

Physical Chemistry 3: – Chemical Kinetics –

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This scriptum contains notes for the lecture “Physical Chemistry 3: Chemical Kinetics” (MNF-chem0405) in the summer term 2013 at the Institute of Physical Chemistry of Christian-Albrechts-University (CAU) Kiel. This module is the last of the three semester lecture course in Physical Chemistry for B.Sc. students of Chemistry and Business Chemistry at CAU Kiel. It includes 3 hours weekly (3 SWS) for lectures and 1 hour weekly (1 SWS) for an exercise class.

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Preface

This scriptum contains lecture notes for the module “Physical Chemistry 3: Chemical Kinetics” (chem0405), the last part of the 3 semester course in Physical Chemistry for B.Sc. students of Chemistry and Business Chemistry at CAU Kiel. It is assumed (but not formally required) that students have previously taken courses on chemical thermodynamics (“Physical Chemistry 1: Chemical Equilibrium” or equivalent) and elementary quantum mechanics (“Physical Chemistry 2: Structure of Matter” or equivalent) as well as “Mathematics for Chemistry” (parts 1 and 2, or equivalent). Module chem0405 includes 3 hours weekly (3 SWS) for lectures and 1 SWS of exercises (56 contact hours combined). Students who started their studies at CAU Kiel should normally be in their 4th semester.

The scriptum gives a summary of the material covered in the scheduled lectures to allow students to repeat the material more economically. It covers basic material that all chemistry students should learn irrespective of their possible inclination towards inorganic, organic or physical chemistry, but goes well beyond the standard Physical Chemistry textbooks used in the PC-1 and PC-2 courses. This is done in recognition of the established research focus at the Institute of Physical Chemistry at CAU to enable students to pursue their B.Sc. thesis project in Physical Chemistry. Some more specialized sections have been marked by asterisks and may be omitted on first reading towards the B.Sc. degree. Useful additional reference material is given in the Appendix.

A brief lecture scriptum can never replace a textbook. For additional review, students are strongly encouraged (and at places required) to consult the recommended books on Chemical Kinetics beyond the standard Physical Chemistry textbooks. The book by Logan¹ is a comprehensive overview of the field of chemical kinetics and a nice introduction; it also has the advantage that it is written in German. The book by Pilling and Seakins² gives a good introduction especially to gas phase kinetics. The book by Houston³ includes more information on the dynamics of chemical reactions. The book by Barrante⁴ is highly recommended for everyone who wants to brush-up some math skills. A highly recommended web site for looking up mathematical definitions and recipies is the *MathWorld* online encyclopedia (<http://mathworld.wolfram.com>).

The computer has become indispensable in modern research. This applies especially to Chemical Kinetics, where only computers can solve (by numerical integration) the coupled nonlinear partial differential equation systems that describe important complex reaction systems (e.g., related to combustion, the atmosphere or climate change). The integration of differential equations, a major task in chemical kinetics, can be performed using *Wolfram Alpha* (<http://www.wolframalpha.com>). More complicated problems can be solved with versatile computer algebra systems, e.g. (in order of increasing power) *Derive*,⁵ *MuPad*, *MathCad*,⁶ *Maple*, *Mathematica*⁷. A graphics program (e.g., *Origin*,⁸

¹ S. R. Logan, *Grundlagen der Chemischen Kinetik*, Wiley-VCH, Weinheim, 1996.

² M. J. Pilling, P. W. Seakins, *Reaction Kinetics*, Oxford University Press, Oxford, 1995.

³ P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw-Hill, 2001.

⁴ J. R. Barrante, *Applied Mathematics for Physical Chemistry*, Prentice Hall, 2003 (\$ 47.11).

⁵ *Derive* is available as shareware without charge.

⁶ *MathCad* is installed in the PC lab.

⁷ *Mathematica* has been used by the author for some of the lecture material.

⁸ Student versions of *Origin* are available for $\approx 35 - 120$ € (depending on run time).

or *Qtiplot*) may be needed for data evaluation and presentation.⁹

As practically all original scientific literature is published in English (British and American; in fact many chemists at some time in their professional lives have to master the subtle differences between both), this scriptum is written in English to introduce students to the predominating language of science at an early stage. Students should also note that the working language of some of the research groups (including that of the author) in the Chemistry Department at CAU is English.

Finally, I would like to encourage all students to ask questions when they appear, whether during the lecture or in the exercise classes!

Kiel, April 13, 2014,

F. Temps

⁹ Excel also allows you to plot simple functions and data, but is not sufficient for serious scientific applications.

Disclaimer

Use of this text is entirely at the reader's risk. Some sections are incomplete, some equations still have to be checked, some figures need to be redrawn, references are still missing, etc. No warranties in any form whatever are given by the author.

Organisational matters

- List of participants
- Lecture schedule
- Exams and grades
 - Homework assignments
 - Short questions
 - Written final exam (“Klausur”)

► **Table 1:** List of participants.

Chemistry (B.Sc.)	82
Business Chemistry (B.Sc.)	25
Biochemistry (B.Sc.)	
Chemistry (2x-B.Sc.)	
Physics (M.Sc.)	1
Other ^{a)}	1
Total	109

^{a)}Not registered for exercise classes and final written exam (“Klausur”).

► **Figure 1:** Physical chemistry courses at CAU Kiel.

C | A | U | I | P | C
Christian-Albrechts-Universität zu Kiel

Physikalische Chemie in den Chemie-Studiengängen an der CAU Kiel

B.Sc. Studiengänge Chemie und Wirtschaftschemie:

- Physikalische Chemie 1: Chemische Thermodynamik (chem0204) 6 LP, 3V + 1Ü
- Physikalische Chemie 2: Aufbau der Materie (chem0304) 6 LP, 3V + 1Ü
- Physikalische Chemie 3: Reaktionskinetik (chem0405) 6 LP, 3V + 1Ü
- Einführung in die Computerchemie (chem0503) 4 LP, 2V + 1Ü
- Physikalisch-Chemisches Grundpraktikum (Chem. Gleichgewicht) 10 LP, 8P + 2S
- Physikalisch-Chemisches Fortgeschrittenenpraktikum (Spektroskopie und Reaktionskinetik) 6 LP, 4P + 2S

M.Sc. Studiengang Chemie:

- Physical Chemistry 4: Molecular Spectroscopy (chem1003) 5 LP, 2V + 1Ü
- Physical Chemistry 5: Statistical Thermodynamics (chem2003) 5 LP, 2V + 1Ü
- Molecular Structure and Molecular Dynamics (chem1004C): Laser Spectroscopy, Chemical Dynamics, Mass Spectrometry, Lab Course on Laser & Mass Spectrometry 15 LP, 6V, 4P, 1S
- Theoretische Chemie & Computerchemie (chem2004C) 15 LP
Quantenchemie, Moleküldynamik, TheoChem-Praktikum

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► **Figure 2:** Organisational matters.

 Organisatorisches	
Christian-Albrechts-Universität zu Kiel	
▪ Vorlesung (3 SWS):	Do, 08:15 – 09:45 Uhr Fr, 09:15 – 10:00 Uhr
▪ Übungen (1 SWS):	Mo, 12:15 – 13:00 Uhr (Beginn: 22.04.2013) <ul style="list-style-type: none"> – (1) Testfragen (10 min), Beispiele, Fragen – (2) Besprechung der Hausaufgaben – Gruppe 1: J. Bahrenburg, kl. HS alte Mensa, R 13, OS 40 – Gruppe 2: F. Temps, Hörsaal alte PC, LMS 8 – Gruppe 3: K. Röttger, Otto-Hahn-Hörsaal, OHP 2
▪ Verlegung:	Fr, 10.05. → Fr. 17.05., 08:15 Uhr !
▪ Keine Vorlesung:	Do + Fr, 23. + 24.05. (Exkursionswoche)
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► **Figure 3:** Requirements and grading.

 Anforderungen für Leistungspunkte zum Modul chem0405	
Christian-Albrechts-Universität zu Kiel	
▪ Übungsaufgaben:	≈ wöchentlich, in der Regel ≈ 3 Aufgaben @ 4 Punkte Abgabe: Mo, 12:00 Uhr (Kasten 1. OG, IPC) Korrektur: Matthias Lipfert, Tim Plöger, Anna Reese
▪ Testfragen:	7 – 14-tägig (unregelmäßig), jeweils ca. 10 min. ⇒ Inhalt der letzten zwei Vorlesungswochen
▪ Klausurtermine:	(1) Do, 11.07.2013, 08 – 10 Uhr, gr. HS OHP 5 (2) Do, 24.10.2013, 08 – 10 Uhr, gr. HS OHP 5
▪ Für die Leistungspunkte werden 60 % der Punkte benötigt, gemäß:	$P = \left(0,3 \times \frac{\text{Übungsaufgaben}}{\sum \text{Übungsaufgaben}} + 0,3 \times \frac{\text{Testfragen}}{\sum \text{Testfragen}} + 0,4 \times \frac{\text{Klausur}}{\sum \text{Klausur}} \right) \times 100\% \geq 60\%$
oder:	$P \left(\frac{\text{Klausur}}{\sum \text{Klausur}} \right) \times 100\% \geq 50\%$
Es zählt das bessere der beiden Ergebnisse.	
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► **Figure 4:** Lecture contents.

C A U I P C		Lecture Topics
Christian-Albrechts-Universität zu Kiel		
Physical Chemistry 3: Chemical Kinetics		
1.	Introduction (Classification & Time Scales of Chemical Reactions)	
2.	Formal Kinetics (Kinetics of Elementary Reactions)	
3.	Kinetics of Complex Reaction Systems	
4.	Experimental Methods for Determining Rate Coefficients	
5.	Collision Theory	
6.	Potential Energy Hypersurfaces for Chemical Reactions	
7.	Transition State Theory	
8.	Unimolecular Reactions	
9.	Chain and Heat Explosions	
10.	Homogeneous and Heterogeneous Catalysis	

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► **Figure 5:** Table of contents (continued).^a

C A U I P C		Lecture Topics
Christian-Albrechts-Universität zu Kiel		
Physical Chemistry 3: Chemical Kinetics		
11.	Reactions in Solution	
12.	Photochemical Reactions*	
13.	Atmospheric Chemistry*	
14.	Combustion Chemistry*	
15.	Astrochemistry*	
16.	Energy Transfer Processes*	
17.	Reaction Dynamics*	
18.	Electrochemical Kinetics*	

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^a Topics marked with asterisks will be omitted in this course for lack of time. They are the subject of specialized lectures for advanced students.

► **Figure 6:** Recommended textbooks on chemical kinetics.

CAU I | P | C
Christian-Albrechts-Universität zu Kiel

Literature Recommendations

- Physical Chemistry Textbooks: Atkins, Wedler, McQuarrie & Simons, Alberty & Silbey, Woodbury
- K. H. Homann, Reaktionskinetik, Steinkopf, Darmstadt, 1975.
- I. W. M. Smith, Kinetics and Dynamics of Elementary Gas Reactions, Butterworths, London, 1980.
- **S. R. Logan, Grundlagen der Chemischen Kinetik, Wiley-VCH, Weinheim, 1996.**
- **M. J. Pilling, P. W. Seakins, Reaction Kinetics, Oxford University Press, Oxford, 1995.**
- **J. I. Steinfeld, J. S. Francisco, W. L. Hase, Chemical Kinetics and Dynamics, Prentice Hall, Englewood Cliffs, 1998.**
- **P. L. Houston, Chemical Kinetics and Reaction Dynamics, McGraw-Hill, 2001.**
- R. G. Gilbert, S. C. Smith, Theory of Unimolecular and Recombination Reactions, Blackwell, Oxford, 1990.
- T. Baer, W. L. Hase, Unimolecular Reactions, Oxford, 1996.
- R. G. K. A. Holbrook, M. J. Pilling, S. H. Robertson, Unimolecular Reactions, 2nd Ed., Wiley, Chichester, 1996.
- **J. R. Barrante, Applied Mathematics for Physical Chemistry, Prentice Hall, 2003.**

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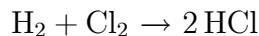
References to original publications and other recommended literature for further reading will be given at the end of each chapter.

1. Introduction

1.1 Types of chemical reactions

- Homogeneous reactions:

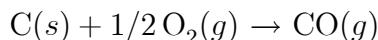
- Reactions in the gas phase, e.g.,



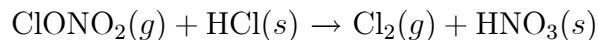
- Reactions in the liquid phase, e.g., H^+ -transfer, reduction/oxidation reactions, hydrolysis, ... (most of organic and inorganic chemistry)
 - Reactions in the solid phase (usually very slow, except for special systems and special conditions; not covered in this lecture).

- Heterogeneous reactions:

- Reactions at the gas-solid interface, e.g.,



- Reactions at the gas-liquid interface, e.g., heterogeneous catalysis, atmospheric reactions on aerosols (e.g., Cl release into the gas phase from polar stratospheric clouds in antarctic spring)

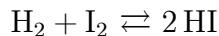


- Reactions at the liquid-solid boundary, e.g., solvation, heterogeneous catalysis, electrochemical reactions (electrode kinetics), ...

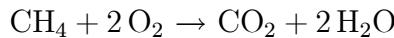
- Irreversible reactions, e.g.,



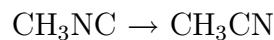
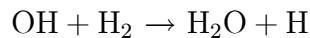
- Reversible reactions, e.g.,



- Composite reactions, e.g.,



- Elementary reactions, e.g.,



1.2 Time scales for chemical reactions

A chemical reaction requires some “contact” between the respective reaction partners. The “time between contacts” thus determines the upper limit for the rate of a reaction.

► Reactions in the gas phase:

- Free mean pathlength $\lambda \gg$ molecular dimension (diameter) d .
- Reaction rate is determined by time between collisions.
- Time between two collisions @ NPT :

$$v \approx 500 \text{ m/s} \quad (1.1)$$

$$\lambda \approx 10^{-7} \text{ m} \quad (1.2)$$



$$\Delta t \approx \lambda/v \approx 2 \times 10^{-10} \text{ s} \quad (1.3)$$



- Gas phase reactions take place on the nanosecond time scale:

$$k_{@NPT}^l \leq \frac{1}{\Delta t} = 5 \times 10^9 \text{ s}^{-1} \quad (1.4)$$

► Reactions in the liquid phase:

- Molecules are permanently in contact with each other.
- Typical distance between neighboring molecules (upper limit allowing for solvation shell):

$$d \approx 2 \times 10^{-8} \dots 10^{-7} \text{ cm} \quad (1.5)$$

- Maximal reaction rate is determined by the rate of diffusion of the reacting molecules in and out of the solvent cage.

► Reactions in the solid phase:

- Atoms and molecules localized on fixed lattice positions.
- Reaction rate is determined by rate of diffusion (“hopping”) of the atoms and molecules *via* vacancies (unoccupied lattice positions, “Fehlstellen”) or interstitial sites (“Zwischengitterplätze”).
- Hopping from one lattice position to another usually requires a corresponding high activation energy.
- Solid state reactions are usually very slow.

► **Time scale of molecular vibrations:**

- The frequencies of the vibrational motions of the atoms in a molecule with respect to each other determine an upper limit for the rate of a unimolecular reaction.
- Uncertainty principle (Fourier relation between frequency and time domain):

$$\Delta E \Delta t \geq \hbar \quad (1.6)$$

↷

$$\Delta\nu \Delta t \geq \frac{1}{2\pi} \quad (1.7)$$

With $\nu = c/\lambda = c\tilde{\nu}$:

$$\Delta t \approx \frac{1}{2\pi c \Delta\tilde{\nu}} \quad (1.8)$$

- Application to a C-C stretching vibration:

$$\tilde{\nu}(\text{C-C}) \approx 1000 \text{ cm}^{-1} \quad (1.9)$$

↷

$$\nu = c/\lambda = c\tilde{\nu} = 3 \times 10^{13} \text{ s}^{-1} \quad (1.10)$$

↷

$$T = \nu^{-1} = 3.33 \times 10^{-14} \text{ s} \approx 33 \text{ fs} \quad (1.11)$$

- Application to slow torsional motions of large molecular groups in solution:

$$\tilde{\nu} \approx 100 \text{ cm}^{-1} \quad (1.12)$$

↷

$$\Delta t \approx 330 \text{ fs} \quad (1.13)$$

- **Femtochemistry:** We can observe ultrafast chemical reactions directly nowadays by following the motions of atoms or groups of atoms in the course of a reaction in real time by femtosecond spectroscopy and femtosecond diffraction techniques. This new area of “femtochemistry” has grown enormously in importance in the last decade, since the award of the Nobel prize in chemistry to A.H. Zewail in 1999.

$$1 \text{ femtosecond} = 1 \text{ fs} = 10^{-15} \text{ s} \quad (1.14)$$

- **Timescale of e^- -jump processes:** Only electron jumps are faster than vibrational motions (by factor of roughly m_e/m_p).

- Estimated time for e^- -jump to another orbital due to absorption/emission of a photon:

$$\Delta t \approx 10^{-18} \text{ s} \quad (1.15)$$

There are indications that electron correlation may slow this time to some 10^{-17} s .¹⁰

¹⁰ The group of F. Krausz (MPI for Quantum Optics, Munich) recently used attosecond metrology based on an interferometric method to measure a delay of $21 \pm 5 \text{ as}$ in the photo-induced emission of electrons from the $2p$ orbitals of neon atoms with respect to emission from the $2s$ orbital by a 100 eV light pulse (Schultze et al, *Science* **328**, 1658 (2010)).

- Other fast electron transfer processes:
 - Autoionization of a doubly excited state, by one electron falling to a lower orbital, while the other is excited into the ionization continuum.
- But “chemical” intra- and intermolecular e^- -transfer reactions are again slower:
 - The electron jump itself is very fast ($\approx 10^{-18}$ s, as above).
 - However, in the Franck-Condon limit, the reactions usually require substantial molecular rearrangements due to the structural differences between the reactants and products (\Rightarrow Marcus theory, Section 11.4). The net reaction rate is thus again limited by the time scale of vibrational motion.

► **Conclusions:**

- The time scales of chemical reactions span the enormous range of some 30 orders of magnitude, from $1\text{ fs} = 10^{-15}\text{ s}$ up to $10^9\text{ y} = 10^{16}\text{ s}!$
- In view of this huge span, a factor-to-two experimental uncertainty in an experimental measurement or a theoretical prediction of a rate constant really means rather little.
- The enormous range of reaction rates, their complex dependencies on temperature, pressure, and species concentrations, and the question of the underlying reaction mechanisms that determine the reaction rates, make the field of chemical reaction kinetics and dynamics very attractive and rewarding!

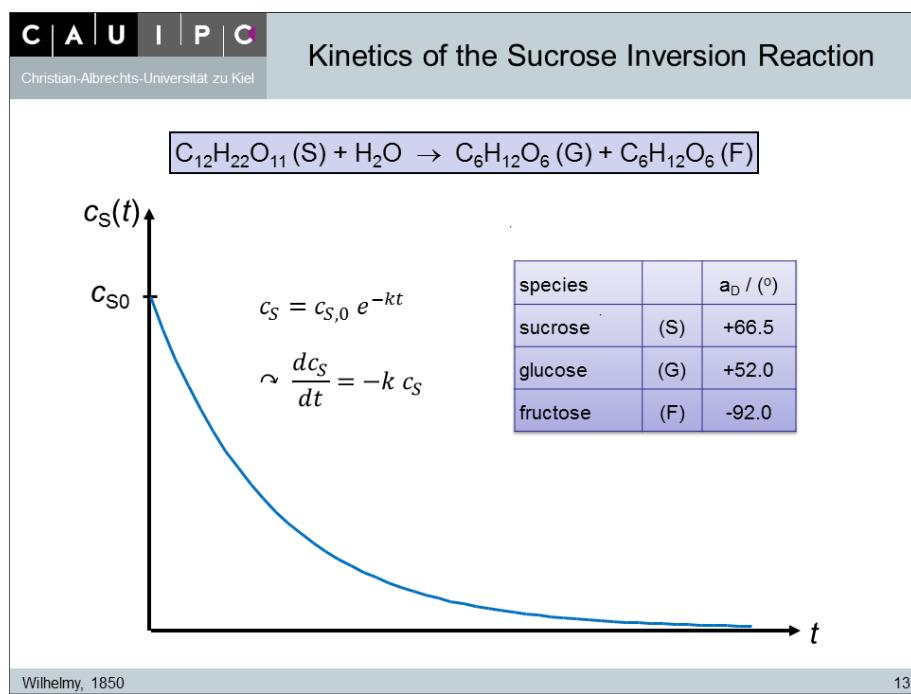
1.3 Historical events

- **Sucrose inversion reaction (Wilhelmy, 1850):** Kinetic investigation of the H^+ catalyzed hydrolysis of sucrose by monitoring the change as function of time of the optical activity of the solution from reactant (sucrose) to products (glucose and fructose).¹¹
- **Table 1.1:** Optical activity parameters for the sucrose inversion reaction.

	$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$		
	sucrose	glucose	fructose
$\alpha_D(1 \text{ M})^a)$	+66.5°	–	+52.0°
$\alpha_D(1 \text{ M})^a)$	$\emptyset = +66.5^\circ$		$\emptyset = -20.0^\circ$

^{a)} $\alpha_D(1 \text{ M})$ = specific angle of rotation of a 1 M solution at $\lambda(\text{Na-}D)$.

- **Figure 1.1:** Observed concentration-time profile of sucrose.



¹¹ This experiment is carried out in the Physical Chemistry Lab Course 1 at CAU ("Grundpraktikum").

► **Empirical rate law:**

$$\ln \frac{c_s}{c_{s,0}} = -k t \quad (1.16)$$

Differentiation gives

$$\frac{d \ln c_s}{dt} - \underbrace{\frac{d \ln c_{s,0}}{dt}}_{=0} = -\frac{d}{dt}(k t) = -k \quad (1.17)$$

or

$$\frac{1}{c_s} \frac{dc_s}{dt} = -k \quad (1.18)$$

↷ Empirical rate law:

$$\frac{dc_s}{dt} = -k c_s \quad (1.19)$$

Reaction rate r :

$$r \equiv -\frac{dc_s}{dt} \quad (1.20)$$

Notice that even though there is one molecule of H_2O taking part in the reaction, $c_{\text{H}_2\text{O}}$ does not appear in the rate law, because it is practically constant in the dilute solution.

► **Figure 1.2:** Milestones in chemical kinetics.

Historic Milestones in Chemical Kinetics	
CAU I P C	Christian-Albrechts-Universität zu Kiel
year	milestone
1850	kinetic measurement of sucrose inversion reaction (Wilhelmy)
≈1888	rate laws and rate constants (van't Hoff)
1889	temperature dependence of chemical reaction rate coefficients (Arrhenius)
≈1900	mechanism of catalysis (Ostwald)
1906	mechanism of the H_2/Br_2 chain reaction (Bodenstein)
1914	kinetics of enzyme reactions (Michaelis & Menten)
1922	pressure dependence for unimolecular reactions (Lindemann)
1927/28	(H)RRK theory for unimolecular reactions (Hinshelwood, Rice, Ramsperger, Kassel)
1925-1927	quantum theory (Heisenberg, Born, Schrödinger)
1935	transition state theory (Eyring, Evans & M. Polanyi, Wigner)
1950-52	flash photolysis - kinetics of fast gas phase reactions (Norrish & Porter)
1954	T-jump method - rate of H^+ transfer reactions (Eigen)
>1954	molecular beam studies (Herschbach, Lee, J. Polanyi, Pauly, Toennies)
1956	theory of electron transfer reactions (Markus), RRKM theory (Markus)
1960	development of the laser (Maiman, Basov & Prokhorov, Townes & Schawlow, ...)
1970-1974	catalytic ozone destruction cycles (Crutzen, Johnston, Rowland & Molina)
>1990	ultrafast molecular dynamics & femtochemistry (Zewail and others)

1.4 References

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2. Formal kinetics

2.1 Definitions and conventions

2.1.1 The rate of a chemical reaction

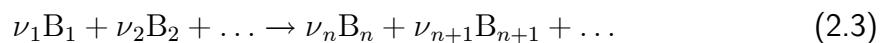
- **Rate of a simple reaction of type $A + B \rightarrow C + D$:**

$$r \equiv -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = +\frac{dc_C}{dt} = +\frac{dc_D}{dt} \quad (2.1)$$

$$= -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt} \quad (2.2)$$

We will usually write the concentrations of a species A by using square brackets, i.e., $[A]$, and understand that $[A]$ is time dependent, i.e., $[A(t)]$.

- **Definition of the rate of reaction:**¹² Using the standard convention for the signs of the stoichiometric coefficients of the reactants (-1) and products ($+1$), we write a generic chemical reaction as



The progress of the reaction from reactants to products can be described using the reaction progress coordinate ξ :

$$d\xi = \frac{dn_i}{\nu_i} \quad (2.4)$$

The time dependence leads to the definition of the reaction rate.

- **Definition 2.1:** The reaction rate r is defined as

$$r \equiv \frac{1}{V} \frac{d\xi}{dt} \quad (2.5)$$

For the above reaction, therefore,

$$r = -\frac{1}{|\nu_1|} \frac{dc_1}{dt} = -\frac{1}{|\nu_2|} \frac{dc_2}{dt} = \dots = +\frac{1}{|\nu_n|} \frac{dc_n}{dt} = +\frac{1}{|\nu_{n+1}|} \frac{dc_{n+1}}{dt} = \dots$$

(2.6)

- **Units:**¹³

- SI unit for the reaction rate:

$$[r] = \text{mol/m}^3 \text{s} \quad (2.7)$$

¹² Reaction rate = Reaktionsgeschwindigkeit. Von manchen Schulen wird auch der Begriff "Reaktionsrate" verwendet. Die bevorzugte "einzig wahre korrekte Übersetzung" wird von der jeweils anderen Seite sehr ernst genommen, allerdings gilt in Kiel in dieser Hinsicht Waffenstillstand.

¹³ For general information on the SI system see (Mills 1988) or (Homann 1995).

- Convenient units for gas phase reactions:

- molar units:

$$[r] = \text{mol/cm}^3 \text{s} \quad (2.8)$$

- molecular units:¹⁴

$$[r] = \text{molecules/cm}^3 \text{s} \Rightarrow \text{cm}^{-3} \text{s}^{-1} \quad (2.9)$$

- We prefer to use molar units for rate constants, because rate constants are inherently quantities that are “averages” of some other quantity, e.g., a molecular cross section weighted by the relevant statistical distribution function (usually the Boltzmann distribution). Rate constants are thus properties of an **ensemble** of molecules, they are **not** original molecular quantities.

- Convenient units for liquid phase reactions:

$$[r] = \text{mol/l s} = \text{M/s} \quad (2.10)$$

2.1.2 Rate laws and rate coefficients

- **The rate equation (rate law):** Experiments show that the reaction rate r generally depends on the concentrations of the reactants. The functional dependence is expressed by the **rate equation** (also called **rate law**),¹⁵ e.g.

$$r = -\frac{1}{|\nu_1|} \frac{d [B_1]}{dt} = \dots \quad (2.11)$$

$$= f([B_1], [B_2], \dots, [B_n], [B_{n+1}], \dots) \quad (2.12)$$

for reaction 2.3.

The rate laws of complex reactions (i.e., the $f([B_1], [B_2], \dots, [B_n], [B_{n+1}], \dots)$) are often rather complicated; only rarely (as in the case of elementary reactions) are they simple and intuitive.

Often (but not always), $f([B_1], [B_2], \dots, [B_n], [B_{n+1}], \dots)$ can be written as a product of a **rate coefficient** k and some power series of the concentrations, for example

$$r = -\frac{1}{|\nu_1|} \frac{d [B_1]}{dt} = k [B_1]^a [B_2]^b \dots \quad (2.13)$$

Note that the exponents a, b, \dots are not usually equal to ν_1, ν_2, \dots

- **The rate constant (rate coefficient):** The **rate constant** (also called **rate coefficient**)¹⁶ k usually depends on temperature ($k = k(T)$) and sometimes also on pressure ($k = k(T, p)$), but **not** on the concentrations ($k \neq f(c)$).

¹⁴ IUPAC has decided that “molecules” is not a unit; see (Mills 1989) or (Homann 1995).

¹⁵ Rate law = Geschwindigkeits- oder Zeitgesetz.

¹⁶ Rate constant = Geschwindigkeitskonstante. Es wird manchmal auch die Übersetzung “Ratenkonstante” verwendet (aber bitte nicht “Ratekonstante”).

- **Rate laws for first-order and second-order reactions:** Simple rate laws describe first-order and second-order reactions:

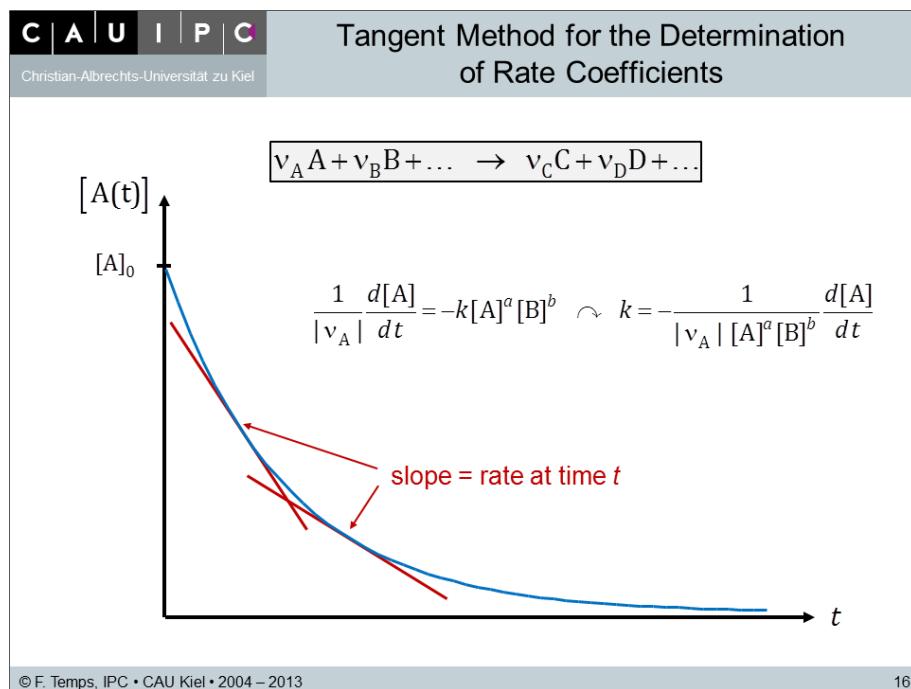
- Example of a first-order reaction: $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$

$$r = -\frac{d[\text{CH}_3\text{NC}]}{dt} = +\frac{d[\text{CH}_3\text{CN}]}{dt} = k [\text{CH}_3\text{NC}] \quad (2.14)$$

- Example of a second-order reaction: $\text{C}_4\text{H}_9 + \text{C}_4\text{H}_9 \rightarrow \text{C}_8\text{H}_{18}$

$$r = -\frac{1}{2} \frac{d[\text{C}_4\text{H}_9]}{dt} = +\frac{d[\text{C}_8\text{H}_{18}]}{dt} = k [\text{C}_4\text{H}_9]^2 \quad (2.15)$$

- **Question:** How can we determine reaction rates r and rate constants k ?
- **Figure 2.1:** The easiest – and always applicable – method for determining the reaction rate r and rate coefficient k is the **tangent method**. To determine r , you simply take the slope of a plot of $c(t)$ at time t ; k then follows via Eq. 2.13.



We'll learn about better methods for determining k for elementary reactions (first-order and second-order reactions) further below.

2.1.3 The order of a reaction

- **Definition 2.2:** The order of a reaction is defined as the sum of the exponents in the rate law (Eq. 2.13).

- **Example:** Considering a generic rate law, like

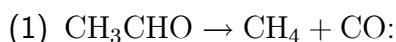
$$-\frac{d[A]}{dt} = |\nu_A| k [A]^a [B]^b \dots, \quad (2.16)$$

the total order of the reaction is $n = a + b$. We also say, the reaction is a -th order in $[A]$ and b -th order in B , ...

The order of a reaction may be determined by the tangent method (Fig. 2.1): Its effects on the reaction rate r are observable by increasing (e.g., doubling) the concentrations of the reaction partners one by one. Better methods will be explored later (\Rightarrow homework assignments).

- **Caveats:**

- The order of a reaction is, in general, an empirical quantity; it has to be determined by an experimental measurement.
- The order of a complex reaction cannot be determined by simply looking at the overall reaction.
- There are reactions with integer order, like the first-order or second-order reactions above (Eqs. 2.14 and 2.15). However, the order can also be fractional, as for the following reactions:



$$\frac{d[\text{CH}_4]}{dt} = k [\text{CH}_3\text{CHO}]^{3/2} \quad (2.17)$$



$$\frac{d[\text{HBr}]}{dt} = \frac{k' [\text{H}_2] [\text{Br}_2]^{1/2}}{1 + k'' [\text{HBr}] / [\text{Br}_2]} \quad (2.18)$$

- A negative order in a concentration means that the respective species acts as an **inhibitor**.
- A positive order in a product concentration means that the reaction rate is enhanced by **autocatalysis**.

2.1.4 The molecularity of a reaction

- **Definition 2.3:** The molecularity of a reaction is the number of molecules in an *elementary* reaction step at the microscopic (molecular) level.

- **There are only three possible cases for the molecularity (one example for each case):**

- monomolecular (= unimolecular) reactions:



- bimolecular reactions:



- termolecular reactions:

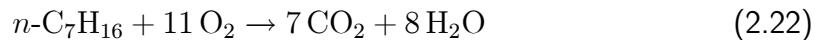


- Events where more than three species come together in the right configuration and react are extremely unlikely and do not play a role.

- **Caveat:** The order of a reaction can be integer or non-integer. However, the molecularity can be only 1 or 2, or at the most 3.

2.1.5 Mechanisms of complex reactions

A stoichiometric formula rarely describes the reactive events happening at the microscopic, molecular level. It is, for example, completely impossible that the combustion of 1 *n*-heptane molecule with 11 molecules of O₂



in an internal combustion engine occurs in a single collision and gives 15 product molecules. Instead, the net reaction is the result of a complex sequence of a very large number (thousands, in this case) of unimolecular, bimolecular, and termolecular elementary reactions.

The identification of the individual elementary reactions, the determination of their rates as a function of *T* and *p*, and the verification of the ensuing reaction mechanism is one of the main tasks in the field of chemical kinetics.

- **Examples for complex reaction systems:**

- H₂/O₂ system (Fig. 2.2),
- Combustion of CH₄ (Fig. 2.3),
- NO_x formation and removal in flames (Fig. 2.4).

- **Figure 2.2:** Reactions in the H_2/O_2 system.

Elementary Reactions in the H_2 / O_2 System			
Christian-Albrechts-Universität zu Kiel			
1.	$\text{H}^{\cdot} + \text{O}_2$	\rightarrow	•OH + •O [·]
2.	•O [·] + H ₂	\rightarrow	•OH + H [·]
3.	•OH + H ₂	\rightarrow	H ₂ O + H [·]
4.	H [·] + O ₂ + M	\rightarrow	HO ₂ [·] + M
5.	H [·] + HO ₂ [·]	\rightarrow	H ₂ + O ₂
6.	H [·] + HO ₂ [·]	\rightarrow	•OH + •OH
7.	•OH + HO ₂ [·]	\rightarrow	H ₂ O + O ₂
8.	•OH + •OH + M	\rightarrow	H ₂ O ₂ + M
9.	...		
	...		
\Rightarrow 8 species (H ₂ , O ₂ , H ₂ O, H ₂ O ₂ , H, O, OH, HO ₂), \approx 20 reactions			
© F. Temps, IPC • CAU Kiel • 2004 – 2013			
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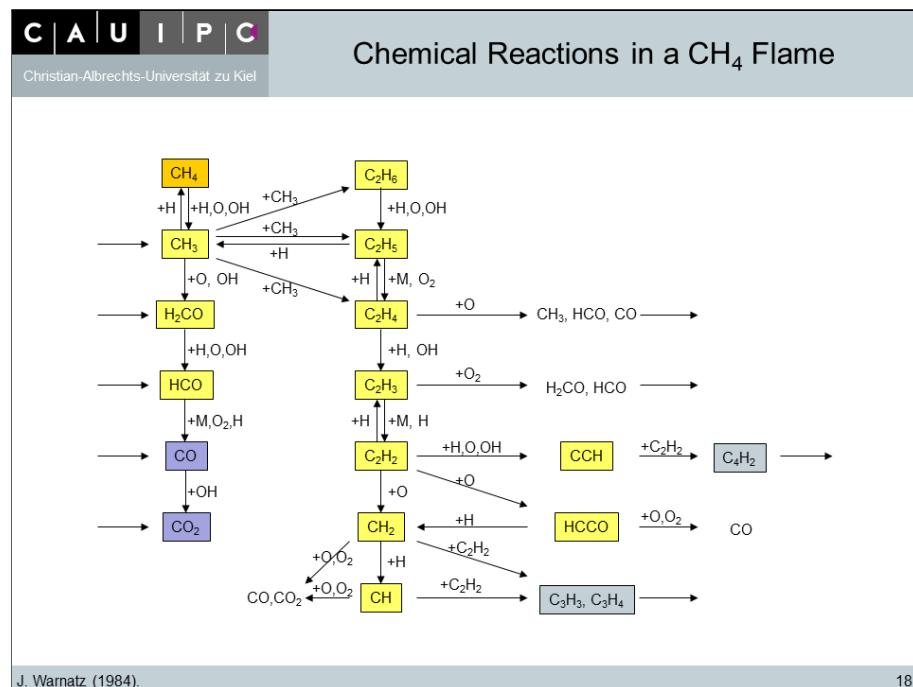
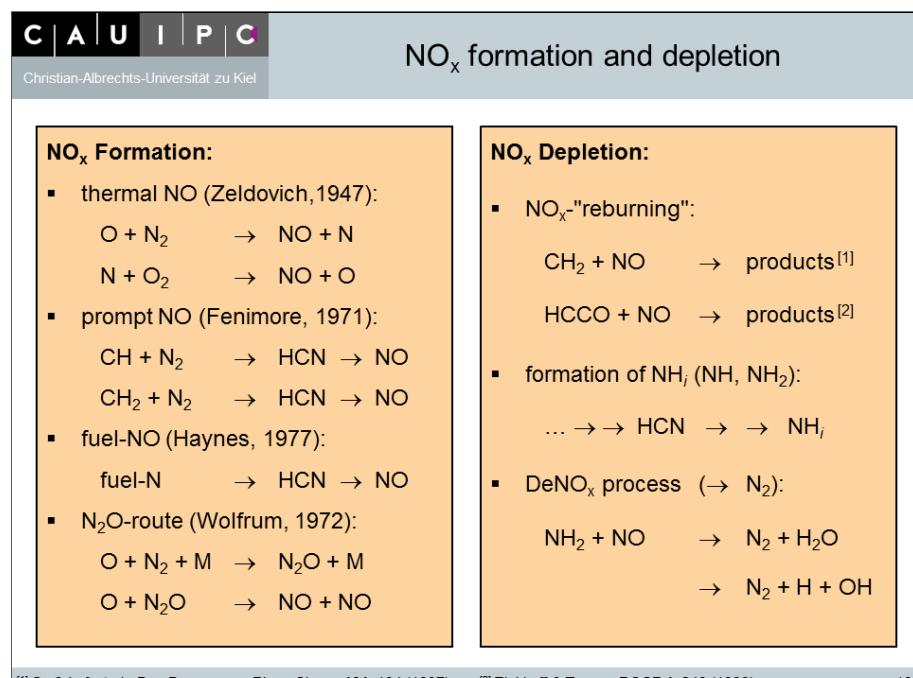
- **Rate equations for the H_2/O_2 system:** Assuming that we know the reaction mechanism (i.e., all elementary reactions contributing), we can write down the rate equations for all species. Doing so, we obtain a set of **coupled non-linear differential equations** (DE's) which can be solved usually only numerically, if we want to describe the net reaction:

$$\frac{d[\text{H}]}{dt} = -k_1 [\text{H}] [\text{O}_2] + k_2 [\text{O}] [\text{H}_2] + k_3 [\text{OH}] [\text{H}_2] - k_4 [\text{H}] [\text{O}_2] [\text{M}] - k_5 [\text{H}] [\text{HO}_2] - k_6 [\text{H}] [\text{HO}_2] + \dots \quad (2.23)$$

$$\frac{d[\text{OH}]}{dt} = k_1 [\text{H}] [\text{O}_2] + k_2 [\text{O}] [\text{H}_2] - k_3 [\text{OH}] [\text{H}_2] + 2k_6 [\text{H}] [\text{HO}_2] - k_7 [\text{OH}] [\text{HO}_2] - 2k_8 [\text{OH}]^2 [\text{M}] + \dots \quad (2.24)$$

$$\frac{d[\text{O}]}{dt} = \dots \quad (2.25)$$

$$\frac{d[\text{O}_2]}{dt} = \dots \quad (2.26)$$

► **Figure 2.3:** Mechanism of CH_4 combustion (Warnatz 1996).► **Figure 2.4:** NO_x in combustion processes (Warnatz 1996).

► **How we will proceed:**

- In the remainder of this Chapter, we shall learn how to analytically solve the rate equations for elementary reactions and for simple composite reactions.
- In Chapter 3, we shall then consider different methods for solving coupled non-linear differential equations for complex reaction systems.
 - These methods are well established for stationary reaction systems.
 - However, the modeling of instationary reaction systems (such as ignition processes, explosions and detonations, 3D or 4D models of atmospheric chemistry and climate evolution, . . .) continues to be a tremendously challenging task.

2.2 Kinetics of irreversible first-order reactions



► Solution of the rate equations for A and B:

$$-\frac{d[A]}{dt} = +\frac{d[B]}{dt} = k [A] \quad (2.28)$$

Mass balance:

$$\frac{d[A]}{dt} + \frac{d[B]}{dt} = 0 \quad (2.29)$$

Integration of the rate equation (Eq. 2.28):

$$-\frac{d[A]}{[A]} = k dt \quad (2.30)$$

$$\int d \ln [A] = \int -k dt = -k \int dt \quad (2.31)$$

↷

$$\ln [A] = -k t + C \quad (2.32)$$

Initial value condition at $t = 0$:

$$[A(t=0)] = [A]_0 \quad (2.33)$$

↷

$$C = \ln [A]_0 \quad (2.34)$$

Solution for $[A(t)]$:

$$\ln [A] = -k t + \ln [A]_0 \quad (2.35)$$

↷

$$[A(t)] = [A]_0 e^{-k t} \quad (2.36)$$

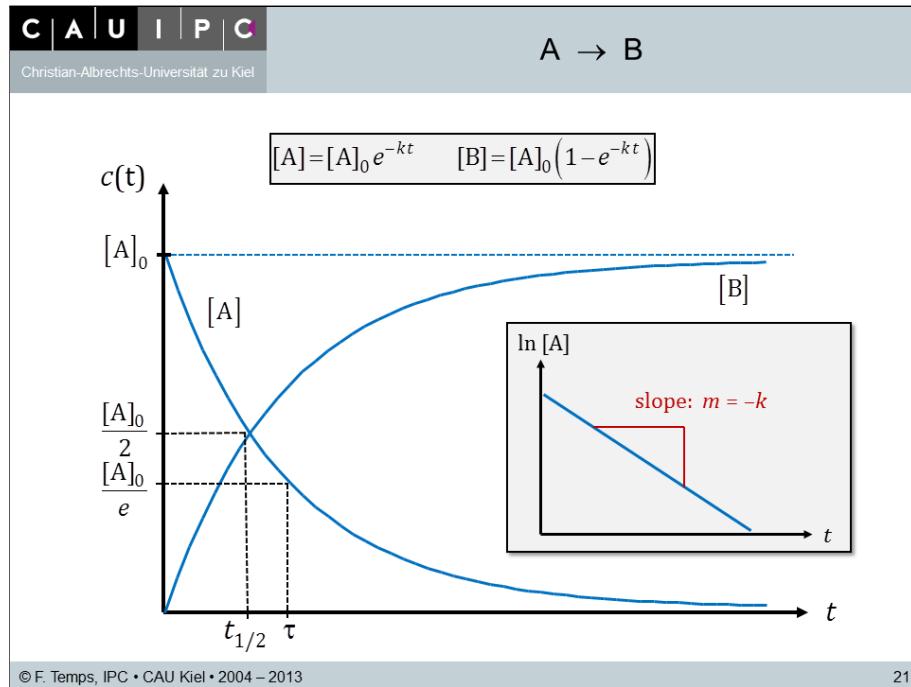
Solution for $[B(t)]$:

$$[B(t)] = [A]_0 - [A(t)] \quad (2.37)$$

↷

$$[B(t)] = [A]_0 (1 - e^{-k t}) \quad (2.38)$$

- **Figure 2.5:** Kinetics of first-order reactions.



- **Time constant:** The rate coefficient k has the dimension of an inverse time. Thus,

$$\tau = \frac{1}{k} \quad (2.39)$$

has dimension of time and is the time after which $[A]$ has dropped to $\frac{1}{e}$ ($= 36.8\%$) of its initial value:

$$[A]_{t=\tau} = [A]_0 e^{-k \tau} = \frac{[A]_0}{e} \approx \frac{[A]_0}{2.718} \quad (2.40)$$

- **Half lifetime:** The half lifetime $t_{1/2}$ is the time after which $[A]$ has dropped to $\frac{1}{2}$ of its initial value (Fig. 2.5):

$$[A(t = t_{1/2})] = [A]_0 e^{-k t_{1/2}} = \frac{[A]_0}{2} \quad (2.41)$$

$$e^{-k t_{1/2}} = \frac{1}{2} \quad (2.42)$$

$$k t_{1/2} = \ln 2 \quad (2.43)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (2.44)$$

► **Conclusion:**

The half lifetime for a first-order reactions is independent of the initial concentration!

► **Experimental determination of k :**

- (1) Plot of $\ln [A]$ vs. t gives a straight line with slope $m = -k$ (see Fig. 2.5):

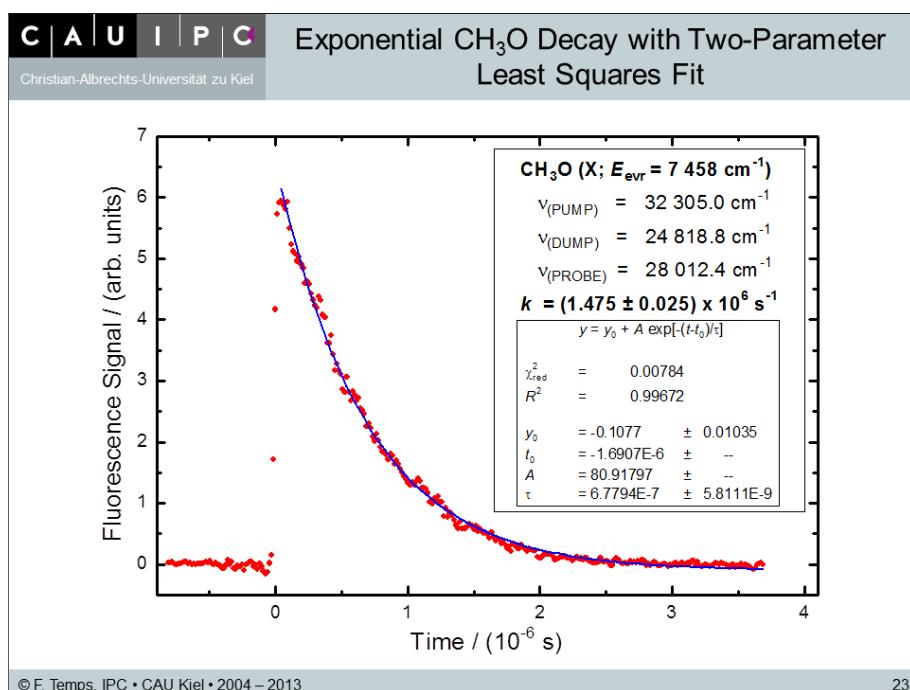
$$\ln ([A] / [A]_0) = -kt \quad (2.45)$$

Advantage: We do not need to know the absolute concentration of $[A]$.

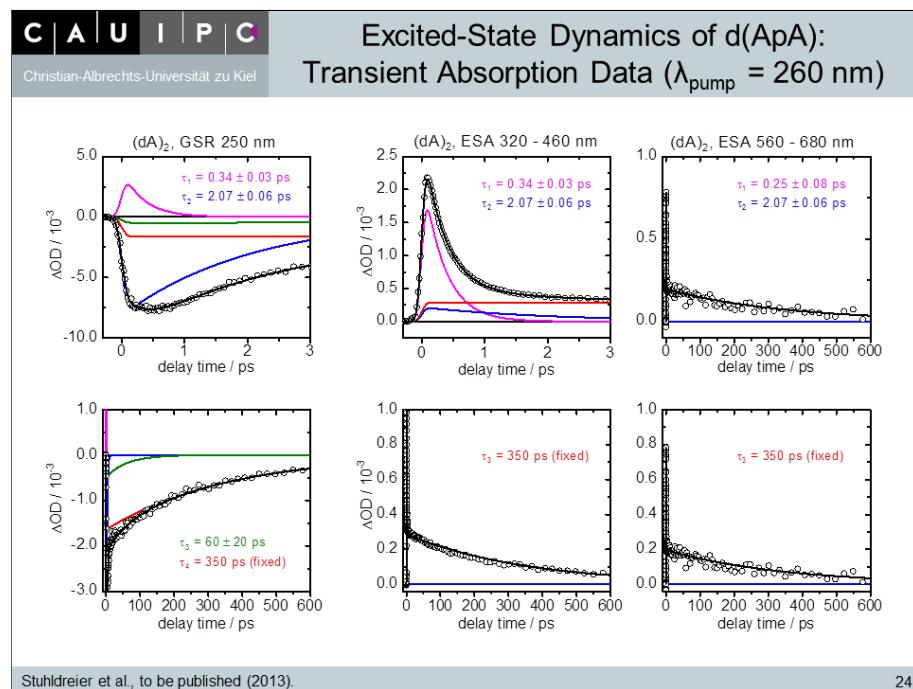
- (2) Numerical fit of k to the exponential decay curve using the Marquardt-Levenberg non-linear least-squares fitting algorithm (Fig. 2.6; see Appendix B for details). This method is useful in particular for analyzing experimental decay curves with a constant background term. Again, we do not need to know the absolute concentration of $[A]$.

Advantages: Can be applied in presence of a constant background signal (noise, weak DC signal). Can also be applied for analyzing data from pump-probe experiments, when the duration of the pump is not short to the decay (deconvolution).

- **Figure 2.6:** Exponential decay curve of a particular vibration-rotation state of the CH_3O radical resulting from its unimolecular dissociation reaction according to $\text{CH}_3\text{O} \rightarrow \text{H} + \text{H}_2\text{CO}$ (Dertinger 1995). The small box is the output box from a fit using the software package ORIGIN.



- **Figure 2.7:** Excited-state relaxation dynamics of the adenine DNA dinucleotide after UV excitation.

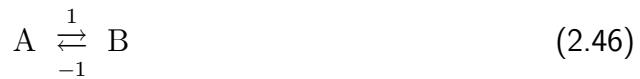


- **Note (and warning):** Anybody who wants to do least-squares fitting is urged to consult appropriate literature before doing the fitting! The book by Bevington¹⁷ is considered required reading for any physical chemistry graduate student.

As the saying goes: With three parameters, you can draw an elephant. With a fourth parameter, you can make him walk.

¹⁷ P. R. Bevington, D. K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, Boston, 1992.

2.3 Kinetics of reversible first-order reactions (relaxation processes)



► **Rate equation:**

$$\frac{d[A]}{dt} = -k_1 [A] + k_{-1} [B] \quad (2.47)$$

► **Equilibrium at $t \rightarrow \infty$:**

$$\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -k_1 [A] + k_{-1} [B] = 0 \quad (2.48)$$

↷

$$\boxed{\frac{[B]_\infty}{[A]_\infty} = \frac{k_1}{k_{-1}} = K_c} \quad (2.49)$$

- The rate constant for the reverse reaction k_{-1} can be calculated from k_1 and K_c .
- Or the equilibrium constant K_c can be determined from measurements of the forward and reverse rate constants. From K_c , we can then determine important thermochemical quantities, for example for reactive free radicals, via

$$K_p = \frac{(p_B/p^\ominus)(p_C/p^\ominus)}{(p_A/p^\ominus)} = \exp \left[-\frac{\Delta_r G^\ominus}{RT} \right] \quad (2.50)$$

• **Important note:**

- In the frequently encountered case that the number of species on the reactant and product side of a reaction differ, one has to be *very* careful with the units of K_c and K_p .

Consider, for example, a gas phase reaction of the type



In this case, K_c has the dimension of mol/cm³:

$$K_c = \frac{k_1}{k_{-1}} = \frac{[B][C]}{[A]} = \frac{\frac{p_B}{RT} \frac{p_C}{RT}}{\frac{p_A}{RT}} = \frac{1}{RT} \frac{p_B p_C}{p_A} = \frac{K'_p}{RT} \quad (2.52)$$

K'_p has the dimension of bar:

$$K'_p = \frac{p_B p_C}{p_A} \quad (2.53)$$

But the thermodynamic equilibrium constant K_p is dimensionless:

$$K_p = \frac{(p_B/p^\ominus)(p_C/p^\ominus)}{(p_A/p^\ominus)} = \frac{K'_p}{p^\ominus} = \exp \left[-\frac{\Delta_r G^\ominus}{RT} \right] \quad (2.54)$$

- General relation between K_p , K'_p , and K_c :

$$K_p = K'_p \times (p^\ominus)^{-\sum_i(\nu_i)} = K_c \times (RT/p^\ominus)^{\sum_i(\nu_i)} \quad (2.55)$$

► **Solution of the rate equations for [A] and [B]:**

Returning to the time dependence of the reaction



we now solve the rate equation

$$\frac{d[A]}{dt} = -k_1 [A] + k_{-1} [B] \quad (2.57)$$

- Mass balance:

$$[B] = [A]_0 - [A] \quad (2.58)$$

- Integration:

$$\frac{d[A]}{dt} = -k_1 [A] + k_{-1} [B] \quad (2.59)$$

$$= -k_1 [A] + k_{-1} ([A]_0 - [A]) \quad (2.60)$$

$$= -(k_1 + k_{-1}) [A] + k_{-1} [A]_0 \quad (2.61)$$

↷

$$\frac{d[A]}{(k_1 + k_{-1}) [A] - k_{-1} [A]_0} = -dt \quad (2.62)$$

- Solution by substitution:

$$x = (k_1 + k_{-1}) [A] - k_{-1} [A]_0 \quad (2.63)$$

$$\frac{dx}{d[A]} = (k_1 + k_{-1}) \quad (2.64)$$

$$d[A] = \frac{dx}{(k_1 + k_{-1})} \quad (2.65)$$

↷

$$\frac{dx}{(k_1 + k_{-1}) x} = -dt \quad (2.66)$$

$$\frac{dx}{x} = -(k_1 + k_{-1}) dt \quad (2.67)$$

↷

$$\ln x = -(k_1 + k_{-1}) t + C \quad (2.68)$$

- Initial value condition at $t = 0$:

$$x = x_0 \quad (2.69)$$

↷

$$C = \ln x_0 \quad (2.70)$$

↷

$$\frac{x}{x_0} = \exp [-(k_1 + k_{-1}) t] \quad (2.71)$$

► **Solution for $[A(t)]$ (Fig. 2.8):**

$$\frac{(k_1 + k_{-1})[A] - k_{-1}[A]_0}{(k_1 + k_{-1})[A]_0 - k_{-1}[A]_0} = \exp[-(k_1 + k_{-1})t] \quad (2.72)$$

or

$$\frac{[A] - \frac{k_{-1}}{k_1 + k_{-1}}[A]_0}{[A]_0 - \frac{k_{-1}}{k_1 + k_{-1}}[A]_0} = \exp[-(k_1 + k_{-1})t] \quad (2.73)$$

This expression is not so easy to memorize, but we may recast it in a simple way:

Using

$$\frac{k_1}{k_{-1}} = \frac{[B]_\infty}{[A]_\infty} = \frac{[A]_0 - [A]_\infty}{[A]_\infty}, \quad (2.74)$$

which gives

$$[A]_\infty = \frac{k_{-1}}{k_1 + k_{-1}} [A]_0, \quad (2.75)$$

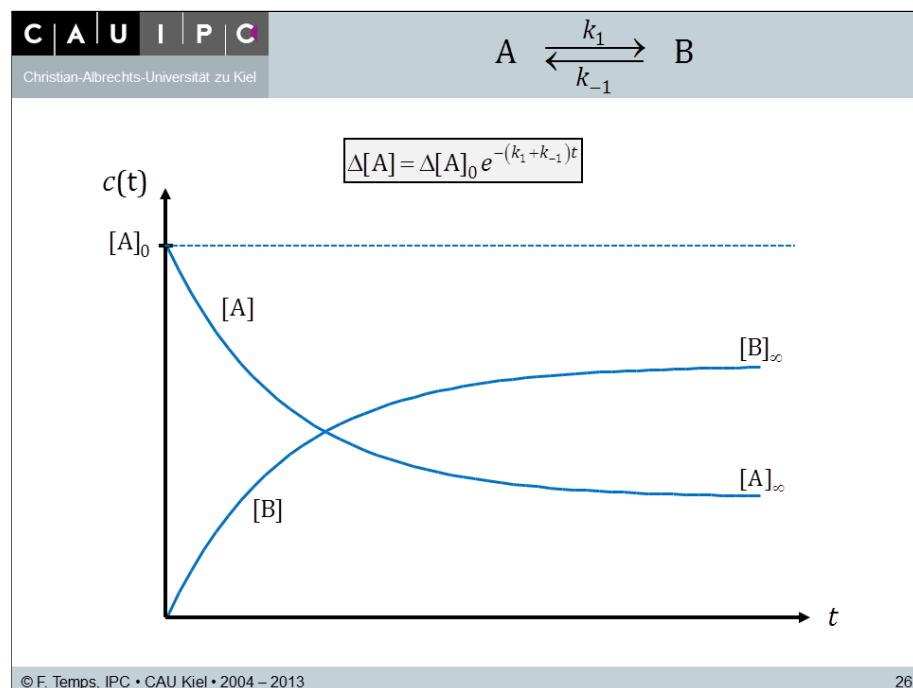
we obtain

$$\boxed{\frac{[A(t)] - [A]_\infty}{[A]_0 - [A]_\infty} = \exp[-(k_1 + k_{-1})t]} \quad (2.76)$$

With $\Delta[A]_t = [A(t)] - [A]_\infty$ and $\Delta[A]_0 = [A]_0 - [A]_\infty$, we write this result in compact form as

$$\boxed{\frac{\Delta[A]_t}{\Delta[A]_0} = \exp[-(k_1 + k_{-1})t]} \quad (2.77)$$

► **Figure 2.8: Kinetics of reversible first-order reactions.**



► **Relaxation processes:**

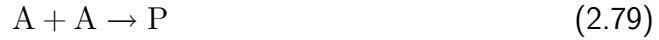
- The transition from a deviation from equilibrium into the equilibrium is called **relaxation**.
- $(k_1 + k_{-1})^{-1}$ has the dimension of time and is called the **relaxation time**,

$$\tau = (k_1 + k_{-1})^{-1} \quad (2.78)$$

- The temporal evolution of relaxation processes from a nonequilibrium to the equilibrium state is determined by the sum of the respective forward and reverse rate constants!

2.4 Kinetics of second-order reactions

2.4.1 $A + A \rightarrow \text{products}$



► **Solution of the rate equation:**

$$-\frac{1}{2} \frac{d[A]}{dt} = k [A]^2 \quad (2.80)$$

Integration:

$$\frac{d[A]}{[A]^2} = -2k dt \quad (2.81)$$

↷

$$-\frac{1}{[A]} = -2kt + C \quad (2.82)$$

Initial value condition at $t = 0$:

$$[A(t=0)] = [A]_0 \quad (2.83)$$

↷

$$C = -\frac{1}{[A]_0} \quad (2.84)$$

Solution for $[A(t)]$ (Fig. 2.15):

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

(2.85)

► **Experimental determination of k :**

(1) Graphical method:

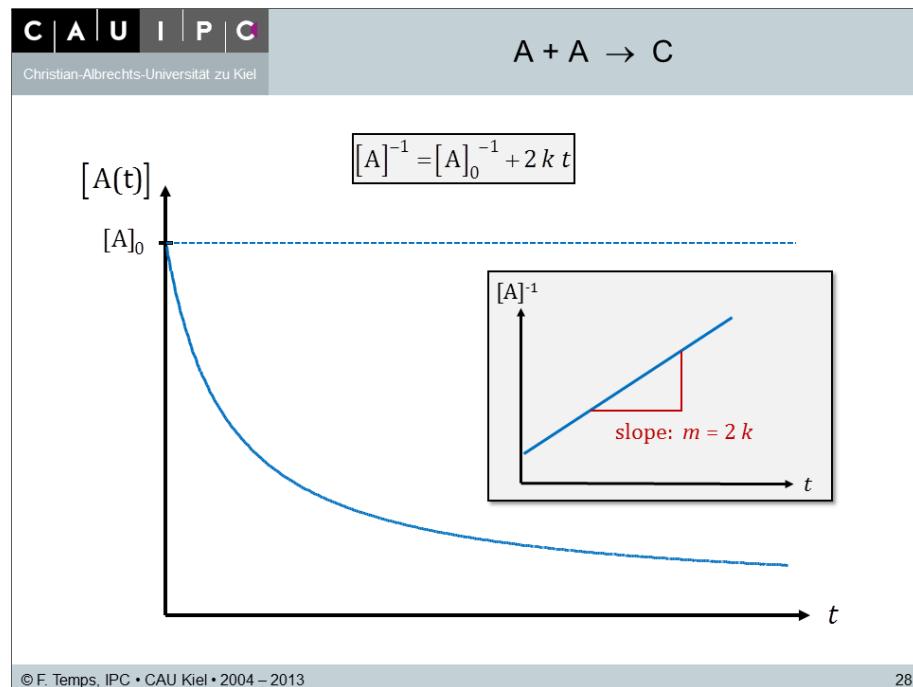
$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt \quad (2.86)$$

⇒ Plot of $[A]^{-1}$ vs. t gives a straight line with slope $m = 2k$ (Fig. 2.9).

⇒ **We do need to know the absolute concentration of $[A]$!**

(2) We can again use a nonlinear least squares fitting method (Appendix B).

- **Figure 2.9:** Kinetics of second-order reactions.



- **Half lifetime:**

$$[A(t_{1/2})] = \frac{[A]_0}{2} \quad (2.87)$$

↷

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + 2k t_{1/2} \quad (2.88)$$

↷

$$t_{1/2} = \frac{1}{2k [A]_0} \quad (2.89)$$

↷

The half lifetime for a second-order reactions depends on the initial concentration!

2.4.2 $A + B \rightarrow$ products



► **Solution of the rate equation:**

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \quad (2.91)$$

(1) Substitution:

$$x = ([A]_0 - [A]_t) = ([B]_0 - [B]_t) \quad (2.92)$$

$$[A] = [A]_0 - x \quad (2.93)$$

↷

$$\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x) \quad (2.94)$$

(2) Integration using partial fractions (skipped here):

...

(3) General solution:

$$\boxed{\frac{[B]_0 [A]_t}{[A]_0 [B]_t} = \exp([A]_0 - [B]_0) k t} \quad (2.95)$$

2.4.3 Pseudo first-order reactions

In experimental studies of second-order reactions of the type $A + B \rightarrow C$, one likes to use a high excess of one of the reactions partners (e.g., $[B] \gg [A]$) so that $[B] \approx \text{const.}$ Under this condition, the reaction is said to be **pseudo first-order**, because

$$k[B] = k' \quad (2.96)$$

↷ Solution of $[A(t)]$:

$$[A] = [A]_0 e^{-k't} = [A]_0 e^{-k[B]t} \quad (2.97)$$

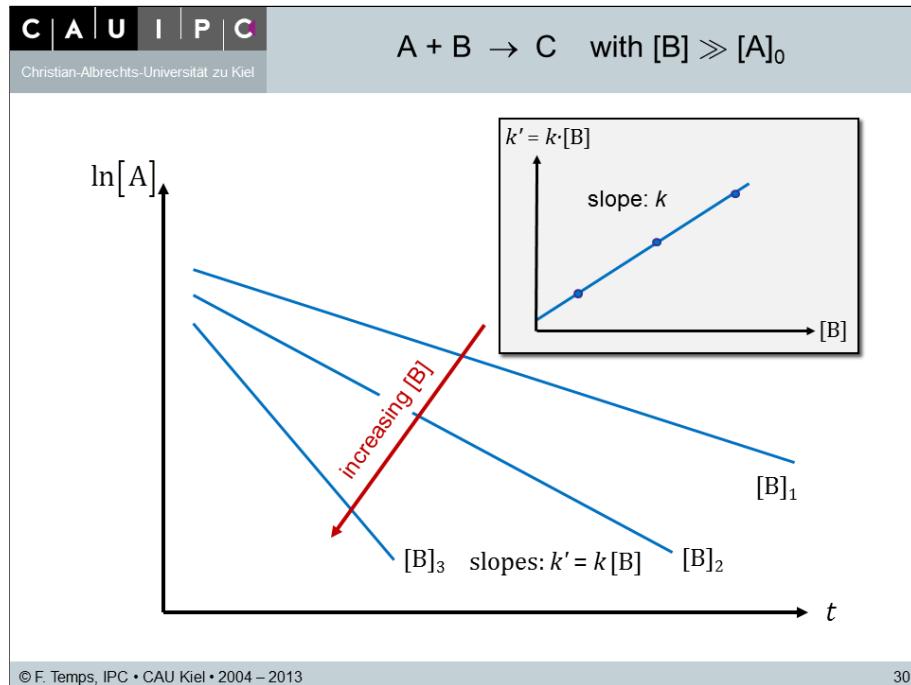
► **Experimental investigation of pseudo first-order reactions:**

(1) Measurements of the pseudo first-order decay of $[A]$ vs. t at different concentrations of $[B]$: Plot of $\ln[A]$ vs. t give pseudo first-order rate constant $k' = k[B]$ for each value of $[B]$.

(2) Plot of $k' = k[B]$ vs. $[B]$ gives straight line with slope k .

⇒ We do not need the absolute concentration of $[A]$, only the concentration of $[B]$ is needed.

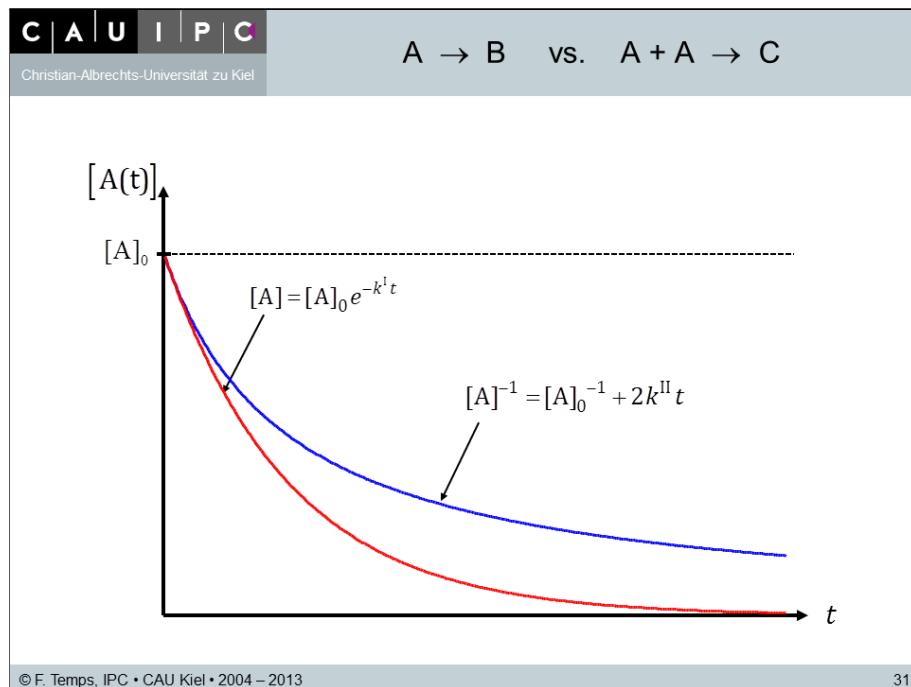
- **Figure 2.10:** Kinetics of pseudo first-order reactions.



2.4.4 Comparison of first-order and second-order reactions

Consider a first-order and a second-order reaction with the same initial concentrations and the same initial rate at $t = 0$. As shown in Fig. 2.11 below, the rate of the second-order reaction rapidly slows down as time increases.

- **Figure 2.11:** Comparison of first-order and second-order reactions.

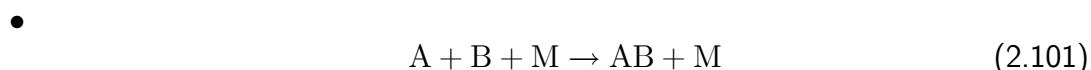
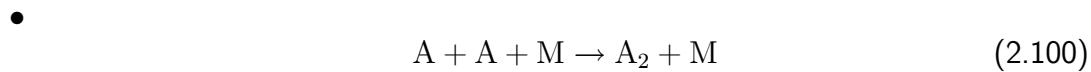


2.5 Kinetics of third-order reactions



$$\text{---} \frac{d [A]}{dt} = k [A] [B] [C] \quad (2.99)$$

- **Pseudo second-order combination reactions:** In combination reactions of two species $A + A \rightarrow A_2$ or $A + B \rightarrow AB$ (for example, the recombination of two free radicals), one of the species (bath gas M) is usually present in large excess ($[M] \gg [A]$, $[B]$), so that the kinetics becomes pseudo second-order, giving the two cases:



M plays the role of an inert collision partner which removes the excess energy from the newly formed A_2 or AB molecules.

2.6 Kinetics of simple composite reactions

2.6.1 Consecutive first-order reactions



► **Coupled differential equations:**

$$\frac{d[A]}{dt} = -k_1 [A] \quad (2.104)$$

$$\frac{d[B]}{dt} = +k_1 [A] - k_2 [B] \quad (2.105)$$

$$\frac{d[C]}{dt} = +k_2 [B] \quad (2.106)$$

In this case, since the DE's are linear, there is an exact solution which we will examine first. We will also look at an approximate solution which can be obtained with the quasi steady-state approximation and at methods to obtain numerical solutions, which we have to use for complex non-linear inhomogeneous DE systems.

► **Mass balance:**

$$[A] + [B] + [C] = [A]_0 \quad (2.107)$$

► **Initial conditions:**

$$[A(t=0)] = [A]_0 \quad (2.108)$$

$$[B(t=0)] = 0 \quad (2.109)$$

$$[C(t=0)] = 0 \quad (2.110)$$

► **Exact solution:**

- First-order decay of [A]:

$$\frac{d[A]}{dt} = -k_1 [A] \quad (2.111)$$

↷

$$[A] = [A]_0 e^{-k_1 t} \quad (2.112)$$

- Inhomogeneous DE for [B]:

$$\frac{d[B]}{dt} = +k_1 [A] - k_2 [B] \quad (2.113)$$

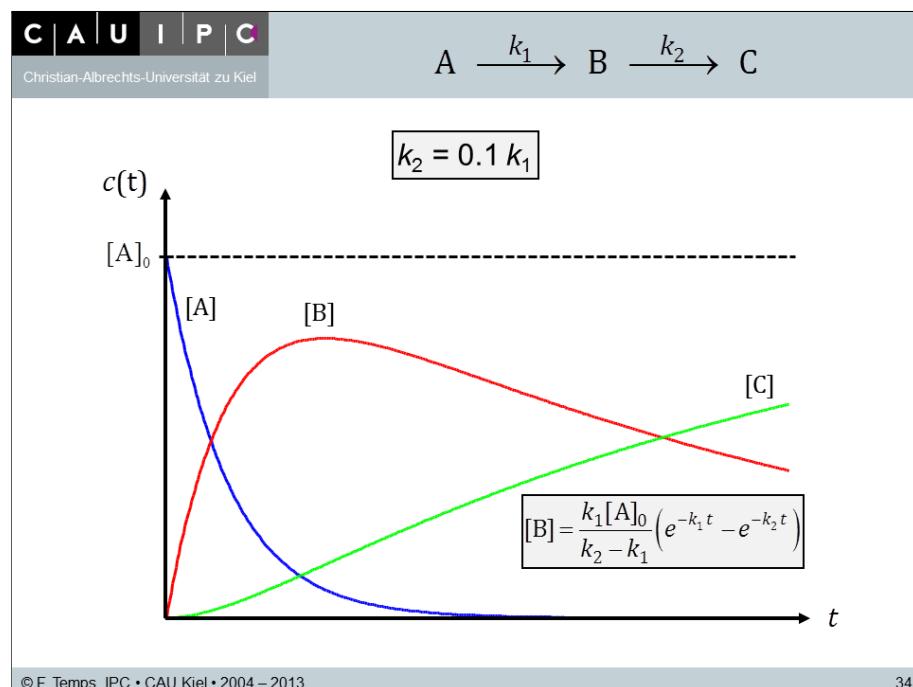
- Solution for $[B(t)]^{18}$:

$$[B(t)] = \begin{cases} \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) & \text{if } k_1 \neq k_2 \\ k_1 [A]_0 t e^{-k_1 t} & \text{if } k_1 = k_2 \end{cases} \quad (2.114)$$

- Reaction products by mass balance:

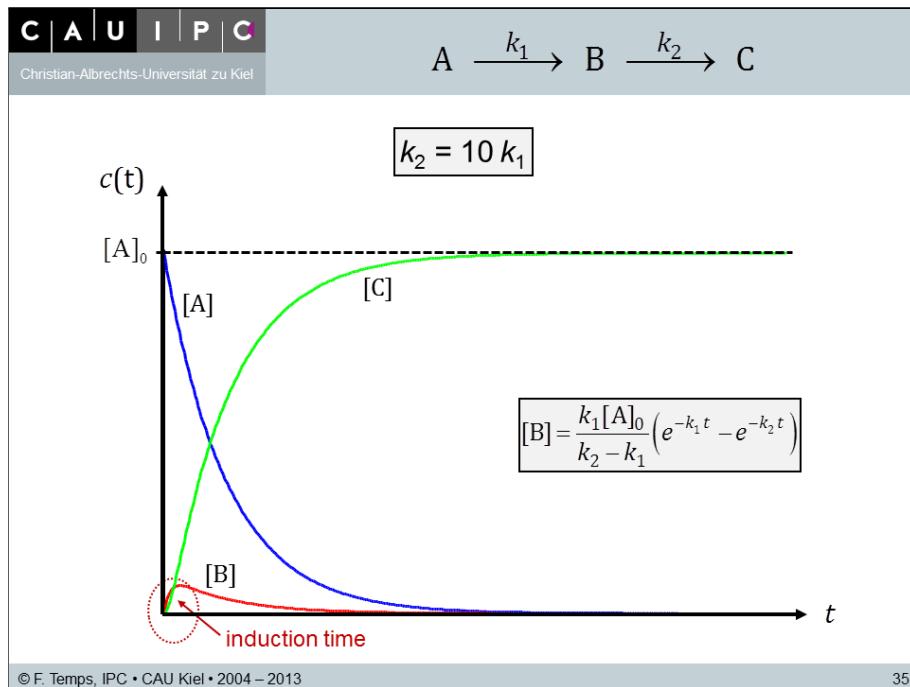
$$[C(t)] = [A]_0 - [A(t)] - [B(t)] = \dots \quad (2.115)$$

- **Figure 2.12:** Kinetics of consecutive first-order reactions (case I).



