vibrations*.

This corresponds, formally, to a slightly *negative* Arrhenius activation energy (not a negative $\Delta^\ddagger E$ barrier!).

- Let us emphasize that such as “inverted” (anti-Arrhenius) temperature dependence for an elementary reaction is only possible when $\Delta^\ddagger E$ is very low. In the case of a large barrier, the exponential increase $\exp(-\Delta^\ddagger E / RT)$ always overweighs any decrease in the pre-exponential factor, eventually leading to the “normal” behavior (where k increases with temperature).

Meaning of $\Delta^\ddagger E$ in the Eyring equation

- The Eyring equation can be expressed through $\Delta^\ddagger E_e$ and partition functions (for a unimolecular reaction):

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A} e^{-\frac{\Delta^\ddagger E_e}{k_B T}} = \frac{k_B T}{h} \frac{Q_{\text{trans}}^\ddagger Q_{\text{rot}}^\ddagger Q_{\text{vib}}^\ddagger}{Q_{\text{trans}}^A Q_{\text{rot}}^A Q_{\text{vib}}^A} e^{-\frac{\Delta^\ddagger E_e}{k_B T}}$$

Here $\Delta^\ddagger E_e = E^\ddagger - E_A$ is the barrier on the potential energy surface (energy difference between the transition state and the reactant minimum).

► Let us consider the vibrational partition function Q_{vib} :

$$\begin{aligned} Q_{\text{vib}} &= \prod_{m=1}^{3N-6} q_{\text{vib},m} = \prod_{m=1}^{3N-6} \frac{e^{-h\nu_m/2k_B T}}{1 - e^{-h\nu_m/k_B T}} = \prod_{m=1}^{3N-6} e^{-h\nu_m/2k_B T} \prod_{m=1}^{3N-6} \frac{1}{1 - e^{-h\nu_m/k_B T}} = \\ &= \exp \left(-\frac{\sum_{m=1}^{3N-6} h\nu_m/2}{k_B T} \right) \cdot \prod_{m=1}^{3N-6} \frac{1}{1 - e^{-h\nu_m/k_B T}} = \exp \left(-\frac{E_{\text{ZP}}}{k_B T} \right) \cdot \tilde{Q}_{\text{vib}} \end{aligned}$$

where $E_{\text{ZP}} = \sum_m h\nu_m/2$ is the *zero-point vibrational energy* (ZPE).

\tilde{Q}_{vib} is another (differently expressed) *vibrational partition function*. When $T \ll \Theta_{\text{vib}}$, $\tilde{Q}_{\text{vib}} \approx 1$. Thus, the ZPE absorbs most of the vibrational effects.

Meaning of $\Delta^\ddagger E$ in the Eyring equation

$$\begin{aligned} \frac{Q_{\text{vib}}^\ddagger}{Q_{\text{vib}}^A} e^{-\frac{\Delta^\ddagger E_e}{k_B T}} &= \frac{\tilde{Q}_{\text{vib}}^\ddagger e^{-E_{\text{ZP}}^\ddagger / k_B T}}{\tilde{Q}_{\text{vib}}^A e^{-E_{\text{ZP}}^A / k_B T}} e^{-\frac{E^\ddagger - E^A}{k_B T}} = \\ &= \frac{\tilde{Q}_{\text{vib}}^\ddagger}{\tilde{Q}_{\text{vib}}^A} e^{-\frac{(E^\ddagger + E_{\text{ZP}}^\ddagger) - (E^A + E_{\text{ZP}}^A)}{k_B T}} = \frac{\tilde{Q}_{\text{vib}}^\ddagger}{\tilde{Q}_{\text{vib}}^A} e^{-\frac{\Delta^\ddagger E_0}{k_B T}} \end{aligned}$$

► Thus,

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^A} e^{-\frac{\Delta^\ddagger E_e}{k_B T}} = \frac{k_B T}{h} \frac{\tilde{Q}^\ddagger}{\tilde{Q}^A} e^{-\frac{\Delta^\ddagger E_0}{k_B T}}$$

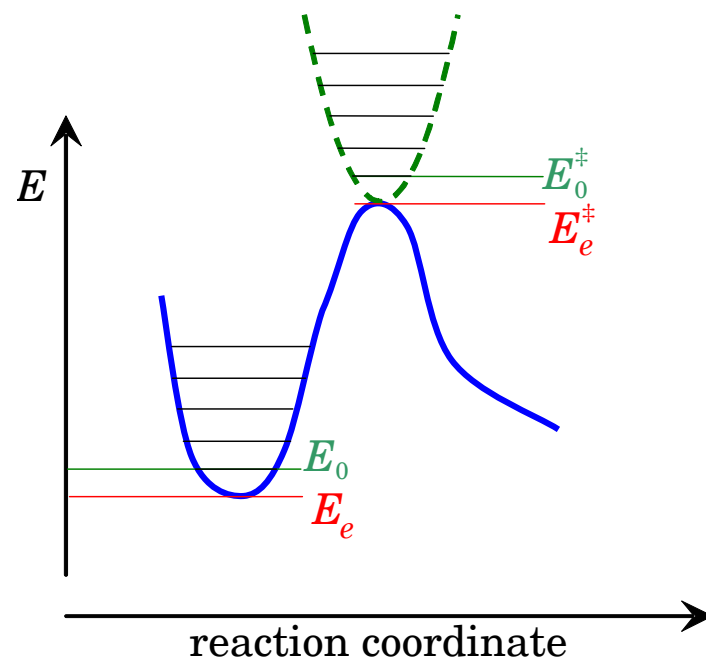
This means that $\Delta^\ddagger E$ in the Eyring equations can have two meanings:

- $\Delta^\ddagger E_e = E^\ddagger - E_A$ is the pure energy barrier
- $\Delta^\ddagger E_0 = (E^\ddagger + E_{\text{ZP}}^\ddagger) - (E^A + E_{\text{ZP}}^A) = \Delta^\ddagger E_e + \Delta E_{\text{ZP}}$

$\Delta^\ddagger E_0$ is the energy barrier including zero-point vibrational energies.

► E_{ZP}^\ddagger has 1 degree of freedom less than E_{ZP}^A , thus usually $E_{\text{ZP}}^\ddagger < E_{\text{ZP}}^A$ and $\Delta^\ddagger E_0 < \Delta^\ddagger E_e$.

► Note that $\Delta^\ddagger E_0$ is isotope-dependent, while $\Delta^\ddagger E_e$ is not (see page 161 for isotope effect)

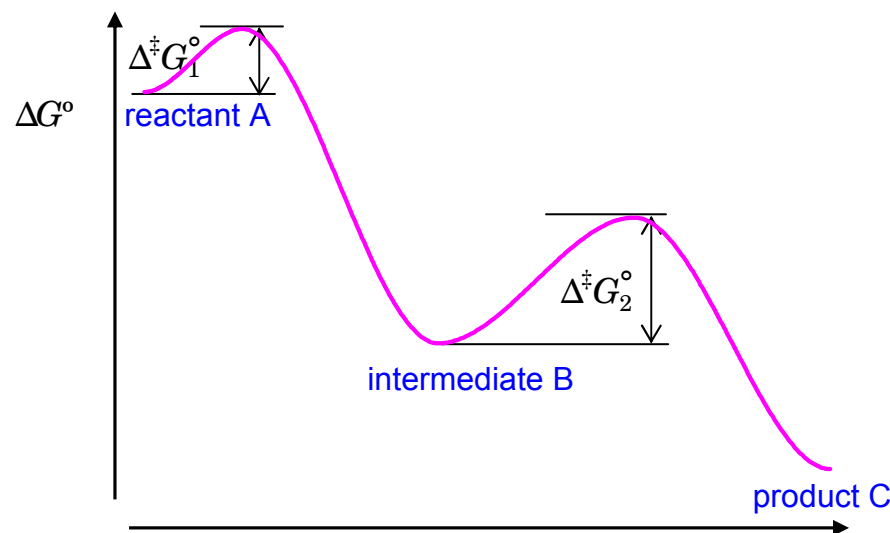


Transition-state theory for complex reactions

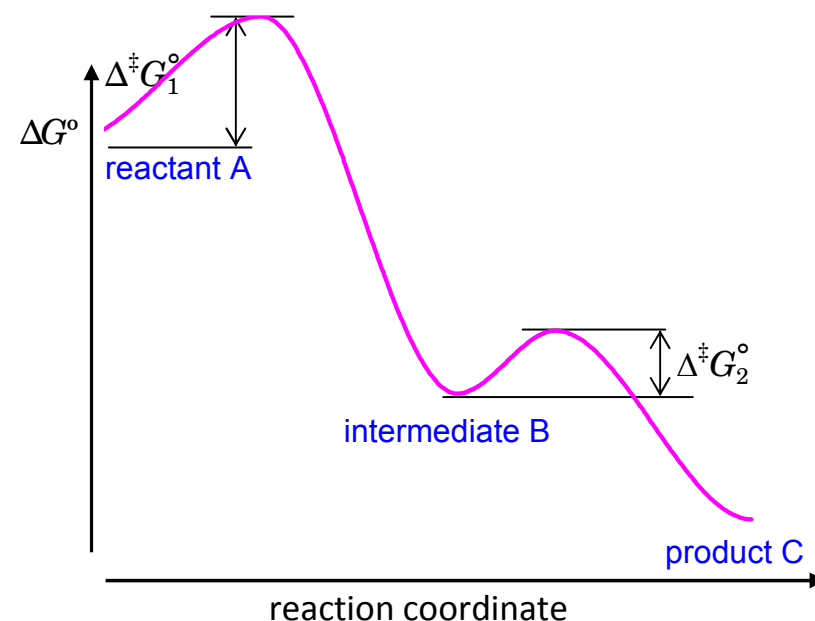
- A one-to-one correspondence between $\Delta^\ddagger G^\circ$ and the rate constant:

$$k = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT} \quad k = \frac{1}{c^\circ} \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$$

- For complex reactions, The Eyring–Polanyi equation should be applied to every elementary step separately.
 - PES for a complex reaction: multiple minima (reactants, products, and intermediates) and TS.
 - Formally, every reaction is reversible. Practically irreversible reactions: $k_{\leftarrow} \ll k_{\rightarrow} \Leftrightarrow \Delta^\ddagger G_{\rightarrow}^\circ \ll \Delta^\ddagger G_{\leftarrow}^\circ \Leftrightarrow \Delta_r G^\circ \ll 0$.



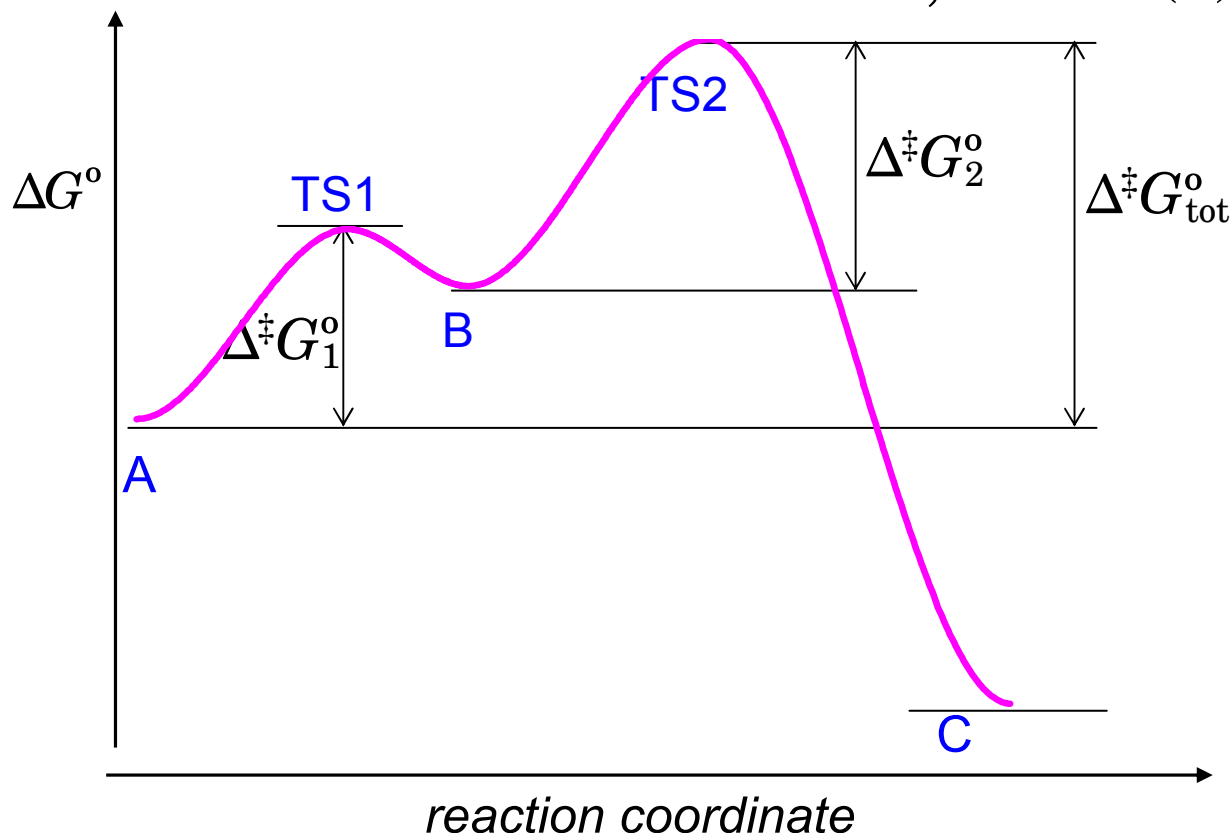
Irreversible consecutive reaction $A \rightarrow B \rightarrow C$,
 $k_1 \gg k_2$, $\Delta^\ddagger G_1^\circ \ll \Delta^\ddagger G_2^\circ$, B \rightarrow C limiting step



Irreversible consecutive reaction $A \rightarrow B \rightarrow C$,
 $k_1 \ll k_2$, $\Delta^\ddagger G_1^\circ \gg \Delta^\ddagger G_2^\circ$, A \rightarrow B limiting step

Transition-state theory for complex reactions

- Reversible consecutive reactions $A \rightleftharpoons B \rightarrow C$, case $G^\circ(B) > G^\circ(A)$:



- Due to pre-equilibrium, $k_{\text{tot}} = K_{\text{eq}(A \rightleftharpoons B)} \cdot k_2$

$$K_{\text{eq}(A \rightleftharpoons B)} = \exp(-(G^\circ(B) - G^\circ(A))/RT)$$

$$k_2 = (k_B T/h) \exp(-(G^\circ(\text{TS2}) - G^\circ(B))/RT)$$

$$\Rightarrow k_{\text{tot}} = K_{\text{eq}(A \rightleftharpoons B)} \cdot k_2 =$$

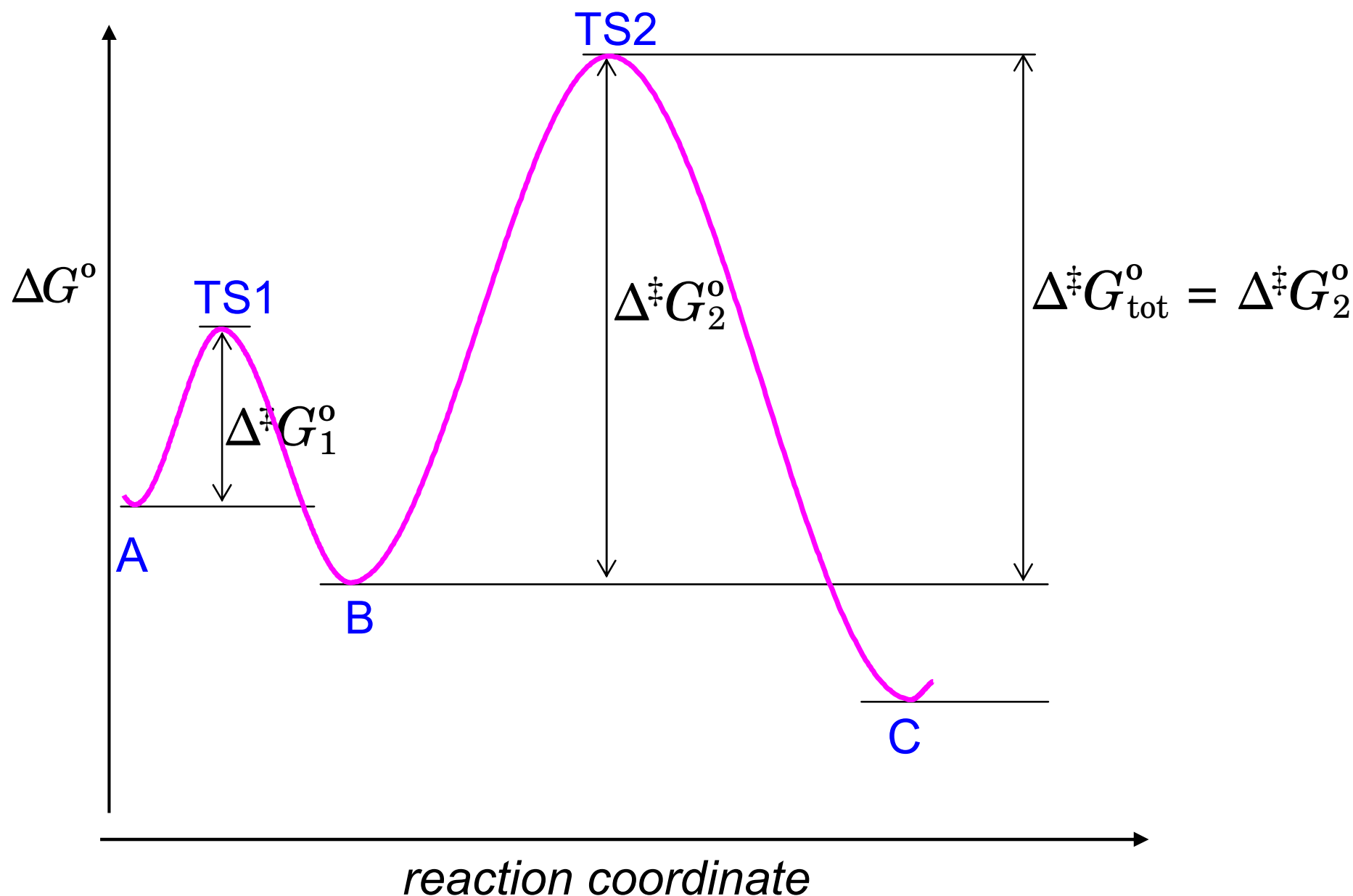
$$= \exp(-(G^\circ(B) - G^\circ(A))/RT) \cdot (k_B T/h) \exp(-(G^\circ(\text{TS2}) - G^\circ(B))/RT) =$$

$$= (k_B T/h) \exp(-(G^\circ(\text{TS2}) - G^\circ(A))/RT)$$

Hence, the actual reaction free energy barrier $\Delta^\ddagger G_{\text{tot}}^\circ = G^\circ(\text{TS2}) - G^\circ(A)$

