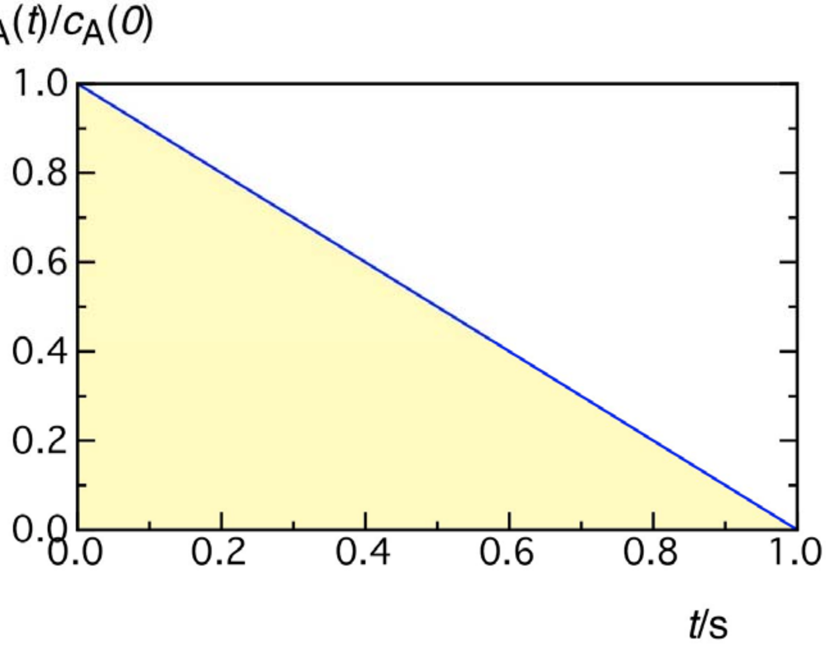
Integration of simple differential rate laws

Zero-order reaction A –> :

$$\frac{\mathrm{d}c_A}{\mathrm{d}t} = -{}^0k; \int_{c_A(0)}^{c_A(t)} \mathrm{d}c_A = -{}^0k\int_0^t \mathrm{d}t; \underline{c_A(t) = c_A(0) - {}^0kt}$$

$[{}^0k]$ = M s^{-1}



This rate law does not represent an ER (something goes to nothing)

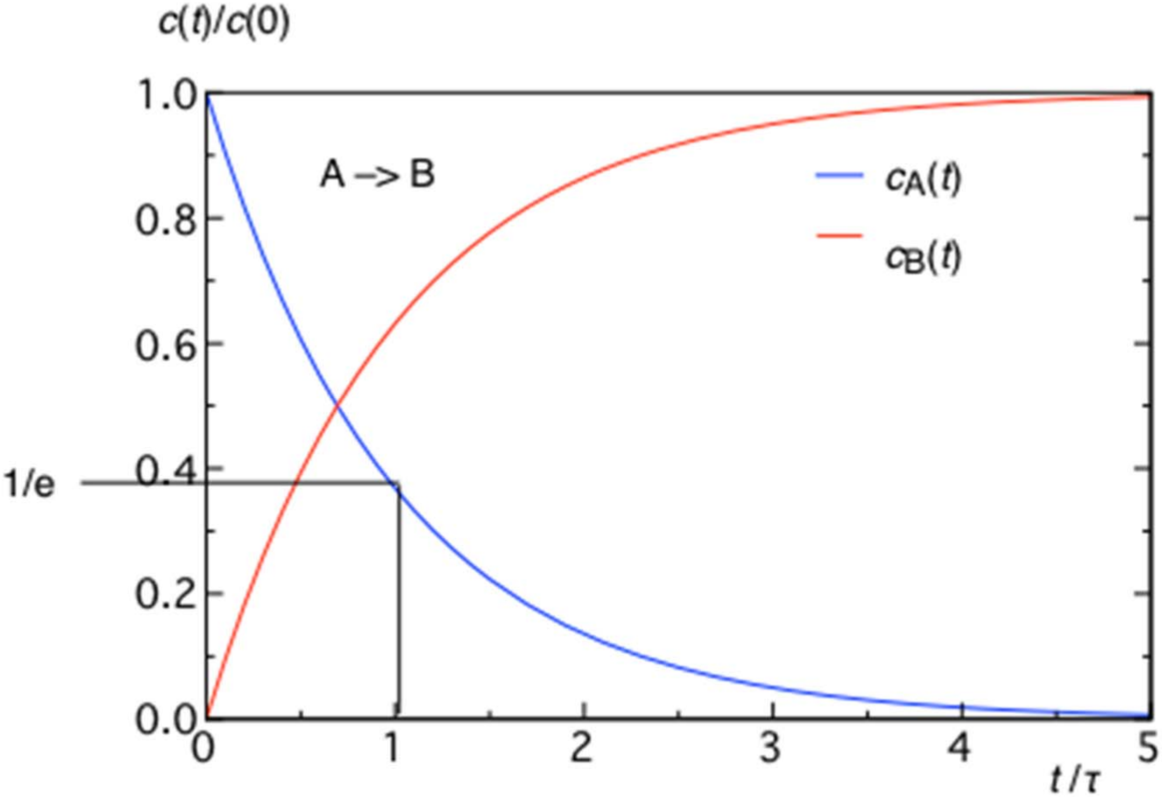
First-order reaction A –> B:

$$\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = -{}^{1}k c_{\mathrm{A}}$$

$$\int_{c_{\mathrm{A}(0)}}^{c_{\mathrm{A}(t)}} \frac{\mathrm{d}c_{\mathrm{A}}}{c_{\mathrm{A}}} = -{}^{1}k\int_{0}^{t}\mathrm{d}t\,;\quad \ln\frac{c_{\mathrm{A}}(t)}{c_{\mathrm{A}}(0)} = -{}^{1}kt$$

$$c_{\mathrm{A}}(t) = c_{\mathrm{A}}(0)\mathrm{e}^{-{}^{1}kt}\,;\quad c_{\mathrm{B}}(t) = c_{\mathrm{A}}(0) - c_{\mathrm{A}}(t)$$

$[{}^{1}k] = \mathrm{s}^{-1}$

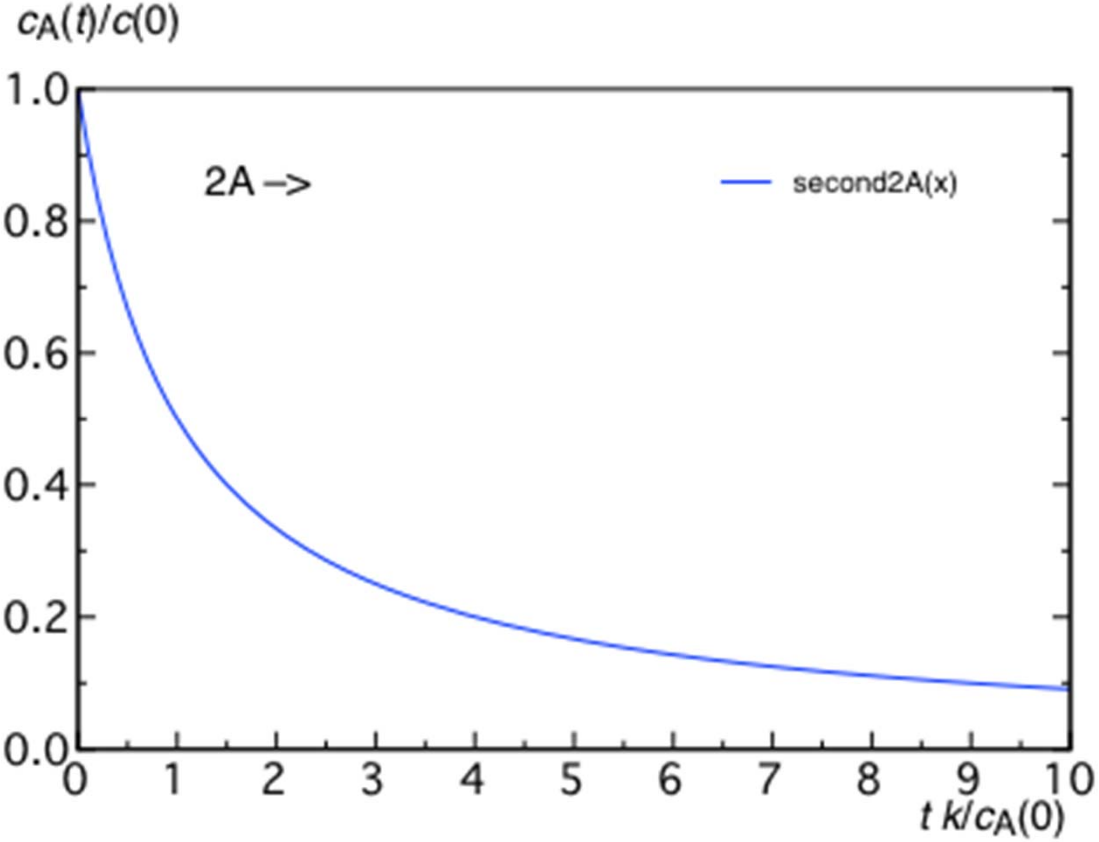


Second-order reaction with a single reactant 2A –> A_2:

$$\frac{dc_A}{dt} = -{}^{2}k c_A^2$$

$$\int_{c_A(0)}^{c_A(t)} \frac{dc_A}{c_A^2} = -{}^{2}k \int_0^t dt\,; \quad \frac{1}{c_A(t)} - \frac{1}{c_A(0)} = {}^{2}kt$$

$$c_A(t) = \frac{c_A(0)}{1 + {}^{2}ktc_A(0)}$$



Second-order reaction with two reactants A+B –> A–B:

$$\frac{\mathrm{d}c_A}{\mathrm{d}t} = -{}^2k c_A c_b$$

If $c_A(0) = c_B(0)$: $c_A(t)/c_B(t) = 1$; same solution as $2A \to A_2$…

If $c_A \neq c_B : \frac{\mathrm{d}c_A}{\mathrm{d}t} = -{}^2k\left(c_A(0)-x\right)\left(c_B(0)-x\right)$; partial fraction expansion ...