¹⁸ The solution is detailed in Appendix C.

- **Figure 2.13:** Kinetics of consecutive first-order reactions (case II).



- **Caveat:** As seen, the general solution for $[B]$ is the difference of two exponentials,

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}), \quad (2.116)$$

One exponential describes the rise, the other the fall of $[B]$. It is sometimes implicitly, but *wrongly* assumed that the rise time corresponds to k_1 and the decay time to k_2 . The truth is that we cannot tell just from the shape of the concentration-time profile whether k_1 or k_2 correspond to the rise or to the fall of $[B]$.

- **Quasi steady-state approximation:** Under the condition that

$$k_2 \gg k_1 \quad (2.117)$$

we can find a simple solution for the DE's. Under this condition, after a short initial *induction time* τ (see Fig. 2.13), the change of $[B]$ is very small compared to that of $[A]$. Therefore, we have approximately

$$\frac{d [B]}{d t} \approx 0 \quad (2.118)$$

This important approximation is known as the **(quasi)steady-state approximation**.¹⁹

¹⁹ Deutsch: Quasistationaritätsannahme.

- **Quasi steady-state solution for $[B(t)]$:** For $t > \tau$ we have

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B] \approx 0 \quad (2.119)$$

$$\curvearrowleft k_1 [A] \approx k_2 [B] \quad (2.120)$$

$$\curvearrowleft [B]_{ss} = \frac{k_1}{k_2} [A] = \frac{k_1}{k_2} [A]_0 e^{-k_1 t} \quad (2.121)$$

For $t > \tau$, $[C(t)]$ is therefore given by

$$\frac{d[C]}{dt} = k_2 [B] \approx k_1 [A] \quad (2.122)$$

$$\curvearrowleft [C] = [A]_0 (1 - e^{-k_1 t}) \quad (2.123)$$

2.6.2 Reactions with pre-equilibrium



- **Equilibrium between $[A]$ and $[B]$:**

$$k_1, k_{-1} \gg k_2 \quad (2.126)$$

$$\curvearrowleft \frac{[B]}{[A]} = \frac{k_1}{k_{-1}} = K_{eq} \quad (2.127)$$

$$[B] = K_{eq} [A] \quad (2.128)$$

- **Time dependence of $[C]$:**

$$\frac{d[C]}{dt} = k_2 [B] = k_2 K_{eq} [A] \quad (2.129)$$

2.6.3 Parallel reactions



$$\curvearrowleft \quad \frac{d[A]}{dt} = - (k_1 + k_2 + k_3) [A] \quad (2.133)$$

$$\curvearrowleft \quad [A] = [A]_0 e^{-(k_1+k_2+k_3)t} \quad (2.134)$$

and

$$[B] = \frac{k_1 [A]_0}{(k_1 + k_2 + k_3)} (1 - e^{-(k_1+k_2+k_3)t}) \quad (2.135)$$

$$[C] = \frac{k_2 [A]_0}{(k_1 + k_2 + k_3)} (1 - e^{-(k_1+k_2+k_3)t}) \quad (2.136)$$

$$[D] = \frac{k_3 [A]_0}{(k_1 + k_2 + k_3)} (1 - e^{-(k_1+k_2+k_3)t}) \quad (2.137)$$

Note that the decay of $[A]$ is determined by the total removal rate constant $k_{total} = k_1 + k_2 + k_3$

2.6.4 Simultaneous first- and second-order reactions*



$$\curvearrowleft \quad \frac{d[A]}{dt} = -k_1 [A] - 2k_2 [A]^2 \quad (2.140)$$

$$\curvearrowleft \quad \frac{1}{[A]} = -\frac{2k_2}{k_1} + \left(\frac{2k_2}{k_1} + \frac{1}{[A]_0} \right) \exp(-k_1 t) \quad (2.141)$$

- **Approximation for $k_1 t \ll 1$:** Power series expansion of the exponential gives

$$\frac{1}{[A]} \approx \frac{1}{[A]_0} + \left(\frac{k_1}{[A]_0} + 2k_2 \right) \times t \quad (2.142)$$

2.6.5 Competing second-order reactions*



► **Solution for the case $[A] \gg [B]$:**

(1)

$$\frac{d[A]}{dt} = -2k_1 [A]^2 - k_2 [A] [B] \quad (2.146)$$

$$\approx -2k_1 [A]^2 \quad (2.147)$$

↷

$$\frac{1}{[A]} - \frac{1}{[A]_0} = 2k_1 t \quad (2.148)$$

or

$$[A] = ([A]_0^{-1} + 2k_1 t)^{-1} \quad (2.149)$$

$$= \frac{[A]_0}{1 + 2k_1 [A]_0 t} \quad (2.150)$$

(2)

$$\frac{d[B]}{dt} = -k_2 [A] [B] - k_3 [B] \quad (2.151)$$

This is another inhomogeneous first-order DE, for which the solution can be found as outlined in Appendix C, giving

$$[B] = [B]_0 \times (1 + 2k_1 [A]_0 t)^{-k_2/2k_1} \times \exp(-k_3 t) \quad (2.152)$$

► **Example:**



In the experimental study of reaction 2.154 (Deters 1998), the rate coefficient for the reaction (k_2 according to Eq. 2.152) was fitted to measured OH concentration-time profiles in the presence of high concentrations of CH_3 using the Marquardt-Levenberg nonlinear least squares fitting algorithm (Press 1992). The rate coefficients k_1 and k_3 were determined by independent measurements. The absolute CH_3 concentrations, which are needed for the evaluation of k_2 according to Eq. 2.152, were obtained using a quantitative titration reaction.

2.7 Temperature dependence of rate coefficients

2.7.1 Arrhenius equation

- ▶ **Arrhenius:**²⁰ Svante Arrhenius (Arrhenius 1889) found the following empirical relation describing the temperature dependence of the reaction rate constant:

$$\boxed{\frac{d \ln k}{d(1/T)} = -\frac{E_A}{R}} \quad (2.156)$$

- ▶ **Definition 2.4:** E_A is called the Arrhenius activation energy of the reaction:

$$\boxed{E_A = -R \frac{d \ln k}{d(1/T)}} \quad (2.157)$$

- ▶ **It is very important to keep in mind the following points:**

- Eq. 2.156 is nothing else but a simple and very convenient way to describe the empirical temperature dependence of reaction rate constants!
- Eq. 2.156 says that, within experimental error, a plot of $\ln k$ vs. $1/T$ should give a straight line. We will see later, however, that this is *rarely* exactly true. The study and the understanding of non-Arrhenius behavior is in fact an important topic in modern kinetics.
- E_A as determined by Eqs. 2.156 and 2.157 is therefore a purely empirical quantity!
- We will use Eq. 2.157 simply as the definition and recipe for determining E_A from experimental data and to relate theoretical models to the experimental data!

- ▶ **The rationale behind the Arrhenius equation (2.156):** The rationale for the Arrhenius equation is that molecules need additional energy so that chemical bonds can be broken, atoms can rearrange, and new bonds can be formed (Fig. 2.14).

Van't Hoff's equation:

$$\Delta_R H = RT^2 \frac{d \ln K}{dT} = RT^2 \frac{d \ln \overrightarrow{k} / \overleftarrow{k}}{dT} \quad (2.158)$$

$$= RT^2 \frac{d \ln \overrightarrow{k}}{dT} - RT^2 \frac{d \ln \overleftarrow{k}}{dT} \quad (2.159)$$

$$= \overrightarrow{E}_A - \overleftarrow{E}_A \quad (2.160)$$

Thus we can write

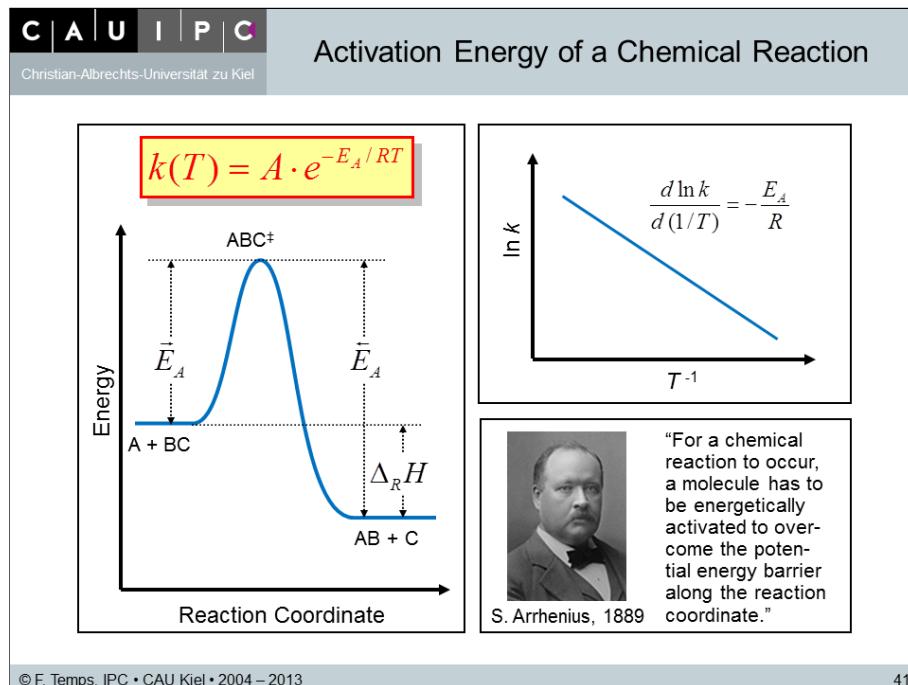
$$\frac{d \ln k}{dT} = \frac{E_A}{RT^2} \quad (2.161)$$

²⁰ Arrhenius is generally regarded as one of the founders of physical chemistry (together with Faraday, van't Hoff, and Ostwald).

or²¹

$$\frac{d \ln k}{d(1/T)} = -\frac{E_A}{R} \quad (2.164)$$

- **Figure 2.14:** Derivation of the Arrhenius equation.



- **Experimental determination of E_A (see Fig. 2.14):** A plot of $\ln k$ vs. $1/T$ gives a straight line with slope $-E_A/R$.
- **Integration of Eq. 2.156:** Assuming that E_A is independent of T , Eq. 2.156 can be integrated:

$$d \ln k = \frac{E_A}{RT^2} dT \quad (2.165)$$

$$\ln k = -\frac{E_A}{RT} + \text{const.} \quad (2.166)$$

$$k(T) = A e^{-E_A/RT} \quad (2.167)$$

Equation 2.167 is used to represent $k(T)$ over a limited T -range using the two parameters E_A and A :

- E_A = Arrhenius activation energy (measure for the energy barrier of the reaction)
- A = pre-exponential factor (frequency factor, collision frequency).

²¹

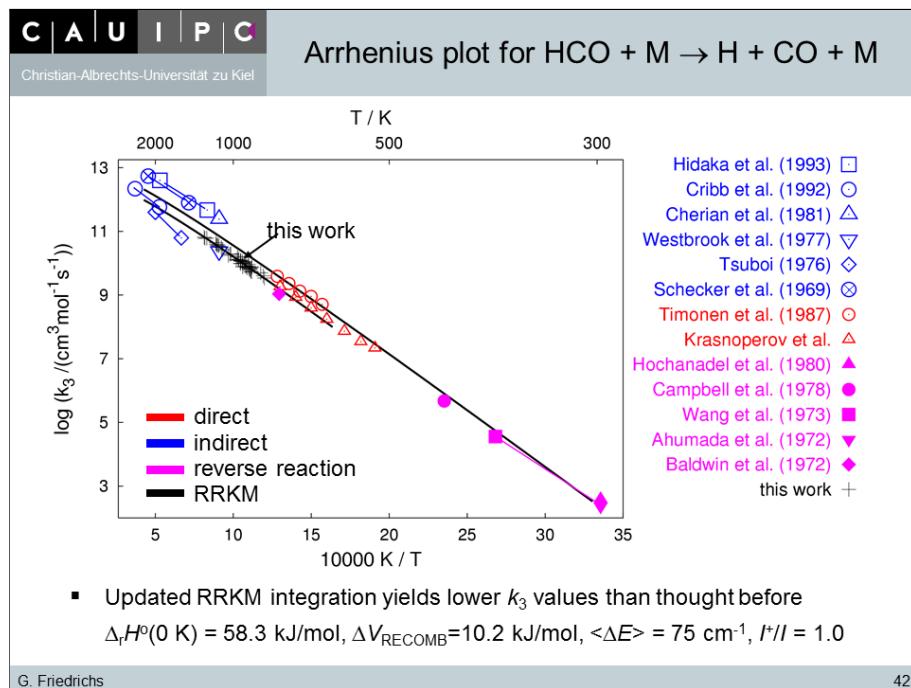
$$\frac{d(1/T)}{dT} = -\frac{1}{T^2} \quad (2.162)$$

$$dT = -T^2 d(1/T) \quad (2.163)$$

- It is important to realize, however, that the value of E_A is not equal to the true height of the potential energy barrier for the reaction!

As said above, E_A is an empirical quantity! Its relation to the true threshold energy E_0 , which is the minimum energy above which reaction may occur, will be a main subject in the theory of bimolecular and unimolecular reactions (Sections 5 – 8). There is also a statistical interpretation of E_A (see Section 8).

- **Figure 2.15:** The reaction $\text{HCO} \rightarrow \text{H} + \text{CO}$ (G. Friedrichs).



2.7.2 Deviations from Arrhenius behavior

In general, A is dependent on temperature, i.e., $A = A(T)$. For gas phase reactions, for example, there is at least the \sqrt{T} dependence of the hard sphere collision frequency. The T -dependence of A is often small compared to E_A so that within experimental error the dependence of $k(T)$ is determined by E_A .

If the T -dependence of A is not small compared to E_A , we will have to use a more general expression for $k(T)$, as explained in the following.

- **Generalized three-parameter expression for $k(T)$:** To account for deviations from Arrhenius because of $A(T)$, one conveniently employs the three parameter expression

$$k(T) = B T^n e^{-E_0/RT} \quad (2.168)$$

with B and E_0 now being T -independent quantities.

Range of n values for specific bimolecular reactions (justified by theory; see later):

$$-1.5 \leq n \leq +3 \quad (2.169)$$

- **Question:** What is the relation of Eq. 2.168 with the Arrhenius equation?
- **Answer:** We have to evaluate the Arrhenius parameters from Eq. 2.168 according to the definitions of E_A and A :

(1) E_A :

$$E_A = +RT^2 \frac{d \ln k}{dT} \quad (2.170)$$

$$= +RT^2 \frac{d}{dT} \left(\ln B + n \ln T - \frac{E_0}{RT} \right) \quad (2.171)$$

↷

$$\boxed{E_A = E_0 + nRT} \quad (2.172)$$

Only in the case that $nRT \ll E_0$ can we neglect the nRT term compared to E_0 !

(2) A : From the expression for E_A , we have

$$E_0 = E_A - nRT \quad (2.173)$$

↷

$$k(T) = B T^n e^{-(E_A - nRT)/RT} \quad (2.174)$$

$$= B T^n e^n e^{-E_A/RT} \quad (2.175)$$

$$= A e^{-E_A/RT} \quad (2.176)$$

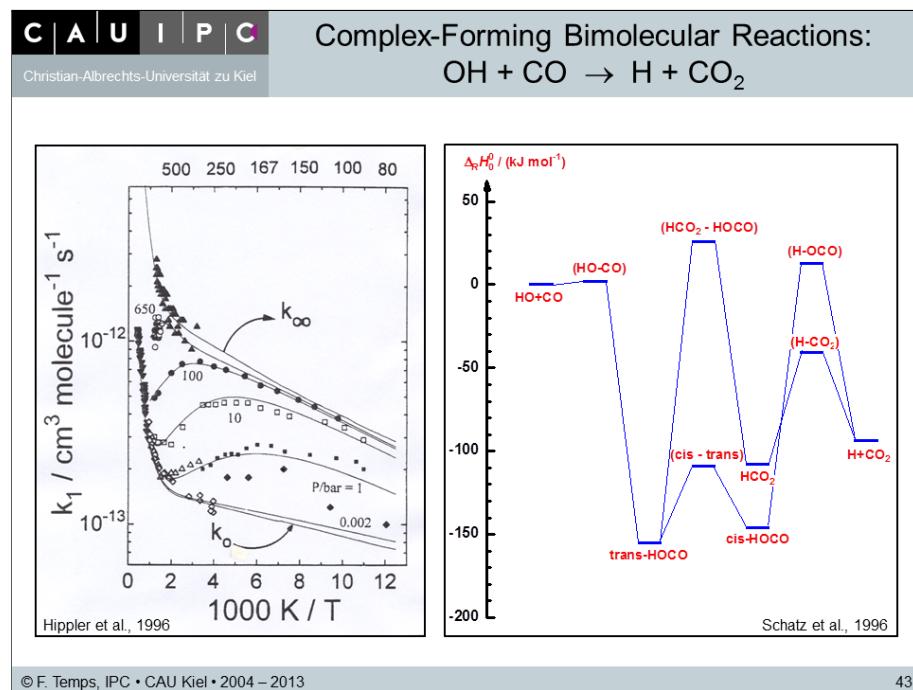
Comparing coefficients, we find

$$\boxed{A = B e^n T^n} \quad (2.177)$$

2.7.3 Examples for non-Arrhenius behavior

Complex forming bimolecular reactions may show extreme non-Arrhenius behavior. An extreme case is the reaction $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$, which incidentally is the single most important reaction in hydrocarbon combustion next to $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$.

► **Figure 2.16:** The reaction $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ (Fulle 1996, Kudla 1992).



Another case is encountered if tunneling plays a role (for example, H^+ transfer reactions at low temperatures). In this case, $k(T)$ tends to a plateau value as $T \rightarrow 0$ (Eisenberger 1991).

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3. Kinetics of complex reaction systems

Real reaction systems are usually much more complicated:

- Net reaction mechanisms may consist of $\approx 100 - 10\,000$ elementary reactions.
- No analytical solutions for the rate laws.
- In favorable cases, one may be able to use certain approximations to simplify the reaction systems, like
 - apply steady-state approximation where possible,
 - take into account reactions in equilibrium,
 - take into account microscopic reversibility (detailed balancing).
- For more accurate descriptions, however, one usually needs **numerical solutions** for the rate equations. Using modern computers, this is not a problem even for $> 10\,000$ reactions, as long as the transport processes are not too complicated (as, for example, 1D reaction systems such premixed flames or 1D models of atmospheric chemistry). However, numerical solutions are still extremely challenging for instationary 3D reaction systems, such as
 - 3D models of atmospheric chemistry including daily/annual variations and couplings to the ocean,
 - ignition processes (internal combustion engines).

3.1 Determination of the order of a reaction

Any reaction mechanism which we may postulate has to explain the observed reaction order. Thus, the determination of the reaction order is a central topic.

We explore some general methods for determining the reaction order by considering an example:

$$r = -\frac{d[A]}{dt} = k [A]^n \quad (3.1)$$

- **First-order and second-order reactions:** Test whether plots of $\ln c$ vs. t or $1/c$ vs. t , give the straight lines expected for first-order or second-order reactions, respectively.
- **Log-log plot of reaction rate vs. concentration:** We see from Eq. 3.1 that a log-log plot of r vs. $[A]$ gives a straight line with slope n :

$\lg r \propto n \lg [A]$

(3.2)

► **Half lifetime method (for $n \neq 1$):**²²

$$-\frac{d[A]}{dt} = k [A]^n \quad (3.3)$$

$$\curvearrowleft \int [A]^{-n} d[A] = \int -k dt \quad (3.4)$$

$$\curvearrowleft -\frac{1}{(n-1)} [A]^{-(n-1)} = -kt + C \quad (3.5)$$

Initial value condition at $t = 0$:

$$[A(t=0)] = [A]_0 \quad (3.6)$$

$$\curvearrowleft C = -\frac{1}{(n-1)} [A]_0^{-(n-1)} \quad (3.7)$$

$$\curvearrowleft \boxed{\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt} \quad (3.8)$$

Half lifetime:

$$[A(t_{1/2})] = \frac{1}{2} [A]_0 \quad (3.9)$$

$$\curvearrowleft \boxed{\frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt_{1/2}} \quad (3.10)$$

$$\curvearrowleft \boxed{t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k} \frac{1}{[A]_0^{n-1}}} \quad (3.11)$$

$$\curvearrowleft \boxed{\lg t_{1/2} \propto -(n-1) \lg [A]_0} \quad (3.12)$$

↷ A log-log plot of $t_{1/2}$ vs. $[A]_0$ gives a straight line with slope $-(n-1)$.

²² We leave aside a usually occurring stoichiometric factor ν here, since we can always define $\nu k = k'$ as rate constant k' .

3.2 Application of the steady-state assumption

The steady state assumption allows us to reduce a large reaction mechanism to a smaller one by eliminating the respective intermediate species.

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

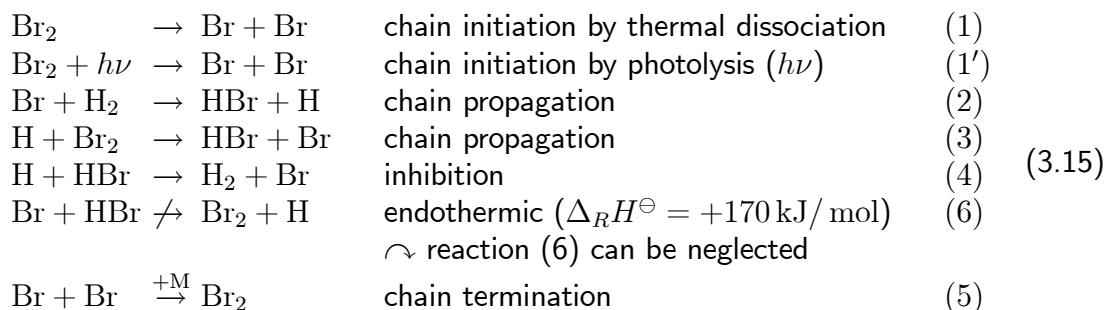
The reaction between H_2 and Br_2 (Bodenstein *et al.*; Christiansen, Polanyi & Herzfeld) runs as a thermal reaction or as a photochemically induced reaction (initiated by light). In the latter case, it is a chain reaction with a quantum yield of

$$\Phi \approx 10^6 \quad (3.13)$$

- **Definition 3.1:** Quantum yield Φ :

$$\Phi = \frac{\text{number of product molecules}}{\text{number of absorbed photons}} \quad (3.14)$$

- **Reaction mechanism (elementary reactions) describing the $\text{H}_2\text{-Br}_2$ system:**



- **Rates equations:** With the steady state approximations (i.e., $d[X]/dt \approx 0$) for $[Br]$ and $[H]$, we obtain²³

$$\frac{d[H]}{dt} = +k_2 [Br] [H_2] - k_3 [H] [Br_2] - k_4 [H] [HBr] \approx 0 \quad (3.16)$$

$$\curvearrowright k_2 [Br] [H_2] - k_4 [H] [HBr] = +k_3 [H] [Br_2] \quad (3.17)$$

$$\curvearrowright [H]_{ss} = \frac{k_2 [Br] [H_2]}{k_3 [Br_2] + k_4 [HBr]} \quad (3.18)$$

$$\frac{d[Br]}{dt} = +2k_1 [Br_2] \underbrace{-k_2 [Br] [H_2] + k_3 [H] [Br_2] + k_4 [H] [HBr]}_{= -\frac{d[H]}{dt} \approx 0} \quad (3.19)$$

$$-2k_5 [Br]^2 \quad (3.20)$$

$$= +2k_1 [Br_2] - 2k_5 [Br]^2 \approx 0 \quad (3.21)$$

$$\curvearrowright [Br]_{ss} = \left(\frac{k_1}{k_5} [Br_2] \right)^{1/2} \quad (3.22)$$

$$\curvearrowright [H]_{ss} = \left(\frac{k_1}{k_5} [Br_2] \right)^{1/2} \times \frac{k_2 [H_2]}{k_3 [Br_2] + k_4 [HBr]} \quad (3.23)$$

$$\frac{d[HBr]}{dt} = k_2 [Br] [H_2] + k_3 [H] [Br_2] - k_4 [H] [HBr] \quad (3.24)$$

Using $k_2 [Br] [H_2] - k_4 [H] [HBr] = +k_3 [H] [Br_2]$ (Eq. 3.17) and substituting $[H]_{ss}$ (Eq. 3.18), the last line simplifies to

$$\frac{d[HBr]}{dt} = 2k_3 [H] [Br_2] \quad (3.25)$$

$$= 2k_3 [Br_2] \times \left(\frac{k_1}{k_5} [Br_2] \right)^{1/2} \times \frac{k_2 [H_2]}{k_3 [Br_2] + k_4 [HBr]} \quad (3.26)$$

$$= \frac{2k_2 (k_1/k_5)^{1/2} [H_2] [Br_2]^{1/2}}{1 + (k_4/k_3) [HBr] / [Br_2]} \quad (3.27)$$

$$= \frac{k' [H_2] [Br_2]^{1/2}}{1 + k'' [HBr] / [Br_2]} \quad (3.28)$$

- **Result:**

$$\boxed{\frac{d[HBr]}{dt} = \frac{k' [H_2] [Br_2]^{1/2}}{1 + k'' [HBr] / [Br_2]}} \quad (3.29)$$

with

$$\boxed{k' = 2k_2 (k_1/k_5)^{1/2} \text{ and } k'' = k_4/k_3} \quad (3.30)$$

- **Conclusion:** We see that HBr acts as an inhibitor of the total reaction.

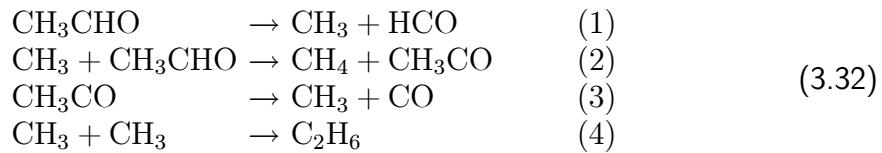
²³ For the photolysis induced reaction, k_1 has to be replaced by $k'_1 I$, where I is the light intensity and k'_1 the corresponding photolysis rate constants (related to the absorption coefficient).

3.2.2 Further examples

- **Exercise 3.1:** The thermal decomposition of acetaldehyde according to the overall reaction



is known to proceed *via* the following elementary steps (Rice-Herzfeld mechanism):



Derive an expression for the production rate of $[\text{CH}_4]$. (Hint: Use the steady-state approximations for $[\text{CH}_3\text{CO}]$ and $[\text{CH}_3]$ and neglect the HCO for the derivation of the expression.) \square

A more complete mechanism takes into account the thermal decomposition of the HCO radicals according to $\text{HCO} \rightarrow \text{H} + \text{CO}$ (5) followed by the reaction $\text{H} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2 + \text{CH}_3\text{CO}$ (6).

- **Solution 3.1:** With the steady state approximations for $[\text{CH}_3\text{CO}]$ and $[\text{CH}_3]$, we obtain

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] - k_3 [\text{CH}_3\text{CO}] \approx 0 \quad (3.33)$$

$$\leadsto [\text{CH}_3\text{CO}]_{ss} = \frac{k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}]}{k_3} \quad (3.34)$$

$$\frac{d[\text{CH}_3]}{dt} = k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] \quad (3.35)$$

$$+ k_3 [\text{CH}_3\text{CO}] - 2k_4 [\text{CH}_3]^2 \quad (3.36)$$

$$= k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] \quad (3.37)$$

$$+ \frac{k_3 k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}]}{k_3} - 2k_4 [\text{CH}_3]^2 \quad (3.38)$$

$$= k_1 [\text{CH}_3\text{CHO}] - 2k_4 [\text{CH}_3]^2 \approx 0 \quad (3.39)$$

$$\leadsto [\text{CH}_3]_{ss} = \left(\frac{k_1 [\text{CH}_3\text{CHO}]}{2k_4} \right)^{1/2} \quad (3.40)$$

and

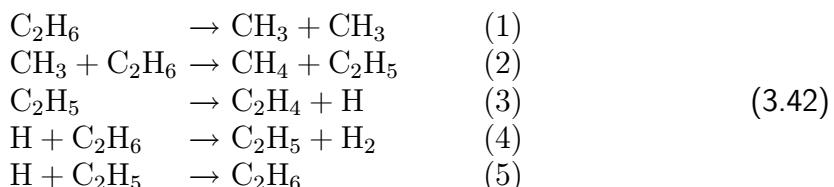
$$\frac{d[\text{CH}_4]}{dt} = k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}]$$

\leadsto

$$\boxed{\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4} \right) [\text{CH}_3\text{CHO}]^{3/2}} \quad (3.41)$$

■

- **Exercise 3.2:** The thermal decomposition of ethane gives mainly $\text{H}_2 + \text{C}_2\text{H}_4$. In addition, small amounts of CH_4 are formed. The decay of the C_2H_6 concentration can be described by the reaction steps



Using the steady-state approximations for the radicals $[\text{CH}_3]$, $[\text{C}_2\text{H}_5]$, and $[\text{H}]$, derive a rate law describing the overall decay of $[\text{C}_2\text{H}_6]$. Note: From the C-H bond dissociation energies in C_2H_6 and C_2H_5 , it is known that $k_3 \gg k_1$. \square

► **Solution 3.2:**

$$-\frac{d[\text{C}_2\text{H}_6]}{dt} = \left[\frac{3}{2}k_1 + \left(\frac{k_1^2}{4} + \frac{k_1 k_3 k_4}{k_5} \right)^{1/2} \right] [\text{C}_2\text{H}_6] \quad (3.43)$$

■

3.3 Microscopic reversibility and detailed balancing

The **principle of microscopic reversibility** is a consequence of the **time reversal symmetry** of classical and quantum mechanics: If all atomic momenta of a molecule that has reached some product state from an initial state are reversed, the molecule will return to its initial state *via* the same path.

A macroscopic manifestation of the principle of microscopic reversibility is **detailed balancing** which states that

- (1) in equilibrium, the forward and reverse rates of a process are equal, i.e., for a reaction $A_1 \xrightleftharpoons[-1]{1} A_2$,

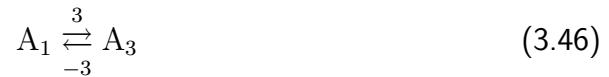
$$k_1 [A_1] = k_{-1} [A_2] \quad (3.44)$$

and

- (2) if molecules A_1 and A_2 are in equilibrium and A_2 and A_3 are in equilibrium, both with respect to each other, there is also equilibrium between A_1 and A_3 :



↷



Thus, we can write

$$\frac{[A_2]_{eq}}{[A_1]_{eq}} = \frac{k_1}{k_{-1}} = K_{12} \quad (3.47)$$

$$\frac{[A_3]_{eq}}{[A_2]_{eq}} = \frac{k_2}{k_{-2}} = K_{23} \quad (3.48)$$

$$\frac{[A_3]_{eq}}{[A_1]_{eq}} = \frac{k_3}{k_{-3}} = K_{13} \quad (3.49)$$

$$= K_{12} K_{23} = \frac{k_1 k_2}{k_{-1} k_{-2}} \quad (3.50)$$

Detailed balancing allows us to simplify complex reaction systems by eliminating $n - 1$ out of a sequence of n reversible reactions that are in equilibrium.

3.4 Generalized first-order kinetics*

3.4.1 Matrix method*

For coupled complex reaction systems with only first-order reactions, the solution of the rate equations can be reduced to an eigenvalue problem (Jost 1974). The solution of the rate equations, i.e., the calculation of the time-dependent concentration profiles, requires finding the eigenvalues and eigenvectors of the rate constant matrix of the system.²⁴

Eigenvalue problems are readily solved in practice using numerical methods (Press 1992).

We consider an example which we solved using conventional methods in Section 2.3.

► **Example:**



The rate equations

$$\frac{d[A_1]}{dt} = -k_1 [A_1] + k_2 [A_2] \quad (3.52)$$

$$\frac{d[A_2]}{dt} = +k_1 [A_1] - k_2 [A_2] \quad (3.53)$$

can be written in a more compact form as a **matrix equation**:

$$\begin{pmatrix} \frac{d[A_1]}{dt} \\ \frac{d[A_2]}{dt} \end{pmatrix} = \begin{pmatrix} -k_1 & +k_2 \\ +k_1 & -k_2 \end{pmatrix} \begin{pmatrix} [A_1] \\ [A_2] \end{pmatrix} \quad (3.54)$$

With the **concentration vector**

$$\mathbf{A} = \begin{pmatrix} [A_1] \\ [A_2] \end{pmatrix} \quad (3.55)$$

and the **rate constant matrix**

$$\mathbf{K} = \begin{pmatrix} -k_1 & +k_2 \\ +k_1 & -k_2 \end{pmatrix} \quad (3.56)$$

this becomes

$$\dot{\mathbf{A}} = \mathbf{K} \cdot \mathbf{A} \quad (3.57)$$

► **Generalized matrix rate equation for coupled first-order reaction systems:**

$$\dot{\mathbf{A}} = \mathbf{K} \cdot \mathbf{A}$$

(3.58)

²⁴ A brief overview on matrices and determinants is given in Appendix D.

- **Ansatz:** The ansatz for solving Eq. 3.58 assumes that we can express \mathbf{A} in terms of another vector \mathbf{B} ,²⁵

$$\mathbf{A} = \mathbf{P} \cdot \mathbf{B} , \quad (3.59)$$

where $\mathbf{P} \cdot \mathbf{B}$ means the dot product, using a rotation matrix \mathbf{P} which is defined so that it diagonalizes \mathbf{K} via the **eigenvalue equation** $\mathbf{K} \cdot \mathbf{P} = \mathbf{P} \cdot \mathbf{\Lambda}$, which by multiplication from the left with \mathbf{P}^{-1} yields

$$\boxed{\mathbf{P}^{-1} \cdot \mathbf{K} \cdot \mathbf{P} = \mathbf{\Lambda}} \quad (3.60)$$

The **eigenvalue matrix** $\mathbf{\Lambda}$ is a diagonal matrix of the form

$$\mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \ddots \end{pmatrix} , \quad (3.61)$$

As defined by Eq. 3.60, its elements on the diagonal $\{\lambda_1, \lambda_2, \dots\}$ are the **eigenvalues of the rate constant matrix**. The matrix \mathbf{P} is called the **eigenvector matrix** associated with \mathbf{K} . The columns of \mathbf{P} are the respective eigenvectors \underline{p}_j associated with the respective eigenvalues λ_j .

- **Solution:** Inserting the ansatz

$$\mathbf{A} = \mathbf{P} \cdot \mathbf{B} \quad (3.62)$$

into our matrix equation²⁶

$$\dot{\mathbf{A}} = \mathbf{K} \cdot \mathbf{A} \quad (3.63)$$

we have

$$\frac{d(\mathbf{P} \cdot \mathbf{B})}{dt} = \mathbf{K} \cdot \mathbf{P} \cdot \mathbf{B} \quad (3.64)$$

or

$$\mathbf{P} \cdot \dot{\mathbf{B}} = \mathbf{K} \cdot \mathbf{P} \cdot \mathbf{B} \quad (3.65)$$

Multiplication of this equation from the left by \mathbf{P}^{-1} gives

$$\mathbf{P}^{-1} \cdot \mathbf{P} \cdot \dot{\mathbf{B}} = \mathbf{P}^{-1} \cdot \mathbf{K} \cdot \mathbf{P} \cdot \mathbf{B} \quad (3.66)$$

or

$$\dot{\mathbf{B}} = \mathbf{\Lambda} \cdot \mathbf{B} \quad (3.67)$$

This DE can be immediately integrated since $\mathbf{\Lambda}$ is diagonal. The solution is

$$\boxed{\mathbf{B} = e^{\mathbf{\Lambda}t} \mathbf{B}_0} \quad (3.68)$$

where $e^{\mathbf{\Lambda}t}$ is a diagonal matrix with elements $\{e^{\lambda_1 t}, e^{\lambda_2 t}, \dots\}$, and $e^{\mathbf{\Lambda}t} \mathbf{B}_0$ means element-wise multiplication. The result gives the time dependence of \mathbf{B} , i.e., $\mathbf{B}(t)$ starting from the initial values \mathbf{B}_0 .

²⁵ The components of \mathbf{B} will be seen to be linear combinations of the components of the concentration vector \mathbf{A} . \mathbf{B} is immediately obtained once we have the matrix of eigenvectors \mathbf{P} (see below).

²⁶ The dot above a concentration vector indicates differentiation by t .

Having $\mathbf{B}(t)$, we can transform back into the original concentration basis by using

$$\mathbf{B} = \mathbf{P}^{-1} \cdot \mathbf{A} \quad (3.69)$$

and

$$\mathbf{B}_0 = \mathbf{P}^{-1} \cdot \mathbf{A}_0 \quad (3.70)$$

Inserting into our solution for \mathbf{B} (Eq. 3.68), we obtain

$$\mathbf{P}^{-1} \cdot \mathbf{A} = e^{\Lambda t} \mathbf{P}^{-1} \cdot \mathbf{A}_0 \quad (3.71)$$

The final step is now a multiplication from the left with \mathbf{P} which yields the solution for Eq. 3.58

$$\boxed{\mathbf{A} = \mathbf{P} \cdot e^{\Lambda t} \mathbf{P}^{-1} \cdot \mathbf{A}_0} \quad (3.72)$$

- ▶ **Note:** This may look complicated to someone who is not used to it. However, once we have set up \mathbf{K} , which is straightforward, everything is done by the computer: The computer computes the
 - eigenvalues of the rate constant matrix \mathbf{K} ,
 - the eigenvector matrix \mathbf{P} of the rate constant matrix \mathbf{K} ,
 - all necessary inverse matrices, etc.,
 - and does all the matrix multiplications.

All you usually have to do is to program the \mathbf{K} matrix.

- ▶ **Application to our example (solution “by hand”):**

- Evaluation of the eigenvalue matrix Λ by solution of the eigenvalue equation

$$\det(\mathbf{K} - \Lambda \cdot \mathbf{I}) = 0 \quad (3.73)$$

with \mathbf{I} as unity matrix:

$$\begin{vmatrix} -k_1 - \lambda & +k_2 \\ +k_1 & -k_2 - \lambda \end{vmatrix} = 0 \quad (3.74)$$

↷

$$(-k_1 - \lambda) \cdot (-k_2 - \lambda) - (k_1 \cdot k_2) = 0 \quad (3.75)$$

$$k_1 k_2 + \lambda k_1 + \lambda k_2 + \lambda^2 - k_1 k_2 = 0 \quad (3.76)$$

$$\lambda (\lambda + (k_1 + k_2)) = 0 \quad (3.77)$$

↷

$$\lambda_1 = 0 \quad (3.78)$$

$$\lambda_2 = -(k_1 + k_2) \quad (3.79)$$

↷

$$\Lambda = \begin{pmatrix} 0 & 0 \\ 0 & -(k_1 + k_2) \end{pmatrix} \quad (3.80)$$

- Conclusions:

- (1) The largest (negative) eigenvalue (λ_2 in this case) determines the shortest time scale and thus the short-time evolution of the reactant concentrations!
- (2) The smallest (negative) eigenvalue (λ_1 in this case) determines the longest time scale of the reaction, i.e., the evolution of the reactant concentrations at long times. The smallest (negative) eigenvalue thus determines the net reaction rate!
- (3) Note that in the example the concentrations at long times are constant (equilibrium!) and therefore $\lambda_1 = 0$.

- Evaluation of the eigenvectors \mathbf{p}_1 und \mathbf{p}_2 by inserting the eigenvalues $\{\lambda_1, \lambda_2, \dots\}$ one by one into

$$\mathbf{K} \cdot \mathbf{P} = \mathbf{\Lambda} \cdot \mathbf{P} \quad (3.81)$$

yields, for each λ_j and the respective \mathbf{p}_j , a linear equation of the type

$$\mathbf{K} \cdot \mathbf{p}_j = \lambda_j \cdot \mathbf{p}_j \quad (3.82)$$

↷

$$(\mathbf{K} - \lambda_j) \cdot \mathbf{p}_j = 0 \quad (3.83)$$

↷

$$(-k_1 - \lambda_j) x_{1,j} + k_2 x_{2,j} = 0 \quad (3.84)$$

$$k_1 x_{1,j} + (-k_2 - \lambda_j) x_{2,j} = 0 \quad (3.85)$$

- Inserting $\lambda_1 = 0$:

$$-k_1 x_1 + k_2 x_2 = 0 \quad (3.86)$$

$$k_1 x_1 + -k_2 x_2 = 0 \quad (3.87)$$

↷

$$k_1 x_1 = k_2 x_2 \quad (3.88)$$

↷

$$x_1 = k_2 \cdot a \quad (3.89)$$

$$x_2 = k_1 \cdot a \quad (3.90)$$

↷

$$\mathbf{p}_1 = \begin{pmatrix} k_2 \cdot a \\ k_1 \cdot a \end{pmatrix} \quad (3.91)$$

- Inserting $\lambda_2 = -(k_1 + k_2)$:

$$(-k_1 + k_1 + k_2) x_1 + k_2 x_2 = 0 \quad (3.92)$$

$$k_1 x_1 + (-k_2 + k_1 + k_2) x_2 = 0 \quad (3.93)$$

↷

$$k_2 x_1 + k_2 x_2 = 0 \quad (3.94)$$

$$k_1 x_1 + k_1 x_2 = 0 \quad (3.95)$$

↷

$$x_1 = -x_2 \quad (3.96)$$

↷

$$x_1 = a \quad (3.97)$$

$$x_2 = -a \quad (3.98)$$

↷

$$\mathbf{p}_2 = \begin{pmatrix} a \\ -a \end{pmatrix} \quad (3.99)$$

- Eigenvector matrix (= rotation matrix \mathbf{P}):

$$\mathbf{P} = \begin{pmatrix} k_2 a & a \\ k_1 a & -a \end{pmatrix} \quad (3.100)$$

- The arbitrary factor a is determined by the initial conditions to be $a = 1$, so that

$$\mathbf{P} = \begin{pmatrix} k_2 & 1 \\ k_1 & -1 \end{pmatrix} \quad (3.101)$$

- Solution for $\mathbf{A}(t)$:

$$\boxed{\mathbf{A} = \mathbf{P} \cdot e^{\Lambda t} \mathbf{P}^{-1} \cdot \mathbf{A}_0} \quad (3.102)$$

► **Solution using symbolic algebra programs:**

- Rate constant matrix \mathbf{K} :

$$\mathbf{K} = \begin{pmatrix} -k_1 & +k_2 \\ +k_1 & -k_2 \end{pmatrix} \quad (3.103)$$

- $\text{eigenvalues}(\mathbf{K}) = \{-k_1 - k_2, 0\}$:

$$\Lambda = \begin{pmatrix} -(k_1 + k_2) & 0 \\ 0 & 0 \end{pmatrix} \quad (3.104)$$

- $\text{eigenvectors}(\mathbf{K}) = \left\{ \begin{pmatrix} -1 \\ 1 \end{pmatrix} \right\} \leftrightarrow -k_1 - k_2, \left\{ \begin{pmatrix} \frac{1}{k_1} k_2 \\ 1 \end{pmatrix} \right\} \leftrightarrow 0 :$

$$\mathbf{P} = \begin{pmatrix} -1 & \frac{k_2}{k_1} \\ +1 & 1 \end{pmatrix} \quad (3.105)$$

- $\text{inverse}(\mathbf{P}) :$

$$\mathbf{P}^{-1} = \begin{pmatrix} -\frac{k_1}{k_1 + k_2} & \frac{k_2}{k_1 + k_2} \\ \frac{k_1}{k_1 + k_2} & \frac{k_1}{k_1 + k_2} \end{pmatrix} \quad (3.106)$$

- $\mathbf{B}_0 = \mathbf{P}^{-1} \mathbf{A}_0$:

$$\mathbf{B}_0 = \mathbf{P}^{-1} \mathbf{A}_0 = \mathbf{P}^{-1} \cdot \begin{pmatrix} A_{1,0} \\ 0 \end{pmatrix} = \begin{pmatrix} -A_{1,0} \frac{k_1}{k_1 + k_2} \\ A_{1,0} \frac{k_1}{k_1 + k_2} \end{pmatrix} \quad (3.107)$$

- Solution for $\mathbf{B}(t)$:

$$\mathbf{B} = e^{\mathbf{\Lambda}t} \mathbf{B}_0 \quad (3.108)$$

$$= \begin{pmatrix} e^{-t(k_1+k_2)} & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -A_{1,0} \frac{k_1}{k_1 + k_2} \\ A_{1,0} \frac{k_1}{k_1 + k_2} \end{pmatrix} \quad (3.109)$$

$$= \begin{pmatrix} -A_{1,0} \frac{k_1}{k_1 + k_2} \times e^{-t(k_1+k_2)} \\ A_{1,0} \frac{k_1}{k_1 + k_2} \times 1 \end{pmatrix} \quad (3.110)$$

- Solution for $\mathbf{A}(t)$:

$$\mathbf{A} = \mathbf{P} \cdot e^{\mathbf{\Lambda}t} \mathbf{P}^{-1} \cdot \mathbf{A}_0 = \mathbf{P} \cdot e^{\mathbf{\Lambda}t} \mathbf{P}^{-1} \cdot \begin{pmatrix} A_{1,0} \\ 0 \end{pmatrix} \quad (3.111)$$

$$= \mathbf{P} \cdot \begin{pmatrix} e^{-t(k_1+k_2)} & 0 \\ 0 & 1 \end{pmatrix} \mathbf{P}^{-1} \cdot \begin{pmatrix} A_{1,0} \\ 0 \end{pmatrix} \quad (3.112)$$

$$= \mathbf{P} \cdot \begin{pmatrix} e^{-t(k_1+k_2)} & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -A_{1,0} \frac{k_1}{k_1 + k_2} \\ A_{1,0} \frac{k_1}{k_1 + k_2} \end{pmatrix} \quad (3.113)$$

$$= \mathbf{P} \cdot \begin{pmatrix} e^{-t(k_1+k_2)} \left(-A_{1,0} \frac{k_1}{k_1 + k_2} \right) \\ 1 \left(A_{1,0} \frac{k_1}{k_1 + k_2} \right) \end{pmatrix} \quad (3.114)$$

$$= \begin{pmatrix} A_{1,0} \frac{k_2}{k_1 + k_2} + A_{1,0} k_1 \frac{e^{-t(k_1+k_2)}}{k_1 + k_2} \\ A_{1,0} \frac{k_1}{k_1 + k_2} - A_{1,0} k_1 \frac{e^{-t(k_1+k_2)}}{k_1 + k_2} \end{pmatrix} \quad (3.115)$$

$$= \begin{pmatrix} A_{1,0} \frac{k_2 + k_1 e^{-t(k_1+k_2)}}{k_1 + k_2} \\ A_{1,0} k_1 \frac{1 - e^{-t(k_1+k_2)}}{k_1 + k_2} \end{pmatrix} \quad (3.116)$$

This result is identical to the result for $[\mathbf{A}(t)]$ obtained in Section 2.3.

3.4.2 Laplace transforms*

The concept of Laplace and inverse Laplace transforms is extremely useful in chemical kinetics because

- (1) Laplace transforms provide a convenient method for solving differential equations,
- (2) Laplace transforms form the connection between microscopic molecular properties and statistically (Boltzmann) averaged quantities.

- **Definition 3.2:** The Laplace transform $\mathcal{L}[f(t)]$ of a function $f(t)$ is defined as the integral

$$F(p) = \mathcal{L}[f(t)] = \int_0^{\infty} f(t) e^{-pt} dt \quad (3.117)$$

where

- t is a real variable,
- $f(t)$ is a real function of the variable t with the property $f(t) = 0$ for $t < 0$,
- p is a complex variable,
- $F(p) = \mathcal{L}[f(t)]$ is a function of the variable p .

- **Definition 3.3:** The inverse Laplace transform $\mathcal{L}^{-1}[F(p)]$ of the function $F(p)$ is defined as the integral

$$f(t) = \mathcal{L}^{-1}[F(p)] = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} F(p) e^{pt} dp \quad (3.118)$$

where

- c is an arbitrary real constant.

- **Relation between $f(t)$ and $F(p)$:** Since $\mathcal{L}^{-1}[F(p)]$ recovers the original function $f(t)$, the pair of functions $f(t)$ and $F(p)$ is said to form a Laplace pair:

$$\mathcal{L}^{-1}[F(p)] = \mathcal{L}^{-1}[\mathcal{L}[f(t)]] = f(t) \quad (3.119)$$

and

$$\mathcal{L}[f(t)] = \mathcal{L}[\mathcal{L}^{-1}[F(p)]] = F(p) \quad (3.120)$$

A list of Laplace and inverse Laplace transforms of some functions can be found in Appendix E (Table E.1).

- **Solution of differential equations using Laplace transforms:** Consider the Laplace transform of the derivative $d f(t)/dt$ of a function $f(t)$:²⁷

$$\mathcal{L}[d f(t)/dt] = \int_0^\infty \frac{d f(t)}{dt} e^{-pt} dt \quad (3.121)$$

$$= f(t) e^{-pt} \Big|_0^\infty - \int_0^\infty f(t) d(e^{-pt}) \quad (3.122)$$

$$= -f(t=0) + p \int_0^\infty f(t) e^{-pt} dt \quad (3.123)$$

$$= -f_0 + p F(p) \quad (3.124)$$

We can solve this equation for $F(p)$ via

$$F(p) = \frac{\mathcal{L}[d f(t)/dt] + f_0}{p} \quad (3.125)$$

and recover the solution $f(t)$ by inverse Laplace transformation,

$$f(t) = \mathcal{L}^{-1} \left[\frac{\mathcal{L}[d f(t)/dt] + f_0}{p} \right] \quad (3.126)$$

- **Example: Application to two consecutive first-order reactions.** As an example, we consider the DE's for two consecutive first-order reactions



We already solved this problem previously (in Section 2.6.1) using conventional methods, and repeat the solution now using the Laplace transform method.

Towards these ends, in this example, we shall denote the concentrations $[A(t)]$ and $[B(t)]$ as $a(t)$ and $b(t)$ and their Laplace transforms as $A(p)$ and $B(p)$. The respective initial concentrations shall be $[A]_0 = a_0$ and $[B]_0 = b_0 = 0$. Thus we have:

- **DE for the concentration $b(t)$:**

$$db/dt = k_1 a_0 e^{-k_1 t} - k_2 b \quad (3.128)$$

- **Laplace transform:** $b(t)$ can be found using Eq. 3.124:

$$\mathcal{L}[db/dt] = -b_0 + p B(p) \quad (3.129)$$

Taking the Laplace transform of the r.h.s. of Eq. 3.128:²⁸

$$\mathcal{L}[db/dt] = \mathcal{L}[k_1 a_0 e^{-k_1 t}] - \mathcal{L}[k_2 b(t)] \quad (3.130)$$

$$= k_1 a_0 \mathcal{L}[e^{-k_1 t}] - k_2 \mathcal{L}[b(t)] = \frac{k_1 a_0}{p + k_1} - k_2 B(p) \quad (3.131)$$

$$= -b_0 + p B(p) \quad (\text{Eq. 3.129}) \quad (3.132)$$

²⁷ We used in line 2: integration by parts; in line 3: the derivative $d(e^{-pt})/dt = -p e^{-pt}$; in line 4: the definition $F(p) = \mathcal{L}[f(t)]$ and the abbreviation $f(t=0) = f_0$.

²⁸ We used $\mathcal{L}[e^{at}] = \frac{1}{p-a}$ from Table E.1 and $\mathcal{L}[b(t)] = B(p)$.

Since we have $b_0 = 0$ from the initial condition, this becomes

$$p B(p) + k_2 B(p) = \frac{k_1 a_0}{p + k_1} \quad (3.133)$$

- **Solution for $B(p)$:**

$$B(p) = k_1 a_0 \frac{1}{p + k_1} \frac{1}{p + k_2} \quad (3.134)$$

- **Inverse Laplace transform:**²⁹

$$b(t) = \mathcal{L}[B(p)] = \frac{k_1 a_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

(3.135)

which is the same as obtained in Section 2.6.1.

²⁹ From Table E.1, we see that $\mathcal{L}^{-1} \left[\frac{1}{(p - a)(p - b)} \right] = \frac{1}{(a - b)} (e^{at} - e^{bt})$.

3.5 Numerical integration

- **Initial value problems:** For complex reaction systems, we have to integrate the coupled nonlinear DE systems numerically using the computer. We start with the known initial values y_i of the concentrations at time t_0 and the associated DE's (\dot{y}_i) and want to compute the values of y_i at time $t > t_0$. In numerics, these problems are known as **initial value problems**. With additional conditions, for example for the spatial distributions of the concentration (fixed values at $(x_0, y_0, z_0, x_1, \dots)$), they become **boundary value problems**.

In solving these problems, we generally have to deal with systems of **stiff nonlinear coupled (ordinary) differential equations** (DE systems are said to be stiff, if the rate constants (more precisely: the eigenvalues) vary by many orders of magnitude; under these conditions, the changes of the dependable variables differ by many orders of magnitude).

Thus we have to solve

- m equations (kinetic equations + transport processes), with
- n variables (concentrations), and the given
- initial values and boundary values.

- **Applications of numerical integration methods:**

- Combustion chemistry:
 - Stationary combustion (for example diffusion flames),
 - Instationary combustion (ignition processes, turbulent combustion) - first successful attempts have been made,
 - Problem: For all but the simplest fuels, we have to deal with hundreds of species and thousands of elementary reactions.
- Atmospheric chemistry:
 - 2D “box” models ($y_i(t, h)$) are straightforward.
 - 4D models are required (time, latitude, longitude, height)!
 - Huge problems, when it comes to
 - * feedback with oceans, etc.?
 - * do we know all reactions?
 - * heterogeneous reactions?
- Physical organic chemistry:
 - Elucidation of reaction mechanisms.
- Macromolecular chemistry (including industrial macromolecular synthesis):
 - Prediction of chain length and other properties of polymers and co-polymers.

► **Survey of methods of numerical integration methods:**

- explicit methods (e.g., Runge-Kutta),
- implicit methods (e.g., Gear),
- extrapolation methods (e.g., Richardson, Bulirsch-Stoer, Deuflhard).

In the following, we consider the basics of the most convenient methods.

3.5.1 Taylor series expansions

The Taylor expansion is the basis for all numerical integration methods. We start from the initial value of $y_i(t_0)$ at some time t_0

$$y_i(t_0) = y_{i,0} \quad (3.136)$$

and want to determine the value $y_i(t_0 + h)$ at time $t_0 + h$. Using the DE for y_i

$$\dot{y}_i(t) = f(t, y_j) \quad (3.137)$$

we expand y_i in a Taylor series around t_0 :

$$y_i(t_0 + h) = y_i(t_0) + h \cdot \dot{y}_i(t_0, y_{j,0}) + \frac{h^2}{2!} \cdot \ddot{y}_i(t_0, y_{j,0}) + \dots \quad (3.138)$$

$$= y_i(t_0) + h \cdot f(t_0, y_{j,0}) + \frac{h^2}{2!} \cdot \dot{f}(t_0, y_{j,0}) + \dots \quad (3.139)$$

Recursion formula:

$$y_{i,n+1} = y_{i,n} + h \cdot f(t_n, y_{j,n}) + \frac{h^2}{2!} \cdot \dot{f}(t_n, y_{j,n}) + \dots \quad (3.140)$$

The first-order term $f(t_n, y_{j,n})$ is given by the rate equation at t_n , the second-order term $\dot{f}(t_n, y_{j,n})$ (which is taken into account for example by the 2nd order Runge-Kutta method) and higher order terms (\Rightarrow higher order Runge-Kutta methods) have to be evaluated numerically by finite differences.

3.5.2 Euler method

The Euler method is based on a 1st order Taylor expansion. If the step size h is small enough, the higher order terms can be neglected:

$$y_i(t_0 + h) = y_i(t_0) + h \cdot \dot{y}_i(t_0) + \mathcal{O}(h^2) \quad (3.141)$$

Initial value problem:

$$\dot{y}_i = f(t, y_j) \quad (3.142)$$

with

$$y_i(t_0) = y_{i,0} \quad (3.143)$$

Result by substituting $\dot{y}_i(t_0) = f(t_0, y_j)$:

$$y_i(t_0 + h) = y_i(t_0) + h f(t_0, y_j) + \mathcal{O}(h^2) \quad (3.144)$$

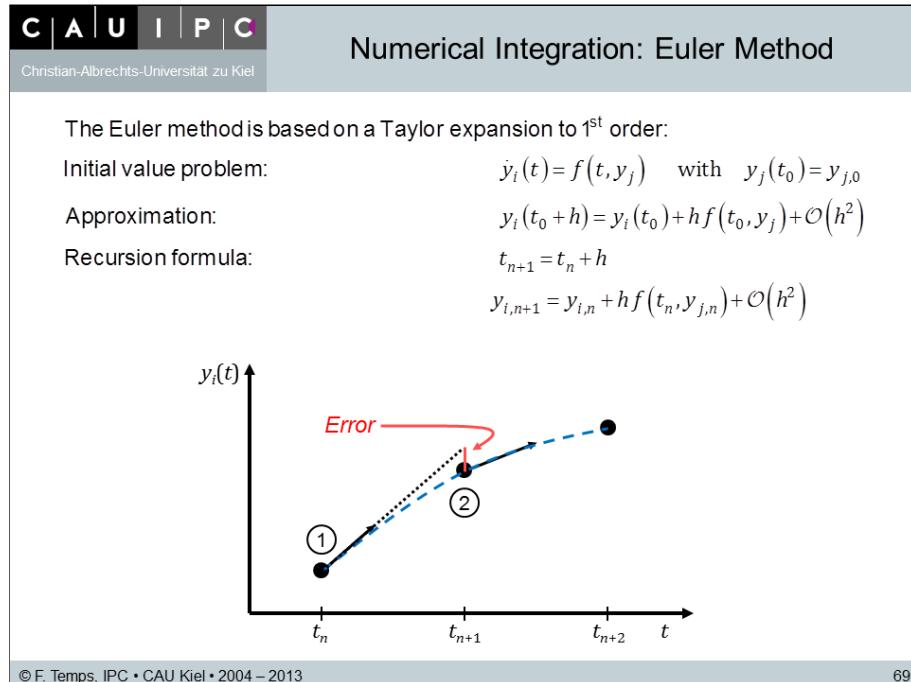
Recursion formula (see Fig. 3.1):

$$t_{n+1} = t_n + h \quad (3.145)$$

$$y_{i,n+1} = y_{i,n} + h f(t_n, y_{j,n}) \quad (3.146)$$

Problem: Large errors for practical step sizes.

- **Figure 3.1:** Euler method.



3.5.3 Runge-Kutta methods

- **2nd order Runge-Kutta method:**

Initial value problem:

$$\dot{y}_i = f(t, y_j) \quad (3.147)$$

with

$$y_i(t_0) = y_{i,0} \quad (3.148)$$

2nd order Runge-Kutta ansatz = Taylor expansion to 2nd order:

$$y_i(t_0 + h) = y_i(t_0) + h\dot{y}_i(t_0) + \frac{h^2}{2!}\ddot{y}_i(t_0) + \mathcal{O}(h^3) \quad (3.149)$$

$$\approx y_i(t_0) + h\dot{y}_i(t_0) + \frac{h^2}{2} \left(\frac{\dot{y}_i(t_0 + h) - \dot{y}_i(t_0)}{h} \right) + \mathcal{O}(h^3) \quad (3.150)$$

$$= y(t_0) + \frac{h}{2} \underbrace{\left(\dot{y}(t_0 + h) + \dot{y}(t_0) \right)}_{=2 \times \text{slope of } y_i(t) \text{ at midpoint}} + \mathcal{O}(h^3) \quad (3.151)$$

Recursion formula:

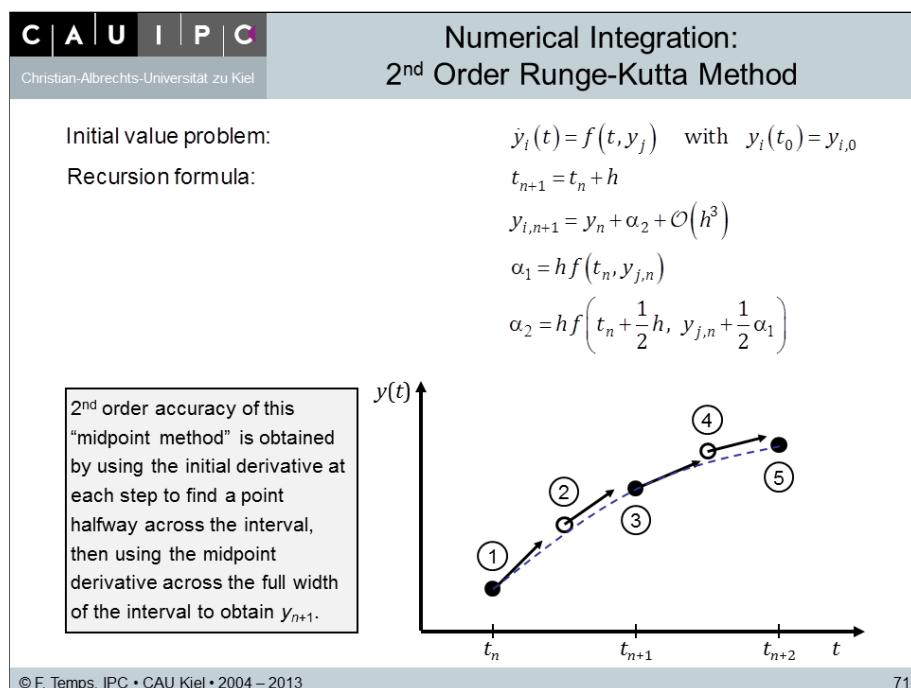
$$t_{n+1} = t_n + h \quad (3.152)$$

$$y_{i,n+1} = y_{i,n} + \alpha_2 + \mathcal{O}(h^3) \quad (3.153)$$

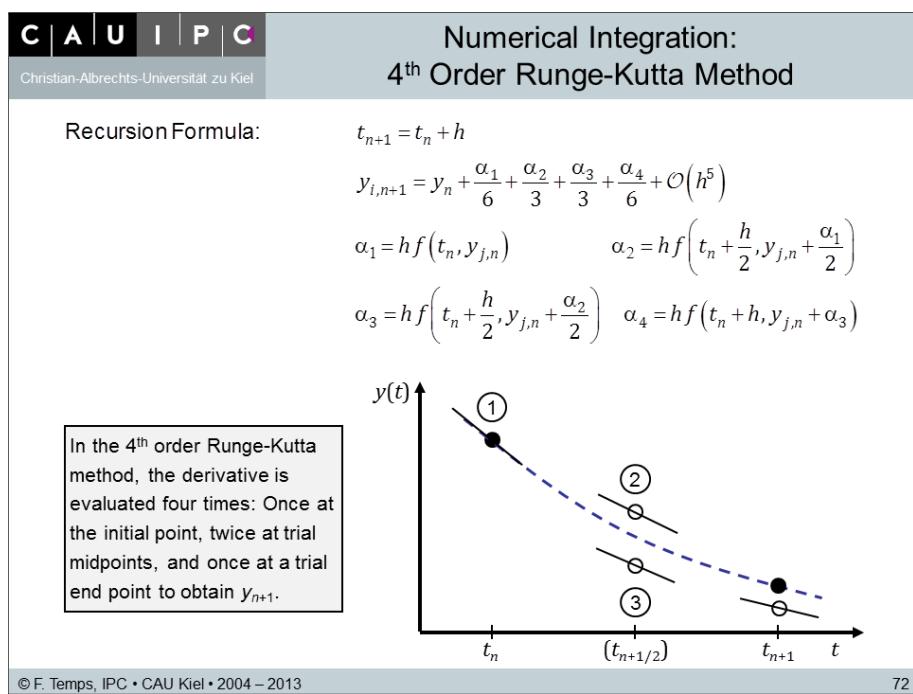
$$\alpha_1 = h f(t_n, y_{j,n}) \quad (3.154)$$

$$\alpha_2 = h f \left(t_n + \frac{h}{2}, y_{j,n} + \frac{\alpha_1}{2} \right) \quad (3.155)$$

► **Figure 3.2:** Illustration of the 2nd order Runge-Kutta method.



- **4th order Runge-Kutta method:** In practice, one frequently uses the 4th order Runge-Kutta method.
- **Figure 3.3:** Illustration of the 4th order Runge-Kutta method.



3.5.4 Implicit methods (Gear):

The Runge-Kutta method becomes unstable for stiff DE systems. In this case, it is preferable to employ *implicit* (also called *iterative* or *backward*) integration methods. The starting point is the implicit form of the Euler method,

$$y_i(t_0 + h) = y_i(t_0) + h \cdot \dot{y}_i(t_0 + h) + \mathcal{O}(h^2) \quad (3.156)$$

For the initial value problem $\dot{y}_i = f(t, y_j)$ with $y_i(t_0) = y_{i,0}$ this leads to the recursion formula:

$$t_{n+1} = t_n + h \quad (3.157)$$

$$y_{i,n+1} = y_{i,n} + h f(t_{n+1}, y_{j,n+1}) \quad (3.158)$$

Using the so-called *predictor-corrector methods*, y_{n+1} is *predicted* in a first step by starting from y_n using one of the *explicit* methods described above. The obtained *trial value* $y_{n+1}^{(0)}$ is then *corrected* by using a backward integration scheme (Gear 1971a, Gear 1971a, Press 1992) to obtain a better estimate $y_{n+1}^{(1)}$. Then, y_n and $y_{n+1}^{(1)}$ are used for a new prediction-correction cycle, giving $y_{n+1}^{(2)}$. The procedure is repeated until the difference between successive iterations falls below some tolerance limit ϵ .

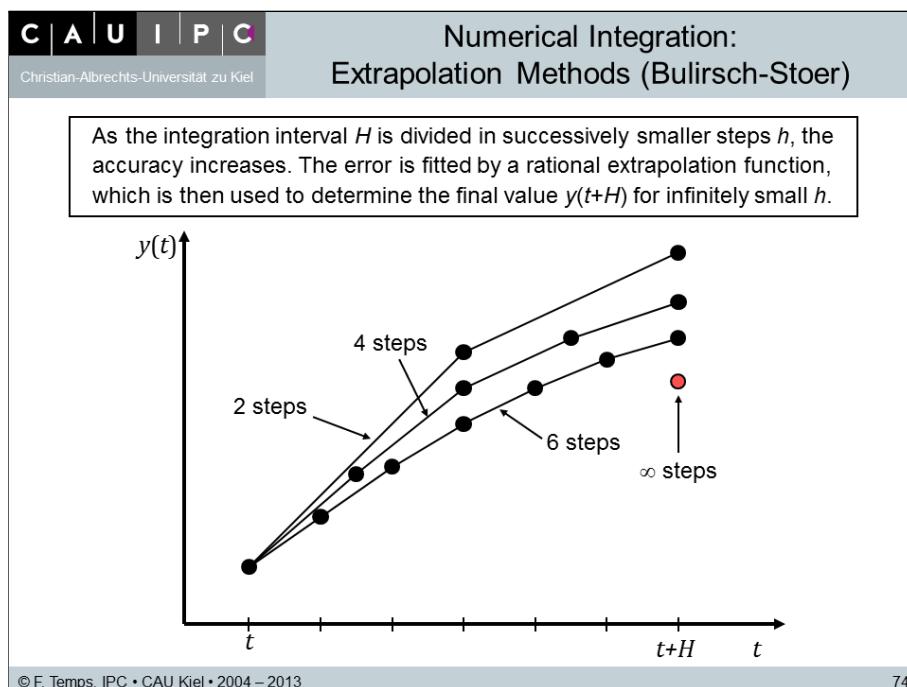
The predictor-corrector method of Gear has been the method of choice for a long time (Gear 1971a, Gear 1971a).

3.5.5 Extrapolation methods (Bulirsch-Stoer)

The idea behind extrapolation methods is that the final answer for y_{n+1} is approximated by an analytical function in the step size h (Richardson extrapolation). The best strategy is to use a rational extrapolating function as the ansatz, and not a polynomial function (Bulirsch-Stoer). This function is determined and fitted to the problem of interest by performing calculations with various values of h . The extrapolating function is then used for extrapolating from y_n to y_{n+1} .

The optimal strategy for stiff DE systems is to follow the Bulirsch-Stoer method (Stoer 1980) in the form implemented by Deuflhard (Bader 1983, Deuflhard 1983, Deuflhard 1985). For Fortran subroutines, see (Press 1992).

► **Figure 3.4:** The principle of extrapolation methods.



3.5.6 Example: Consecutive first-order reactions

As an example, we solve the DE's for two consecutive first-order reactions



- (a) exactly, using symbolic algebra software like MathCad, Maple, Mathematica, or MuPad (the math engine built-in into SWP, the program used to write this script)
- (b) using numeric integration.

► **Exact solution using symbolic algebra software:**

- (1) To set-up the initial value problem for the program,³⁰ we enter the following a 1×6 matrix:

$$\begin{bmatrix} a' = -k_1 a \\ b' = +k_1 a - k_2 b \\ c' = +k_2 b \\ a(0) = a_0 \\ b(0) = 0 \\ c(0) = 0 \end{bmatrix} \quad (3.160)$$

- (2) To obtain the solution, we select the menu item "SolveODE, Exact". The program gives the output:

Exact solution is:

$$\begin{bmatrix} c(t) = \frac{1}{k_1} \left(a_0 k_1 - a_0 k_1 k_2 \frac{e^{-tk_1}}{k_2 - k_1} + a_0 k_1^2 \frac{e^{-tk_2}}{k_2 - k_1} \right) \\ b(t) = a_0 k_1 \frac{e^{-tk_1}}{k_2 - k_1} - a_0 k_1 \frac{e^{-tk_2}}{k_2 - k_1} \\ a(t) = \frac{1}{k_1} \left(a_0 k_1 k_2 \frac{e^{-tk_1}}{k_2 - k_1} - a_0 k_1^2 \frac{e^{-tk_2}}{k_2 - k_1} \right) \end{bmatrix} \quad (3.161)$$

- (3) After simplifying, factorizing, and rewriting the output, we obtain

$$\begin{bmatrix} c(t) = \frac{a_0}{k_2 - k_1} (k_2 - k_1 + k_1 e^{-tk_2} - k_2 e^{-tk_1}) \\ b(t) = a_0 \frac{k_1}{k_1 - k_2} (e^{-tk_2} - e^{-tk_1}) \\ a(t) = a_0 e^{-tk_1} \end{bmatrix} \quad (3.162)$$

We immediately recognize these results from section 2.

- **Numerical solutions:** Numerical integration is performed by the different symbolic algebra programs using one of the methods outlined in the preceding subsection. We have to specify the DE's, the initial values, and the values for the rate constants.³¹

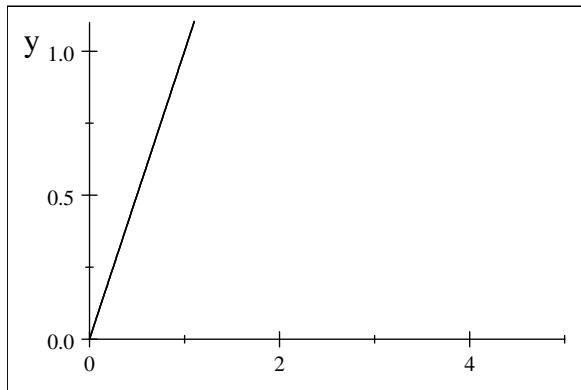
- (1) We adopt the rate constant values $k_1 = 1.00$ and $k_2 = 10.0$.
(2) We define the problem (now using capital letters):

$$\begin{bmatrix} A' = -A \\ B' = +A - 10B \\ C' = +10B \\ A(0) = 1 \\ B(0) = 0 \\ C(0) = 0 \end{bmatrix} \quad (3.163)$$

³⁰ The different software packages differ in the ways in which the problems have to be set up.

³¹ SWP can handle the problem only if the rate constant values are explicitly entered in the DE's. Other software does better.

, Functions defined: A, B, C

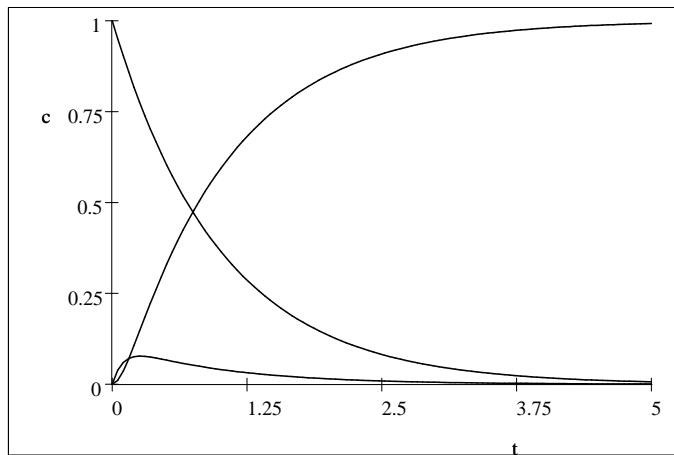


(3) Application of "SolveODE, Numeric" gives the output:

, Functions defined: A, B, C

This means that the program now "knows" these functions.