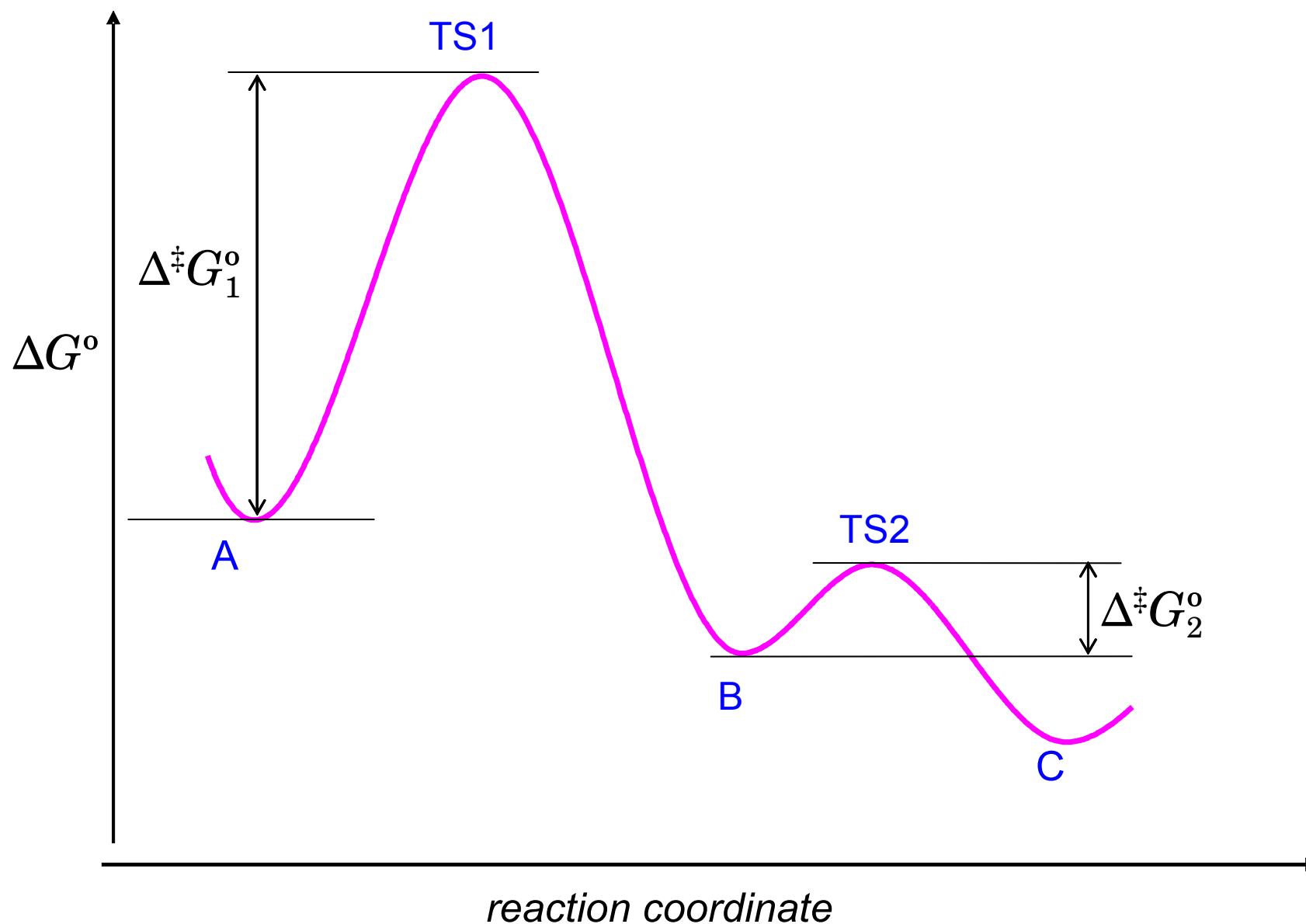
Transition-state theory for complex reactions

- Reversible consecutive reactions $A \rightleftharpoons B \rightarrow C$, case $G^\circ(B) < G^\circ(A)$:



- In this case, almost all of the reactant(s) A swiftly transforms to B ($[B] \approx [A]_0$), and the rate-determining step will be the B \rightarrow C step.

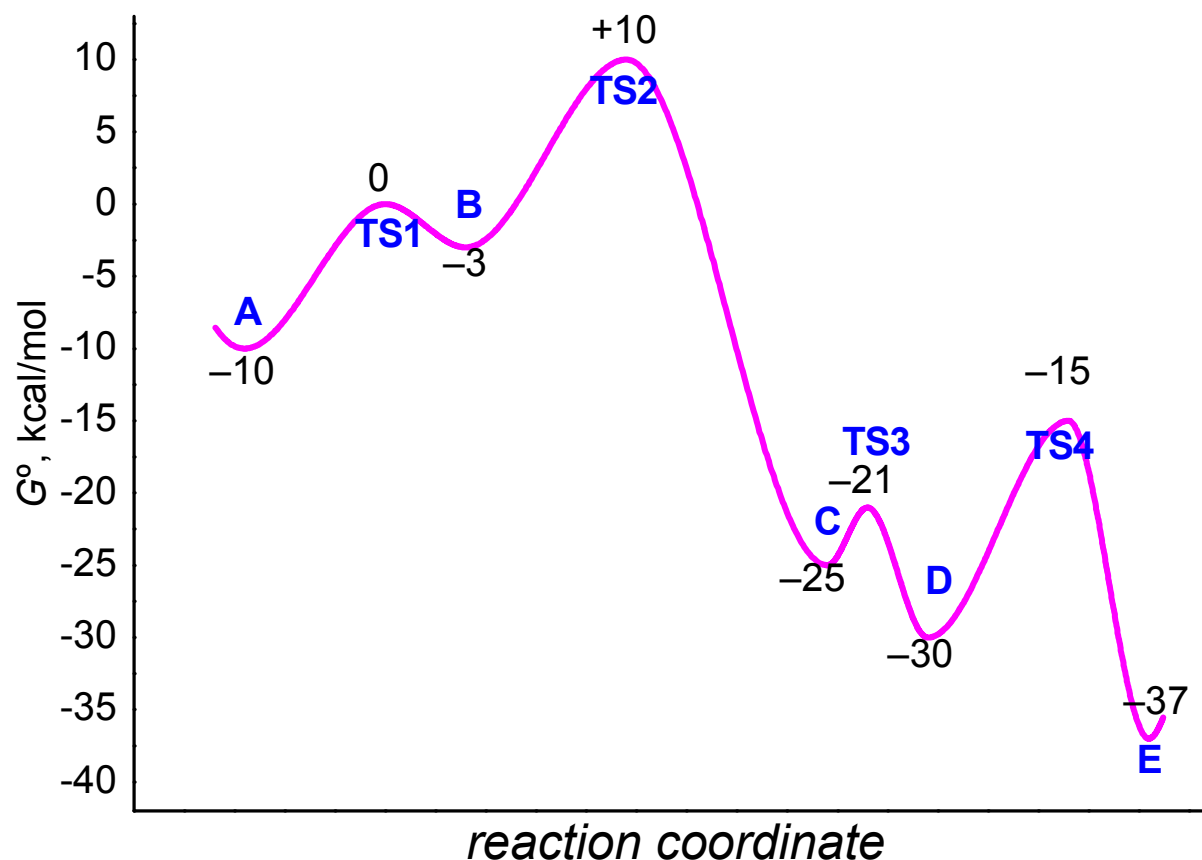
Transition-state theory for complex reactions



- **Summary:** in all cases $\Delta^\ddagger G_{\text{tot}}^\circ$ should be evaluated starting from the lowest (not necessarily the nearest) *left-hand* minimum.

Transition-state theory for complex reactions – example

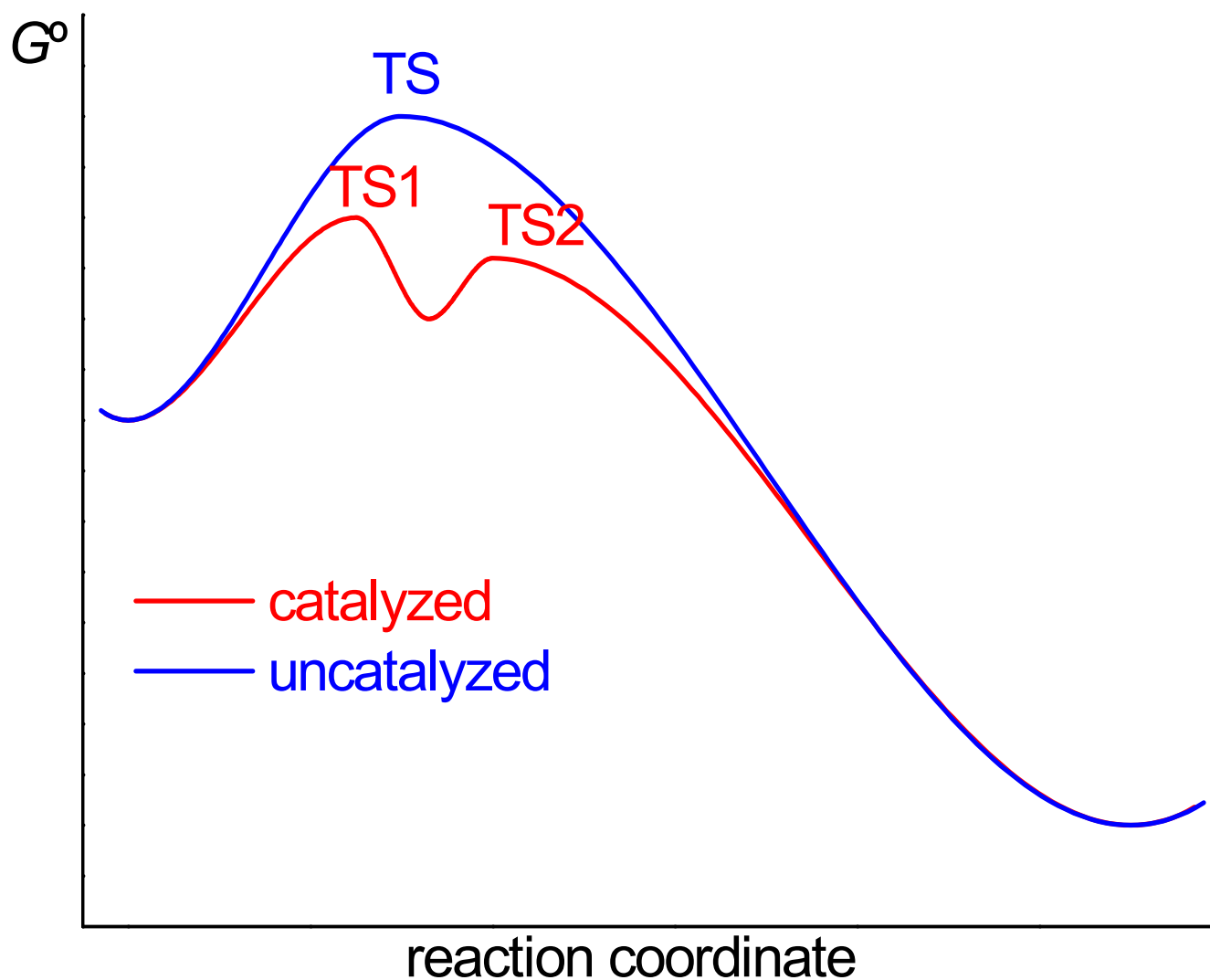
- Analysis of the potential energy surface for a complex reaction – an example:



- Checking all the transition states:
 - **TS1**: The only minimum to the left is **A**, thus $\Delta^\ddagger G_1^\circ = 10$ kcal/mol;
 - **TS2**: The lowest minimum to the left is **A**, thus $\Delta^\ddagger G_2^\circ = 20$ kcal/mol;
 - **TS3**: The lowest minimum to the left is **C**, thus $\Delta^\ddagger G_3^\circ = 4$ kcal/mol;
 - **TS4**: The lowest minimum to the left is **D**, thus $\Delta^\ddagger G_4^\circ = 15$ kcal/mol.
- Comparing $\Delta^\ddagger G_1^\circ$, $\Delta^\ddagger G_2^\circ$, $\Delta^\ddagger G_3^\circ$, and $\Delta^\ddagger G_4^\circ$: $\Delta^\ddagger G_2^\circ$ is the largest \Rightarrow **A** \rightarrow **TS2** is the rate-determining step. The total $\Delta^\ddagger G_{\text{tot}}^\circ = 20$ kcal/mol.

Potential energy surface – a catalytic reaction

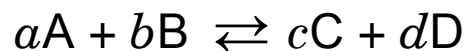
- A catalyzed *vs.* an uncatalyzed reaction:



- A **catalyzed** reaction goes through intermediate(s) and has a lower $\Delta^\ddagger E$, $\Delta^\ddagger G^\circ$, and $\Delta^\ddagger H^\circ$ and also the Arrhenius activation energy E_a .

Reactions at equilibrium and Microscopic Reversibility

- Consider an elementary reversible reaction of any molecularity:



The forward v_1 and reverse v_{-1} reaction rates are:

$$v_1 = k_1[A]^a[B]^b ; v_{-1} = k_{-1}[C]^c[D]^d$$

- At equilibrium (i.e., at $t = \infty$) the rates must be equal: $v_1 = v_{-1}$. Therefore,

$$k_1[A]^a[B]^b = k_{-1}[C]^c[D]^d \Rightarrow \frac{k_1}{k_{-1}} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_{\text{eq}}$$

Thus, we have obtained the *law of chemical equilibrium* and provided a *link* between the chemical kinetics and thermodynamics.

- Now consider a more general case of a complex reversible reaction that has arrived to equilibrium: $aA + bB \rightleftharpoons cC + dD \rightleftharpoons eE + fF \rightleftharpoons \dots \rightleftharpoons wW + xX \rightleftharpoons yY + zZ$

- The **Microscopic Reversibility Principle** (TOLMAN 1928) states that *at equilibrium* the rate of every forward elementary reaction must be equal to the rate of the corresponding reverse reaction:

$$k_1[A]^a[B]^b = k_{-1}[C]^c[D]^d ; k_2[C]^c[D]^d = k_{-2}[E]^e[F]^f ; \dots ; k_n[W]^w[X]^x = k_{-n}[Y]^y[Z]^z$$

Multiplying all the above equations, we obtain:

$$k_1 k_2 \dots k_n [A]^a [B]^b [C]^c [D]^d \dots [W]^w [X]^x = k_{-1} k_{-2} \dots k_{-n} [C]^c [D]^d [E]^e [F]^f \dots [Y]^y [Z]^z$$

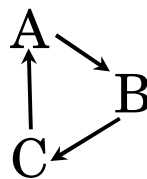
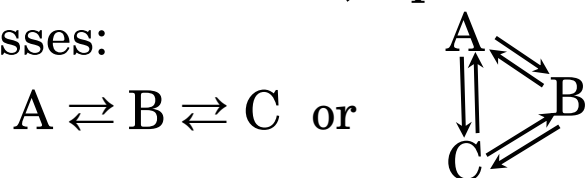
which gives, upon cancellation of identical terms, the following expression for the equilibrium constant:

$$K_{\text{eq}} = \frac{k_1 k_2 \dots k_n}{k_{-1} k_{-2} \dots k_{-n}} = \frac{[Y]^y [Z]^z}{[A]^a [B]^b}$$

Therefore, the equilibrium constant expression is determined only by the reactant concentrations $[A]^a$ and $[B]^b$ (with the powers a and b corresponding to the stoichiometric coefficients) and the product concentrations $[Y]^y$ and $[Z]^z$ and *does not* depend on a particular reaction mechanism or intermediate concentrations.