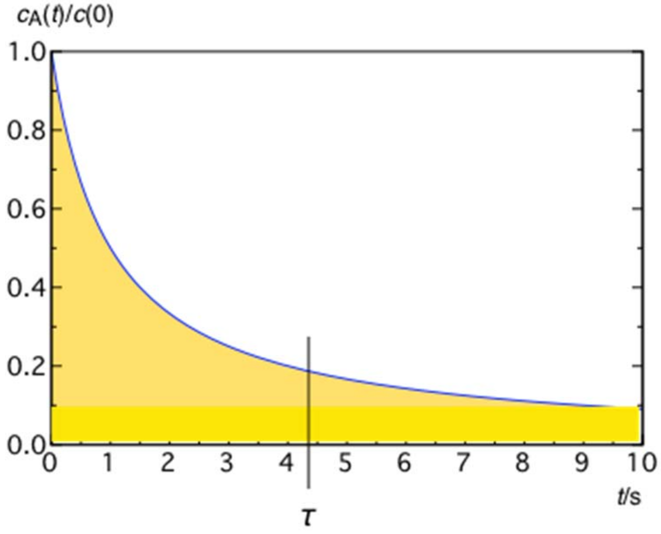
$$\ln \frac{c_A(t)/c_A(0)}{c_B(t)/c_B(0)} = \left(c_A(0)-c_B(0)\right)^2 kt$$

Note: this solution becomes indefinite for $c_A \approx c_B$ (Taylor expansion)

Hence: Avoid

Average lifetime τ of reacting species

$$\tau \equiv \frac{1}{c_A(0)} \int_0^\infty t \mathrm{d} c_A(t)$$



This is the gravity center of the area under the curve $c_A(t)$

First-order reaction:

$$\tau = -{}^1k \int_0^\infty t e^{-{}^1kt} \mathrm{d}t = \frac{1}{{}^1k},\ c_A(t) = c_A(0) e^{-t/\tau}$$

$$c_A(\tau) = c_A(0) e^{-1} = 0.368 c_A(0)$$

Half-life $t_{1/2}$: time, at which ½ of the conversion at t = inf is reached.
If $c_A(\text{inf}) = 0$ (irreversible reaction): $t_{1/2} = \ln 2/{}^1k = 0.693/{}^1k$; $= \tau_{2}/\ln 2 = 1.443\ t_{1/2}$

Second-order reaction, 2A or $c_A = c_B = c$, $c(\text{inf}) = 0$
τ = inf(!), $t_{1/2} = 1/\{c_A(0)\ {}^2k\}$ is inversely proportional to $c_A(0)$!

Complex reactions (combinations of ERs)

a) Reversible first-order reactions

$$\mathrm{A} \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftharpoons}} \mathrm{B}$$

$$\frac{\mathrm{d}c_\mathrm{A}(t)}{\mathrm{d}t} = -k_\mathrm{f}c_\mathrm{A}(t) + k_\mathrm{b}c_\mathrm{B}(t)$$

$$\text{initial condition: } c_\mathrm{B}(0) = 0$$

$$\text{conservation of mass: } c_\mathrm{A}(t) + c_\mathrm{B}(t) = c_\mathrm{A}(0)$$

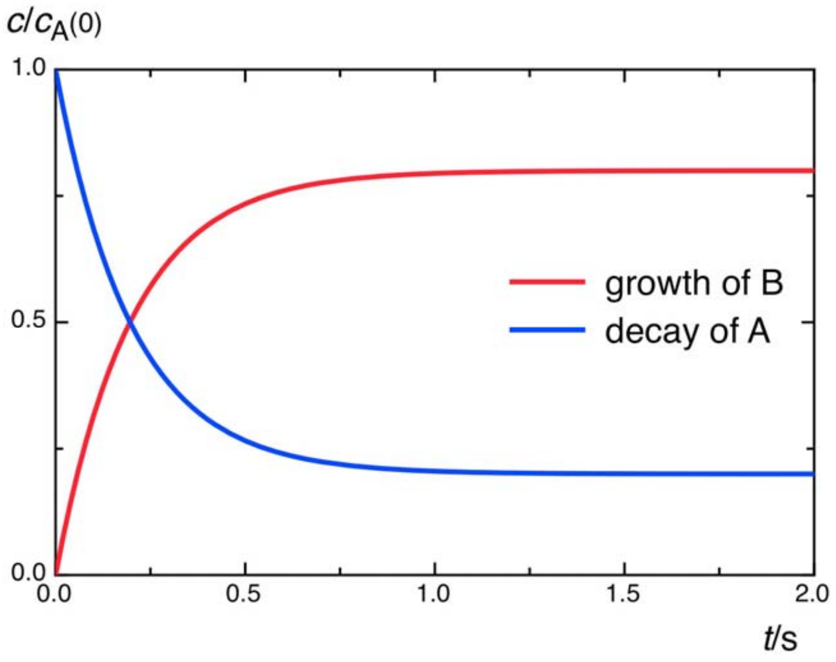
$$\frac{\mathrm{d}c_\mathrm{A}(t)}{\mathrm{d}t} = -k_\mathrm{f}c_\mathrm{A}(t) + k_\mathrm{b}\left[c_\mathrm{A}(0) - c_\mathrm{A}(t)\right] = -(k_\mathrm{f} + k_\mathrm{b})c_\mathrm{A}(t) + k_\mathrm{b}c_\mathrm{A}(0)$$

$$\text{at equilibrium, } t = \infty: \quad \frac{\mathrm{d}c_\mathrm{A}(t)}{\mathrm{d}t} = 0, \text{ hence } k_\mathrm{b}c_\mathrm{A}(0) = (k_\mathrm{f} + k_\mathrm{b})c_\mathrm{A}(\infty)$$

$$\frac{\mathrm{d}c_\mathrm{A}(t)}{\mathrm{d}t} = (k_\mathrm{f} + k_\mathrm{b})\left[c_\mathrm{A}(\infty) - c_\mathrm{A}(t)\right]$$

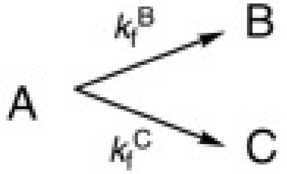
$$\int_{c_\mathrm{A}(0)}^{c_\mathrm{A}(t)} \frac{\mathrm{d}c_\mathrm{A}(t)}{c_\mathrm{A}(t) - c_\mathrm{A}(\infty)} = -(k_\mathrm{f} + k_\mathrm{b})\int_0^t \mathrm{d}t$$

$$\ln\left[\frac{c_\mathrm{A}(t) - c_\mathrm{A}(\infty)}{c_\mathrm{A}(0) - c_\mathrm{A}(\infty)}\right] = -(k_\mathrm{f} + k_\mathrm{b})t$$



Example: $k_\mathrm{f} = 4\ \mathrm{s}^{-1}$, $k_\mathrm{b} = 1\ \mathrm{s}^{-1}$

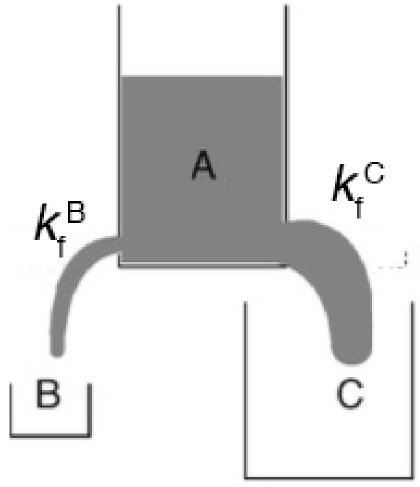
b) Parallel reactions

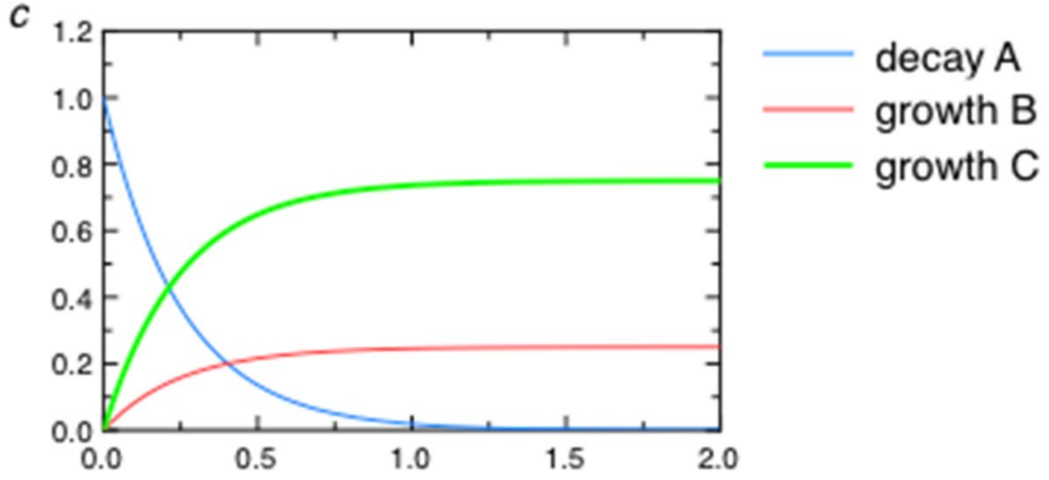


$$\frac{dc_A(t)}{dt} = -k_f^B c_A(t) - k_f^C c_A(t) = -\left(k_f^B + k_f^C\right) c_A(t)$$

$$c_A(t) = c_A(0)\,e^{-\left(k_f^B + k_f^C\right)t}, \quad c_B(t) = c_A(0)\frac{k_f^B}{k_f^B + k_f^C}\left(1 - e^{-\left(k_f^B + k_f^C\right)t}\right), \quad c_C(t) = c_A(0)\frac{k_f^C}{k_f^B + k_f^C}\left(1 - e^{-\left(k_f^B + k_f^C\right)t}\right)$$