(4) We can plot A, B , and C using the Plot2D menu point:



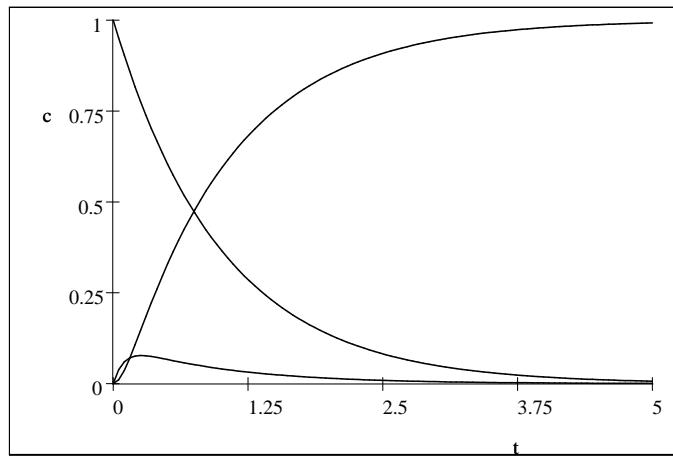
(We add the plots for B and C by dragging both symbols to the plot window)

(5) With $a_0 = 1$, $k_1 = 1$, and $k_2 = 10$, we also plot the exact solutions a, b , and c

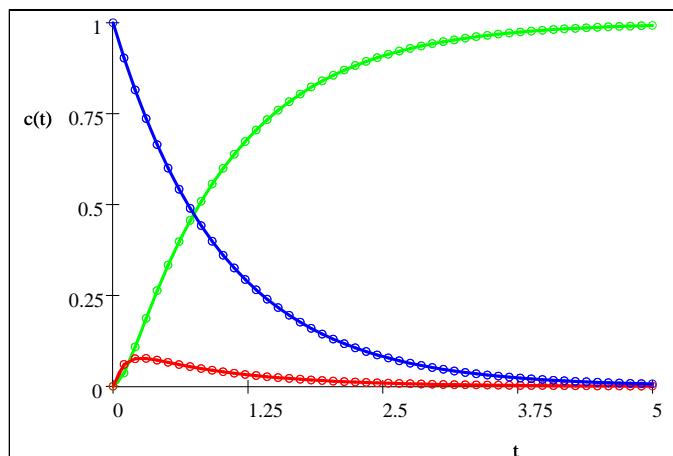
$$c = \frac{a_0}{k_2 - k_1} (k_2 - k_1 + k_1 e^{-tk_2} - k_2 e^{-tk_1}) \quad (3.164)$$

$$b = a_0 \frac{k_1}{k_1 - k_2} (e^{-tk_2} - e^{-tk_1}) \quad (3.165)$$

$$a = a_0 e^{-tk_1} \quad (3.166)$$



- (6) The rest is just some fixing up: We combine the two plots, with an increased number of points plotted, add axis labels and colors:



Numerical solution of the DE system defined by Eq. 3.163. Full lines: numeric solutions. Dotted lines: exact solutions.

The exact and the numerical solutions are identical within numeric precision.

3.6 Oscillating reactions*

The reactant and product concentrations normally approach equilibrium in a smooth (often exponential) fashion. Under special circumstances, however, the concentrations may also show *oscillations* and/or *bistability* as they approach equilibrium. Such behavior can occur only if there is a chemical *feedback* by *autocatalysis*.

3.6.1 Autocatalysis

Example for autocatalysis:



Rate law:

$$-\frac{d[A]}{dt} = k[A][B] \quad (3.168)$$

To solve this DE, we substitute for $[B(t)]$ using the mass balance relation $[A]_0 - [A(t)] = [B(t)] - [B]_0$ and introduce $x = [A(t)]$ as reaction *progress variable*:

$$[B(t)] = [A]_0 + [B]_0 - [A(t)] \quad (3.169)$$

$$= [A]_0 + [B]_0 - x \quad (3.170)$$

This gives the DE

$$-\frac{dx}{dt} = kx([A]_0 + [B]_0 - x) \quad (3.171)$$

↷

$$\int \frac{dx}{([A]_0 + [B]_0)x - x^2} = - \int k dt \quad (3.172)$$

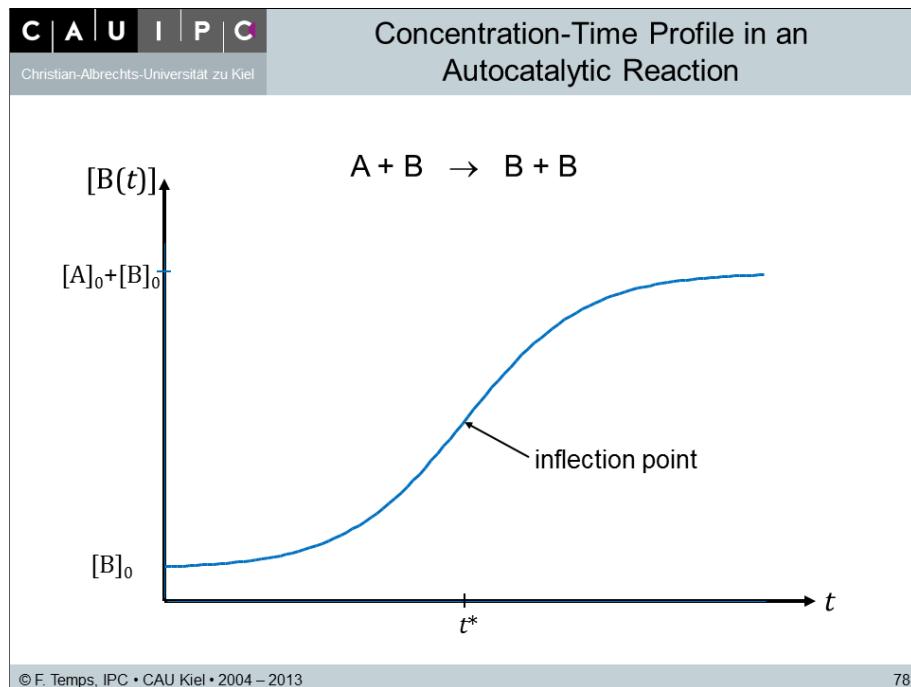
Solution:

$$\frac{1}{[A]_0 + [B]_0} \ln \left(\frac{[A]_0 [B(t)]}{[B]_0 [A(t)]} \right) = -kt \quad (3.173)$$

or

$$[B(t)] = \frac{[A]_0 + [B]_0}{1 + ([A]_0 / [B]_0) \exp[-k([A]_0 + [B]_0)t]} \quad (3.174)$$

► **Figure 3.5:** Autocatalysis.



- As can be seen from the sigmoid (*S*-shaped) concentration-time profile of [B] in Fig. 3.5, the rate of increase of [B] increases up to the inflection point t^* .
- This curve is typical for a population increase from a low plateau to a new (higher) plateau after a favorable change of the environment due to, e.g., the availability of more food, a technical revolution, a reduction of mortality by a medical breakthrough, ...

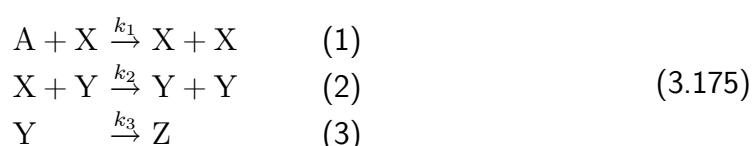
Many interesting games which can be played based on these ideas are described in (Eigen 1975).

3.6.2 Chemical oscillations

The presence of one or more autocatalytic steps in a reaction mechanism can lead to chemical oscillations.

a) The Lotka mechanism

The origin of chemical oscillations can be understood by considering the reaction mechanism proposed by Lotka in 1910 (see Lotka 1920):



- Both reactions (1) and (2) are autocatalytic.
- The Lotka mechanism illustrates the principle, but it does not correspond to an existing chemical reaction system.
- A real oscillating reaction is the Belousov-Zhabotinsky reaction; this reaction may be described using a more complicated mechanism (see below).

In order to model the resulting chemical oscillations, we assume that the reaction takes place in a flow reactor, which is constantly supplied with new A such that the concentration of A stays constant ($[A] = [A]_0$), while the product Z is constantly removed.

► **Rate equations and steady-state solutions:**

$$\frac{d[X]}{dt} = +k_1 [A]_0 [X] - k_2 [X] [Y] \quad (3.176)$$

$$\frac{d[Y]}{dt} = +k_2 [X] [Y] - k_3 [Y] \quad (3.177)$$

Steady-state solutions:

$$\frac{d[X]}{dt} = +k_1 [A]_0 [X] - k_2 [X] [Y] = 0 \quad (3.178)$$

$$\frac{d[Y]}{dt} = +k_2 [X] [Y] - k_3 [Y] = 0 \quad (3.179)$$

Dividing these equations by $[X]$ and $[Y]$, respectively, we find

$$k_2 [Y]_{ss} = k_1 [A]_0 \quad (3.180)$$

$$k_2 [X]_{ss} = k_3 \quad (3.181)$$

Since $[A] = [A]_0$, the steady state solutions for $[X]$ and $[Y]$ are independent of time!

► **Displacements from steady-state solutions:** What happens if the concentrations are displaced from the steady-state values by small amounts x and y ?

(1) **Ansatz:**

$$[X] = [X]_{ss} + x \quad (3.182)$$

$$[Y] = [Y]_{ss} + y \quad (3.183)$$

(2) Rate equations:

$$\frac{dx}{dt} = +k_1 [A]_0 ([X]_{ss} + x) - k_2 ([X]_{ss} + x) ([Y]_{ss} + y) \quad (3.184)$$

$$= +k_1 [A]_0 [X]_{ss} + k_1 [A]_0 x - \underbrace{k_2 [X]_{ss} [Y]_{ss}}_{=k_1 [A]_0 [X]_{ss}}$$

$$-k_2 [X]_{ss} y - \underbrace{k_2 [Y]_{ss} x}_{=k_1 [A]_0 x} - k_2 x y$$

$$= -k_2 [X]_{ss} y - k_2 x y \quad (3.185)$$

$$\frac{dy}{dt} = +k_2 ([X]_{ss} + x) ([Y]_{ss} + y) - k_3 ([Y]_{ss} + y) \quad (3.186)$$

$$= k_2 [X]_{ss} [Y]_{ss} + k_2 [X]_{ss} y + k_2 [Y]_{ss} x \\ + k_2 x y - \underbrace{k_3 [Y]_{ss}}_{=k_2 [X]_{ss}} - \underbrace{k_3 y}_{=k_2 [X]_{ss}}$$

$$= +k_2 [Y]_{ss} x + k_2 x y \quad (3.187)$$

(3) **Simplified DE's for small displacements:** We may neglect the terms containing xy . Thus, we obtain two coupled first-order DE's

$$\frac{dx}{dt} = -k_2 [X]_{ss} y \quad (3.188)$$

$$\frac{dy}{dt} = +k_2 [Y]_{ss} x \quad (3.189)$$

which can be converted to a single second-order DE by the ansatz

$$\dot{x} = -a y \quad (3.190)$$

$$\dot{y} = +b x \quad (3.191)$$

Second-order DE:

$$\ddot{x} = -a \dot{y} = -a b x \quad (3.192)$$

Formal solution of this second-order DE:

$$x(t) = [X(t)] - [X]_{ss} = c_1 e^{\lambda t} + c_2 e^{-\lambda t} \quad (3.193)$$

(4) **Eigenvalues:** To determine the eigenvalue belonging to the linear DE's, we have to solve the determinant

$$\begin{vmatrix} 0 - \lambda & -a \\ +b & 0 - \lambda \end{vmatrix} = \begin{vmatrix} \lambda & -k_2 [X]_{ss} \\ k_2 [Y]_{ss} & \lambda \end{vmatrix} = 0 \quad (3.194)$$

↷

$$\lambda^2 + k_2 [X]_{ss} [Y]_{ss} = 0 \quad (3.195)$$

↷ The solutions for λ are purely imaginary:

$$\lambda_{1,2} = \pm i (k_2^2 [X]_{ss} [Y]_{ss})^{1/2} \quad (3.196)$$

$$= \pm i (k_1 k_3 [A]_0)^{1/2} \quad (3.197)$$

(5) **Solution for $x(t)$:**

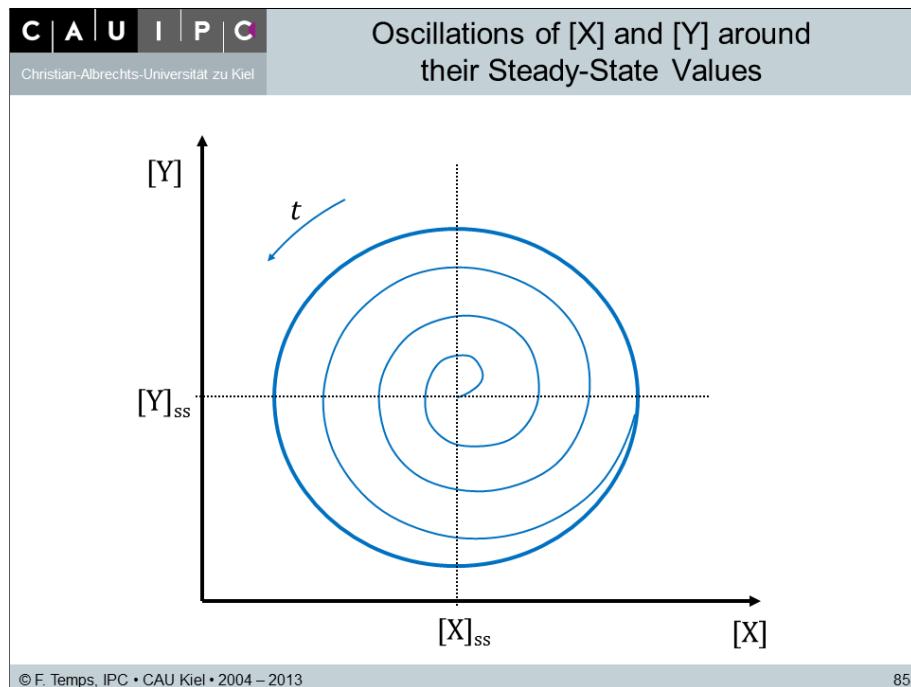
$$x(t) = c_1 e^{i\omega t} + c_2 e^{-i\omega t} = x_0 \cos \omega t \quad (3.198)$$

with

$$\omega = (k_1 k_3 [A]_0)^{1/2} \quad (3.199)$$

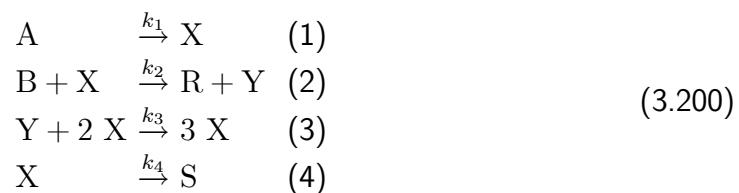
This means that if the system is displaced from its steady-state, the species concentrations will start to oscillate and the displacements may even grow in magnitude until the amplitude reaches the limiting value x_0 (see limit cycle diagram in Fig. 3.6).

- **Figure 3.6:** Limit cycle diagram for chemical oscillations according to the Lotka mechanism.



b) The Brusselator³²

Reaction scheme:



³² The name 'Brusselator' stems from the workplace of its inventor Prigogine (Brussels). The model does not correspond to a real chemical system.

Here, A and B are reactants, R and S are final products, and X and Y are intermediates. The autocatalytic reaction is reaction (3).

Rate equations (using “dimensionless time” $\tau = k_4 t$) and steady-state concentrations:

$$\frac{d[X]}{d\tau} = \dot{[X]} = \frac{k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X]}{k_4} \quad (3.201)$$

$$\frac{d[Y]}{d\tau} = \dot{[Y]} = \frac{k_2[B][X] - k_3[X]^2[Y]}{k_4} \quad (3.202)$$

Steady-state concentrations:

$$[X]_{ss} = \frac{k_1[A]}{k_4} \quad (3.203)$$

$$[Y]_{ss} = \frac{k_2 k_4 [B]}{k_1 k_3 [A]} \quad (3.204)$$

We now investigate the effect of small displacements from steady-state by $\delta[X]$ and $\delta[Y]$. The reaction rates respond to these displacements according to

$$\left(\frac{\partial \dot{[X]}}{\partial [X]} \right)_{ss} \delta[X] \quad \text{and} \quad \left(\frac{\partial \dot{[Y]}}{\partial [Y]} \right)_{ss} \delta[Y] \quad (3.205)$$

↷

- The steady-state is stable if

$$\left(\frac{\partial \dot{[X]}}{\partial [X]} \right)_{ss} + \left(\frac{\partial \dot{[Y]}}{\partial [Y]} \right)_{ss} < 0 \quad (3.206)$$

- The steady-state is unstable if

$$\left(\frac{\partial \dot{[X]}}{\partial [X]} \right)_{ss} + \left(\frac{\partial \dot{[Y]}}{\partial [Y]} \right)_{ss} \geq 0 \quad (3.207)$$

- Stability criterion:

$$\left(\frac{\partial \dot{[X]}}{\partial [X]} \right)_{ss} + \left(\frac{\partial \dot{[Y]}}{\partial [Y]} \right)_{ss} = \frac{k_2[B]}{k_4} - \frac{k_1^2 k_3 [A]^2}{k_4^2} - 1 \quad (3.208)$$

c) Belousov-Zhabotinsky reaction

Oxidation of malonic acid to CO_2 by bromate, catalyzed by cerium ions in acidic solution:



The reaction is probed by addition of the redox indicator ferroin/ferriin: The color varies between *red* and *blue* depending on the concentrations of Ce^{4+} and Ce^{3+} .

► **Figure 3.7:** Mechanism of the Belousov-Zhabotinsky reaction.

Belousov-Zhabotinsky Reaction	
C A U I P C	Christian-Albrechts-Universität zu Kiel
1.	$2 \text{H}^+ + \text{BrO}_3^- + \text{Br}^- \rightarrow \text{HBrO}_2 + \text{HOBr}$
2.	$\text{H}^+ + \text{HBrO}_2 + \text{Br}^- \rightarrow 2 \text{HOBr}$
3.	$\text{Br}^- + \text{HOBr} + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$
4.	$\text{Br}_2 + \text{CH}_2(\text{COOH})_2 \rightarrow \text{BrCH}(\text{COOH})_2 + \text{H}^+ + \text{Br}^-$
5.	$\text{H}^+ + \text{BrO}_3^- + \text{HBrO}_2 \rightarrow 2 \text{BrO}_2 + \text{H}_2\text{O}$
6.	$\text{H}^+ + \text{BrO}_2 + \text{Ce}^{3+} \rightarrow \text{HBrO}_2 + \text{Ce}^{4+}$
7.	$2 \text{HBrO}_2 \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+$
8.	$\text{BrCH}(\text{COOH})_2 + 4\text{Ce}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{Br}^- + \text{HCOOH} + 2\text{CO}_2 + 4\text{Ce}^{3+} + 6\text{H}^+$
9.	$\text{HOBr} + \text{HCOOH} \rightarrow \text{Br}^- + \text{CO}_2 + \text{H}^+ + \text{H}_2\text{O}$

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► **Figure 3.8:** Phases I - III of the Belousov-Zhabotinsky reaction.

Belousov-Zhabotinsky Reaction: Phases I - III	
C A U I P C	Christian-Albrechts-Universität zu Kiel
(I)	BrO_3^- oxidizes malonic acid to brominated malonic acid with consumption of Br^- ions: $\text{BrO}_3^- + 2\text{Br}^- + 3\text{CH}_2(\text{COOH})_2 + 3\text{H}^+ \rightarrow 3\text{BrCH}(\text{COOH})_2 + 3\text{H}_2\text{O}$
(II)	Br^- has been consumed, but the oxidation of malonic acid continues. At the same time, Ce^{3+} is oxidized to Ce^{4+} : $\text{BrO}_3^- + 4\text{Ce}^{3+} + \text{CH}_2(\text{COOH})_2 + 5\text{H}^+ \rightarrow \text{BrCH}(\text{COOH})_2 + 4\text{Ce}^{4+} + 3\text{H}_2\text{O}$
(III)	The brominated malonic acid is further oxidized by Ce^{4+} , which regenerates the Br^- ions: $4\text{Ce}^{4+} + \text{BrCH}(\text{COOH})_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ce}^{3+} + \text{Br}^- + 2\text{CO}_2 + \text{HCOOH} + 5\text{H}^+$

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► **Figure 3.9:** Key steps of the Belousov-Zhabotinsky reaction.

C | A | U | I | P | C
Christian-Albrechts-Universität zu Kiel

**Belousov-Zhabotinsky Reaction:
The Autocatalysis Step**

1.	$\text{BrO}_3^- + \text{Br}^- + 2 \text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{HOBr}$	
2.	$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2 \text{BrO}_2 + \text{H}_2\text{O}$	
3.	$\text{Ce}^{3+} + \text{BrO}_2 + \text{H}^+ \text{ (blue)} \rightarrow \text{Ce}^{4+} + \text{HBrO}_2 \text{ (red)}$	
<hr/>		
Σ	$2 \text{Ce}^{3+} + \text{BrO}_3^- + \text{HBrO}_2 + 3 \text{H}^+ \rightarrow 2 \text{Ce}^{4+} + 2 \text{HBrO}_2 + \text{H}_2\text{O}$	(R2) + 2 x (R3)
<hr/>		

These reactions predict oscillations of the concentrations of Br^- and Ce^{4+} :

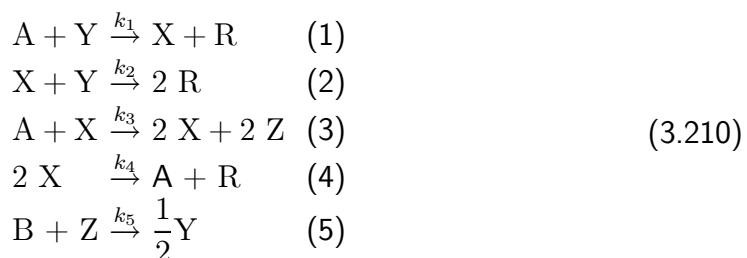
- The autocatalytic reaction Σ leads to a decrease of $[\text{Br}^-]$ to the point that phase I (and reaction 1) are stopped.
- Phase II begins, which converts Ce^{4+} to Ce^{3+} .
- This starts phase III of the reaction, which uses Ce^{4+} and regenerate Br^- .

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d) The Oregonator³³

The Oregonator model can be used to describe the *Belousov-Zhabotinsky reaction*.

► **Schematic model and kinetic equations:**



with $A = \text{BrO}_3^-$, $B = \text{CH}_2(\text{COOH})_2 + \text{BrCH}(\text{COOH})_2$, $R = \text{HOBr}$, $X = \text{HBrO}_2$, $Y = \text{Br}^-$, $Z = \text{Ce}^{4+}$.

Using dimensionless time ($\tau = k_5 [B] t$), we obtain

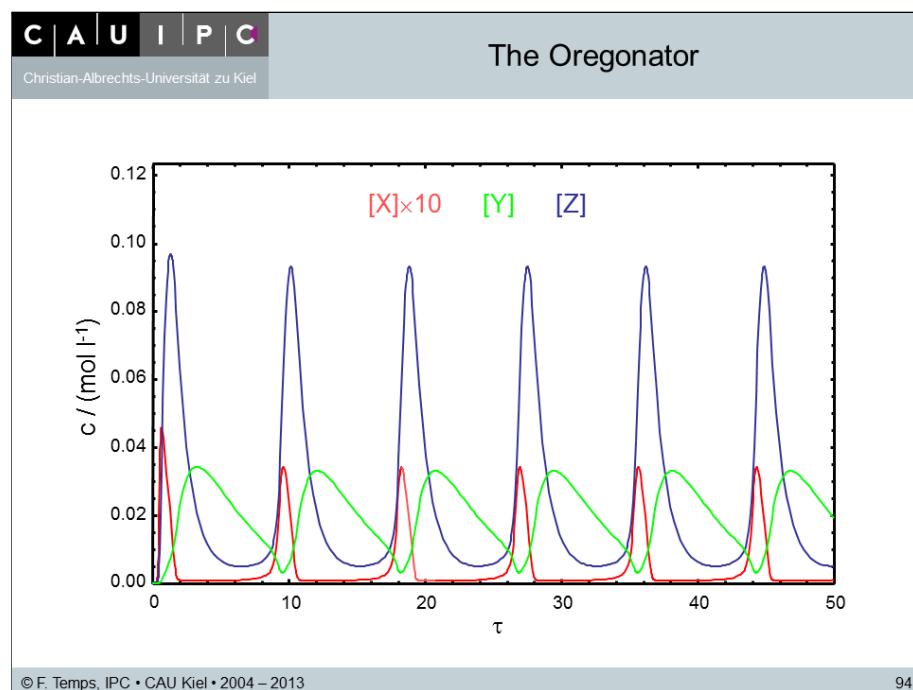
³³ The name 'Oregonator' stems from the workplace of its inventor Noyes (University of Oregon).

$$\frac{d[X]}{d\tau} = \frac{k_1[A][Y] - k_2[X][Y] + k_3[A][X] - 2k_4[X^2]}{k_5[B]} \quad (3.211)$$

$$\frac{d[Y]}{d\tau} = \frac{-k_1[A][Y] - k_2[X][Y] + \frac{1}{2}k_5[B][Z]}{k_5[B]} \quad (3.212)$$

$$\frac{d[Z]}{d\tau} = \frac{2k_3[A][X] - k_5[B][Z]}{k_5[B]} \quad (3.213)$$

- **Figure 3.10:** Numerical integration of the Oregonator model (rate constants in $1\text{ mol}^{-1}\text{s}^{-1}$: $k_1 = 0.005$, $k_2 = 1.0$, $k_3 = 1.0$, $k_4 = 1.0$, $k_5 = .0004$; initial concentrations in mol l^{-1} : $[A] = 0.01$, $[B] = 1.0$, $[X]_0 = 0.0$, $[Y]_0 = 0.0$, $[Z]_0 = 0.00025$.)



3.7 References

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4. Experimental methods

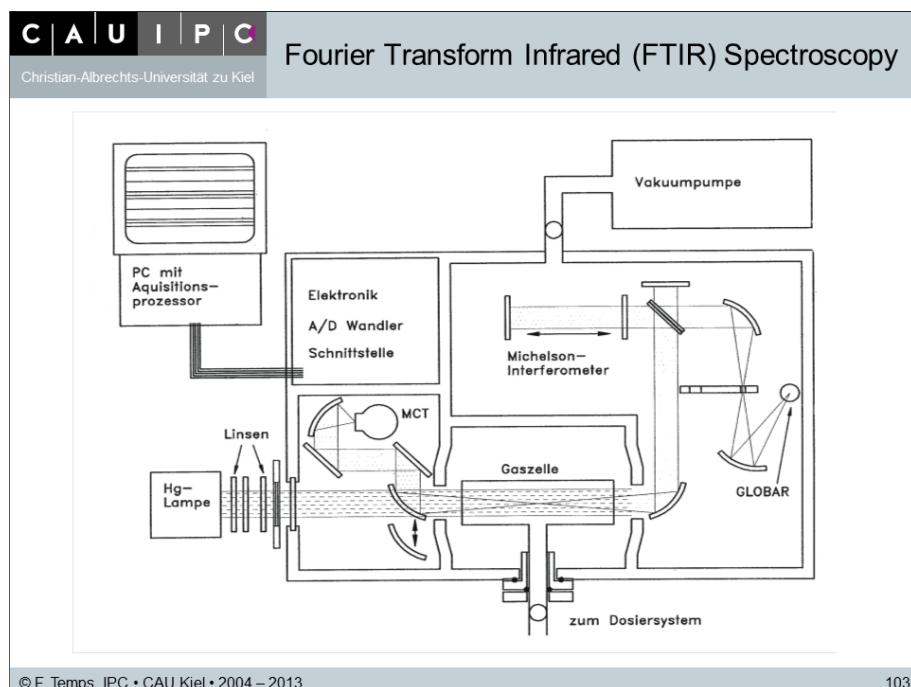
In this section we consider experimental techniques for determining rate coefficients. We'll get to faster reactions as we go down the list.

Special techniques used in quantum state-resolved reaction dynamics, photodissociation, or transition state spectroscopy (molecular beams, state specific detection, photofragment translational spectroscopy, photofragment imaging, other pump-probe techniques, fluorescence up-conversion, fs-CARS, fs-DFWM) will be considered later (in advanced courses), but we'll briefly touch photochemistry and "femtochemistry".

4.1 End product analysis

- first step for setting up reaction mechanisms,
- all convenient analytical techniques (HPLC, GC, GC-MS, MS, UV, FTIR, . . .),
- Problem: No "direct" kinetic information because of lack of time resolution.

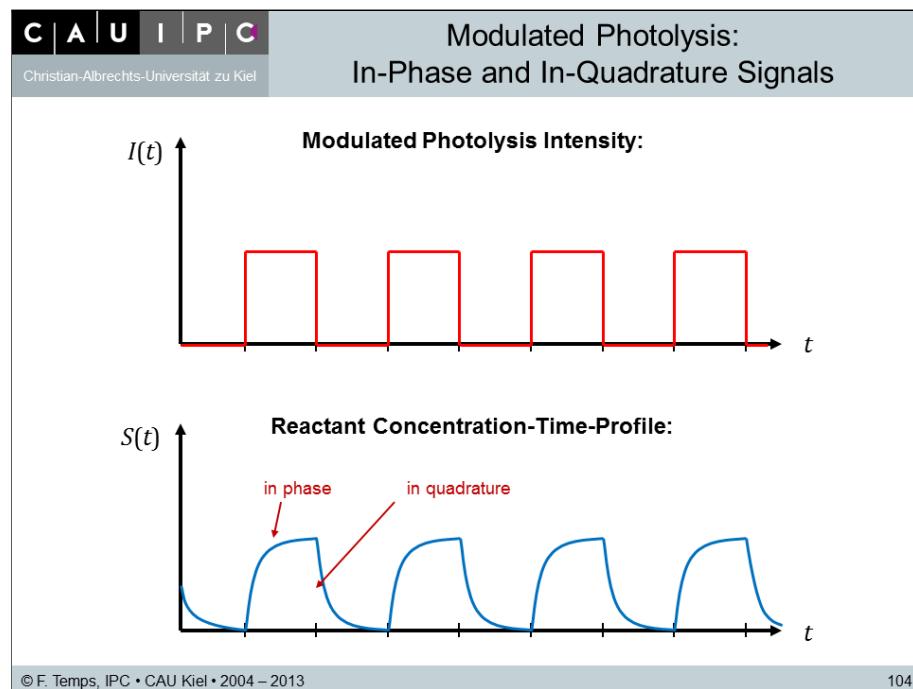
► **Figure 4.1:** FTIR spectrometer for kinetic studies of photolysis-induced reactions.



4.2 Modulation techniques

- especially for photo-induced reactions.
- photolysis light has to be modulated at a frequency that is comparable to that of the reaction \curvearrowright time scale of 10's of ms and longer.
- kinetic information is derived from the “in-phase” and the “in-quadrature” components of the reactant and product concentrations as function of modulation frequency.

► **Figure 4.2:**



4.3 The discharge flow (DF) technique

DF technique is used for gas phase reactions on ms timescale:

- laminar flow along tubular reactor:

$$\Delta t = \frac{\Delta z}{\bar{v}} \quad (4.1)$$

with \bar{v} = mean flow speed, Δz = distance along the flow tube.

- \curvearrowright first-order reaction gives exponential decay of concentration along Δz .
- in reality \Rightarrow Hagen-Poiseuille flow (parabolic flow profile),
- but fast radial diffusion of reactants (at pressures of 1 to 10 mbar) gives “plug shaped” radial concentration profiles despite parabolic flow profile.
- more complicated, when “back diffusion” and radial diffusion have to be taken into account (at higher pressures).
- problem: heterogeneous reactions lead to first-order decay of reactive radicals even in the absence of a reactant.

Combinations with numerous highly sensitive detection techniques, for instance:

- mass spectrometry (MS): universal, but often low sensitivity; problems with fragmentation of molecules in the ion source,
- laser induced fluorescence (LIF): excitation to electronically excited state followed by relaxation by spontaneous emission. very sensitive (e.g., for OH (${}^2\Sigma \leftarrow {}^2\Pi$) detection limit below 10^6 molecules/cm 3),
- electron spin resonance (ESR): for paramagnetic atoms by exploiting the Zeeman effect depending on magnetic field B

$$E = E_0 + g\mu_B M_J B \quad (4.2)$$

$$\Delta M_J = 1 \curvearrowright \Delta E = g\mu_B B \quad (4.3)$$

ESR transitions are in the microwave region (X band: 9 GHz).

- laser magnetic resonance (LMR): very sensitive; based on observation of rotational transitions between Zeeman-shifted rotational levels of paramagnetic radicals (B_{rot} = rotational constant).

$$E'' = B_{\text{rot}} J(J+1) + g_J'' \mu_B M_J'' B \quad (4.4)$$

$$E' = B_{\text{rot}} J(J+1) + g_J' \mu_B M_J' B \quad (4.5)$$

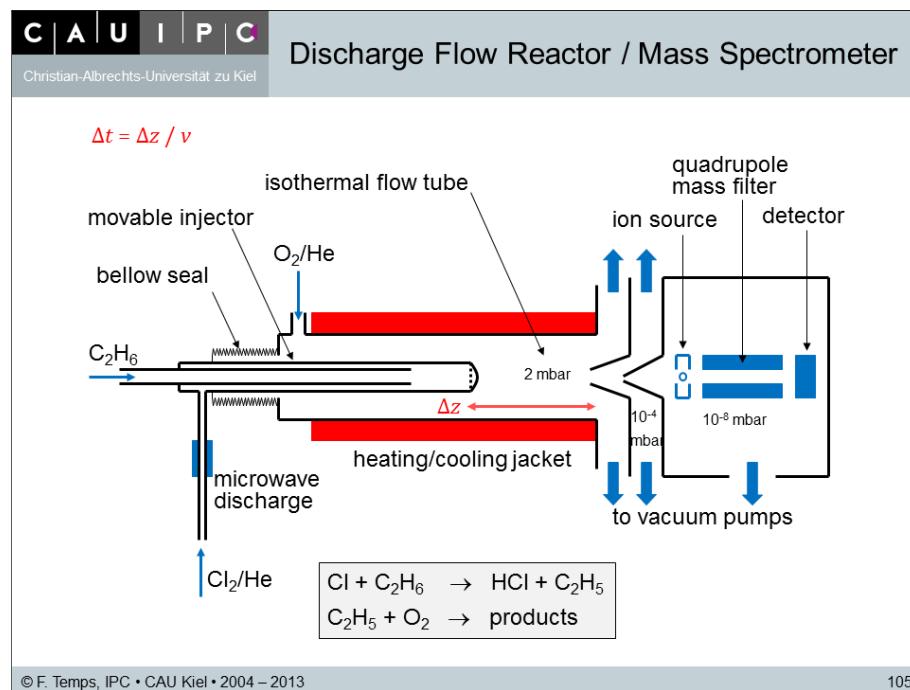
$$\Delta J = \pm 1, \Delta M_J = 0, \pm 1 : \quad (4.6)$$

$$\curvearrowright E' = B_{\text{rot}} (J''+1)(J''+2) + g_J' \mu_B M_J' B \quad (4.7)$$

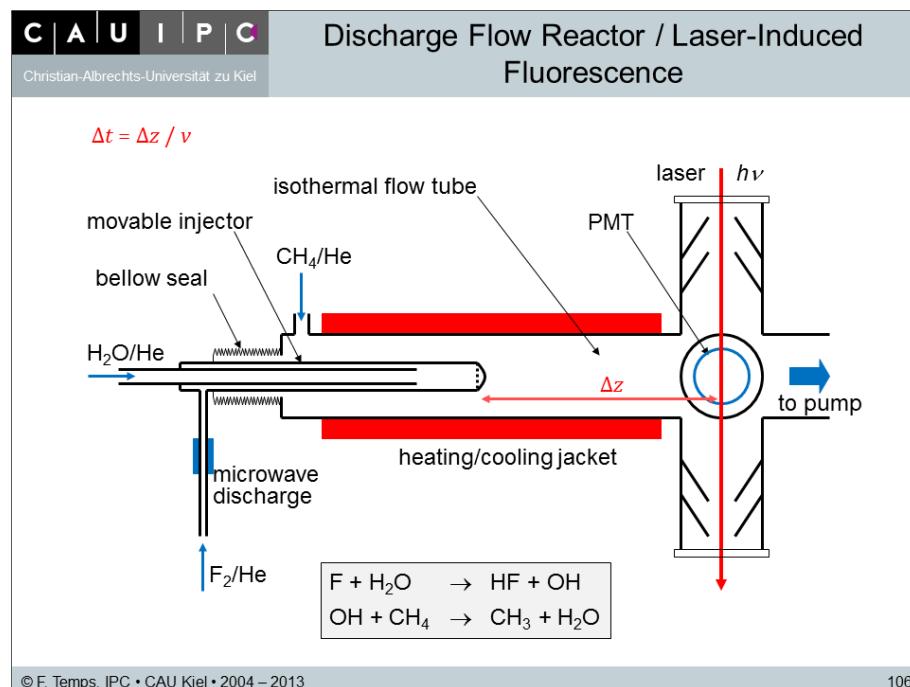
$$\curvearrowright \Delta E = h\nu_{\text{Laser}} = 2B_{\text{rot}}(J''+1) + \mu_B B (g_J' M_J' - g_J'' M_J'') \quad (4.8)$$

LMR transitions are in the FIR region ($100 \mu\text{m} \leq \lambda \leq 2000 \mu\text{m}$).

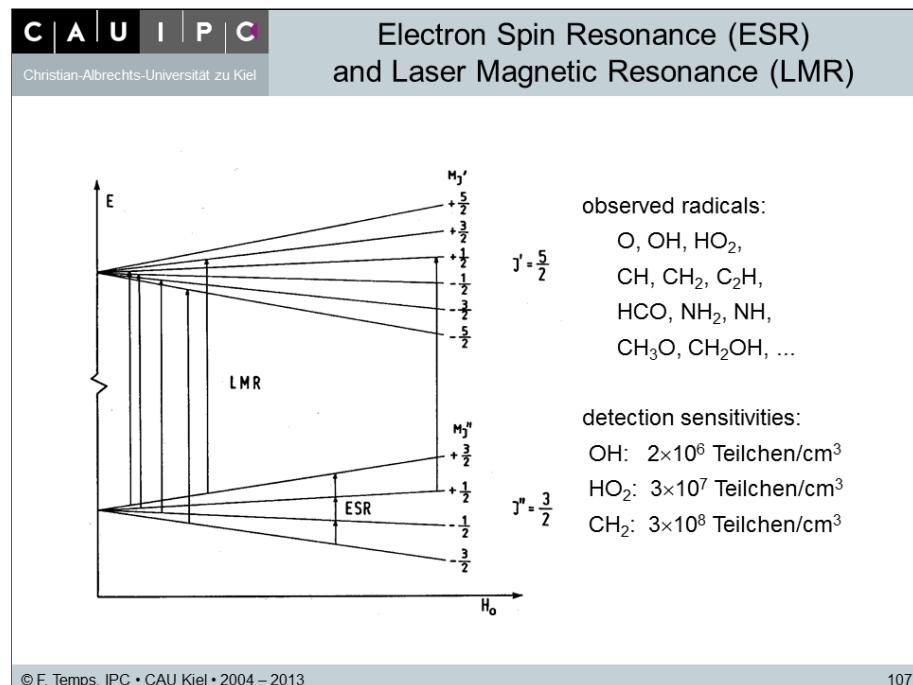
- **Figure 4.3:** Schematic diagram of a DF/MS combination.



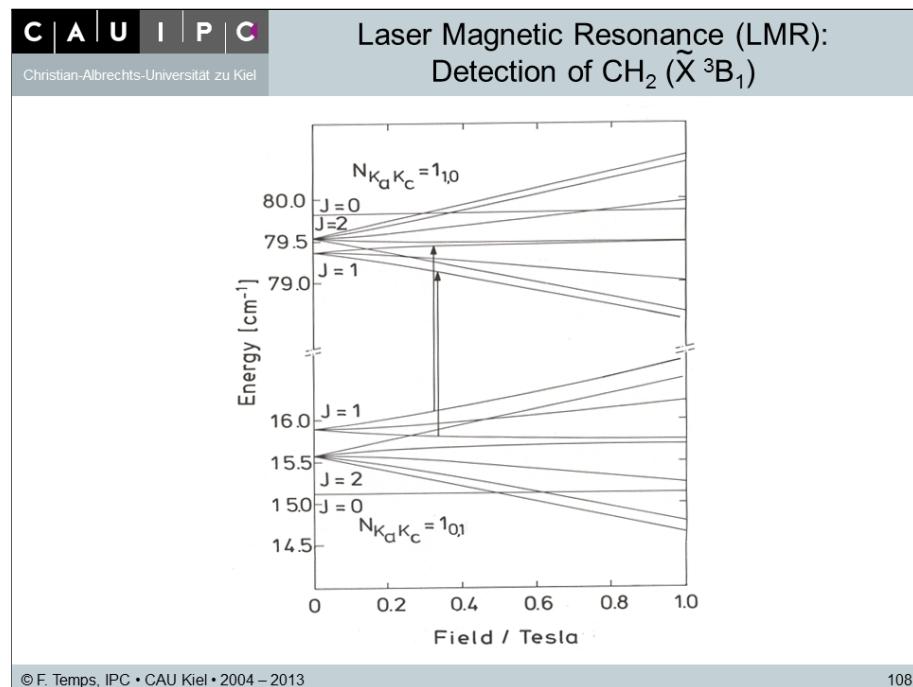
- **Figure 4.4:** Schematic diagram of a DF/LIF combination.



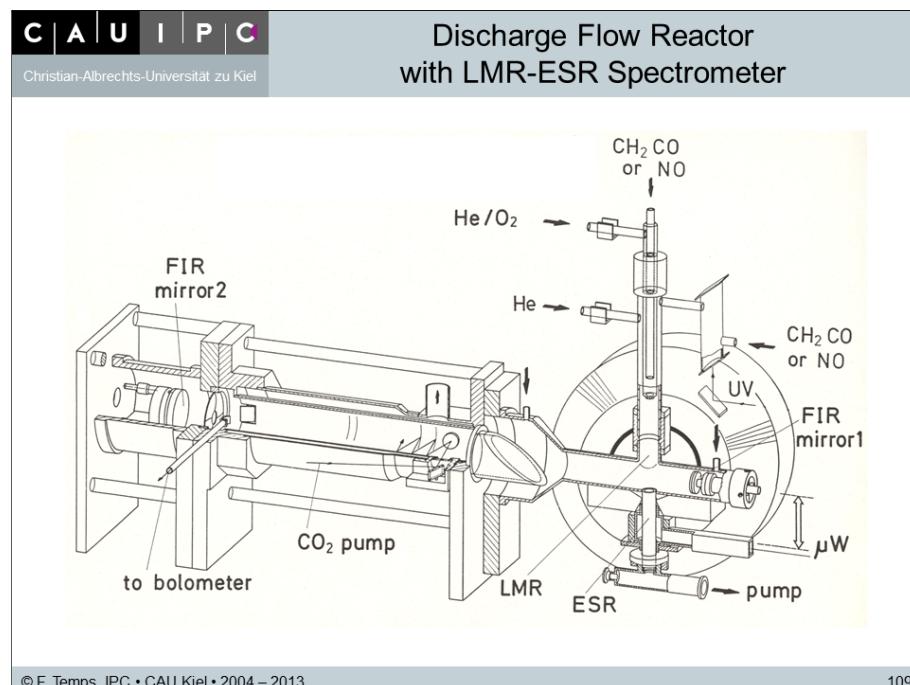
- **Figure 4.5:** Principles of Electron Spin Resonance (ESR) and Laser Magnetic Resonance (LMR).



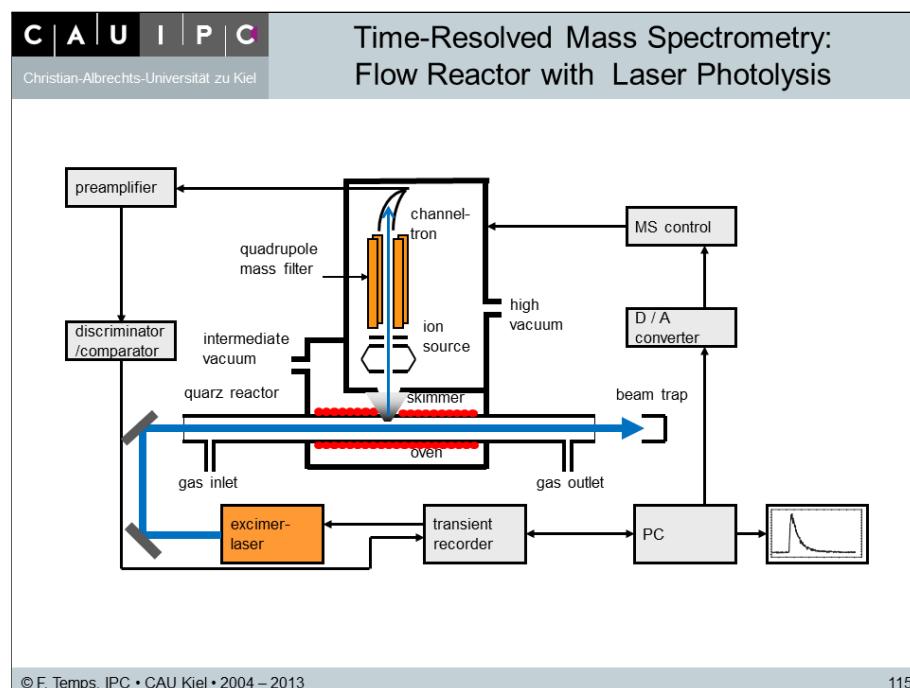
- **Figure 4.6:** Laser Magnetic Resonance (LMR).



- **Figure 4.7:** Schematic diagram of a DF/LMR combination



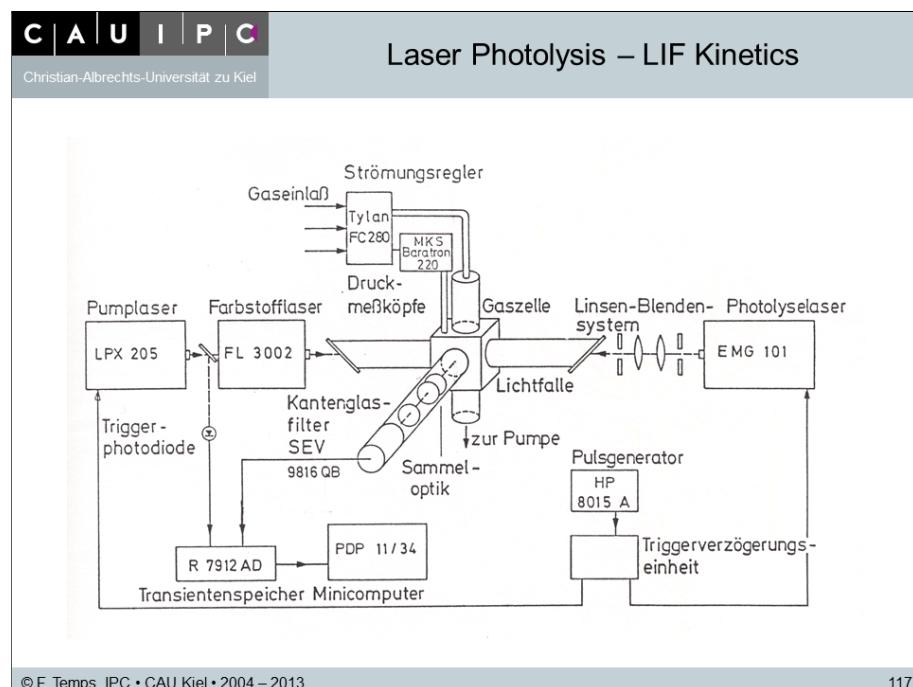
- **Figure 4.8:** Flow reactor with laser flash photolysis and time-resolved mass spectrometric detection of transient reactants and products.



4.4 Flash photolysis (FP)

- “pump-probe” technique:
 - generation of transient species by flash photolysis using fast flash lamp or pulsed lasers (“pump”),
 - fast detection of transient species by UV absorption spectrometry, laser induced fluorescence (LIF), cavity ringdown spectroscopy (CRDS) (“probe”).
- for gas and liquid phase reactions on nanosecond timescale (Norrish & Porter).

- **Figure 4.9:** Typical “Pump-Probe” set-up for kinetics studies by pulsed laser photolysis and detection by laser-induced fluorescence.



- **Cavity Ringdown Spectroscopy (CRDS):**

- CRDS is an ideal method for absorption spectroscopy with pulsed lasers despite of their large ($\pm 5\%$) amplitude fluctuations.
- The absorption measurement is transformed into the time domain:
 - time dependence of signal transmitted through a resonator:

$$I = I_0 \exp(-t/\tau) \quad (4.9)$$

- decay of intensity for pass through cavity (length L , mirror reflectivity R , absorption path length l):

$$\frac{dI}{dx} = - \underbrace{\left(\frac{1-R}{L} \right) I}_{dI/L \text{ due to reflection losses at mirrors}} - \underbrace{\frac{\alpha l}{L} I}_{dI/L \text{ due to absorption}} \quad (4.10)$$

- with

$$dx = c dt \quad (4.11)$$

$$\overset{\curvearrowright}{\frac{dI}{dt}} = -\frac{c}{L} [(1-R) + \alpha l] I \quad (4.12)$$

- empty cavity ($\alpha = 0$):

$$\boxed{\tau_0^{-1} = \frac{c(1-R)}{L}} \quad (4.13)$$

- with absorber ($\alpha \neq 0$):

$$\boxed{\tau^{-1} = \frac{c[(1-R) + \alpha l]}{L}} \quad (4.14)$$

- The difference of the ringdown times measures the absorption coefficient and is related to absorber concentration $[A]$ by

$$\boxed{\tau^{-1} - \tau_0^{-1} = \alpha l / L = c\sigma [A] l / L} \quad (4.15)$$

- Performance of a CRD spectrometer:

- mirrors:

$$R = 99.999\% \quad (4.16)$$

- measured empty cavity decay time:

$$\tau_0 \approx 300 \mu\text{s} \quad (4.17)$$

- effective absorption pathlength (1 m cell):

$$l_{\text{eff}} = 90 \text{ km} \quad (4.18)$$

- applications to chemical kinetics:

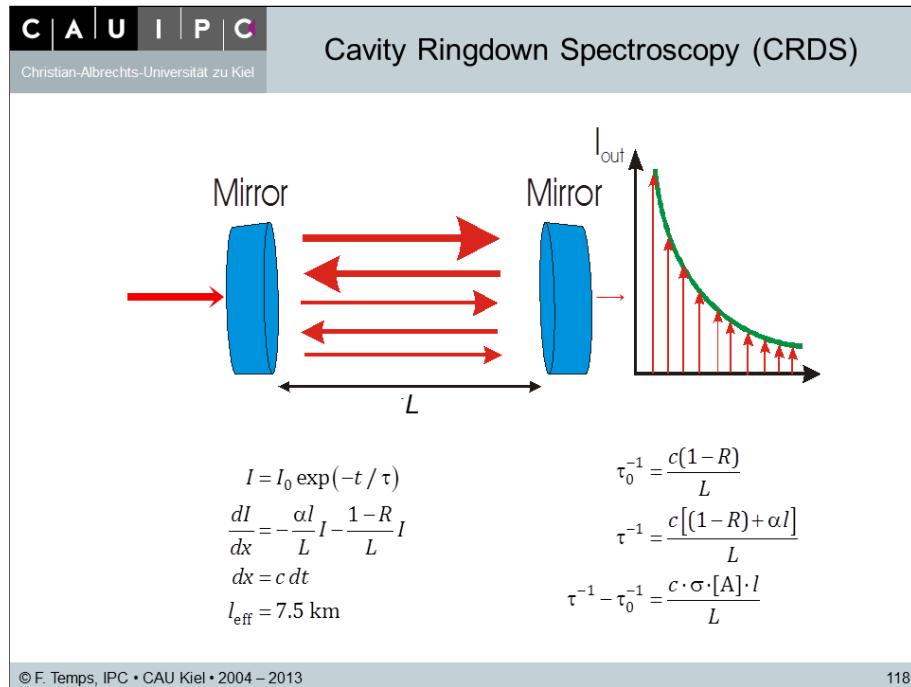
- slow reactions: pump-probe scheme with variable time delay.
first-order reaction with rate constant k_1 :

$$[A] = [A]_0 e^{-k_1 t} \quad (4.19)$$

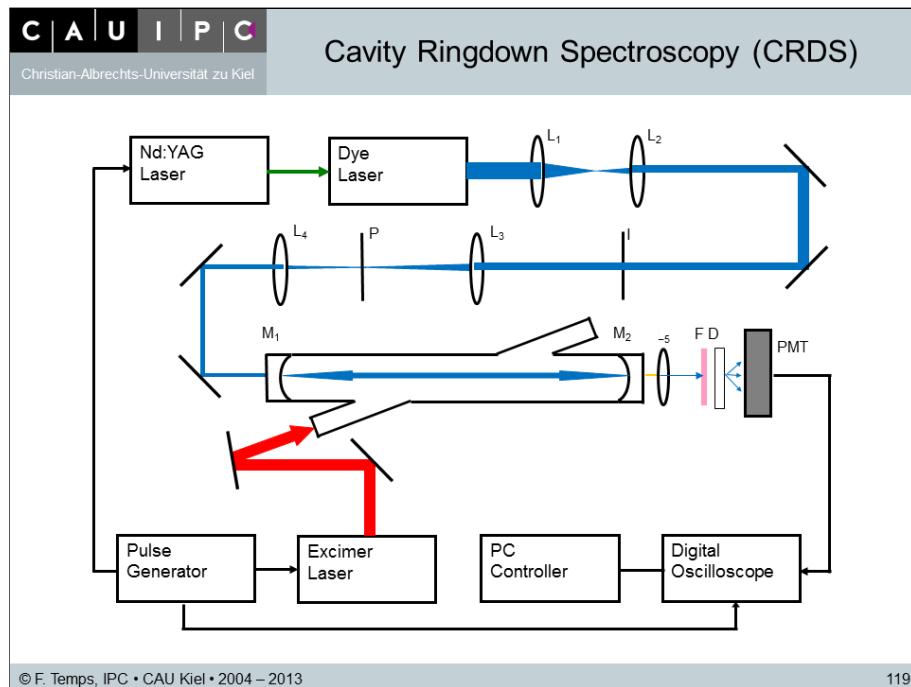
$$\overset{\curvearrowright}{\ln (\tau^{-1} - \tau_0^{-1})} = B - k_1 t \quad (4.20)$$

- fast reactions: kinetics and ringdown occur on the same time scale. \curvearrowright
(extended) Kinetics and Ringdown model ((e)SKaR); see Brown2000 and Guo2003 for details.

► **Figure 4.10:**



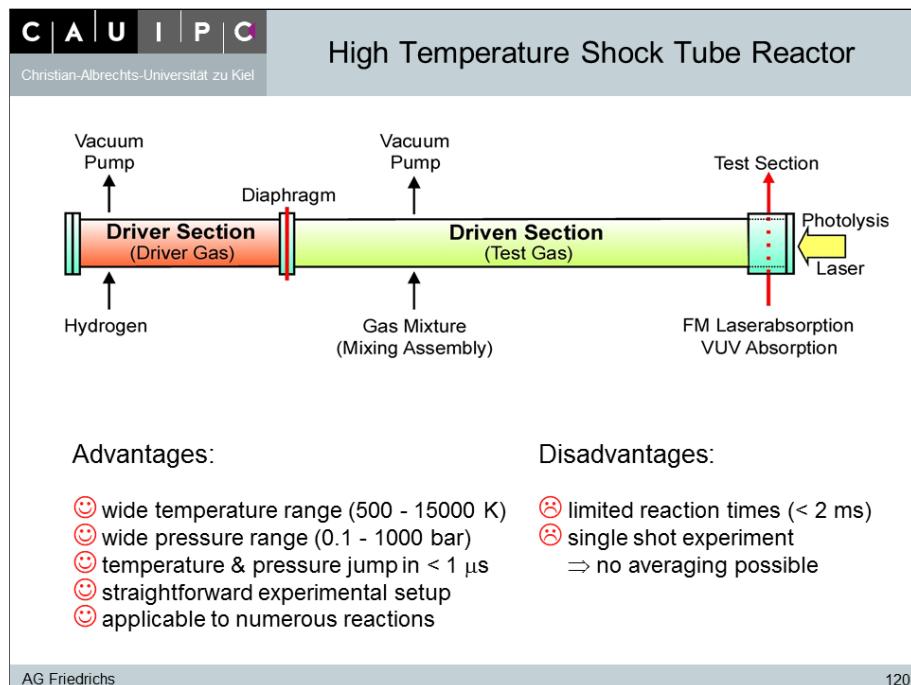
► **Figure 4.11:**



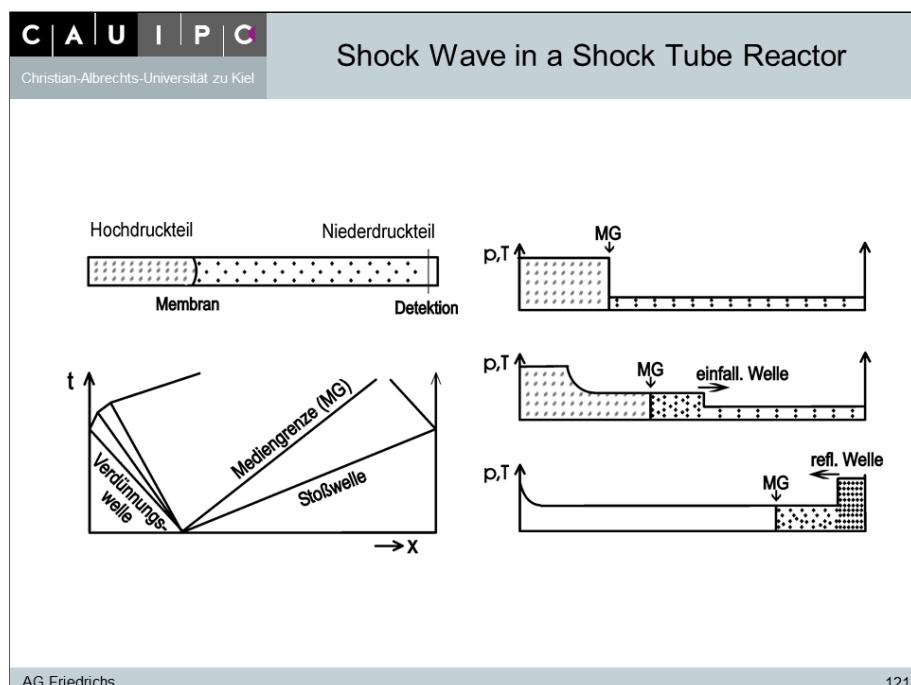
4.5 Shock tube studies of high temperature kinetics

- Detection of atoms by atomic resonance absorption spectrometry (ARAS),
- Detection of small radicals by frequency modulation absorption spectrometry (FM-AS)

► Figure 4.12:



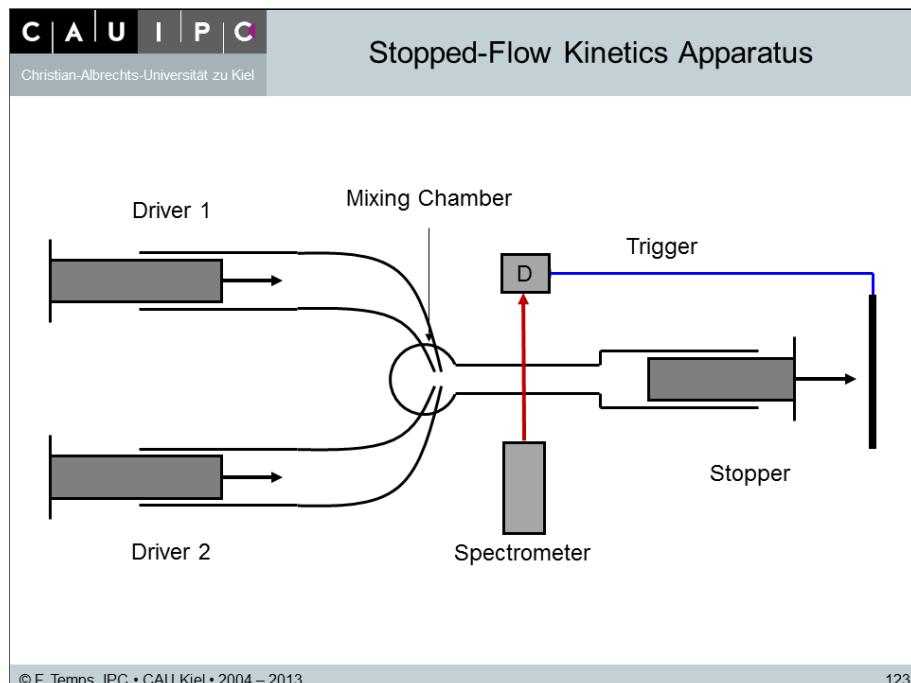
► Figure 4.13:



4.6 Stopped flow studies

- the analogue of the flow tube technique for liquid phase reactions.
- applications mainly kinetics of enzyme reactions, studies of protein folding dynamics

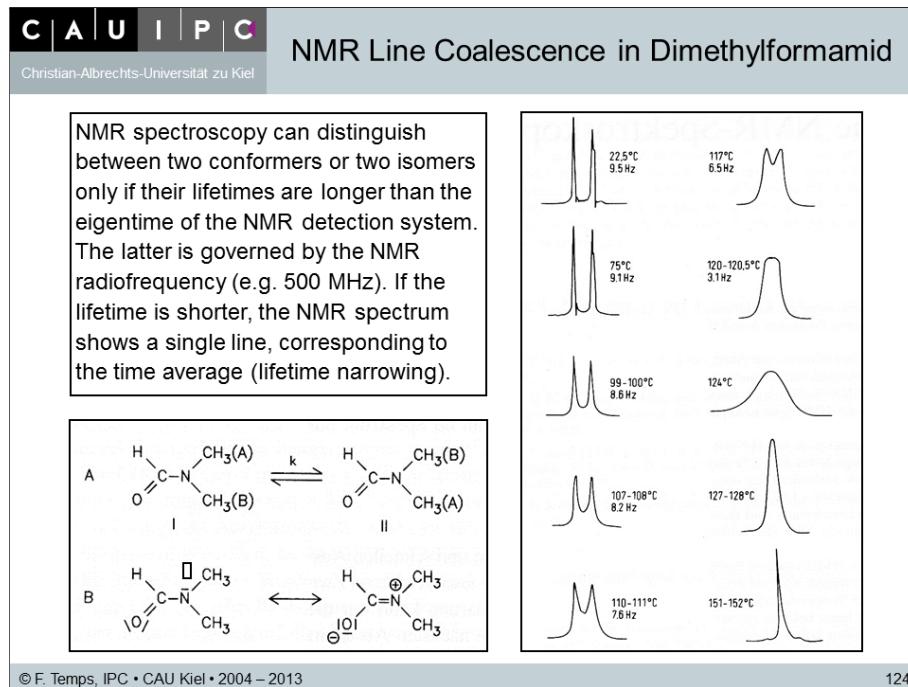
► **Figure 4.14:**



4.7 NMR spectroscopy

- line coalescence
- good for interconversion of two conformers ("isomerization")

► **Figure 4.15:**

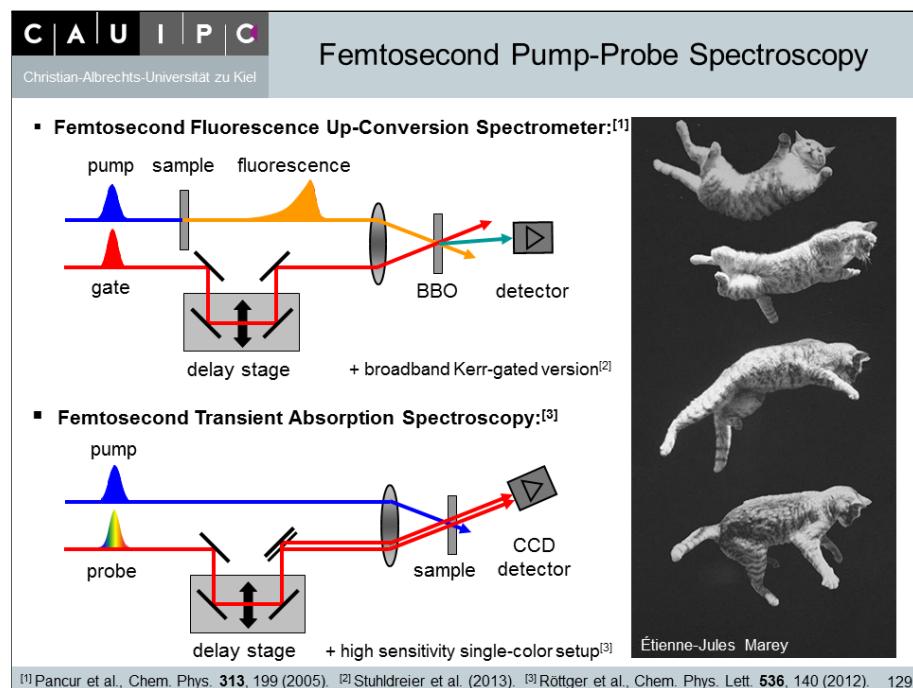


4.8 Relaxation methods

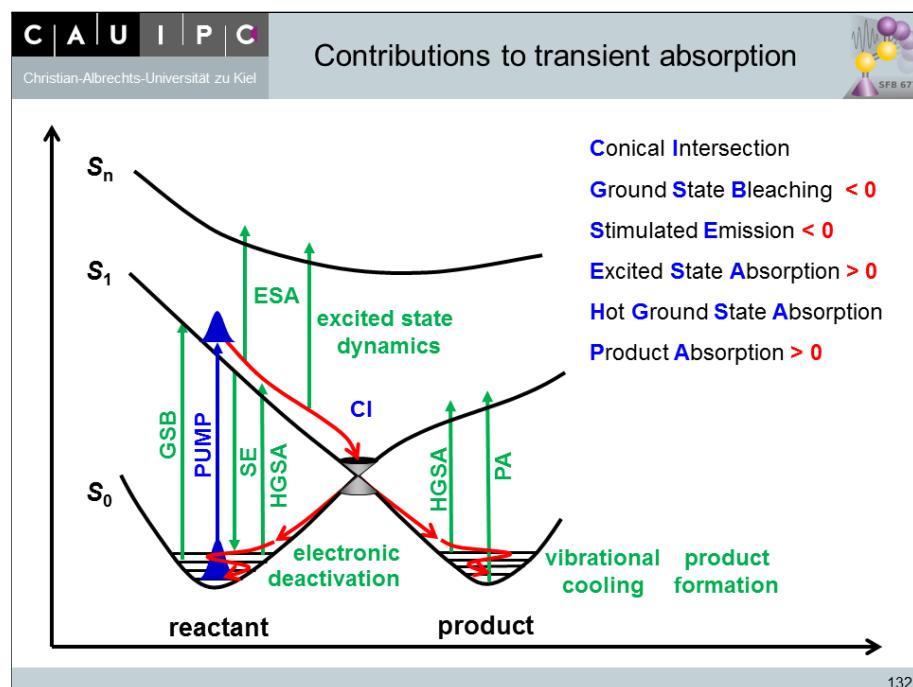
- application to fast reactions in the liquid phase (Eigen)
- T -jump, p -jump, pH -jump, . . . :
 - (1) \Rightarrow displacement from equilibrium
 - (2) \Rightarrow measurements of relaxation into new equilibrium state by transient absorption spectroscopy, conductivity, . . .

4.9 Femtosecond spectroscopy

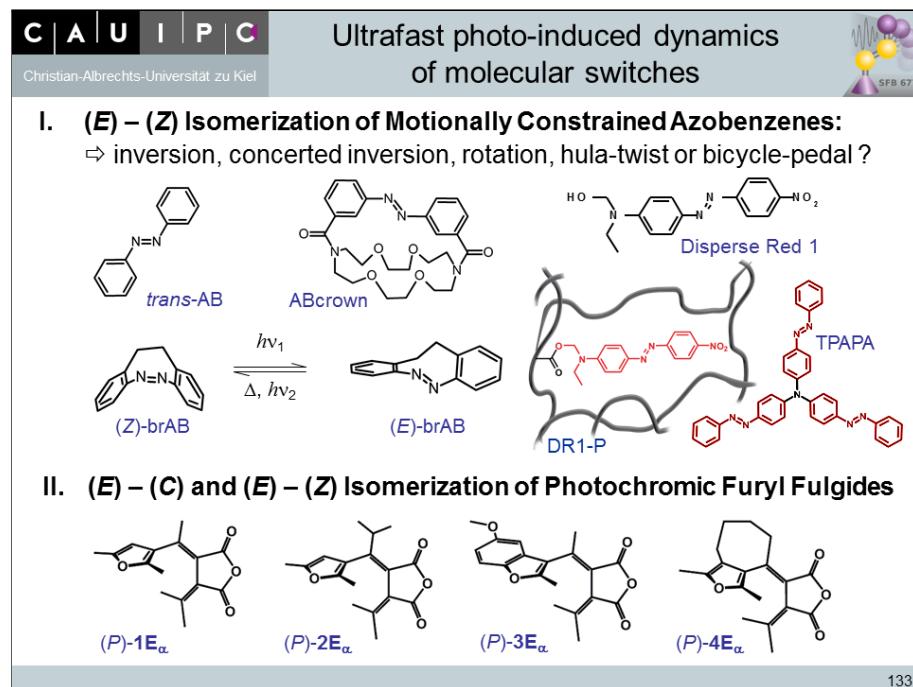
- **Figure 4.16:** Femtosecond pump-probe spectroscopy for the investigation of ultrafast reactions (time resolution down to the order of 10 fs).



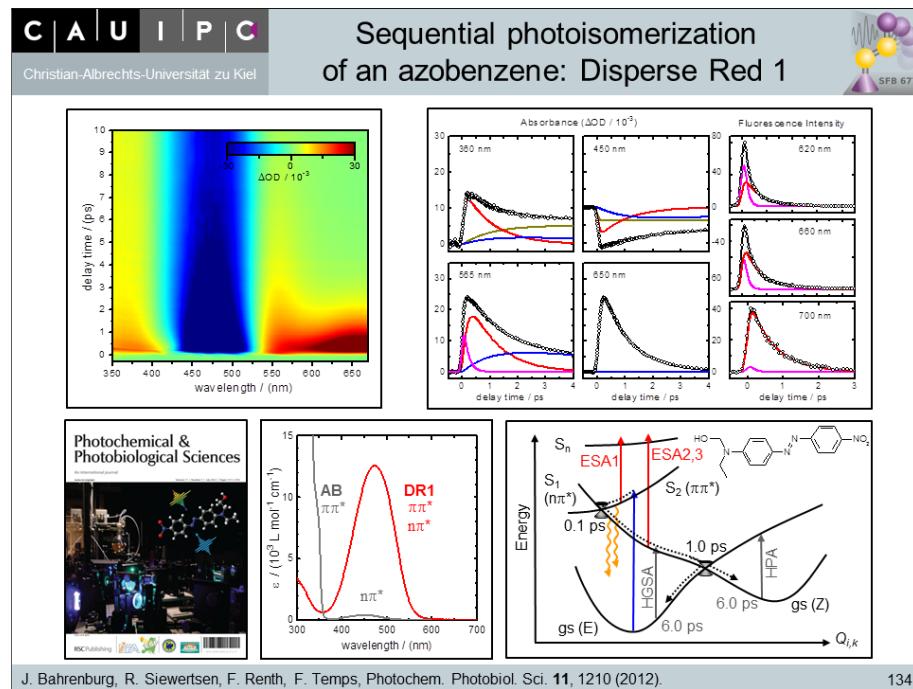
- **Figure 4.17:** Signals in broadband femtosecond transient absorption spectroscopy.



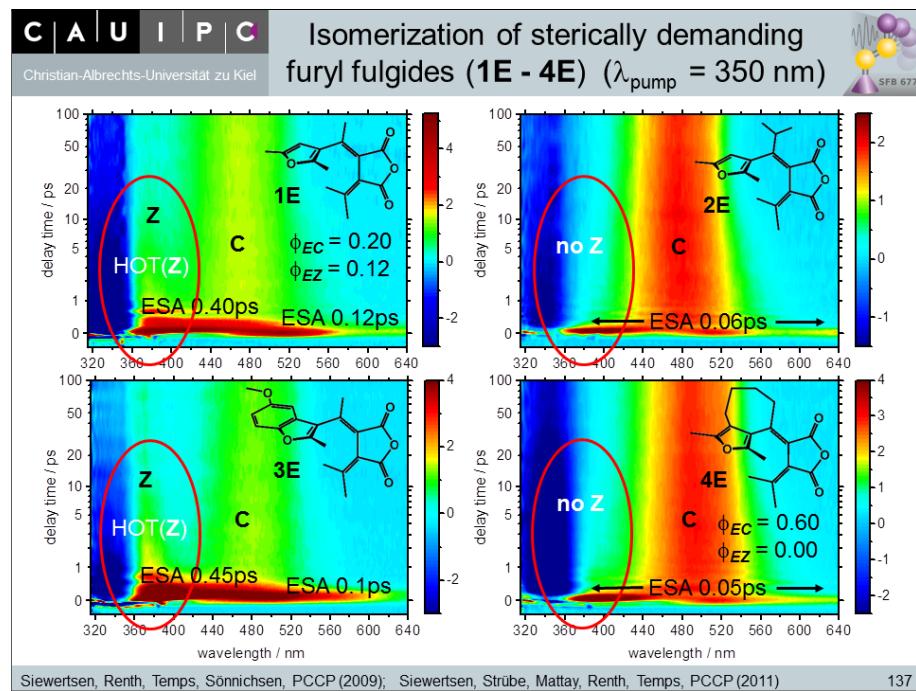
- **Figure 4.18:** Broadband femtosecond transient absorption spectroscopy of photochromic molecular switches in SFB 677.