This is different from the kinetics *outside of* equilibrium, where the rate law in general depends on the mechanism.

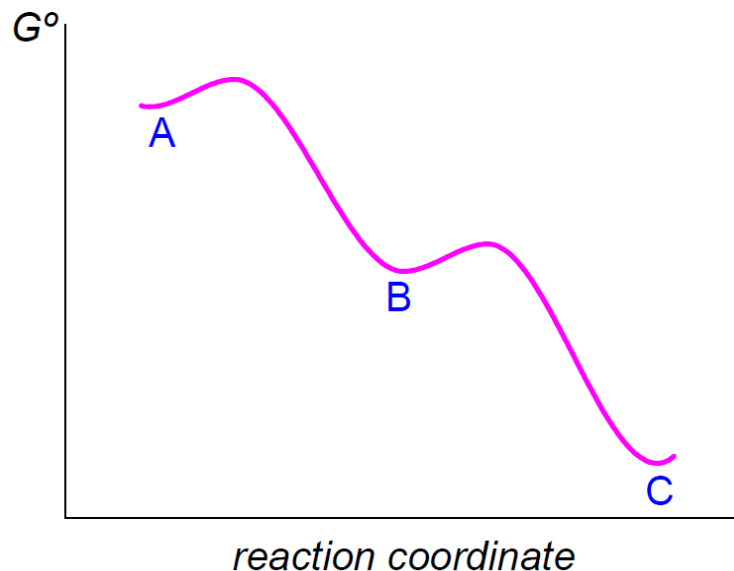
- **FOWLER** (1936) later augmented the microscopic reversibility principle by the **de-tailed balance principle** that states that in a complex reversible reaction every elementary step of the forward reaction must be mirrored by a reverse elementary step. In other words, equilibrium can be maintained by any of the following processes:



while a cyclic process such as this: is *not* possible, since it would mean different mechanisms for the $A \rightarrow C$ and $C \rightarrow A$ reactions: A transforms to C through the intermediate B, while the reverse process $C \rightarrow A$ is an elementary reaction, i.e., the forward and reverse processes would have different mechanisms, which is forbidden.

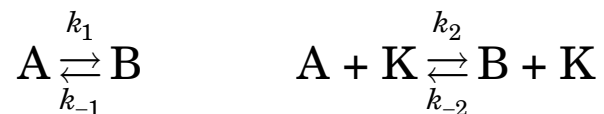
- It is not possible to justify the microscopic reversibility principle or the detailed balance principle theoretically just using the phenomenological kinetics. Their foundations come from the consideration of the potential energy surface. The basic idea is as follows: if a pathway linking the reactant(s) A and the product B is passable (in terms of $\Delta^\ddagger G^\circ$ and $\Delta_r G^\circ$) in the direction $A \rightarrow B$, it should be also passable in the reverse direction $B \rightarrow A$. Let us consider, for instance, the cyclic mechanism shown before. We will demonstrate that it is impossible.

Indeed, the irreversibility of the $A \rightarrow B$ steps means that $G^\circ(B) \ll G^\circ(A)$. Analogously, $G^\circ(C) \ll G^\circ(B)$. Hence, $G^\circ(C) \ll G^\circ(A)$. If, nevertheless, the $C \rightarrow A$ reaction is kinetically affordable in terms of $\Delta^\ddagger G^\circ$ (as shown in the scheme above), the $C \rightarrow A$ transition state must lie fairly low with respect to C. But then it must be even lower with respect to A, and the direct $A \rightarrow C$ process must be even easier than the $C \rightarrow A$ process!



- Using purely phenomenological (“macroscopic”) arguments, it can be shown that without microscopic reversibility, one could obtain effects that contradict to the classical thermodynamics.

For example, let’s imagine a reversible reaction $A \rightleftharpoons B$ that can occur both with and without a catalyst K according to two following mechanisms:



At equilibrium, *without* taking into account the microscopic reversibility principle, we could write down $v_1 + v_2 = v_{-1} + v_{-2}$. Thus,

$$k_1[A] + k_2[A][K] = k_{-1}[B] + k_{-2}[B][K]$$

Therefore,

$$K_{\text{eq}} = \frac{[B]}{[A]} = \frac{k_1 + k_2[K]}{k_{-1} + k_{-2}[K]}$$

which would mean that the equilibrium constant K_{eq} would depend on the catalyst concentration. In other words, the catalyst would be able to *shift* the equilibrium. This is impossible according to thermodynamics, since, if we actually had a catalyst that could shift the equilibrium, we would be able to build a *perpetuum mobile*.

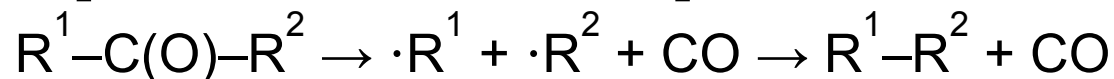
The paradox is resolved as follows: using the detailed-balance principle, we have to write down two separate equations for the rates: $v_1 = v_{-1}$ and $v_2 = v_{-2}$:

$k_1[A] = k_{-1}[B]$ and $k_2[A][K] = k_{-2}[B][K]$. Hence,

$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}} .$$

- Solvents have a strong influence on a chemical reaction:
 - Much higher concentrations are available than in the gas phase.
 - Ionic substances dissociate into ions, which has a profound effect on the reaction mechanism. (cf. S_N1, S_N2, E1, E2, electrophilic additions/ substitutions...)
 - Solvent can differently stabilize the reactants, transition state, and products, causing the kinetic ***solvent effect***.
 - For bimolecular reactions, $\Delta^\ddagger S^\circ$ is less negative in the solvent than in the gas phase.
 - “Cage effect” (= *efecte de gàbia*) (Franck–Rabinowitch effect):
Intermediates can be temporarily confined in a *cage* of surrounding solvent molecules.

Example: Norrish reaction – photochemical decomposition of ketones:

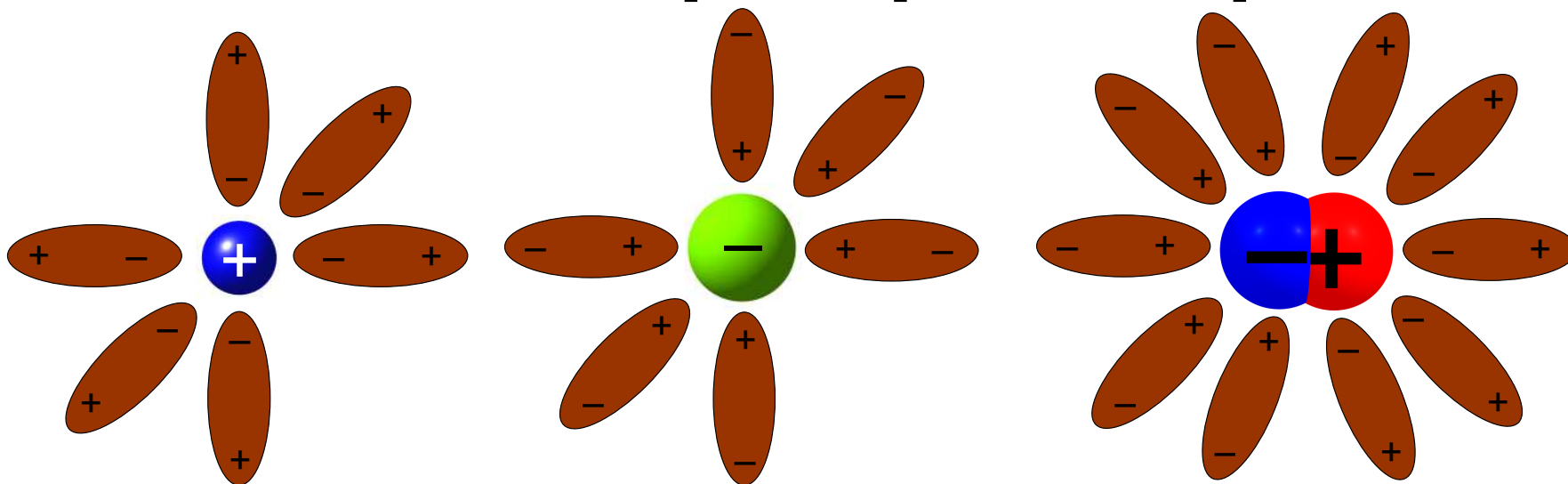


In the gas phase, $\cdot R^1$ and $\cdot R^2$ undergo recombination randomly, yielding R^1R^1 , R^1R^2 , and R^2R^2 in statistic fractions 1:2:1.

In solvent, $\cdot R^1$ and $\cdot R^2$ recombine in the same solvent *cage*, where they were formed, giving predominantly the R^1R^2 product.

Solvent effect – solvation energy

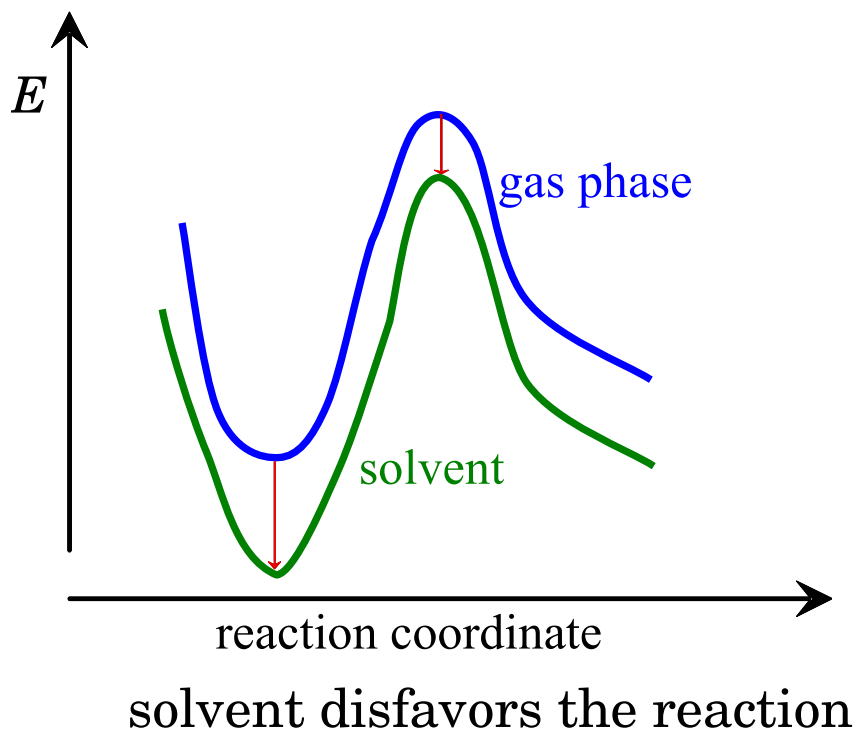
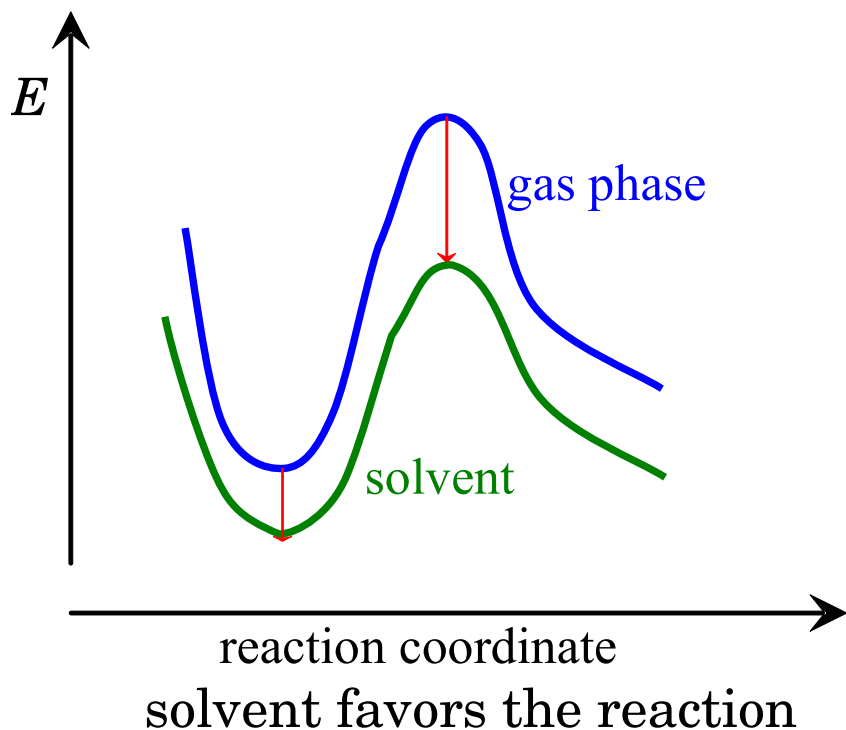
- The potential energy surface E changes in solution *vs.* gas phase. The thermodynamic functions (H , G , S) also change:
 $G^\circ(\text{solution}) = G^\circ(\text{gas}) + \Delta G^\circ_{\text{solvation}}$ $\Delta G^\circ_{\text{solvation}}$ is the *solvation free energy*.
- Solvation energy comes mostly from solute-solvent interaction (negative contribution): electrostatics + dispersion + polarization + specific interactions



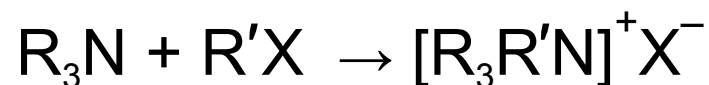
- Specific interactions: hydrogen bonds between solute and a polar protic solvent (H_2O , NH_3 , alcohols,...).
- Another contribution to solvation energy is *cavitation energy* (positive!).
- The total $\Delta G^\circ_{\text{solvation}}$ is usually negative, but sometimes small positive values can be obtained for poorly soluble substances due to cavitation energy.

Solvent effect – solvation energy

- Kinetic **solvent effect** is the change of reaction rate (constant) in solvent compared to the gas phase.
 - The solvent effect is due to unequal stabilization of the reactant(s) and the transition state in solution, leading to a change in the reaction barrier. Thus, $\Delta^\ddagger E$, $\Delta^\ddagger H^\circ$, and $\Delta^\ddagger G^\circ$ can be either *larger* or *smaller* in the solvent than in the gas phase, depending on whether the reactants or the transition state is stabilized more:



- Menshutkin reaction



The product is *ionic*; the transition state $[\text{R}_3\text{N}\cdots\text{R}'\cdots\text{X}]^\ddagger$ (albeit not ionic) is strongly polar. Therefore, such a reaction proceeds much **faster** in more **polar** solvents.

► Menshutkin reaction rate constants:

Solvent	$k \cdot 10^5, \text{M}^{-1} \cdot \text{s}^{-1}$	dielectric constant ϵ	dipole moment μ (D)
Hexane	0.5	1.9	0
Toluene	25.3	2.4	0.43
Bromobenzene	166	5.2	1.55
Acetone	265	20.7	2.85
Nitrobenzene	1380	34.8	4.02

Solvent effect – solvation energy

- The quantitative theories of solvation are relatively complex. However, for a *spherical ions* or a *spherical dipole*, the electrostatic component $E_{\text{el.st.}}$ of $\Delta G^\circ_{\text{solvation}}$ can be estimated as follows:

Spherical ion – Born formula (1920)

$$E_{\text{el.st.}} = -\frac{1}{2} \left(1 - \frac{1}{\varepsilon} \right) k_e \frac{q^2}{r}$$

$q = ez$ is the charge

r is the radius, ε is the dielectric constant

$k_e = 1/(4\pi\varepsilon_0) \approx 9 \cdot 10^9 \text{ J} \cdot \text{m} \cdot \text{C}^{-2}$ is the Coulomb constant

Spherical dipole – Onsager formula (1936)

$$E_{\text{el.st.}} = - \left(\frac{\varepsilon - 1}{2\varepsilon + 1} \right) k_e \frac{\mu^2}{r^3}$$

μ is the dipole moment

Note: both formulae are approximate and describe the electrostatics only.