Example: $k_f^B = 1\ \mathrm{s}^{-1}$, $k_f^C = 3\ \mathrm{s}^{-1}$





The rate constants for the decay of A and the growth of B and of C are all equal to $k_{obs} = k_f^B + k_f^C$, but the partition ratios or efficiencies are k_f^B/k_{obs} and k_f^C/k_{obs} different.

c) Sequential reactions: $A \xrightarrow{k_f^B} \boxed{B} \xrightarrow{k_f^C} \boxed{C}$

$$\frac{\mathrm{d}c_A(t)}{\mathrm{d}t} = -k_f^B c_A(t), \quad \frac{\mathrm{d}c_B(t)}{\mathrm{d}t} = k_f^B c_A(t) - k_f^C c_B(t), \quad \frac{\mathrm{d}c_C(t)}{\mathrm{d}t} = k_f^C c_B(t)$$

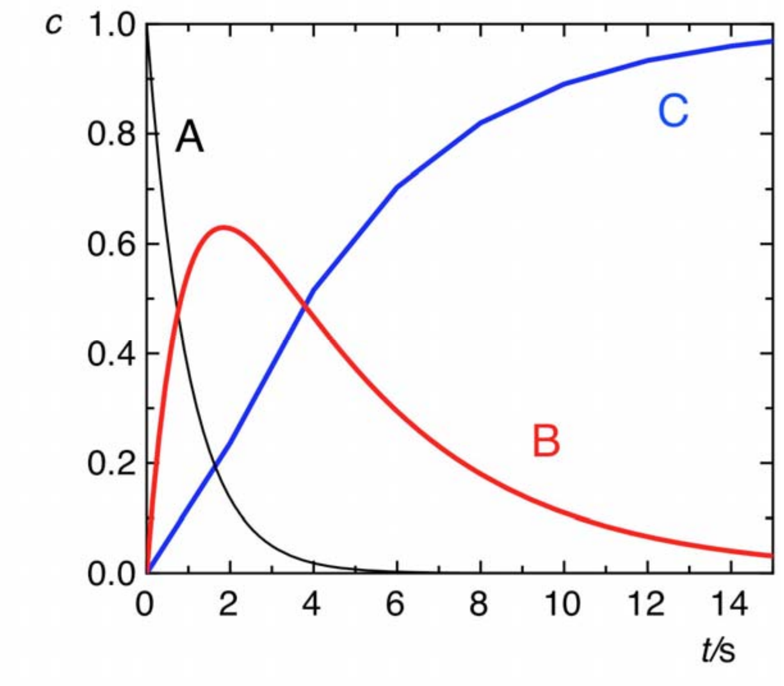
initial conditions: $c_B(0) = c_C(0) = 0$

conservation of mass: $c_A(0) = c_A(t) + c_B(t) + c_C(t)$

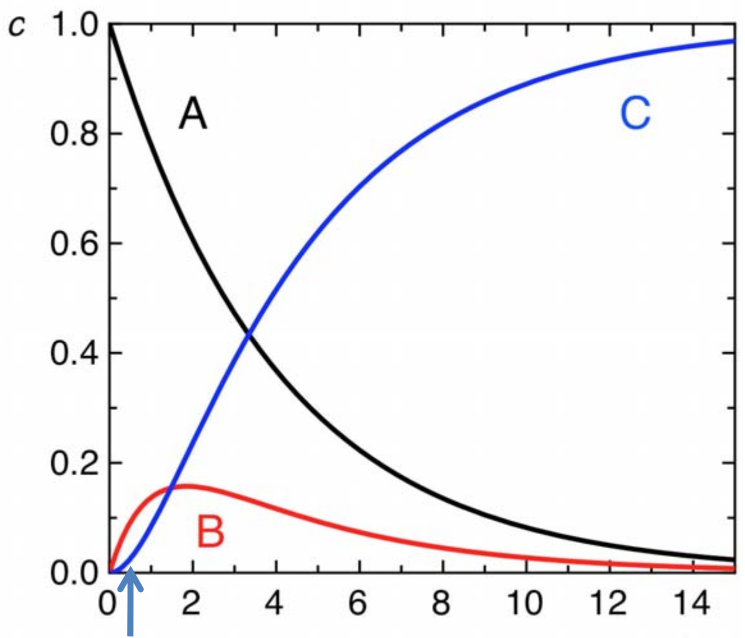
integration ($e^{-k_f^C t}$ is "integrating factor"):

$$c_B(t) = \frac{c_A(0) k_f^B}{k_f^C - k_f^B}\left(e^{-k_f^B t} - e^{-k_f^C t}\right)$$

Example: $k_f^B = 1\ \mathrm{s}^{-1}$, $k_f^C = 0.25\ \mathrm{s}^{-1}$



$k_f^B = 0.25\ \mathrm{s}^{-1}$, $k_f^C = 1\ \mathrm{s}^{-1}$



Induction period

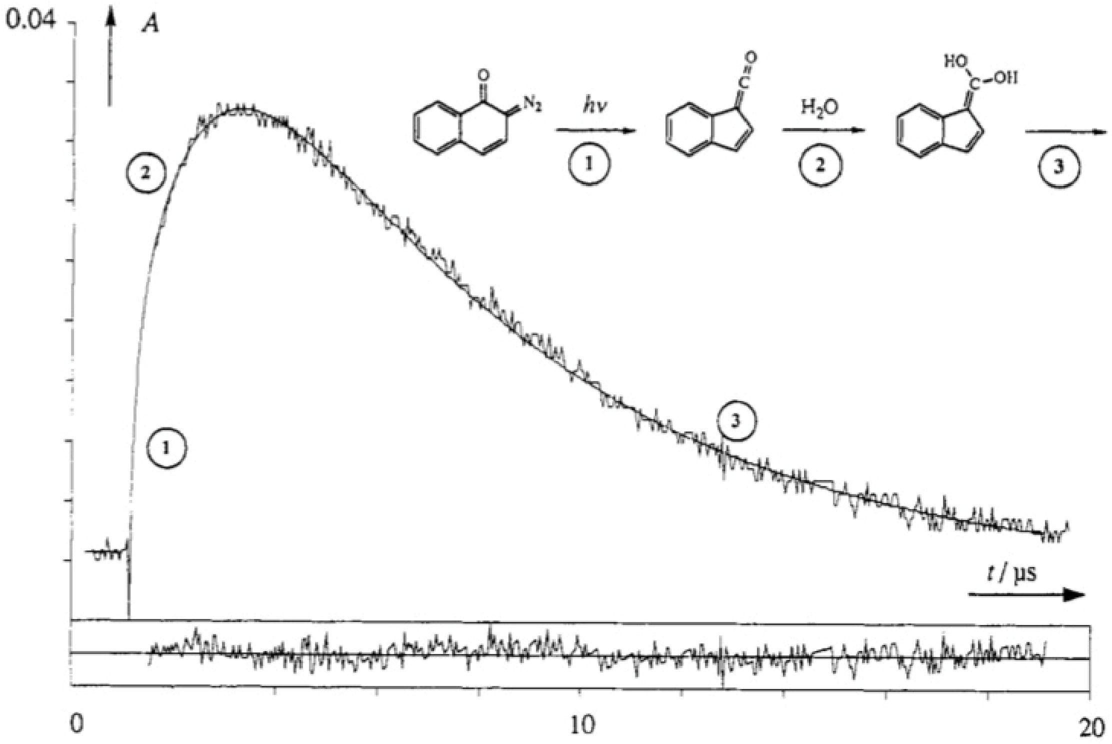
A note regarding c) sequential reactions