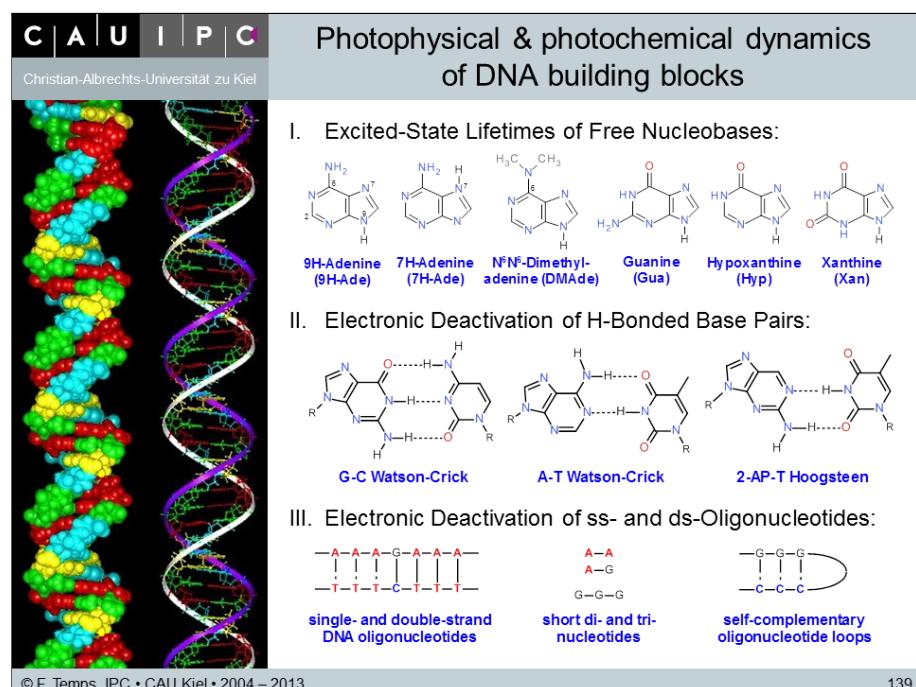
- **Figure 4.19:** Broadband femtosecond transient absorption spectroscopy of Disperse Red 1.



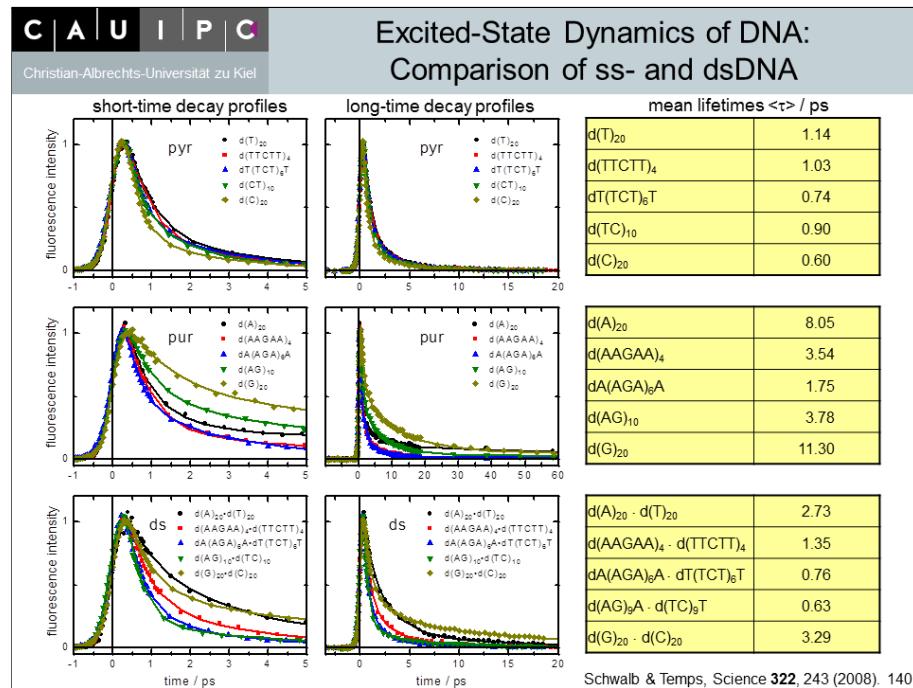
- **Figure 4.20:** Broadband femtosecond transient absorption spectroscopy of Furyl Fulgides.



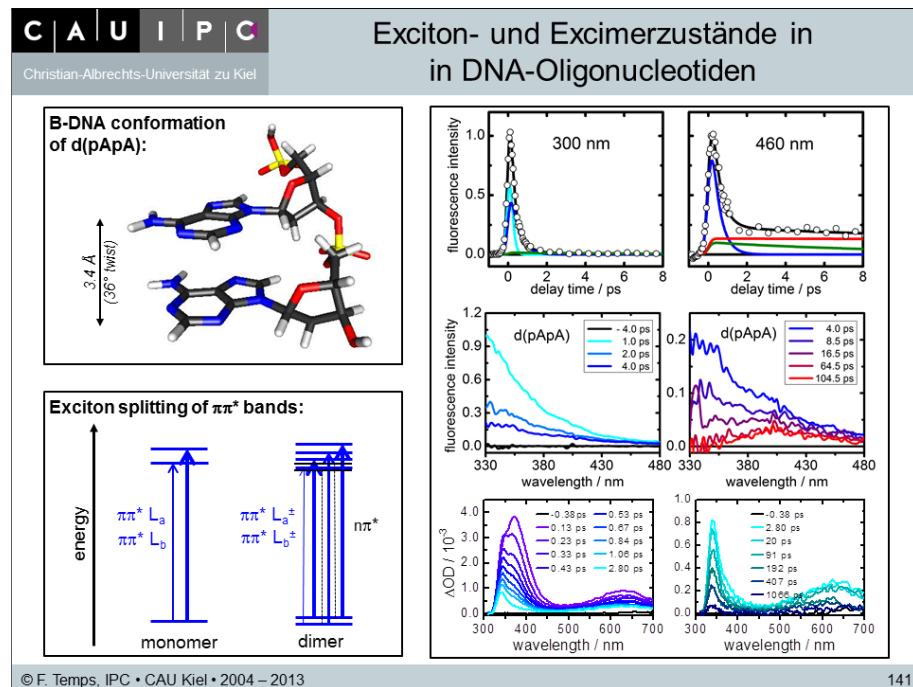
- **Figure 4.21:** Ultrafast Electronic Deactivation in DNA Building Blocks.



- **Figure 4.22:** Femtosecond fluorescence up-conversion data for DNA strands.



- **Figure 4.23:** Ultrafast Electronic Deactivation in DNA Building Blocks: d(pApA) as Model System.



4.10 References

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5. Collision theory

So far, we have considered more or less complex chemical reactions following more or less complicated rate laws, but we have only considered the rate coefficients appearing in the rate laws as empirical quantities, which had to be determined experimentally.

We shall now ask the question, whether we can rationalize and predict those rate coefficients using theoretical models. Towards these ends, we have to look at the reactions at a microscopic, molecular level. In particular, we have to

- consider the relation between the microscopic (individual molecule) properties and the macroscopic (thermally averaged) rate quantities (rate constants, product branching ratios)
- develop models for the microscopic (molecular level) progress of individual elementary reactions, including the different molecular degrees of freedom (quantum states).
- develop sufficiently simplified models averaging over the molecular degrees of freedom which still allow us to make practically useful, relevant, and sufficiently accurate predictions.

We shall do so in the next four chapters.

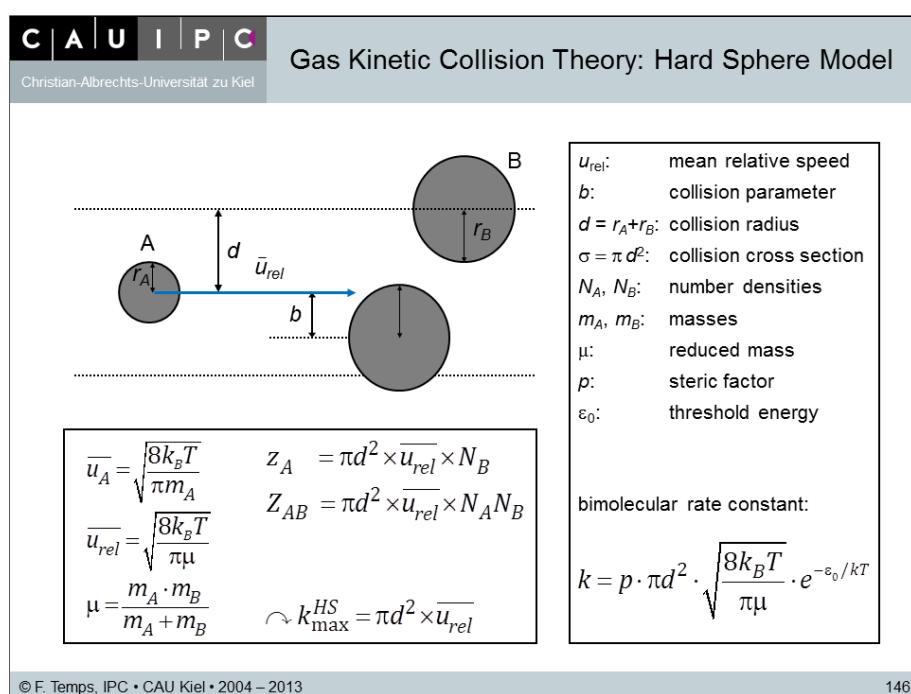
► **Collision theory:** To begin with, this chapter considers bimolecular reactions in the gas phase. These obviously require a collision between two molecules as condition for a reaction to take place.

- We start with the hard sphere collision model of structureless particles as the simplest model for bimolecular reactions. Although this model has two major flaws, it leads to the right result because of a compensation of errors.
- We then consider results of kinetic gas theory, which allow us to properly take into account the molecular speed distributions.
- We apply the hard sphere collision model to understand transport processes in the gas phase (diffusion, heat conductivity, viscosity).
- We then proceed with a correct derivation of advanced collision theory models starting from differential cross sections (which can be measured in crossed molecular beam experiments). Advanced collision theory is the method of choice for fast gas phase reactions which can be studied in detail by molecular beam experiments and handled by quantum theory.

5.1 Hard sphere collision theory

5.1.1 The gas kinetic collision frequency

- **The gas kinetic collision frequency as upper limit for rate constants of bimolecular reactions:** The gas kinetic collision frequency constitutes an upper limit for the rate constant of bimolecular gas phase reactions. We assume that the molecules A and B are structureless hard spheres (radii r_A, r_B) moving around with fixed mean speeds u_A and u_B and look at the number of collisions between A and B per unit time.
- **Figure 5.1:** Derivation of the hard sphere gas kinetic collision frequency.



- **Discussion of the molecular quantities affecting the rate constant:**

- collision parameter (= projected distance between centers of gravity):

$$b \quad (5.1)$$

- maximal collision parameter = max b value leading to a collision b_{\max} :

$$b \leq b_{\max} = r_A + r_B = d \quad (5.2)$$

- collision cross section $\sigma = \pi d^2$ (= reactive cross section)³⁴:

$$\sigma^{HS} = \pi d^2 = \pi (r_A + r_B)^2 \quad (5.3)$$

³⁴ Deutsch: reaktiver Wirkungsquerschnitt.

- mean speed of A and B:

$$\overline{u_A} = \sqrt{\frac{8k_B T}{\pi m_A}} = \sqrt{\frac{8RT}{\pi M_A}} \quad (5.4)$$

$$\overline{u_B} = \sqrt{\frac{8k_B T}{\pi m_B}} = \sqrt{\frac{8RT}{\pi M_B}} \quad (5.5)$$

- mean relative speed (2 different molecules, i.e., A \neq B):³⁵

$$\boxed{\overline{u_{rel}} = \sqrt{\frac{8k_B T}{\pi \mu}}} \quad (5.9)$$

with the reduced mass

$$\boxed{\mu = \frac{m_A m_B}{m_A + m_B}} \quad (5.10)$$

- mean relative speed (single type of molecules, i.e., A = B):

$$\mu = \frac{m_A m_A}{m_A + m_A} = \frac{1}{2} m_A \quad (5.11)$$

↷

$$\overline{u_{rel}} = \sqrt{2} \times \sqrt{\frac{8k_B T}{\pi m_A}} \quad (5.12)$$

► Hard sphere gas kinetic collision frequency:

- We want to determine the number of collisions z_A of a single molecule A with molecules B in time dt . This is given by the product of the (volume that A has swept in dt) \times (number density of B):

- volume of cylinder that A has swept in time dt :

$$\text{volume} = \text{cross section} \times dl \quad (5.13)$$

↷

$$\pi d^2 \times \overline{u_{rel}} dt \quad (5.14)$$

³⁵ The mean relative speed of two molecules with velocities \mathbf{u}_A and \mathbf{u}_B is found by looking at the square of the difference speed

$$u_{rel}^2 = |\mathbf{u}_A - \mathbf{u}_B|^2 = |u_A|^2 + |u_B|^2 - 2|u_A||u_B|\cos\theta \quad (5.6)$$

The third term averaged over $\cos\theta$ is 0, therefore

$$u_{rel}^2 = |u_A|^2 + |u_B|^2 = \frac{3k_B T}{m_A} + \frac{3k_B T}{m_B} = \frac{3k_B T (m_A + m_B)}{m_A m_B} = \frac{3k_B T}{\mu} \quad (5.7)$$

Since \overline{u} and $(\overline{u^2})^{1/2}$ differ only by a constant factor, we also find that

$$\overline{u_{rel}} = \sqrt{\frac{8k_B T}{\pi \mu}} \quad (5.8)$$

- number density of B

$$N_B \quad (5.15)$$

- Number of collisions of a single A in time dt : \Rightarrow number of molecules B in that volume

$$z_A = \pi d^2 \times \overline{u_{rel}} \times N_B \quad (5.16)$$

- Number of all collisions between A and B:

$$Z_{AB} = \pi d^2 \times \overline{u_{rel}} \times N_A N_B \quad (5.17)$$

- Modification for collisions between identical molecules (collisions must not be counted twice):

$$Z_{AA} = \frac{1}{2} \times \pi d^2 \times \overline{u_{rel}} \times N_A N_A \quad (5.18)$$

$$= \frac{\sqrt{2}}{2} \times \pi d^2 \times \overline{u_A} \times N_A N_A \quad (5.19)$$

- Comparison with rate expression:

$$-\frac{dN_A}{dt} = -\frac{dN_B}{dt} = k \times N_A N_B = Z_{AB} \quad (5.20)$$

↷

- Expression for rate constant for collisions A + B:

$$k_{\max}^{HS} = \pi d^2 \times \overline{u_{rel}} = \sigma^{HS} \times \overline{u_{rel}} \quad (5.21)$$

↷

$$k_{\max}^{HS} = \pi d^2 \times \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \quad (5.22)$$

- Modification for collisions between identical molecules (A + A):

$$k_{\max}^{HS} = \frac{1}{2} \pi d^2 \times \overline{u_{rel}} = \frac{1}{\sqrt{2}} \pi d^2 \times \left(\frac{8k_B T}{\pi m_A} \right)^{1/2} \quad (5.23)$$

These expressions give the **upper limits for the rate constants of bimolecular reactions**. The upper limits are reached only if

- there are no energetic restrictions (no energy barriers),
- all collisions lead to reaction (no steric constraints),
- molecules can be approximated as hard spheres (unrealistic, usually one has $\sigma^{rxn} < \sigma^{HS}$),
- all molecules collide with the same relative speed (in reality there is a distribution of speeds).

► **Mean free pathlength:**

- The mean free pathlength is the distance that a molecule flies between two successive collisions:

$$\lambda = \frac{\text{distance}}{\#\text{ of collisions}} = \frac{\text{distance/time}}{\#\text{ of collisions/time}} = \frac{\overline{u_{rel}}}{z_A} \quad (5.24)$$

↷

$$\boxed{\lambda = \frac{1}{\pi d^2 \times N_B} \propto \frac{1}{N}} \quad (5.25)$$

- Modification for collisions between identical molecules (A + A):

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi d^2 \times N_A} \quad (5.26)$$

► **Time between two collisions:**

$$\frac{1}{z_A} = \frac{1}{\pi d^2 \overline{u_{rel}} \times N_B} \quad (5.27)$$

► **Example 5.1:** Collision frequency for O₂ - N₂ @ T = 298 K, p = 1000 mbar:

Molecular parameters:

$$d_{O_2} = 2r_{O_2} = 3.467 \text{ \AA} \quad (5.28)$$

$$d_{N_2} = 2r_{N_2} = 3.798 \text{ \AA} \quad (5.29)$$

$$\curvearrowright d = 3.6 \text{ \AA} = 3.6 \times 10^{-10} \text{ m} \quad (5.30)$$

$$\sigma^{HS} = \pi d^2 = 41 \text{ \AA}^2 \quad (5.31)$$

$$\mu = \frac{28 \times 32}{28 + 32} \times 10^{-3} \text{ kg/mol} \times \frac{1}{N_L} \quad (5.32)$$

$$\overline{u_{rel}} = \sqrt{\frac{8RT}{\pi\mu}} = 650 \text{ m/s} \quad (5.33)$$

$$(\text{but } \overline{u}(\text{O}_2) = 444 \text{ m/s}) \quad (5.34)$$

Rate constant:

$$k_{\max}^{HS} = \pi d^2 \times \left(\frac{8k_B T}{\pi\mu} \right)^{1/2} \quad (5.35)$$

$$= 2.6 \times 10^{-10} \text{ cm}^3/\text{s} \quad (5.36)$$

$$= 1.6 \times 10^{14} \text{ cm}^3/\text{mol s} \quad (5.37)$$

Mean free pathlength:

$$p = 1000 \text{ mbar} \quad (5.38)$$

$$N_B = 4.0 \times 10^{-5} \text{ mol/cm}^3 \quad (5.39)$$

$$= 2.5 \times 10^{25} / \text{m}^3 \quad (5.40)$$

$$d = 3.6 \times 10^{-10} \text{ m} \quad (5.41)$$

$$\lambda = 1 \times 10^{-7} \text{ m} \quad (5.42)$$

Rule-of-thumb:

$$p = 0.3 \text{ mbar} \curvearrowright \lambda = 0.3 \text{ mm} \quad (5.43)$$

Time between collisions:

$$p = 1000 \text{ mbar} \quad (5.44)$$

$$\frac{1}{z_A} = \frac{1}{\pi d^2 \overline{u_{rel}} \times N_B} \quad (5.45)$$

$$= 1.5 \times 10^{-10} \text{ s} \quad (5.46)$$

$$\approx 0.1 \text{ ns} \quad (5.47)$$

□

5.1.2 Allowance for a threshold energy for reaction

- **The threshold energy E_0 :** The majority of reactions exhibit a threshold energy, below which the reaction does not occur (quantum mechanical tunneling is excluded here). The molecules must have a minimum energy ϵ_{\min} to overcome this reaction threshold energy ϵ_0 . For our structureless spherical molecules, we consider only translational energy ϵ_T .³⁶

$$\epsilon_T < \epsilon_0 : \text{no reaction} \quad (5.48)$$

$$\epsilon_T > \epsilon_0 : \text{reaction} \quad (5.49)$$

- **Boltzmann distribution:** Fraction of molecules with translational energy $\epsilon_T > \epsilon_0$:

$$\frac{dN(\epsilon_T > \epsilon_0)}{N} = \exp\left(-\frac{\epsilon_0}{k_B T}\right) dN = \exp\left(-\frac{E_0}{RT}\right) dN \quad (5.50)$$

- **Resulting rate constant:**

$$k_{\max}^{HS} = \pi d^2 \times \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \times e^{-\epsilon_0/k_B T} \quad (5.51)$$

or

$$k_{\max}^{HS} = \pi d^2 \times \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \times e^{-E_0/RT} \quad (5.52)$$

- **Arrhenius activation energy:** Applying the definition of the apparent (Arrhenius) activation energy E_A , we find that

$$E_A = RT^2 \frac{d \ln k}{dt} = E_0 + \frac{1}{2} RT \quad (5.53)$$

As we see, E_A is not constant but (slightly) T -dependent: The slope of a plot of $\ln k_{\max}^{HS}$ vs. T^{-1} increases as $T \rightarrow \infty$ (or $T^{-1} \rightarrow 0$). The Arrhenius preexponential factor A would not be constant as well, it is also slightly T -dependent.

³⁶ We use ϵ_T and ϵ_0 to indicate the energies in molecular units, and E_T and E_0 for the respective values in molar units.

5.1.3 Allowance for steric hindrance

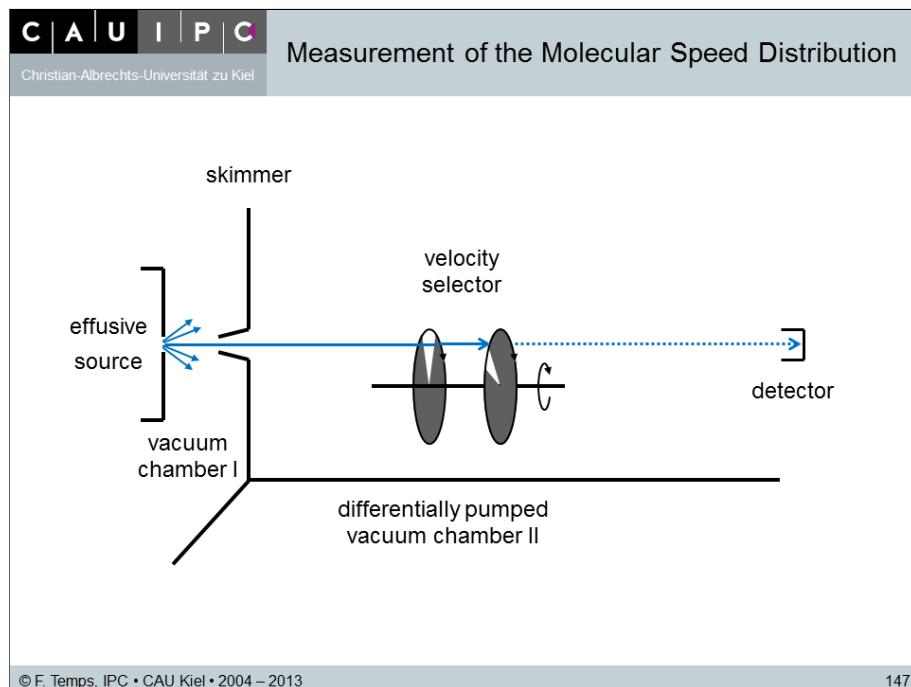
- **The sterical factor p :** In addition, even if $\epsilon_T > \epsilon_0$, not every collision will lead to a reaction, because real molecules are not structureless: A reaction requires a specific orientation of the molecules. This is taken into account by introducing a sterical factor p :

$$k_{\max}^{HS} = p \times \pi d^2 \times \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \times e^{-\epsilon_0/kT} \quad (5.54)$$

5.2 Kinetic gas theory

5.2.1 The Maxwell-Boltzmann speed distributions of gas molecules in 1D and 3D

- **Figure 5.2:** Experimental measurement of molecular speed distribution using a rotating disk velocity selector and an effusive molecular beam (orifice diameter $\ll \lambda$).



- **Rotating disk velocity selector:**

- Flight time of molecules with velocity u_x between two rotating disks (distance L):

$$\tau_1 = \frac{L}{u_x} \quad (5.55)$$

- Time delay of second slit with respect to first slit (δ = angle, ω = angular velocity):

$$\tau_2 = \frac{\delta}{\omega} \quad (5.56)$$

- Transmission only if

$$\tau_1 = \tau_2 \quad (5.57)$$

$$u_x = L \times \frac{\omega}{\delta} \quad (5.58)$$

In practice, one uses a number of velocity selectors in series. A measurement of the 1D speed distribution $f(u_x) du_x = \frac{N(u_x)}{N} du_x$ using this method gives

► **The 1D Maxwell-Boltzmann speed distribution (Fig. 5.3):**

$$f(u_x) du_x = \sqrt{\frac{m}{2\pi k_B T}} \times \exp\left(-\frac{mu_x^2}{2k_B T}\right) du_x \quad (5.59)$$

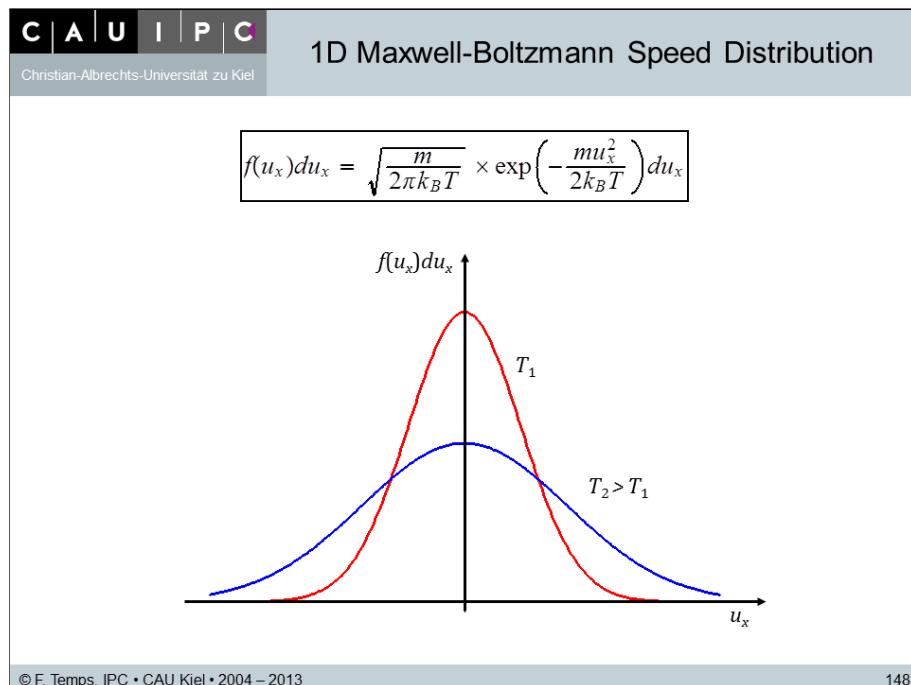
Note that this distribution is already normalized for $\int_{-\infty}^{\infty} f(u_x) du_x = 1$. We check this by substituting

$$t = \sqrt{\frac{m}{2k_B T}} u_x \curvearrowright dt = \sqrt{\frac{m}{2k_B T}} du_x \curvearrowright du_x = \sqrt{\frac{2k_B T}{m}} dt \quad (5.60)$$

\curvearrowright

$$\int_{-\infty}^{\infty} f(u_x) du_x = \sqrt{\frac{m}{2\pi k_B T}} \int_{-\infty}^{\infty} \sqrt{\frac{2k_B T}{m}} e^{-t^2} dt = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2} dt = \frac{1}{\sqrt{\pi}} \sqrt{\pi} = 1 \quad (5.61)$$

► **Figure 5.3:** 1D Maxwell-Boltzmann speed distribution.



- **Velocity distribution in 3 dimensions:** Since the velocities in x , y , z direction are independent, the probability that a molecule has a velocity between u_x and $u_x + du_x$, u_y and $u_y + du_y$, and u_z and $u_z + du_z$ is given be the product of $f(u_x) du_x$, $f(u_y) du_y$, and $f(u_z) du_z$:

$$\begin{aligned} \frac{N(u_x, u_y, u_z)}{N} du_x du_y du_z &= f(u_x) f(u_y) f(u_z) du_x du_y du_z \\ &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times \exp \left(-\frac{m(u_x^2 + u_y^2 + u_z^2)}{2k_B T} \right) du_x du_y du_z \end{aligned} \quad (5.62)$$

We are, however, not interested in the distribution of velocities pointing into a specific direction (u_x, u_y, u_z) , but in the probability that a molecule has a certain speed $|u|$ in any direction, i.e., that the velocity vector ends somewhere on a sphere with radius

$$|u| = \sqrt{u_x^2 + u_y^2 + u_z^2} \quad (5.63)$$

To obtain this distribution, we must integrate over all polar angles ϕ and θ . This corresponds to replacing the volume element $du_x du_y du_z$ with the volume $4\pi u^2 du$ of a spherical shell with radius u and thickness du . \curvearrowright

- **The 3D Maxwell-Boltzmann speed distribution (Fig. 5.4):**

$$f(u) du = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times 4\pi u^2 \times \exp \left(-\frac{mu^2}{2k_B T} \right) du \quad (5.64)$$

Note that this distribution is also normalized for $\int_0^\infty f(u) du = 1$. We check this by substituting

$$t = \sqrt{\frac{m}{2k_B T}} u \curvearrowright dt = \sqrt{\frac{m}{2k_B T}} du \curvearrowright du = \left(\frac{2k_B T}{m} \right)^{1/2} dt \quad (5.65)$$

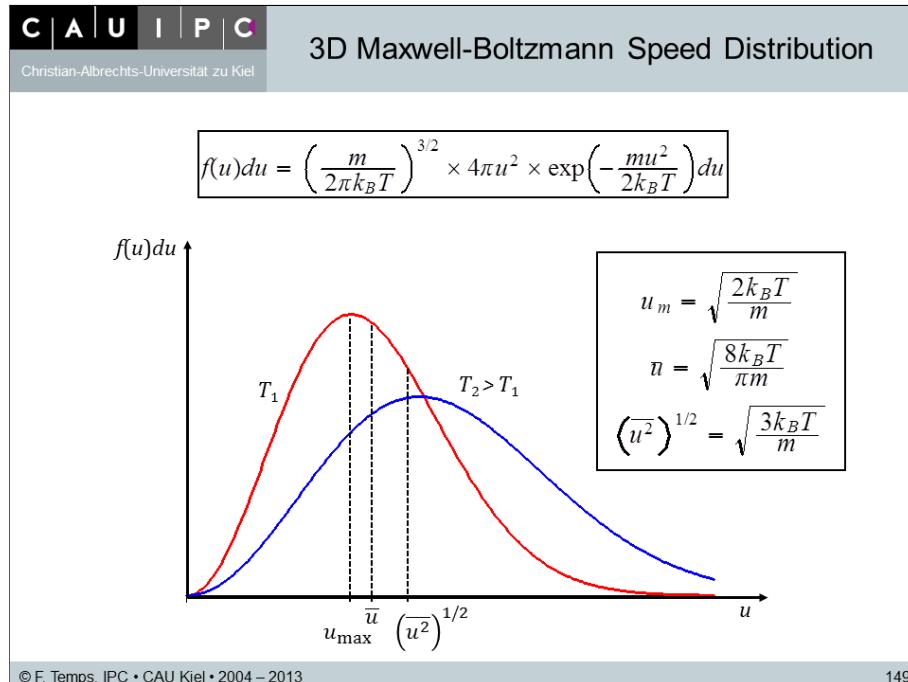
$$u^2 = \frac{2k_B T}{m} t^2 \quad (5.66)$$

\curvearrowright

$$\int_0^\infty f(u) du = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times 4\pi \int_0^\infty \frac{2k_B T}{m} t^2 e^{-t^2} \left(\frac{2k_B T}{m} \right)^{1/2} dt \quad (5.67)$$

$$= 4\pi \times \left(\frac{1}{\pi} \right)^{3/2} \int_0^\infty t^2 e^{-t^2} dt = 4\pi \times \left(\frac{1}{\pi} \right)^{3/2} \times \frac{1}{4} \sqrt{\pi} = 1 \quad (5.68)$$

- **Figure 5.4:** 3D Maxwell-Boltzmann speed distribution.



- **Notice the differences between the following quantities:**

- Value at maximum of $f(u)$:

$$u_{\max} = \sqrt{\frac{2k_B T}{m}} \quad (5.69)$$

- Mean speed:

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m}} \quad (5.70)$$

- Root mean square value:

$$(\bar{u^2})^{1/2} = \sqrt{\frac{3k_B T}{m}} \quad (5.71)$$

- **Table 5.1:** Mean molecular speed values for some gases @ $T = 298$ K.

gas	\bar{u} [m / s]
H	2511
H_2	1776
He	1255
O_2	444
CO_2	379
Hg	178
^{238}U	163

- **Kinetic energy distribution function:** We may substitute ϵ_T for u in Eq. 5.64:

$$\epsilon_T = \frac{1}{2}mu^2 \quad (5.72)$$

$$\curvearrowright u = \left(\frac{2\epsilon_T}{m} \right)^{1/2} \quad (5.73)$$

$$\curvearrowright \frac{du}{d\epsilon_T} = \left(\frac{2}{m} \right)^{1/2} \times \frac{1}{2} \times (\epsilon_T)^{-1/2} = \left(\frac{1}{2m} \right)^{1/2} (\epsilon_T)^{-1/2} \quad (5.74)$$

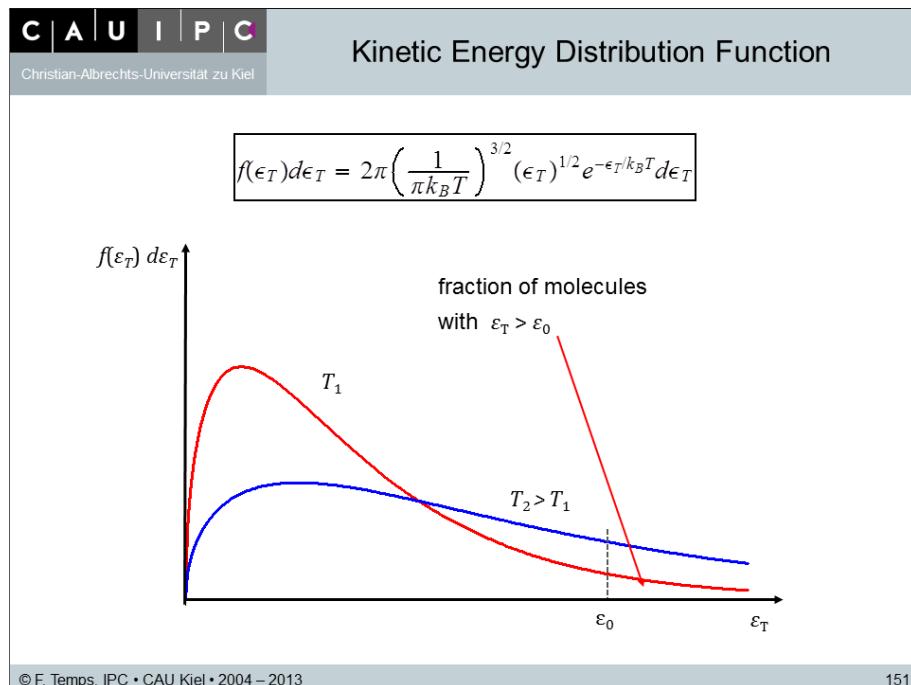
$$\curvearrowright du = \left(\frac{1}{2m} \right)^{1/2} (\epsilon_T)^{-1/2} d\epsilon_T \quad (5.75)$$

Insertion into Eq. 5.64 gives (see Fig. 5.5)

$$f(\epsilon_T) d\epsilon_T = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times 4\pi \left(\frac{2\epsilon_T}{m} \right) \times e^{-\epsilon_T/k_B T} \times \left(\frac{1}{2m} \right)^{1/2} \left(\frac{1}{\epsilon_T} \right)^{1/2} d\epsilon_T \quad (5.76)$$

$$\curvearrowright \boxed{f(\epsilon_T) d\epsilon_T = 2\pi \left(\frac{1}{\pi k_B T} \right)^{3/2} (\epsilon_T)^{1/2} e^{-\epsilon_T/k_B T} d\epsilon_T} \quad (5.77)$$

- **Figure 5.5:** Maxwell-Boltzmann distribution function for the kinetic energy.



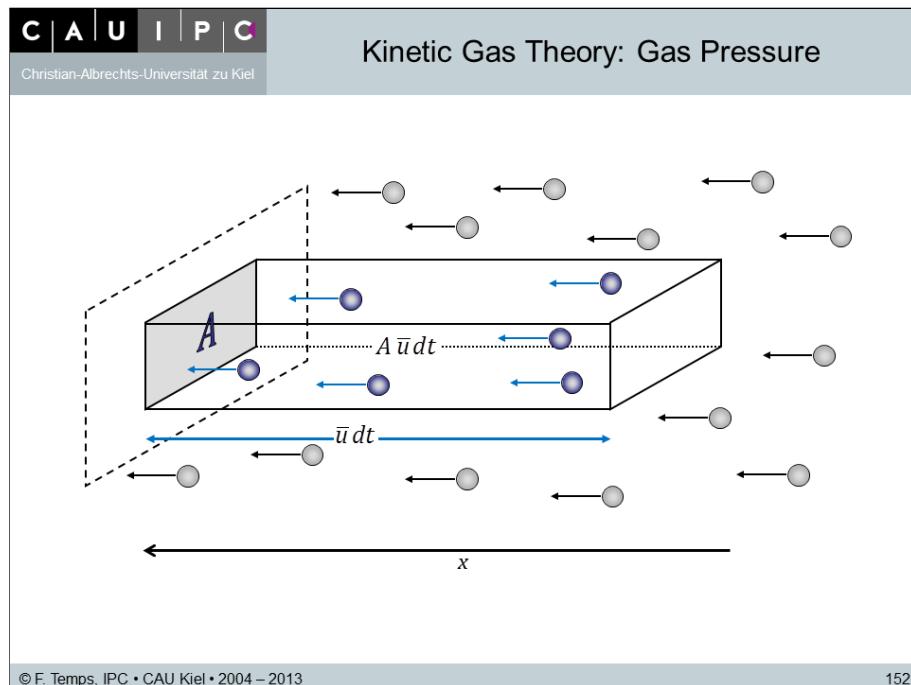
The fraction of molecules with $\epsilon_T > \epsilon_0$ is temperature dependent.

5.2.2 The rate of wall collisions in 3D

Earlier, we calculated the rate of wall collisions of the molecules of a gas with mass m and number density N in a container of volume V and the resulting gas pressure P using a simplified model by assuming that $\frac{1}{6}$ of all molecules have a fixed speed $\bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$ in $+x$ direction (cf. Fig. 5.6). In this simple picture, we neglected the 3D molecular velocity distribution. We obtained the correct result only due to a cancelation of two errors (assumption of fixed $\frac{1}{6}\bar{u}$ and 3D distribution). In the following,

- (1) we briefly review the simplified picture,
- (2) we then proceed to derive the correct results by appropriate averaging over the velocity/speed distribution.

► **Figure 5.6:** Simplified model for the calculation of the pressure of an ideal gas.



► **Simplified model for the calculation of the pressure of an ideal gas:**

- In the time dt , all gas molecules (mass m) in the volume $A \bar{u}_{+x} dt$ hit the wall area A .
- Number of wall collisions dZ in time dt (with number density N):

$$dZ = N \times \frac{1}{6} \times A \times \bar{u} dt \quad (5.78)$$

- Momentum change dp due to wall collision, force on wall, and pressure:

$$dp = 2m\bar{u} \times N \frac{1}{6} A \bar{u} dt \quad (5.79)$$

- Gas pressure:

$$P = \frac{F}{A} = \frac{1}{A} \frac{dp}{dt} = \frac{1}{A} \times 2m\bar{u} \times N \frac{1}{6} A \bar{u} \quad (5.80)$$

↷

$$P = \frac{1}{3} N m \bar{u}^2 \quad (5.81)$$

- Result for 1 mol ($N = \frac{N_L}{V}$ with $N_L = 6.022 \times 10^{23} \text{ mol}^{-1}$ and $\bar{\epsilon}_{\text{kin}} = \frac{m\bar{u}^2}{2}$):

$$P\bar{V} = \frac{1}{3} N_L m \bar{u}^2 = \frac{2}{3} N_L \bar{\epsilon}_{\text{kin}} = \frac{2}{3} N_L \times \frac{3}{2} k_B T = RT \quad (5.82)$$

► **Correct derivation of the gas kinetic wall collision frequency:**

- Number of molecules with velocities u_x, u_y, u_z in a volume of $A u dt$ with $u = \sqrt{u_x^2 + u_y^2 + u_z^2}$ (cf. Fig. 5.7) that will hit the area A in the time dt :

$$dN(u_x, u_y, u_z) = N A |u_x| dt \frac{N(u_x)}{N} du_x \frac{N(u_y)}{N} du_y \frac{N(u_z)}{N} du_z \quad (5.83)$$

- To find the number of all molecules hitting A in dt , we have to integrate over all positive u_x and over all (positive and negative) u_y and u_z , using the 1D-Maxwell-Boltzmann distributions $f(u_x) du_x = \frac{N(u_x)}{N} du_x$, etc.:

$$dN = N A dt \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty |u_x| \exp\left(-\frac{mu_x^2}{2k_B T}\right) \exp\left(-\frac{mu_y^2}{2k_B T}\right) \exp\left(-\frac{mu_z^2}{2k_B T}\right) du_z du_y du_x \quad (5.84)$$

We know that the distributions over u_y and u_z are normalized to 1. Hence, we only have to solve the integral over u_x , which we do by the substitution

$$t = \left(\frac{m}{2k_B T} \right)^{1/2} u_x \curvearrowright dt = \left(\frac{m}{2k_B T} \right)^{1/2} du_x \curvearrowright du_x = \left(\frac{2k_B T}{m} \right)^{1/2} dt \quad (5.85)$$

↷

$$\int_0^\infty |u_x| \exp\left(-\frac{mu_x^2}{2k_B T}\right) du_x = \int_0^\infty \left(\frac{2k_B T}{m} \right)^{1/2} |t| e^{-t^2} \left(\frac{2k_B T}{m} \right)^{1/2} dt \quad (5.86)$$

$$= \frac{2k_B T}{m} \int_0^\infty t e^{-t^2} dt = \frac{2k_B T}{m} \frac{1}{2} = \frac{k_B T}{m} \quad (5.87)$$

- Result:³⁷

$$dN = N A dt \left(\frac{m}{2\pi k_B T} \right)^{1/2} \times \frac{k_B T}{m} = N A dt \times \left(\frac{k_B T}{2\pi m} \right)^{1/2} \quad (5.88)$$

↷

$$Z_{\text{wall}} = \frac{dN}{A dt} = N \times \left(\frac{k_B T}{2\pi m} \right)^{1/2} \quad (5.89)$$

This can be rewritten using the mean molecular speed \bar{u} , because

$$Z_{\text{wall}} = N \times \frac{1}{4} \left(\frac{16k_B T}{2\pi m} \right)^{1/2} = N \times \frac{1}{4} \left(\frac{8k_B T}{\pi m} \right)^{1/2} \quad (5.90)$$

With

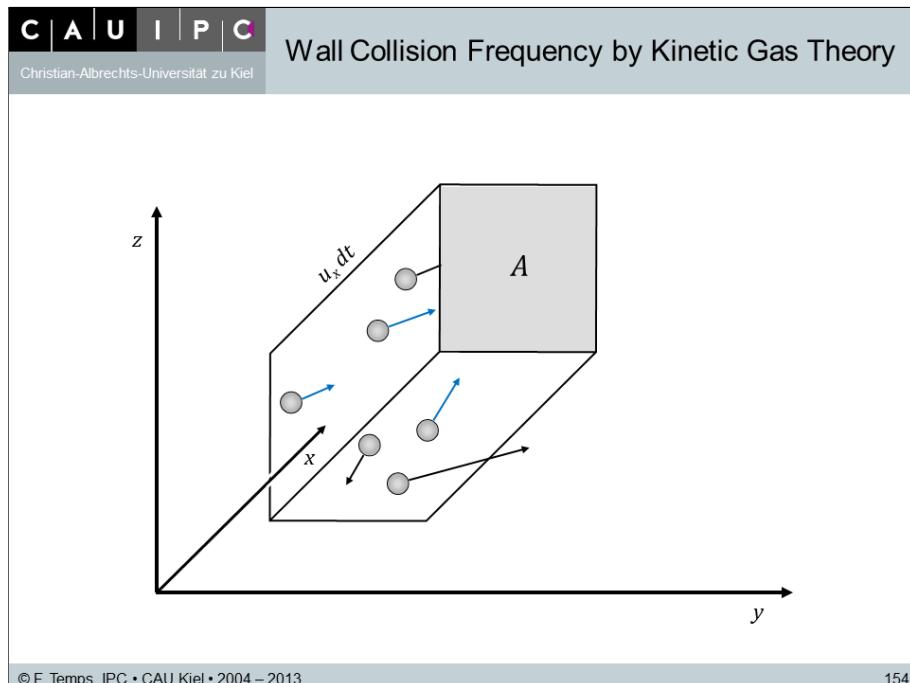
$$\boxed{\bar{u} = \left(\frac{8k_B T}{\pi m} \right)^{1/2}} \quad (5.91)$$

we thus obtain the

- Final result for the gas kinetic collision frequency:

$$\boxed{Z_{\text{wall}} = \frac{1}{4} N \bar{u}} \quad (5.92)$$

- **Figure 5.7:** On the derivation of the gas kinetic wall collision frequency.



³⁷ Notice that two of the three $\left(\frac{m}{2\pi k_B T} \right)^{1/2}$ factors in Eq. 5.84 above are compensated by the integrations over u_y and u_z , only one $\left(\frac{m}{2\pi k_B T} \right)^{1/2}$ factor remains.

► **Correct derivation of the gas pressure and the ideal gas equation:**

- Likewise, we take the differential number of wall collisions for specific speeds (Eq. 5.83) to compute the momentum change $dp_x(u_x, u_y, u_z)$ in time dt

$$dp_x(u_x, u_y, u_z) = 2m |u_x| \times N A |u_x| dt \times f(u_x) du_x f(u_y) du_y f(u_z) du_z \quad (5.93)$$

- Inserting again the 1D-Maxwell-Boltzmann distributions and integrating over all positive u_x and all u_y, u_z , we find the total momentum change in time dt :

$$dp_x = N A dt \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times 2m \times \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty u_x^2 \exp\left(-\frac{mu_x^2}{2k_B T}\right) \exp\left(-\frac{mu_y^2}{2k_B T}\right) \exp\left(-\frac{mu_z^2}{2k_B T}\right) du_x du_y du_z \quad (5.94)$$

- Pressure P for $N = \frac{N_L}{\bar{V}}$, again using the substitution $t = \left(\frac{m}{2k_B T}\right)^{1/2} u_x$

$$P = \frac{dp_x}{A dt} = \frac{N_L}{\bar{V}} \left(\frac{m}{2\pi k_B T} \right)^{1/2} \times 2m \int_0^\infty u_x^2 \exp\left(-\frac{mu_x^2}{2k_B T}\right) du_x \quad (5.95)$$

↷

$$P = \frac{N_L}{\bar{V}} \left(\frac{1}{\pi} \right)^{1/2} 2m \frac{2k_B T}{m} \int_0^\infty t^2 e^{-t^2} dt = \frac{N_L}{\bar{V}} k_B T \quad (5.96)$$

↷

$$\boxed{p\bar{V} = RT} \quad (5.97)$$

Thus, we have fixed our earlier simple derivations by appropriately integrating over the Maxwell-Boltzmann velocity distribution of the molecules.

5.3 Transport processes in gases

5.3.1 The general transport equation

- **Definition of the flux \vec{J} of a quantity:** We consider a generic *transport property*

$$\Gamma \quad (5.98)$$

which differs in magnitude along the z direction, i.e., has the gradient

$$\text{grad } \Gamma \quad (5.99)$$

The flux of Γ through an area A in time dt is defined as

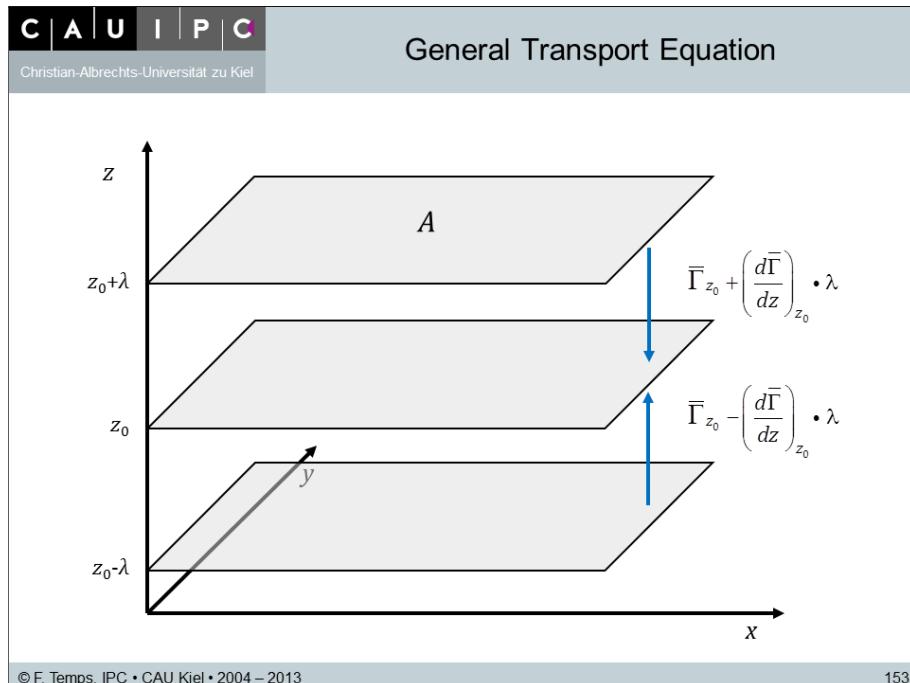
$$\vec{J}_\Gamma = \frac{d\Gamma}{A dt} \quad (5.100)$$

and can be written as

$$\vec{J}_\Gamma = -a \text{grad } \Gamma \quad (5.101)$$

Kinetic gas theory allows us to derive a general equation for the proportionality constant a .

- **Figure 5.8:** Derivation of the general transport equation.



► **The general transport equation:** We consider the net flux of Γ through an area A at $z = z_0$ that is transported by gas molecules coming from an area above at $z = z_0 + \lambda$ and from below from an area above at $z = z_0 - \lambda$ (where λ is the mean free pathlength). Denoting the respective transport quantity per molecule as $\bar{\Gamma}$, these partial fluxes are given by the number of gas kinetic collisions hitting on A ($z = z_0$) times the $\bar{\Gamma}$ carried by each gas molecule (number density N):

- Using the gas kinetic wall collision frequency $Z_{\text{wall}} = \frac{1}{4} N \bar{u}$ (Eq. 5.92), we obtain

$$d\Gamma_+ = \frac{1}{4} N \bar{u} \times A \times \left(\bar{\Gamma}_{z_0} + \left(\frac{d\bar{\Gamma}}{dz} \right) \lambda \right) dt \quad (5.102)$$

and

$$d\Gamma_- = \frac{1}{4} N \bar{u} \times A \times \left(\bar{\Gamma}_{z_0} - \left(\frac{d\bar{\Gamma}}{dz} \right) \lambda \right) dt \quad (5.103)$$

- Net effect:

$$d\Gamma = d\Gamma_+ - d\Gamma_- = \frac{1}{2} N \bar{u} \times A \times \left(\frac{d\bar{\Gamma}}{dz} \right) \lambda dt \quad (5.104)$$

- Net flux (with $-$ sign to account for the fact that the flux is directed along the downhill gradient of $\bar{\Gamma}$):

$$\boxed{\vec{J}_\Gamma = \frac{d\Gamma}{A dt} = -\frac{1}{2} \bar{u} \lambda N \left(\frac{d\bar{\Gamma}}{dz} \right)} \quad (5.105)$$

with \bar{u} given by (see the derivation of Z_{wall} above)

$$\boxed{\bar{u} = \left(\frac{8k_B T}{\pi m} \right)^{1/2}} \quad (5.106)$$

and, for only one type of gas molecules A (i.e., A - A collisions),

$$\boxed{\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi d^2 \times N}} \quad (5.107)$$

- If N also varies along z (diffusion), Eq. 5.105 may be recast by defining the overall transport quantity $\bar{\Gamma}'$ from the transport quantity per molecule $\bar{\Gamma}$ as

$$\bar{\Gamma}' = N \bar{\Gamma} \quad (5.108)$$

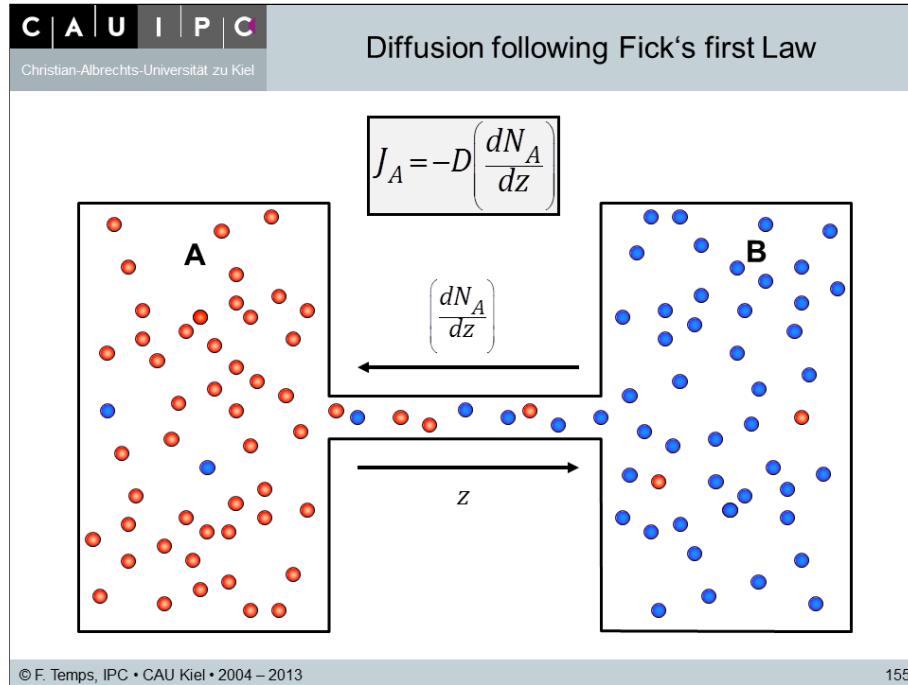
into the form

$$\boxed{\vec{J}_\Gamma = -\frac{1}{2} \bar{u} \lambda \left(\frac{d\bar{\Gamma}'}{dz} \right)} \quad (5.109)$$

In the following, we shall apply Eqs. 5.105 or 5.109 to determine the self-diffusion coefficient ($\bar{\Gamma} = 1$, $\bar{\Gamma}' = N$), the heat conductivity ($\bar{\Gamma} = U$), and the viscosity ($\bar{\Gamma} = \mu u_x$) of gases.

5.3.2 Diffusion

- **Figure 5.9:** The diffusion in a mixture A + B of one sort of molecules A against a time-independent concentration gradient $\frac{dN_A}{dz}$ is described by Fick's first law.



- Fick's first law:

$$\vec{J}_A = \frac{dN_A}{A dt} = -D \left(\frac{dN_A}{dz} \right) \quad (5.110)$$

- In order to derive an expression for the self-diffusion coefficient D (diffusion of an isotope of A in normal A), we make the ansatz

$$\bar{\Gamma} = 1, \bar{\Gamma}' = N_A \quad (5.111)$$

↷

$$\vec{J}_A = -\frac{1}{2} \bar{u} \lambda \left(\frac{dN_A}{dz} \right) \quad (5.112)$$

- Result:

$$D = \frac{1}{2} \bar{u} \lambda \quad (5.113)$$

- Fick's second law (time-dependent concentration gradient):

$$\frac{\partial N_A}{\partial t} = D \frac{\partial^2 N_A}{\partial z^2} \quad (5.114)$$

- Einstein's diffusion law in 1D:

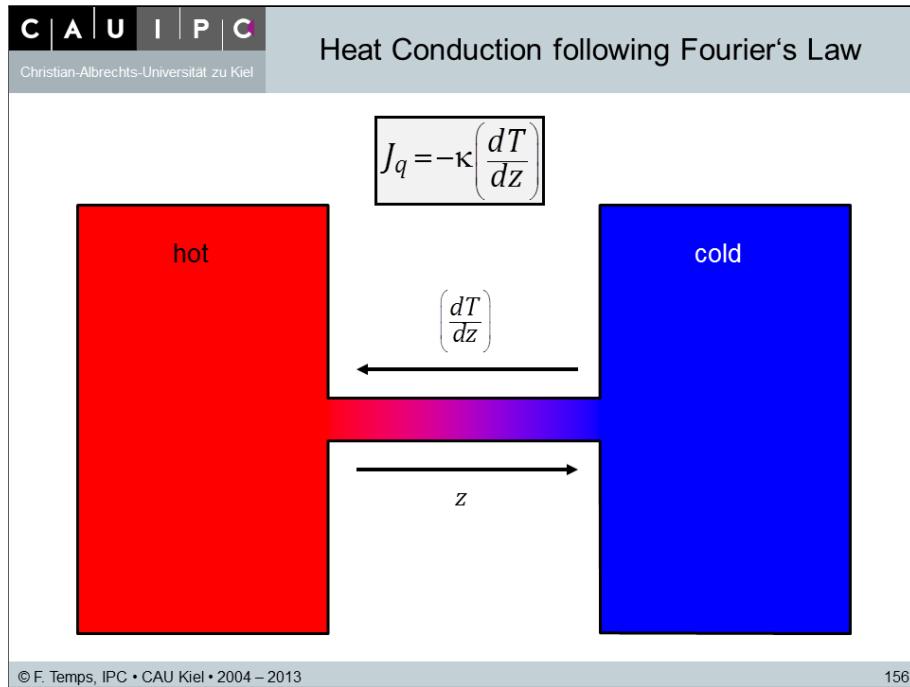
$$\Delta z^2 = 2Dt \quad (5.115)$$

- Einstein's diffusion law in 3D:

$$\Delta s^2 = 6Dt \quad (5.116)$$

5.3.3 Heat conduction

- **Figure 5.10:** Heat conduction is described by Fourier's law.



- Fourier's law (for constant temperature gradient):

$$\vec{J}_q = \frac{dq}{A dt} = -\kappa \left(\frac{dT}{dz} \right) \quad (5.117)$$

- Ansatz:

$$\bar{\Gamma} = U = \text{internal energy per molecule} \quad (5.118)$$

↷

$$\vec{J}_q = -\frac{1}{2} \bar{u} \lambda N \left(\frac{dU}{dz} \right) \quad (5.119)$$

$$= -\frac{1}{2} \bar{u} \lambda N \left(\frac{dU}{dT} \right) \left(\frac{dT}{dz} \right) \quad (5.120)$$

$$= -\frac{1}{2} \bar{u} \lambda N \left(\frac{dc_V dT}{dT} \right) \left(\frac{dT}{dz} \right) \quad (5.121)$$

$$= -\frac{1}{2} \bar{u} \lambda N c_V \left(\frac{dT}{dz} \right) \quad (5.122)$$

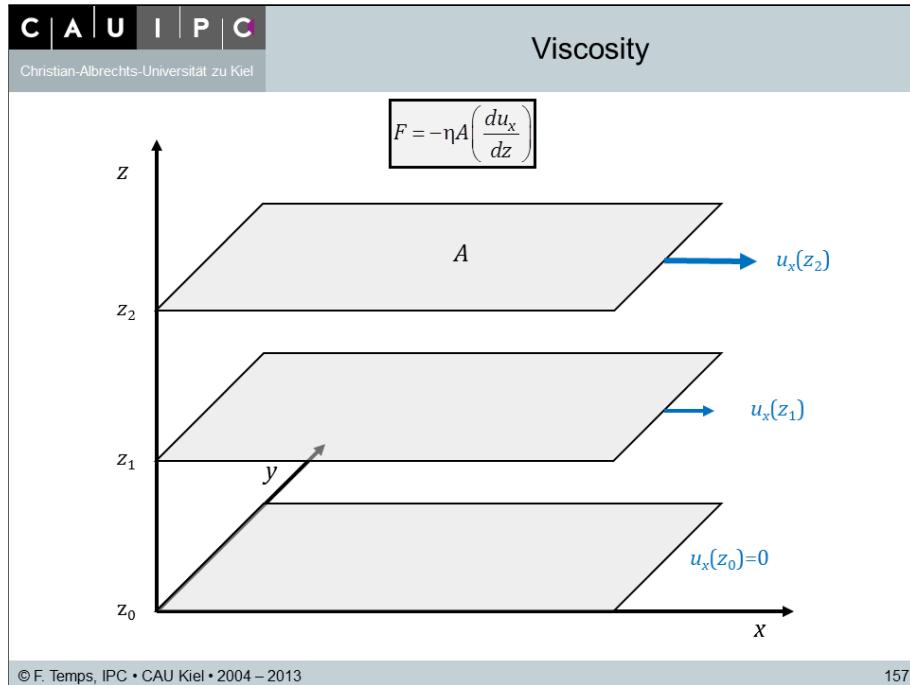
- Result:

$$\kappa = \frac{1}{2} \bar{u} \lambda N c_V \quad (5.123)$$

with N = number density and c_V = specific heat per molecule.

5.3.4 Viscosity

► **Figure 5.11:** Newton's law describes the inner friction in laminar flow.



- Newton's law:

$$\frac{F}{A} = -\eta \left(\frac{du_x}{dz} \right) \quad (5.124)$$

- Ansatz:

$$\bar{\Gamma} = mu_x = \text{momentum per molecule in } x \text{ direction} \quad (5.125)$$

↷

$$\begin{aligned} \vec{J}_{px} &= -\frac{1}{2} \bar{u} \lambda N \left(\frac{d(mu_x)}{dz} \right) \\ &= \frac{1}{A} \frac{d(mu_x)}{dt} = \frac{1}{A} \frac{dp}{dt} = \frac{F}{A} \end{aligned}$$

- Result:

$$\eta = \frac{1}{2} \bar{u} \lambda m N \quad (5.126)$$

with N = number density and m = mass of molecule.

5.4 Advanced collision theory

The hard sphere model is a very primitive model. In reality, we have to account for the following:

- The reaction probability depends on exact details of the collision, i.e.,

$$\text{hard sphere model} \rightarrow P(\epsilon_T, b, \dots) \quad (5.127)$$

- Molecules are not hard spheres with $\sigma^{HS} = \pi d^2$ but “soft”, i.e., the reactive cross section depends on the relative speed (or kinetic energy)

$$\sigma^{HS} \rightarrow \sigma(u) \rightarrow \sigma(\epsilon_T) \quad (5.128)$$

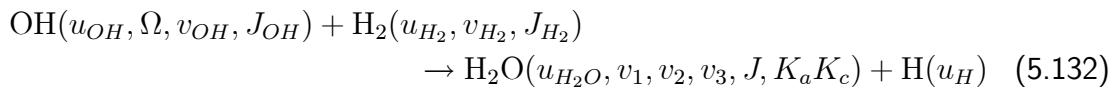
- The speed distribution follows the Maxwell-Boltzmann distribution, i.e.,

$$\overline{u_{rel}} \rightarrow f(u) \rightarrow f(\epsilon_T) \quad (5.129)$$

- Molecules in different quantum states α_i behave differently, i.e.,

$$\sigma \rightarrow \sigma(\alpha_i; \epsilon_T) \quad (5.130)$$

- **Examples:** The complexity of the problem is illustrated in Fig. 5.12 by two examples:



As can be seen, the reaction rate is expected to depend on u_i (speed, translational energy), v_i (vibrational quantum numbers (ν_1 = symmetric stretch, ν_2 = bend, ν_3 = antisymmetric stretch)), J_i , K_a , K_c (rotational quantum numbers), Ω (fine structure state, electronic state). In addition, the products are scattered into the spatial angles θ , ϕ .

- **Figure 5.12:** Quantum state-specific elementary reactions.

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Microscopic Treatment of Elementary Chemical Reactions

Examples of elementary reactions in specific quantum states:

$$\text{D}(u_D) + \text{H}_2(u_{H_2}, v_{H_2}, J_{H_2}) \rightarrow \text{HD}(u_{HD}, v_{HD}, J_{HD}) + \text{H}(u_H)$$

$$\text{OH}(u_{OH}, \Omega_{OH}, v_{OH}, J_{OH}) + \text{H}_2(u_{H_2}, v_{H_2}, J_{H_2}) \rightarrow \text{H}_2\text{O}(u_{H_2\text{O}}, v_1, v_2, v_3, J, K_a, K_c) + \text{H}(u_H)$$

u_i : speeds (translational energy)
 v_i : vibrational quantum numbers
 J, K_a, K_c : rotational quantum numbers
 Ω_{OH} : fine structure (electronic state)
 θ, ϕ : spatial scattering angle

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We shall now derive the **fundamental equation of collision theory** that allows us to account for those effects.

5.4.1 Fundamental equation for reactive scattering in crossed molecular beams

- Consider the following reactive scattering process (Fig. 5.13):



- Intensity of beam of A:

$$I_A = u \times N_A \quad (5.134)$$

Is this reasonable? \Rightarrow Look at the physical dimensions of $u \times N_A$:

$$[\text{cm/s}] \times [\text{molecules/cm}^3] = [\text{molecules/cm}^2 \text{s}] = [\text{intensity}] \quad (5.135)$$

- Depletion of intensity of A due to scattering by B:

$$\frac{dI_A}{u dN_A} = -\sigma(u) \times \frac{I_A}{u N_A} \times N_B \times \frac{dl}{u dt} \quad (5.136)$$

\curvearrowright rate equation:

$$\frac{dN_A}{dt} = -\sigma(u) u N_A N_B \quad (5.137)$$

- Rate coefficient for a given value of u :

$$k(u) = \sigma(u) u \quad (5.138)$$

- Averaging over the speed distribution $f(u)$ leads to the **fundamental equation** of all improved collision theories:

$$k(T) = \langle u \sigma(u) \rangle \quad (5.139)$$

i.e.,

$$k(T) = \int_0^\infty u \sigma(u) f(u, T) du \quad (5.140)$$

- Frequently used approximation: Since the explicit form of $\sigma(u)$ is usually not known, we write

$$k(T) = \langle u \rangle \langle \sigma(u) \rangle \quad (5.141)$$

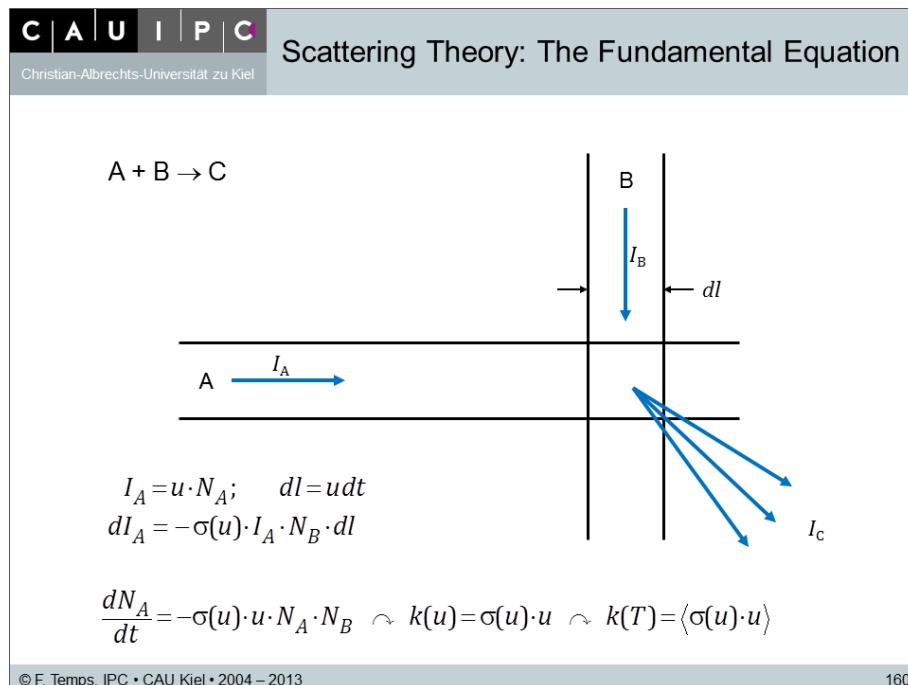
with

$$\langle u \rangle = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \quad (5.142)$$

and

$$\langle \sigma(u) \rangle = u\text{-averaged (reactive) cross section} \quad (5.143)$$

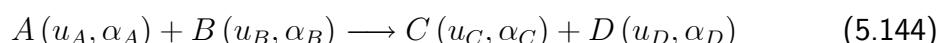
- **Figure 5.13:** Derivation of the fundamental equation.



5.4.2 Crossed molecular beam experiments

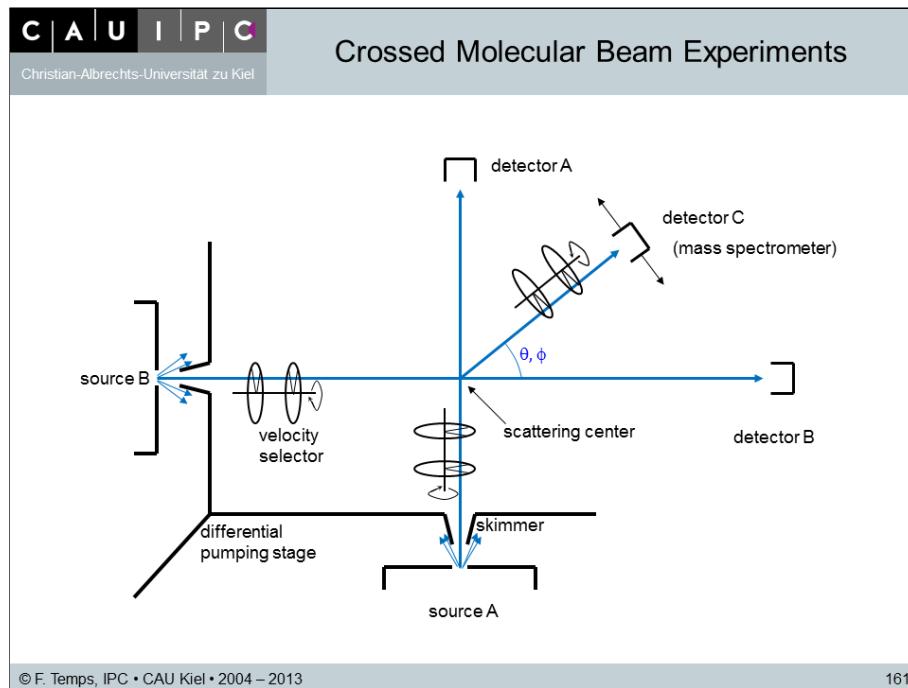
- **Differential and integral reactive cross sections:** Experiments with crossed molecular beams allow us to measure **differential** and **integral reactive cross sections** (Herschbach 1987, Lee 1987).

We consider the reaction



where u_i denotes the speeds of the molecules and α_i stands for the quantum numbers of their energy states (electronic, vibrational, rotational, nuclear spin). In an ideal experiment (which has yet to be performed), all α_i of the reactants are defined by, e.g., a specific excitation using laser, and the α_i of the products are determined by some probe laser. The u_i can be determined in a molecular beam experiment using a rotating disk velocity selector (see Fig. 5.14).

- **Figure 5.14:** Measurement of differential cross sections in crossed molecular beam experiments.



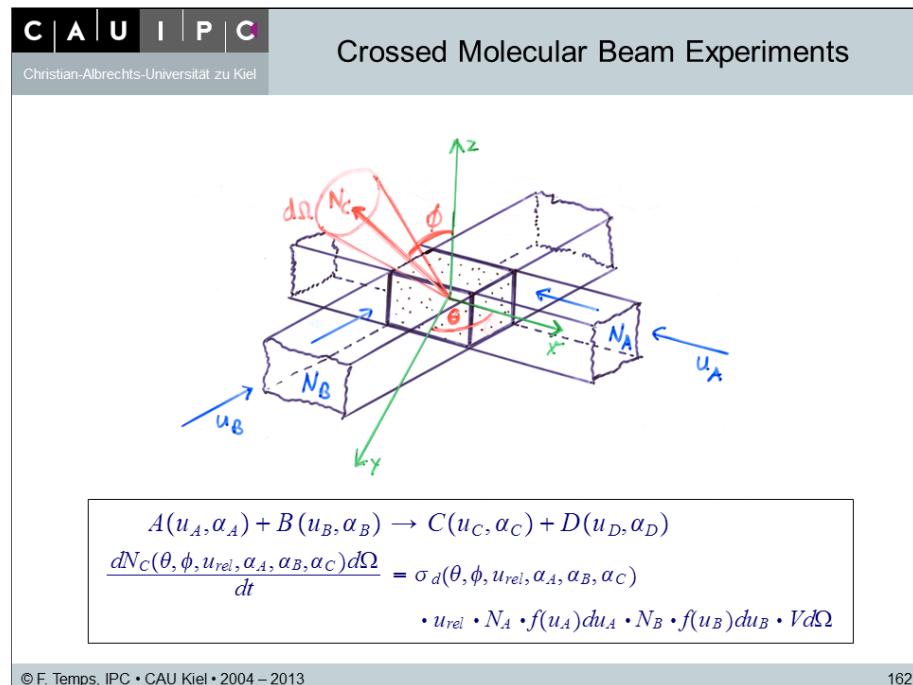
- **Differential and integral cross sections from crossed molecular beam experiments:**

- We define the **differential cross section** $\sigma_d(\theta, \phi, u_{rel}, \alpha_A, \alpha_B, \alpha_C)$ for scattering of products C into the solid angle element $d\Omega$ at θ, ϕ such that

$$\frac{dN_C(\theta, \phi, u_{rel}, \alpha_A, \alpha_B, \alpha_C) d\Omega}{dt} = \sigma_d(\theta, \phi, u_{rel}, \alpha_A, \alpha_B, \alpha_C) \times u_{rel} \times N_A \times f(u_A) \times N_B \times f(u_B) \times V d\Omega \quad (5.145)$$

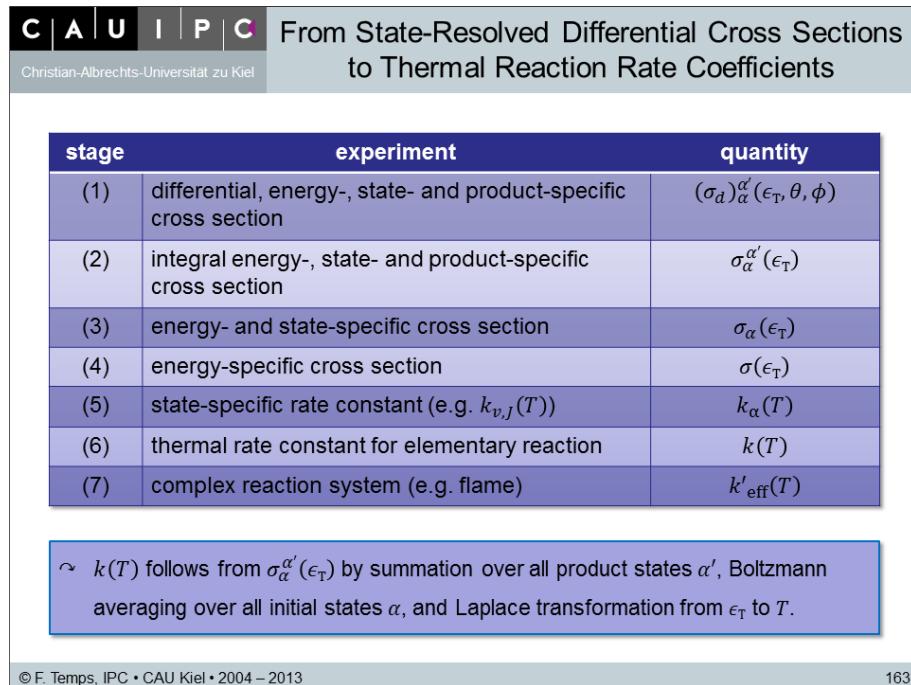
- Corresponding **integral cross sections** are obtained by integration over θ and ϕ .
- Depending on the scattering process of interest, we distinguish between
 - elastic cross sections ($\sigma_{elast.}$): measure of the size of the molecules,
 - inelastic cross sections ($\sigma_{inelast.}$): measure of the efficiency of energy transfer processes,
 - reactive cross sections ($\sigma_{react.}$): measure of reactivity.