- Consider a bimolecular reaction involving ions: $A + B \rightarrow C$ and assume that the Born formula yields a correction to the $G^\circ(A)$, $G^\circ(B)$, and $G^\circ(\text{TS})$. Thus, the $\Delta^\ddagger G^\circ$ in solution will be:

$$\Delta^\ddagger G^\circ_{\text{solution}} = \Delta^\ddagger G^\circ_{\text{gas}} - \frac{1}{2} \left(1 - \frac{1}{\varepsilon} \right) k_e \frac{\overbrace{(q_A + q_B)^2}^{\text{charge of TS}}}{r_{\text{TS}}} + \frac{1}{2} \left(1 - \frac{1}{\varepsilon} \right) k_e \frac{q_A^2}{r_A} + \frac{1}{2} \left(1 - \frac{1}{\varepsilon} \right) k_e \frac{q_B^2}{r_B}$$

$$\Delta^\ddagger G^\circ_{\text{solution}} = \Delta^\ddagger G^\circ_{\text{gas}} + \frac{1}{2} \left(1 - \frac{1}{\varepsilon} \right) k_e \left(-\frac{(q_A + q_B)^2}{r_{\text{TS}}} + \frac{q_A^2}{r_A} + \frac{q_B^2}{r_B} \right)$$

if we further assume that $r_A = r_B = r_{TS} = r$, a simpler expression is obtained:

$$\Delta^\ddagger G^\circ_{\text{solution}} = \Delta^\ddagger G^\circ_{\text{gas}} - \left(1 - \frac{1}{\varepsilon}\right) k_e \frac{q_A q_B}{r}$$

Note: we have just described (in a simplified manner) the solvation effect on a ionic reaction. For ions of the same sign, the activated complex $(A \cdots B)^{q_A + q_B}$ is more charged and therefore stronger solvated than individual ions A and B. For ions of opposite signs, the activated complex is weaker solvated. The effect on the rate constant:

$$\frac{k_{\text{solution}}}{k_{\text{gas}}} = e^{-(\Delta^\ddagger G^\circ_{\text{solution}} - \Delta^\ddagger G^\circ_{\text{gas}})/k_B T} = e^{\left(1 - \frac{1}{\varepsilon}\right) k_e \frac{q_A q_B}{r k_B T}}$$

The solvent effect has nothing to do with repulsion (or attraction) *between* ions. Of course, it is important, but it is already included in $\Delta^\ddagger G^\circ_{\text{gas}}$. Of course, with increasing dielectric constant the solvent effect $k_{\text{solution}}/k_{\text{gas}}$ increases, since the factor $(1 - 1/\varepsilon)$ increases. The rate constant ratio between two solvents with different dielectric constants ε_1 and ε_2 is as follows (SCATCHARD 1932):

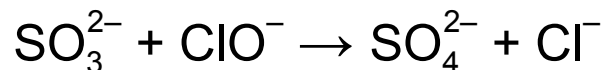
$$\frac{k_{\text{solvent1}}}{k_{\text{solvent2}}} = e^{\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right) k_e \frac{q_A q_B}{r k_B T}}$$

Primary kinetic salt effect – qualitative explanation

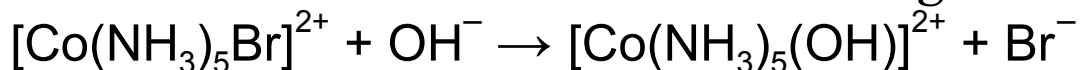
- The **salt effect** is the influence of electrolytes that are *not* involved into the reaction on the reaction's rate constant.
- With increasing ionic strength, each ion surrounded by a denser ionic atmosphere composed of other ions. This atmosphere provides a shielding (*=apantallament*) for the given ion, thus weakening the interaction between the ions. This is favorable for reaction of ions of the same charge (less repulsion), but unfavorable for reaction of ions of opposite charge (less attraction).
- Note: the ionic strength (and thus the salt effect) depends on *all* ions present in the solutions, not just those participating in the reaction. Thus, even addition of an inert salt will influence the rate constant!

► Examples:

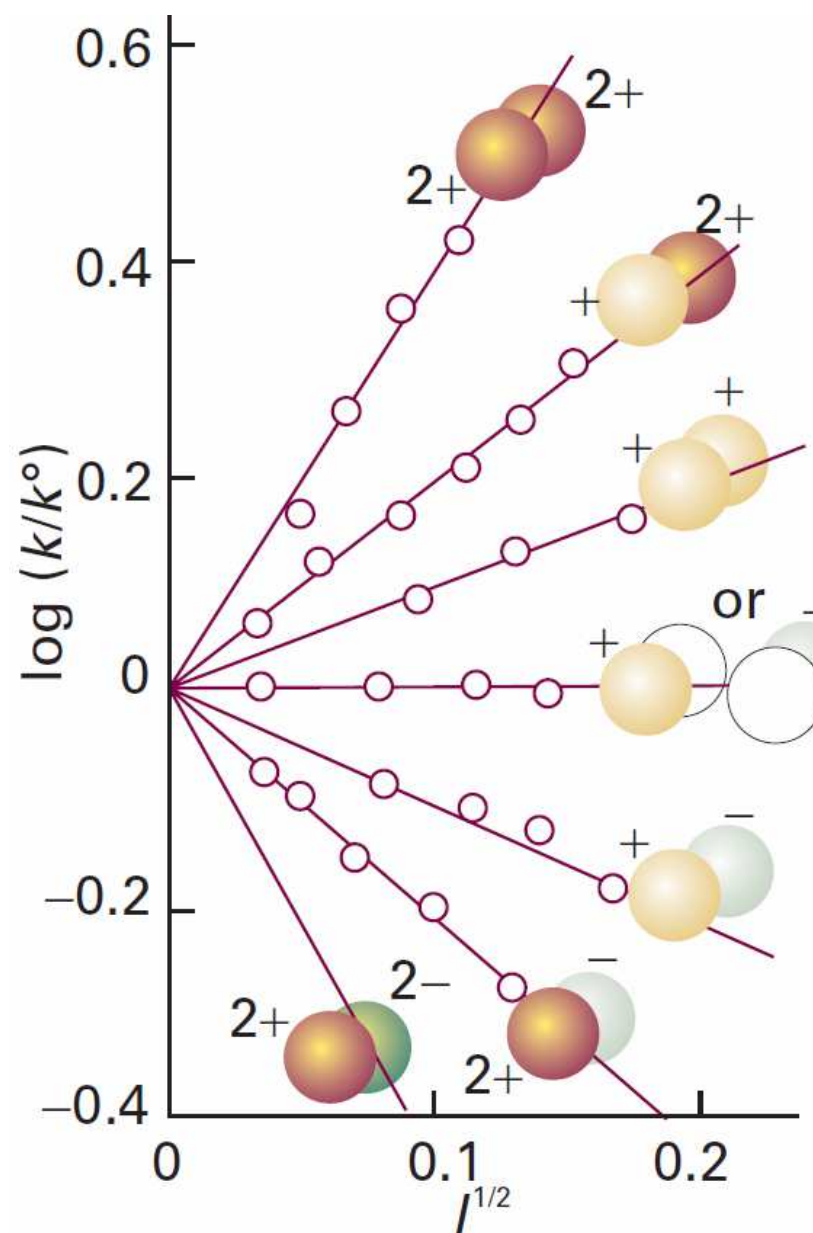
- Reaction rate *increases* with increasing I :



- Reaction rate *decreases* with increasing I :



Vyboishchikov (157)



Ionic strength (*força iònica*):

$$I = 1/2 \sum_i c_i z_i^2$$

Primary kinetic salt effect

- Let us go back to the derivation of the Eyring equation (page 128), but now consider that the solutions are *not ideal*:

$$\frac{a_{(A\cdots B)^\ddagger}}{a_A a_B} = \frac{\gamma^\ddagger [(A\cdots B)^\ddagger] / c^\circ}{(\gamma_A [A] / c^\circ) (\gamma_B [B] / c^\circ)} = K^\ddagger \Rightarrow [(A\cdots B)^\ddagger] = \frac{\gamma_A \gamma_B}{\gamma^\ddagger} \frac{1}{c^\circ} K^\ddagger [A] [B]$$

where γ_A , γ_B , γ^\ddagger are the *activity coefficients* of the reactants and activated complex, correspondingly; $0 < \gamma < 1$.

- For diluted solutions of *non-electrolytes*, γ is close to 1 and does not influence the rate constant substantially.
- For *electrolytes* γ must be taken into account.
- The rate constant in an electrolyte solution is given by:

$$k_{\text{solv}}(I) = \frac{k_B T}{h} \frac{\gamma_A \gamma_B}{\gamma^\ddagger} \frac{1}{c^\circ} e^{-\Delta^\ddagger G_{\text{solv}}^\circ / RT} = \frac{\gamma_A \gamma_B}{\gamma^\ddagger} k_{\text{solv}}(0)$$

where $k(0)$ is the rate constant at zero ionic strength.

Primary kinetic salt effect – Brønsted–Bjerrum equation

- The rate constant at non-zero ionic strength I :

$$\frac{k(I)}{k(0)} = \frac{\gamma_A \gamma_B}{\gamma^\ddagger}$$

- The activity coefficient γ depends on the ionic strength I as described by the Debye–Hückel theory:

$$\log_{10} \gamma_i = -Az_i^2 \sqrt{I} \quad (\text{Debye–Hückel limiting law})$$

where A is a constant ($\approx 0.51 \text{ M}^{-1/2}$ in H_2O solutions at 25°C);

z_i is the charge of i -th ion;

I is the *ionic strength*: $I = \frac{1}{2} \sum_i c_i z_i^2$

$$\log_{10} \frac{k(I)}{k(0)} = \log_{10} \frac{\gamma_A \gamma_B}{\gamma^\ddagger} = \log_{10} \gamma_A + \log_{10} \gamma_B - \log_{10} \gamma^\ddagger = -Az_A^2 - Az_B^2 + A \underbrace{(z_A + z_B)^2}_{\text{charge of TS}}$$

Brønsted–Bjerrum equation:

$$\log_{10} \frac{k(I)}{k(0)} = 2Az_A z_B \sqrt{I}$$

- The Brønsted–Bjerrum equation describes the **primary** kinetic **salt effect**: the rate constant for an ionic reaction *increases* with ionic strength if the reacting ions are of the same charge ($z_A z_B > 0$) and *decreases* if the ions are of opposite charge ($z_A z_B < 0$).



Jonannes Brønsted
(1879–1947)

- Ionic strength can affect the concentration of a reactant or a catalysts due to changing in ionization constant.
 - ▶ Example: Catalysis of sucrose inversion with acetic acid.
Addition of NaCl accelerates the reaction because of enhanced dissociation of acetic acid due to presence of Na^+ and Cl^- .
 - ▶ Reactions in which the ionic form of a reactant reacts, get faster in the presence of an electrolyte.

Kinetic isotope effect (KIE)

- The ***Kinetic Isotope Effect*** (KIE) is the change in the rate constant upon isotope substitution in the reactant (e.g., H→D). Usually, $KIE = k_H/k_D > 1$. The ***primary*** KIE takes place when the isotope-substituted bond is broken in the reaction.
- For simplicity, let us consider a *unimolecular* reaction in which a X–H (X–D) bond is broken:

$$k = \frac{k_B T}{h} \frac{\tilde{Q}^\ddagger}{\tilde{Q}^A} e^{-\frac{\Delta^\ddagger E_0}{k_B T}} = \frac{k_B T}{h} \frac{Q_{\text{trans}}^\ddagger}{Q_{\text{trans}}^A} \frac{Q_{\text{rot}}^\ddagger}{Q_{\text{rot}}^A} \frac{\tilde{Q}_{\text{vib}}^\ddagger}{\tilde{Q}_{\text{vib}}^A} e^{-\frac{\Delta^\ddagger E_0}{k_B T}}$$

$$k_H / k_D \approx \frac{Q_{\text{vib}}^\ddagger(\text{H}) / Q_{\text{vib}}^\ddagger(\text{D})}{Q_{\text{vib}}^A(\text{H}) / Q_{\text{vib}}^A(\text{D})}$$

- Neglecting Q_{trans} and Q_{rot} because Q_{trans}^A and $Q_{\text{trans}}^\ddagger$ cancel exactly, while $Q_{\text{rot}}^A(\text{H}) \approx Q_{\text{rot}}^\ddagger(\text{D})$.

$$k_H / k_D = \frac{\tilde{Q}_{\text{vib}}^\ddagger(\text{H}) / \tilde{Q}_{\text{vib}}^\ddagger(\text{D})}{\tilde{Q}_{\text{vib}}^A(\text{H}) / \tilde{Q}_{\text{vib}}^A(\text{D})} e^{-\frac{\Delta\Delta^\ddagger E_0}{RT}}, \text{ where } \Delta\Delta^\ddagger E_0 = \Delta^\ddagger E_0(\text{H}) - \Delta^\ddagger E_0(\text{D}) = \\ = \Delta E_{\text{ZP}}(\text{H}) - \Delta E_{\text{ZP}}(\text{D}) < 0 \text{ because } \Delta E_{\text{ZP}}(\text{H}) < \Delta E_{\text{ZP}}(\text{D}).$$

Primary kinetic isotope effect

- Limiting case 1 (high frequencies, low temperatures):

$$h\nu / k_B T \gg 1 \Rightarrow \frac{1}{1 - e^{-h\nu_m / k_B T}} \approx 1 \Rightarrow \tilde{Q}_{\text{vib}}(\text{H}) \approx \tilde{Q}_{\text{vib}}(\text{D})$$

The isotope effect will be solely due to difference in $\Delta^\ddagger E_0$: $\Delta^\ddagger E_0(\text{D}) > \Delta^\ddagger E_0(\text{H})$:

$$k_{\text{H}} / k_{\text{D}} = e^{-\frac{\Delta\Delta^\ddagger E_0}{k_B T}} = e^{-\frac{h(\nu_{\text{H}} - \nu_{\text{D}})}{2k_B T}}$$

Here we used the approximation $e^{-x} \approx 0 \Rightarrow 1 - e^{-x} \approx 1$ for $x \gg 1$.

- Limiting case 2 (low frequencies, high temperatures): $h\nu / k_B T \ll 1$

$$\tilde{Q}_{\text{vib}}(\text{H}) / \tilde{Q}_{\text{vib}}(\text{D}) = \frac{1 - e^{-h\nu(\text{H}) / k_B T}}{1 - e^{-h\nu(\text{D}) / k_B T}} \approx \frac{h\nu(\text{H}) / k_B T}{h\nu(\text{D}) / k_B T} = \frac{\nu(\text{H})}{\nu(\text{D})}$$

Here we used the approximation $e^{-x} \approx 1 - x \Rightarrow 1 - e^{-x} \approx x$ for $x \ll 1$.

$$k_{\text{H}} / k_{\text{D}} = \frac{\tilde{Q}_{\text{vib}}(\text{H})}{\tilde{Q}_{\text{vib}}(\text{D})} e^{-\frac{\Delta\Delta^\ddagger E_0}{k_B T}} \approx \frac{\nu(\text{H})}{\nu(\text{D})} e^{-\frac{h(\nu_{\text{H}} - \nu_{\text{D}})}{2k_B T}}$$

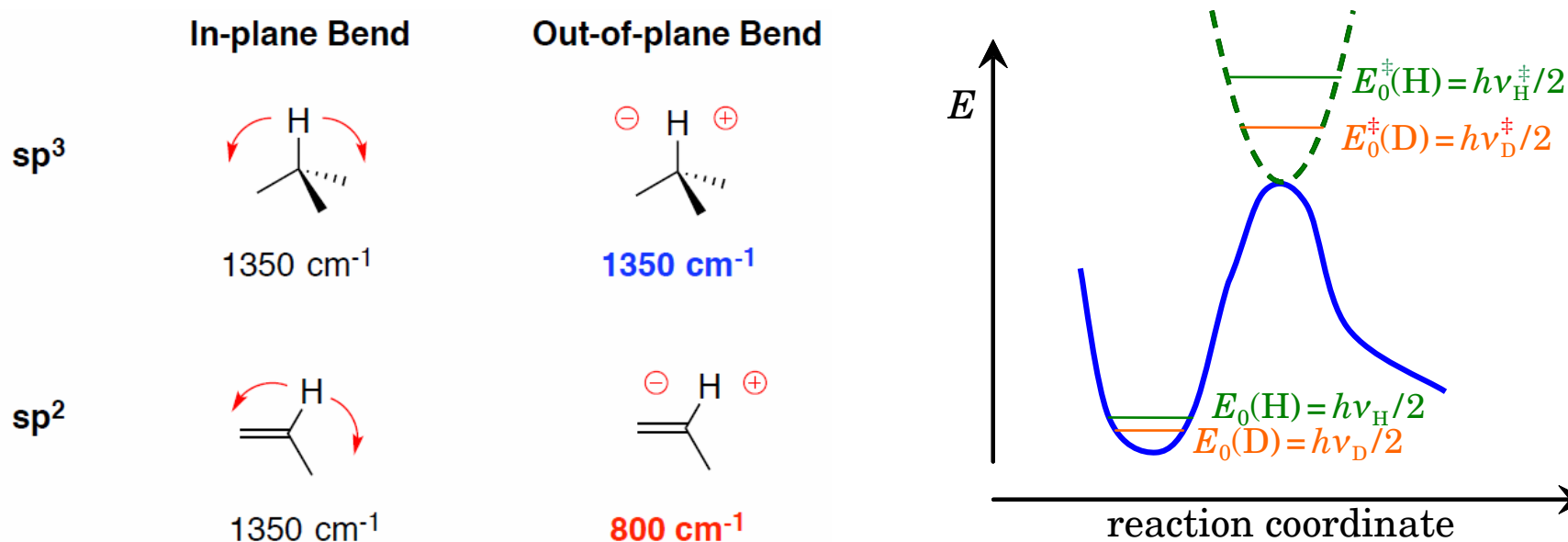
- The frequency ratio:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}} \Rightarrow \frac{\nu(\text{H})}{\nu(\text{D})} = \sqrt{\frac{m_{\text{D}}}{m_{\text{H}}}} \approx \sqrt{2}$$

- Not necessarily any of the two limiting cases take place.
- Typical primary KIE for H/D is between 1 and 8.
- For other elements, KIE is much smaller (i.e., 1.03–1.05 for $^{12}\text{C}/^{13}\text{C}$).