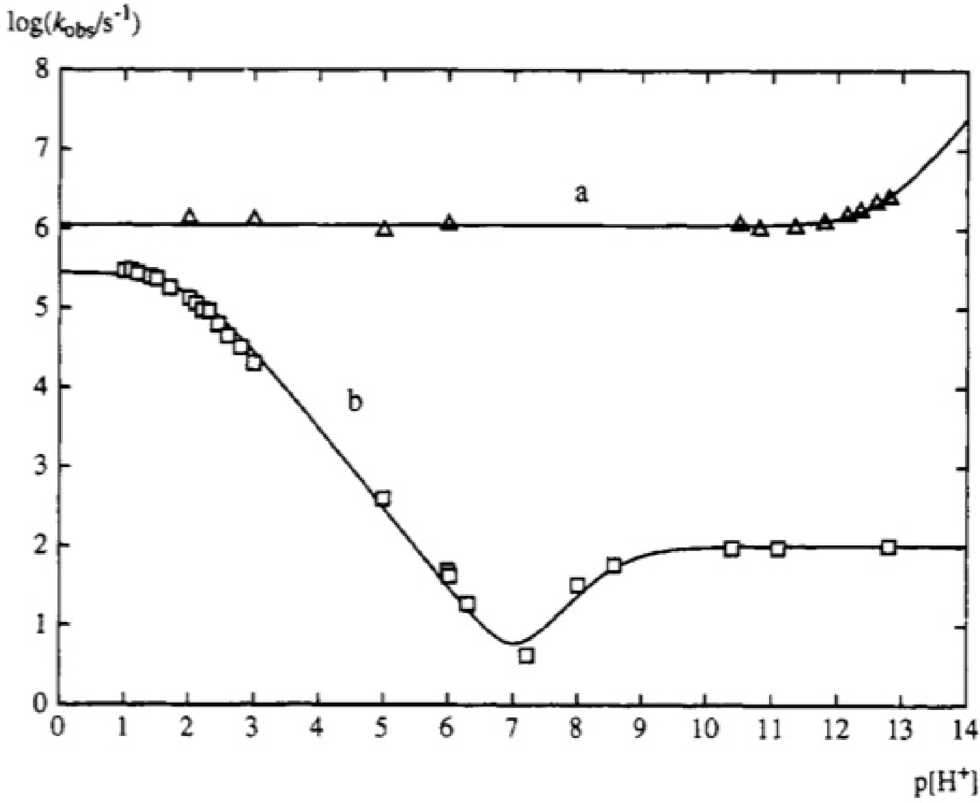
The equation

$$c_B(t) = \frac{c_A(0)k_f^B}{k_f^C - k_f^B}\left(e^{-k_f^B t} - e^{-k_f^C t}\right)$$

is unchanged upon exchange of the rate constants k_f^B and k_f^C!

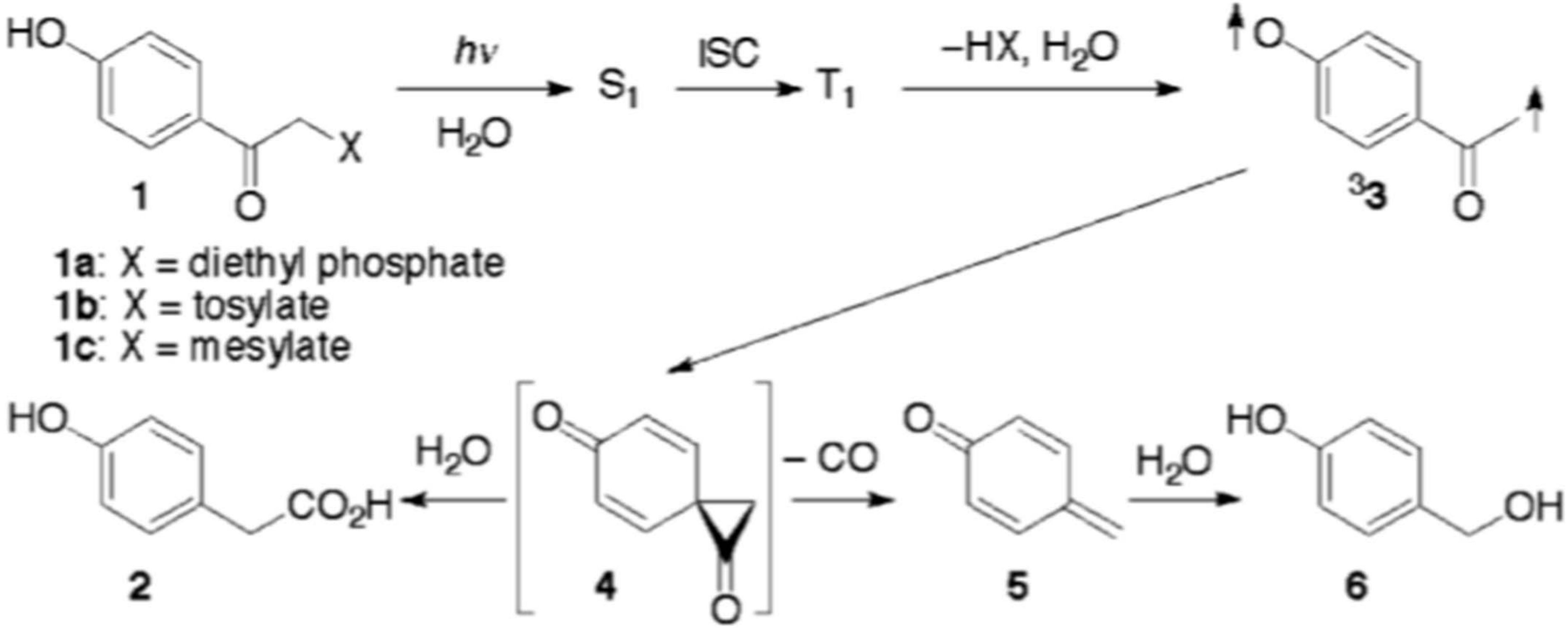
The growth part of the growth–decay curve B always corresponds to the faster reaction, but it does not follow that it corresponds to the step A–>B. For an assignment, other information is needed., e.g.:





JACS, **1994**, *116*, 954

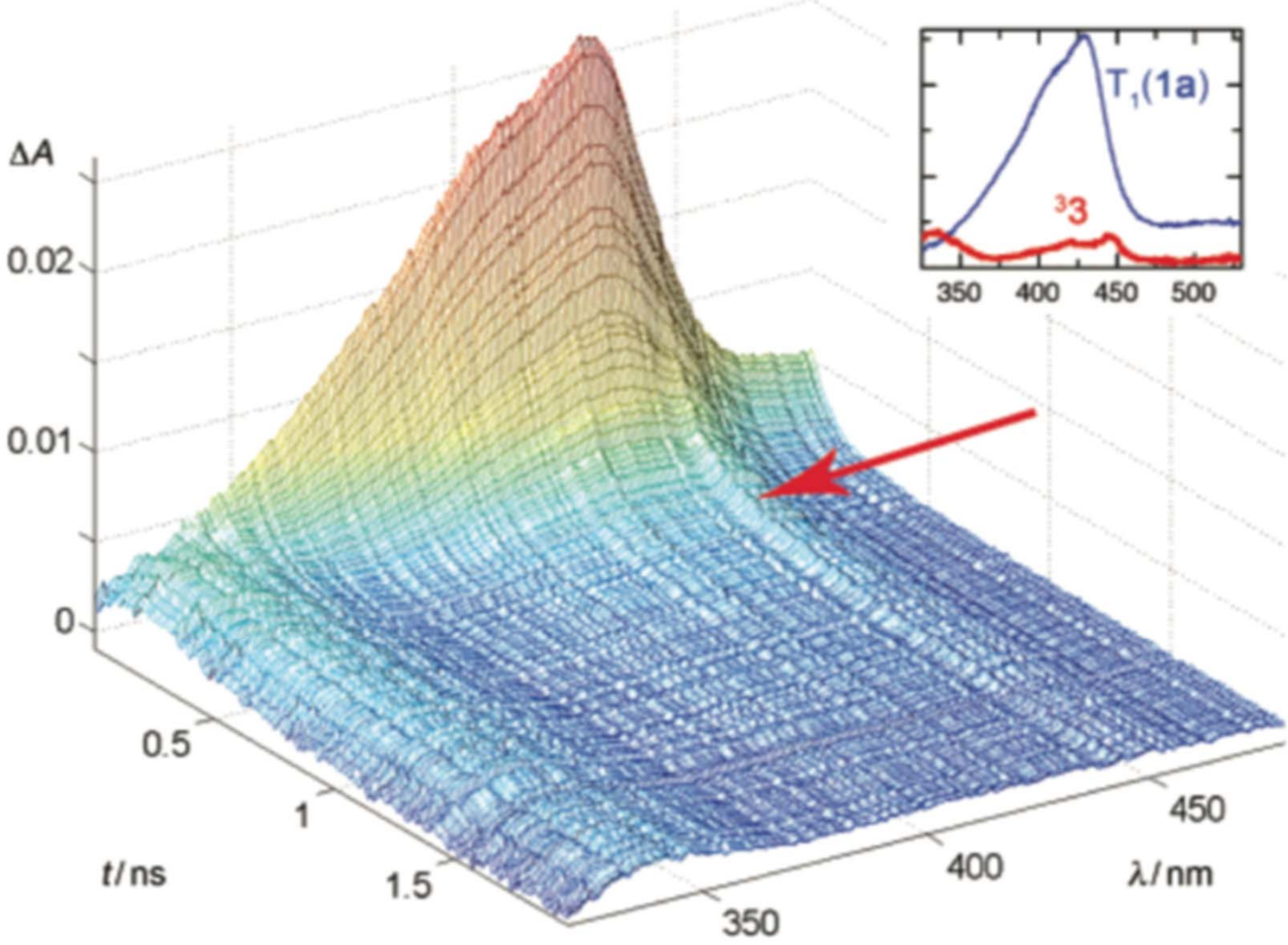
Scheme 1. Mechanism of the Photo-Favorskii Rearrangement **1** → **2**