- **Figure 5.15:** Measurement of differential cross sections in crossed molecular beam experiments.



5.4.3 From differential cross sections $\sigma(\dots)$ to reaction rate constants $k(T)$

- **Figure 5.16:** The strategy.



- **1 → 2 : Integration over angles:**

$$\sigma_{\alpha}^{\alpha'}(\epsilon_T) = \int_0^{2\pi} \int_0^{\pi} (\sigma_d)_{\alpha}^{\alpha'}(\epsilon_T, \theta, \phi) \sin \theta d\theta d\phi \quad (5.146)$$

- **2 → 3 : Summation over all product quantum states α' :**

$$\sigma_{\alpha}(\epsilon_T) = \sum_{\alpha'} \sigma_{\alpha}^{\alpha'}(\epsilon_T) \quad (5.147)$$

- **3 → 4 : Thermal averaging over initial quantum states α :**

$$\sigma(\epsilon_T) = \sum_{\alpha} f_{\alpha} \times \sigma_{\alpha}(\epsilon_T) \quad (5.148)$$

with the **Boltzmann factor** f_{α} and the **partition function** Q_{α}

$$f_{\alpha} = \frac{g_{\alpha} e^{-\epsilon_{\alpha}/k_B T}}{\sum g_{\alpha} e^{-\epsilon_{\alpha}/k_B T}} = \frac{g_{\alpha} e^{-\epsilon_{\alpha}/k_B T}}{Q_{\alpha}} \quad (5.149)$$

$$Q_{\alpha} = \sum_{\alpha} g_{\alpha} e^{-\epsilon_{\alpha}/k_B T} \quad (5.150)$$

↷

$$\sigma(\epsilon_T) = \sum_{\alpha} \sigma_{\alpha}(\epsilon_T) \times \frac{g_{\alpha} e^{-\epsilon_{\alpha}/k_B T}}{Q} \quad (5.151)$$

- **5 → 6 : Thermal averaging over all ϵ_T :**

$$\begin{aligned}
 k(T) &= \sum_{\alpha} f_{\alpha} \times k_{\alpha}(T) \\
 &= \sum_{\alpha} \frac{g_{\alpha} e^{-\epsilon_{\alpha}/k_B T}}{Q_{\alpha}} \times k_{\alpha}(T) \\
 &= \int_{\alpha} \frac{g_{\alpha} e^{-\epsilon_{\alpha}/k_B T}}{Q_{\alpha}} \times k_{\alpha}(T) d\epsilon_{\alpha}
 \end{aligned}$$

- **3 → 5 and 4 → 6 : Laplace Transformation:**

$$k(T) \propto \int_0^{\infty} \epsilon_T \times \sigma(\epsilon_T) \times e^{-\epsilon_T/k_B T} d\epsilon_T \quad (5.152)$$

This expression follows from the fundamental equation (Eq. 5.140) by substituting ϵ_T for u . The exact transformation (giving the correct factors before the integral) will be carried out below (see Eq. 5.162).

5.4.4 Laplace transforms in chemistry

Formally, the transformation (Eq. 5.152) is a *Laplace transformation* (see Appendix E). A Laplace transform generally described the transformation from a microscopic ("microcanonical") quantity such as $\sigma(\epsilon_T)$ to a macroscopic ("macrocanonical", i.e., T dependent) quantity such as $k(T)$.

- **Definition of the Laplace Transformation:** The Laplace transform $\mathcal{L}[f(t)]$ of a function $f(t)$ is defined as the integral

$$F(p) = \mathcal{L}[f(t)] = \int_0^{\infty} f(t) e^{-pt} dt \quad (5.153)$$

- **Inverse Laplace Transformation:**

$$f(t) = \mathcal{L}^{-1}[F(p)] = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} F(p) e^{pt} dp \quad (5.154)$$

with an arbitrary real number c .

► **Notes:**

(1) The so far best known Laplace transform to us is the partition function

$$Q(T) = \sum_i g_i e^{-\epsilon_i/k_B T} = \int_0^{\infty} \rho(\epsilon) e^{-\epsilon/k_B T} d\epsilon \quad (5.155)$$

(2) While the pathway from $\sigma(\epsilon_T)$ to $k(T)$ by forward Laplace transformation is straightforward, it is not generally straightforward to derive $\sigma(\epsilon_T)$ by inverse Laplace transformation from $k(T)$, because $k(T)$ would be needed from $T = 0$ to $T = \infty$.

5.4.5 Bimolecular rate constants from collision theory

- **Transformation from velocity to energy space:** Taking our results from kinetic gas theory, we are now in the position to apply the fundamental equation of collision theory (Eq. 5.140)

$$k(T) = \int_0^\infty u \sigma(u) f(u, T) du \quad (5.156)$$

using various functional forms for σ . Towards these ends, we first transform from u to ϵ_T by inserting $f(u)$ from Eq. 5.64 (with the reduced mass μ instead of m). We thus obtain

$$k(T) = 4\pi \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \int_0^\infty u^3 \sigma(u) \exp\left(-\frac{\mu u^2}{2k_B T}\right) du \quad (5.157)$$

As done above, we substitute for u according to

$$\epsilon_T = \frac{1}{2}\mu u^2 \quad (5.158)$$

$$\curvearrowright u = \left(\frac{2\epsilon_T}{\mu} \right)^{1/2} \quad (5.159)$$

$$\curvearrowright \frac{du}{d\epsilon_T} = \left(\frac{2}{\mu} \right)^{1/2} \frac{1}{2} \left(\frac{1}{\epsilon_T} \right)^{1/2} = \left(\frac{1}{2\mu} \right)^{1/2} \left(\frac{1}{\epsilon_T} \right)^{1/2} \quad (5.160)$$

$$\curvearrowright du = \left(\frac{1}{2\mu} \right)^{1/2} \left(\frac{1}{\epsilon_T} \right)^{1/2} d\epsilon_T \quad (5.161)$$

and obtain

$$k(T) = \left(\frac{1}{\pi\mu} \right)^{1/2} \left(\frac{2}{k_B T} \right)^{3/2} \int_{\epsilon_0}^\infty \epsilon_T \sigma(\epsilon_T) \exp\left(-\frac{\epsilon_T}{k_B T}\right) d\epsilon_T$$

$$(5.162)$$

The integration from ϵ_0 to ∞ takes into account that a reaction can occur only if $\epsilon_T > \epsilon_0$.

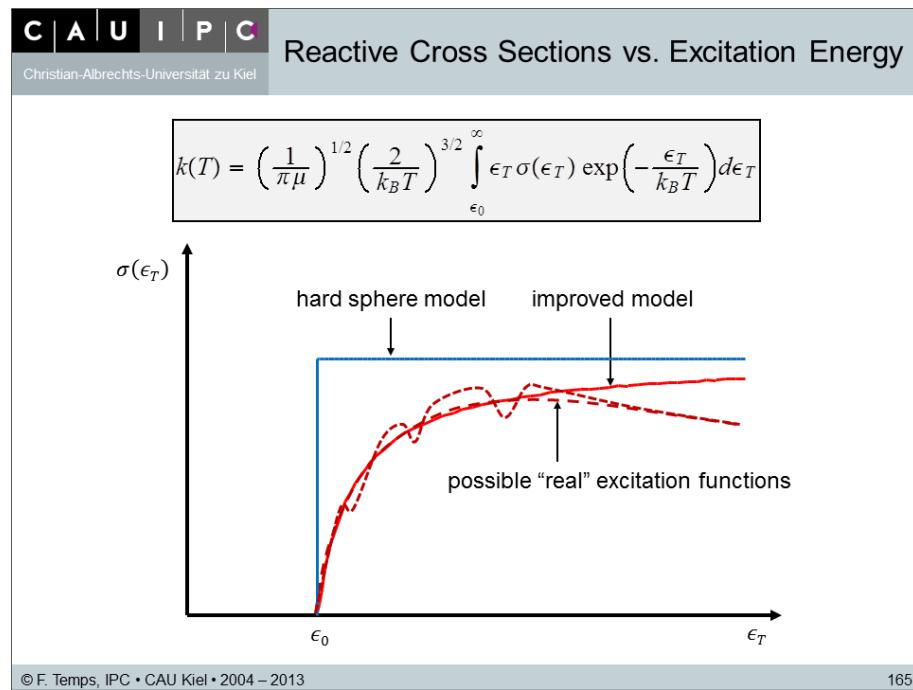
This expression is interpreted as follows:

- The function $\epsilon_T e^{-\epsilon_T/k_B T}$ describes the fraction of molecules with energy ϵ_T .
- The function $\sigma(\epsilon_T)$ in the integrand is called the **excitation function**³⁸. This can, in general, be a rather complicated (and not necessarily smooth) function (see Fig. 5.17).
- The complete integrand $\epsilon_T \sigma(\epsilon_T) e^{-\epsilon_T/k_B T}$ is called the **reaction function**³⁹, because it describes the **reactive** fraction of the molecules.
- The rate constant $k(T)$ corresponds to the area under the reaction function.

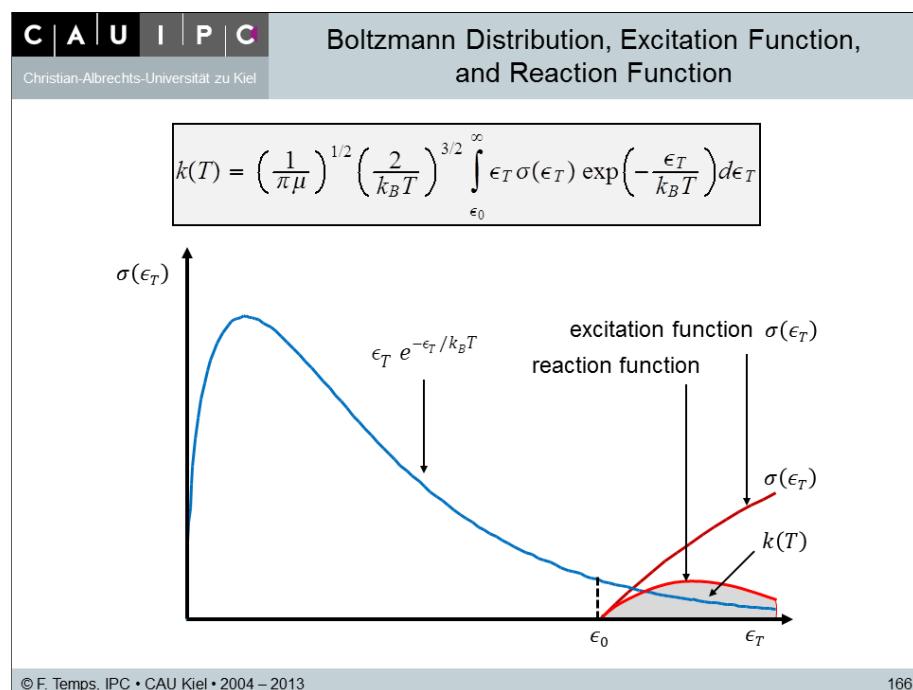
³⁸ “Anregungsfunktion”

³⁹ “Reaktionsfunktion”

- **Figure 5.17:** Advanced collision theory: The excitation function.



- **Figure 5.18:** Advanced collision theory: The reaction function.



- **Non-equilibrium energy distribution:*** The above expression for $k(T)$ is valid if the reacting molecules are in internal equilibrium, i.e., the energy states are populated according to the Boltzmann distribution.

Deviations from the Boltzmann distributions will occur in the case of very fast reactions, if the reaction is faster than the relaxation between the energy states. In this case, $k(T)$ decreases because the mean energy of the reacting molecule decreases.

Mean energy of the reacting molecules (see Fig. 5.19):

$$\bar{\epsilon} = \sum_i p_i \epsilon_i = \int_{\epsilon_0}^{\infty} p(\epsilon) \epsilon d\epsilon \quad (5.163)$$

- (1) For thermal equilibrium:

$$p(\epsilon) = f(\epsilon) \quad (5.164)$$

with $f(\epsilon)$ being the Boltzmann distribution.

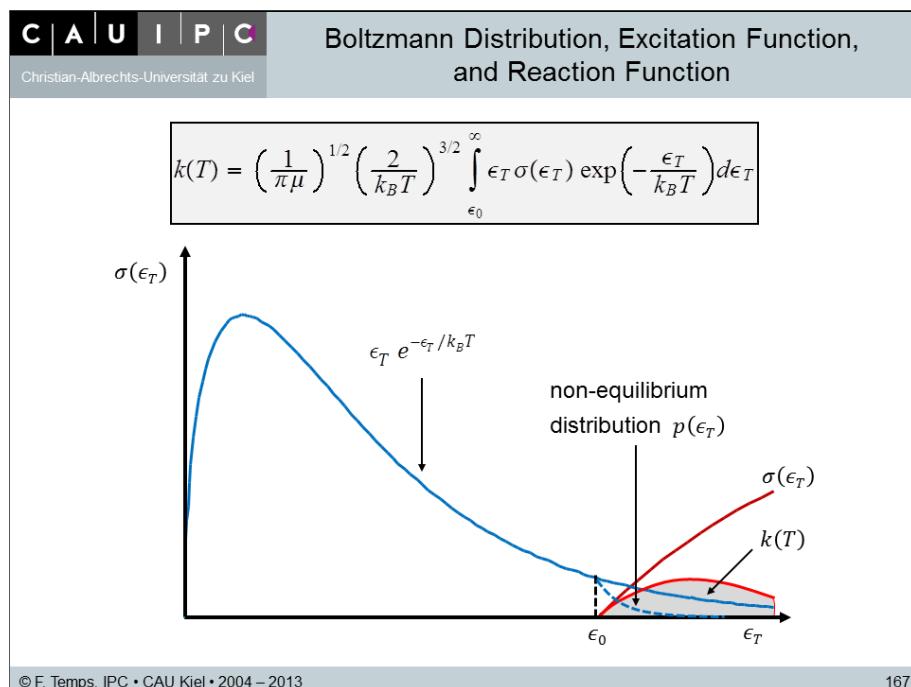
- (2) Non-equilibrium:

$$p(\epsilon) < f(\epsilon) \quad (5.165)$$

↷

$$\overline{\epsilon}_{\text{non-eq.}} < \overline{\epsilon}_{\text{eq.}} \quad (5.166)$$

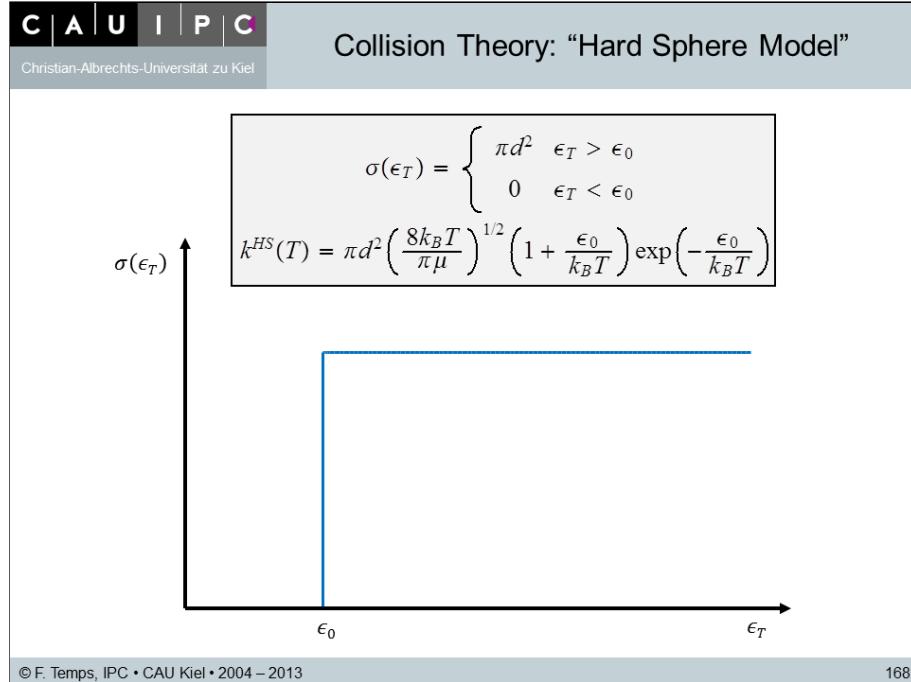
- **Figure 5.19:** Mean energy of the reacting molecules in thermal equilibrium and for a non-equilibrium situation.



- **Conclusion:** The non-equilibrium distribution leads to a *reduced* rate coefficient.

a) Advanced collision theory for hard spheres (Fig. 5.20)

► **Figure 5.20:** The hard sphere model.



(1) Ansatz for the reactive cross section:

$$\sigma(\epsilon_T) = \begin{cases} \pi d^2 & \epsilon_T > \epsilon_0 \\ 0 & \epsilon_T < \epsilon_0 \end{cases} \quad (5.167)$$

(2) Inserting this ansatz into Eq. 5.162:

$$k^{HS}(T) = \left(\frac{1}{\pi \mu} \right)^{1/2} \left(\frac{2}{k_B T} \right)^{3/2} \int_{\epsilon_0}^{\infty} \pi d^2 \epsilon_T \exp\left(-\frac{\epsilon_T}{k_B T}\right) d\epsilon_T \quad (5.168)$$

(3) Result for $k^{HS}(T)$: With

$$\int x e^{ax} dx = \frac{e^{ax}}{a^2} (ax - 1) \quad (5.169)$$

we obtain

$$\begin{aligned} k^{HS}(T) &= \left(\frac{1}{\pi \mu} \right)^{1/2} \left(\frac{2}{k_B T} \right)^{3/2} \pi d^2 \\ &\times (k_B T)^2 \times \exp\left(-\frac{\epsilon_0}{k_B T}\right) \left(-\frac{\epsilon_0}{k_B T} - 1 \right) \Big|_{\epsilon_0}^{\infty} \end{aligned} \quad (5.170)$$

↷

$$k^{HS}(T) = \pi d^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \left(1 + \frac{\epsilon_0}{k_B T} \right) \exp\left(-\frac{\epsilon_0}{k_B T}\right) \quad (5.171)$$

(4) Arrhenius activation energy:

$$E_A = RT^2 \frac{d \ln k}{dT} \quad (5.172)$$

$$\ln k \propto \frac{1}{2} \ln T + \ln \left(1 + \frac{E_0}{RT} \right) - \frac{E_0}{RT} \quad (5.173)$$

$$\frac{d \ln k}{dT} = \frac{1}{2} \frac{1}{T} + \frac{1}{1 + E_0/RT} \left(-\frac{E_0}{RT^2} \right) + \left(\frac{E_0}{RT^2} \right) \quad (5.174)$$

↷

$$E_A = E_0 + \frac{1}{2} RT - \frac{E_0}{1 + E_0/RT} \quad (5.175)$$

b) Line-of-Centers model (Figs. 5.21 - 5.22)

Even for hard spheres, because of angular momentum conservation (see below), not the entire collision energy, but only the fraction “directed” along the line of centers (*LC*) is effective.

In particular, we have

- for a collision with $b = 0$:

$$\epsilon_{LC} = \epsilon_T \quad (5.176)$$

↷ central collisions are most effective,

- for a collision with $b = d$:

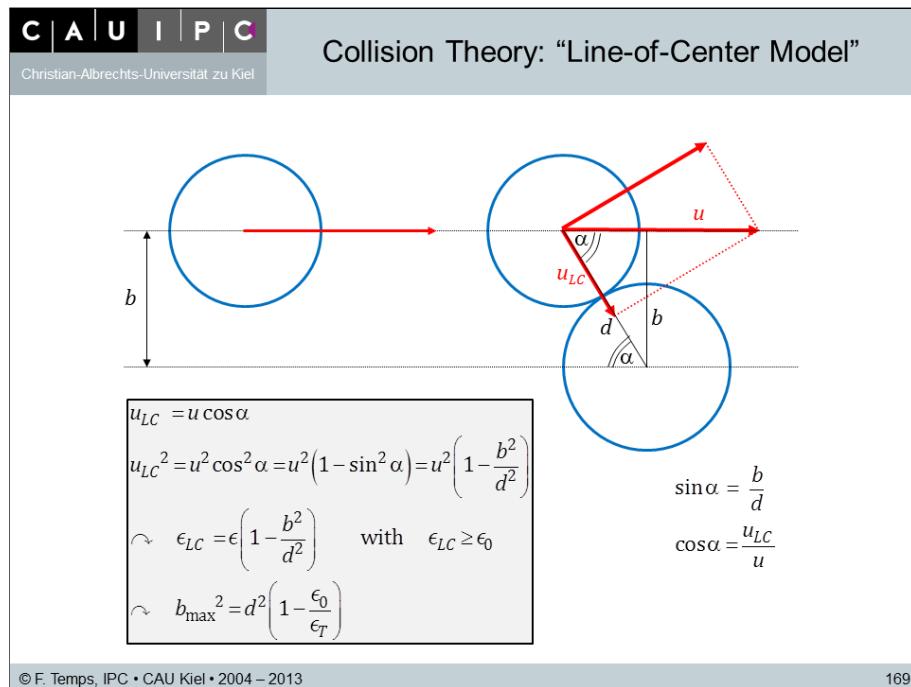
$$\epsilon_{LC} = 0 \quad (5.177)$$

↷ glancing collisions are ineffective because $\epsilon_{LC} = 0$,

- general expression (see below):

$$\epsilon_{LC} = \epsilon_T \left(1 - \frac{b^2}{d^2} \right) \quad (5.178)$$

↷ ϵ_{LC} decreases with increasing b .

► **Figure 5.21:** Collision energy along line-of-centers

Functional expression for $\sigma(\epsilon_T)$:

(1) We assume that a reaction can occur only if $\epsilon_{LC} \geq \epsilon_0$. Thus, we first determine ϵ_{LC} (see Fig. 5.21):

$$u_{LC} = u \cos \alpha \quad (5.179)$$

$$u_{LC}^2 = u^2 \cos^2 \alpha \quad (5.180)$$

$$= u^2 (1 - \sin^2 \alpha) \quad (5.181)$$

$$= u^2 \left(1 - \frac{b^2}{d^2}\right) \quad (5.182)$$

↷

$$\epsilon_{LC} = \epsilon_T \left(1 - \frac{b^2}{d^2}\right) \quad (5.183)$$

(2) We see from this expression that ϵ_{LC} decreases with increasing b . Thus, for a given ϵ_T , we have a maximal value of b (i.e., a value b_{\max}), for which $\epsilon_{LC} \geq \epsilon_0$. We determine b_{\max} from the condition that

$$\epsilon_{LC} = \epsilon_T \left(1 - \frac{b^2}{d^2}\right) \geq \epsilon_0 \quad (5.184)$$

↷

$$b^2 \leq d^2 \left(1 - \frac{\epsilon_0}{\epsilon_T}\right) = b_{\max}^2 \quad (5.185)$$

↷

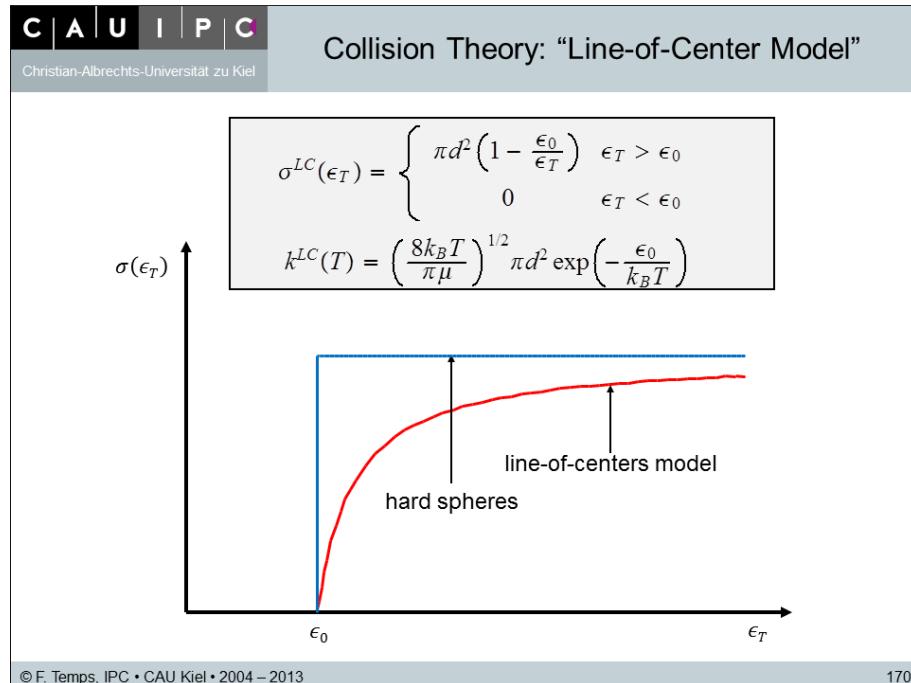
$$\sigma^{LC}(\epsilon_T) = \pi b_{\max}^2 = \pi d^2 \left(1 - \frac{\epsilon_0}{\epsilon_T}\right) \quad (5.186)$$

↷

$$\sigma^{LC}(\epsilon_T) = \begin{cases} \pi d^2 \left(1 - \frac{\epsilon_0}{\epsilon_T}\right) & \epsilon_T > \epsilon_0 \\ 0 & \epsilon_T < \epsilon_0 \end{cases} \quad (5.187)$$

$\sigma^{LC}(\epsilon_T)$ is shown as function of ϵ_T in Fig. 5.22. Crossed molecular beam experiments have indeed shown similar dependencies for a number of reactions.

- **Figure 5.22:** Reactive cross section for the line-of-centers model.



(3) Result for $k(T)$ from Eq. 5.162:

$$k^{LC}(T) = \left(\frac{1}{\pi \mu}\right)^{1/2} \left(\frac{2}{k_B T}\right)^{3/2} \times \int_{\epsilon_0}^{\infty} \pi d^2 \left(1 - \frac{\epsilon_0}{\epsilon_T}\right) \epsilon_T \exp\left(-\frac{\epsilon_T}{k_B T}\right) d\epsilon_T \quad (5.188)$$

$$= \left(\frac{1}{\pi \mu}\right)^{1/2} \left(\frac{2}{k_B T}\right)^{3/2} \times \int_{\epsilon_0}^{\infty} \pi d^2 (\epsilon_T - \epsilon_0) \exp\left(-\frac{\epsilon_T}{k_B T}\right) d\epsilon_T \quad (5.189)$$

↷

$$k^{LC}(T) = \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \pi d^2 \exp\left(-\frac{\epsilon_0}{k_B T}\right) \quad (5.190)$$

This result is identical to that of our primitive “hard sphere-fixed mean relative speed” model from Section 5.1!

(4) Arrhenius activation energy:

$$E_A = RT^2 \frac{d \ln k}{dT} \quad (5.191)$$

↷

$$E_A = E_0 + \frac{1}{2}RT$$

(5.192)

c) Allowance for the “steric effect”

In order to account for the “structures” of the molecules which can undergo a reaction only if the reaction partners have a specific relative orientation, we introduce a (generally T -dependent) steric factor $p(T)$:

$$k(T) = p(T) \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \pi d^2 \exp \left(-\frac{\epsilon_0}{k_B T} \right) \quad (5.193)$$

In $p(T)$, we include all sorts of factors leading to deviations from the predictions by simple collision theory. In favorable cases, $p(T)$ can be predicted by theory. Towards these ends, we define a **reaction probability** $P(\epsilon_T, b)$ (also called the **opacity function**, and calculated by theory) and integrate according to

$$\sigma(\epsilon_T) = \int_0^{b'_{\max}} P(\epsilon_T, b) 2\pi b db \quad (5.194)$$

In other cases, it may be convenient to define an angle dependent reaction threshold energy ϵ_0^* :

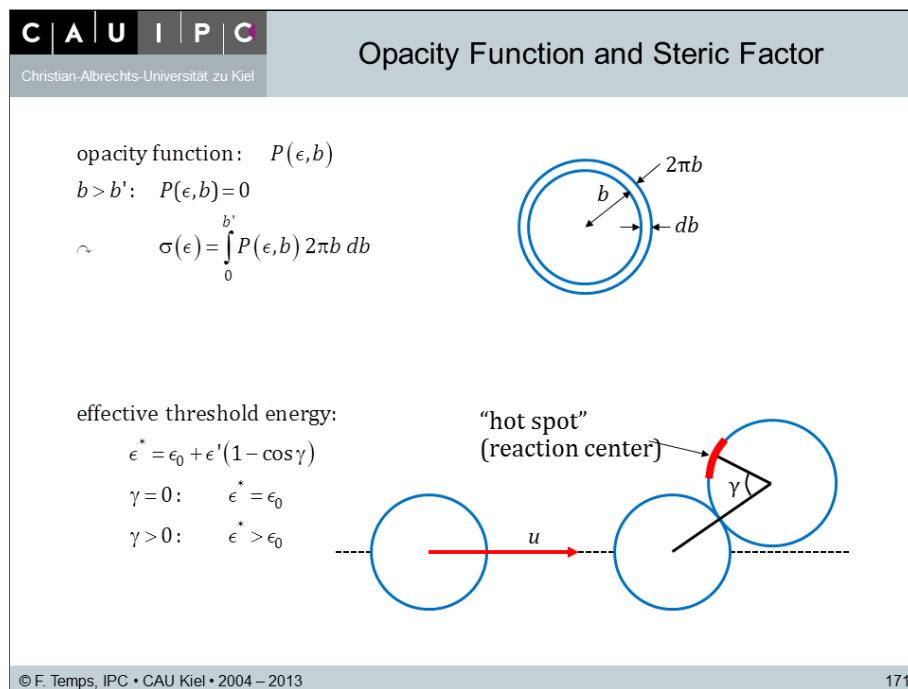
$$\epsilon_0^* = \epsilon_0 + \epsilon' (1 - \cos \gamma) \quad (5.195)$$

↷

$$\begin{aligned} \epsilon_0^* &= \epsilon_0 \text{ for } \gamma = 0 \\ \epsilon_0^* &> \epsilon_0 \text{ for } \gamma \neq 0 \end{aligned} \quad (5.196)$$

Such models are helpful for explaining steric factors in the range of $1 \leq p \leq 0.001$.

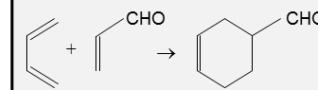
► **Figure 5.23:** Collision theory: Allowance for steric effects.



► **Table 5.2:** Comparison of predictions by collision theory with experimental data.

Collision Theory: Predictions vs. Experiments

Christian-Albrechts-Universität zu Kiel

Reaction	E_0 kJ mol ⁻¹	$10^{-14} A_{\text{expt}}$ cm ³ mol ⁻¹ s ⁻¹	$10^{-14} A_{\text{calc}}$ cm ³ mol ⁻¹ s ⁻¹	$p(T)$
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	0	10.0	2.1	4.90
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	0	0.24	1.1	0.22
$\text{NOCl} + \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$	102	0.094	0.6	0.16
	83	$1.5 \cdot 10^{-5}$	3.0	$5 \cdot 10^{-6}$

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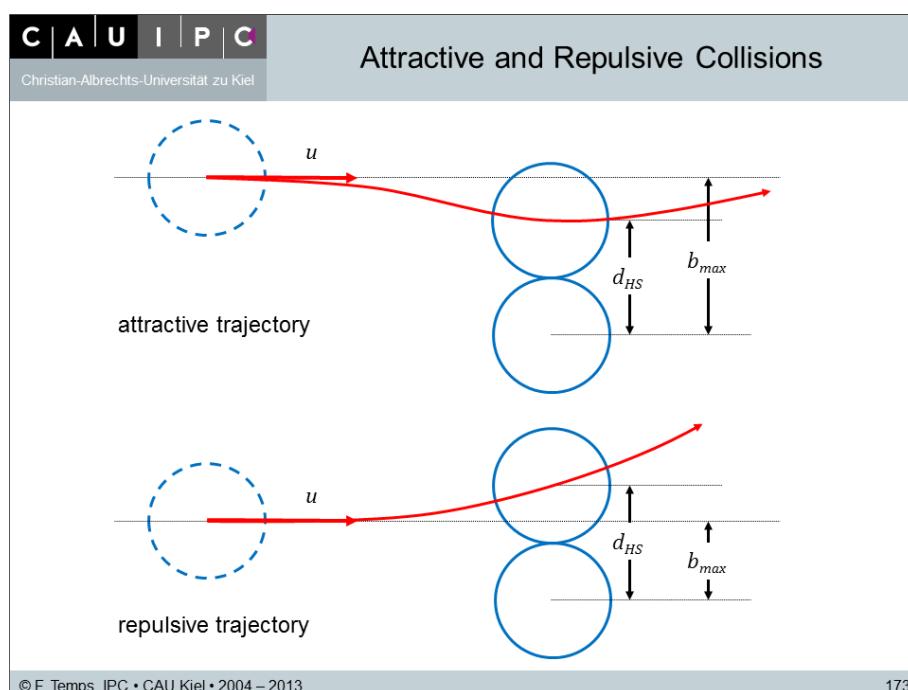
- **Harpooning:** The value of ≥ 1 for the steric factor of the $\text{K} + \text{Br}_2$ reaction can be understood by the “harpooning mechanism”: An electron jumps from the K to the Br_2 at a long intermolecular distance. The subsequent collision and reaction at closer distance then occurs between a K^+ and Br_2^- . The collision between these two is strongly affected by the Coulomb attraction.

5.4.6 Long-range intermolecular interactions

To this point, we have neglected any interactions between the reacting molecules other than the the collision itself. Thus, only straight line trajectories were allowed. In reality, however, there will be attractive or repulsive interactions between the colliding molecules (see Fig. 5.24). These will inevitably affect the collision dynamics. An extreme example is the $\text{K} + \text{Br}_2$ reaction mentioned above.

We will investigate the potential energy hypersurfaces governing the reactions in Section 6. Here, we will consider only long-range intermolecular interactions which can be easily implemented in collision theory.

- **Figure 5.24:** Examples of attractive and repulsive trajectories for the collision between two molecules.



a) Types of long-range interactions

The long-range interactions between molecules can be described using multipole expansions of the potentials (charge: 1; dipole: 2; induced dipole: 3; quadrupole: 3 ...). In general, the interaction potential between two multipoles of ranks l and l' is proportional to r^{-n} with $n = l + l' - 1$:

$$V(r) = - \left(\frac{C_n}{r} \right)^n \quad (5.197)$$

- **Table 5.3:** Types of long-range intermolecular interactions.

system	$V(r)$
charge-charge (Coulomb)	$V_{QQ}(r) = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 r}$
charge-dipole	$V_{Q\mu}(r, \theta) = \vec{\mu} \cdot \vec{E} = -\frac{ze\mu \cos\theta}{4\pi\epsilon_0 r^2}$
dipole-dipole	$V_{\mu\mu}(r, \theta_1, \theta_2) = \frac{\mu_1 \cdot \mu_2 - \frac{3(\mu_1 \cdot \mathbf{r})(\mu_2 \cdot \mathbf{r})}{r^2}}{4\pi\epsilon_0 r^3}$
charge-quadrupole	$V_{Q\Theta} \propto r^{-3}$
dipole-quadrupole	$V_{\mu\Theta} \propto r^{-4}$
charge-induced dipole	$V_{Q\mu_{ind}} \propto r^{-4}$
quadrupole-quadrupole	$V_{\Theta\Theta} \propto r^{-5}$
induced dipole-induced dipole	$V_{\mu_{ind}\mu_{ind}} \propto r^{-6}$

- **Table 5.4:** Long-range intermolecular interactions ($\mu = 1.5 \text{ D}$, $\alpha = 3 \text{ \AA}^3$, $z = 1$, $\theta = 0$; energies in kJ/mol ; for comparison: $RT = 2.5 \text{ kJ/mol}$ @ $T = 298 \text{ K}$).

system	$V(r = 5 \text{ \AA})$	$V(r = 10 \text{ \AA})$
ion-ion	278	139
ion-dipole	17.4	4.35
ion-induced dipole	3.34	0.21
dipole-dipole	2.17	0.27

b) Lennard-Jones (6-12) potential for nonpolar molecules

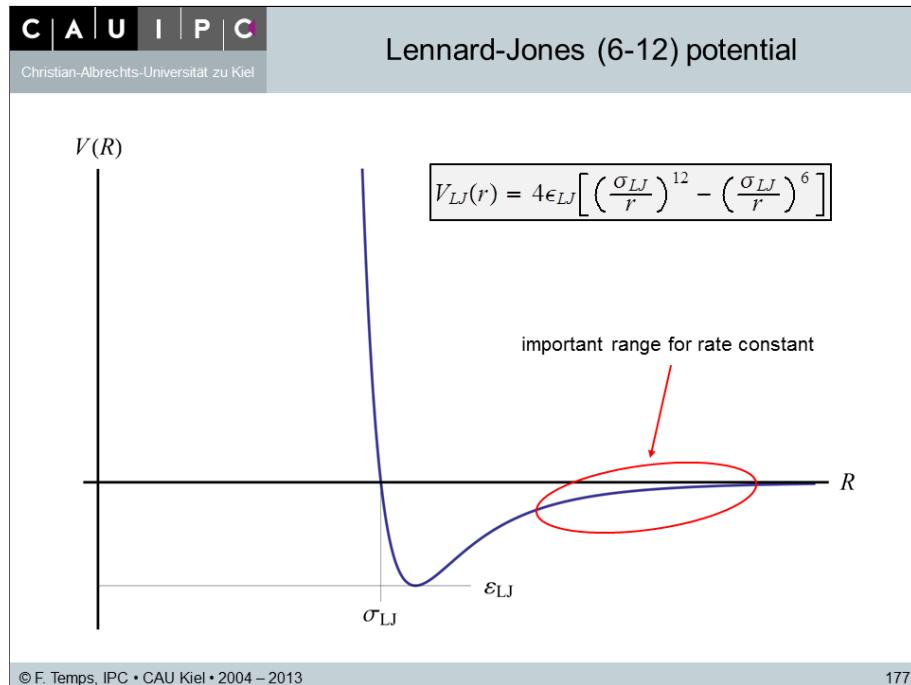
A realistic intermolecular potential for non-polar molecules is the Lennard-Jones (6-12) potential

$$V_{\text{LJ}}(R) = 4\epsilon_{\text{LJ}} \left[\left(\frac{\sigma_{\text{LJ}}}{R} \right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{R} \right)^6 \right] \quad (5.198)$$

ϵ_{LJ} is usually given in reduced form in units of K as

$$\epsilon_{\text{LJ}}^* = \frac{\epsilon_{\text{LJ}}}{k_B} \quad (5.199)$$

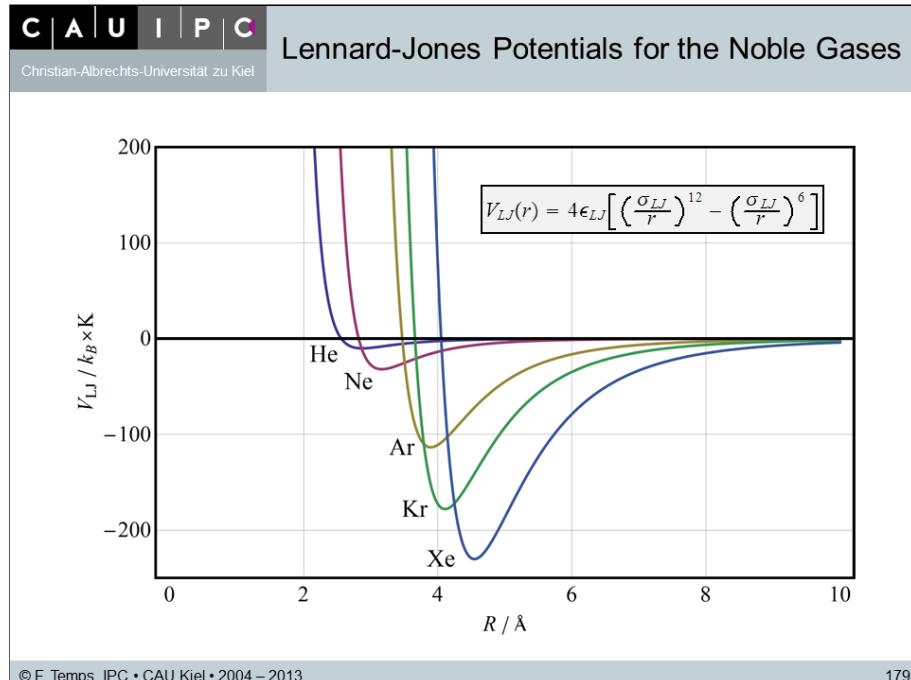
- **Figure 5.25:** Schematic plot of the Lennard-Jones potential.



- **Estimation of LJ parameters:** Values for σ_{LJ} and ϵ_{LJ} are typically derived from transport properties (e.g., viscosity), thermodynamic data (vdW parameters), or – if there is no better way – from empirical correlations (see, e.g., Svehla1963) with critical data, boiling temperatures, . . .
- **Table 5.5:** Lennard-Jones for some gases (Mourits1977).

	σ_{LJ} / (pm)	(ϵ_{LJ}/k_B) / (K)		σ_{LJ} / (pm)	(ϵ_{LJ}/k_B) / (K)
He	256.0	10.2	N_2	373.8	82.0
Ne	282.2	32.0	O_2	3480	102.6
Ar	346.5	113.5	CH_4	379.0	142.1
Kr	366.2	178.0	CF_4	448.6	167.3
Xe	405.0	230.2	CCl_4	561.1	415.5
H_2	293.0	37.0	CO_2	394.3	200.9
			SF_6	519.9	212.0

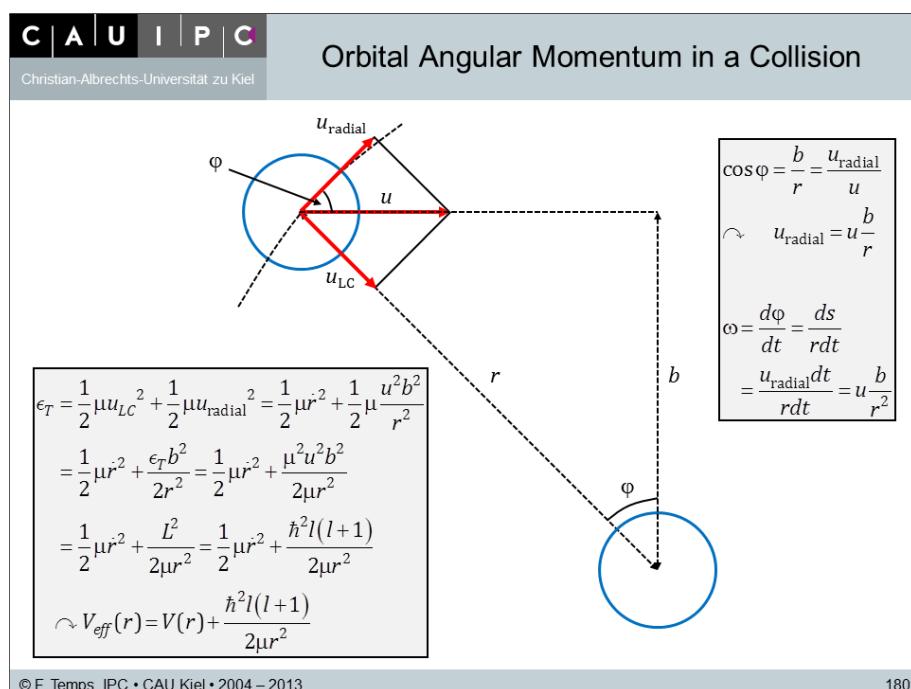
- **Figure 5.26:** Lennard-Jones interaction potentials for He, Ne, Ar, Kr, and Xe.



c) Orbital angular momentum and centrifugal barrier*

In the case of a non-central collision, part of the translational energy is converted to “rotational energy” (orbital angular momentum; see Fig. 5.27). This is seen by partitioning the velocity u vector between the LC direction ($u_{central}$) and the radial direction (u_{radial}). The component u_{radial} corresponds to a rotational motion.

- **Figure 5.27:** Orbital angular momentum in binary collisions.



- Radial velocity component:

$$\cos \varphi = \frac{b}{r} = \frac{u_{radial}}{u} \quad (5.200)$$

↷

$$u_{radial} = u \frac{b}{r} \quad (5.201)$$

- Kinetic energy:

$$\epsilon_T = \underbrace{\frac{1}{2}\mu u_{LC}^2}_{\text{translation via LC}} + \underbrace{\frac{1}{2}\mu u_{radial}^2}_{=\frac{1}{2}\mu r^2\omega^2 \text{ (rotation)}} \quad (5.202)$$

- Angular velocity:

$$\omega = \frac{d\varphi}{dt} = \frac{ds}{r dt} = \frac{u_{radial} dt}{r dt} = \frac{u_{radial}}{r} = u \frac{b}{r^2} \quad (5.203)$$

- Kinetic energy:

$$\epsilon_T = \frac{1}{2}\mu (u_{LC})^2 + \frac{1}{2}\mu (u_{radial})^2 \quad (5.204)$$

$$= \frac{1}{2}\mu r^2 + \frac{1}{2}\mu \frac{u^2 b^2}{r^2} \quad (5.205)$$

$$= \frac{1}{2}\mu r^2 + \frac{1}{2}\epsilon_T \frac{b^2}{r^2} \quad (5.206)$$

$$= \frac{1}{2}\mu r^2 + \frac{1}{2}\frac{\mu^2 u^2 b^2}{\mu r^2} \quad (5.207)$$

- Orbital angular momentum: μub is the orbital angular momentum L

$$\mu ub = \mu b^2 \frac{u}{b} = I\omega = L \quad (5.208)$$

↷

$$\epsilon_T = \frac{1}{2}\mu r^2 + \frac{L^2}{2\mu r^2} \quad (5.209)$$

From quantum mechanics, $L^2 = \hbar^2 l(l+1)$ with l as orbital angular momentum quantum number. ↷

$$\epsilon_T = \frac{1}{2}\mu r^2 + \frac{\hbar^2 l(l+1)}{2\mu r^2} \quad (5.210)$$

$$= \frac{1}{2}\mu r^2 + C_2 l(l+1) \quad (5.211)$$

where $C_2 = \frac{\hbar^2}{2\mu r^2}$ is formally an r -dependent rotational constant.

- Centrifugal barrier: The centrifugal kinetic energy term $\frac{\hbar^2 l(l+1)}{2\mu r^2}$ acts as a centrifugal barrier

$$V_{\text{centrifugal}} = \frac{1}{2}\epsilon_T \frac{b^2}{r^2} = \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

(5.212)

- With a long-range attractive term of the form $-\left(\frac{C_n}{r}\right)^n$, the intermolecular potential thus has the form

$$V_{eff}(r) = -\left(\frac{C_n}{r}\right)^n + \epsilon_T \frac{b^2}{r^2} \quad (5.213)$$

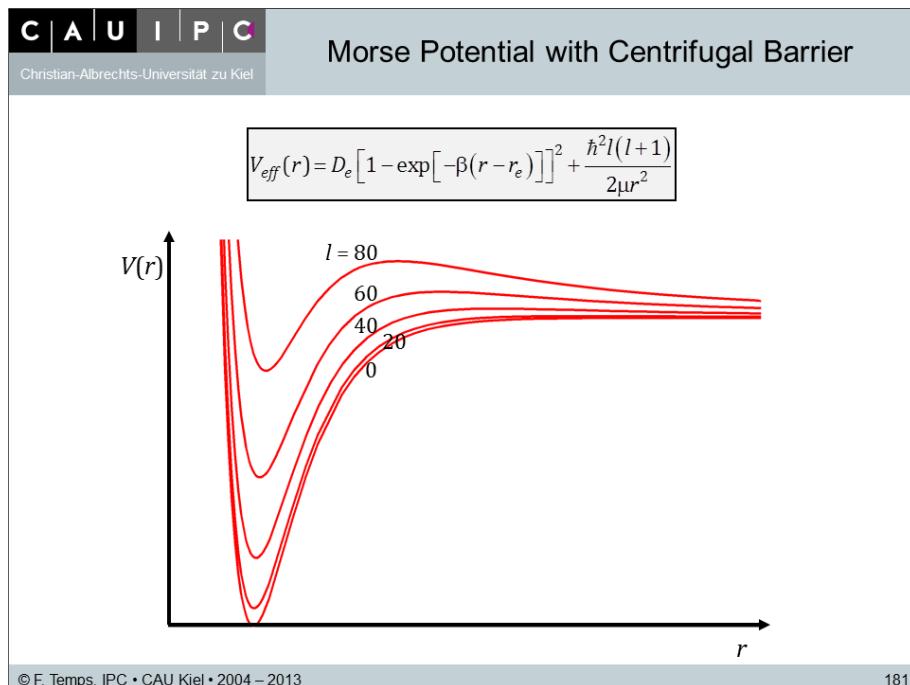
$$= -\left(\frac{C_n}{r}\right)^n + \frac{\hbar^2 l(l+1)}{2\mu r^2} \quad (5.214)$$

i.e.,

$$V_{eff}(r) \propto -r^{-n} + r^{-2} \quad (5.215)$$

- The r^{-2} term is important in practice if $n > 3$. In effect, it leads to an effective energy barrier ("centrifugal" barrier).
- The larger b for a given ϵ_T , the larger the orbital angular momentum l .

- **Figure 5.28:** Potential energy curves with centrifugal barriers for a diatomic system.



d) Langevin "capture" rate constant for ion-molecule reactions*

An nice illustration of the above results is the rate constant for ion-molecule reactions. The intermolecular interaction is governed by the point charge-induced dipole interaction.⁴⁰ In addition, the centrifugal barrier has to be taken into account, so that

$$V(r) = -\frac{\alpha (ze)^2}{(4\pi\epsilon_0)^2 2r^4} + \epsilon_T \left(\frac{b}{r}\right)^2 \quad (5.216)$$

The resulting expression for the rate constant is

$$k^L(T) = \left(\frac{4\alpha (ze)^2}{(4\pi\epsilon_0)^2 \mu} \right)^{1/2} \times \Gamma\left(\frac{1}{2}\right) \quad (5.217)$$

Typical values of k^L are $100 \times k^{HS}$.

⁴⁰ $V(r)$ needs to be checked again!!

6. Potential energy surfaces for chemical reactions

6.1 Diatomic molecules

- **Morse potential (anharmonic oscillator):**

$$V(r) = D_e [1 - \exp(-\beta_e(r - r_e))]^2 \quad (6.1)$$

- **Vibrational states of a harmonic oscillator:**

$$\epsilon_v = \hbar\omega_e \left(v + \frac{1}{2}\right) = h\nu_e \left(v + \frac{1}{2}\right) \quad (6.2)$$

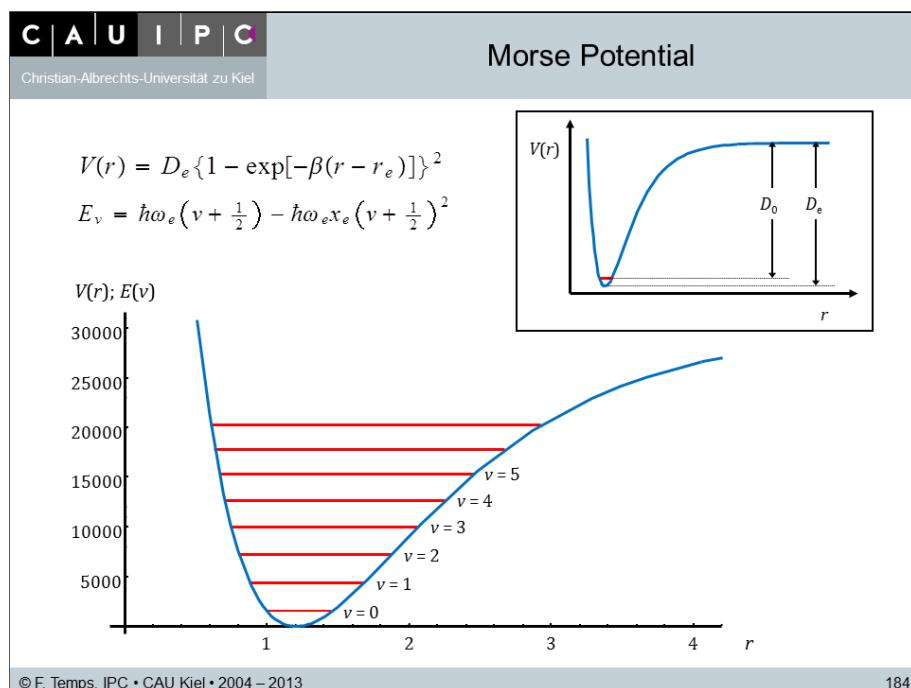
- **Vibrational states of an anharmonic oscillator:**

$$\epsilon_v = \hbar\omega_e \left(v + \frac{1}{2}\right) - \hbar\omega_e x_e \left(v + \frac{1}{2}\right)^2 + \dots \quad (6.3)$$

- **Dissociation energies D_e and D_0 :**

$$D_e = D_0 + \frac{1}{2}\hbar\omega_e - \frac{1}{4}\hbar\omega_e x_e + \dots \quad (6.4)$$

- **Figure 6.1:** Potential energy curve of diatomic molecules.



6.2 Polyatomic molecules

The potential energy becomes dependent of the different internal coordinates.

- **Question:** How many internal coordinates (dimensions) do we need?
- **Answer:**

- Total number of degrees of freedom of an N -atomic molecule:

$$3N \quad (6.5)$$

- for translational motion of center of gravity:

$$3 \quad (6.6)$$

- for rotational motion around center of gravity

$$2 \text{ for linear molecules} \quad (6.7)$$

$$3 \text{ for nonlinear molecules} \quad (6.8)$$

- resulting number of vibrational coordinates:

- linear molecules:

$$3N - 5 \quad (6.9)$$

- nonlinear molecules:

$$3N - 6 \quad (6.10)$$

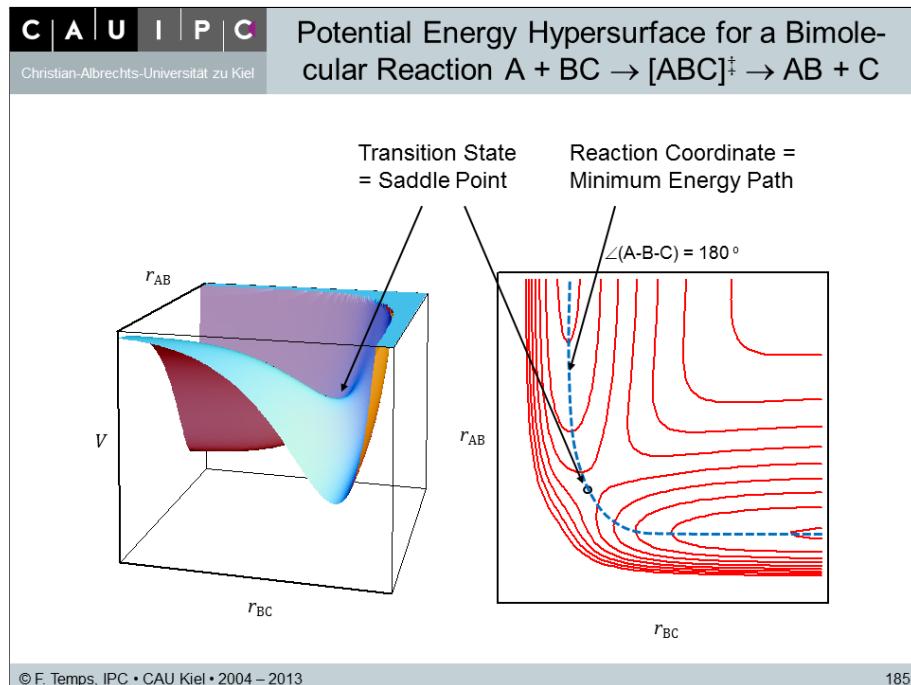
- **$3N - 6$ dimensional potential energy hypersurface:**

- The internal coordinates are described using the normal coordinates Q_j (vibrational displacements).
- The potential energy function

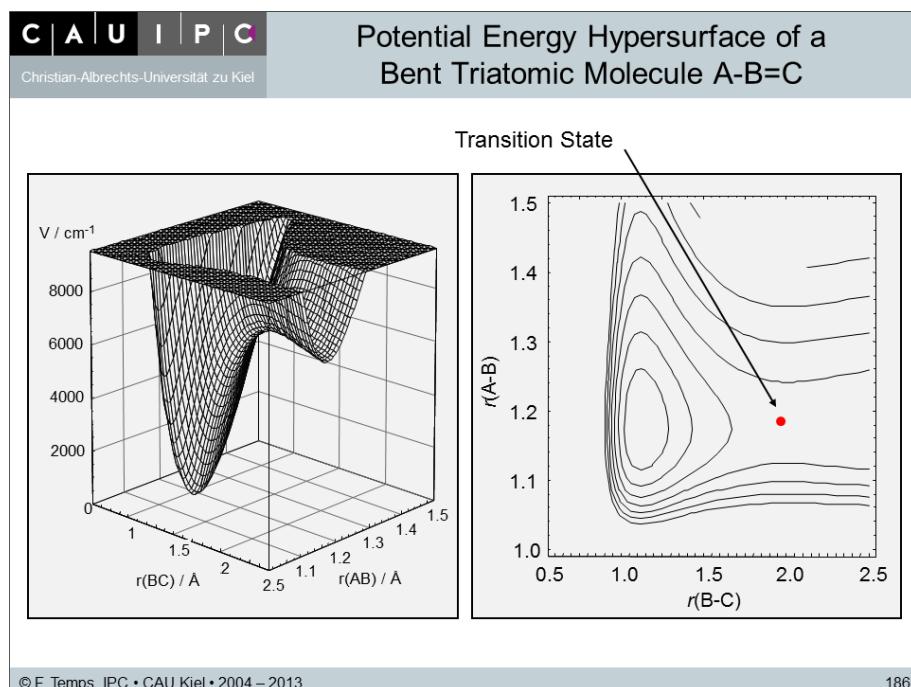
$$V(Q_1, Q_2, \dots, Q_{3N-6}) \quad (6.11)$$

is a hypersurface in a $3N - 6$ ($3N - 5$) dimensional hyperspace. But we can plot V only in 2-D or 3-D space.

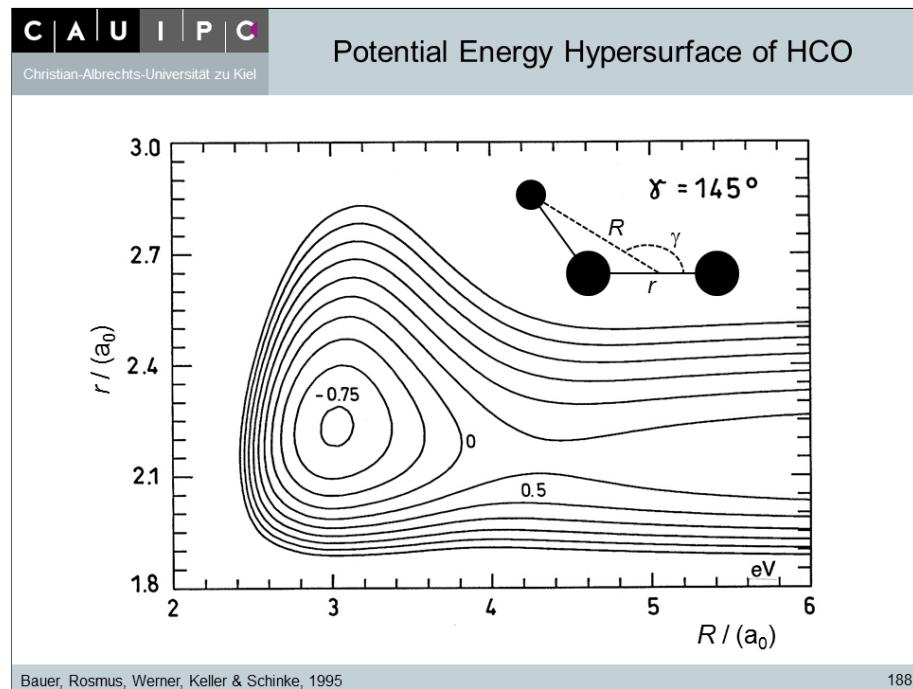
- **Figure 6.2:** Potential energy hypersurface for a simple atom transfer reaction (plot for fixed angle, e.g., collinear collision and other fixed coordinates depending on dimensionality of the system).



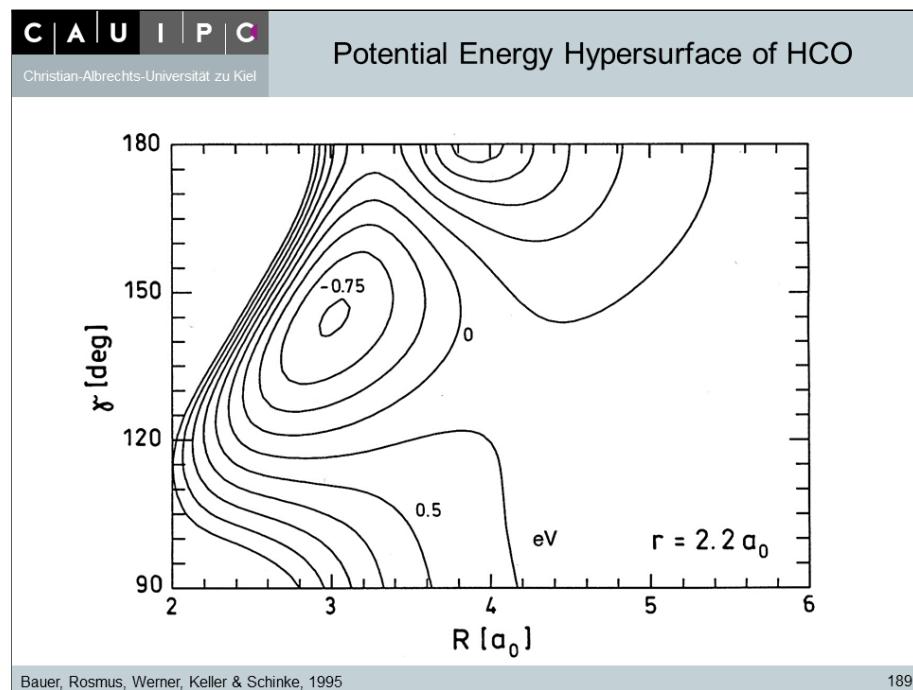
- **Figure 6.3:** Schematic potential energy hypersurface of a triatomic molecule.



- **Figure 6.4:** Potential energy hypersurface of HCO.



- **Figure 6.5:** Potential energy hypersurface of HCO.



► **Models of potential energy surfaces:**

- (1) Empirical or semiempirical models (e.g., LEPS),
- (2) Single points $V(Q_i)$ by *ab initio* calculations using quantum chemistry. Problem:
Fitting the surface to the computed points.

► **Kinetics and Dynamics:**

- (1) TST = Transition State Theory (statistical theory),
- (2) Classical trajectory calculations (by solving Newton's equations),
- (3) Fully quantum mechanical wave packet calculations (by solving the time-dependent Schrödinger equation).

6.3 Trajectory Calculations

The “exact” dynamics of the molecules on a potential energy hypersurface can be followed by classical trajectory calculations.

- **Phase Space:** $6N$ -dimensional space spanned by the spatial coordinates (Q_j) and the conjugated momenta (P_j):

$$Q_j \leftrightarrow P_j \quad (6.12)$$

where

$$P_j = \mu_j \frac{\partial Q_j}{\partial t} = \mu_j \dot{Q}_j \quad (6.13)$$

- **Hamilton function:**

$$H = T + V = \frac{P^2}{2\mu} + V(Q) \quad (6.14)$$

Note that T depends only on P and V depends only on Q .

- **Equations of motion:**

- for a 1 particle system:

(1)

$$F = ma = \frac{\partial P}{\partial t} = -\frac{\partial V(Q)}{\partial Q} \quad (6.15)$$

↷

$$\dot{P} = -\frac{\partial V}{\partial Q} = -\frac{\partial H}{\partial Q} \quad (6.16)$$

since T contains only P not Q .

(2)

$$H = \frac{P^2}{2\mu} + V \quad (6.17)$$

↷

$$\frac{\partial H}{\partial P} = \frac{1}{\mu} \times P = \frac{1}{\mu} \times \left(\mu \dot{Q} \right) = \dot{Q} \quad (6.18)$$

↷

$$\dot{Q} = \frac{\partial H}{\partial P} \quad (6.19)$$

- for an N atomic system:

$$H = T + V = \sum_{j=1}^{3N} \frac{\mu_j}{2} P_j^2 + V(Q_1, Q_2, \dots, Q_{3N-6}) \quad (6.20)$$

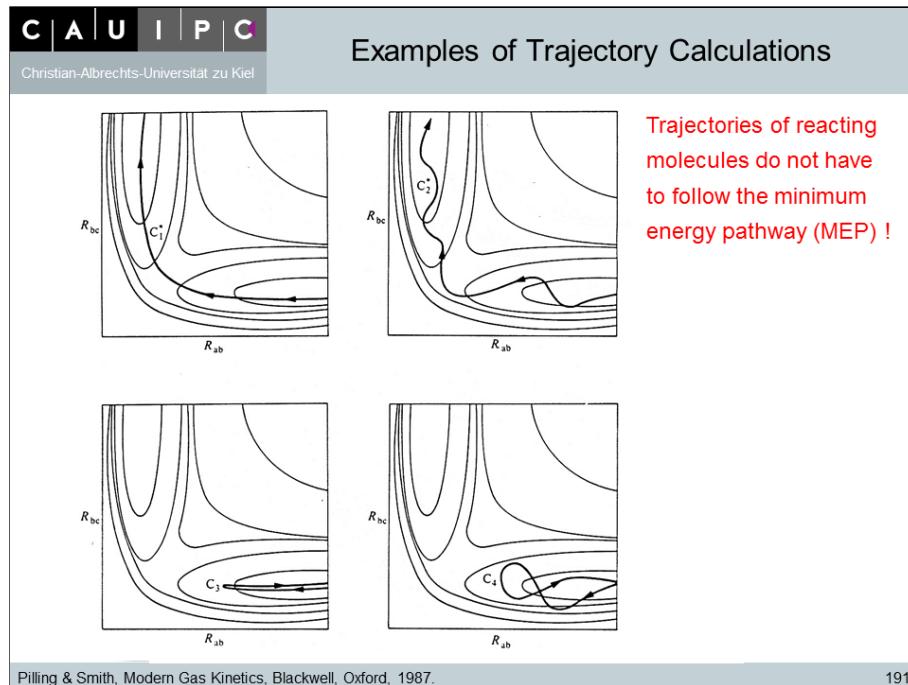
$$\dot{P}_j = -\frac{\partial H}{\partial Q_j} \quad (6.21)$$

$$\dot{Q}_j = \frac{\partial H}{\partial P_j} \quad (6.22)$$

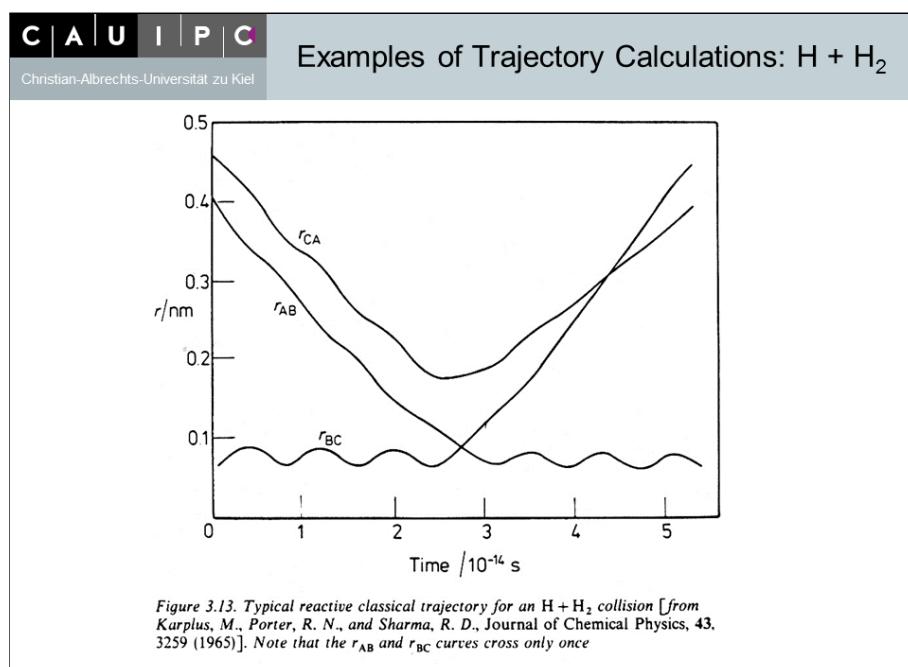
Thus we obtain a set of coupled differential equations which can be solved using the Runge-Kutta or Gear methods.

- Thermal rate constants $k(T)$ follow by suitable averaging over the initial conditions (u , vibrational states, rotational states, angles, ...).
- Major problems: Zero-point energy? Tunneling? Surface crossings?

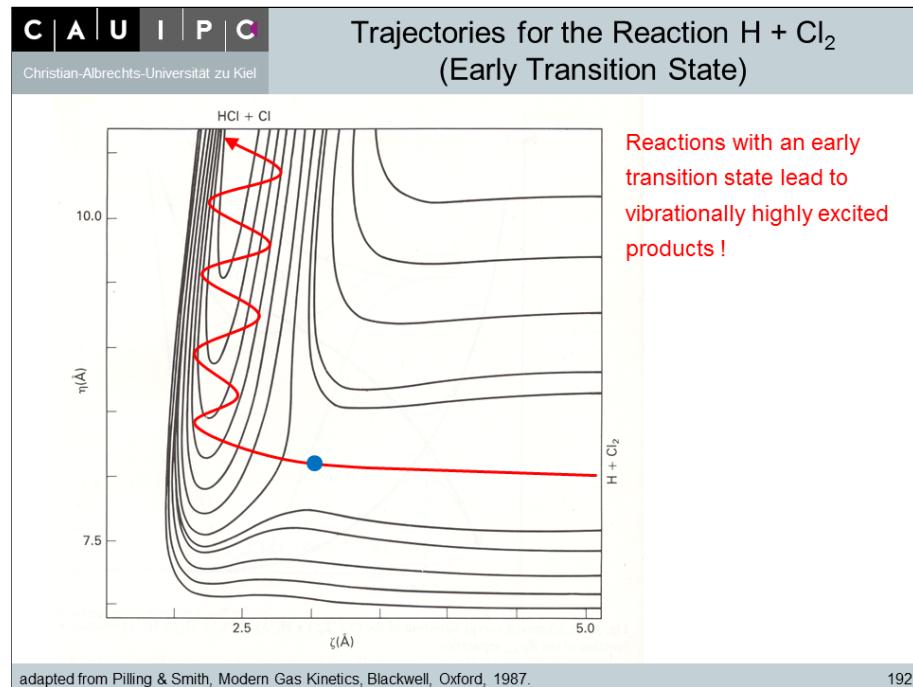
► **Figure 6.6:** Trajectory calculations.



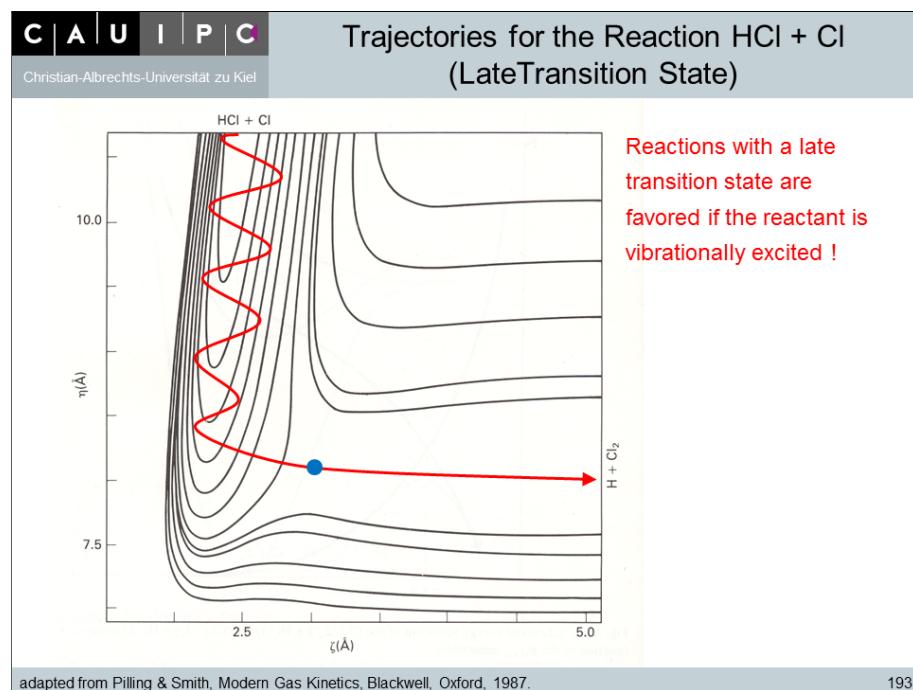
► **Figure 6.7:** Trajectory calculations.



- **Figure 6.8:** The reaction $\text{H} + \text{Cl}_2$ is a reaction with an early TS. The reaction is known to yield HCl with an inverted vibrational state distribution ($\Rightarrow \text{HCl-Laser}$).



- **Figure 6.9:** Bimolecular reaction with a late TS.



7. Transition state theory

7.1 Foundations of transition state theory

The concept of transition state theory (TST) or activated complex theory (ACT) goes back to H. Eyring and M. Polanyi (1935). TST is a statistical theory; it does not give information on the exact dynamics of a reaction. It does, however, give (statistical) information on product state distributions.