Secondary kinetic isotope effect (SKIE)

- When the H/D isotope substitution takes place at a bond different from the one broken in the reaction, this is the **secondary kinetic isotope effect**.
- SKIE typically occurs when the *hybridization* of a reacting carbon atom changes and based on the changes in the *bending* (rather than stretching!) vibrations:
 - $sp^2 \rightarrow sp^3$: bending vibration becomes stronger $\Rightarrow \Delta^\ddagger E_0(\text{H}) - \Delta^\ddagger E_0(\text{D}) < 0$
“inverse” SKIE with $k_{\text{H}}/k_{\text{D}}$ about 0.7 to 0.9:

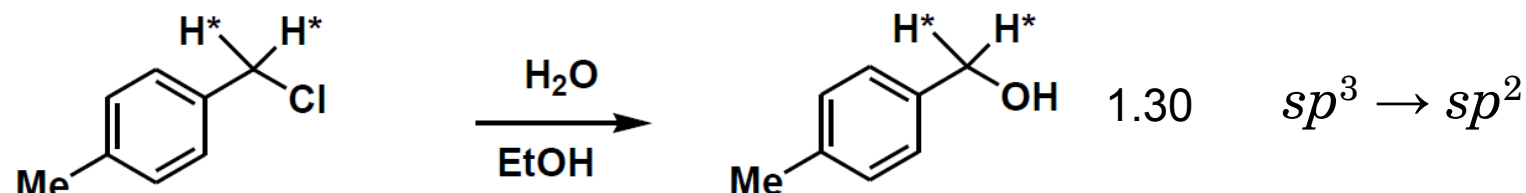
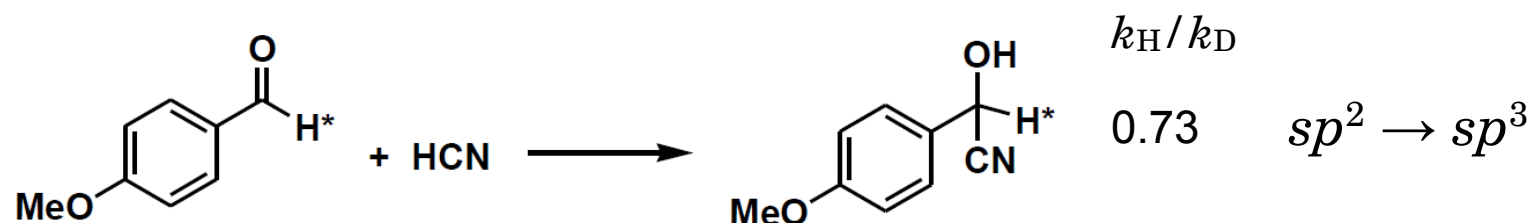


- $sp^3 \rightarrow sp^2$: “normal” SKIE with $k_{\text{H}}/k_{\text{D}}$ about 1.1 to 1.2.

See pages 816–818 of Atkins’s book for more detail.

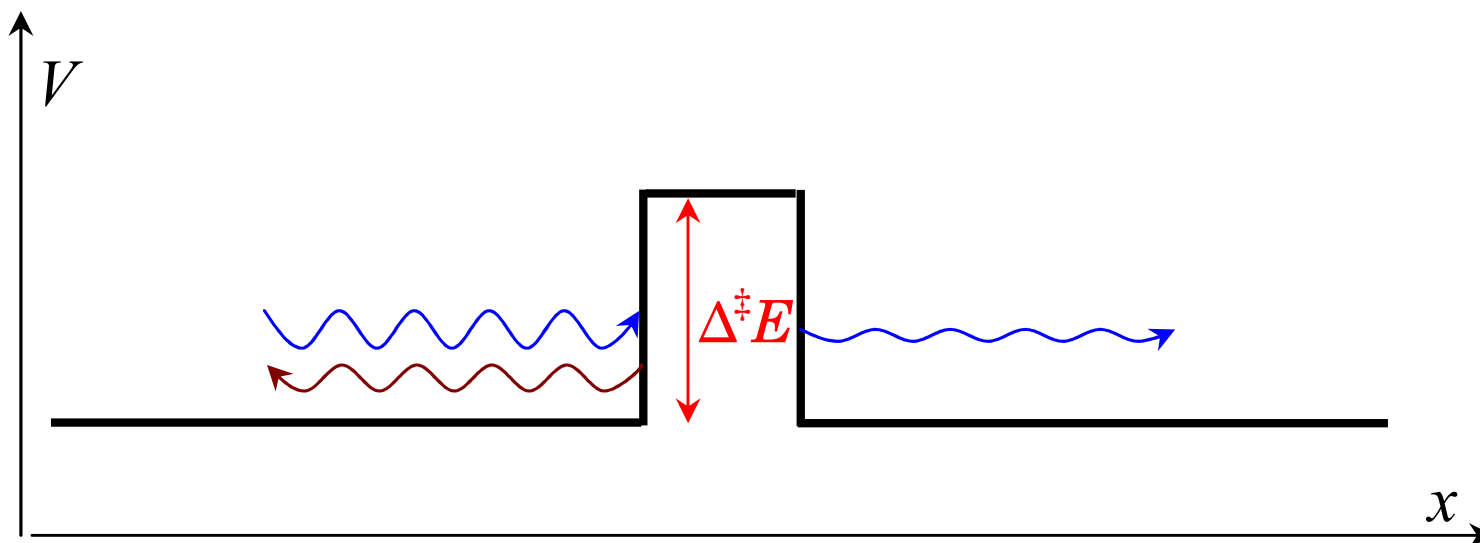
Secondary kinetic isotope effect – examples

- The isotope effect (or its absence) is helpful to make conclusion about the rate-determining step of a complex reaction.



Tunnelling

- The Transition-State Theory is a classical (not quantum) theory \Rightarrow quantum-mechanical effects such as **tunnelling** are not taken into account.
- *Tunnelling*: penetration of a quantum particle with $E < \Delta^\ddagger E$ through the barrier.
 - ▶ Transmission probability $P_t(E)$ increases with increasing particle *energy* E ($P_t = 1$ for $E > \Delta^\ddagger E$).
 - ▶ Transmission probability decreases with increasing particle *mass* m , barrier *height* $\Delta^\ddagger E$ and barrier *width*.
- Tunnelling is very important for *electron transfer* processes and may be important for *proton* transfer. Not important for other reactions.
- Tunnelling is more important at low temperatures (see next page).

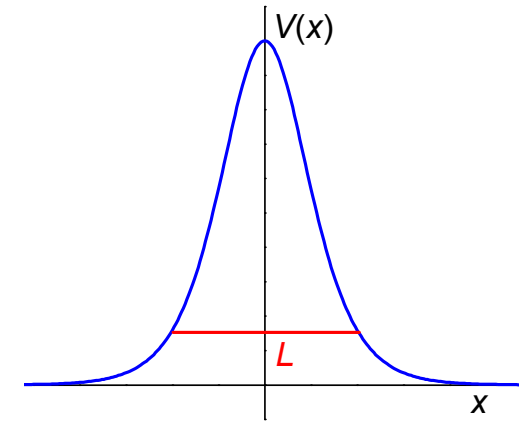


- The tunneling correction $\kappa_t(T)$ at temperature T is obtained by Boltzmann averaging of transmission probability $P_t(E)$:

$$\kappa_t(T) = \frac{1}{k_B T} \int_0^{\infty} P_t(E) e^{-E/k_B T} dE$$

- $P_t(E)$ is derived analytically for a model potential of certain mathematical form – the *Eckart potential*:

$$V(x) = \frac{\Delta^\ddagger E}{\cosh^2(x\pi/L)} \quad P_t(E) = \frac{1}{1 + \exp\left(\frac{4\pi L \sqrt{2m\Delta^\ddagger E}}{h} \left(1 - \sqrt{\frac{E}{\Delta^\ddagger E}}\right)\right)}$$



- After a lengthy derivation, the following WIGNER correction to the rate constant is obtained. Note that this is an approximation only:

$$\kappa_t(T) = \frac{h|v_{\text{im}}|}{2k_B T \sin(h|v_{\text{im}}|/(2k_B T))} \approx 1 + \frac{1}{24} \left(\frac{h|v_{\text{im}}|}{k_B T} \right)^2$$

$$k_{\text{full}} = \kappa_t(T) \cdot k_{\text{Eyring}}(T)$$

where v_{im} is the *imaginary frequency* at the transition state:

$$v_{\text{im}} = \frac{i}{L} \sqrt{\frac{\Delta^\ddagger E}{2m}}; \quad |v_{\text{im}}| = \frac{1}{L} \sqrt{\frac{\Delta^\ddagger E}{2m}}$$

Tunnelling – example

- $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$ reaction $\Delta^\ddagger E = 40 \text{ kJ/mol}$, $\nu_{\text{im}} = 1511 \text{ cm}^{-1} = 4.53 \cdot 10^{13} \text{ Hz}$

$T, \text{ K}$	200	225	250	300	400	500	1000
$\kappa_t(T)$	864	169	54	14	4	2.4	1.2

- Such a strong tunnelling is not typical: it is due to an unusually small TS mass for this reaction

- Formal kinetics:
 - ▶ Horiuti–Temkin theory of steady-state reactions
 - ▶ Experimental methods of studying fast reactions
 - ▶ Polythermic kinetics
- Kinetics theory:
 - ▶ Collision theory
 - ▶ Unimolecular reactions (Lindemann–Hinshelwood, RRK, RRKM theories)
 - ▶ Dynamics of the elementary act
 - ▶ Electron-transfer processes; Marcus theory
 - ▶ Diffusion-control reactions
 - ▶ Reactions in open systems; macrokinetics
 - ▶ Photochemical reactions

<https://tinyurl.com/1storderkinetics>

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

- Solution

- ▶ Variable separation:

$$-\frac{d[A]}{[A]} = kdt$$

- ▶ Version 1 – Indefinite integration

$$-\int \frac{d[A]}{[A]} = \int kdt + C \quad -\ln[A] = kt + C$$

C is the *integration constant*, the value of which is determined from the initial condition: $[A](t=0) = [A]_0 \Rightarrow C = -\ln [A]_0$

$$-\ln[A] = kt - \ln[A]_0$$

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

$$\frac{[A]}{[A]_0} = e^{-kt} \equiv \exp(-kt)$$

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

► Version 2 – Definite integration

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t k dt'$$

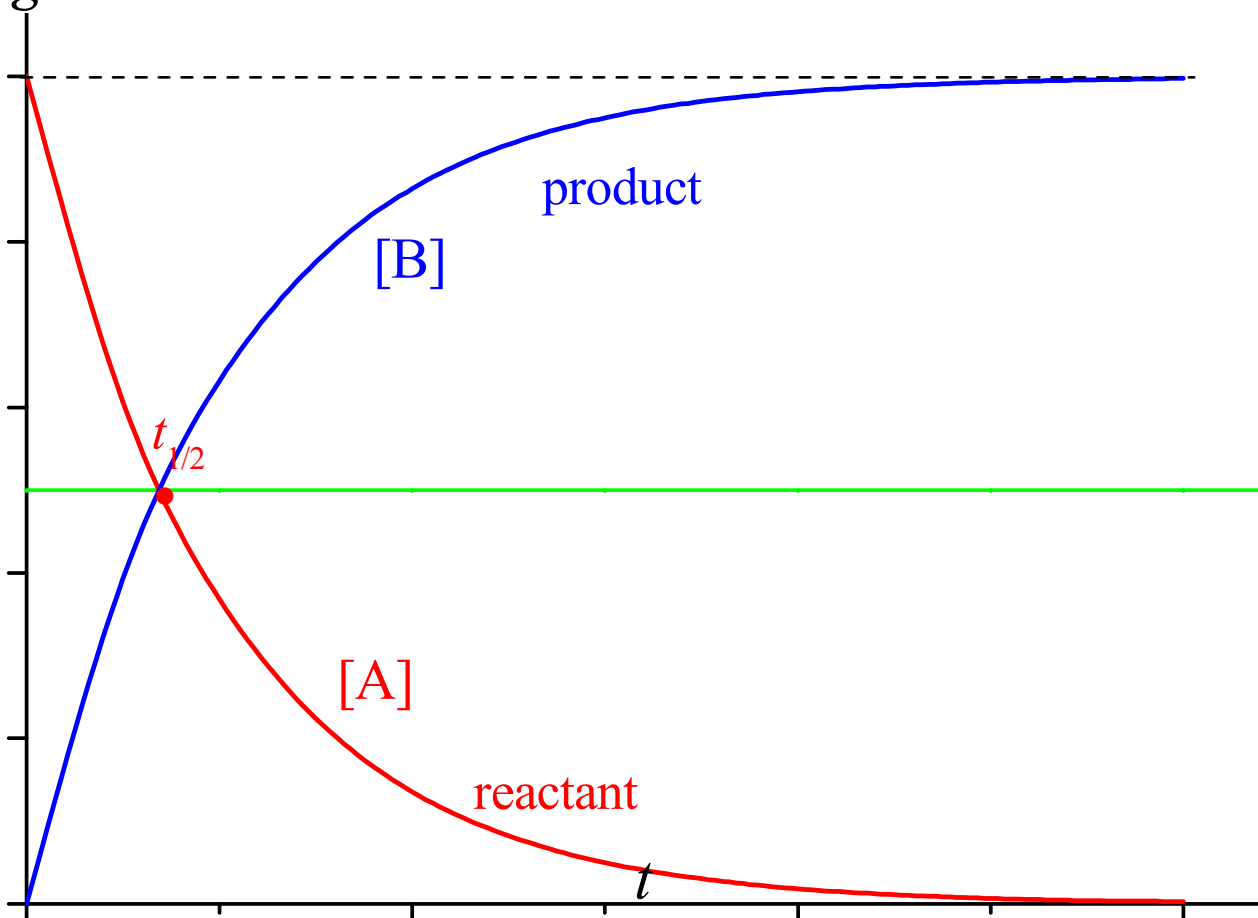
$$-\ln[A] \Big|_{[A]_0}^{[A]_t} = kt' \Big|_0^t$$

$$-(\ln[A]_t - \ln[A]_0) = kt$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

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

$$[\text{Product}]_t = [A]_0 - [A]_t$$



Appendix 2. Second-order reaction kinetics – one substrate

See <https://tinyurl.com/2ndorderkinetics>

- $2A \rightarrow B$: (k in $M^{-1} \cdot s^{-1}$):

$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A]^2 \quad \left\{ \begin{array}{l} \frac{d[A]}{dt} = -2k[A]^2 \\ \frac{d[B]}{dt} = k[A]^2 \end{array} \right.$$

- Solution:

- For a *one*-substrate reaction: $2A \rightarrow B$: rate law (k in $M^{-1} \cdot s^{-1}$):

$$-\frac{1}{2} \frac{d[A]}{dt} = k[A]^2 \quad \Leftrightarrow \quad \frac{d[A]}{dt} = -2k[A]^2$$

► Variable separation: $\frac{d[A]}{dt} = -2k[A]^2 \Rightarrow -\frac{d[A]}{[A]^2} = 2k dt$

► Version 1 – Indefinite integration Initial condition:

$$-\int \frac{d[A]}{[A]^2} = \int 2k dt \quad [A](t=0) = [A]_0 \Rightarrow C = \frac{1}{[A]_0}$$

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

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

► Version 2 – Definite integration:

$$\begin{aligned} \frac{d[A]}{dt} &= -2k[A]^2 & - \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} &= \int_0^t 2k dt \\ - \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} &= \int_0^t 2k dt & \frac{1}{[A]} \Big|_{[A]_0}^{[A]_t} = 2k dt \Big|_0^t &\Rightarrow \frac{1}{[A]_t} - \frac{1}{[A]_0} = 2kt \end{aligned}$$

Appendix 3 – Guggenheim relation

The Guggenheim relation (which is not actually due to E.A.Guggenheim) is enormously useful for solving kinetics problems, as it links any measurable quantity (“signal”) Y that characterizes the advance of a chemical reaction with the concentration of the reactant $[A]$:

$$\boxed{\frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty}}$$

The only condition of applicability of the Guggenheim relation is that the quantity Y depends *linearly* on the concentration of all components of the reaction mixture:

$$Y = Y_M + \sum_i \lambda_i [A_i]$$

Thus, the signal Y can be optical absorbance in spectrophotometry, electrical conductivity, total pressure of a gas mixture, angle of rotation of polarized light, a concentration of a species other than the reactant, and many other quantities. However, it *cannot* be optical transmittance, electrical resistance, or pH, as they are not linear functions of the concentrations.

A rigorous derivation of the Guggenheim relation is presented on Pages 21–22 of the *Llibret de problemes*. We will now discuss how it can be used for solving chemical kinetics problems.

First of all, the Guggenheim relation expresses laws of stoichiometry. On its own, it does not carry any information about the kinetics of the process under study. Therefore, it must be combined with a valid kinetic rate law in the integrated form. We will consider four distinct cases: (a) first-order irreversible reaction; (b) first-order reversible reaction; (c) second-order irreversible reaction with equal reactant concentrations: $[A]_0 = [B]_0$; (d) zeroth-order irreversible reaction.