1a: X = diethyl phosphate
1b: X = tosylate
1c: X = mesylate

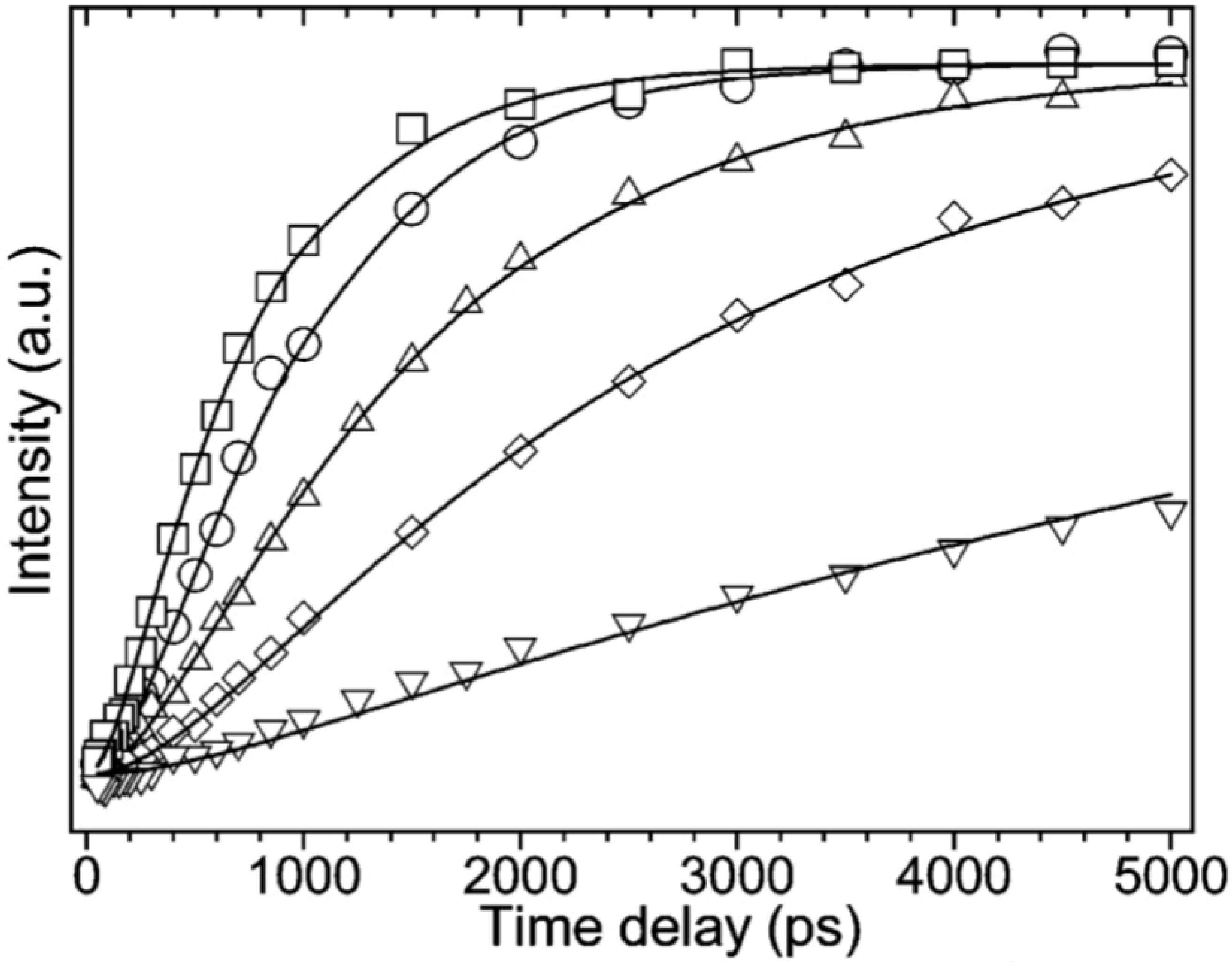
JACS, **2008**, *130*, 3307

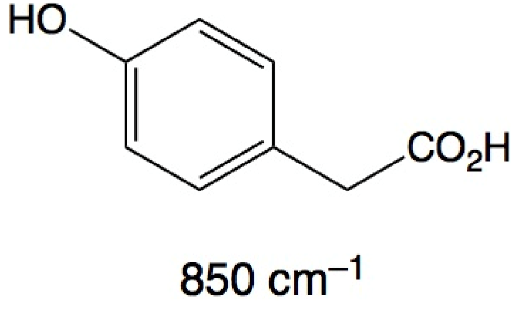
Pump–probe spectroscopy



ps Time-resolved resonance Raman

Phillips et al. *JACS*, **2006**, *128*, 2558



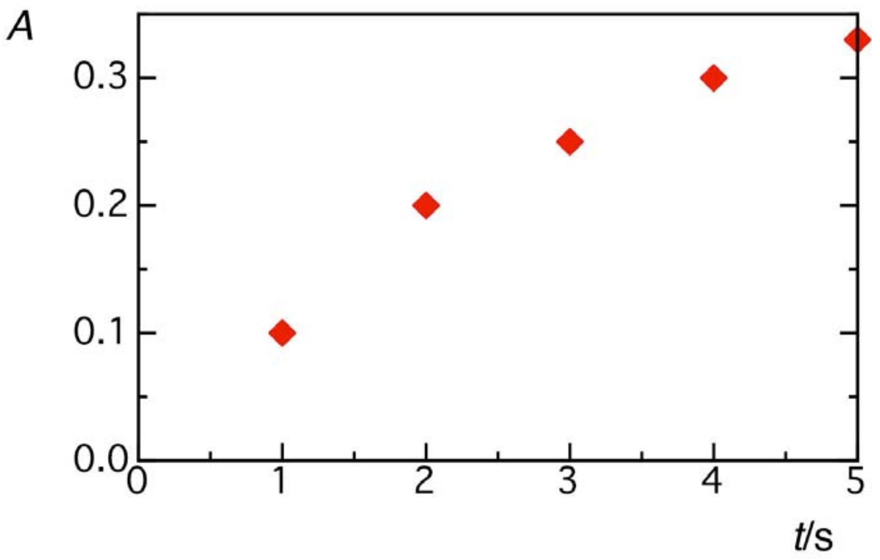


Time dependence of formation of the final product

Analysis of experimental data

Given: A set of data pairs A(*t*)

Task: Define a model (rate law) and determine the model parameter(s) by fitting the rate law to the data



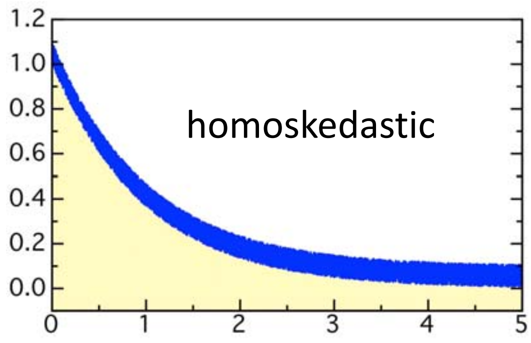
Pre-computer times (and still many textbooks):

Linearise the model and fit by linear regression

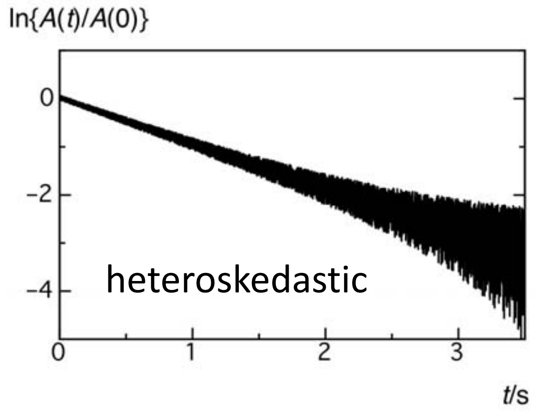
E.g., 1st-order: $A = \varepsilon c d$

$$A_A(t) = A_A(0)e^{-{}^1kt};\ \ln\left(\frac{A_A(t)}{A_A(0)}\right) = -{}^1kt$$

This not recommended, because errors in *A*(*t*) are usually homoskedastic and become heteroskedastic upon linearisation:

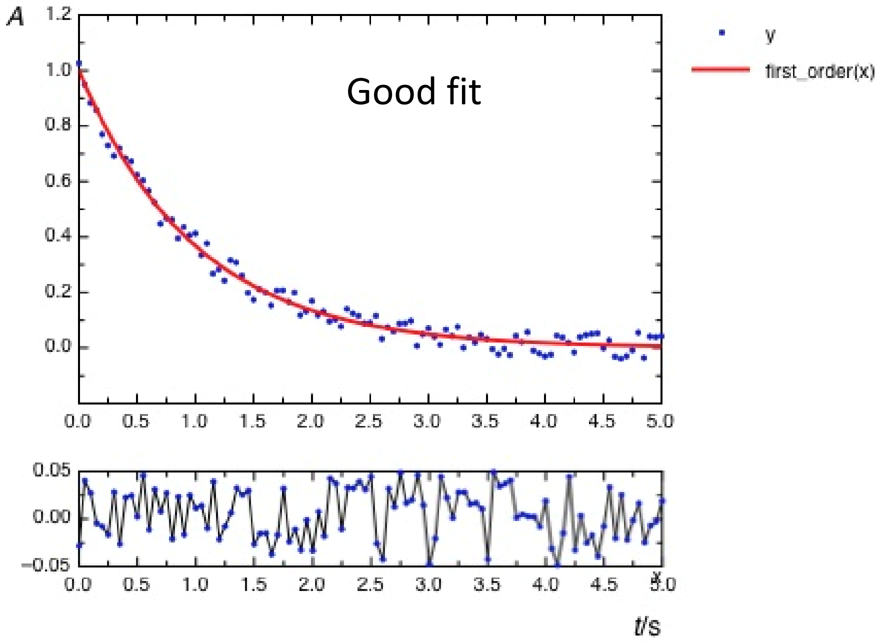


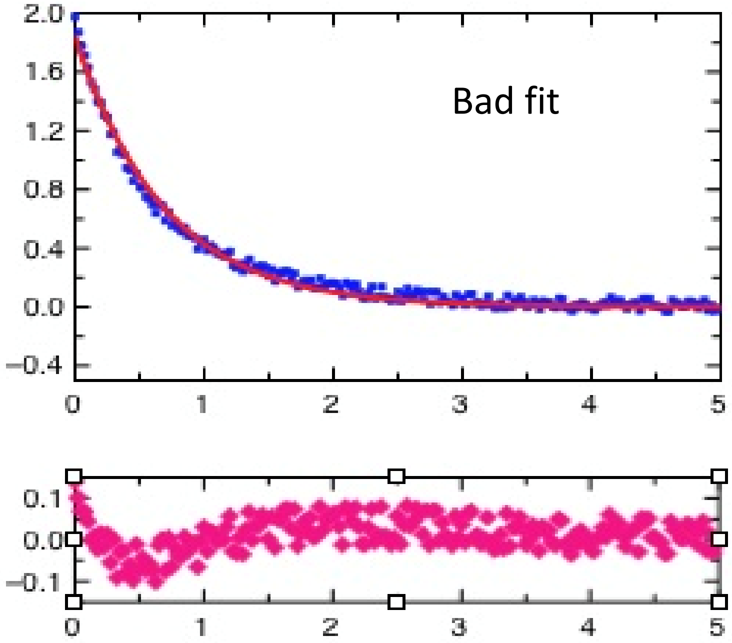
ansformed:



Proper fitting

- Least-squares fitting of nonlinear functions (e.g., y= c*exp(–*kt*) to a given data set can be done only iteratively (Levenberg–Marquart algorithm), but fitting is very fast with modern computers (seconds with 500 data pairs) and provides fit parameters (rate constants) with error limits.
- Never state: “The data were fitted to function xy”!
- Enlarge the time scale settings to define the end point (*t* = inf) accurately.
- A second-order decay can look very similar to a sum of two exponentials!
- Plot and check residuals (A_{calc}–A_{exp}) in a normalized window.



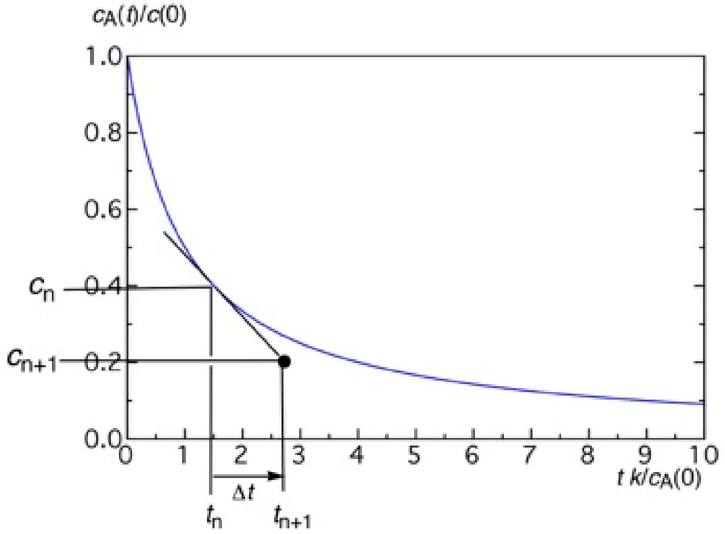


Numerical integration of complex differential rate laws

Given: A differential rate law $\mathrm{d}c/\mathrm{d}t = \mathrm{f}(c, t)$

Replace the differential quotient by a difference quotient and use a recursive formula:

$\mathrm{d}c/\mathrm{d}t \sim (c_{n+1} - c_n)/\Delta t,\ \underline{c_{n+1} \sim c_n + \mathrm{f}(c_n, t)/\Delta t}$



This is Euler's method

Note: errors are cumulative!

Improved method: Runge–Kutta

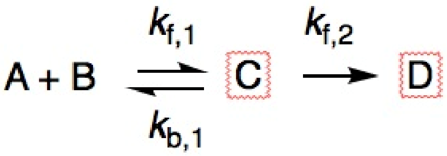
Determine $(c_{n+1} - c_n)/\Delta t$ as the average in the interval Δt (2nd order RK)

Better: divide the interval Δt into 4 parts (4th order RK)

This approximation is commonly used in computer programs.

Important approximations

a) Pre-equilibrium:



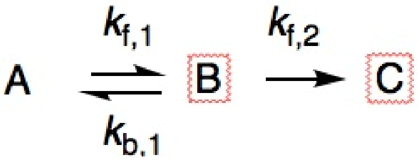
$$A + B \underset{k_{b,1}}{\overset{k_{f,1}}{\rightleftharpoons}} \boxed{C} \xrightarrow{k_{f,2}} \boxed{D}$$

Under what condition is the pre-equilibrium approximation valid?

$K = c_C/(c_A c_B) = k_{f,1}/k_{b,1}$ (note the units!)

$dc_D/dt = k_{f,2}c_C = k_{f,2}Kc_Ac_B$ (approximately a 1st order reaction with $k_{obs} = k_{f,2}K$

b) Stationary-state approximation (Bodenstein):

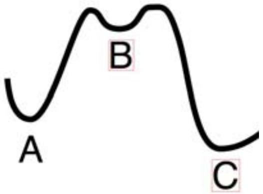


$$A \underset{k_{b,1}}{\overset{k_{f,1}}{\rightleftharpoons}} \boxed{B} \xrightarrow{k_{f,2}} \boxed{C}$$

Note: This scheme contains only 1st order reactions –> exact integration is possible

Write the set of differential equations:

$$\frac{dc_A}{dt} = -k_{f,1}c_A + k_{b,1}c_B, \quad (1) \qquad \frac{dc_B}{dt} = k_{f,1}c_A - \left(k_{b,1} + k_{f,2}\right)c_B, \quad (2) \qquad \frac{dc_C}{dt} = k_{f,2}c_B \quad (3)$$



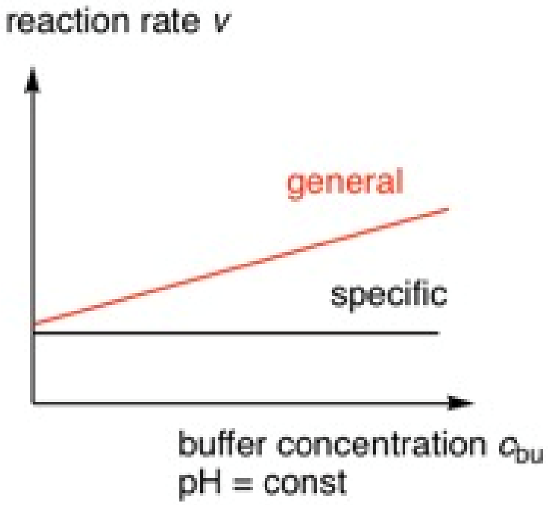
If $k_{b,1} + k_{f,2} >> k_{f,1}$, then c_B will always be small:

Assume $dc_B/dt \sim 0$ (in fact: $dc_B/dt << k_{f,1}c_A$), then (2): $c_B \sim k_{f,1}c_A/(k_{b,1} + k_{f,2})$

Replace c_B in (1): $dc_A/dt = k_{f,1}k_{f,2}c_A/(k_{b,1} + k_{f,1})$; 1st order eq., $k_{obs} = k_{f,1}k_{f,2}/(k_{b,1} + k_{f,1})$

$c_A(t) = c_A(0)\exp(-k_{obs}t)$; $c_C(t) = c_A(0)\{1\text{-}\exp(-k_{obs}t)\}$.

General and specific acid catalysis



$$V = dc/dt = k_0 + \underbrace{k_{H^+}[H^+]}_{\text{specific}} + \underbrace{k_{HA}[HA]}_{\text{general}}$$

How can it be that a reaction is catalyzed only by H^+ and not by general acids HA?

Specific acid catalysis is observed when a reaction proceeds by pre-equilibrium protonation:

$$A + H^+ \xrightleftharpoons{\text{fast}} AH^+ \xrightarrow[k_1]{\text{slow}} BH^+ \xrightarrow{\text{fast}} B + H^+$$

$$v = k_1 c_{AH^+} = (k_1/K_a) c_A c_{H^+},\ K_a = c_A c_{H^+}/c_{H^+}$$

The pre-equilibrium is not affected by any general acid present.

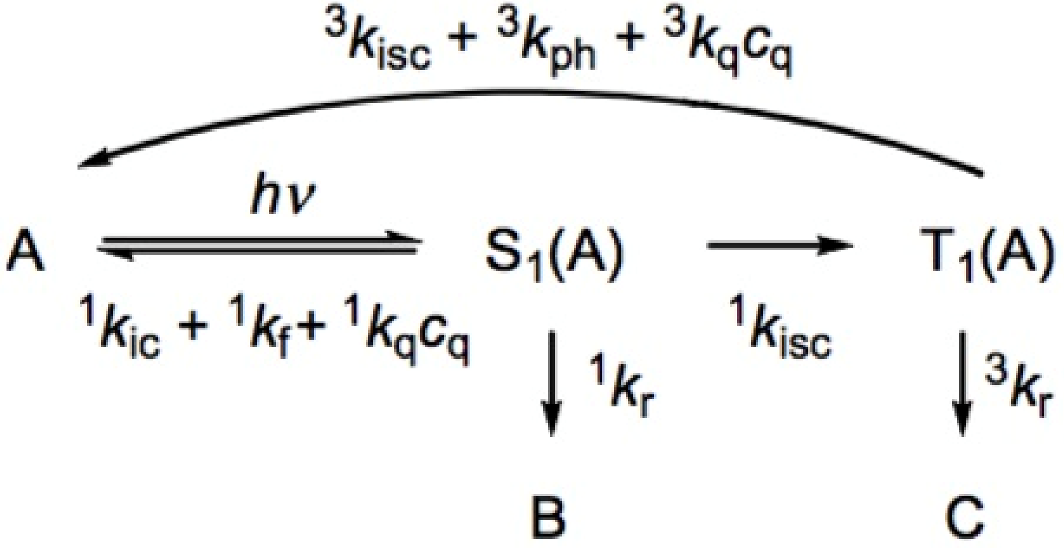
General acid is not involved in the transition state between A and B, but H^+ is.