There are two forms of TST:

- Macrocanonical TST $\Rightarrow k(T)$ for a macrocanonical ensemble of molecules with a constant T (an ensemble of molecules with energy states populated according to the Boltzmann distribution - each state being equally likely.)
- Microcanonical TST (μ TST) $\Rightarrow k(E)$ for a microcanonical ensemble of molecules with specific energy E .

We will consider only the first version.

The detailed application of TST also depends on whether or not the reaction has a distinctive potential energy barrier (\Rightarrow conventional TST or variational TST).

- **Figure 7.1:** Transition State Theory (TST): Fundamental equations and applications.

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Transition State Theory: Applications

$$k(T) = \kappa \frac{k_B T}{h} \frac{Q_{ABC}^{\ddagger}}{Q_A Q_{BC}} e^{-\Delta E_0/k_B T}$$

$$= \kappa \frac{k_B T}{h} e^{\Delta S_{0K}^{\ddagger}/R} e^{-\Delta H_{0K}^{\ddagger}/RT}$$

Applications of TST:

- values of preexponential factors A ,
- difference between E_0 and E_A ,
- T -dependence of E_A ,
- gas phase and liquid phase reactions (proton transfer, electron transfer, organic chemistry, reactions of ions in solutions),
- pressure dependence of reaction rate constants (activation volumes),
- kinetic isotope effects,
- structure-reactivity relations (e.g., Hammett relations in organic chemistry),
- features of biological reactions
- heterogeneous reactions: heterogeneous catalysis, electrode reactions, ...



Henry Eyring



Michael Polanyi

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7.1.1 Basic assumptions of TST

- (1) The Born-Oppenheimer approximation (separation of electronic and nuclear motion) is a valid approximation. Thus we can describe the nuclear motion during the reaction on a single electronic potential energy surface (PES; see Fig. 7.2).⁴¹
- (2) The reactant molecules are in internal equilibrium (the quantum states are populated according to the Boltzmann distribution).
- (3) “Transition state” and “dividing surface”:
 - a) Conventional TST (valid for so-called “type I” PES’s = PES’s with a distinctive energy barrier along the reaction coordinate (RC)): We can localize a distinctive “transition state” (TS) for the reaction at the saddle point on the PES that separates the reactant and product “valleys”. The TS is located at the maximum of the PES along the minimum energy path (MEP; see Fig. 7.3).
 - b) Variational TST (version that can be used for so-called “type II” PES’s = PES’s without a clear energy barrier along the RC (we can’t localize a simple TS)): We can localize a $3N - 7$ -dimensional “dividing surface” (DS) on the $3N - 6$ -dimensional PES that separates the reactant and product regions on the PES in such a way that the “reactive flux” through the DS becomes minimal (Fig. 7.2). The TS is then placed at the point where the MEP intersects the DS. In this case, the position of the TS depends strongly on the finer details such as angular momentum (because of centrifugal barriers which move inwards with increasing l or increasing b).
- (4) The motion along the minimum energy path across the TS (through the DS) can be separated from other degrees of freedom and treated as translational motion. At the TS, we therefore have 1 translational degree of freedom q^\ddagger (the RC) and $3N - 7$ (vibrational) degrees of freedom ξ_i orthogonal to the RC.
- (5) Reactant molecules passing through the DS never come back (no recrossing).
- (6) The states of the TS are in quasi-equilibrium with the states of the reactant molecule even if we have no equilibrium between reactants and products (the individual molecules don’t know that this equilibrium is not present - this quasi-equilibrium assumption can be dropped in dynamical derivations of TST; see below).

► **Conditions for TS at the saddle point:**

- (1) V has maximum along q^\ddagger :

$$\frac{\partial V}{\partial q^\ddagger} = 0 \text{ and } \frac{\partial^2 V}{\partial q^{\ddagger 2}} < 0 \quad (7.1)$$

↷ 1 imaginary frequency (criterion for TS in quantum chemical calculations)!

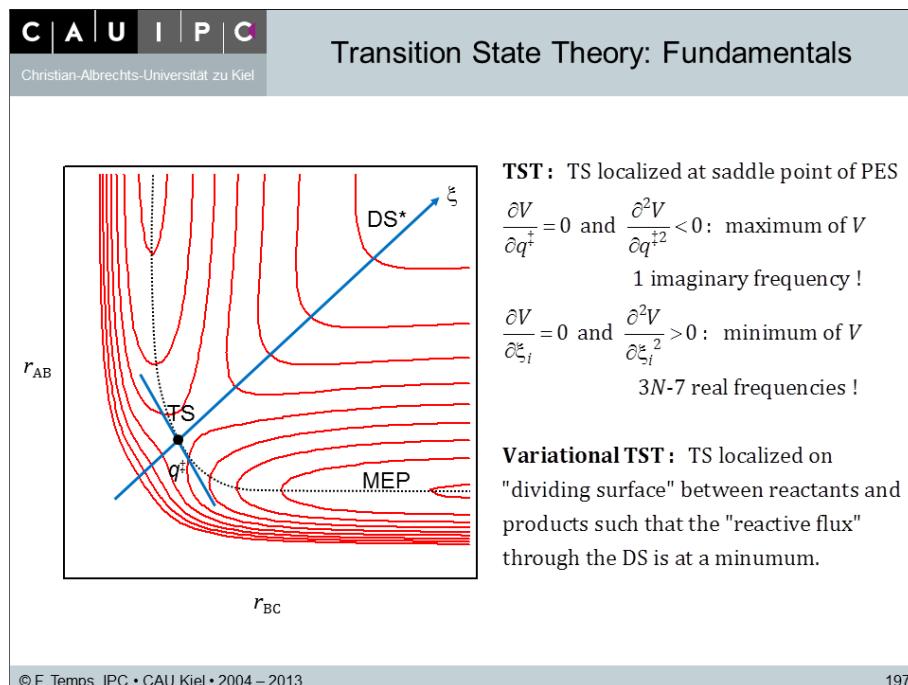
⁴¹ TST cannot be used at least in the simple form considered in this lecture when two potential surfaces are involved that are energetically close to each other (or even become degenerate) and the reaction involves a “non-adiabatic transition” between these two potentials.

(2) V has minimum along all $3N - 7$ other coordinates:

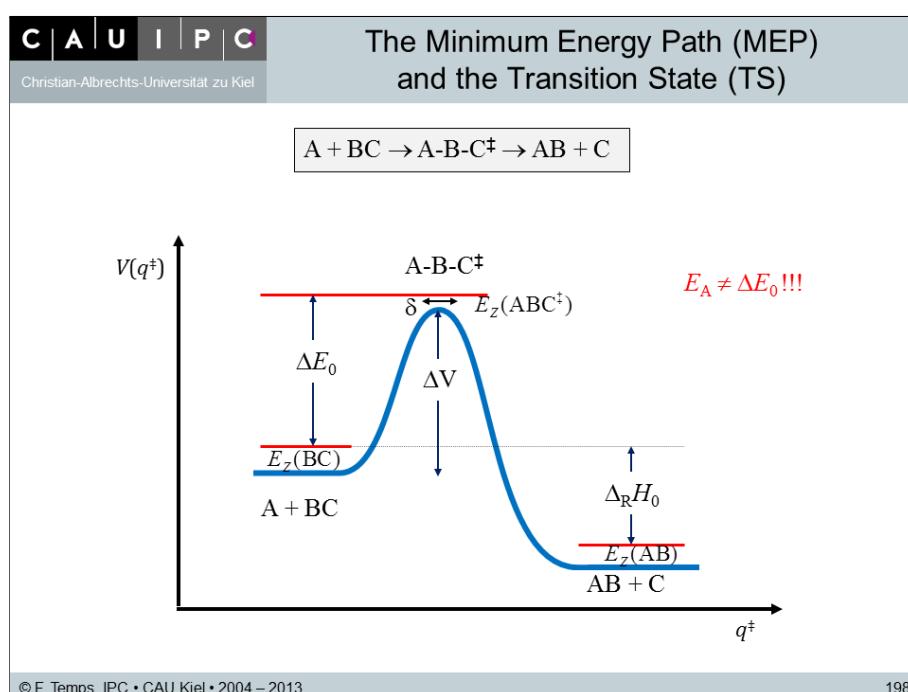
$$\frac{\partial V}{\partial \xi_i} = 0 \text{ and } \frac{\partial^2 V}{\partial \xi_i^2} > 0 \quad (7.2)$$

$\sim 3N - 7$ real other frequencies.

► **Figure 7.2:** Transition state theory: The dividing surface with minimal reactive flux.



► **Figure 7.3:** Minimum energy path (MEP) and transition state (TS) of a simple atom transfer reaction.



7.1.2 Formal kinetic model

In order to derive the TST expression for $k(T)$, we first look at a simple formal kinetic model. This formal kinetic model has its roots in the original idea that the TS can be considered as some sort of an “activated complex” with a local energy minimum on the PES. It is not a good derivation of the TST expression for $k(T)$, but leads to the correct expression.

► **Activated complex model of TST:**



↷

$$[ABC^\ddagger]_{ss} = \frac{k_1 [A] [BC]}{k_2 + k_3} \quad (7.4)$$

► **Assumption:** $k_3 \ll k_2$ ↷

$$[ABC^\ddagger]_{ss} = \frac{k_1}{k_2} [A] [BC] = K_{12} [A] [BC] \quad (7.5)$$

↷ Equilibrium between the reactants ($A + BC$) and the TS (ABC^\ddagger):

$$\frac{d[P]}{dt} = k_3 [ABC^\ddagger]_{ss} \quad (7.6)$$

$$= \underbrace{k_3 K_{12}}_{=k} [A] [BC] \quad (7.7)$$

↷

► **ACT expression for rate constant:**

$$k = k_3 K_{12} \quad (7.8)$$

Below, we will find that

$$k_3 = \nu^\ddagger = \frac{k_B T}{h} \quad (7.9)$$

and

$$K_{12} \propto \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (7.10)$$

7.1.3 The fundamental equation for $k(T)$

The above derivation of the TST rate constant was based on an oversimplified picture, since the TS is not at a local minimum but at a saddle point on the PES. In this section, we derive the TST fundamental equation more carefully by bringing in some dynamical aspects. In (1) - (4), we explore the implications of the quasi-equilibrium assumption, and in (5) - (9) we develop a dynamical semiclassical model:⁴²

⁴² Semiclassical because the translation is handled classically while all other degrees of freedom are described quantum mechanically.

(1) We start by assuming equilibrium between the reactants and products:



(2) We consider two dividing surfaces at the TS separated by a distance of $\leq \delta$.

δ is the “length” of a “phase space cell” in semiclassical theory which is determined by Heisenberg’s uncertainty principle:

$$\Delta q^\ddagger \times \Delta p^\ddagger = \delta \times \Delta p^\ddagger = h \quad (7.12)$$

(3) We now consider the number densities of molecules passing through these surfaces from left to right ($\overrightarrow{N^\ddagger}$) and from right to left ($\overleftarrow{N^\ddagger}$). The total number density N^\ddagger at the TS in equilibrium is their sum, i.e.,

$$N^\ddagger = \overrightarrow{N^\ddagger} + \overleftarrow{N^\ddagger} = K_c^\ddagger N_A N_{BC} \quad (7.13)$$

In equilibrium, we must have

$$\overrightarrow{N^\ddagger} = \overleftarrow{N^\ddagger} \quad (7.14)$$

Thus,

$$\overrightarrow{N^\ddagger} = \overleftarrow{N^\ddagger} = \frac{1}{2} N^\ddagger = \frac{K_c^\ddagger}{2} N_A N_{BC} \quad (7.15)$$

(4) We now suddenly remove all the products. Then $\overleftarrow{N^\ddagger} = 0$. However, there is no reason for $\overrightarrow{N^\ddagger}$ to change, because the molecules on the reactant side remain in internal equilibrium (this is the quasi-equilibrium assumption).⁴³ ↗

$$\overrightarrow{N^\ddagger} = \frac{N^\ddagger}{2} = \frac{K_c^\ddagger}{2} N_A N_{BC} \quad (7.16)$$

Thus, we can still express $\overrightarrow{N^\ddagger}$ using the equilibrium constant K_c^\ddagger even if there is no equilibrium between reactants and products.

(5) We now turn to the reaction rate, which is given by the number density of molecules $d\overrightarrow{N^\ddagger}$ in the time interval dt that are crossing the DS in the forward direction. We can write this as

$$\frac{d\overrightarrow{N^\ddagger}}{dt} = \overrightarrow{\nu^\ddagger} N^\ddagger = \frac{\overrightarrow{u^\ddagger}}{\delta} N^\ddagger \quad (7.17)$$

where

- $\overrightarrow{\nu^\ddagger}$ is the decay rate of the TS in the forward direction (or the frequency factor for the molecules crossing the DS in the forward direction),

⁴³ The quasi-equilibrium assumption for $\overrightarrow{N^\ddagger}$ is made in canonical TST. In a microcanonical derivation of the TST expression for $k(E)$, we consider the fluxes $\overrightarrow{N^\ddagger}$ and $\overleftarrow{N^\ddagger}$ through the dividing surface at the TS. Then, the individual molecules “don’t know” that the products have been removed and $\overleftarrow{N^\ddagger} = 0$. Since they don’t know about this, the flux $\overrightarrow{N^\ddagger}$ has to remain unchanged.

- $\overrightarrow{u^\ddagger} = \delta \overrightarrow{v^\ddagger}$ is the mean speed of the molecules crossing the DS in the forward direction.

(6) We now use the equilibrium constant to determine N^\ddagger via

$$K_c^\ddagger = \frac{N_{ABC}^\ddagger}{N_A N_{BC}} \quad (7.18)$$

$$\curvearrowleft N^\ddagger = N_{ABC}^\ddagger = K_c^\ddagger N_A N_{BC} \quad (7.19)$$

$$\curvearrowleft \frac{d\overrightarrow{N^\ddagger}}{dt} = \frac{\overrightarrow{u^\ddagger}}{\delta} K_c^\ddagger N_A N_{BC} = k N_A N_{BC} \quad (7.20)$$

with

$$k = \frac{\overrightarrow{u^\ddagger}}{\delta} K_c^\ddagger \quad (7.21)$$

(7) From statistical thermodynamics (see Appendix G), we have the following expression for the equilibrium constant $K_c^\ddagger(T)$ in terms of the molecular partition functions:

$$K_c^\ddagger(T) = \frac{Q_{ABC}^*}{Q_A Q_{BC}} = \frac{Q_{ABC}}{Q_A Q_{BC}} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \quad (7.22)$$

- The Q 's are the respective molecular partition functions (per unit volume).
- Q_{ABC}^* is written with respect to the zero-point level of the reactants.
- The $\exp(-\Delta\epsilon_0/k_B T)$ factor arises subsequently, because we now express the value of partition function for the TS relative to the zero-point level of the TS ($Q_{ABC}^* = Q_{ABC} \exp(-\Delta\epsilon_0/k_B T)$).

(8) Separating the motion along the reaction coordinate q^\ddagger from the other degrees of freedom, we write

$$Q_{ABC} = Q_{q^\ddagger} Q_{ABC}^\ddagger \quad (7.23)$$

where Q_{q^\ddagger} is the 1-D (translational) partition function describing the translational motion of the molecules along q^\ddagger across the TS and Q_{ABC}^\ddagger is the partition function for all $3N - 7$ other (rotational-vibrational-electronic) degrees of freedom.

Here,

- the 1-D translational partition function is

$$Q_{q^\ddagger} = \left(\frac{2\pi\mu k_B T}{h^2} \right)^{1/2} \times \delta \quad (7.24)$$

- the mean speed along q^\ddagger for crossing the DS in the forward direction is given by

$$\overrightarrow{u^\ddagger} = \frac{\int_0^\infty u e^{-\mu u^2/2k_B T} du}{\int_{-\infty}^\infty e^{-\mu u^2/2k_B T} du} = \left(\frac{k_B T}{2\pi\mu} \right)^{1/2} \quad (7.25)$$

(9) Collecting and inserting the results into

$$k(T) = \frac{u^\ddagger}{\delta} K_c(T) \quad (7.26)$$

we obtain

$$k(T) = \frac{1}{\delta} \left(\frac{k_B T}{2\pi\mu} \right)^{1/2} \times \left(\frac{2\pi\mu k_B T}{h^2} \right)^{1/2} \delta \times \frac{Q_{ABC}^\ddagger}{Q_A Q_{BC}} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \quad (7.27)$$

↷

$$k(T) = \frac{k_B T}{h} \frac{Q_{ABC}^\ddagger}{Q_A Q_{BC}} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \quad (7.28)$$

- **Result:** In order to account (i) for some recrossing of the TS and (ii) for quantum mechanical tunneling, we add an additional factor κ , called the transmission coefficient. For well-behaved reactions, $\kappa \approx 1$. Thus, we end up with the **fundamental equation of TST** in the form:

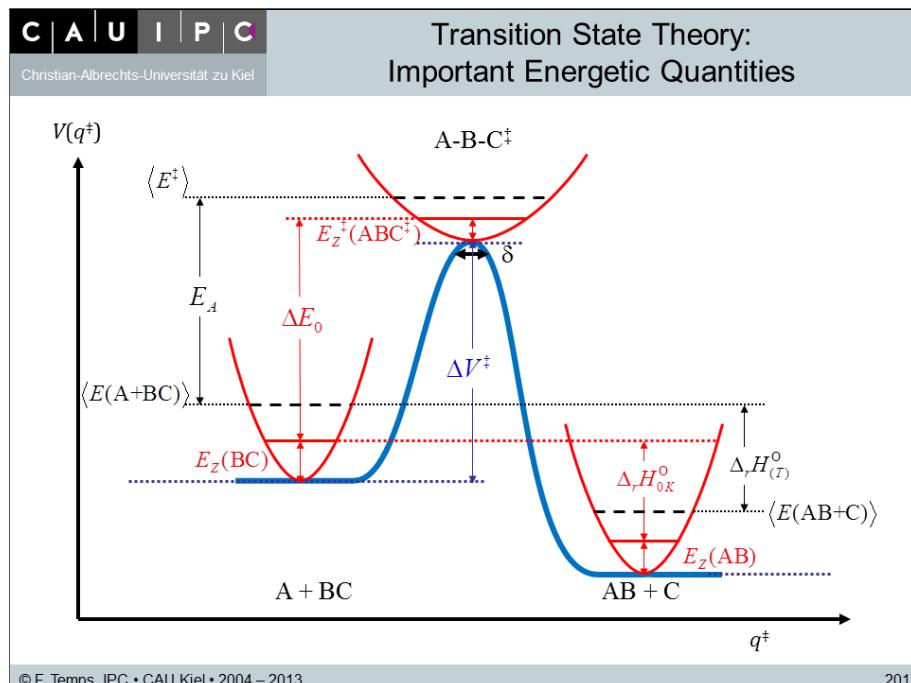
$$k(T) = \kappa \frac{k_B T}{h} \frac{Q_{ABC}^\ddagger}{Q_A Q_{BC}} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \quad (7.29)$$

Note that Q_{ABC}^\ddagger is the partition function of the TS excluding the RC.

Equation 7.29 allows us to calculate $k(T)$ using the following data:

- The threshold energy for the reaction $\Delta\epsilon_0$ (or, per mol, ΔE_0). ΔE_0 has to be obtained from ab initio quantum chemistry calculations, and
- structural information on the reactants and the TS (i.e., bond lengths and angles, vibrational frequencies).

- **Figure 7.4:** Illustration of ΔV^\ddagger , ΔE_0 , and E_A .



$$\Delta V^\ddagger : \text{ Born-Oppenheimer potential energy barrier} \quad (7.30)$$

$$\Delta E_0 : \text{ zero-point corrected threshold energy for the reaction} \quad (7.31)$$

$$E_A : \text{ Arrhenius activation energy} \quad (7.32)$$

ΔE_0 is given with respect to the zero-point energies of the reactants and the TS,

$$E_z = \frac{1}{2} \sum h\nu_i \quad (7.33)$$

7.1.4 Tolman's interpretation of the Arrhenius activation energy

- We now understand the difference between E_A and ΔE_0 :

$$E_A = RT^2 \frac{d \ln k(T)}{dT} \quad (7.34)$$

$$= RT^2 \frac{d}{dT} \ln \left(N_L \frac{k_B T}{h} \frac{Q_{ABC}^\ddagger}{Q_A Q_{BC}} \exp \left(-\frac{\Delta E_0}{RT} \right) \right) \quad (7.35)$$

$$= \underbrace{\Delta E_0 + RT + RT^2 \frac{d \ln Q_{ABC}^\ddagger}{dT}}_{= \langle E_{\text{reacting molecules}} \rangle} - \underbrace{\left(RT^2 \frac{d \ln Q_A}{dT} + RT^2 \frac{d \ln Q_{BC}}{dT} \right)}_{= \langle E_{\text{all molecules}} \rangle} \quad (7.36)$$

- ΔE_0 is difference of the zero-point levels of the reactants and the TS,
- the RT term is the mean translational energy in the RC (from the $k_B T/h$ factor),
- the $RT^2 \frac{d \ln Q}{dT}$ terms are the internal (vibration-rotation) energies of the TS and the reactants, respectively. ↗

- Tolman's interpretation of E_A (see Fig. 7.4):

$E_A = \langle E_{\text{reacting molecules}} \rangle - \langle E_{\text{all molecules}} \rangle$

(7.37)

7.2 Applications of transition state theory

$$k(T) = \kappa \frac{k_B T}{h} \frac{Q_{ABC}^{\ddagger}}{Q_A Q_{BC}} \exp\left(-\frac{\Delta E_0}{k_B T}\right) \quad (7.38)$$

TST has gained enormous importance in all areas of physical chemistry because it provides the basis for understanding — and/or calculating —

- quantitative values of preexponential factors,
- ΔE_0 from measured E_A values,
- T -dependence of E_A and deviations from Arrhenius behavior,
- gas phase and liquid phase reactions (proton transfer, electron transfer, organic reactions, reactions of ions in solutions),
- pressure dependence of reaction rate constants (activation volumes),
- kinetic isotope effects,
- structure-reactivity relations (e.g., Hammett relations in organic chemistry),
- features of biological reactions (enzyme reactions),
- heterogeneous reactions (heterogeneous catalysis, electrode kinetics), ...

7.2.1 The molecular partition functions

In order to evaluate Eq. 7.29 for a given reaction, we need, besides ΔE_0 , the molecular partition functions for the reactants and the TS. We summarize only the main points here; further information is given in Appendix G.

► **Definition:**

$$Q = \sum_i g_i e^{-\epsilon_i/k_B T} \quad (7.39)$$

► **Physical interpretation:**

- The molecular partition function is a number which describes how many states are available to the molecule at a given temperature T .
- The ratio

$$\frac{Q_{ABC}^{\ddagger}}{Q_A Q_{BC}} \quad (7.40)$$

in Eq. 7.29 is thus the ratio of the number of states available to the TS and the reactant molecules. Since each state is equally likely, $\frac{Q_{ABC}^{\ddagger}}{Q_A Q_{BC}}$ is the relative probability of the TS *vs.* the probability of the reactants.

Note again that Q_{ABC}^{\ddagger} is the partition function of the TS *excluding* the translational motion along the RC.

- **Separation of degrees of freedom:** For separable degrees of freedom, we can write the molecular partition function Q as

$$Q = Q_{trans} \times Q_{rot} \times Q_{vib} \times Q_{el} \quad (7.41)$$

Nuclear spin (Q_{ns}) may have to be taken into account in some cases as well.

- **Table 7.1:** Molecular partition functions.

type of motion	energy	partition function	magnitude
translation (1-D)	$\frac{\hbar^2}{8m} \frac{n^2}{L^2}$	$\left(\frac{2\pi m k_B T}{\hbar^2}\right)^{1/2} L$	$10^8 \times L$
translation (3-D)	$\frac{\hbar^2}{8m} \left(\frac{n_x^2}{L_y^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$	$\left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2} V$	$10^{24} \times V$
rotation (1-D) ^a	$\frac{\hbar^2}{2I} M^2$	$\left(\frac{2I k_B T}{\hbar^2 \sigma}\right)^{1/2}$	10
rotation (2-D) ^b	$\frac{\hbar^2}{2I} J(J+1)$	$\left(\frac{2I k_B T}{\hbar^2 \sigma}\right)$	10^2
rotation (3-D) ^c	$\epsilon_{J,K}$ or $\epsilon_{J,K_a K_c}$	$\frac{\pi^{1/2}}{\sigma} \left(\frac{2k_B T}{\hbar^2}\right)^{3/2} (I_x I_y I_z)^{1/2}$	$10^3 \dots 10^4$
vibration ^d	$\hbar \nu_i v$	$[1 - \exp(-\hbar \nu_i / k_B T)]^{-1}$	$1 \dots 10$
electronic	ϵ_i	$\sum_i g_i \exp(-\epsilon_i / k_B T)$	1

^a Free internal rotor. For a hindered rotor (torsional vibrational mode), the partition function has to be determined by an explicit calculation over the hindered rotor quantum states.

^b Linear molecule.

^c Nonlinear molecule.

^d For each harmonic oscillator degree of freedom measured from zero-point level.

7.2.2 Example 1: Reactions of two atoms $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{A} \cdots \mathbf{B}^\ddagger \rightarrow \mathbf{AB}$

This example is somewhat artificial unless there is some mechanism to remove the bond energy (for example, in associative ionization, $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{A} \cdots \mathbf{B}^\ddagger \rightarrow \mathbf{AB}^+ + e^-$).

$$k(T) = \frac{k_B T}{h} \frac{Q_{AB}^\ddagger}{Q_A Q_B} \exp\left(-\frac{\Delta E_0}{RT}\right) \quad (7.42)$$

$$= \frac{k_B T}{h} \left(\frac{Q_{AB}^\ddagger / V}{(Q_A / V)(Q_B / V)} \right)_{trans} \left(\frac{Q_{AB}^\ddagger}{1} \right)_{rot} \exp\left(-\frac{\Delta E_0}{RT}\right) \quad (7.43)$$

$$= \frac{k_B T}{h} \left(\frac{2\pi(m_A + m_B)k_B T}{h^2} \frac{h^2}{2\pi m_A k_B T} \frac{h^2}{2\pi m_B k_B T} \right)^{3/2} \left(\frac{8\pi^2 I^\ddagger k_B T}{h^2} \right) \times \exp\left(-\frac{\Delta E_0}{RT}\right) \quad (7.44)$$

$$= \frac{k_B T}{h} \left(\frac{h^2}{2\pi k_B T} \frac{m_A + m_B}{m_A m_B} \right)^{3/2} \left(\frac{8\pi^2 k_B T}{h^2} \frac{m_A m_B (r_A + r_B)^2}{m_A + m_B} \right) \times \exp\left(-\frac{\Delta E_0}{RT}\right) \quad (7.45)$$

↷

$$k(T) = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \pi (r_A + r_B)^2 \exp\left(-\frac{\Delta E_0}{RT}\right) \quad (7.46)$$

This result is identical to that obtained by the LC model in collision theory!

7.2.3 Example 2: The reaction $\text{F} + \text{H}_2 \rightarrow \text{F}\cdots\text{H}\cdots\text{H}^\ddagger \rightarrow \text{FH} + \text{H}$

- **Exercise 7.1:** Evaluate the rate constant for the reaction



using the data in Table 7.2 at $T = 200, 300, 500, 1000$ and 2000 K , determine the Arrhenius parameters, and compare the results with the experimental value of

$$k = 2 \times 10^{14} \exp(-800/T) \text{ cm}^3/\text{mol s} \quad (7.48)$$

□

- **Table 7.2:** Properties of the reactants and transition state of the reaction $\text{F} + \text{H}_2$.

parameter	$\text{F}\cdots\text{H}\cdots\text{H}^\ddagger$	F	H_2
$r_2(\text{F}\cdots\text{H})/(\text{\AA})$	1.602		
$r_1(\text{H}\cdots\text{H})/(\text{\AA})$	0.756		0.7417 ^b
$\nu_1/(\text{cm}^{-1})$	4007.6		4395.2
$\nu_2/(\text{cm}^{-1})$	397.9		
$\nu_3/(\text{cm}^{-1})$	397.9		
$\nu_4/(\text{cm}^{-1})$	310.8 ⁱ ^c		
$m/(\text{u})$	21.014	18.9984	2.016
$I/\left(\text{u\AA}^2\right)$	7.433		0.277
σ	1		2
g_{el}^d	4	4	1
$E_0/(\text{kJ mol}^{-1})$	6.57	0.00	

^a The transition state FHH^\ddagger is assumed to be linear.

^b $= r(\text{H}-\text{H})$.

^c One imaginary frequency describes the TS along the RC.

^d The electronic ground state of F is ${}^2P_{3/2}$. We neglect the ${}^2P_{1/2}$ spin-orbit component at $E({}^2P_{1/2}) = 404 \text{ cm}^{-1}$ because it does not correlate with the products $\text{H} + \text{HF}$. The electronic state of linear FHH^\ddagger is ${}^2\Pi$. The ground state of H_2 is ${}^2\Sigma_g^+$.

- **Solution 7.1:**

$$k(T) = \frac{k_B T}{h} \frac{Q_{FHH}^\ddagger}{Q_F Q_{H_2}} \exp\left(-\frac{\Delta E_0}{RT}\right) \quad (7.49)$$

$$= \frac{k_B T}{h} \left(\frac{Q_{FHH}^\ddagger/V}{(Q_F/V)(Q_{H_2}/V)} \right)_{trans} \left(\frac{Q_{FHH}^\ddagger}{Q_F Q_{H_2}} \right)_{rot} \left(\frac{Q_{FHH}^\ddagger}{Q_F Q_{H_2}} \right)_{vib} \left(\frac{Q_{FHH}^\ddagger}{Q_F Q_{H_2}} \right)_{el} \times \exp\left(-\frac{\Delta E_0}{RT}\right) \quad (7.50)$$

The different factors can be evaluated separately:

$$\left(\frac{Q_{FHH}^\ddagger/V}{(Q_F/V)(Q_{H_2}/V)} \right)_{trans} = \left(\frac{m_F + m_{H_2}}{m_F m_{H_2}} \right)^{3/2} \left(\frac{h^2}{2\pi k_B T} \right)^{3/2} \quad (7.51)$$

$$\left(\frac{Q_{FHH}^\ddagger}{Q_F Q_{H_2}} \right)_{rot} = \left(\frac{8\pi^2 k_B T I^\ddagger / h^2}{8\pi^2 k_B T I_{H_2} / \sigma_{H_2} h^2} \right) = \sigma_{H_2} \frac{I^\ddagger}{I_{H_2}} \quad (7.52)$$

$$\left(\frac{Q_{FHH}^\ddagger}{Q_F Q_{H_2}} \right)_{vib} = \frac{1 - \exp(-h\nu_{H_2}/k_B T)}{\prod_{i=1}^3 [1 - \exp(-h\nu_i^\ddagger/k_B T)]} \quad (7.53)$$

$$\left(\frac{Q_{FHH}^\ddagger}{Q_F Q_{H_2}} \right)_{el} = \frac{4}{4 \times 1} \quad (7.54)$$

Note: The difference between the TST result and experiment can be ascribed (a) to tunneling and (b) deficiencies of the *ab initio* PES. Indeed, according to newer *ab initio* calculations, the TS is actually slightly bent and the TS parameters differ slightly, yielding better agreement with experiment. ■

7.2.4 Example 3: Deviations from Arrhenius behavior (T^n dependence of $k(T)$)*

- **Exercise 7.2:** The temperature dependence of bimolecular gas phase reactions of the type $A + B \rightarrow$ products can usually be expressed in the form

$$k(T) = B \times T^n \times \exp(-\Delta E_0/RT) \quad (7.55)$$

Using the TST expression for $k(T)$

$$k(T) = \frac{k_B T}{h} \frac{Q_{AB}^\ddagger}{Q_A Q_B} \exp\left(-\frac{\Delta E_0}{RT}\right), \quad (7.56)$$

determine the values of n for the types of reactions in Table 7.3, assuming that the vibrational degrees of freedom are not excited. \square

- **Table 7.3:**

A	+ B	\rightarrow TS ‡	$\frac{k_B T}{h}$	transl.	rot.	n
atom	atom	linear TS	T^1	$\frac{T^{3/2}}{T^{3/2}T^{3/2}}$	$\frac{T^1}{1}$	+0.5
atom	linear molecule	linear TS	T^1	$T^{-3/2}$	$\frac{T^1}{T^{3/2}}$	-0.5
atom	linear molecule	nonlin. TS	T^1	$T^{-3/2}$	$\frac{T^1}{T^{3/2}}$	0.0
atom	nonlin. molecule	nonlin. TS	T^1	$T^{-3/2}$	$\frac{T^{3/2}}{T^{3/2}}$	-0.5
linear molecule	linear molecule	linear TS	T^1	$T^{-3/2}$	$\frac{T^1}{T^1T^1}$	-1.5
linear molecule	linear molecule	nonlin. TS	T^1	$T^{-3/2}$	$\frac{T^{3/2}}{T^1T^1}$	-1.0
linear molecule	nonlin. molecule	nonlin. TS	T^1	$T^{-3/2}$	$\frac{T^{3/2}}{T^1T^{3/2}}$	-1.5
nonlin. molecule	nonlin. molecule	nonlin. TS	T^1	$T^{-3/2}$	$\frac{T^{3/2}}{T^{3/2}T^{3/2}}$	-2.0

- **Solution 7.2:** See Table 7.3. ■

Using the above results, we can recast $k(T)$ and determine the following expression for the Arrhenius activation energy, with n as above:

$$E_A = \Delta E_0 + nRT + RT^2 \frac{d \ln Q_{vib}^\ddagger}{dT} - RT^2 \sum_{\text{Reactants}} \frac{d \ln Q_{vib}^{\text{reactants}}}{dT} \quad (7.57)$$

We see that the value for E_A depends on the vibrational frequencies of the TS and the reactants. Often, the frequencies of the reactants are very high so that $Q_{vib}^{\text{reactant}} = 1$. However, the TS may have soft vibrations so that Q_{vib}^\ddagger may approach the classical value

$$Q_{vib} = [1 - \exp(-h\nu/k_B T)]^{-1} \rightarrow \frac{k_B T}{h\nu} \text{ for } T \rightarrow \infty \quad (7.58)$$

Thus, each “soft” vibrational mode in the TS increases n by 1, each “soft” vibrational mode in the reactants decreases n by 1.

7.3 Thermodynamic interpretation of transition state theory

7.3.1 Fundamental equation of thermodynamic transition state theory

As shown above,

$$k(T) = \frac{k_B T}{h} K_c^\ddagger \quad (7.59)$$

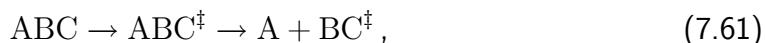
K_c^\ddagger can often be interpreted using thermodynamic arguments, i.e., ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger . For liquid phase reactions, this is straightforward. For gas phase reactions, we have to take into account the difference between K_c^\ddagger and K_p^\ddagger .

a) Thermodynamic transition state theory for unimolecular gas phase reactions

For unimolecular isomerization and dissociation reactions of the type



or



we have

$$K_c^\ddagger(T) = \frac{[ABC^\ddagger]}{[ABC]} = \frac{p_{ABC^\ddagger}}{p_{ABC}} = K_p^\ddagger(T) \quad (7.62)$$

$K_c^\ddagger(T) = K_p^\ddagger(T) = K^\ddagger(T)$ is dimensionless ($\Delta\nu^\ddagger = 0$) and we do not have to worry about a difference between $K_c^\ddagger(T) = K_p^\ddagger(T)$ and about units or different standard states.

► **Results:** Eq. 7.59 thus gives the following results:

- **Rate constant:**

$$k(T) = \frac{k_B T}{h} K^\ddagger(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (7.63)$$

↷

$$k(T) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (7.64)$$

- **Arrhenius activation energy:**

$$E_A = RT^2 \frac{d \ln k}{dT} = RT^2 \frac{d}{dT} \ln \left[\frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \right] \quad (7.65)$$

↷

$$E_A = \Delta H^\ddagger + RT + RT^2 \frac{d \Delta S^\ddagger}{dT} \quad (7.66)$$

$$= \Delta H^\ddagger + RT + RT \frac{d \Delta c_p^\ddagger}{dT} \quad (7.67)$$

If $\Delta S^\ddagger = f(T)$ in the temperature range of interest, we obtain

$$E_A = \Delta H^\ddagger + RT \quad (7.68)$$

- **Arrhenius preexponential factor:**

$$\Delta H^\ddagger = E_A - RT \quad (7.69)$$

$$k(T) = e \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{E_A}{RT}\right) \quad (7.70)$$

$$A = e \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (7.71)$$

b) Thermodynamic transition state theory for bimolecular gas phase reactions

► **Conversion from $K_c^\ddagger(T)$ to $K_p^\ddagger(T)$:** For bimolecular reactions



we have to account for the different numbers of species $\Delta\nu^\ddagger = \nu^\ddagger - \nu_{\text{reactants}}$:

$$\Delta\nu^\ddagger = -1. \quad (7.73)$$

We therefore have to convert from $K_c^\ddagger(T)$ to $K_p^\ddagger(T)$ via

$$K_c^\ddagger(T) = \frac{[ABC^\ddagger]}{[A][BC]} = \frac{\frac{p_{ABC^\ddagger}}{RT}}{\frac{p_A}{RT} \frac{p_{BC}}{RT}} = \frac{\frac{p_{ABC^\ddagger}/p^\ominus}{RT}}{\frac{p_A/p^\ominus}{RT} \frac{p_{BC}/p^\ominus}{RT}} \times \frac{1}{p^\ominus} = K_p^\ddagger(T) \times \left(\frac{RT}{p^\ominus}\right)^{-\Delta\nu^\ddagger}. \quad (7.74)$$

Here, $K_c^\ddagger(T)$ is conveniently given in units of 1 mol^{-1} .⁴⁴ However, K_p^\ddagger , ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger are related to the standard state at $p^\ominus = 1\text{ bar}$.⁴⁵ To keep track of units in the conversion, it is useful to apply R in $\frac{1\text{ bar}}{\text{mol K}}$ by writing

$$R = 8.3145 \frac{\text{J}}{\text{mol K}} = 8.3145 \frac{\text{m}^3 \text{Pa}}{\text{mol K}} = 0.083145 \frac{1\text{ bar}}{\text{mol K}} = R' \quad (7.76)$$

⁴⁴ With $K_c^\ddagger(T)$ in units of $(\text{mol l}^{-1})^{\Delta\nu}$, we get as close as possible to the standard state $m^* = 1\text{ mol kg}^{-1}$ for reactions in aqueous solution.

⁴⁵ We recall that the thermodynamic equilibrium constant $K_p(T) = \exp(-\Delta_R G^\ominus/RT)$ referred to the standard state at $p^\ominus = 1\text{ bar}$ is dimensionless. Instead of the dimensionless $K_p^\ddagger(T)$, one may also decide to use the equilibrium constant in pressure units $K_p^{\ddagger'}$:

$$K_c^\ddagger(T) = \frac{[ABC^\ddagger]}{[A][BC]} = \frac{\frac{p_{ABC^\ddagger}}{RT}}{\frac{p_A}{RT} \frac{p_{BC}}{RT}} = K_p^{\ddagger'}(T) \times R'T \quad (7.75)$$

so that, with $\Delta\nu^\ddagger = -1$, we obtain

$$K_c^\ddagger(T) = \frac{\frac{p_{ABC^\ddagger}/p^\ominus}{RT}}{\frac{p_A/p^\ominus}{RT} \frac{p_{BC}/p^\ominus}{RT}} \times \frac{1}{p^\ominus} = K_p^\ddagger(T) \times \left(\frac{R'T}{p^\ominus} \right). \quad (7.77)$$

Thus, via Eq. 7.59:

$$k(T) = \frac{k_B T}{h} \frac{R'T}{p^\ominus} K_p^\ddagger(T) = \frac{k_B T}{h} \frac{R'T}{p^\ominus} \exp\left(-\frac{\Delta G^{\ominus\ddagger}}{RT}\right), \quad (7.78)$$

in units of

$$\dim(k(T)) = \dim\left(\frac{k_B T}{h}\right) \times \dim\left(\frac{R'T}{p^\ominus}\right) = \frac{1}{\text{mol s}} \quad (7.79)$$

and with the standard state for the thermodynamics quantities explicitly indicated by the \ominus symbol.

► Results:

- **Rate constant:**

$$k(T) = \frac{k_B T}{h} \frac{R'T}{p^\ominus} \exp\left(\frac{\Delta S^{\ominus\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ominus\ddagger}}{RT}\right) \quad (7.80)$$

- **Arrhenius activation energy:**

$$E_A = RT^2 \frac{d \ln k}{dT} \quad (7.81)$$

If $\Delta S^{\ominus\ddagger} \neq f(T)$ in the temperature range of interest:

$$E_A = \Delta H^{\ominus\ddagger} + 2RT \quad (7.82)$$

- **Arrhenius preexponential factor:**

$$\Delta H^{\ominus\ddagger} = E_A - 2RT \quad (7.83)$$

↷

$$k(T) = \frac{k_B T}{h} \frac{R'T}{p^\ominus} \exp\left(\frac{\Delta S^{\ominus\ddagger}}{R}\right) \exp\left(-\frac{E_A - 2RT}{RT}\right) \quad (7.84)$$

$$= e^2 \frac{k_B T}{h} \frac{R'T}{p^\ominus} \exp\left(\frac{\Delta S^{\ominus\ddagger}}{R}\right) \exp\left(-\frac{E_A}{RT}\right) \quad (7.85)$$

Comparison with the Arrhenius expression $k = A \exp(-E_A/RT)$ thus gives

$$A = e^2 \frac{k_B T}{h} \frac{R'T}{p^\ominus} \exp\left(\frac{\Delta S^{\ominus\ddagger}}{R}\right) \quad (7.86)$$

- **Note:** k and A are given above in units of $1\text{ mol}^{-1}\text{ s}^{-1}$ (we may denote this by writing them as k_c and A_c), while ΔH^{\ddagger} and ΔS^{\ddagger} used above are referred to the standard state for gases of $p^\ominus = 1\text{ bar}$.

- For ideal gases, ΔH^\ddagger and ΔU^\ddagger are related via

$$\Delta H^{\ddagger} = \Delta U^{\ddagger} + \Delta \nu^\ddagger (pV) = \Delta U^{\ddagger} - RT = \Delta U^{+\ddagger} - RT \quad (7.87)$$

- Likewise, ΔS^{\ddagger} and $\Delta S^{+\ddagger}$ for are related via

$$\Delta S^{+\ddagger} - \Delta S^{\ddagger} = \int_{p^\ominus}^{c^+} \frac{\delta q}{T} = \int_{p^\ominus}^{c^+} \frac{pdV}{T} = \int_{p^\ominus}^{c^+} \frac{pdV}{T} = \int_{p^\ominus}^{c^+} \frac{\Delta n^\ddagger R}{V} dV \quad (7.88)$$

$$\begin{aligned} &= \Delta n^\ddagger R \ln \frac{V^+}{n^+ R' T / p^\ominus} = \Delta n^\ddagger R \ln \frac{V^+}{n^+ R' T / p^\ominus} = \Delta n^\ddagger R \ln \frac{p^\ominus}{c^+ R' T} \\ &= \Delta n^\ddagger R \ln \frac{c^+ R' T}{p^\ominus} \end{aligned} \quad (7.90)$$

↷

$$\Delta S^{\ddagger} = \Delta S^{+\ddagger} - R \ln \frac{c^+ R' T}{p^\ominus} \quad (7.91)$$

with $p^\ominus = 1\text{ bar}$ and $c^+ = \frac{n^+}{V^+} = 1\text{ mol l}^{-1}$.

c) Thermodynamic transition state theory for reactions in the liquid phase

For reactions in condensed phases,

$$\Delta H \approx \Delta U \quad (7.92)$$

and

$$K_c^\ddagger(T) = \frac{[\text{ABC}^\ddagger]}{[\text{A}][\text{BC}]} = (c^+)^{\Delta \nu^\ddagger} \exp\left(-\frac{\Delta S^{+\ddagger}}{R}\right) \exp\left(-\frac{\Delta U^{+\ddagger}}{RT}\right) \quad (7.93)$$

$$\approx (c^+)^{\Delta \nu^\ddagger} \exp\left(-\frac{\Delta S^{+\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{+\ddagger}}{RT}\right) \quad (7.94)$$

↷

- for unimolecular reactions:

$$k(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta S^{+\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{+\ddagger}}{RT}\right) \quad (7.95)$$

- for bimolecular reactions:

$$k(T) = \frac{k_B T}{c^+ h} \exp\left(-\frac{\Delta S^{+\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{+\ddagger}}{RT}\right) \quad (7.96)$$

Note: The conversion between values for $\Delta H^{+\ddagger}$ and ΔH^{\ddagger} and, likewise, between values for $\Delta S^{+\ddagger}$ and ΔS^{\ddagger} for a given reaction in the liquid and gas phase requires some caution.⁴⁶

⁴⁶ See, e.g., D. M. Golden, J. Chem. Ed. **48**, 235 (1971).

7.3.2 Applications of thermodynamic transition state theory

a) Comparison of ΔS^\ddagger -values for different types of transition states

► Bimolecular reactions:



↷

$$\Delta S^\ddagger < 0 \quad (7.98)$$

or even

$$\Delta S^\ddagger \ll 0 \quad (7.99)$$

Furthermore, for chemically otherwise similar molecules

$$S \text{ (nonlinear molecule)} > S \text{ (linear molecule)} \gg S \text{ (cyclic molecule)} \quad (7.100)$$

Thus,

$$|\Delta S^\ddagger \text{ (nonlinear molecule)}| < |\Delta S^\ddagger \text{ (linear molecule)}| \ll |\Delta S^\ddagger \text{ (cyclic molecule)}| \quad (7.101)$$

For example:

$$\left| \Delta S^\ddagger \left(\begin{array}{ccc} A & \cdots & B \\ & \ddots & \\ & & C \end{array} \right) \right| < \left| \Delta S^\ddagger \left(\begin{array}{ccc} A & \cdots & B & \cdots & C \end{array} \right) \right| \ll \left| \Delta S^\ddagger \left(\begin{array}{ccc} A & \cdots & B \\ \vdots & & \vdots \\ C & \cdots & D \end{array} \right) \right| \quad (7.102)$$

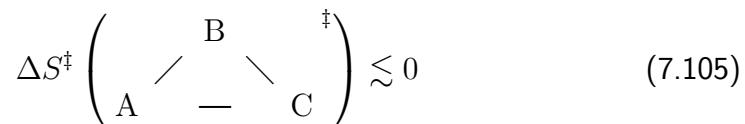
↷

$$A_{\text{cyclic}} \ll A_{\text{linear}} < A_{\text{nonlinear}} \quad (7.103)$$

► Unimolecular reactions:



- For isomerization reactions with a tight transition state:



- For bond fission reactions with a loose transition state:

$$\Delta S^\ddagger (AB \cdots C^\ddagger) > 0 \quad (7.106)$$

↷

$$A_{\text{loose}} > A_{\text{tight}} \quad (7.107)$$

b) Thermochemical estimation of A-factors*

Equations 7.71 and 7.86 allow us to estimate the A -factors of chemical reaction rate constants by the following procedure (Benson 1976):

- (1) We setup a model for the TS, with a certain structure and vibrational frequencies.
- (2) We take a reference molecule that is similar to the TS and use the S^{ref} of the reference molecule for a zero-order estimation of ΔS^\ddagger according to

$$\Delta S^\ddagger = S^{\text{ref}} - \sum_{\text{reactants}} (S^{\text{reactants}}) \quad (7.108)$$

- (3) We apply corrections for the differences between S^{ref} and S^\ddagger based on the statistical thermodynamics result of

$$S = R \ln Q + RT \frac{d \ln Q}{dT} \quad (7.109)$$

↷

$$\Delta S^{\text{cor}} = S^\ddagger - S^{\text{ref}} = R \ln \frac{Q^\ddagger}{Q^{\text{ref}}} + RT \frac{d}{dT} \ln \left(\frac{Q^\ddagger}{Q^{\text{ref}}} \right) \quad (7.110)$$

Usually, the correction term accounts for differences of the entropies for translation, rotation, internal rotations, vibrations, symmetry, electron spin, plus sometimes other terms (e.g., optical isomers).

- **Example 7.1:** Estimation of the A -factor for the reaction $\text{O} + \text{CH}_4 \rightarrow (\text{O} \cdots \text{H} \cdots \text{CH}_3)^\ddagger \rightarrow \text{OH} + \text{CH}_3$.

$$\Delta S^\ddagger = S(\text{O} \cdots \text{H} \cdots \text{CH}_3)^\ddagger - S(\text{O}) - S(\text{CH}_4) \quad (7.111)$$

$$S^{\text{ref}} = S(\text{CH}_3\text{F}) \quad (7.112)$$

ΔS^{cor} thus depends on a comparison of CH_3F and OHCH_3^\ddagger (see Table). □

- **Table 7.4:** Estimation of the A -factor for the reaction $\text{O} + \text{CH}_4 \rightarrow (\text{O} \cdots \text{H} \cdots \text{CH}_3)^\ddagger \rightarrow \text{OH} + \text{CH}_3$.

Contribution	$\Delta S^\ddagger / (\text{J mol}^{-1} \text{K}^{-1})$
$S_f^\ominus(\text{CH}_3\text{F}) - S_f^\ominus(\text{O}) - S_f^\ominus(\text{CH}_4)$	-124.3
Spin: $+R \ln 3$	+ 9.1
external rotation: $\frac{1}{3} R \ln \frac{(I_1 I_2 I_3)^\ddagger}{(I_1 I_2 I_3)^{\text{ref}}}$	+ 7.9
translation	- 0.4
$\nu_{\text{CF}} = 1000 \text{ cm}^{-1} \rightarrow RC$	- 0.4
$\nu_{\text{OH}} = 2000 \text{ cm}^{-1}$	+ 0.0
$2\nu_{\text{OHC}}(\text{bend}) = 600 \text{ cm}^{-1}$	+ 4.2
$\Delta S^\ddagger = S_f^\ominus(\text{O} \cdots \text{H} \cdots \text{CH}_3^\ddagger) - S_f^\ominus(\text{O}) - S_f^\ominus(\text{CH}_4)$	-103.9

Correction $\Delta S_p^\ddagger \rightarrow \Delta S_c^\ddagger: +R \ln(R'T) \quad \curvearrowright \quad \Delta S^\ddagger = -19.8 \text{ J mol}^{-1} \text{K}^{-1}$.

Estimated A -value:

$$A = e^2 \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (7.113)$$

$$= 7.39 \times 6.25 \times 10^{12} \times \exp\left(\frac{-19.7 \text{ J mol}^{-1} \text{ K}^{-1}}{8.31 \text{ J mol}^{-1} \text{ K}^{-1}}\right) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (7.114)$$

$$= 4.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (7.115)$$

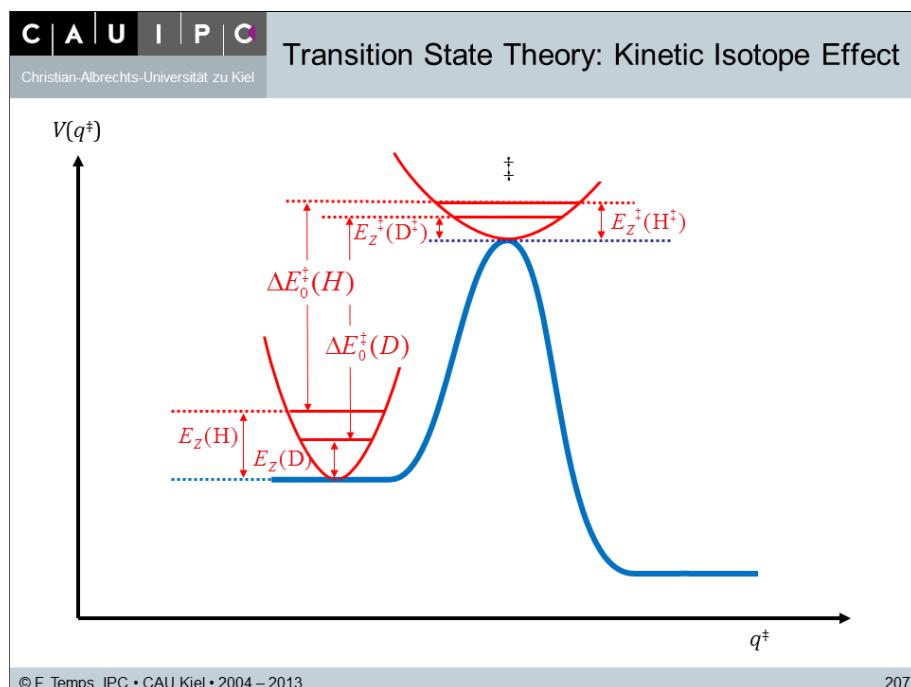
Experimental A -value:

$$A_{\text{expt}} = 1.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (7.116)$$

The difference is probably due to a poor estimate of the TS structure – one can do much better, I just didn't try hard enough here.⁴⁷

7.3.3 Kinetic isotope effects

- **Figure 7.5:** The kinetic isotope effect due to the difference in the zero-point energies of the reactants and the respective TS structures.



⁴⁷ For H abstraction reactions from a series of hydrocarbons by ${}^3\text{CH}_2$, the agreement that was achieved was better than $\pm 30\%$.

Kinetic isotope effects occur in particular in the case of H/D atom transfer reactions. The reason is that the threshold energy ΔE_0^\ddagger depends on the vibrational zero-point energies.

We consider the reactions



where

$$\Delta E_0^\ddagger(H-R) = \Delta V^\ddagger + E_z^\ddagger(A-H-R) - E_z(H-R) \quad (7.119)$$

$$\Delta E_0^\ddagger(D-R) = \Delta V^\ddagger + E_z^\ddagger(A-D-R) - E_z(D-R) \quad (7.120)$$

with

$$E_z = N_L \frac{1}{2} \sum_i h\nu_i \quad (7.121)$$

↷

$$\Delta E_{0(D/H)}^\ddagger = \Delta E_0^\ddagger(D-R) - \Delta E_0^\ddagger(H-R) \quad (7.122)$$

$$= +E_z^\ddagger(A-D-R) - E_z^\ddagger(A-H-R) - (E_z(D-R) - E_z(H-R)) \quad (7.123)$$

↷

$$\frac{k(D-R)}{k(H-R)} = \exp\left(-\frac{\Delta E_{0(D/H)}^\ddagger}{RT}\right) \quad (7.124)$$

- **Example 7.2:** R-H/R-D substitution. The vibrational frequencies depend on the force constants f and reduced masses μ :

$$\nu = \frac{1}{2\pi} \left(\frac{f}{\mu}\right)^{1/2} \quad (7.125)$$

For H/D substitution:

$$\frac{\mu(HR)}{\mu(DR)} \approx \frac{1}{2} \quad (7.126)$$

↷

$$\frac{\nu(HR)}{\nu(DR)} = \left(\frac{\mu(HR)}{\mu(DR)}\right)^{1/2} \approx \sqrt{2} \quad (7.127)$$

With $\nu(HR) = 3000 \text{ cm}^{-1}$ and $\nu(DR) = 2100 \text{ cm}^{-1}$, we find $\Delta E_Z = \frac{1}{2}(3000 - 2100) \text{ cm}^{-1} = 450 \text{ cm}^{-1}$, by which the DR reactant is stabilized compared to the HR reactant. For $T = 300 \text{ K}$:

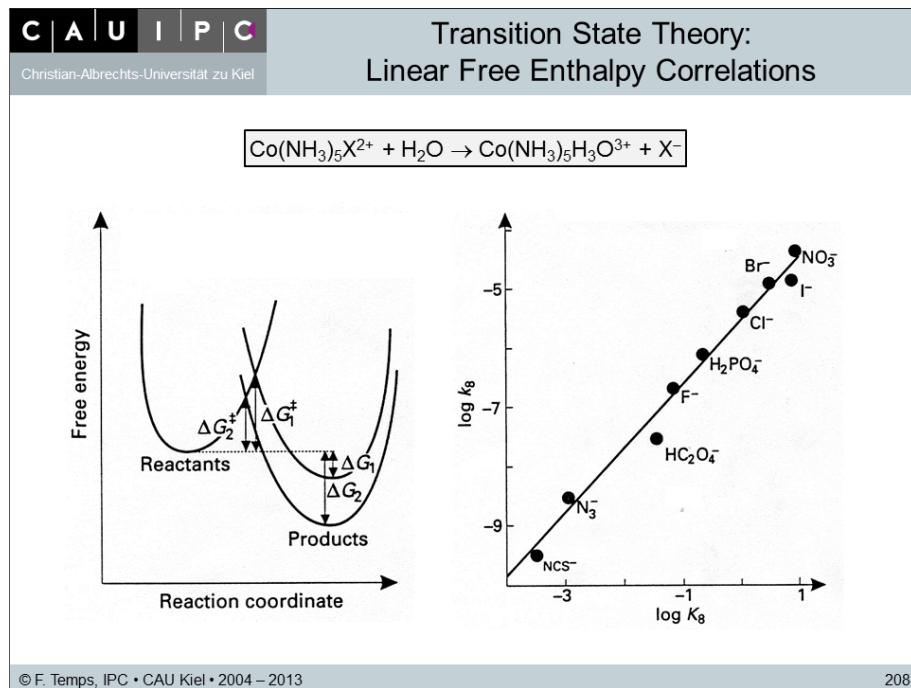
$$\frac{k(DR)}{k(HR)} = \exp\left(-\frac{450}{200}\right) \approx e^{-2.25} \approx 0.1 \quad (7.128)$$

□

For more realistic estimates, one has to take into account the change of all vibrational frequencies in the reacting molecules and the TS.

7.3.4 Gibbs free enthalpy correlations

► **Figure 7.6:** Linear free enthalpy correlations.



Application of the TST expression

$$k = \frac{k_B T}{h} \exp \left(-\frac{\Delta G^\ddagger}{RT} \right) \quad (7.129)$$

to a series of related reactions (1) and (2) often gives a relation of the type⁴⁸

$$\Delta G_1^\ddagger - \Delta G_2^\ddagger = \alpha (\Delta G_1^\ominus - \Delta G_2^\ominus) \quad (7.130)$$

↷

$$\ln \frac{k_1}{k_2} = \alpha \ln \frac{K_1}{K_2} \quad (7.131)$$

7.3.5 Pressure dependence of k

Liquid phase reactions often show a pressure dependence of the rate constant. Using the relation

$$\left(\frac{\partial G}{\partial P} \right)_T = V \quad (7.132)$$

we can predict this pressure dependence. Starting with

$$k = \frac{k_B T}{h} \exp \left(-\frac{\Delta G^\ddagger}{RT} \right) \quad (7.133)$$

we find

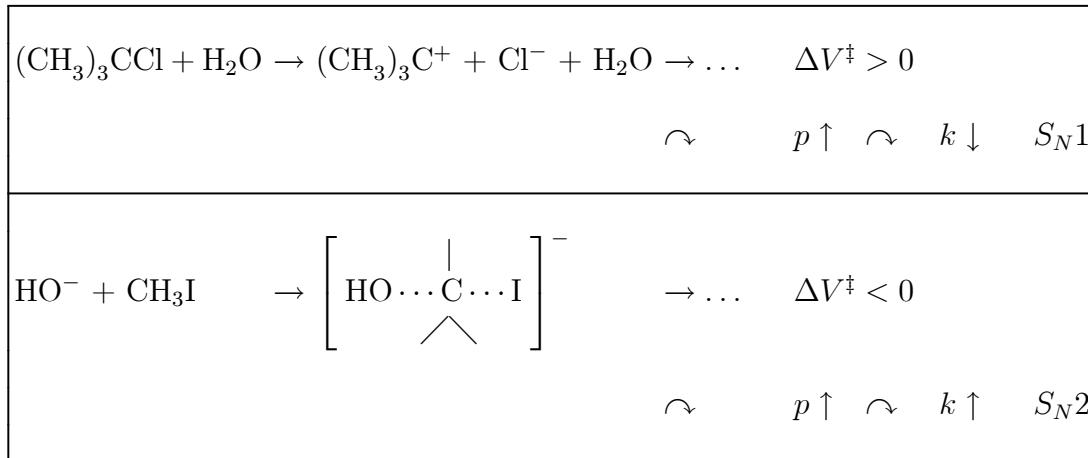
$$\left(\frac{\partial \ln k}{\partial p} \right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (7.134)$$

⁴⁸ A well-known example is the Hammett correlation in organic chemistry.

► **Activation volume:**

$$\Delta V^\ddagger \quad (7.135)$$

- **Example 7.3:** Comparison of the pressure dependencies of the rate constants for S_N1 and S_N2 reactions:

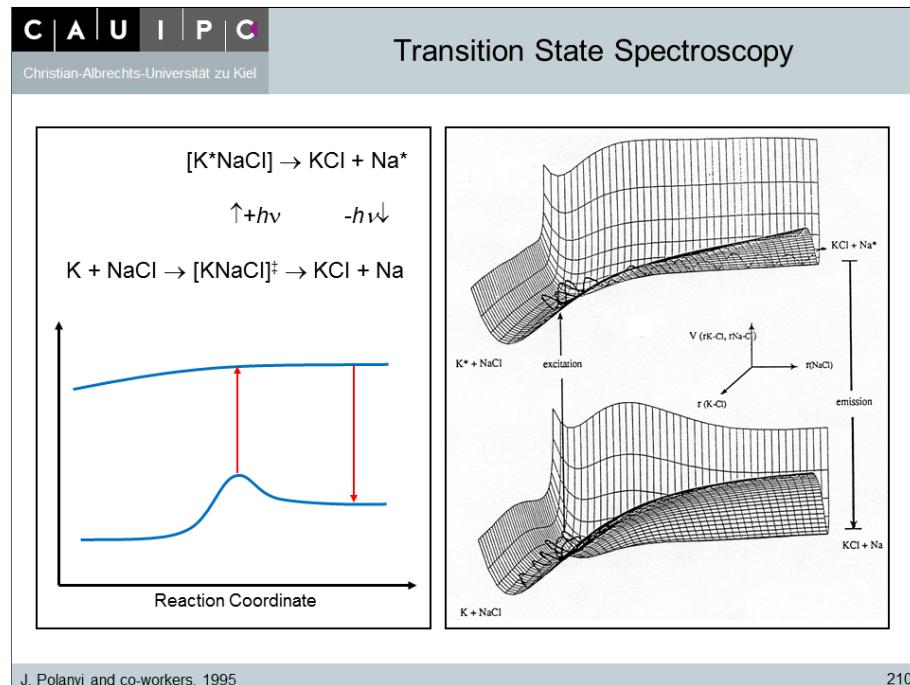


□

7.4 Transition state spectroscopy

Until a few years ago, the “transition state” was a rather “elusive and strange” species. This situation has completely changed (a) because of the rapidly improving quantum chemical methods for computing TS properties and (b) because of transition state spectroscopy, in the frequency domain (J. Polanyi, Kinsey), and in the time domain (Zewail).

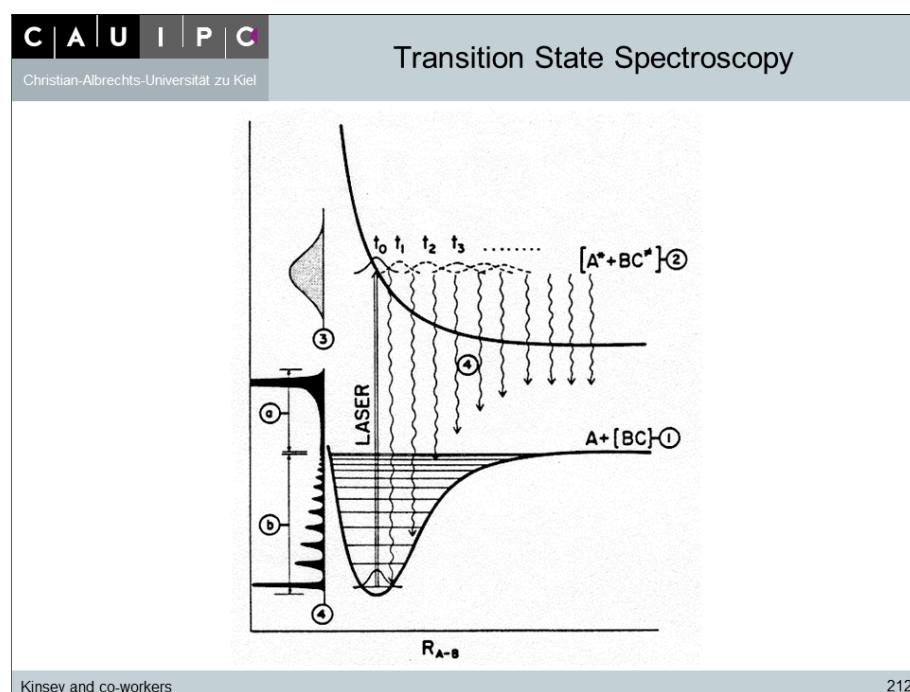
- **Figure 7.7:** Transition state spectroscopy: The reaction $\text{K} + \text{NaCl}$.



J. Polanyi and co-workers, 1995

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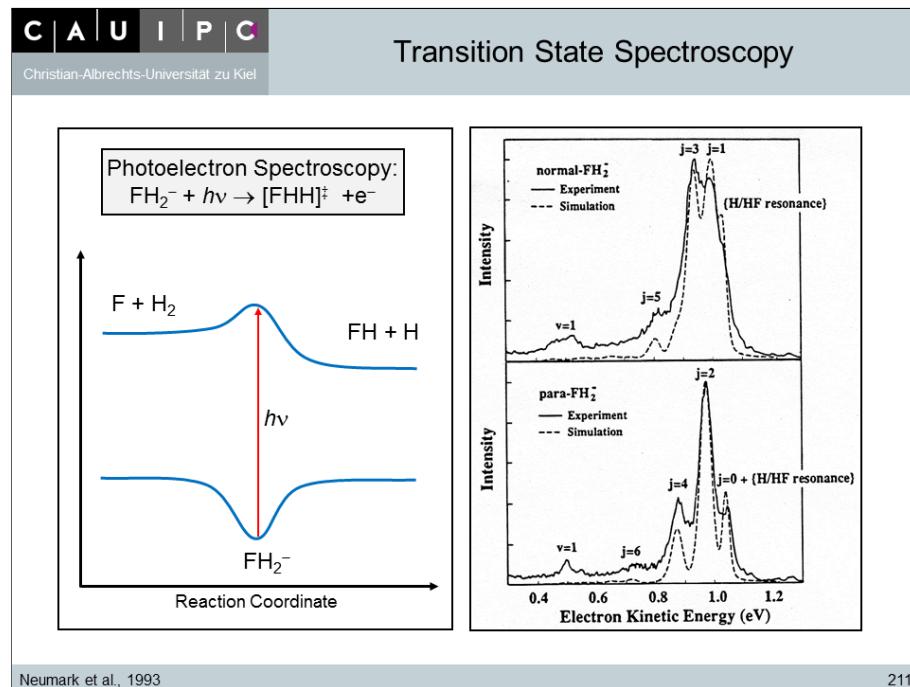
- **Figure 7.8:** Transition state spectroscopy: Raman emission of dissociating molecules.



Kinsey and co-workers

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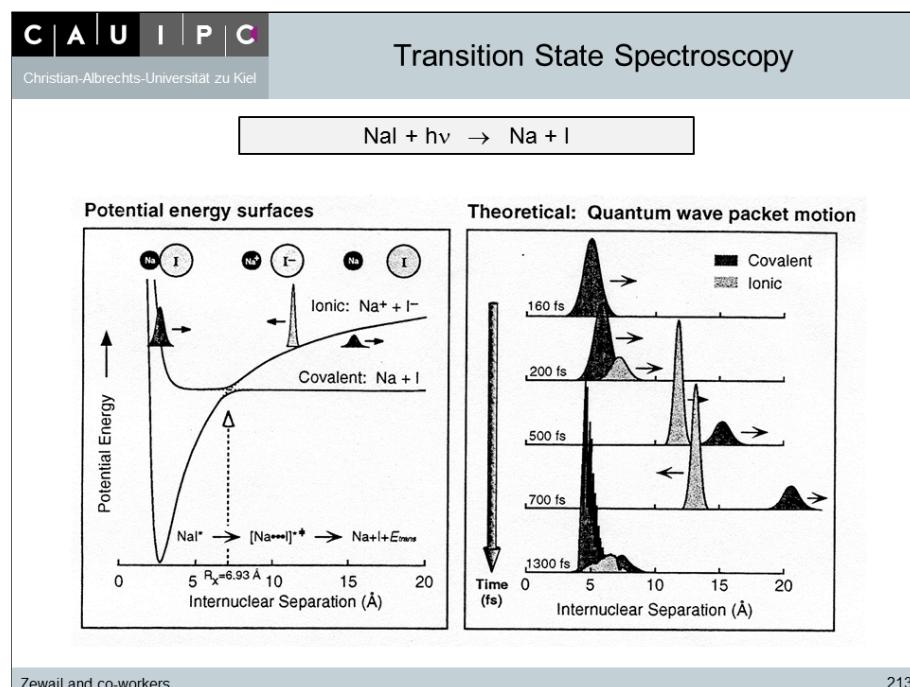
► **Figure 7.9:** Transition state spectroscopy: The reaction $\text{F} + \text{H}_2$.



Neumark et al., 1993

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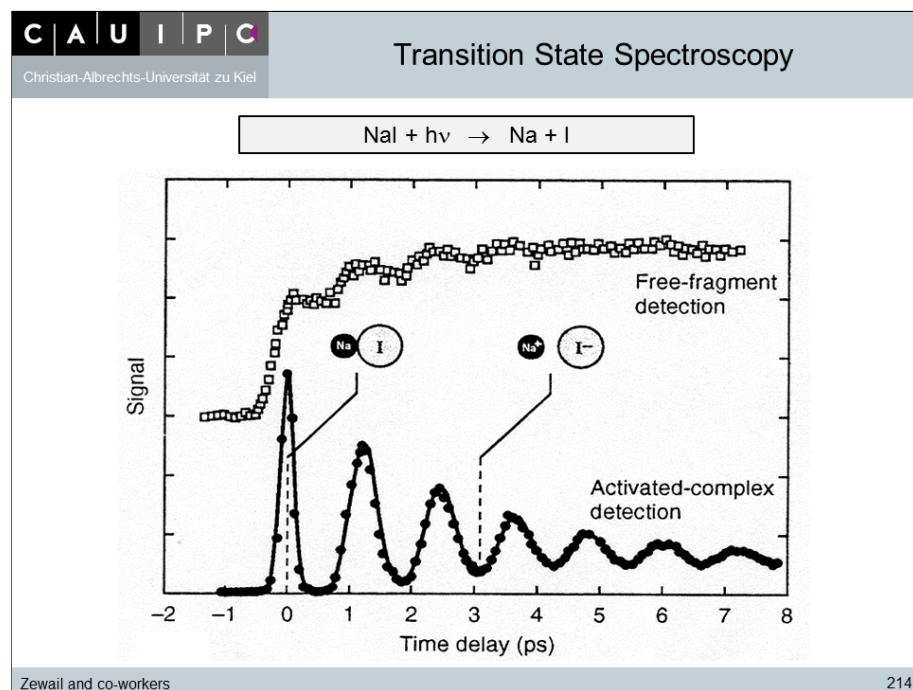
► **Figure 7.10:** Transition state spectroscopy: NaI Photodissociation.



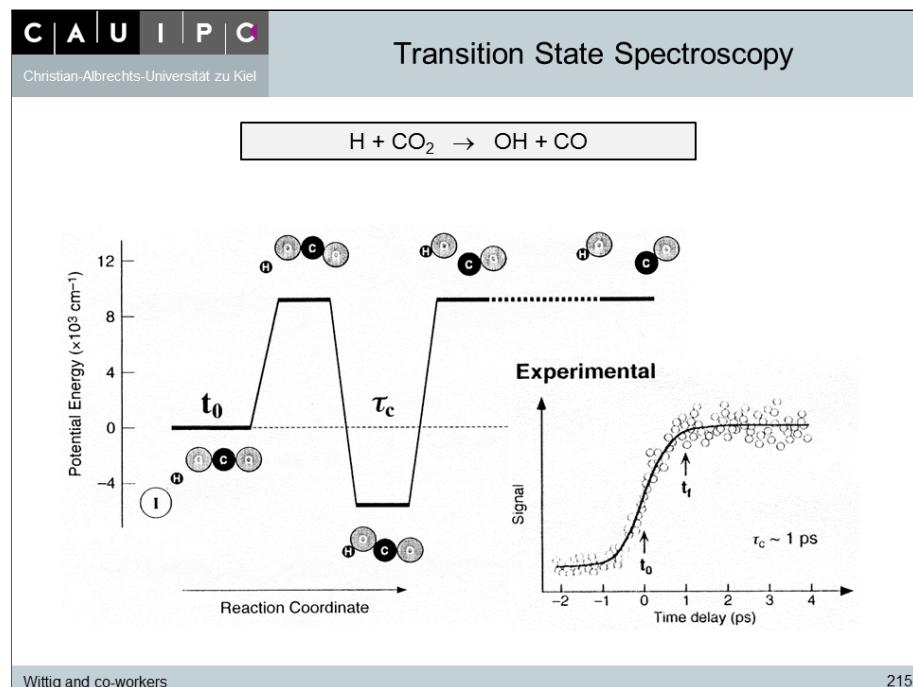
Zewail and co-workers

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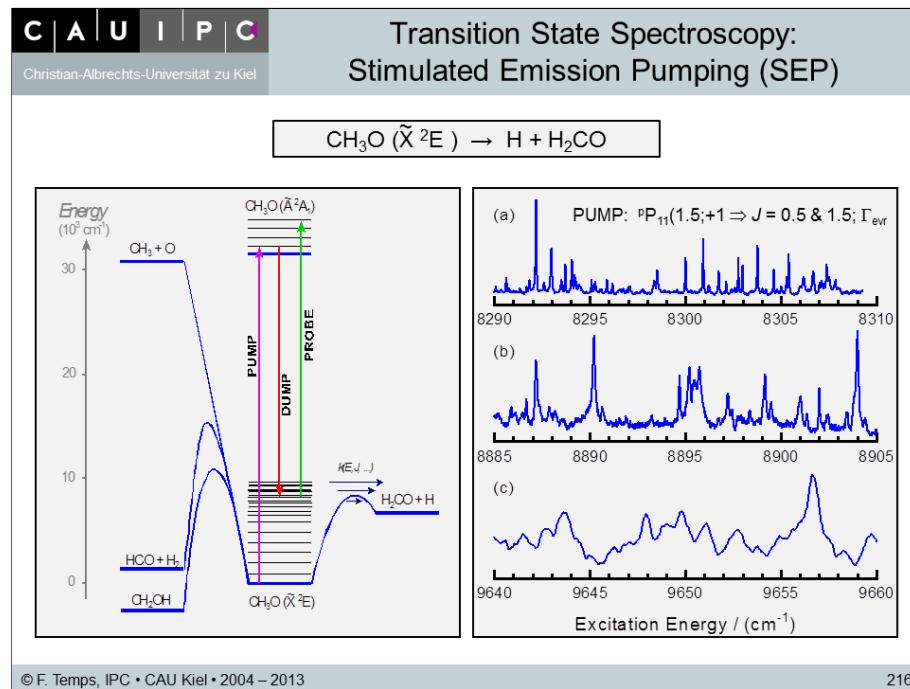
- **Figure 7.11:** Transition state spectroscopy: NaI Photodissociation.