(a) **first-order irreversible reaction – Guggenheim I method** (not actually due to E.A.Guggenheim)

Rate law:

Guggenheim relation (taking into account that $[A]_{\infty} = 0$):

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

$$\frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}} = \frac{[A]_t - [A]_{\infty}}{[A]_0 - [A]_{\infty}} = \frac{[A]_t}{[A]_0}$$

Therefore,

$$\frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}} = e^{-kt} \Rightarrow Y_t - Y_{\infty} = (Y_0 - Y_{\infty})e^{-kt} \Rightarrow \ln(Y_t - Y_{\infty}) = \ln(Y_0 - Y_{\infty}) - kt$$

If $Y_t < Y_{\infty}$, the latter equation should be rewritten as follows: $\ln(Y_{\infty} - Y_t) = \ln(Y_{\infty} - Y_0) - kt$

In general, the final equation will be:

$$\boxed{\ln |Y_t - Y_{\infty}| = \ln |Y_0 - Y_{\infty}| - kt} \text{ – Guggenheim I method (requires } Y_{\infty})$$

This one is directly suitable for doing a linear regression in the coordinates $\ln |Y_t - Y_{\infty}| (t)$.

The slope will give the rate constant k .

(a1) **first-order irreversible reaction – Guggenheim II method** (E.A.Guggenheim 1926):

Consider the situation that we do *not* have Y_{∞} available, but the data are *equidistant* in term of time. That is, we have $Y_t, Y_{t+\Delta t}, Y_{t+2\Delta t}, Y_{t+3\Delta t}, Y_{t+4\Delta t}, \dots$. Then considering applying the equation for Y_t and $Y_{t+\Delta t}$, we get the following:

$$Y_t - Y_{\infty} = (Y_0 - Y_{\infty})e^{-kt} \text{ and } Y_{t+\Delta t} - Y_{\infty} = (Y_0 - Y_{\infty})e^{-k(t+\Delta t)}$$

Subtracting these two equations:

$$Y_{t+\Delta t} - Y_t = (Y_{\infty} - Y_0)(e^{-kt} - e^{-k(t+\Delta t)})$$

$$Y_{t+\Delta t} - Y_t = (Y_{\infty} - Y_0)(1 - e^{-k\Delta t})e^{-kt}$$

$$\boxed{\ln |Y_{t+\Delta t} - Y_t| = \ln(|Y_{\infty} - Y_0|(1 - e^{-k\Delta t})) - kt} \text{ – Guggenheim II method (requires equidistant data)}$$

The latter equation can be applied for a linear regression in the coordinates $\ln |Y_{t+\Delta t} - Y_t| (t)$. Note that the equidistance of the data ($\Delta t = \text{const}$) is important, because otherwise the intercept is not a constant and the regression will be invalid.

(a2) **first-order irreversible reaction – KMS method** (Kezdy–Mangelsdorf–Swinbourne): Like in Guggenheim II method, we do *not* need Y_∞ , but we need *equidistant* data. We start the derivation from the expression of the Guggenheim I method:

$$(Y_t - Y_\infty)/(Y_0 - Y_\infty) = e^{-kt} \Rightarrow Y_t - Y_\infty = (Y_0 - Y_\infty)e^{-kt}$$

and subsequently get:

$$Y_{t+\Delta t} - Y_\infty = (Y_0 - Y_\infty)e^{-k(t+\Delta t)} \Rightarrow (Y_{t+\Delta t} - Y_\infty)e^{k\Delta t} = (Y_0 - Y_\infty)e^{-kt}$$

Thus:

$$Y_t - Y_\infty = (Y_{t+\Delta t} - Y_\infty)e^{k\Delta t}$$

Multiplying by $e^{-k\Delta t}$:

$$Y_{t+\Delta t} - Y_\infty = (Y_t - Y_\infty)e^{-k\Delta t}$$

$$Y_{t+\Delta t} = (Y_t - Y_\infty)e^{-k\Delta t} + Y_\infty$$

$$Y_{t+\Delta t} = Y_t e^{-k\Delta t} - Y_\infty e^{-k\Delta t} + Y_\infty$$

$$Y_{t+\Delta t} = (Y_\infty - Y_\infty e^{-k\Delta t}) + Y_t e^{-k\Delta t}$$

$$\boxed{Y_{t+\Delta t} = Y_\infty(1 - e^{-k\Delta t}) + e^{-k\Delta t}Y_t} \text{ – the KMS method (requires equidistant data)}$$

This latter is suitable for a linear regression in the coordinates $Y_{t+\Delta t}(Y_t)$. The slope will be $e^{-k\Delta t}$, from which we can get k .

(a3) **R/R method** for a **first-order irreversible reaction** – when the signal *derivative* values $R(t) = dY/dt$ are available, not just the signal y itself. Taking the derivative of the equation

$$Y_t - Y_\infty = (Y_0 - Y_\infty)e^{-kt} \Rightarrow Y_t = (Y_0 - Y_\infty)e^{-kt} + Y_\infty$$

we obtain for the time t :

$$R_t = dY_t/dt = -k(Y_0 - Y_\infty)e^{-kt}$$

and then for the time $t + \Delta t$:

$$R_{t+\Delta t} = -k(Y_0 - Y_\infty)e^{-k(t+\Delta t)}$$

Dividing two above equations by each other, we obtain: $R_t/R_{t+\Delta t} = e^{-k\Delta t}$ and hence:

$$k = \frac{\ln(R_{t+\Delta t} / R_t)}{\Delta t}$$

Thus, if we have the signal *derivatives*, we can easily calculate k from any two subsequent time points t and $t + \Delta t$ directly. The values of k can be then averaged over various datapoints.

(b) **first-order reversible reaction:**

$$\text{Rate law: } [A]_t = [A]_\infty + ([A]_0 - [A]_\infty)e^{-(k_1+k_{-1})t} \Rightarrow \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty} = e^{-(k_1+k_{-1})t}$$

$$\text{Guggenheim relation: } \frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty} \quad (\text{this time } [A]_\infty \neq 0)$$

Therefore,

$$\frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = e^{-(k_1+k_{-1})t} \Rightarrow \boxed{\ln|Y_t - Y_\infty| = \ln|Y_0 - Y_\infty| - (k_1 + k_{-1})t}$$

The linear regression is also done in the coordinates $\ln|Y_t - Y_\infty|(t)$. The slope gives the *sum* of the rate constants $k_1 + k_{-1}$.

The Guggenheim II and the KMS methods can be also used to find $k_1 + k_{-1}$.

(c) **second-order irreversible reaction, equal initial concentrations** ($[A]_0 = [B]_0$):

Rate law:

Guggenheim relation (taking into account that $[A]_\infty = 0$):

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

$$\frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty} = \frac{[A]_t}{[A]_0}$$

Multiplying the above equation by $[A]_0$ and substituting $[A]_t/[A]_0$ in the denominator from the Guggenheim relation:

$$\begin{aligned} \frac{1}{[A]_t} - \frac{1}{[A]_0} &= kt \Rightarrow \frac{[A]_0}{[A]_t} - 1 = k[A]_0 t = k[A]_0 t \Rightarrow \frac{1}{\frac{Y_t - Y_\infty}{Y_0 - Y_\infty}} - 1 = k[A]_0 t \Rightarrow \\ \Rightarrow \frac{Y_0 - Y_\infty}{Y_t - Y_\infty} - 1 &= k[A]_0 t \Rightarrow \frac{(Y_0 - Y_\infty) - (Y_t - Y_\infty)}{Y_t - Y_\infty} = k[A]_0 t \Rightarrow \frac{Y_0 - Y_t}{Y_t - Y_\infty} = k[A]_0 t \Rightarrow \\ \Rightarrow \frac{Y_t - Y_\infty}{Y_0 - Y_t} &= \frac{1}{k[A]_0 t} \Rightarrow \boxed{Y_t = \frac{1}{k[A]_0} \left(\frac{Y_0 - Y_t}{t} \right) + Y_\infty} \end{aligned}$$

The linear regression is done in the coordinates $Y_t((Y_0 - Y_t)/t)$. The slope gives $1/(k[A]_0)$, which is equal to the half-life (see page 27.) Note that in this case you do *not* need to know Y_∞ , but you have to know $[A]_0$. Another problem is that at small t values, evaluation of $(Y_0 - Y_t)/t$, can be quite inaccurate.

(c2) **second-order irreversible reaction, equal initial concentrations** ($[A]_0 = [B]_0$):

There is another choice of coordinates for the regression:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \Rightarrow \frac{[A]_0}{[A]_t} = 1 + k[A]_0 t \Rightarrow \frac{Y_0 - Y_\infty}{Y_t - Y_\infty} = 1 + k[A]_0 t$$

The regression is done in coordinates $(Y_0 - Y_\infty)/(Y_t - Y_\infty)$ vs. t . The slope is $k[A]_0$, from which k can be obtained. Note that Y_∞ is needed in this case

(d) **zeroth-order irreversible reaction:**

Rate law:

Guggenheim relation (taking into account that $[A]_{\infty} = 0$):

$$[A]_t = [A]_0 - kt \qquad \frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}} = \frac{[A]_t - [A]_{\infty}}{[A]_0 - [A]_{\infty}} = \frac{[A]_t}{[A]_0} \Rightarrow [A]_t = [A]_0 \frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}}$$

$$[A]_0 \frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}} = [A]_0 - kt$$

$$\frac{Y_t - Y_{\infty}}{Y_0 - Y_{\infty}} = 1 - \frac{k}{[A]_0} t$$

$$Y_t = Y_0 + \frac{k(Y_{\infty} - Y_0)}{[A]_0} t$$

This is suitable for a linear regression in the coordinates $Y_t(t)$. The slope is $k(Y_{\infty} - Y_0)/[A]_0$, from which k can be obtained.

Summary on Guggenheim and related methods

Method	Equation	Requirement
1st order – Guggenheim I	$\ln Y_t - Y_\infty = \wp - kt$	Y_∞ is needed
1st order – Guggenheim II	$\ln Y_{t+\Delta t} - Y_t = \wp - kt$	equidistant data ($\Delta t = \text{const}$) are needed
1st order – KMS	$Y_{t+\Delta t} = \wp + e^{-k\Delta t} Y_t$	
2nd order – Guggenheim I	$Y_t = \wp + (1/(k[A]_0))((Y_0 - Y_t)/t)$	Y_∞ is <i>not</i> needed
2nd order – Guggenheim II	$(Y_0 - Y_\infty)/(Y_t - Y_\infty) = 1 + k[A]_0 t$	Y_∞ is needed
0th order – Guggenheim	$Y_t = \wp + k((Y_\infty - Y_0)/[A]_0)t$	Y_∞ is needed

The rate constant in all these methods is eventually obtained from the *slope*. The Georgian letter \wp (“tsil”) means here an intercept, which is not used and the exact form of which is unimportant.

Appendix 4. Reversible reactions – elementary derivation

- Below is a derivation of first-order reversible reaction using elementary calculus (without using the **K** matrix formalism):

- $$\begin{array}{lll}
 k_1 & \frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] & \frac{d[B]}{dt} = k_1[A] - k_{-1}[B] \\
 A \rightarrow B & & \\
 k_{-1} & [B] = [A]_0 - [A] & \\
 B \rightarrow A & \frac{d[A]}{dt} = -k_1[A] + k_{-1}([A]_0 - [A]) & \\
 & \frac{d[A]}{dt} = -(k_1 + k_{-1})[A] + k_{-1}[A]_0 &
 \end{array}$$

- Separation of variables:

$$\frac{1}{-(k_1 + k_{-1})[A] + k_{-1}[A]_0} d[A] = dt$$

Taking a definite integral:

$$\begin{aligned}
 \int_{[A]_0}^{[A]} \frac{1}{-(k_1 + k_{-1})[A] + k_{-1}[A]_0} d[A] &= \int_0^t dt \\
 -\frac{1}{k_1 + k_{-1}} \ln \left(-(k_1 + k_{-1})[A] + k_{-1}[A]_0 \right) \Big|_{[A]_0}^{[A]} &= t \Big|_0^t \\
 -\frac{1}{k_1 + k_{-1}} \ln \left(\frac{-(k_1 + k_{-1})[A] + k_{-1}[A]_0}{-(k_1 + k_{-1})[A]_0 + k_{-1}[A]_0} \right) &= t \\
 -\frac{1}{k_1 + k_{-1}} \ln \left(\frac{-(k_1 + k_{-1})[A] + k_{-1}[A]_0}{-k_1[A]_0} \right) &= t \\
 -\frac{1}{k_1 + k_{-1}} \ln \left(\frac{(k_1 + k_{-1})[A] - k_{-1}[A]_0}{k_1[A]_0} \right) &= t \\
 \frac{(k_1 + k_{-1})[A] - k_{-1}[A]_0}{k_1[A]_0} &= e^{-(k_1 + k_{-1})t} \\
 (k_1 + k_{-1})[A] &= k_{-1}[A]_0 + k_1[A]_0 e^{-(k_1 + k_{-1})t}
 \end{aligned}$$

Therefore

$$\boxed{[A] = \frac{k_{-1}[A]_0}{k_1 + k_{-1}} + \frac{k_1[A]_0}{k_1 + k_{-1}} e^{-(k_1 + k_{-1})t}}$$

Appendix 5. Parallel reactions – elementary derivation

- Below is a derivation of first-order parallel reactions using elementary calculus (without using the **K** matrix formalism):

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A] = -(k_1 + k_2)[A] \quad \begin{array}{l} A \rightarrow B \quad k_1 \\ A \rightarrow C \quad k_2 \end{array}$$

$$\frac{d[B]}{dt} = k_1[A]$$

$$\frac{d[C]}{dt} = k_2[A]$$

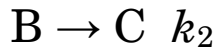
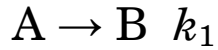
$$[A] = [A]_0 e^{-(k_1 + k_2)t}$$

$$\frac{d[B]}{dt} = k_1[A] = k_1[A]_0 e^{-(k_1 + k_2)t} \Rightarrow [B] = \int_0^t k_1[A]_0 e^{-(k_1 + k_2)t} dt = \frac{k_1[A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t})$$

$$\text{Analogously, } [C] = \int_0^t k_2[A]_0 e^{-(k_1 + k_2)t} dt = \frac{k_2[A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t})$$

Appendix 6. Consecutive reactions

- Below is a derivation of first-order consecutive reactions using elementary calculus (without using the **K** matrix formalism):



$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

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

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

- The equation is not separable. There are at least two ways of solving this equations: multiplying by $e^{k_2 t}$ or substitution $[B] = K(t)e^{-k_2 t}$:

- Solution by a substitution $[B](t) = K(t)e^{-k_2 t}$:

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

Let us make the substitution $[B](t) = K(t)e^{-k_2 t}$, where $K(t)$ is a new (auxiliary) unknown function. Then:

$$\frac{d[B]}{dt} = \frac{dK}{dt} e^{-k_2 t} + K(t) \frac{d}{dt} (e^{-k_2 t}) = \frac{dK}{dt} e^{-k_2 t} - k_2 K(t) e^{-k_2 t}$$

Inserting this into then left-hand side of equation

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

we obtain a differential equation with respect to the new (auxiliary) unknown function

$$\frac{dK}{dt}e^{-k_2t} - k_2K(t)e^{-k_2t} = k_1[A]_0e^{-k_1t} - k_2K(t)e^{-k_2t}$$

$$\frac{dK}{dt}e^{-k_2t} = k_1[A]_0e^{-k_1t}$$

$$\frac{dK}{dt} = k_1[A]_0e^{-(k_1-k_2)t}$$

Integration of the latter equation yields:

$$K(t) = k_1[A]_0e^{(k_2-k_1)t} \cdot \frac{1}{k_2 - k_1} + C = \frac{k_1[A]_0}{k_2 - k_1}e^{(k_2-k_1)t} + C$$

and

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

Therefore,

$$[B](t) = K(t)e^{-k_2t} = \left(\frac{k_1[A]_0}{k_2 - k_1}e^{(k_2-k_1)t} + C \right) e^{-k_2t} = \frac{k_1[A]_0}{k_2 - k_1}e^{-k_1t} + Ce^{-k_2t}$$

To determine the value of C , we need the initial condition $[B](t=0) = 0$, since the concentration of the intermediate is 0 at the beginning. Thus, we obtain $C = -k_1[A]_0/(k_2-k_1)$

$$[B](t) = \frac{k_1[A]_0}{k_2 - k_1}e^{-k_1t} + Ce^{-k_2t} = \frac{k_1[A]_0}{k_2 - k_1}e^{-k_1t} - \frac{k_1[A]_0}{k_2 - k_1}e^{-k_2t} = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t})$$

In a **special case** $k_1 = k_2 = k$ the derivation (and the resulting equation) is different:

$$\frac{dK}{dt} = k_1[A]_0 e^{-(k_1-k_2)t} = k[A]_0$$

$$K(t) = k[A]_0 t + C$$

$$[B](t) = K(t)e^{-kt} = (k[A]_0 t + C)e^{-kt} = k[A]_0 te^{-kt} + Ce^{-kt}$$

Using the initial condition $[B](t=0) = 0$, we obtain $C = 0$. Thus, $[B](t) = k[A]_0 te^{-kt}$