Quantum yield

Definition: The quantum yield $\Phi_x(\lambda)$ ${}_x/n_\mathrm{p}$, where n_x is the amount of photophysical or photochemical events that occurred, and n_p is the amount of photons at the irradiation wavelength tλat were absorbed by the reactant. $[n_x] = [n_\mathrm{p}]$ = mol; [$\Phi_x(\lambda)$] = 1.

The quantum yield of a single-step process *x* is equal to its efficiency $\eta_x = k_x/\Sigma k_i$ here k_i are the rate constants of all processes competing for the depletion of the reactant. The overall quantum yield for a complex reaction (several ER steps) is equal to the product of the efficiencies of all reaction steps. (Note: Stationary-state approximation not needed for derivation!)

A typical photochemical reaction sequence (different notation!):

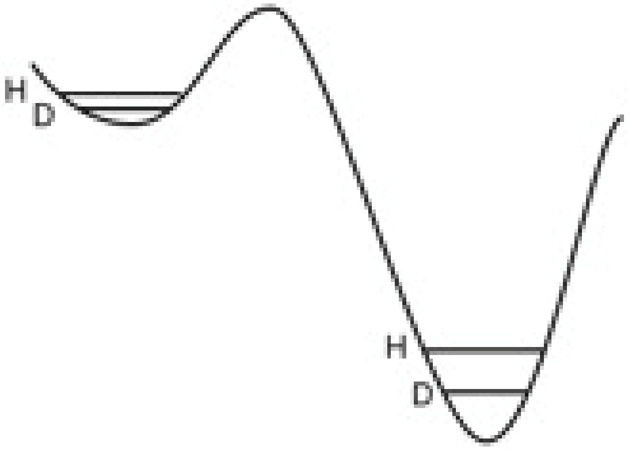


Kinetic and thermodynamic isotope effects

Thermodynamic: $HT + H_2O \overset{K}{\rightleftharpoons} H_2 + H_2O \qquad K = 6.3$

The heavy isotope prefers to be in the strong bond, because of the zero-point vibrational energy.

Kinetic: maximal effect, when the bond to H/D/T is broken.



$$\varepsilon_0 = \frac{h\nu}{2} = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}},\ \mu = \frac{m_1 m_2}{m_1 + m_2} \approx m_2 \text{ if } m_1 >> m_2$$

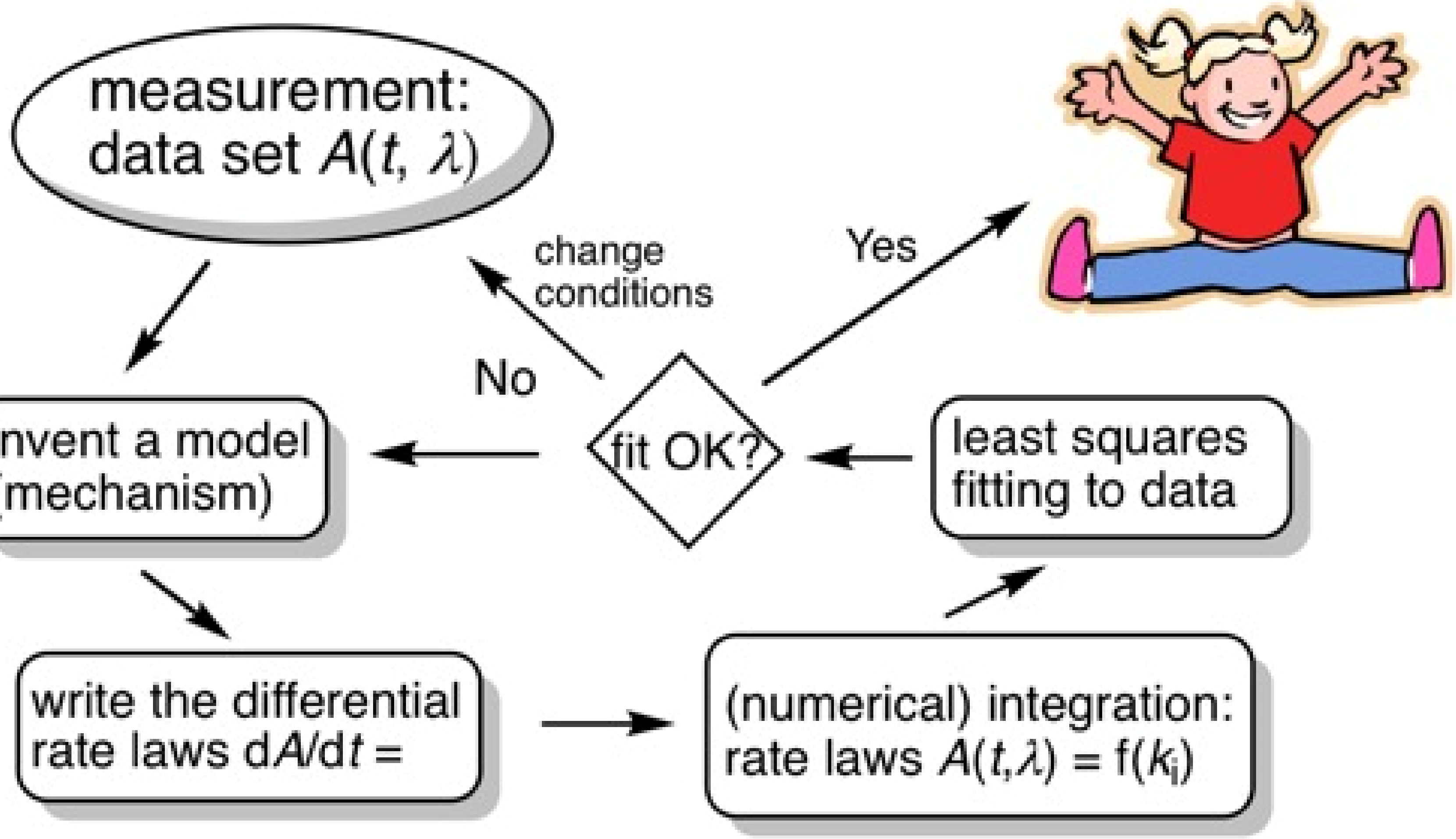
$$\frac{\varepsilon_0(\mathrm{H})}{\varepsilon_0(\mathrm{D})} \approx \sqrt{2},\ \frac{\varepsilon_0(\mathrm{H})}{\varepsilon_0(\mathrm{T})} \approx \sqrt{3}$$

$$\varepsilon_0(\mathrm{H}) - \varepsilon_0(\mathrm{D}) = \frac{h\nu_\mathrm{H}}{2}(1 - 1/\sqrt{2}) \approx 0.15 h\nu_\mathrm{H}$$

For ν_H= 3000 cm^{-1}, T ~ 300 K: $k_\mathrm{H}/k_\mathrm{D}$ ~ 7 (±2) primary isotope effect

When H/D are only “spectators”: $k_\mathrm{H}/k_\mathrm{D}$ ~ 1 (±0.2) secondary isotope effect

Summary



measurement: data set $A(t, \lambda)$

invent a model (mechanism)

write the differential rate laws $dA/dt =$

(numerical) integration: rate laws $A(t,\lambda) = f(k_i)$

least squares fitting to data

fit OK?

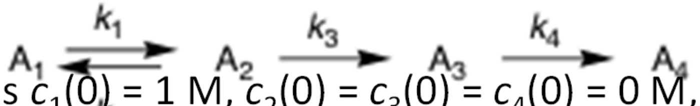
No

change conditions

Yes

Exercises

1. Express the equilibrium concentrations of A and B in a reversible 1st-order reaction in terms of the rates constants k_f and k_b and c_{tot}.
2. Explain why the hypothetical cyclopropanone reaction intermediate **4** is not observed in the photo-Favorskii rearrangement.
3. The chemical yield of B in a photoreaction is 100%, yet the quantum yield of formation of B may be <1. Explain.
4. Express the quantum yields of formation of products B and C as a function of the reaction rate constants shown in the Scheme on the slide "quantum yields".
5. The equilibrium constant of the Diels–Alder reaction of anthracene (A) with a diene (D) in hexane is $K^{o}(298\text{ K}) = 2$. The decrease of the initial concentration of A, $c_A(t = 0) = 1 \times 10^{-4}$ M, in a 1 M solution of D is measured by the UV-absorption of A. It obeys a first-order rate law, $k_{obs} = 0.01\ s^{-1}$.
   a) How big is the end concentration of A, $c_A(t = \inf)$?
   b) How big is the second-order rate constant ${}^2k$ of the Diels-Alder reaction?
   c) Give the integrated first-order rate law for the decrease of A.
   d) How big is the first-order rate for the dissociation of the Diels–Alder adduct DA?
5. Compound A_4 is formed by the following reaction mechanism:



$$A_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_2 \xrightarrow{k_3} A_3 \xrightarrow{k_4} A_4$$

With the initial conditions $c_1(0) = 1$ M, $c_2(0) = c_3(0) = c_4(0) = 0$ M, one observes the following kinetics for the formation of A_4: $c_4(t) = \{1 - \exp(-k_{obs}t)\}$ M, where $k_{obs} = 1\ s^{-1}$.