- **Figure 7.12:** Transition state spectroscopy: Reaction a in van-der-Waals Complex.



- **Figure 7.13:** Transition state spectroscopy: Stimulated Emission Pumping.



7.5 References

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8. Unimolecular reactions

Unimolecular reactions are reactions in which only one species experiences chemical change.

► **Figure 8.1:** Examples of unimolecular reactions.

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Unimolecular reactions: examples

- Bond fission (dissociation):

$$\text{I}_2 \longrightarrow \text{I} + \text{I}$$

$$\text{C}_2\text{H}_6 \longrightarrow \text{CH}_3 + \text{CH}_3$$
- Recombination:

$$\text{CH}_3 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_6$$
- Isomerization:
- Reactions of „chemically activated“ molecules:

$${}^1\text{CH}_2 + \text{---} \longrightarrow \text{---} \longrightarrow \text{---}$$
- Reactions of photochemically activated molecules:

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8.1 Experimental observations

(1) There are many reactions governed by a first-order rate law,

$$\frac{d[\text{A}]}{dt} = -k_\infty [\text{A}] , \quad (8.1)$$

for example isomerization and dissociation reactions like



(2) In these reactions, no other species than the reactants experience any chemical change.

(3) These reactions have the same rates in the gas phase and in solution,

$$k_{\text{gas phase}} \approx k_{\text{solution phase}} , \quad (8.6)$$

i.e., the environment has no effect on the reaction rates!

- (4) There are many similar other reactions, however, for which the rate law is second-order, i.e.,

$$\frac{d[A]}{dt} = -k_0 [A] [M] \quad (8.7)$$

Examples are



- (5) More detailed measurements show that at a given temperature the order of the reaction may depend on pressure (see Fig. 8.2), for instance for the reaction



one has found that

- a) for $p \rightarrow 0$:

$$\frac{d[\text{CH}_3\text{NC}]}{dt} = -k_0 [\text{CH}_3\text{NC}] [M] \quad (8.11)$$

This is called the "low pressure range" for the reaction.

- b) for $p \rightarrow \infty$:

$$\frac{d[\text{CH}_3\text{NC}]}{dt} = -k_\infty [\text{CH}_3\text{NC}] \quad (8.12)$$

This is called the "high pressure range" for the reaction".

- (6) The transition from the low to the high pressure range depends

- a) on the size of the molecule (see Fig. 8.3),
b) for a given molecule, it depends on temperature.

- (7) The activation energy in the low pressure regime is much smaller than in the high pressure regime:

$$E_A = RT^2 \frac{d \ln k}{dT} \quad (8.13)$$

where

$$E_{A,0} < E_{A,\infty} \quad (8.14)$$

and

$$E_{A,\infty} \approx E_0 \quad (8.15)$$

- (8) The preexponential factors in the low pressure regime are much higher than the collision frequencies, i.e.,

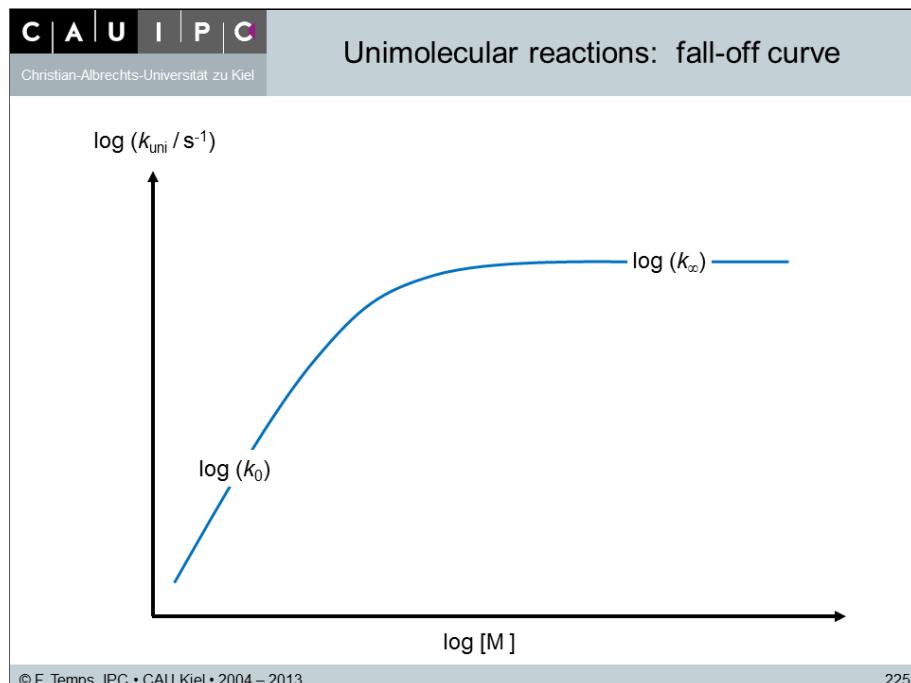
$$A_0 > Z_{AM} \quad (8.16)$$

- (9) For all these reactions, the molecules must somehow be "energized". There are other reactions, in which the molecules are energized chemically ("chemically activated reactions") or by photons. At the microscopic, i.e., molecular level, these reactions should have related mechanisms.

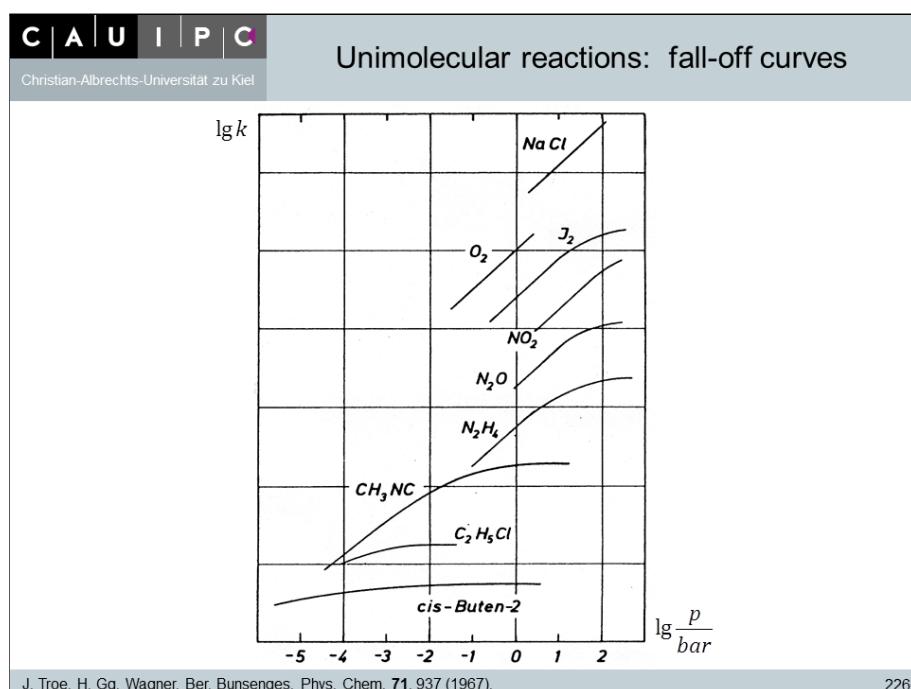
► **Questions:**

- (1) What are the differences of the reactions under (1), (4) and (5)?
- (2) How can we rationalize their reaction mechanisms?

► **Figure 8.2:** Schematic fall-off curve of the unimolecular rate constant.



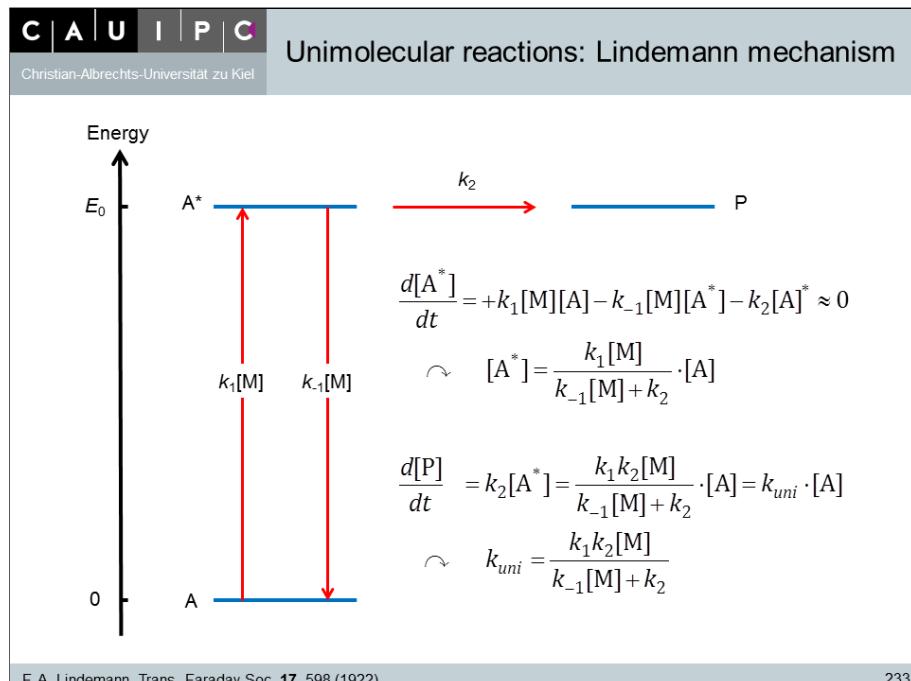
► **Figure 8.3:** Experimentally observed fall-off curves of unimolecular reactions.



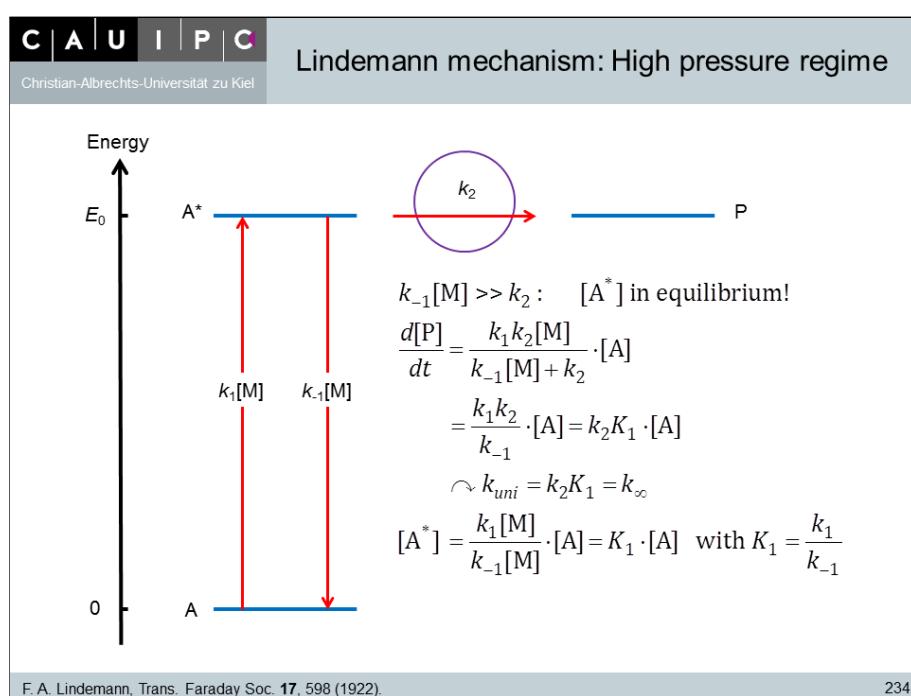
8.2 Lindemann mechanism

First attempts to explain the pressure dependence of unimolecular reaction rate constants due to radiation and the dissociation dynamics due to centrifugal forces (rotational excitation) proved to be wrong. In addition, the historic examples for unimolecular reactions, for instance the N_2O_5 decomposition, were later proven to have more complex reaction mechanisms. The first “realistic” model that explained the pressure dependence of k_{uni} was that proposed by Lindemann (1922).

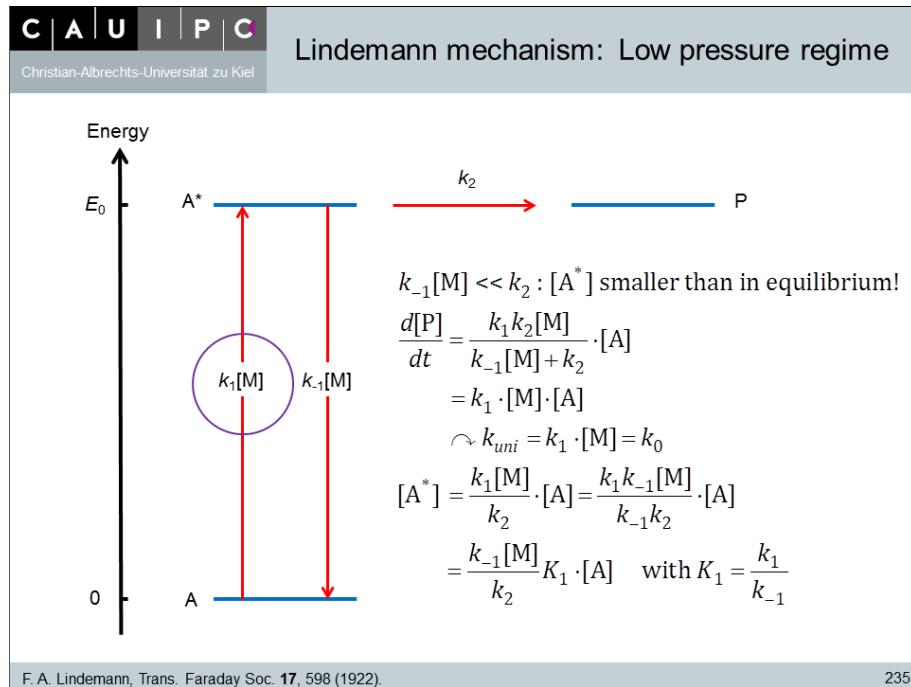
► **Figure 8.4:** Lindemann mechanism.



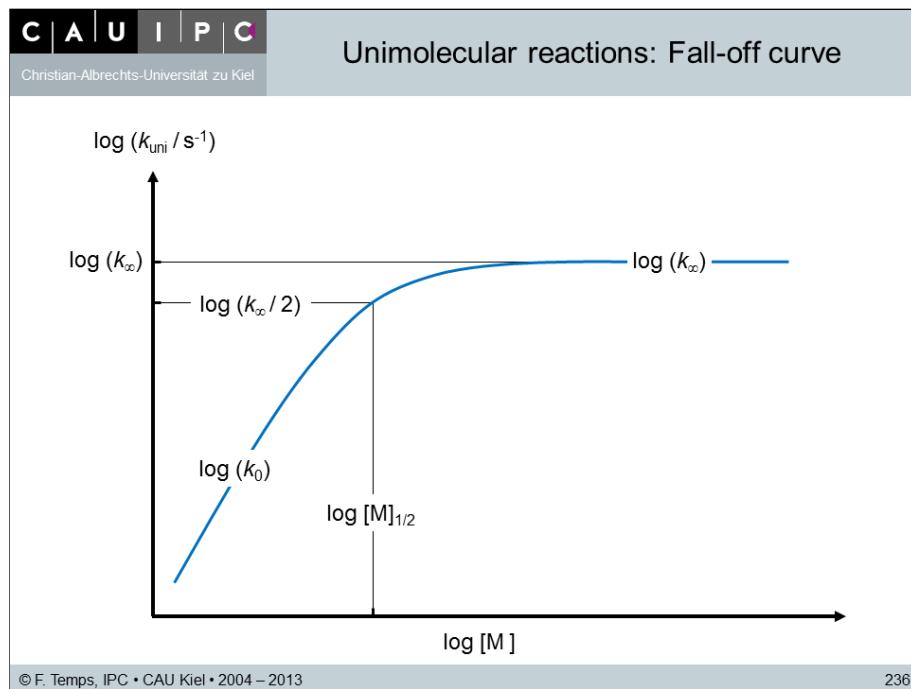
► **Figure 8.5:** Lindemann mechanism: High pressure regime.



- **Figure 8.6:** Lindemann mechanism: Low pressure regime.



- **Figure 8.7:** Fall-off curve: The proper way to plot $\log k_{uni}$ is vs. $\log [M]$.^{a,b}



^a Since $k_0 \propto [M]$, we can also plot $\log k_{uni}$ vs. $\log k_0$. This gives the so-called doubly reduced fall-off curves.

^b In reality, the fall-off regime extends over several orders of magnitude in $[M]$.

- **Half-pressure:** We have found the following results:

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2} \quad (8.17)$$

$$k_{\infty} = k_2 \frac{k_1}{k_{-1}} \quad (8.18)$$

$$k_0 = k_1 [M] \quad (8.19)$$

Thus, if $k_{-1} [M] = k_2$, we have

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2} = \frac{k_2 k_1 [M]}{2k_{-1} [M]} = \frac{1}{2} \frac{k_2 k_1}{k_{-1}} = \frac{1}{2} k_{\infty} \quad (8.20)$$

Half “pressure”:

$$[M]_{1/2} = \frac{k_2}{k_{-1}} \quad (8.21)$$

- **Lifetimes of energized molecules:** It is instructive to look at the reciprocal values:

$$\frac{1}{k_{-1} [M]} = \frac{1}{k_2} \quad (8.22)$$

- $\frac{1}{k_{-1} [M]}$ is the time between two collisions. This is, in fact, the lifetime of the energized molecules with respect to collisional deactivation.
- $\frac{1}{k_2}$ is the lifetime of the excited molecules with respect to reaction.

Thus, at the half pressure, we have

$$\tau_{\text{Collisional Deactivation}} = \tau_{\text{Unimolecular Decay}} \quad (8.23)$$

- **Determination of k_{∞} :**

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2} \quad (8.24)$$

↷

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{1}{[M]} \quad (8.25)$$

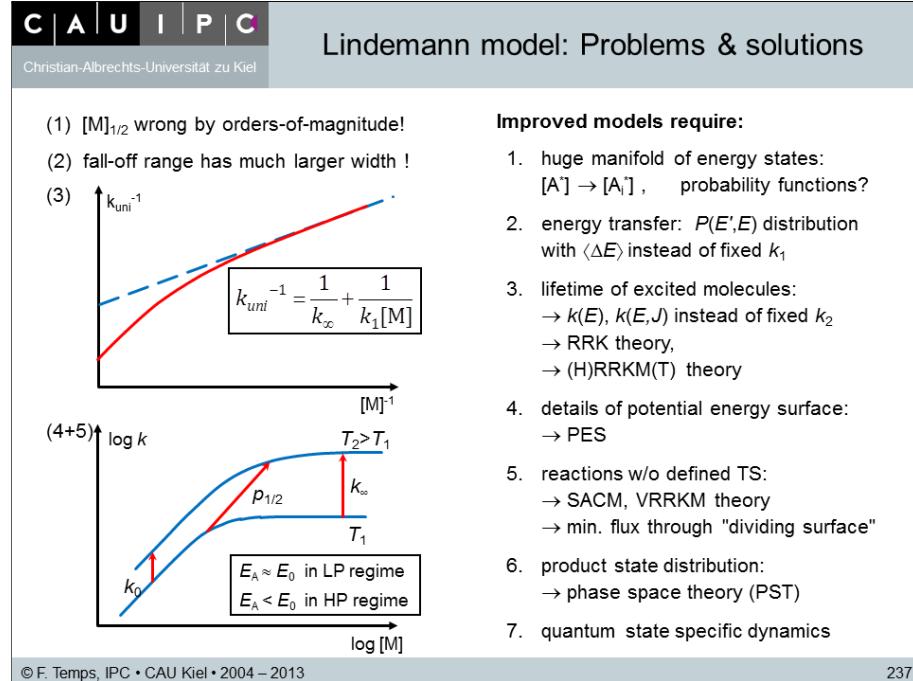
$$= \frac{1}{k_{\infty}} + \frac{1}{k_1} \frac{1}{[M]} \quad (8.26)$$

$$= \frac{1}{k_{\infty}} + \frac{1}{k_0} \quad (8.27)$$

↷ Plot of k_{uni}^{-1} vs. $[M]^{-1}$ should give a straight line with slope k_1^{-1} and intercept k_{∞}^{-1} .

► **Deficiencies of the Lindemann model:**

► **Figure 8.8:**



• Activation energies:

$$E_{A,0} < E_{A,\infty} \quad (8.28)$$

In particular:

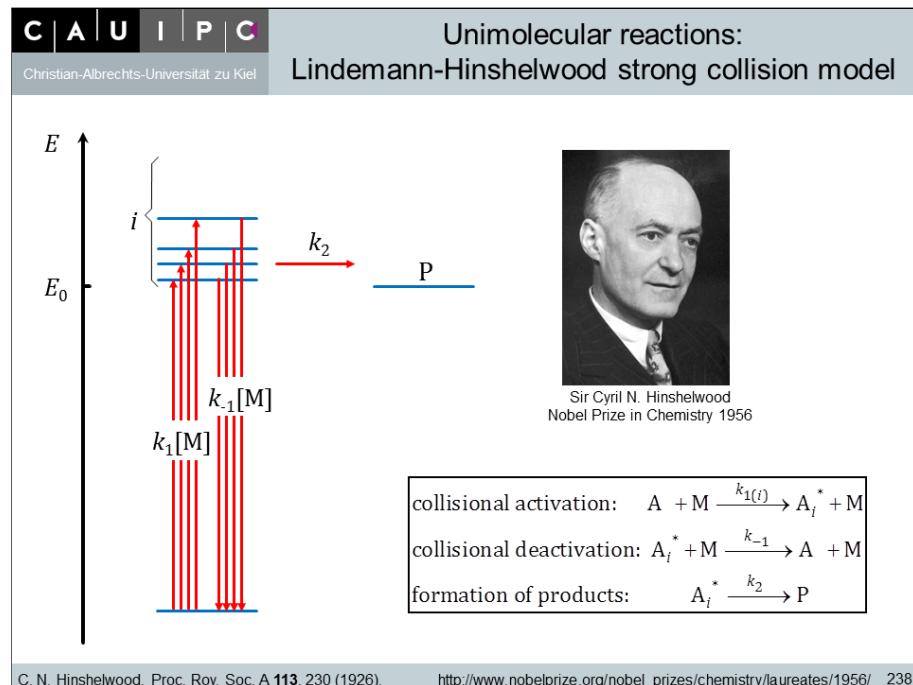
$$E_{A,\infty} \approx E_0 \quad (8.29)$$

$$E_{A,0} \approx E_0 - (s - 1.5) RT \quad (8.30)$$

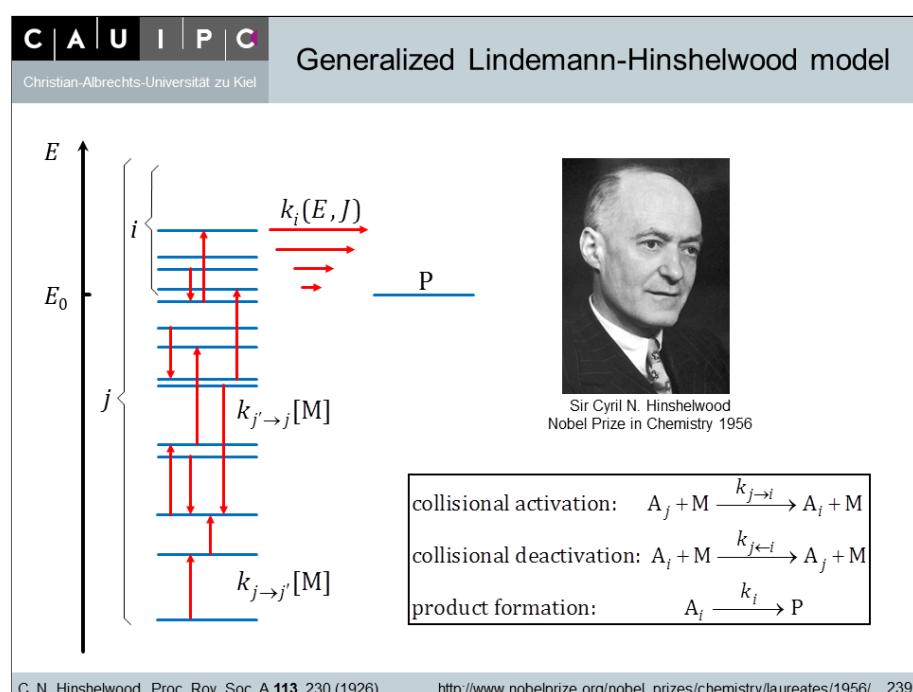
8.3 Generalized Lindemann-Hinshelwood mechanism

8.3.1 Master equation

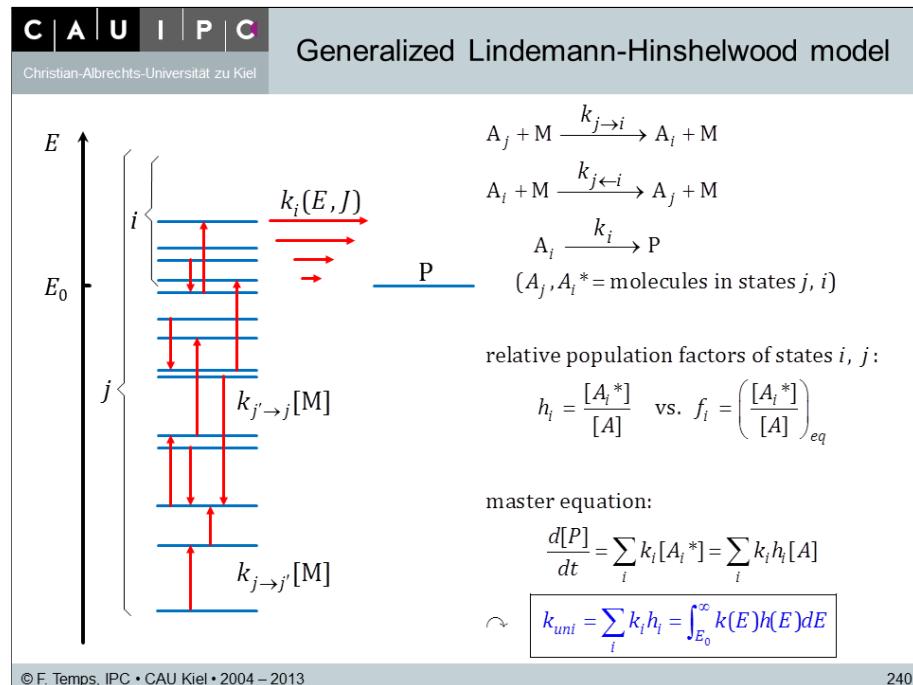
► **Figure 8.9:** Strong collision model.



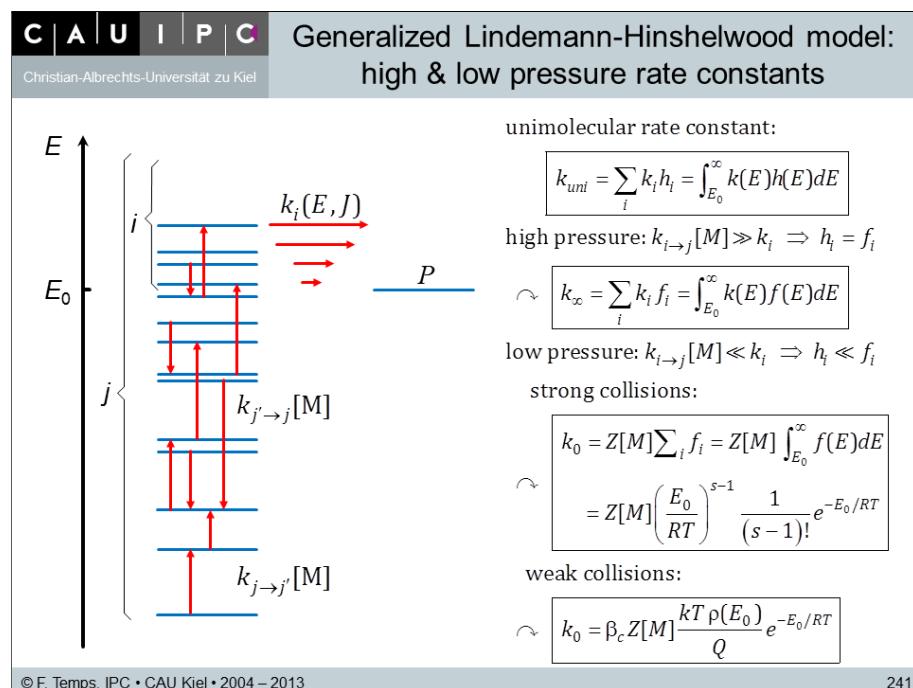
► **Figure 8.10:** Generalized Lindemann-Hinshelwood weak collision model.



- **Figure 8.11:** Generalized Lindemann-Hinshelwood weak collision model.



- **Figure 8.12:** Generalized Lindemann-Hinshelwood model: Rate constants in the high and low pressure (strong and weak collision) limits.



8.3.2 Equilibrium state populations

As seen from the master equation analysis, the unimolecular reaction rate constant in the high and in the low pressure regimes depends on the equilibrium (Boltzmann) state distributions f_i (for discrete states) or $f(E)$ (continuous state distributions). In a polyatomic molecule, due to the large number of vibrational degrees of freedom, the number of vibrational states increases very rapidly with increasing vibrational excitation energy. The quanta of vibrational excitation can be distributed over the oscillators. In order to calculate the number of combinations, we start with a single oscillator and expand our scope first to two oscillators and then to $s = 3N - 6$ oscillators.

a) Equilibrium state population for a single oscillator:

► **Boltzmann distribution:**

$$f_i = \frac{g_i e^{-\epsilon_i/k_B T}}{Q_{vib}} \quad (8.31)$$

with the energy quanta

$$\epsilon_i = h\nu \times v ; \quad v = 0, 1, 2, \dots \quad (8.32)$$

the degeneracy factor

$$g_i \quad (8.33)$$

and the partition function

$$Q_{vib} = \frac{1}{1 - e^{-h\nu/k_B T}} \quad (8.34)$$

► **Limiting case for high T (transition to classical mechanics):** $h\nu \ll k_B T \curvearrowright$

$$Q_{vib}^{\text{classical}} = \frac{k_B T}{h\nu} \quad (8.35)$$

since

$$e^{-x} \approx 1 - x \text{ for } x \rightarrow 0 \quad (8.36)$$

Note that this classical description of vibrations is not so bad for unimolecular reactions, where we are interested in the kinetic behavior at high temperatures.

b) Equilibrium state population for s oscillators:

$$g(E) \rightarrow \rho(E) dE \quad (8.37)$$

\curvearrowright

$$f(E) dE = \frac{\rho(E) e^{-E/k_B T} dE}{Q_{vib}} \quad (8.38)$$

with $\rho(E)$ being the *density of vibrational states* at the energy E and

$$Q_{vib} = \prod_{k=1}^s \frac{1}{1 - e^{-h\nu_k/k_B T}} \quad (8.39)$$

and

$$s = 3N - 6 \quad (\text{resp. } s = 3N - 5) \quad (8.40)$$

8.3.3 The density of vibrational states $\rho(E)$

The density of vibrational states is defined as

$$\rho(E) = \frac{\text{number of states in energy interval}}{\text{energy interval}} \quad (8.41)$$

i.e.,

$$\boxed{\rho(E) = \frac{dN(E)}{dE}} \quad (8.42)$$

In a polyatomic molecule, as we shall see in the following, $\rho(E)$ increases with E very rapidly owing to the large number of overtone and combination states, and reaches truly astronomical values:

a) $s = 1$:

$$\rho(E) = \frac{1}{h\nu} \quad (8.43)$$

b) $s = 2$:

We consider the ways, in which we can distribute two identical energy quanta $h\nu$ between the two oscillators:

E	Osc. 1	Osc. 2	Osc. 1	Osc. 2	Osc. 1	Osc. 2	g_i
0	-	-					1
$h\nu$		-	-				2
$2h\nu$		-			-		3
$3h\nu$		-					4
$4h\nu$							5
$5h\nu$							6
⋮	⋮	⋮					⋮

(8.44)

c) s oscillators:

- For simplicity, we consider a molecule with s *identical harmonic oscillators*.
 - This molecule shall be excited with j *quanta*, each of size $h\nu$, i.e., the molecule has the excitation energy $E = j h\nu$
- **Question:** How can we distribute these j quanta over the s oscillators?

- **Answer:** We are asking for the *number of distinguishable possibilities to distribute j quanta between s oscillators*, $P(j)$. This is identical to the problem of distributing j balls between s boxes, for example for $j = 11$ and $s = 8$:

$$\bullet \bullet \bullet | \bullet | \bullet | \quad | \bullet | \bullet \bullet | \bullet | \bullet \bullet \quad (8.45)$$

That number is identical to the *number of distinguishable permutations of j balls (•) and $s - 1$ walls (|)*,

$$P(j) = \frac{(j + s - 1)!}{j! (s - 1)!} \quad (8.46)$$

where $(j + s - 1)!$ is the total number of permutations, which is corrected by dividing through $j! (s - 1)!$ to account for the number of indistinguishable permutations among the balls ($j!$) and walls ($(s - 1)!$) among each other (which give indistinguishable results).

- **Answer:** We make the following approximation for $j \gg s$:⁴⁹

$$\frac{(j + s - 1)!}{j! (s - 1)!} \approx \frac{j^{s-1}}{(s - 1)!} \quad (8.49)$$

- **Question:** How can we compute $\rho(E)$?

- **Answer:**

$$\rho(E) = \frac{dN(E)}{dE} \quad (8.50)$$

(1) We consider the energy interval

$$\Delta E = h\nu \quad (8.51)$$

at the excitation energy

$$E = j \times h\nu \quad (8.52)$$

In this energy interval, we have the number of states

$$\Delta N(E) = P(j) \quad (8.53)$$

$$\rho(E) = \frac{dN(E)}{dE} \approx \frac{\Delta N(E)}{\Delta E} = \frac{1}{h\nu} \frac{(j + s - 1)!}{j! (s - 1)!} \quad (8.54)$$

⁴⁹ The approximation

$$\frac{(j + s - 1)!}{j!} \approx j^{s-1} \quad (8.47)$$

can be derived using Stirling's formula ($\ln N! = N \ln N - N$) and the power series expansion of

$$\ln(1 - x) \approx x \quad (8.48)$$

for $|x| \ll 1$ (see homework assignment).

(2) Using the approximation $\frac{(j+s-1)!}{j!(s-1)!} \approx \frac{j^{s-1}}{(s-1)!}$ (Eq. 8.49) for $j \gg s$ gives

$$\rho(E) = \frac{1}{h\nu} \frac{j^{s-1}}{(s-1)!} \quad (8.55)$$

(3) Inserting $j = E/h\nu$ into $\rho(E)$, we obtain

$$\rho(E) = \frac{1}{h\nu} \frac{(E/h\nu)^{s-1}}{(s-1)!} \quad (8.56)$$

(4) Result:

$$\boxed{\rho(E) = \frac{E^{s-1}}{(s-1)! (h\nu)^s}} \quad (8.57)$$

d) Notes:*

- (1) The above derivation may seem artificial because in a real molecule not all oscillators are identical. However, the derivation can be easily generalized.
- (2) For instance, we can start from the number of states of the first oscillator $N_1(E_1)$ and convolute this with the density of states $\rho_2(E)$ of the second oscillator

$$\rho_2(E_2) = \rho_2(E - E_1) = \frac{1}{h\nu} \quad (8.58)$$

and compute the total (combined) density of states for two oscillators by convolution according to

$$\rho(E) = \int_0^E N_1(E_1) \rho_2(E - E_1) dE_1 \quad (8.59)$$

etc. up to s oscillators. The result is

$$\boxed{\rho(E) = \frac{E^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i}} \quad (8.60)$$

- (3) We can also use inverse Laplace transforms: Since Q_{vib} is the Laplace transform of $\rho(E)$ according to

$$Q_{vib} = \int_0^\infty \rho(E) e^{-E/k_B T} dE = \mathcal{L}[\rho(E)] \quad (8.61)$$

we can determine $\rho(E)$ from Q_{vib} (which we know) by inverse Laplace transformation.

- (4) With corrections for zero-point energy:

$$\boxed{\rho(E) = \frac{(E + E_Z)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i}} \quad (8.62)$$

(5) With (empirical) Whitten-Rabinovitch corrections:

$$\rho(E) = \frac{(E + a(E) E_Z)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i} \quad (8.63)$$

where $a(E)$ is a correction factor that is of the order of 1 except at very low energies.

- (6) Exact values of $\rho(E)$ for harmonic oscillators can be obtained by direct state counting algorithms.
- (7) Corrections for anharmonicity can be applied using different means.

8.3.4 Unimolecular reaction rate constant in the low pressure regime

From the master equation analysis above, we obtained the thermal unimolecular reaction rate constant in the low pressure regime as

$$k_0 = \sum_i \sum_j k_{-1(ij)} [\text{M}] \frac{h_j}{f_j} f_i \quad (8.64)$$

The reduction of the excited state populations compared to the equilibrium (Boltzmann) distribution is shown in Fig. 8.13. Two cases can be distinguished:

- (1) With the strong collision assumption ($\langle \Delta E_c \rangle \gg RT$), we can apply the so-called equilibrium theories which assume that $h_j = f_j$ for $E \leq E_0$. Thus, the state population below E_0 remains as in the high pressure regime, whereas it is reduced above E_0 . Then,

$$k_0 = \sum_i \sum_j k_{-1(ij)} [\text{M}] \frac{h_j}{f_j} f_i = \sum_i \sum_j k_{-1(ij)} [\text{M}] f_i = Z [\text{M}] \sum_i f_i \quad (8.65)$$

↷

$$k_0 = Z [\text{M}] \int_{E_0}^{\infty} f(E) dE \quad (8.66)$$

Using the expressions for $f(E)$, $\rho(E)$ and Q in the classical limit ($h\nu \ll k_B T$) derived above and doing the integration by parts, we obtain the Hinshelwood equation for k_0 :

$$k_0 = Z_{AM} [\text{M}] \left(\frac{E_0}{k_B T} \right)^{s-1} \frac{1}{(s-1)!} e^{-E_0/k_B T} \quad (8.67)$$

This equation is usually used to describe experimental data with s as a fit parameter (usually about half the real s).

Since $Z_{AM} \propto T^{0.5}$ and $E_A = RT^2 d \ln k / dT$, the low pressure activation energy becomes

$$E_{A,0,sc} = E_0 - (s - 1.5) RT \quad (8.68)$$

Thus, E_A may be significantly smaller than E_0 . This can be understood as illustrated in Fig. 8.14.

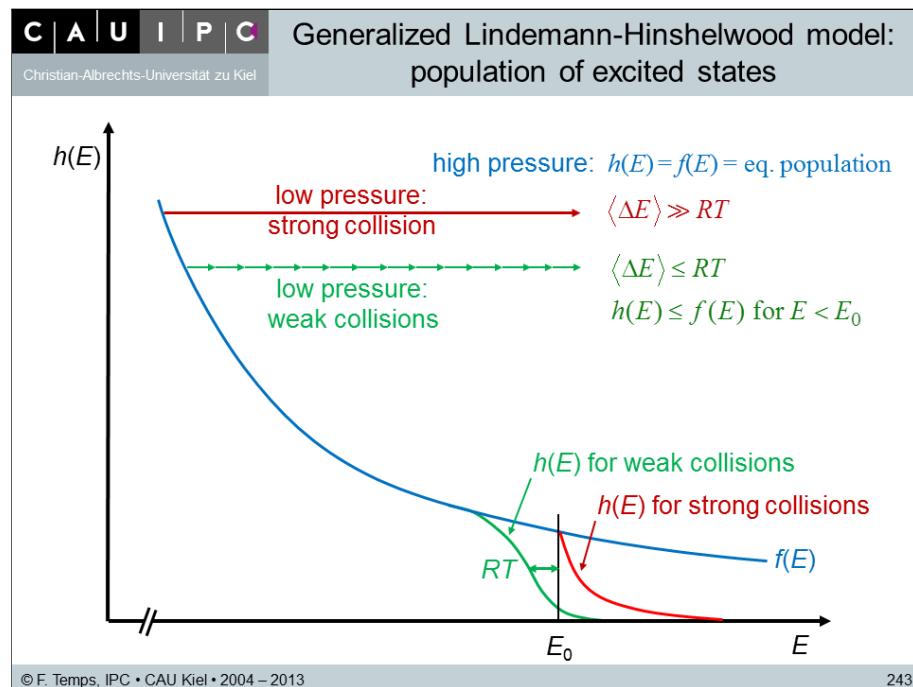
- (2) With the weak collision assumption ($\langle \Delta E_c \rangle \leq RT$) made by the so-called non-equilibrium theories, the bottleneck in the state population falls below the equilibrium distribution already below E_0 (see Fig. 8.14). Using the weak collision assumption, Troe derived the expression

$$k_0 = \beta_c Z [M] \frac{k_B T \rho_{rovib}(E_0)}{Q_{rovib}} e^{-E_0/k_B T} \quad (8.69)$$

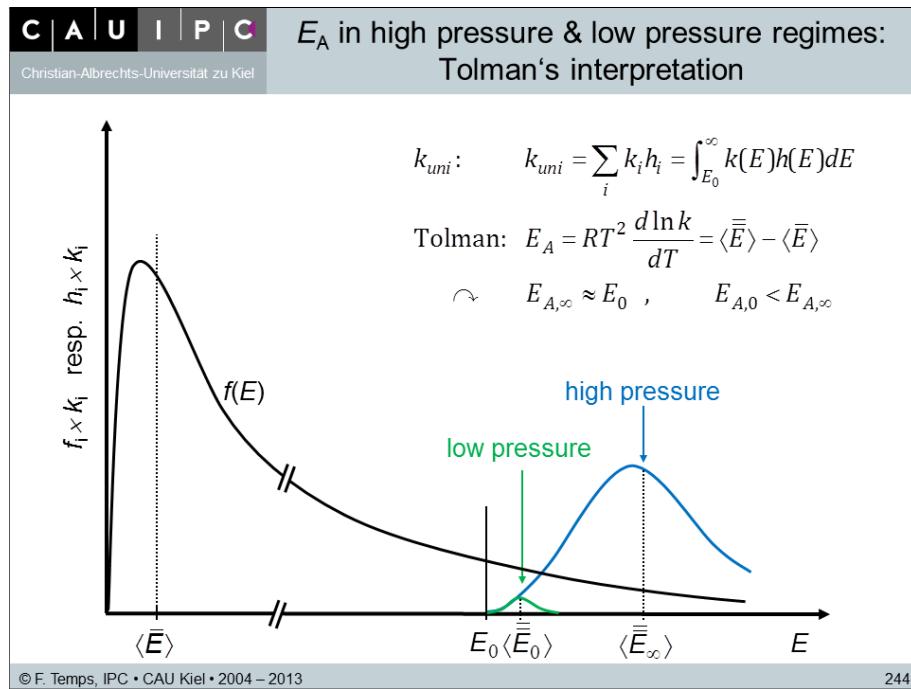
where β_c is the so-called collision efficiency ($\beta_c \leq 1$) which can be expressed in terms of the average energy transferred per collision $\langle \Delta E_c \rangle$. E_A becomes even smaller than the Hinshelwood E_A above. A simple estimate of the weak collision effect based on Fig. 8.14 may lead to

$$E_{A,0,wc} \approx E_0 - (s - 0.5) RT \quad (8.70)$$

- **Figure 8.13:** State populations.



- **Figure 8.14:** Activation energies for unimolecular reactions in the high pressure, the low pressure strong collision, and the low pressure weak collision limits.



8.3.5 Unimolecular reaction rate constant in the high pressure regime

From the master equation analysis above, the thermal unimolecular reaction rate constant in the high pressure regime is (see Fig. 8.12)

$$k_\infty = \int_0^{\infty} k(E) f(E) dE \quad (8.71)$$

with the Boltzmann distribution

$$f(E) dE = \frac{\rho(E) e^{-E/k_B T} dE}{Q_{vib}} \quad (8.72)$$

as shown in Fig. 8.13.

Averaging over the Boltzmann distribution gives the TST expression

$$k(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} e^{-E_0/k_B T} \quad (8.73)$$

8.4 The specific unimolecular reaction rate constants $k(E)$

We may intuitively expect that the specific unimolecular reaction rate constants $k(E)$ depend on the energy content (i.e., the excitation energy E) of the energetically activated molecules A^* . More precisely, we will also have to take into account the dependence of the specific rate constants on other conserved degrees of freedom, in particular total angular momentum J ($\Rightarrow k(E, J)$), and perhaps other quantities (symmetry, components of J if K -mixing is weak, ($\Rightarrow k(E, J; \sigma; \alpha_i)$)).

8.4.1 Rice-Ramsperger-Kassel (RRK) theory

- **RRK model:** In order to derive an expression for the specific rate constants $k(E)$, we realize that it is not enough that the molecules are energized to above E_0 . Indeed, for the reaction to take place, the energy also has to be in the right oscillator, namely in the RC. In particular, for the reaction to take place, of the total excitation energy E , the amount E^\dagger has to be concentrated in the RC such that $E^\dagger \geq E_0$. Thus, we can write the reaction scheme as



where A^\dagger denotes those excited molecules that have enough energy in the RC to overcome E_0 . We assume that once this critical configuration (A^\dagger) is reached, the molecules will immediately cross the TS and go to the product side.

- **Probabilities of A^\dagger and A^* :** The probability of A^\dagger compared to A^* can be derived using statistical arguments by considering the ratio of the density of states. We consider a molecule with

- s oscillators,
- $j = E/h\nu$ quanta which have to be distributed over the s oscillators,
- a threshold energy of E_0 such that a minimum of $m = E_0/h\nu$ quanta have to be concentrated in the RC and only $j - m$ quanta can be distributed freely,
- $j \gg s$ and $j - m \gg s$.

The probability of A^\dagger relative to A^* is given by

$$\frac{P(A^\dagger)}{P(A^*)} = \frac{\rho(A^\dagger)}{\rho(A^*)} \quad (8.75)$$

where

$$\rho(A^*) \propto \rho^*(E) = \frac{1}{h\nu} \frac{(j + s - 1)!}{j! (s - 1)!} \quad (8.76)$$

and, since in the critical configuration only $j - m$ quanta can be distributed freely,

$$\rho(A^\dagger) \propto \rho^\dagger(E) = \frac{1}{h\nu} \frac{(j - m + s - 1)!}{(j - m)! (s - 1)!} \quad (8.77)$$

↷

$$\frac{P(A^\dagger)}{P(A^*)} = \frac{(j-m+s-1)!}{(j-m)!(s-1)!} \times \frac{j!(s-1)!}{(j+s-1)!} \quad (8.78)$$

$$= \frac{(j-m+s-1)!}{(j-m)!} \times \frac{j!}{(j+s-1)!} \quad (8.79)$$

- **Specific rate constant:** The critical configuration A^\dagger is reached with the rate coefficient (\equiv frequency factor) ν^\dagger (see the reaction scheme above). Since the energy is now in place (in the RC), A^\dagger will cross the TS to products.

The specific rate constant $k(E)$ is therefore simply

$$k(E) = \nu^\dagger \times \frac{P(A^\dagger)}{P(A^*)} \quad (8.80)$$

↷

$$k(E) = \nu^\dagger \times \frac{(j-m+s-1)!}{(j-m)!} \times \frac{j!}{(j+s-1)!} \quad (8.81)$$

- **Kassel formula:** With the approximations according to Eq. 8.49),

$$\frac{(j+s-1)!}{j!} \approx j^{s-1} \text{ for } j \gg s \quad (8.82)$$

and

$$\frac{(j-m+s-1)!}{(j-m)!} \approx (j-m)^{s-1} \text{ for } j-m \gg s, \quad (8.83)$$

we obtain

$$\frac{P(A^\dagger)}{P(A^*)} = \frac{(j-m)^{s-1}}{j^{s-1}} = \left(\frac{j-m}{j}\right)^{s-1} \quad (8.84)$$

↷

$$\frac{P(A^\dagger)}{P(A^*)} = \left(\frac{E-E_0}{E}\right)^{s-1} \quad (8.85)$$

so that the specific rate constant becomes

$$k(E) = \nu^\dagger \left(\frac{E-E_0}{E}\right)^{s-1} \quad (8.86)$$

This expression is known as the *Kassel formula* for $k(E)$.

- **Notes on the Kassel formula:**

- Owing to the approximations $j \gg s$ and $j-m \gg s$, the Kassel formula is valid only at $E \gg E_0$.

- The Kassel formula describes experimental data qualitatively well. However, instead of the full value of $s = 3N - 6$, one usually has to use an effective number s_{eff} . As suggested by Troe, s_{eff} can be estimated from the specific heat of the reactant molecules via

$$c_V = \left(\frac{dU}{dT} \right)_V = N_L \frac{d}{dT} \left(k_B T^2 \frac{d \ln Q_{\text{vib}}}{dT} \right) \approx s_{\text{eff}} R \quad (8.87)$$

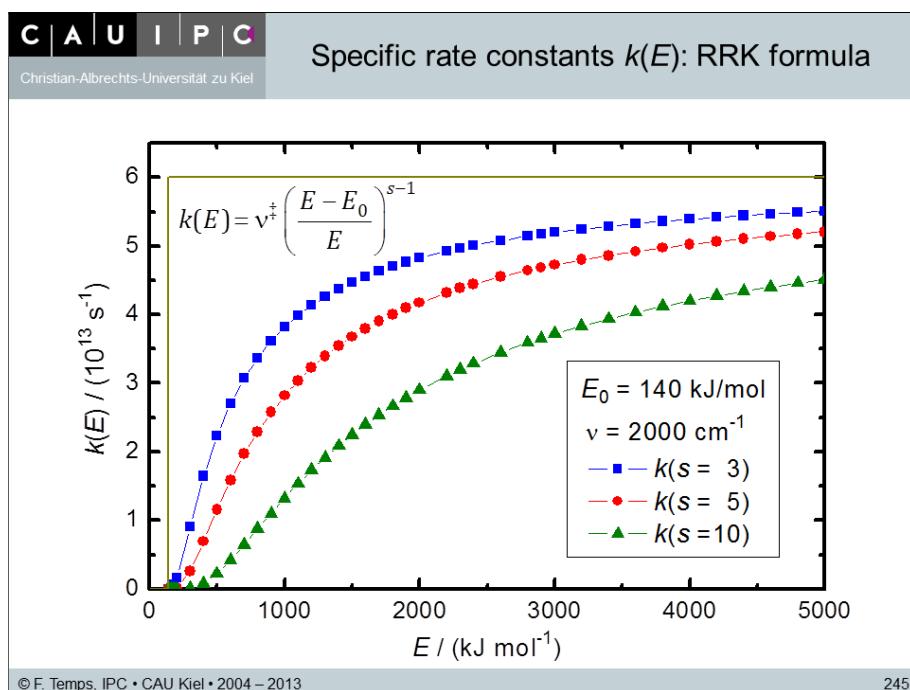
using the known expression for Q_{vib} ,

$$Q_{\text{vib}} = \prod_{k=1}^s \frac{1}{1 - \exp(-h\nu_k/k_B T)} \quad (8.88)$$

- Often, s_{eff} is equal to about one half of the number of oscillators,

$$s_{\text{eff}} \approx \frac{(3N - 6)}{2} \quad (8.89)$$

► **Figure 8.15:** Specific rate constants: RRK formula.



8.4.2 Rice-Ramsperger-Kassel-Marcus (RRKM) theory

RRK theory fails in the following points:

- It can be used only with s as an effective parameter (s_{eff}).
- It leads to the wrong results close to threshold, where $E \rightarrow E_0$ (see the conditions above).
- It is difficult to derive for oscillators with different frequencies.
- RRK theory is essentially a classical theory. It does not know about zero-point energy.

- **RRKM expression:** These problems are essentially solved by RRKM theory which gives the expression

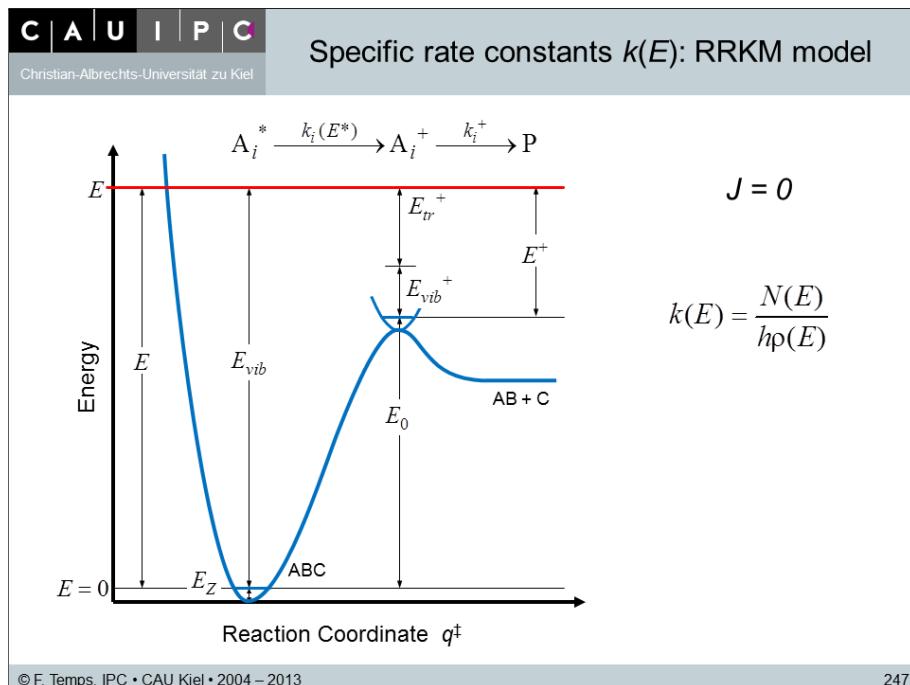
$$k(E) = \frac{N^\ddagger(E - E_0)}{h\rho(E)} \quad (8.90)$$

where

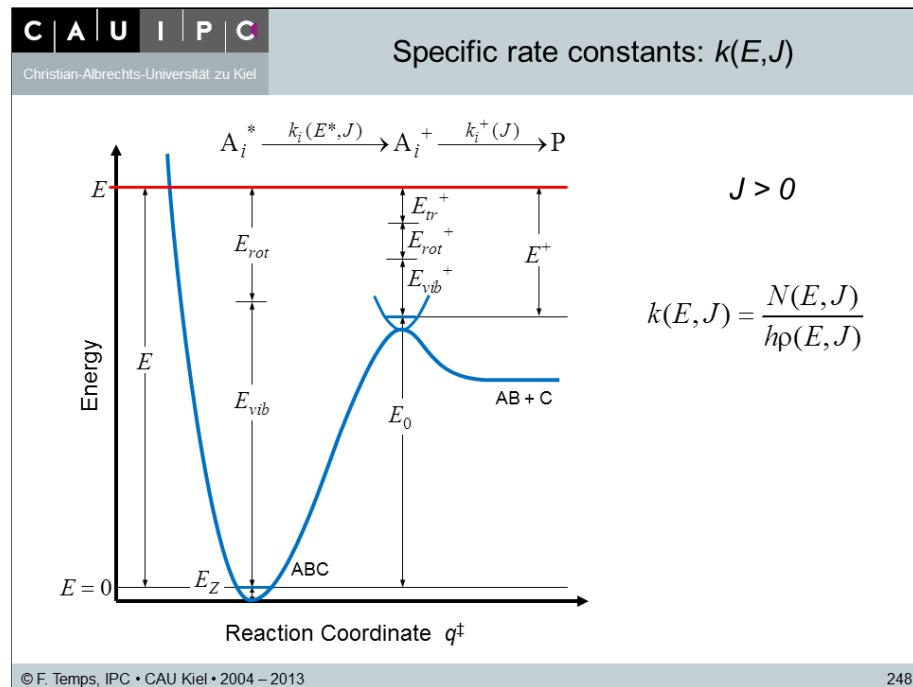
- $N^\ddagger(E - E_0)$ is the number of open channels (essentially the number of states at the transition state configuration excluding the RC), counted from the zero-point level of the TS, at the energy $E - E_0$,
- $\rho(E)$ is the density of states of the reacting molecules at the energy E .

These quantities are the two critical quantities in microcanonical transition state theory.

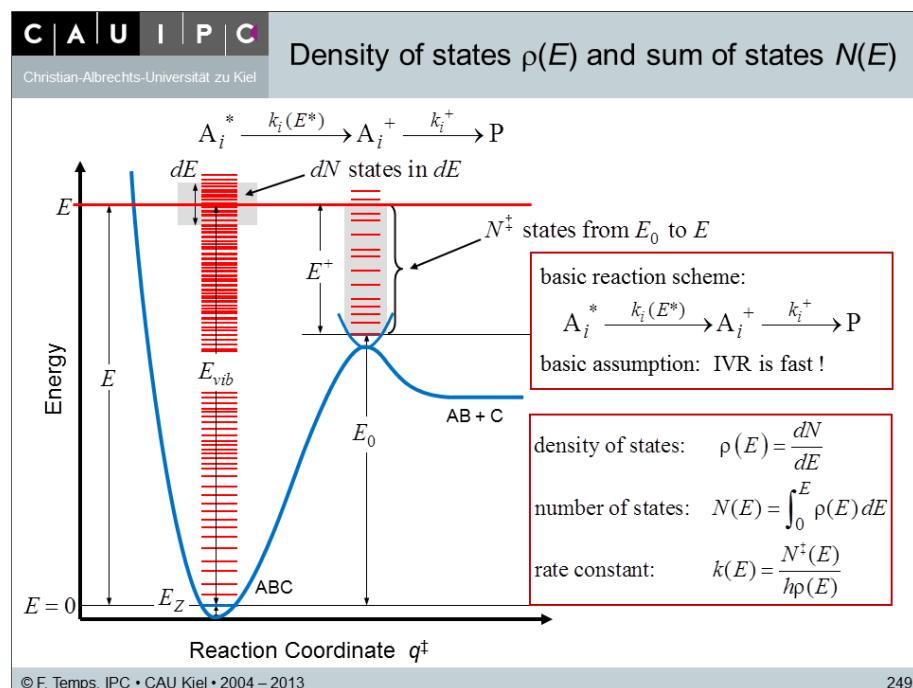
- **Figure 8.16:** RRKM expression for $k(E)$.



- **Figure 8.17:** RRKM expression for $k(E, J)$ with angular momentum conservation.



- **Figure 8.18:** The sum and the density of states.



- **RRKM expression with angular momentum conservation:** Eq. 8.90 can be generalized to include other conserved quantities, e.g., total angular momentum,

$$k(E, J) = \frac{N^\ddagger(E - E_0, J)}{h\rho(E, J)} \quad (8.91)$$

- **Relation between RRKM and RRK theory:** To elucidate the relation between Eqs. 8.86 and 8.90, we look at $\rho(E)$ and $N(E - E_0)$ more closely.

- (1) Density of vibrational states $\rho(E)$:

$$\rho(E) = \frac{\text{number of states in energy interval}}{\text{energy interval}} = \frac{dN(E)}{dE} \quad (8.92)$$

- a) RRK result for the number of indistinguishable permutations of j quanta over s oscillators; $j = \frac{E}{h\nu} \gg s$:

$$\rho(E) = \frac{1}{h\nu} \frac{(j + s - 1)!}{j! (s - 1)!} \approx \frac{1}{h\nu} \frac{j^{s-1}}{(s - 1)!} = \frac{1}{h\nu} \frac{(E/h\nu)^{s-1}}{(s - 1)!} \quad (8.93)$$

↷

$$\boxed{\rho(E) = \frac{E^{s-1}}{(s - 1)! (h\nu)^s}} \quad (8.94)$$

- b) It is relatively easy to show that for oscillators with different frequencies, the expression for $\rho(E)$ becomes

$$\boxed{\rho(E) = \frac{E^{s-1}}{(s - 1)! \prod_{i=1}^s h\nu_i^s}} \quad (8.95)$$

- c) With corrections for zero-point energy:

$$\boxed{\rho(E) = \frac{(E + E_Z)^{s-1}}{(s - 1)! \prod_{i=1}^s h\nu_i^s}} \quad (8.96)$$

- d) With (empirical) Whitten-Rabinovitch correction:

$$\boxed{\rho(E) = \frac{(E + a(E) E_Z)^{s-1}}{(s - 1)! \prod_{i=1}^s h\nu_i^s}} \quad (8.97)$$

where $a(E)$ is a correction factor that is of the order of 1 except at very low energies.

- e) Exact values of $\rho(E)$ for harmonic oscillators can be obtained by direct state counting algorithms. Corrections for anharmonicity can be applied using different means.

(2) **Number of states $N(E)$ and $N^\ddagger(E - E_0)$:** Since $\rho(E) = dN(E)/dE$, the number of states from $E = 0$ to E can be obtained by integration,

$$N(E) = \int_0^E \rho(E) dE \quad (8.98)$$

a) RRK expression:

$$N(E) = \int_0^E \rho(E) dE = \int_0^E \frac{E^{s-1}}{(s-1)! (h\nu)^s} dE = \frac{1}{(s-1)!} \frac{1}{(h\nu)^s} \int_0^E E^{s-1} dE \quad (8.99)$$

↷

$$\boxed{N(E) = \frac{E^s}{s! (h\nu)^s}} \quad (8.100)$$

b) Allowing for different frequencies, we modify this expression to

$$\boxed{N(E) = \frac{E^s}{s! \prod_{i=1}^s h\nu_i}} \quad (8.101)$$

c) As above, a correction for zero-point energy gives

$$\boxed{N(E) = \frac{(E + E_Z)^s}{s! \prod_{i=1}^s h\nu_i}} \quad (8.102)$$

d) With the Whitten-Rabinovitch correction, this becomes

$$\boxed{N(E) = \frac{(E + a(E) E_Z)^s}{s! \prod_{i=1}^s h\nu_i}} \quad (8.103)$$

e) Correction for $E \rightarrow 0$: At $E = 0$, we must have at least one state, i.e.,

$$\boxed{N^\ddagger(E) = 1 + \frac{(E + a(E) E_Z)^s}{s! \prod_{i=1}^s h\nu_i} - \frac{(a(0) E_Z)^s}{s! \prod_{i=1}^s h\nu_i}} \quad (8.104)$$

(3) Application to unimolecular reactions:

a) At the TS, we have only $s - 1$ oscillators since the RC has to be excluded. Furthermore, the states range from the zero-point energy E_0 of the TS to E , while we count E from the zero-point of the reactants. ↷

$$\boxed{N^\ddagger(E - E_0) = 1 + \frac{\left(E - E_0 + a^\ddagger(E - E_0) E_Z^\ddagger\right)^{s-1}}{(s-1)! \prod_{i=1}^{s-1} h\nu_i^\ddagger} - \frac{\left(a^\ddagger(0) E_Z^\ddagger\right)^{s-1}}{(s-1)! \prod_{i=1}^{s-1} h\nu_i^\ddagger}} \quad (8.105)$$

This expression gives the correct value of $N^\ddagger(E - E_0) = 1$ at $E = E_0$.

b) Density of states:

$$\rho(E) = \frac{(E + a(E) E_Z)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i} \quad (8.106)$$

c) Specific rate constant:

$$k(E) = \frac{1}{h\rho(E)} + \frac{\left(E - E_0 + a^\ddagger(E - E_0) E_Z^\ddagger\right)^{s-1}}{h\rho(E)(s-1)! \prod_{i=1}^{s-1} h\nu_i^\ddagger} - \frac{\left(a^\ddagger(0) E_Z^\ddagger\right)^{s-1}}{h\rho(E)(s-1)! \prod_{i=1}^{s-1} h\nu_i^\ddagger} \quad (8.107)$$

(4) For energies sufficiently above E_0 , we can use the expressions

$$N^\ddagger(E - E_0) = \frac{\left(E - E_0 + E_Z^\ddagger\right)^{s-1}}{(s-1)! \prod_{i=1}^{s-1} h\nu_i^\ddagger} \quad (8.108)$$

and

$$\rho(E) = \frac{(E + E_Z)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i} \quad (8.109)$$

to obtain

$$k(E) = \frac{N^\ddagger(E - E_0)}{h\rho(E)} = \frac{\prod_{i=1}^s h\nu_i}{\prod_{i=1}^{s-1} h\nu_i^\ddagger} \frac{\left(E - E_0 + E_Z^\ddagger\right)^{s-1}}{h(E + E_Z)^{s-1}} \quad (8.110)$$

↷

$$k(E) = \frac{\prod_{i=1}^s \nu_i}{\prod_{i=1}^{s-1} \nu_i^\ddagger} \left(\frac{E - E_0 + E_Z^\ddagger}{E + E_Z} \right)^{s-1} \quad (8.111)$$

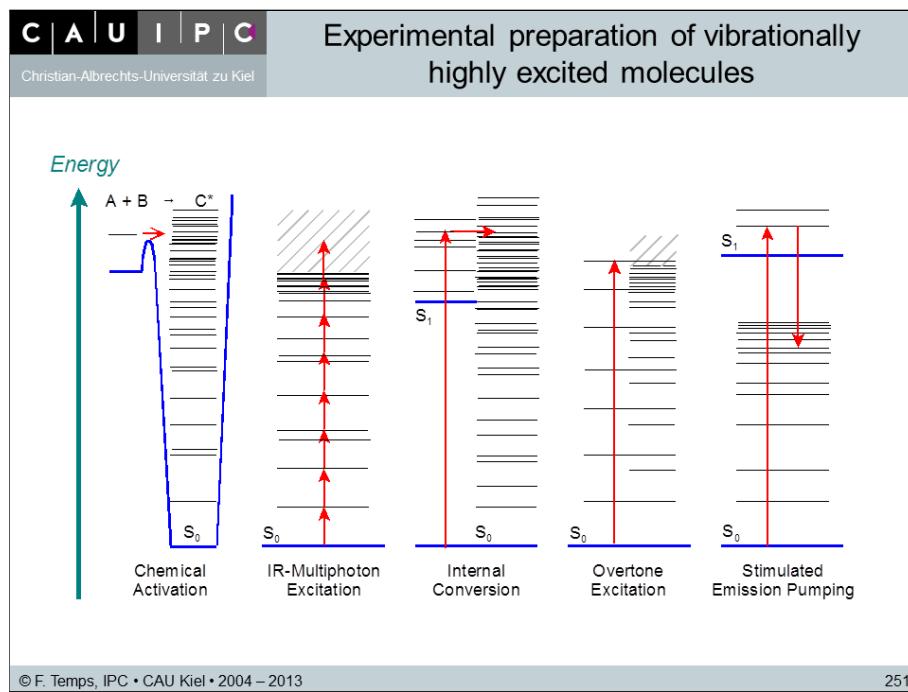
The resemblance to the Kassel formula is obvious.

8.4.3 The SACM and VRRKM model

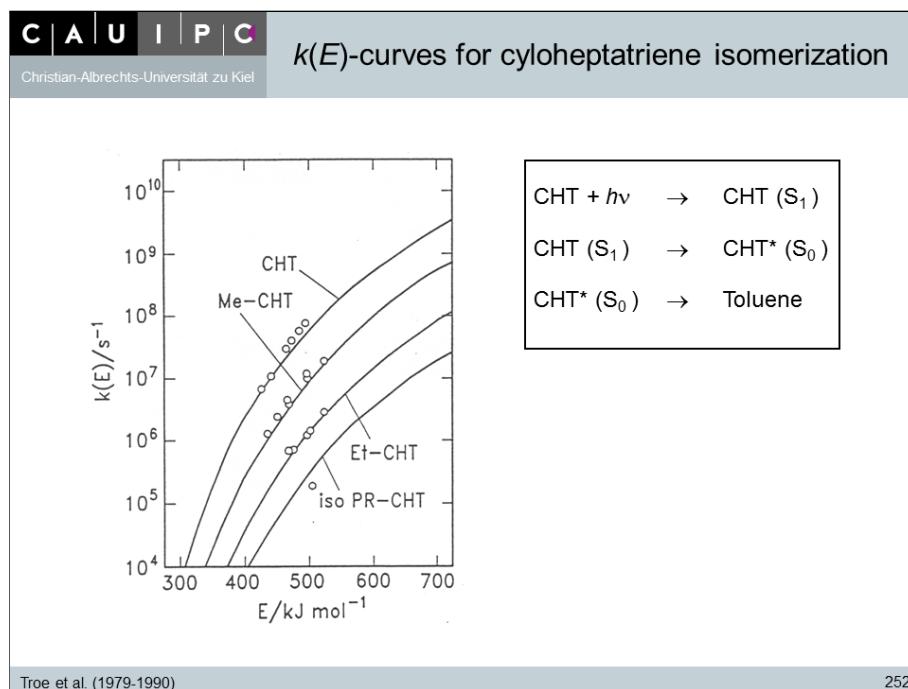
More advanced models allow for the tightening of the TS with increasing J (variational RRKM theory = VRRKM theory) or even for individual adiabatic channel potential curves (statistical adiabatic channel model = SACM). The latter model has to be used for reactions with loose transition states.

8.4.4 Experimental results

- **Figure 8.19:** Experimental methods for the preparation of highly vibrationally excited molecules with defined excitation energy.



- **Figure 8.20:** Comparison of theoretically predicted specific rate constants $k(E)$ for unimolecular isomerization of cycloheptatrienes with directly measured experimental data.



8.5 Collisional energy transfer*

Skipped for lack of time.

8.6 Recombination reactions

See homework assignment.

8.7 References

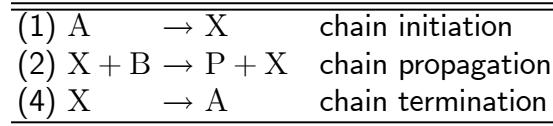
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9. Explosions

9.1 Chain reactions and chain explosions

9.1.1 Chain reactions without branching

► Reaction scheme:



► Rate laws:

$$\frac{d[X]}{dt} = k_1 [A] - k_4 [X] \quad (9.1)$$

$$\frac{d[P]}{dt} = k_2 [B] [X] \quad (9.2)$$

As we see, reaction (2) does not appear in the rate law because $X \rightarrow X$!

► Solutions of Eq. 9.1 for two limiting cases (cf. Fig. 9.1):

(1) Solution for $t \rightarrow 0$ and $[A] \approx \text{const}$ by substitution, using

$$y = k_1 [A] - k_4 [X]$$

↷

$$\frac{dy}{d[X]} = -k_5 \curvearrowright d[X] = -\frac{dy}{k_4}$$

↷

$$-\frac{1}{k_4} \frac{dy}{dt} = y \curvearrowright \frac{dy}{y} = -k_4 dt$$

↷

$$y = C e^{-k_4 t} = k_1 [A] - k_4 [X] \quad (9.3)$$

↷

$$[X] = \frac{k_1}{k_4} [A] - C e^{-k_4 t} \quad (9.4)$$

$t = 0$:

$$[X] = 0 \curvearrowright C = \frac{k_1}{k_4} [A] \quad (9.5)$$

↷

$$[X] = \frac{k_1 [A]}{k_4} \left(1 - e^{-k_4 t} \right) \quad (9.6)$$

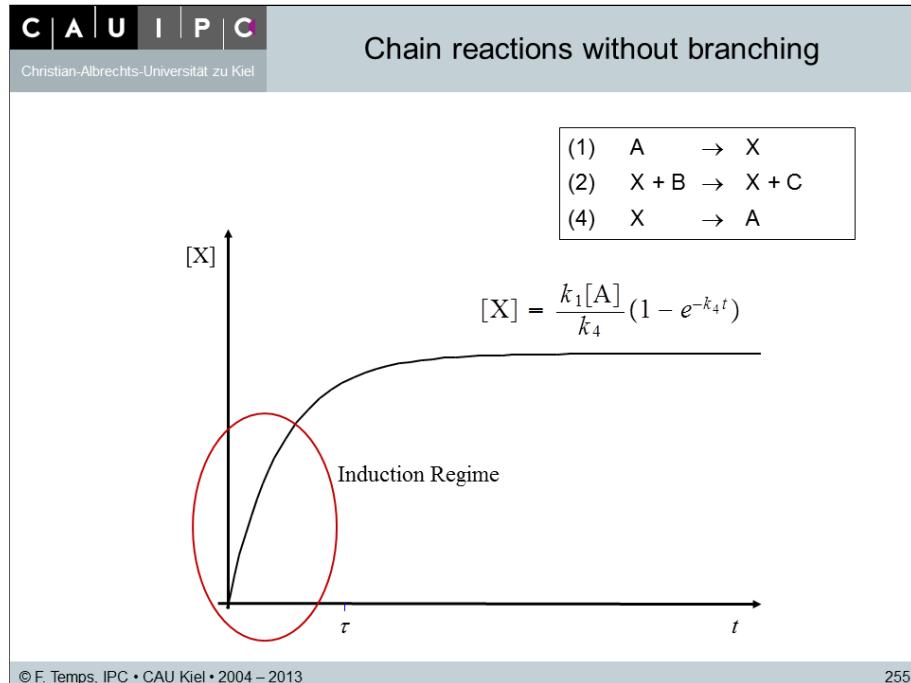
(2) Solution with steady state assumption for $[X]$ at $t \gg \tau$ (i.e, after the induction time τ):

$$\frac{d[X]}{dt} \approx 0 \quad (9.7)$$

$$[X]_{ss} = \frac{k_1}{k_4} [A] \quad (9.8)$$

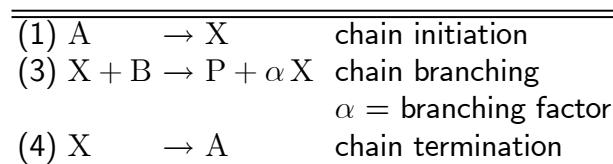
Considering the free radical concentration profile $[X(t)]$, no disasters are happening.