- Solution by an integrating factor:

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

Let us multiply both parts by $e^{k_2 t}$:

$$e^{k_2 t} \frac{d[B]}{dt} = k_1[A]_0 e^{k_2 t} e^{-k_1 t} - k_2 e^{k_2 t} [B]$$

$$e^{k_2 t} \frac{d[B]}{dt} + \textcolor{blue}{k_2} e^{k_2 t} [B] = k_1[A]_0 e^{(k_2-k_1)t}$$

Note that $\textcolor{blue}{k_2} e^{k_2 t}$ is the derivative of $e^{k_2 t}$ and, thus, the entire left-hand side is the derivative of $e^{k_2 t} [B]$:

$$\frac{d}{dt} (e^{k_2 t} [B]) = k_1[A]_0 e^{(k_2-k_1)t}$$

Now we should simply integrate the above equation with respect to t :

$$e^{k_2 t} [B] = \int k_1[A]_0 e^{(k_2-k_1)t} dt$$

$$e^{k_2 t} [B] \Big|_0^t = \frac{k_1[A]_0}{k_2 - k_1} e^{(k_2-k_1)t} \Big|_0^t$$

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

$$e^{k_2 t} [B]_t = k_1[A]_0 \frac{e^{(k_2-k_1)t} - 1}{k_2 - k_1} \Rightarrow [B]_t = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}); \quad k_1[A]_0 t e^{-k_1 t} \quad (k_1 = k_2)$$

The solution for [C] is found by direct integration with the initial condition $[C](t = 0) = 0$

$$\begin{aligned} \frac{d[C]}{dt} &= k_2[B] = k_2 \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \Rightarrow [C] = [A]_0 - \frac{[A]_0}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) = \\ &= \frac{k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})}{k_2 - k_1} [A]_0 \end{aligned}$$

In a **special case** $k_1 = k_2 = k$ the derivation (and the resulting equation) is different:

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-kt} - k[B]$$

$$e^{kt} \frac{d[B]}{dt} = k_1[A]_0 - k[B]e^{kt}$$

$$e^{kt} \frac{d[B]}{dt} + k e^{kt} [B] = k_1[A]_0$$

$$\frac{d}{dt} (e^{kt} [B]) = k_1[A]_0$$

$$e^{kt} [B] = \int k_1[A]_0 dt$$

$$e^{kt} [B] = k_1[A]_0 t + C$$

$$[B] = k_1[A]_0 t e^{-kt} + C e^{-kt}$$

Using the initial condition $[B]_{t=0} = 0$, we obtain $C = 0$. Thus, $[B]_t = k[A]_0 t e^{-kt}$

- Reversible reaction:

$$\frac{d[A]}{dt} = -(k_1 + k_{-1})[A] + k_{-1}[A]_0$$

Separating variables $[A]$ and t :

$$\frac{1}{-(k_1 + k_{-1})[A] + k_{-1}[A]_0} d[A] = dt$$

Taking a definite integral:

$$\int_{[A]_0}^{[A]} \frac{1}{-(k_1 + k_{-1})[A] + k_{-1}[A]_0} d[A] = \int_0^t dt$$

$$-\frac{1}{k_1 + k_{-1}} \ln(-(k_1 + k_{-1})[A] + k_{-1}[A]_0) \Big|_{[A]_0}^{[A]} = t \Big|_0^t$$

$$-\frac{1}{k_1 + k_{-1}} \ln\left(\frac{-(k_1 + k_{-1})[A] + k_{-1}[A]_0}{-(k_1 + k_{-1})[A]_0 + k_{-1}[A]_0}\right) = t$$

$$-\frac{1}{k_1 + k_{-1}} \ln\left(\frac{-(k_1 + k_{-1})[A] + k_{-1}[A]_0}{-k_1[A]_0}\right) = t$$

$$-\frac{1}{k_1 + k_{-1}} \ln\left(\frac{(k_1 + k_{-1})[A] - k_{-1}[A]_0}{k_1[A]_0}\right) = t$$

$$\frac{(k_1 + k_{-1})[A] - k_{-1}[A]_0}{k_1[A]_0} = e^{-(k_1 + k_{-1})t}$$

$$(k_1 + k_{-1})[A] = k_{-1}[A]_0 + k_1[A]_0 e^{-(k_1 + k_{-1})t}$$

Therefore

$$[A] = \frac{k_{-1}[A]_0}{k_1 + k_{-1}} + \frac{k_1[A]_0}{k_1 + k_{-1}} e^{-(k_1 + k_{-1})t}$$

• Langmuir adsorption isotherm (1916)

If we have just adsorption, the application of the steady-state approximation to the “reaction” $A + Z \rightleftharpoons AZ$ with rate constants k_1 and k_{-1} results to:

$$d[AZ]/dt = k_1[A][Z] - k_{-1}[AZ]$$

$$[Z] = [Z]_0 - [AZ]$$

$$\begin{aligned} d[AZ]/dt &= k_1[A][Z] - k_{-1}[AZ] = k_1[A]([Z]_0 - [AZ]) - k_{-1}[AZ] = \\ &= k_1[A][Z]_0 - (k_1[A] + k_{-1})[AZ] = 0 \quad \Rightarrow [AZ] = \frac{k_1[A][Z]_0}{k_{-1} + k_1[A]} \end{aligned}$$

$$\frac{[AZ]}{[Z]_0} = \frac{(k_1/k_{-1})[A]}{1 + (k_1/k_{-1})[A]} = \frac{K_{eq}[A]}{1 + K_{eq}[A]}$$

where $K_{eq} = k_1/k_{-1}$ is the equilibrium constant. It is more common to express this result through *coverage* $\theta_A = [AZ]/[Z]_0$ and partial pressure P_A :

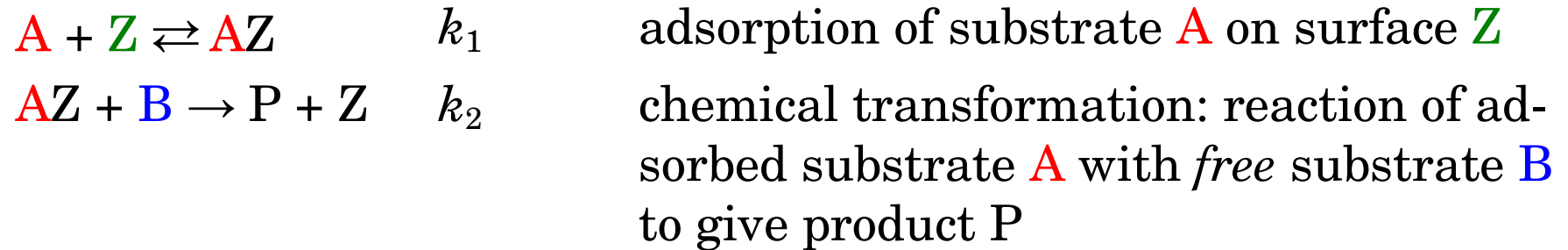
$$\theta_A = \frac{K_{eq}P_A}{1 + K_{eq}P_A}$$

The latter equation is referred to as *Langmuir adsorption isotherm*.

Note that the steady-state condition for such a simple process is equivalent to equilibrium, since $k_1[A][Z] - k_{-1}[AZ] = 0$ is equivalent to

$$\frac{[AZ]}{[A][Z]} = \frac{k_1}{k_{-1}} = K_{eq}$$

• Eley–Rideal model – derivation



$$d[AZ]/dt = k_1[A][Z] - k_{-1}[AZ] - k_2[AZ][B] = k_1[A][Z] - (k_{-1} + k_2[B])[AZ]$$

$$[Z] = [Z]_0 - [AZ]$$

$$\begin{aligned} d[AZ]/dt &= k_1[A][Z] - (k_{-1} + k_2[B])[AZ] = k_1[A]([Z]_0 - [AZ]) - (k_{-1} + k_2[B])[AZ] = \\ &= k_1[A][Z]_0 - (k_1[A] + k_{-1} + k_2[B])[AZ] = 0 \quad \Rightarrow [AZ] = \frac{k_1[A][Z]_0}{k_{-1} + k_2[B] + k_1[A]} \end{aligned}$$

$$\frac{d[B]}{dt} = k_2[AZ][B] = \frac{k_1k_2[A][B][Z]_0}{k_{-1} + k_2[B] + k_1[A]}$$

$$v = \frac{d[B]/dt}{[Z]_0} = \frac{k_1k_2[A][B]}{k_1[A] + k_2[B] + k_{-1}}$$

Appendix 10

- To calculate the average chain length, we have to find the following infinite series:

$$L = \sum_{s=0}^{\infty} sP(s) = \sum_{s=0}^{\infty} s(1-\beta)^s \beta = \beta \sum_{s=0}^{\infty} s(1-\beta)^s = \beta \sum_{s=0}^{\infty} sx^s$$

where $x = 1 - \beta$.

$$\sum_{s=0}^{\infty} sx^s = x \sum_{s=0}^{\infty} sx^{s-1} = x \sum_{s=0}^{\infty} sx^{s-1} = x \sum_{s=0}^{\infty} (x^s)' = x \left(\sum_{s=0}^{\infty} x^s \right)'$$

The series under the derivative sign in the right-hand side is just the infinite geometric progression, which can be found easily:

$$S = \sum_{s=0}^{\infty} x^s = 1 + x + x^2 + \dots = 1 + x(1 + x + \dots) = 1 + xS$$

$$S = 1 + xS \Rightarrow S = \frac{1}{1-x}$$

Therefore, $\sum_{s=0}^{\infty} sx^s = x \left(\frac{1}{1-x} \right)' = x \frac{1}{(1-x)^2} = \frac{x}{(1-x)^2}$

and $L = \beta \sum_{s=0}^{\infty} sx^s = \beta \cdot \frac{1-\beta}{\beta^2} = \frac{1-\beta}{\beta}$

- For characterizing a stationary point we actually need the *signs* of the eigenvalues $\text{sign}(\lambda_k)$ rather than λ_k 's themselves. To determine the signs, the following simple rule (***Sylvester criterion***) can be employed:

$$\mathbf{H} = \begin{pmatrix} h_{11} & h_{12} & \cdots & h_{1N} \\ h_{21} & h_{22} & \cdots & h_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ h_{N1} & h_{N2} & \cdots & h_{NN} \end{pmatrix}$$

where M_1, M_2, \dots, M_N are *principal minors* of \mathbf{H} .

$$\text{sign}(\lambda_1) = \text{sign}(M_1) = \text{sign}(h_{11})$$

$$\text{sign}(\lambda_1 \lambda_2) = \text{sign}(M_2) = \text{sign} \begin{vmatrix} h_{11} & h_{12} \\ h_{12} & h_{22} \end{vmatrix}$$

$$\text{sign}(\lambda_1 \lambda_2 \lambda_3) = \text{sign}(M_3) = \text{sign} \begin{vmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{33} \end{vmatrix}$$

...

$$\text{sign}(\lambda_1 \lambda_2 \lambda_3 \dots \lambda_N) = \text{sign}(M_N) = \text{sign}(\det(\mathbf{H}))$$

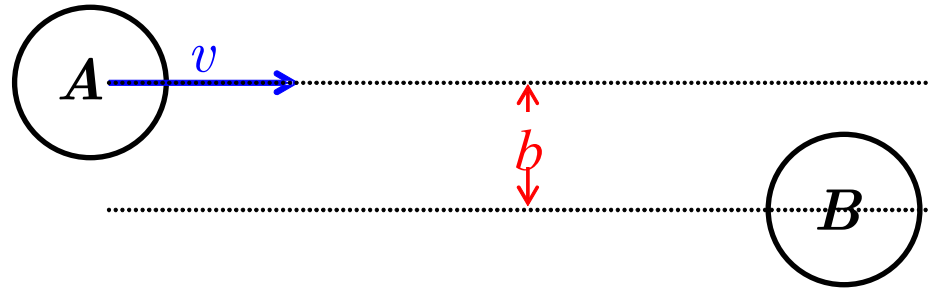
Using the Sylvester criterion, we have to calculate N determinants of various size (from 1 to N), but we do not need to find the eigenvalues. *Note* that the Sylvester criterion is *not* a method for finding eigenvalues!

- The Sylvester criterion is a very convenient tool for matrices 2×2 and 3×3 matrices when working without computer.

- In the ***collision theory***, we consider reacting molecules as hard spheres, paying attention to the collision between them but not to what happens *within* the reacting molecule.
- The idea is to calculate the *number of collisions* between molecules of reactants A and B per unit time per unit volume (*collision frequency*) and derive the *rate* of the reaction from it.
- ***Collision classification:***
 - ▶ Elastic collisions:
 - Exchange of kinetic energy only;
 - Velocity and the direction of translational motion *change*;
 - Translational energy of each molecule *change*; the total translational energy does *not*;
 - Rotational and vibrational energy do *not* change.
 - *No chemical changes* (bond formation or breaking) occur.
 - ▶ Inelastic collisions:
 - A part of *kinetic* energy is transferred to vibrational and rotational energy;
 - The molecule(s) become(s) *vibrationally* and *rotationally* excited;
 - *No chemical changes* (bond formation or breaking) occur.
 - ▶ Reactive collisions:
 - Chemical changes leading to formation of product(s) from the reactants (bond breaking and/or formation).

Collision theory

- Let's consider a collision of two *hard spheres* **A** and **B** moving at a *relative velocity* v :



- b (**impact parameter**) is defined as minimum distance between the sphere centers.
- *Kinetic energy* of two particles moving at velocities \mathbf{v}_A and \mathbf{v}_B :

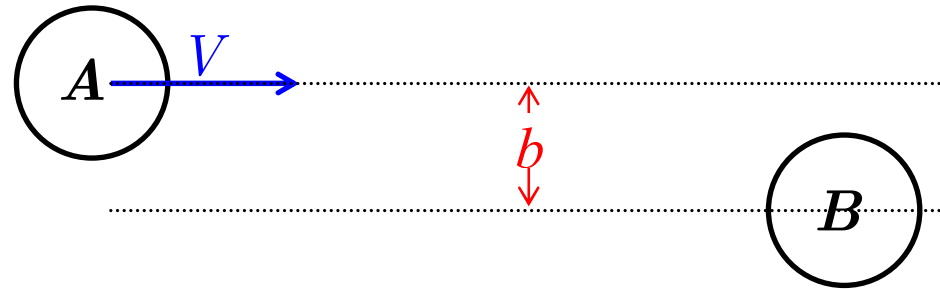
$$E_{\text{kin}} = \frac{\mu v^2}{2} + \frac{(m_A + m_B) v_{\text{c.m.}}^2}{2}$$

where $\mu = m_A m_B / (m_A + m_B)$ is the **reduced mass**; $v = |\mathbf{v}_1 - \mathbf{v}_2|$ is the relative velocity and $v_{\text{c.m.}}$ is the velocity of the center of mass.

Thus, the *relative* kinetic energy is given by $E_{\text{kin}} = \mu v^2 / 2$.

Collision theory – collision cross-section

- Let's consider again a collision of two *hard spheres* **A** and **B**:

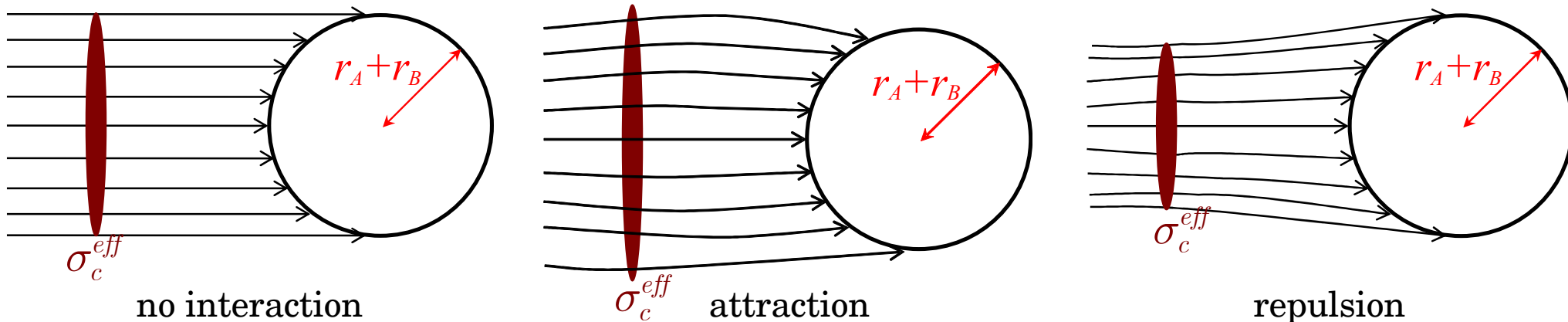


- The collision occurs if $b \leq r_A + r_B$.
- The **collision cross-section** (*secció de col·lisió*) for *non-interacting* spheres is defined as

$$\sigma_c = \pi(r_A + r_B)^2 = \pi d^2$$

$d = r_A + r_B$ is referred to as *collision diameter*.