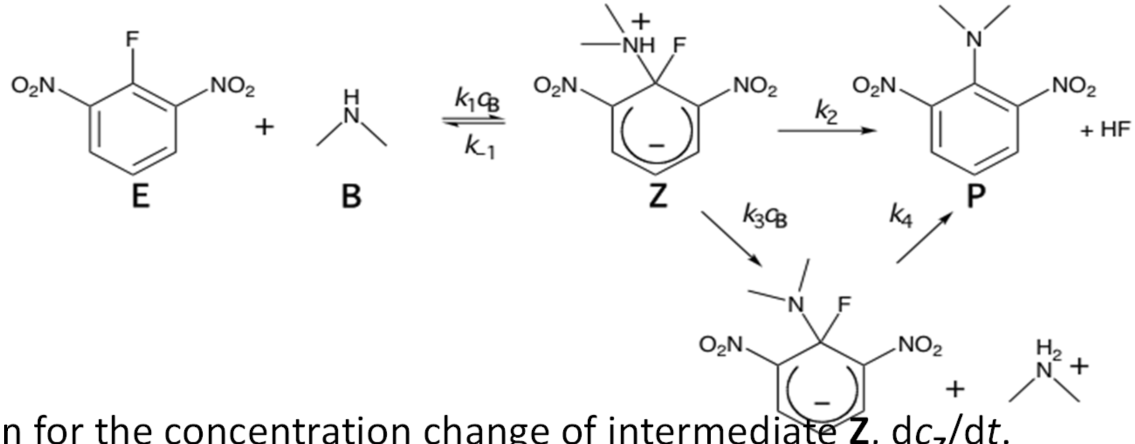
a) Draw a qualitative concentration diagram $c_4(t)$. Both axes must be labelled correctly.

b) Give a combination of boundary conditions for the rate constants k_1 .. k_4, for which the observed, simple rate law would hold [e.g., $k_1 >> k_2$, etc.].

c) Indicate, how k_{obs} depends on the microscopic rate constants [e.g., $k_{obs} = k_1/k_4$] for the boundary conditions given under b).

Exercises

6) The mechanism for the substitution of fluorine in 2,6-dinitrofluorbenzene (**E**) by dimethylamine (**B**) is shown in the following scheme. The concentrations of the intermediates **Z** and **Z'** is very small at all times. Dimethylamine **B** is used in great excess ($c_\mathbf{B} \approx$ const.)



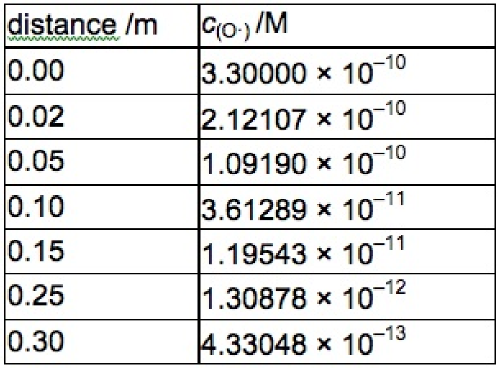
a) Give a differential equation for the concentration change of intermediate **Z**, dc_Z/dt.
b) The decrease of compound **E** obeys a first-order rate law, $c_\mathbf{E}(t) = c_\mathbf{E}(0)\exp(-k_\mathrm{obs}t)$. Give a relation between k_obs and microscopic rate constants k_i shown in the scheme.

7) Oxygen radicals O· are mixed with chlorine gas in a stopped-flow apparatus. The reaction $Cl_2 + O\cdot \rightarrow ClO + Cl\cdot$ is second order (first order in each component). The concentration of O· was measured at various distances from the mixing point:

The initial concentration of Cl_2 is 2.54×10^{-7} M and remains essentially constant after mixing of the

w after mixing amounts to 6.6 m s^{-1}.

(f the reaction.



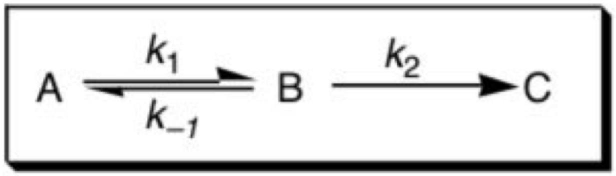
distance /m	$c_{(O\cdot)}$ /M
0.00	3.30000×10^{-10}
0.02	2.12107×10^{-10}
0.05	1.09190×10^{-10}
0.10	3.61289×10^{-11}
0.15	1.19543×10^{-11}
0.25	1.30878×10^{-12}
0.30	4.33048×10^{-13}

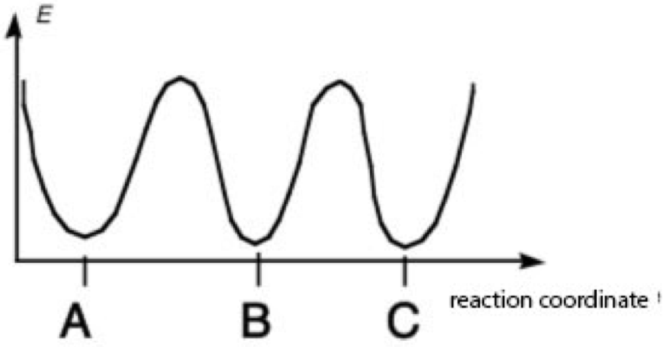
10) Consider three limiting cases for the reaction shown below:

a) The Bodenstein-approximation holds for B ($\mathrm{d}c_\mathrm{B}/\mathrm{d}t \approx 0$), but B is not in a rapid pre-equilibrium with A,

b) B is in rapid pre-equilibrium with A, but the Bodenstein-approximation does not hold, and

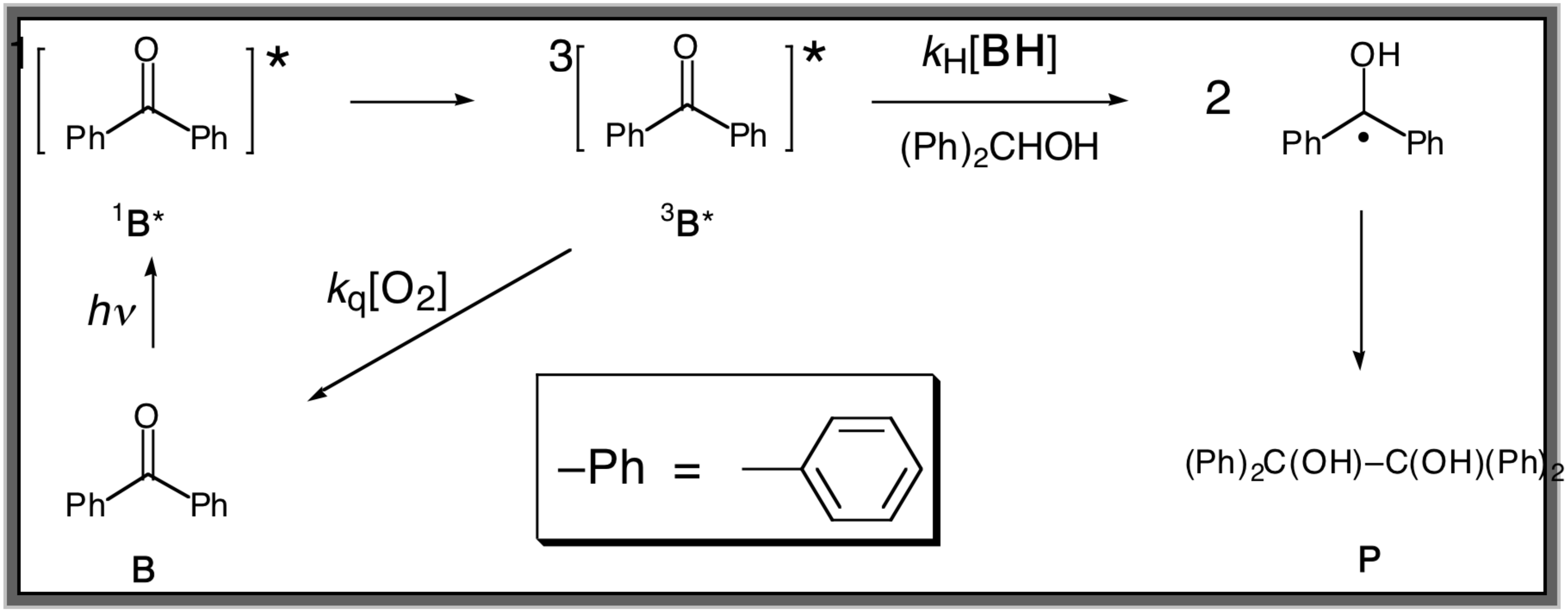
c) both conditions (Bodenstein-approximation und and rapid pre-equilibrium) hold.





Sketch three energy diagrams (as indicated on the right) for the three limiting cases and state, which conditions the three rate constants must obey in each case.

11) The photoreaction of benzophenone (**B**) in the presence of benzhydrole (**BH**) gives benzpinakole (**P**). The electronically excited triplet state of benzophenone (^{3}**B***) is formed very rapidly (< 50 ps) and quantitatively after excitation of **B**. The decay of ^{3}**B*** obeys a first-order rate law, because [**BH**] >> [^{3}**B***], i.e., [**BH**] ≈ const. The lifetime of ^{3}**B*** is 1.0 μs in a degassed solution with [**BH**] = 0.1 mol dm^{-3}. Saturation of the solution with air reduces the lifetime of ^{3}**B*** to 200 ns. The oxygen concentration in air-saturated solution is $[O_2] = 2 \times 10^{-3}$ mol dm^{-3}.



a) Calculate the second-order rate constants k_H und k_q. (hint: Consider only the reactions starting from ^{3}**B***)

b) By which factor is the quantum yield of **P** reduced, when the degassed solution is saturated with air?