- A real collision of two spheres with velocities \mathbf{v}_A and \mathbf{v}_B and masses m_A and m_B will be replaced by shooting of a point mass (*massa puntual*) μ and velocity v on a fictitious fixed target with area σ_c .
- The collision cross-section for *interacting* molecules is influenced by intermolecular interaction:



- σ_c^{eff} is referred to as **effective collision cross-section** (*secció eficaç de col·lisió*)

Collision theory – collision frequency

- We want to calculate the collision frequency Z (*number of collisions* per unit time per unit volume) of molecules moving with given velocities v_A and v_B .

- ▶ The collision frequency Z_{AB} is then calculated as

$$Z_{AB} = \sigma_c^{eff} v \cdot n_A n_B,$$

where n_A and n_B is the number of molecules A and B per unit volume. *A detailed derivation is give in the other file.*

Units SI: $\text{m}^2 \cdot (\text{m} \cdot \text{s}^{-1}) \cdot (\text{m}^{-3}) \cdot (\text{m}^{-3}) = \text{m}^{-3} \cdot \text{s}^{-1}$

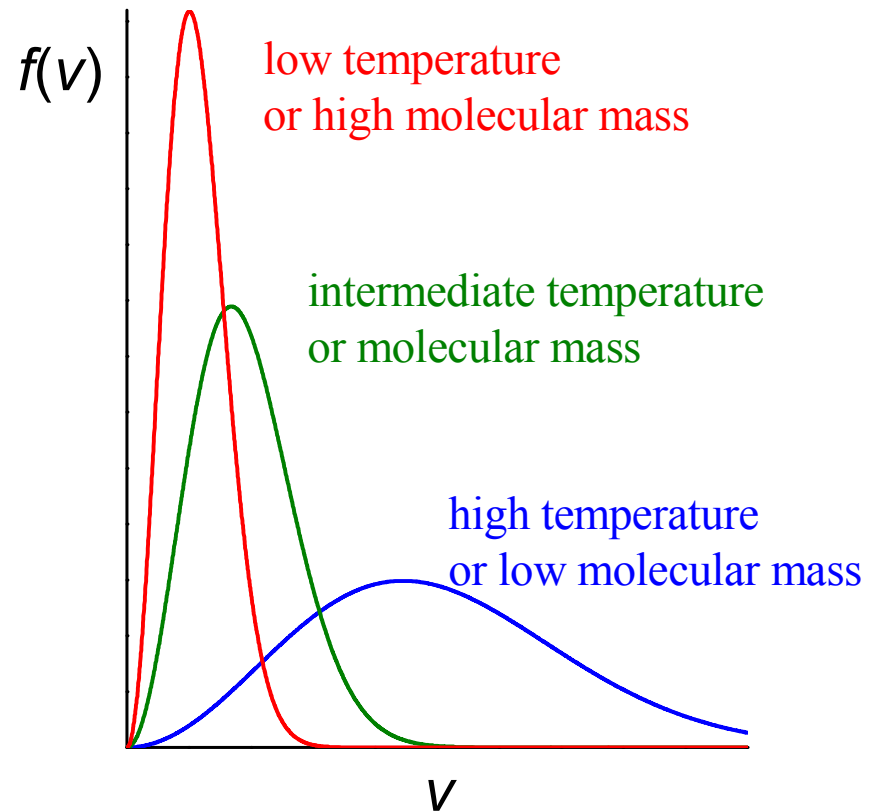
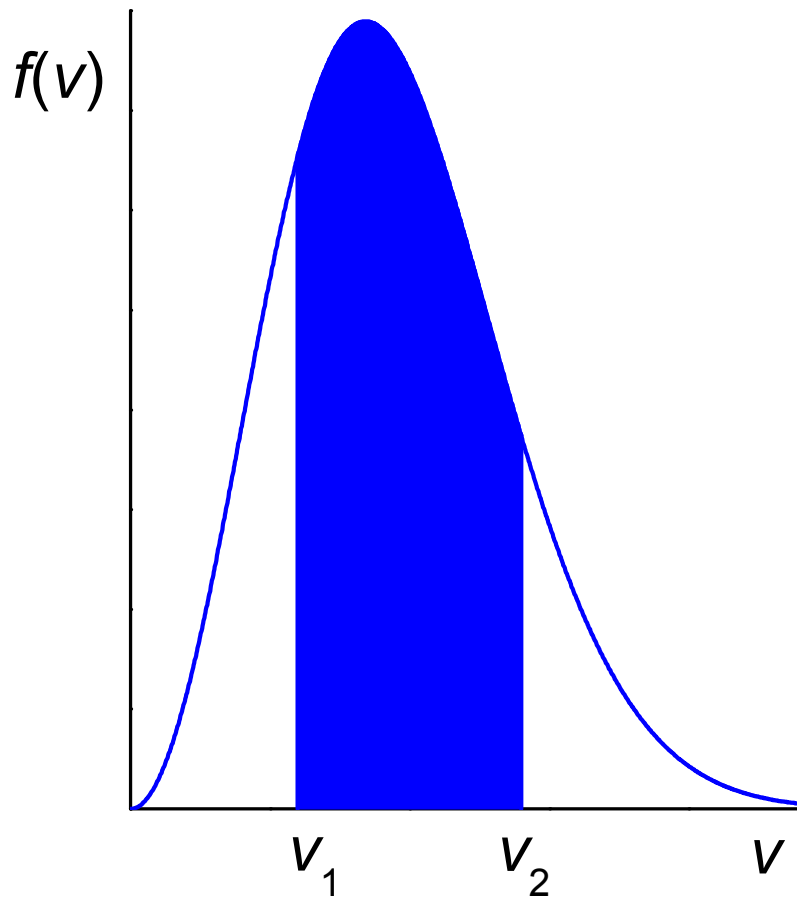
- ▶ The collision frequency Z_{AA} for *identical* molecules:

$$Z_{AA} = \frac{1}{2} \sigma_c^{eff} v \cdot n_A^2$$

Collision theory – Maxwell distribution

- To use the formula for the collision frequency we have to know the *mean relative velocity* v , which is obtained from the **Maxwell distribution**.
- *Mean relative velocity* from the Maxwell distribution:

$$\langle v \rangle = \int_0^{\infty} v f(v) dv = \sqrt{\frac{8k_B T}{\pi \mu}}$$



Mean molecular velocities at various temperatures, $\text{m}\cdot\text{s}^{-1}$

	298 K	1273 K
He	1256	2596
N ₂	475	981
CO ₂	379	783
C ₆ H ₆	284	589

- *Mean* relative velocity (μ is the reduced mass):

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi \mu}}$$

- *Collision frequency* in general case:

$$Z_{AB} = \sigma_c^{eff} \langle v \rangle n_A n_B$$

$$Z = \sigma_c^{eff} \sqrt{\frac{8k_B T}{\pi \mu}} n_A n_B$$

- *Collision frequency* in the case of *identical* molecules ($\mu = m_A m_A / (m_A + m_A) = m_A / 2$):

$$Z_{AA} = \frac{1}{2} \sigma_c^{eff} \sqrt{\frac{8k_B T}{\pi (m / 2)}} n_A^2 = 2 \sigma_c^{eff} \sqrt{\frac{k_B T}{\pi m}} n_A^2$$

Collision theory – requirement of minimum energy

- Not all the collisions (by far not all!) are reactive ones (cf. elastic and inelastic ones). It is reasonable to assume that a collision is *reactive* when the relative kinetic energy is greater than a certain *threshold energy* (= *energia llindar*) E_0 . Then the *frequency of reactive collisions* will be as follows:

$$Z_{\text{react}} = Z_{\text{AB}} e^{-\frac{E_0}{k_B T}} = \sigma_c^{\text{eff}} \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{E_0}{k_B T}} n_A n_B$$

- Let's express Z_{react} in terms of molar concentrations:

$$Z_{\text{react}} = N_A^2 \sigma_c^{\text{eff}} \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{E_0}{k_B T}} [A][B]$$

Now Z_{react} is essentially the *reaction rate*, but expressed in terms of number of reacting molecules per unit volume per unit time ($\text{m}^{-3} \cdot \text{s}^{-1}$). To get the reaction rate in molar units ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$), we have to divide Z_{react} by N_A :

$$v = \frac{Z_{\text{react}}}{N_A} = N_A \sigma_c^{\text{eff}} \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{E_0}{k_B T}} [A][B]$$

Here v is the reaction rate, not the molecular velocity!

Collision theory – steric factor and Trautz–Lewis equation

- Still, not all the collisions (even with a kinetic energy above the threshold) are reactive, because the reaction only occurs when the molecules are favorably oriented. Thus, the reaction rate must be multiplied by a steric factor P ($0 < P < 1$):

$$v = N_A P \sigma_c^{eff} \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{E_0}{k_B T}} [A][B] = N_A \sigma_{react}^{eff} \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{E_0}{k_B T}} [A][B]$$

This is the ***Trautz–Lewis equation***.

► For a one-substrate reaction:

$$v = 2N_A P \sigma_c^{eff} \sqrt{\frac{k_B T}{\pi m}} e^{-\frac{E_0}{k_B T}} [A]^2 = 2N_A \sigma_{react}^{eff} \sqrt{\frac{k_B T}{\pi m}} e^{-\frac{E_0}{k_B T}} [A]^2$$

- Relation between the threshold energy E_0 in the Trautz–Lewis equation and the Arrhenius activation energy E_a is as follows (see page 97):

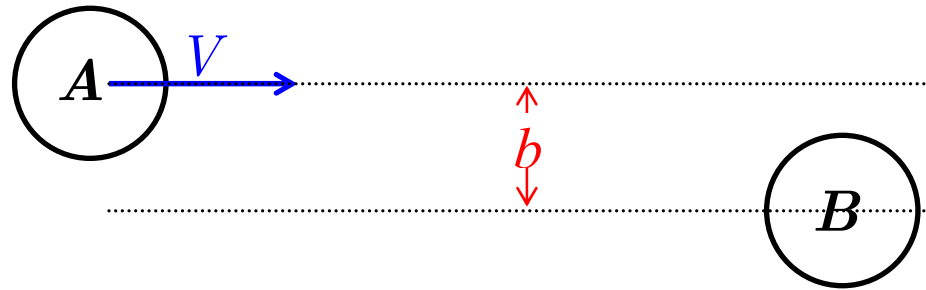
$$E_0 = E_a - \frac{1}{2}RT$$

This is because in the Trautz–Lewis equation the rate constant temperature dependence is

of type $k = k(T) = aT^{1/2}e^{-\frac{E_0}{RT}}$.

Collision theory – opacity function

- When we considered a collision of two *hard spheres* **A** and **B**:



we assumed that the collision occurs if and only if $b \leq r_A + r_B$.

- We can now take a more general view, assuming that for any impact parameter b there is some *probability* $P(b)$ that the collision takes place:

$$\sigma_c^{eff} = \int_0^{\infty} P(b) d(\pi b^2) = \int_0^{\infty} 2\pi b P(b) db$$

- The function $P(b)$ is referred to as **opacity function**.

- In the above example of non-interacting hard spheres, the opacity function is

$$P(b) = \begin{cases} 1, & \text{if } b \leq r_A + r_B \\ 0, & \text{if } b > r_A + r_B \end{cases}$$

$$\text{Then } \sigma_c^{eff} = \int_0^{r_A + r_B} 2\pi b db = \pi(r_A + r_B)^2$$

Appendix 13 – Transition-state theory – link to the collision theory

- Application for a **bi**molecular reaction of two atoms: $A + B \rightarrow \text{Pr}$.

► For **bi**molecular reactions (see page 129):

$$k = N_A \frac{k_B T}{h} \frac{(Q^\ddagger / V^\circ)}{(Q^A / V^\circ)(Q^B / V^\circ)} e^{-\frac{\Delta^\ddagger E}{RT}}$$

► Rotational partition functions:

$$Q_{\text{rot}}^A = Q_{\text{rot}}^B = 1; \quad Q_{\text{rot}}^\ddagger = \frac{8\pi^2 I^\ddagger}{h^2} k_B T = \frac{8\pi^2 \mu d^{\ddagger 2}}{h^2} k_B T$$

$$Q_{\text{vib}}^A = Q_{\text{vib}}^B = Q_{\text{vib}}^\ddagger = 1$$

where $\mu = m_A m_B / (m_A + m_B)$ is the reduced mass and d^\ddagger is the inter-atomic distance in the transition state.

► Translational partition functions:

$$Q_{\text{trans}}^A / V^\circ = \frac{(2\pi m_A k_B T)^{3/2}}{h^3}; \quad Q_{\text{trans}}^B / V^\circ = \frac{(2\pi m_B k_B T)^{3/2}}{h^3}$$

$$Q_{\text{trans}}^\ddagger / V^\circ = \frac{(2\pi(m_A + m_B)k_B T)^{3/2}}{h^3}$$

$$\frac{Q_{\text{trans}}^\ddagger / V^\circ}{(Q_{\text{trans}}^A / V^\circ)(Q_{\text{trans}}^B / V^\circ)} = h^3 \frac{((m_A + m_B)/(m_A m_B))^{3/2}}{(2\pi k_B T)^{3/2}} = \frac{h^3}{(2\pi \mu k_B T)^{3/2}}$$

where $\mu = m_A m_B / (m_A + m_B)$ is again the *reduced mass*.

$$\begin{aligned}
k &= N_A \frac{k_B T}{h} \frac{(Q_{\text{trans}}^\ddagger / V^\circ)}{(Q_{\text{trans}}^A / V^\circ)(Q_{\text{trans}}^B / V^\circ)} \frac{Q_{\text{rot}}^\ddagger}{Q_{\text{rot}}^A Q_{\text{rot}}^B} \frac{Q_{\text{vib}}^\ddagger}{Q_{\text{vib}}^A Q_{\text{vib}}^B} e^{-\frac{\Delta^\ddagger E}{RT}} = \\
&= N_A \frac{k_B T}{h} \frac{h^3}{(2\pi\mu k_B T)^{3/2}} \frac{8\pi^2 \mu d^{\ddagger 2}}{h^2} k_B T e^{-\frac{\Delta^\ddagger E}{RT}} = \\
&= N_A d^{\ddagger 2} \left(\frac{8\pi k_B T}{\mu} \right)^{1/2} e^{-\frac{\Delta^\ddagger E}{RT}} \\
&= N_A \sigma_{\text{react}} \left(\frac{8k_B T}{\pi\mu} \right)^{1/2} e^{-\frac{\Delta^\ddagger E}{RT}}
\end{aligned}$$

where σ_{react} is defined by $\sigma_{\text{react}} = \pi d^{\ddagger 2}$. The above expression, which is valid for a reaction of two atoms only, is identical to the Trautz–Lewis equation of the *collision theory* (not a part of our course; see page 200 in interested)!

- For a **one-substrate** bimolecular reaction of two identical atoms: $2 A \rightarrow \text{Pr}$ the result will be a *half* of the previous one, because in this case

$$Q_{\text{rot}}^\ddagger = \frac{1}{2} \frac{8\pi^2 I^\ddagger}{h^2} k_B T = \frac{1}{2} \frac{8\pi^2 \mu d^{\ddagger 2}}{h^2} k_B T$$

where “2” in the denominator is the *symmetry number* (see page 135). Thus,

$$k = \frac{1}{2} N_A \sigma_{\text{react}} \left(\frac{8k_B T}{\pi\mu} \right)^{1/2} e^{-\frac{\Delta^\ddagger E}{RT}} = 2 N_A \sigma_{\text{react}} \left(\frac{k_B T}{\pi m} \right)^{1/2} e^{-\frac{\Delta^\ddagger E}{RT}}$$

Transition-state theory – approximate link to Arrhenius equation

- Link (approximate) between the Eyring and the Arrhenius equations:

► Normally: $\Delta^\ddagger E \approx E_a - RT$ (see page 97)

In this expression, “ $-RT$ ” originates from the $k_B T$ factor in the Eyring–Polanyi equation

► $\Delta^\ddagger H^\circ \approx \Delta^\ddagger E \approx E_a - RT$ $\Delta^\ddagger E \approx \Delta^\ddagger H^\circ$

► Special case for **bimolecular** reactions in the gas phase, when the standard condition is a fixed *pressure* (e.g. $P^\circ = 1$ atm) and k is given in $\text{atm}^{-1} \cdot \text{s}^{-1}$:

$$\Delta^\ddagger H^\circ \approx E_a - 2RT$$

This is because

$$\begin{aligned} k &= \frac{1}{c^\circ} \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT} = \frac{1}{P^\circ / RT} \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT} = \\ &= \frac{RT}{P^\circ} \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT} \end{aligned}$$

► Thus, *for the gas phase*, $\Delta^\ddagger H^\circ \approx E_a - (1 - \Delta^\ddagger n)RT$, where $\Delta^\ddagger n$ is the *change* in the number of particles (0 for unimolecular reactions, -1 for bimolecular).

► The Eyring–Polanyi equation then adopts the following form:

$$k = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S^\circ}{R}} e^{-\frac{\Delta^\ddagger H^\circ}{RT}} = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S^\circ}{R}} e^{-\frac{E_a - (1 - \Delta^\ddagger n)RT}{RT}} = \frac{k_B T}{h} e^{\frac{\Delta^\ddagger S^\circ}{R}} e^{1 - \Delta^\ddagger n} e^{-\frac{E_a}{RT}}$$