► **Figure 9.1:** Evolution of the free radical concentration in a normal chain reaction.



9.1.2 Chain reactions with branching

► **Reaction scheme:**



► **Most important example for a chain branching reaction:**



This reaction is responsible for flame propagation in all hydrocarbon flames: Since H is small, it has the highest diffusion coefficient and diffuses rapidly into the unburnt gases.

► **Rate laws:**

$$\frac{d[X]}{dt} = k_1 [A] + (\alpha - 1) k_3 [X] [B] - k_4 [X] \quad (9.10)$$

$$\frac{d[P]}{dt} = k_3 [B] [X] \quad (9.11)$$

► **Solutions for three limiting cases:**

(1) $\alpha = 1$ or $k_4 > k_3(\alpha - 1)[B]$:

$$\frac{d[X]}{dt} \approx 0 \quad (9.12)$$

↷

$$[X] = \frac{k_1 [A]}{k_4 - (\alpha - 1) k_3 [B]} \quad (9.13)$$

↷

$$\frac{d[P]}{dt} = k_3 [B] [X] = \dots \quad (9.14)$$

The overall reaction is stable, because the radical concentration is stable. The product formation rate is final (constant, well behaved).

(2) $k_4 = k_3(\alpha - 1)[B]$: At short times, $[A], [B] \approx \text{const}$ ↷

$$\frac{d[X]}{dt} = k_1 [A] = \text{const} \quad (9.15)$$

↷

$$[X] \rightarrow \infty \quad (9.16)$$

The overall reaction turns unstable, because the radical concentration goes to infinity and thus the product formation rate too, leading to chain explosion!

(3) $k_4 < k_3(\alpha - 1)[B]$: At short times, $[A], [B] \approx \text{const}$ ↷

$$\frac{d[X]}{dt} + k_4 [X] - k_3(\alpha - 1) [X] [B] = k_1 [A] \quad (9.17)$$

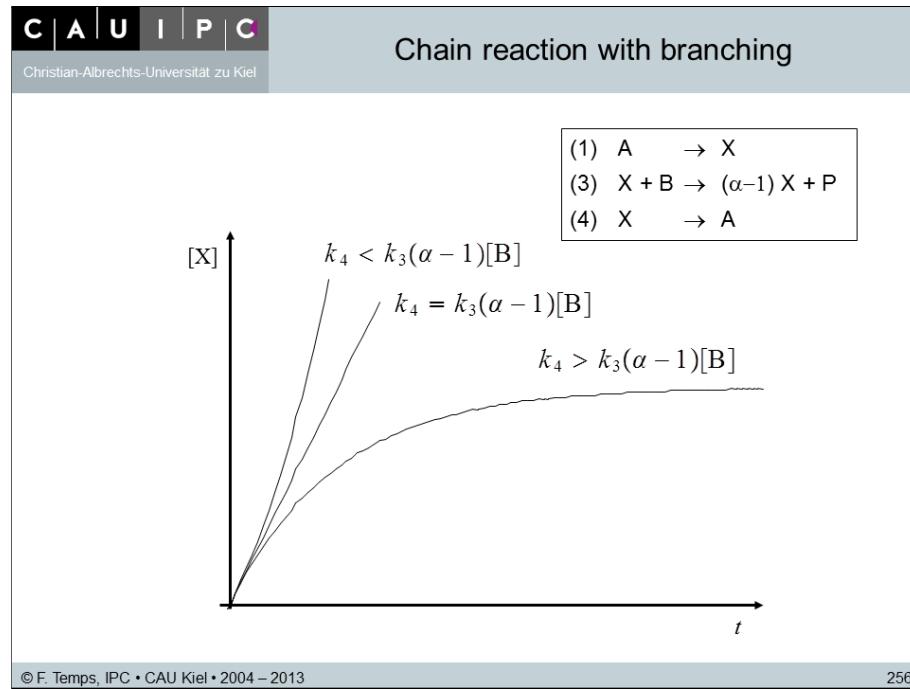
$$\frac{d[X]}{dt} + [X] (k_4 - k_3(\alpha - 1) [B]) = k_1 [A] \quad (9.18)$$

↷

$$[X] = \frac{k_1 [A]}{(\alpha - 1) k_3 [B] - k_4} \times \left(\exp [(\alpha - 1) k_3 [B] t] - 1 \right) \quad (9.19)$$

The overall reaction turns unstable, because the radical concentration increases exponentially, leading to an exponentially growing product formation rate, and therefore chain explosion!

- **Figure 9.2:** Evolution of the free radical concentrations in a chain reaction with branching (three limiting cases).



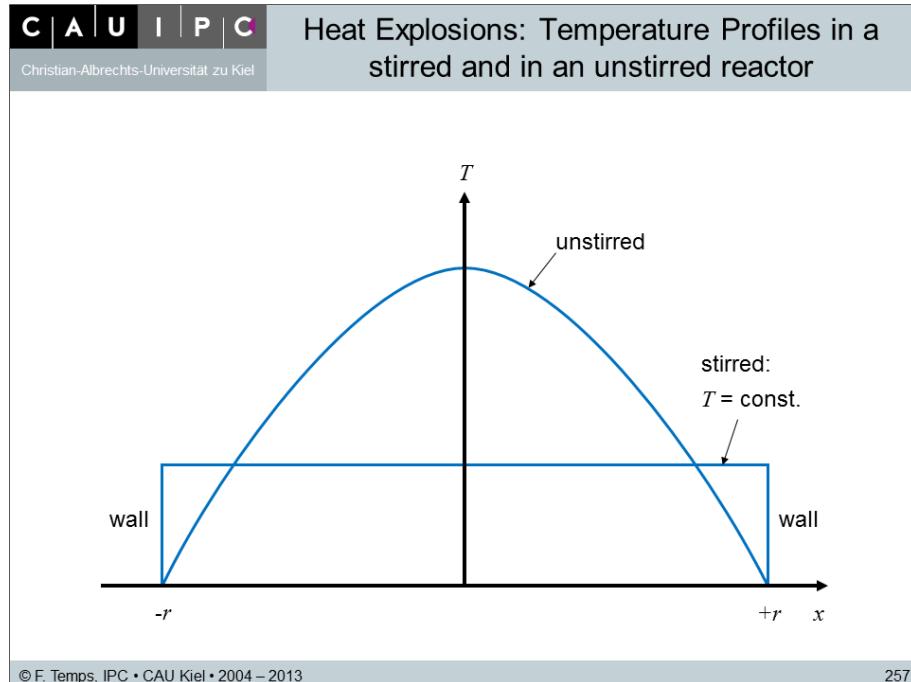
9.2 Heat explosions

We consider an exothermic bimolecular reaction in a closed reactor



and look at the radial temperature profile in the reactor.

- **Figure 9.3:** Temperature profiles in a stirred and in an unstirred reactor.



9.2.1 Semenov theory for “stirred reactors” ($T = \text{const.}$)

- **Heat production in an exothermic reaction ($\Delta_R H^\ominus < 0$):**

- **Energy released per volume:**

$$\Delta c \Delta_R H^\ominus \quad [\text{kJ}/\text{cm}^3] \quad (9.21)$$

- **Reaction rate:**

$$\frac{dc_A}{dt} = -k [A] [B] \quad (9.22)$$

- **heat release:**

$$q_R = V \Delta_R H^\ominus \frac{dc_A}{dt} \quad (9.23)$$

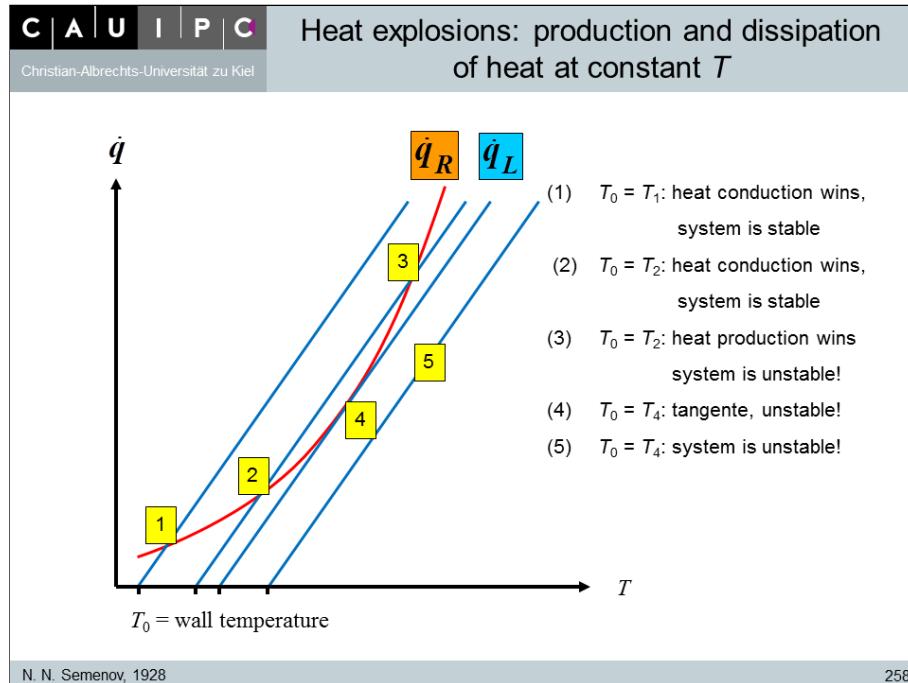
$$= V \Delta_R H^\ominus \underbrace{k_0 e^{-E_A/RT}}_{\text{Arrhenius rate constant in pressure units}} \underbrace{p_A p_B}_{(9.24)}$$

Arrhenius rate constant in pressure units

- **positive feedback effect:**

reaction rate increases
 ↵ temperature $T \uparrow$
 ↵ reaction rate \uparrow
 ↵ heat explosion !!

► **Figure 9.4:** Heat explosions.



► **Heat removal:** At constant temperature in the *stirred* reactor, we use Newton's law

$$\dot{q}_L = \alpha F (T - T_0) \quad (9.25)$$

where

α : heat conduction coefficient (depends on material) (9.26)

F : reactor surface area

T : temperature

T_0 : wall temperature

As we see, the heat removal increases (becomes steeper), when we increase the reactor surface area (at constant reactor volume).

► **Stability limits:**

- (1) $T_0 = T_1$: Heat removal wins over heat production ↵ negative feedback ↵ stable.
- (2) $T_0 = T_2$: Heat removal wins over heat production ↵ negative feedback ↵ stable.
- (3) $T_0 = T_3$: Heat production wins over heat removal ↵ positive feedback ↵ heat explosion, but the system should never reach point [3].
- (4) $T_0 = T_4$: tangent ↵ stability limit, the system runs away upon the smallest perturbation!
- (5) $T_0 = T_5$: always unstable!

► **Conclusions:**

- The quantity that determines whether the system is stable or not is the wall temperature T_0 , because T_0 determines the initial point of the heat removal line.
- Smaller surface-to-volume ratio is dangerous, because smaller surface at a given volume leads to a smaller slope of the heat removal line \curvearrowright *instability!*
- Security measure: internal cooling system (cold water pipes, heat exchanger).
- Emergency measure: when cooling system fails, the reaction mixture should be strongly diluted by addition of solvent immediately!

► **Quantitative estimation of the stability limits:*** At point (4) in Fig. 9.4, we have:

$$\dot{q}_L = \dot{q}_R \quad (9.27)$$

$$\curvearrowright \alpha F (T - T_0) = V \Delta_R H^\ominus k_0 e^{-E_A/RT} p_A p_B \quad (9.28)$$

$$\frac{\partial \dot{q}_L}{\partial T} = \frac{\partial \dot{q}_R}{\partial T} \quad (9.29)$$

$$\curvearrowright \alpha F = V \Delta_R H^\ominus k_0 e^{-E_A/RT} p_A p_B \frac{E_A}{RT^2} \quad (9.30)$$

$$\frac{\text{Eq. } I}{\text{Eq. } II} \curvearrowright \frac{RT^2}{E_A} = (T - T_0) \quad (9.31)$$

$$\curvearrowright T_2 - \frac{E_A}{R} T + \frac{E_A}{R} T_0 = 0 \quad (9.32)$$

$$\curvearrowright T = \frac{E_A}{2R} \pm \sqrt{\left(\frac{E_A}{2R}\right)^2 - \frac{E_A}{R} T_0} \quad (9.33)$$

Solution is:

$$\left\{ \begin{array}{l} T = \frac{1}{2R} \left(E_A + \sqrt{(E_A^2 - 4RT_0 E_A)} \right) \\ T = \frac{1}{2R} \left(E_A - \sqrt{(E_A^2 - 4RT_0 E_A)} \right) \end{array} \right\} \quad (9.34)$$

This can be simplified:

- (1) For practically important reactions, we have:

$$E_A \gg RT_0 \curvearrowright T_0 \ll \frac{E_A}{R} \quad (9.35)$$

- (2) We also can exclude unreasonably high temperatures \curvearrowright only the --sign before $\sqrt{}$ counts: \curvearrowright

$$T^* = \frac{E_A}{2R} - \sqrt{\left(\frac{E_A}{2R}\right)^2 - \frac{E_A}{R} T_0} \quad (9.36)$$

$$= \frac{E_A}{2R} - \frac{E_A}{2R} \sqrt{1 - \frac{4RT_0}{E_A}} \quad (9.37)$$

$$= \frac{E_A}{2R} \left(1 - \sqrt{1 - \frac{4RT_0}{E_A}} \right) \quad (9.38)$$

(3) We can expand the $\sqrt{ } :$

$$x = \frac{4RT_0}{E_A} ; \quad x < 1 ; \quad (9.39)$$

$$\curvearrowright \sqrt{1-x} = 1 - \frac{1}{2}x - \frac{1}{2 \cdot 4}x^2 - \dots \quad (9.40)$$

$$\curvearrowright T^* = \frac{E_A}{2R} \left(1 - 1 + \frac{2RT_0}{E_A} + \frac{16 \cdot R^2 T_0^2}{2 \cdot 4 \cdot (E_A)^2} + \dots \right) \quad (9.41)$$

$$\curvearrowright T^* = T_0 + \frac{RT_0^2}{E_A} \quad (9.42)$$

$$\curvearrowright T^* - T_0 = \frac{RT_0^2}{E_A} \quad (9.43)$$

(4) Insert into in (1) and power expansion:

$$\alpha \cdot F \cdot \left(\frac{RT_0^2}{E_A} \right) = V \cdot \Delta_R H^\ominus \cdot k_0 \cdot \exp \left[-\frac{E_A}{RT_0 \left(1 + \frac{RT_0}{E_A} \right)} \right] \cdot p_A \cdot p_B \quad (9.44)$$

$$= V \cdot \Delta_R H^\ominus \cdot k_0 \cdot e \cdot \exp \left[-\frac{E_A}{RT_0} \right] \cdot p^2 \cdot x_A \cdot x_B \quad (9.45)$$

(5) Explosion limit:

$$\frac{p^2}{T_0^2} \cdot \exp \left[-\frac{E_A}{RT_0} \right] = \frac{\alpha \cdot F \cdot R}{e \cdot \Delta_R H^\ominus \cdot V \cdot E_A \cdot k_0 \cdot x_A \cdot x_B} = \text{const.} \quad (9.46)$$

$$\curvearrowright p \propto T \cdot e^{E_A/RT} \quad (9.47)$$

Power expansion of the exponent in step (4):

$$\exp \left[-\frac{E_A}{RT_0 \left(1 + \frac{RT_0}{E_A} \right)} \right] = \exp \left[-\frac{1}{x} \frac{1}{1+x} \right] \quad \text{mit } x = \frac{RT_0}{E_A} \ll 1 \quad (9.48)$$

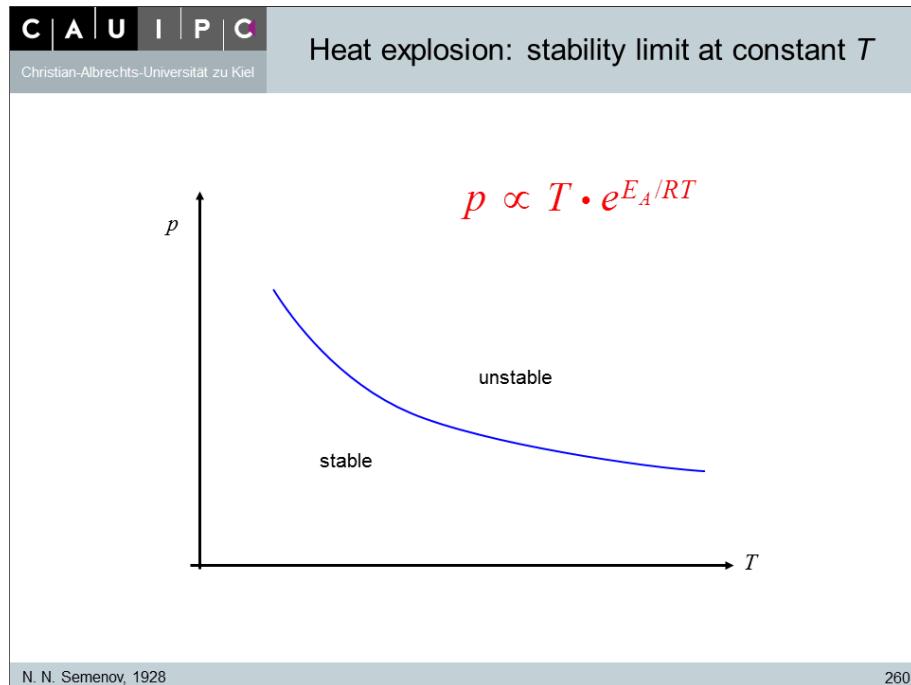
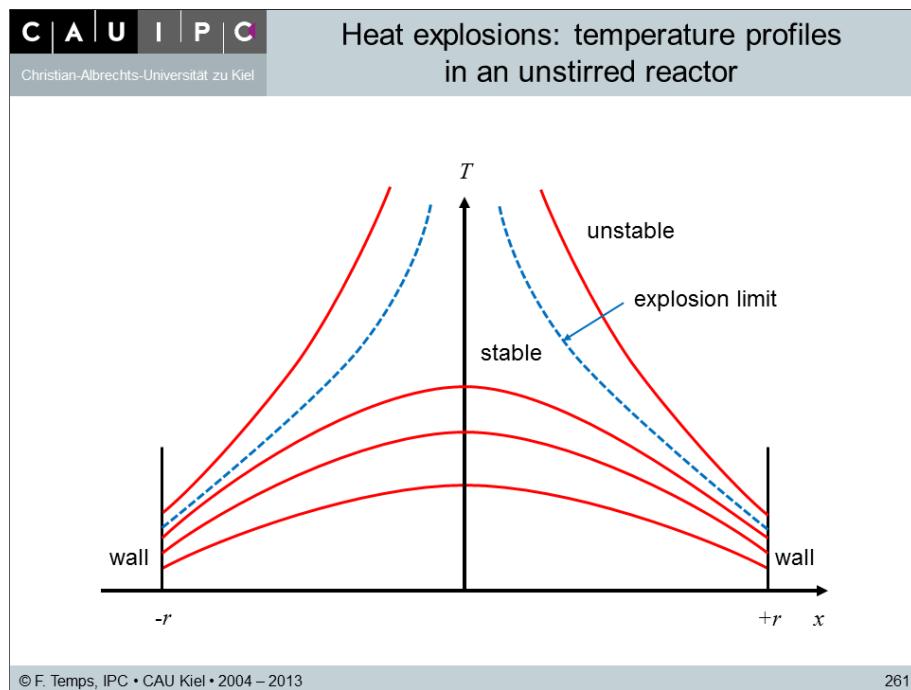
$$= \exp \left[-\frac{1}{x} (1 - x + x^2 \dots) \right] \quad (9.49)$$

$$\approx \exp \left[-\frac{1}{x} (1 - x) \right] \quad (9.50)$$

$$= \exp \left[1 - \frac{1}{x} \right] \quad (9.51)$$

$$= e^1 \cdot \exp \left[-\frac{1}{x} \right] \quad (9.52)$$

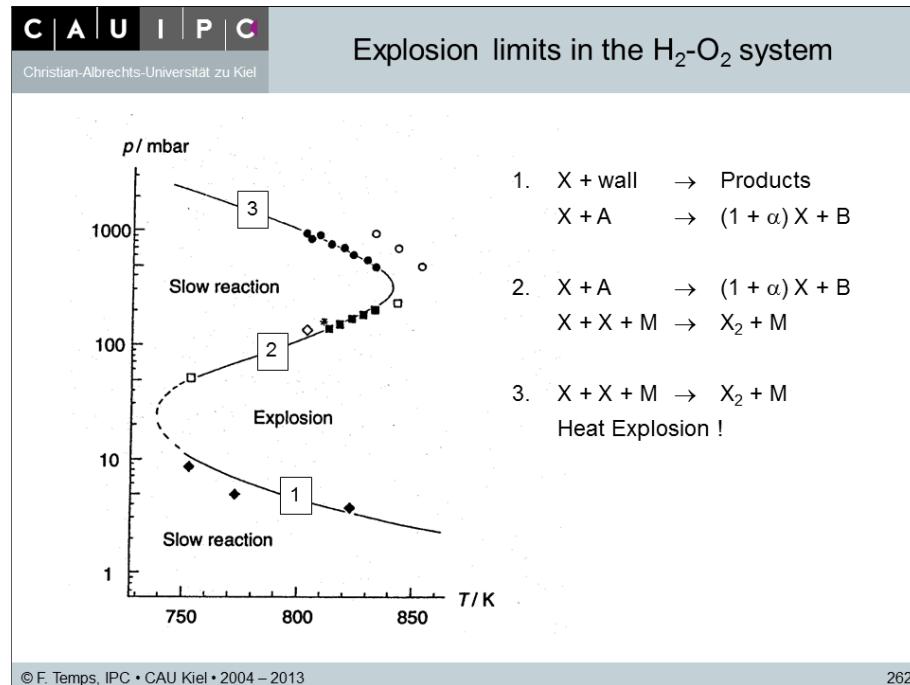
$$= e \cdot \exp \left[-\frac{E_A}{RT_0} \right] \quad (9.53)$$

► **Figure 9.5:****9.2.2 Frank-Kamenetskii theory for “unstirred reactors”**► **Figure 9.6:** Temperature profiles in an unstirred reactor.

Boundary effects are neglected in the Figure. In reality, there is a smooth transition in the boundary layer.

9.2.3 Explosion limits

► **Figure 9.7:** Explosion limits in the H₂/O₂ system.



9.2.4 Growth curves and catastrophe theory

► **Exponential growth:**

$$x \propto e^{k \cdot t} \curvearrowright \frac{dx}{dt} = k x \quad (9.54)$$

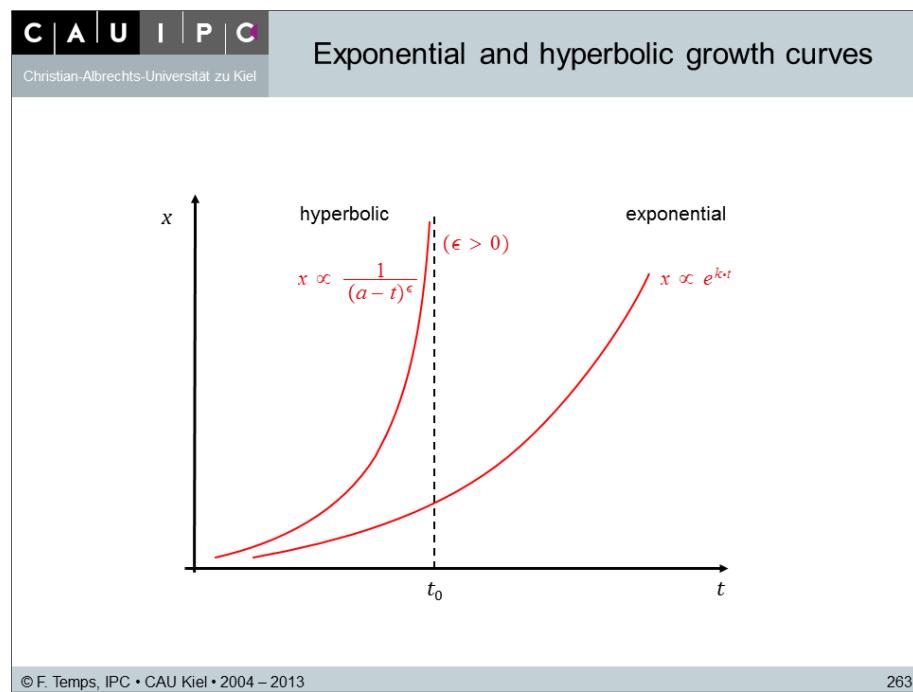
► **Hyperbolic growth:**

$$x \propto \frac{1}{(a - t)^\epsilon} \curvearrowright \frac{dx}{dt} = k x^{1+\epsilon} \quad \text{mit } 1 + \epsilon > 1 \quad (9.55)$$

► **Heat explosion:**

$$q_R \propto k c_A c_B \quad \text{quadratic, i.e. we get hyperbolic growth !} \quad (9.56)$$

- **Figure 9.8:** Growth curves.



10. Catalysis

The net rate of a chemical reaction may be affected by the presence of a third species even though that species is neither consumed nor produced by the reaction. If the rate increases, we speak of **catalysis**. If the rate decreases, we speak of **inhibition**.

In general, we have to distinguish

- homogeneous catalysis,
- heterogeneous catalysis.

10.1 Kinetics of enzyme catalyzed reactions (homogeneous catalysis)

The mechanism describing the homogeneous catalytical activity of enzymes has first been elucidated by Michaelis and Menten (1914).

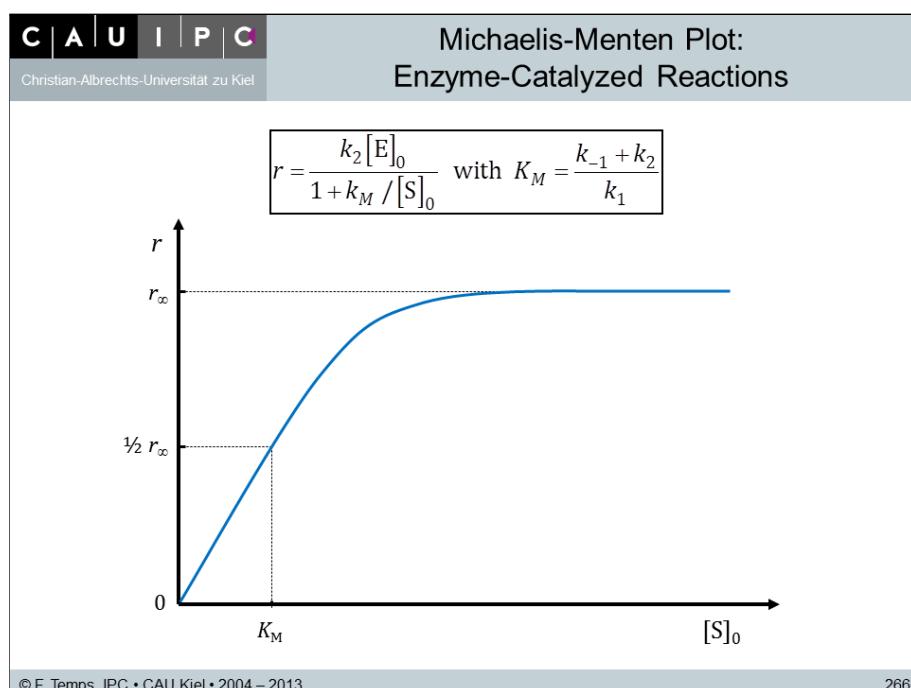
► **Experimental observations on enzyme catalysis:**

- (1) For constant substrate concentration $[S]_0$, the reaction rate r is proportional to the concentration of the enzyme $[E]_0$

$$r \propto [E]_0 \quad \text{for } [S]_0 = \text{const} \quad (10.1)$$

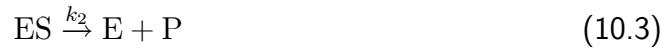
- (2) At an applied enzyme concentration $[E]_0$, the reaction rate r first increases with increasing substrate concentrations $[S]_0$ and then reaches saturation, as is shown in Fig. 10.1.

► **Figure 10.1:** Enzyme catalysis: Michelis-Menten kinetics.



10.1.1 The Michaelis-Menten mechanism

Basic reaction scheme:



Typical values of k_2 :

$$k_2 \approx 10^2 \dots 10^3 \text{ s}^{-1} \quad (\text{in some cases up to } 10^6 \text{ s}^{-1}) \quad (10.4)$$

Reaction rate:

$$\frac{d[P]}{dt} = -\frac{d[S]}{dt} = k_2 [ES] \quad (10.5)$$

$$\frac{d[ES]}{dt} = k_1 [E] [S] - k_{-1} [ES] - k_2 [ES] \quad (10.6)$$

$$\approx 0 \quad (10.7)$$

Mass balance:

$$[E]_0 = [E] + [ES] \quad (10.8)$$

$$\curvearrowright [E] = [E]_0 - [ES] \quad (10.9)$$

$$[S]_0 = [S] + [ES] + [P] \quad (10.10)$$

$$\curvearrowright [S] = [S]_0 - [ES] - [P] \quad (10.11)$$

Steady state ES concentration:

$$\frac{d[ES]}{dt} = k_1 ([E]_0 - [ES]) ([S]_0 - [ES] - [P]) - (k_{-1} + k_2) [ES] \quad (10.12)$$

$$\approx 0 \quad (10.13)$$

Approximations:

$$[E]_0 \ll [S]_0 \quad (10.14)$$

$$[ES] \ll [S]_0 \quad (10.15)$$

$$[P] \approx 0 \quad \text{for early times} \quad (10.16)$$

\curvearrowright

$$\frac{d[ES]}{dt} = k_1 [E]_0 [S]_0 - k_1 [S]_0 [ES] - (k_{-1} + k_2) [ES] \quad (10.17)$$

$$\approx 0 \quad (10.18)$$

Steady state ES concentration:

$$[ES]_{ss} = \frac{k_1 [E]_0 [S]_0}{k_1 [S]_0 + k_{-1} + k_2} \quad (10.19)$$

Resulting rate expression:

$$r = \frac{d[P]}{dt} = k_2 [ES] \quad (10.20)$$

$$= \frac{k_1 k_2 [E]_0 [S]_0}{k_1 [S]_0 + k_{-1} + k_2} \quad (10.21)$$

$$= \frac{k_2 [E]_0}{1 + \frac{k_{-1} + k_2}{k_1 [S]_0}} \quad (10.22)$$

↷

$$r = \frac{k_2 [E]_0}{1 + K_M / [S]_0} \quad (10.23)$$

with the **Michaelis-Menten constant**

$$K_M = \frac{k_{-1} + k_2}{k_1} \quad (10.24)$$

Limiting cases:

$$(1) [S]_0 \rightarrow \infty \curvearrowright \frac{K_M}{[S]_0} \ll 1: \curvearrowright$$

$$r = \frac{d[P]}{dt} = k_2 [E]_0 \quad (10.25)$$

$$(2) [S]_0 \rightarrow 0 \curvearrowright \frac{K_M}{[S]_0} \gg 1: \curvearrowright$$

$$r = \frac{d[P]}{dt} = \frac{k_2 [E]_0 [S]_0}{K_M} \quad (10.26)$$

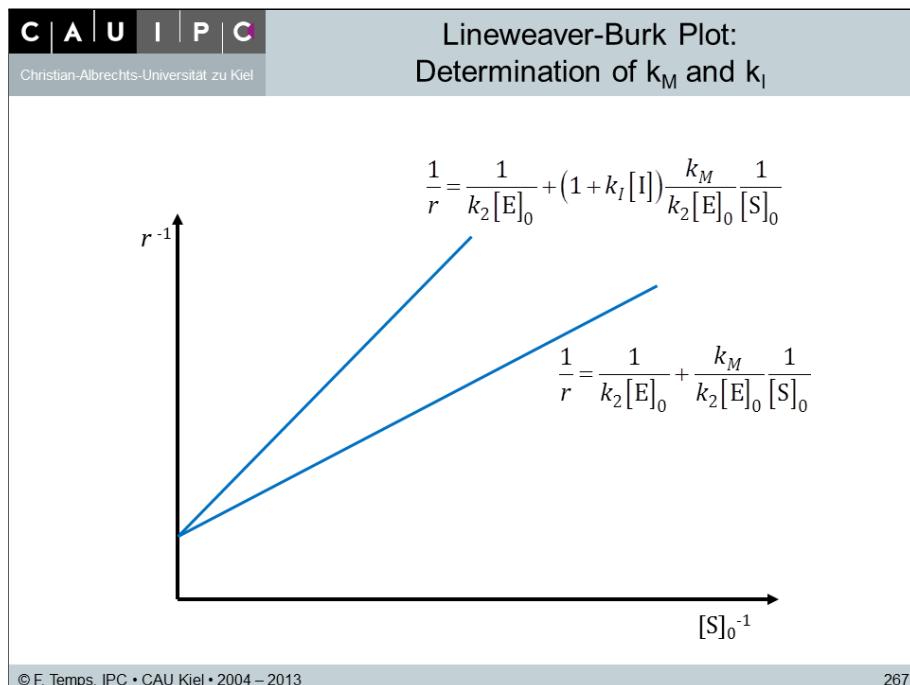
Determination of k_2 and K_M from a Lineweaver-Burk plot (Fig. 10.2):

$$\frac{1}{r} = \frac{1}{k_2 [E]_0} + \frac{K_M}{k_2 [E]_0} \frac{1}{[S]_0} \quad (10.27)$$

⇒ A plot of r^{-1} vs. $[S]_0^{-1}$ should give a straight line with intercept $(k_2 [E]_0)^{-1}$ and slope $K_M/k_2 [E]_0$. ↷

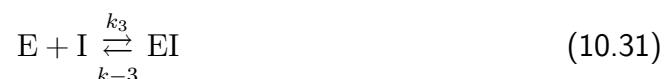
$$\frac{\text{slope}}{\text{intercept}} = K_M = \frac{k_{-1} + k_2}{k_1} \quad (10.28)$$

- **Figure 10.2:** Lineweaver-Burk plot.



10.1.2 Inhibition of enzymes:

Extended reaction mechanism:



The EI complex is catalytically inactive, since I blocks the active site of E.

Inhibition constant:

$$K_I = \frac{[EI]}{[E][I]} = \frac{k_3}{k_{-3}} \quad (10.32)$$

Reaction rate (Fig. 10.2):

$$\frac{d[ES]}{dt} = \dots \approx 0 \quad (10.33)$$

↷

$$\left[\frac{1}{r} = \frac{1}{k_2[E]_0} + (1 + k_I[I]) \times \frac{K_M}{k_2[E]_0} \frac{1}{[S]_0} \right] \quad (10.34)$$

↷ The slope of the plot of r^{-1} vs. $[S]_0^{-1}$ goes up (see Fig. 10.2).

- **Exercise 10.1:** Derive Eq. 10.34 with a reasonable assumption for the concentrations of I. □

10.2 Kinetics of heterogeneous reactions (surface reactions)

- **Examples for heterogeneous reactions (gas-solid interface):** Many reactions, which are very slow in the gas phase, take place as heterogeneous reactions in the presence of a heterogeneous catalyst:

- catalytic hydrogenation
- NH_3 synthesis (Haber-Bosch)
- catalytic exhaust gas treatment (internal combustion engines)
- catalytic DeNO_x processes
- CO oxidation
- oxidative coupling reactions of CH_4 (oxide catalysts)
- atmospheric reactions (at gas-solid and gas-liquid interface)

10.2.1 Reaction steps in heterogeneous catalysis

Heterogeneous reactions take place via a series of steps:

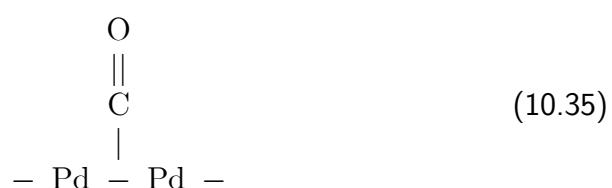
- Diffusion in gas (or liquid) phase to catalyst surface.
- Adsorption:
 - “physical” adsorption (“physisorption”),
 - “chemical” adsorption (“chemisorption”).
- Diffusion on the surface.
- Chemical reaction on the surface.
- Desorption.
- Diffusion away from surface.

10.2.2 Physisorption and chemisorption

We distinguish between “physical” adsorption (“physisorption”) and “chemical” adsorption (“chemisorption”) on a surface based upon the adsorption energies (surface binding energies). ⇒ Fig. 10.3.

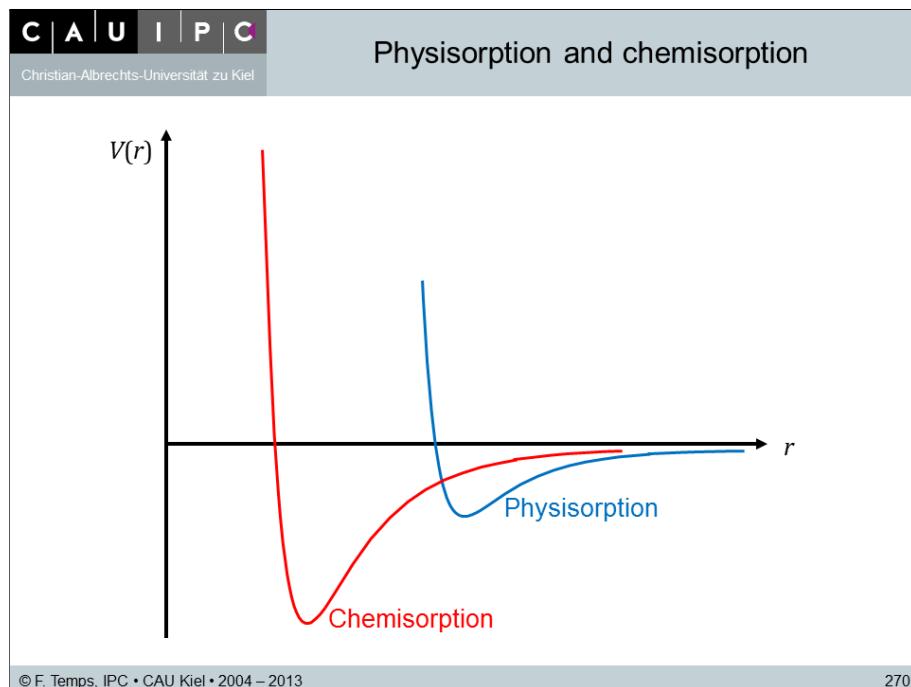
- Physisorption:
 - van-der-Waals type interaction,
 - typical bond energy: $\Delta H_{ads} \leq -40 \text{ kJ mol}^{-1}$,

- example: Ar on a metal or oxide surface.
- Chemisorption:
 - formation of a chemical bond between adsorbate and surface.
 - typical bond energy: $\Delta H_{ads} \leq -100.. -300 \text{ kJ mol}^{-1}$,
 - example: CO on Pd:



- * chemical bond by overlap of n orbital of the C atom with free bands of Pd,
- * back donation from occupied bands into π^* orbital of the CO substrate.
- * Experiment shows that $\nu(\text{Pd} - \text{C} = \text{O}) \approx 236 \text{ cm}^{-1}$.

- **Figure 10.3:** Potential curves for physisorption and chemisorption.



10.2.3 The Langmuir adsorption isotherm

- **Reaction scheme:**



► **Fraction of occupied active surface sites Θ :**

- Adsorption rate:

$$k_1 \times (1 - \Theta) \times p \quad (10.38)$$

- Desorption rate:

$$k_{-1} \times \Theta \quad (10.39)$$

- Steady state:

$$k_1 (1 - \Theta) p = k_{-1} \Theta \quad (10.40)$$

↷

$$k_1 p = (k_{-1} + k_1 p) \Theta \quad (10.41)$$

↷

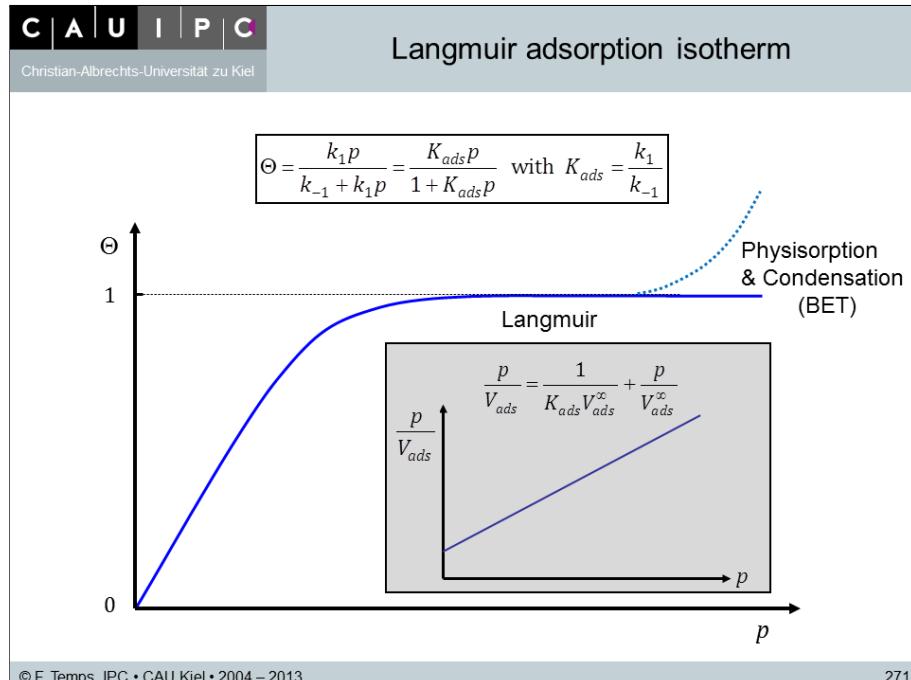
► **Langmuir isotherm (Fig. 10.4):**

$$\Theta = \frac{k_1 p}{k_{-1} + k_1 p} = \frac{K_{ads} p}{1 + K_{ads} p} \quad (10.42)$$

with

$$K_{ads} = \frac{k_1}{k_{-1}} \quad (10.43)$$

► **Figure 10.4: Langmuir adsorption isotherm.**



- **Determination of V_{ads} , V_{ads}^∞ , and the adsorption enthalpy ΔH_{ads} :** At a series of temperatures T , we need to measure $\Theta(p, T) = \frac{V_{ads}(p, T)}{V_{ads}^\infty(T)}$ as function of p by pressure/volume measurements in an ultrahigh vacuum apparatus.

- From Eq. 10.42:

$$\frac{1}{\Theta} = \frac{V_{ads}^\infty}{V_{ads}} = 1 + \frac{1}{K_{ads} p} \quad (10.44)$$

- Multiplication of l.h.s. and r.h.s. with $\frac{p}{V_{ads}^\infty}$:

$$\frac{p}{V_{ads}} = \frac{1}{K_{ads} V_{ads}^\infty} + \frac{p}{V_{ads}^\infty} = a + mp \quad (10.45)$$

- A plot of $\frac{p}{V_{ads}}$ vs. p gives a straight line (see the inset in Fig. 10.4) with slope

$$m = (V_{ads}^\infty)^{-1} \quad (10.46)$$

and intercept

$$a = (K_{ads} V_{ads}^\infty)^{-1} \quad (10.47)$$

-

$$K_{ads} = \frac{\text{slope}}{\text{intercept}} = \frac{m}{a} \quad (10.48)$$

- van't Hoff plot:

$$\frac{d \ln K_{ads}}{d(1/T)} = -\frac{\Delta H_{ads}}{R} \quad (10.49)$$

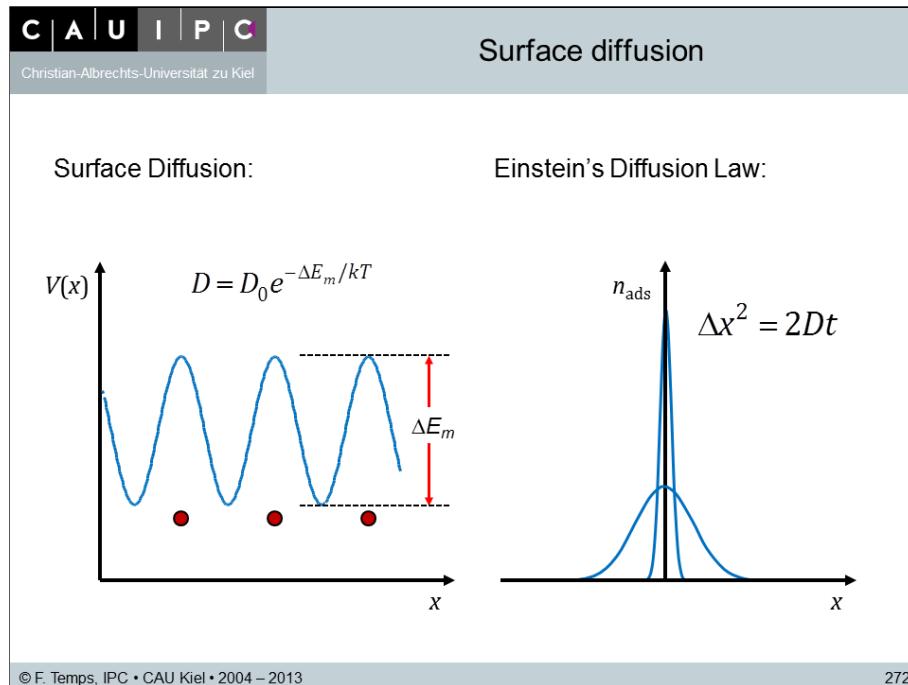
- **Desorption rate:** If $\Delta\epsilon_0 > 0$, we can describe the desorption rate by TST (see Figs. 10.3 und 10.6).

$$k_{-1} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_S} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \quad (10.50)$$

The Q 's are partition functions per unit area.

10.2.4 Surface Diffusion

► **Figure 10.5:** Surface Diffusion.



► **Diffusion is an activated process:**

$$D = D_0 \exp\left(-\frac{\Delta E_m}{kT}\right) \quad (10.51)$$

ΔE_m = energy barrier of jump of adsorbate from one site to another.

► **Fick's 2nd law:**

$$\frac{\partial n_{ads}(x, t)}{\partial t} = D \times \frac{\partial^2 n_{ads}(x, t)}{\partial x^2} \quad (10.52)$$

► **Einstein's diffusion law:**

- 1D:

$$\Delta x^2 = 2Dt \quad (10.53)$$

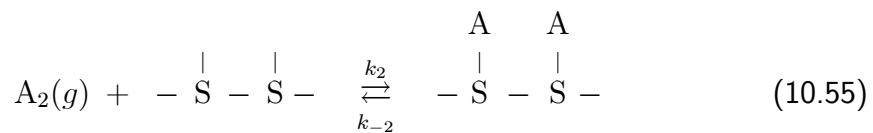
- 2D:

$$\Delta x^2 = 4Dt \quad (10.54)$$

10.2.5 Types of heterogeneous reactions

a) Dissociative Adsorption

► **Scheme:**



► **Adsorption isotherm:**

- Adsorption rate:

$$k_2 p_{A_2} (1 - \Theta)^2 \quad (10.56)$$

- Desorption rate:

$$k_{-2} \Theta^2 \quad (10.57)$$

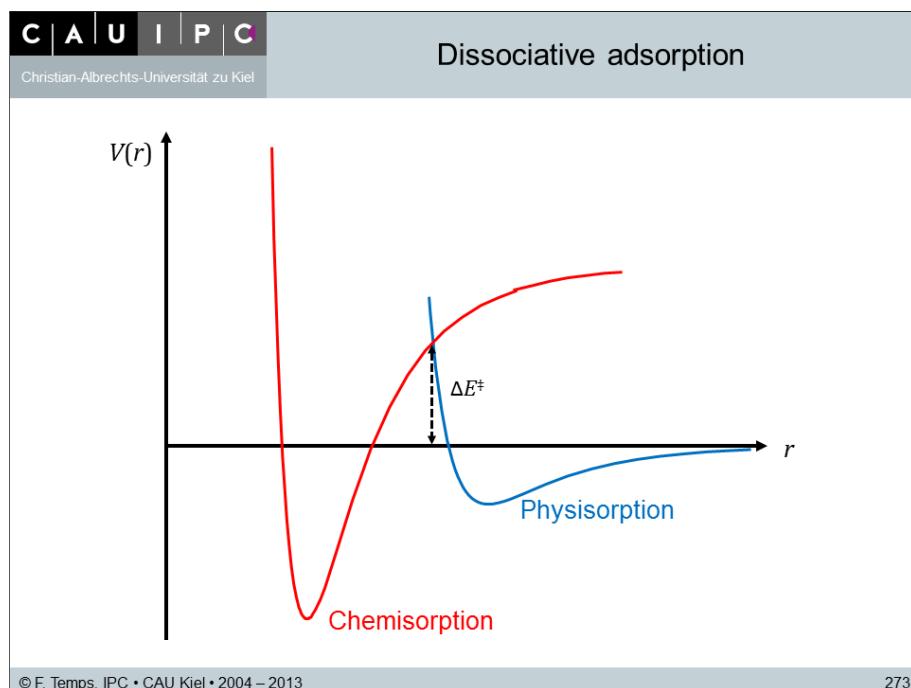
↷

$$\Theta = \frac{(p_{A_2} \times K_{ads})^{1/2}}{1 + (p_{A_2} \times K_{ads})^{1/2}} \quad (10.58)$$

with

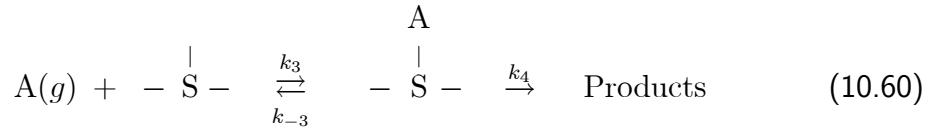
$$K_{ads} = \frac{k_2}{k_{-2}} \quad (10.59)$$

► **Figure 10.6:** Potential energy curves for dissociative adsorption.



b) Surface catalyzed unimolecular dissociation

► **Scheme:**



► **Example:** Decomposition of PH_3 on a W metal surface.

► **Decomposition rate and two limiting cases:**

$$\frac{d[\text{P}]}{dt} = k_4 \Theta_A = k_4 \times \frac{K_{ads} p_A}{1 + K_{ads} p_A} \quad (10.61)$$

(1) $K_{ads} p_A \ll 1$: The reaction becomes first-order in p_A .

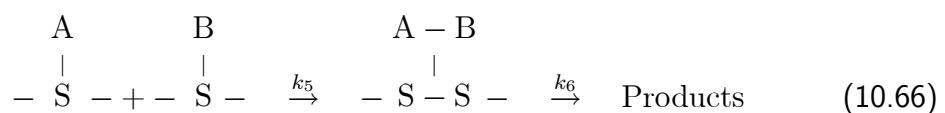
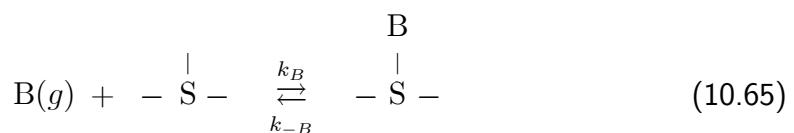
$$\frac{d[\text{P}]}{dt} = k_4 K_{ads} p_A \quad (10.62)$$

(2) $K_{ads} p_A \gg 1$: The reaction becomes zeroth order, i.e., independent of p_A !

$$\frac{d[\text{P}]}{dt} = k_4 \quad (10.63)$$

c) Bimolecular reactions

► **Scheme:**



► **Reaction rate:** Assuming that A and B compete for the same active sites, we have

$$k_A p_A (1 - \Theta_A - \Theta_B) = k_{-A} \Theta_A \quad (10.67)$$

$$k_B p_B (1 - \Theta_A - \Theta_B) = k_{-B} \Theta_B \quad (10.68)$$

↷

$$\frac{d[\text{P}]}{dt} = k_5 \Theta_A \Theta_B = \frac{k_5 K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \quad (10.69)$$

- **Limiting cases:** It is often the case that one species is adsorbed much more strongly than the other.

- Assume, for instance, that $K_A p_A \ll K_B p_B$. Then,

$$\frac{d[P]}{dt} = \frac{k_5 K_A K_B p_A p_B}{(1 + K_B p_B)^2} \quad (10.70)$$

(1) $K_B p_B \gg 1$:

$$\frac{d[P]}{dt} = \frac{k_5 K_A p_A}{K_B p_B} \quad (10.71)$$

The reaction is inhibited by B, which is strongly adsorbed: At high p_B , all active sites are blocked by B.

(2) $K_B p_B \ll 1$:

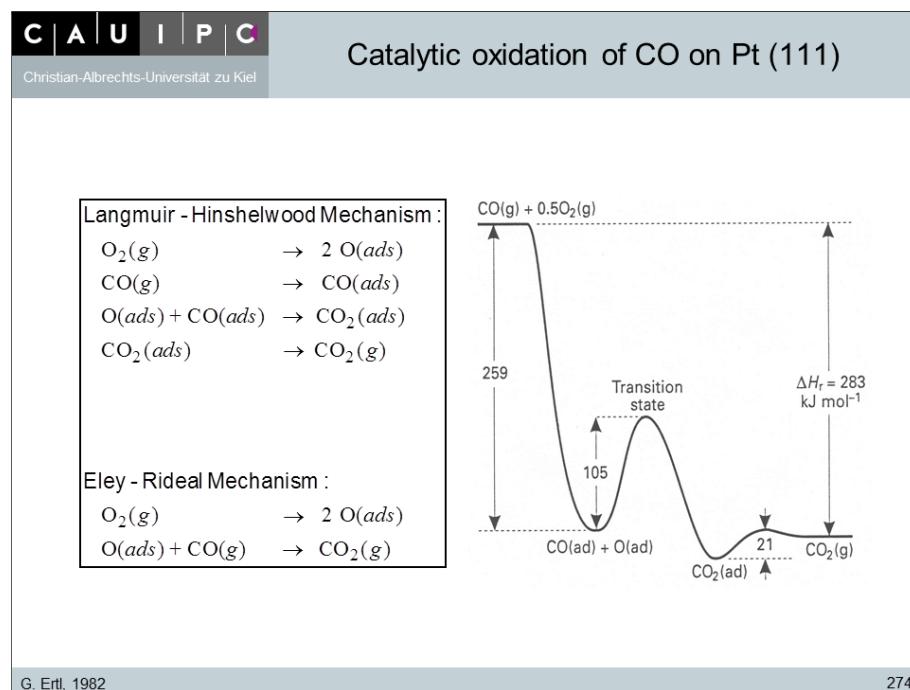
$$\frac{d[P]}{dt} = k_5 K_A K_B p_A p_B \quad (10.72)$$

The reaction is truly second order.

⇒ We can see from these two cases that, as p_B increases, the rate $\frac{d[P]}{dt}$ first increases, reaches a maximum, and then decreases again.

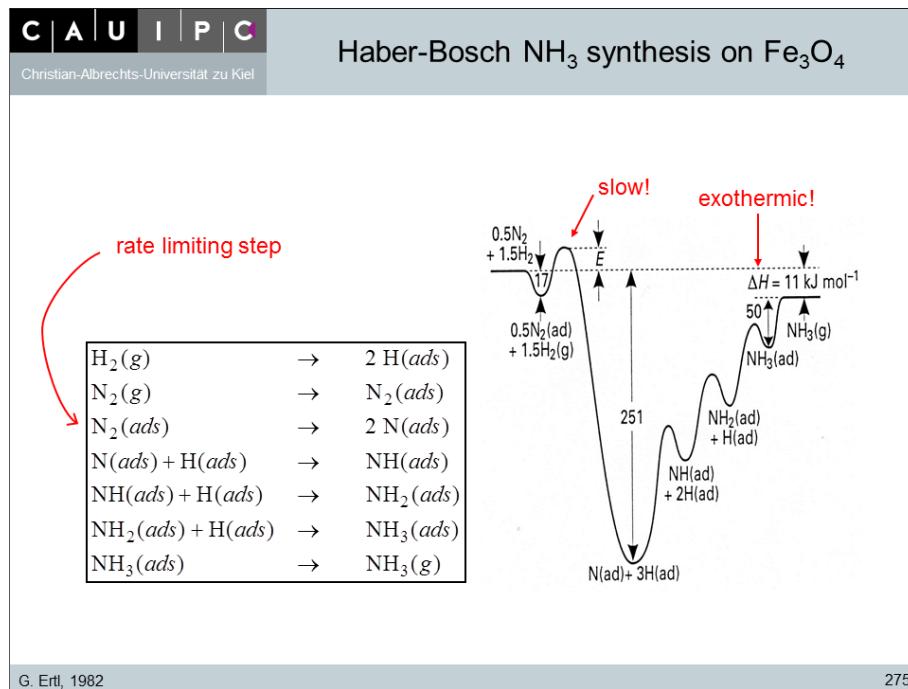
d) Example 1: Heterogeneous oxidation of CO

- **Figure 10.7:** Heterogeneous oxidation of CO on Pt. (a) Langmuir-Hinshelwood and Eley-Rideal mechanisms, (b) potential energy diagram (values in kJ mol^{-1}).



e) Example 2: Haber-Bosch NH₃ synthesis

- **Figure 10.8:** Potential energy diagram for the catalytic reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2 \text{NH}_3$ on a Fe_3O_4 catalyst according to Ertl and co-workers (1982). Energies in kJ mol^{-1} .



f) How can we control and accelerate heterogeneous reactions?

The answer depends on which step is rate determining:

- If diffusion to/from the surface is the rate determining step, we can accelerate the reaction by stirring
- If the adsorption step is rate determining (because of an activation energy), we can accelerate the reaction by increasing T and p and, in particular, by increasing surface area.

11. Reactions in solution

"Everyone has problems - chemists have solutions."

► **Comparison of gas and liquid phase reactions (@ $T = 298 \text{ K}$ and $p = 1 \text{ bar}$):**

- Molecules in the gas phase occupy $\approx 0.2 \text{ \%}$ of the total volume, while molecules in the liquid phase occupy $\approx 50 \text{ \%}$ of the total volume.
- Molecules in liquid are in permanent contact with each other, and undergo permanent collisions with each other.
- The crossing of a potential barrier in a reaction is not continuous as in gas phase but affected by multiple collisions during the crossing.
- As a result of the permanent collisions, we can expect the reactant molecules to be in thermodynamic equilibrium even above E_0 . Thus TST should be applicable.
- However, it is very difficult to evaluate the partition functions in liquids. Hence, one usually employs the thermodynamic version TST.
- Solvent molecules act as an efficient heat bath.

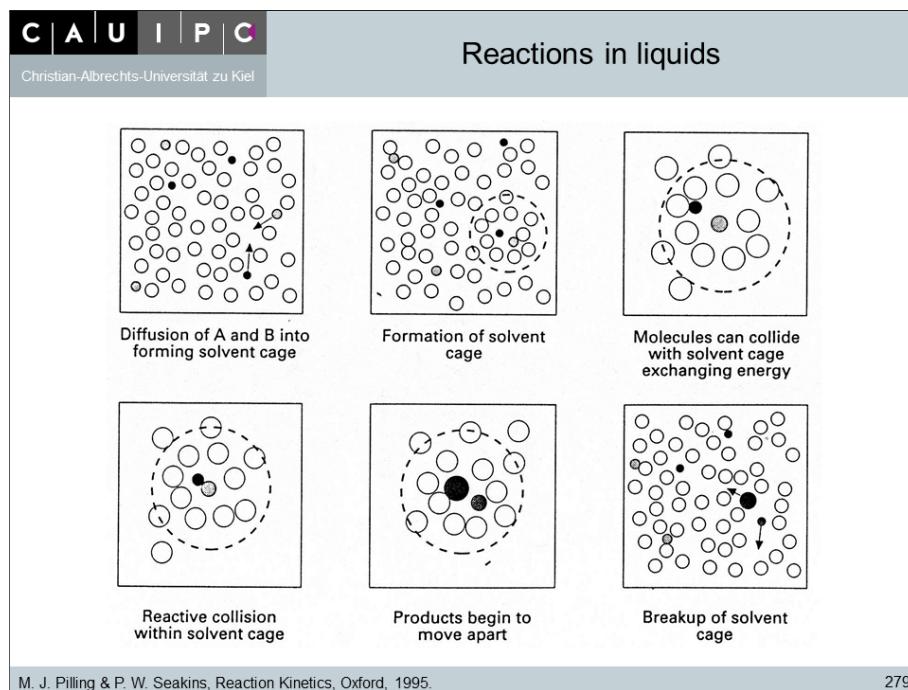
► **Observations on liquid phase reactions:** Experience has shown that reactions in liquids have similar rates as in the gas phase, except if

- the reaction occurs with the solvent,
- there are strong interactions of the reactant molecules with the solvent (e.g., ionic reactions; \Rightarrow solvent shells),
- the reactions are diffusion controlled.

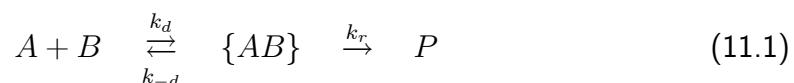
11.1 Qualitative model of liquid phase reactions

In contrast to gas phase reactions for which we have advanced theories (\Rightarrow transition state theory, unimolecular rate theory), the theory for liquid phase reactions is much less well developed. However, we can understand the required basic reaction steps as sketched in Fig. 11.1 and a number of limiting cases resulting from these steps.

- **Figure 11.1:** Structure and dynamics of solutions.



- **Formal kinetics:** We distinguish between the formation of the encounter complex in the solvent cage (by diffusion) and the actual reaction:



$$\curvearrowleft \quad \frac{d[\{AB\}]}{dt} = k_d [A][B] - k_{-d}[\{AB\}] - k_r[\{AB\}] \approx 0 \quad (11.2)$$

$$[\{AB\}] = \frac{k_d}{k_{-d} + k_r} [A][B] \quad (11.3)$$

$$\curvearrowleft \quad \frac{d[P]}{dt} = k_r [\{AB\}] = \frac{k_d k_r}{k_{-d} + k_r} [A][B] = k [A][B] \quad (11.4)$$

with

$$k = \frac{k_d k_r}{k_{-d} + k_r} \quad (11.5)$$

- **Rate constant for liquid phase reactions:**

$$k = \frac{k_d k_r}{k_{-d} + k_r}$$

(11.6)

► **Two limiting cases:**

(1) **Diffusion control:** $k_r \gg k_{-d} \curvearrowright$

$$k = k_d \quad (11.7)$$

This case is observed when $E_A = 0$ and the diffusion coefficient D_{AB} is small. We shall find below that

$$k_d = 4\pi r_{AB} D_{AB} \quad (11.8)$$

(2) **Reaction (or activation) control:** $k_r \ll k_{-d} \curvearrowright$

$$k = \frac{k_d}{k_{-d}} k_r = K_{\{AB\}} k_r \quad (11.9)$$

In this case, the reaction is said to be activation controlled because usually it has a sizable E_A .

k_r can be described by TST:

$$k_r = \frac{k_B T}{h} e^{\Delta S^+ / R} e^{-\Delta H^+ / RT} \quad (11.10)$$

11.2 Diffusion-controlled reactions

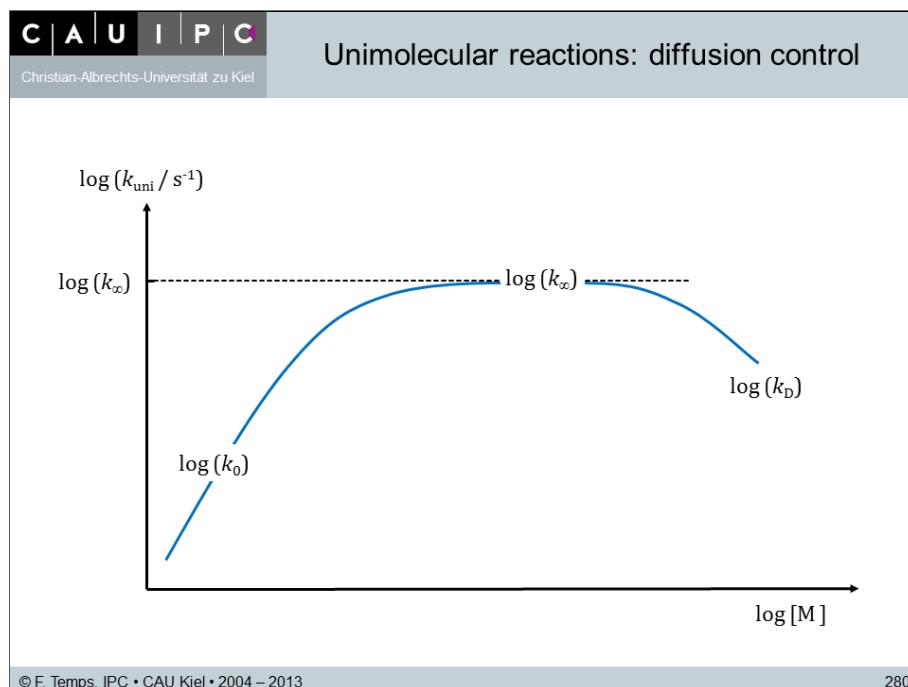
11.2.1 Experimental observations

The transition to diffusion control can be observed in the gas phase by studying the kinetics in highly compressed gases (up to $p = 1000$ bar) or, even better, in supercritical media. At $p \approx 1000$ bar, the gas density reaches the density of the liquid phase.

- **Smoluchowsky-Kramers limit:** At high densities, the rate constant becomes

$$k \propto D \propto \frac{1}{\eta} \quad (11.11)$$

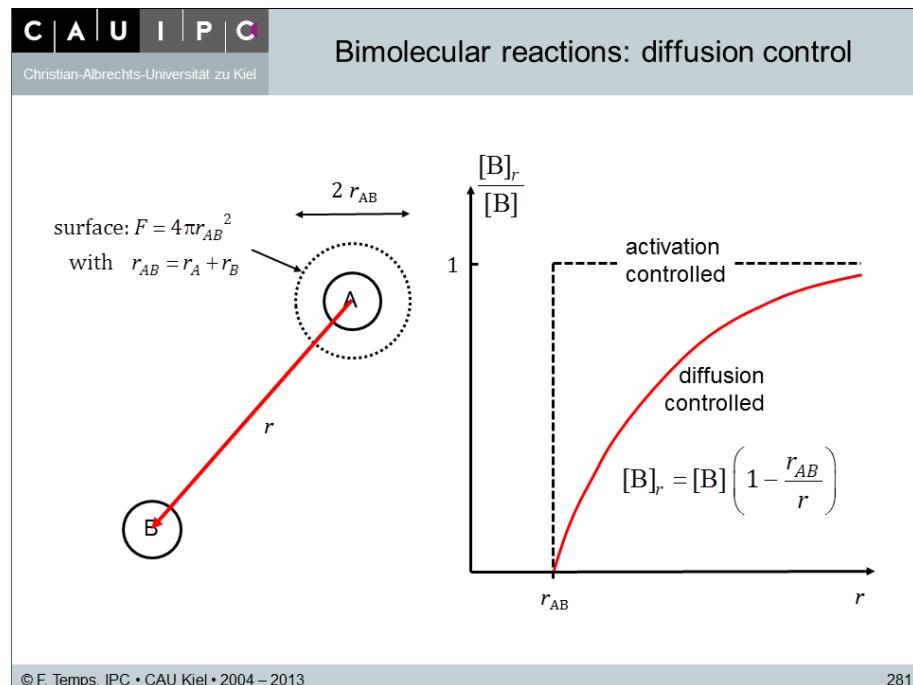
- **Figure 11.2:** Diffusion control of a unimolecular reaction: At very high pressures, the fragments recombine before they become separated by diffusion \curvearrowright the reaction becomes diffusion controlled.



11.2.2 Derivation of k_D

In order to derive a theoretical expression for k_D , we consider the distribution of the molecules B around a molecule A in the center of a sphere as shown in Fig. 11.3.

► **Figure 11.3:** Radial distribution of reactants in a diffusion-controlled reaction.



(1) We start by considering the boundary conditions for the concentration $[B]$ (cf. Fig. 11.3):

- At a distance $r \rightarrow \infty$, the concentration of B is identical to the mean concentration in the solution, i.e.,

$$r \rightarrow \infty \curvearrowright [B]_r = [B]_{r=\infty} = [B] \quad (11.12)$$

- At the distance $r = r_{AB}$, for a diffusion controlled reaction, the concentration of B vanishes because of its fast reaction with A , i.e.,

$$r \rightarrow 0 \curvearrowright [B]_{r=0} = 0 \quad (11.13)$$

(2) The result is a concentration gradient $\frac{d[B]_r}{dr}$ around A , which gives rise to a net flux \overleftarrow{J} by diffusion as described by Fick's first law:

$$J = D_{AB} \times F \times \frac{d[B]_r}{dr} \quad (11.14)$$

We define this flux, measured in units of molecules/s, in the direction from $r = \infty$ (high concentration) to $r = r_{AB}$ (low concentration); thus there is no $-$ sign in the usually written form of Fick's law.

D_{AB} is the mean diffusion coefficient, measured in m^2/s ,

$$D_{AB} = D_A + D_B \quad (11.15)$$

(3) With $F = 4\pi r^2$ as the surface of the sphere with radius r around A , we obtain

$$J = D_{AB} \times 4\pi r^2 \times \frac{d[B]_r}{dr} \quad (11.16)$$

(4) To determine the concentration profile $[B]_r$, we integrate over $d[B]_r$:

$$\int_{[B]_r}^{[B]_\infty} d[B]_r = \int_r^\infty \frac{J}{4\pi r^2 D_{AB}} dr \quad (11.17)$$

$$[B]_r^\infty = - \frac{J}{4\pi r D_{AB}} \Big|_r^\infty \quad (11.18)$$

$$[B] - [B]_r = \frac{J}{4\pi r D_{AB}} - 0 \quad (11.19)$$

(5) J is found from the boundary conditions that $[B]_r = 0$ at $r = r_{AB}$:

$$J = 4\pi r_{AB} D_{AB} \times [B] \quad (11.20)$$

(6) The concentration gradient of $[B]$ is obtained by inserting the above result for J into Eq. 11.19:

$$[B] - [B]_r = \frac{r_{AB} [B]}{r} \quad (11.21)$$

$$[B]_r = [B] \left(1 - \frac{r_{AB}}{r}\right) \quad (11.22)$$

This expression is plotted in Fig. 11.3.

(7) To determine k_D , we write the rate of the diffusion controlled reaction as

$$\frac{d[P]}{dt} = J [A] \quad (11.23)$$

Inserting the expression for J from Eq. 11.20, we obtain

$$\frac{d[P]}{dt} = 4\pi r_{AB} D_{AB} \times [A] [B] \quad (11.24)$$

The diffusion-limited rate constant is thus (in molecular units)

$$k_D = 4\pi r_{AB} D_{AB} \quad (11.25)$$

(8) Nernst-Einstein relation between diffusion constant and viscosity for spherical particles with radius r_S :

$$D = \frac{k_B T}{6\pi\eta r_S} \quad (11.26)$$

$$k_D \propto \frac{k_B T}{\eta} \quad (11.27)$$

(9) Keep in mind that diffusion is an activated process:

$$D = D_0 e^{-E_A/RT} \quad (11.28)$$

Typical value for H_2O : $E_A \approx 15 \text{ kJ mol}^{-1}$.

► **Typical values:**

$$D_{AB} \approx 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \quad (11.29)$$

$$r_{AB} \approx 5 \times 10^{-8} \text{ cm} \quad (11.30)$$

↷ Typical magnitude of k_D :

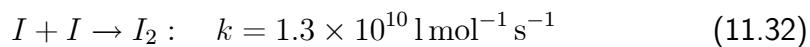
$$k_D \approx 8 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \quad (11.31)$$

► **Table 11.1:** Diffusion constants of ions in aqueous solution at $T = 298 \text{ K}$.

ion	$D / (\text{cm}^2 \text{ s}^{-1})$	ion	$D / (\text{cm}^2 \text{ s}^{-1})$
H^+	9.1×10^{-5}	OH^-	5.2×10^{-5}
Li^+	1.0×10^{-5}	Cl^-	2.0×10^{-5}
Na^+	1.3×10^{-5}	Br^-	2.1×10^{-5}

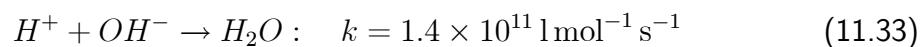
► **Examples of diffusion controlled reaction in solution:**

- radical recombination reactions, e.g.



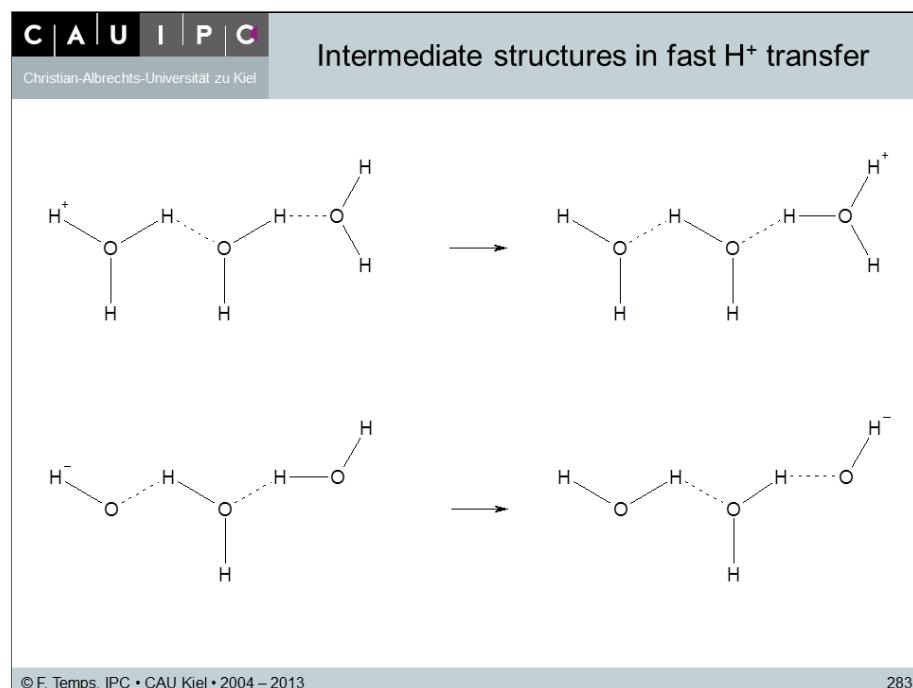
- electronic deactivation (quenching) in solution

- H^+ transfer reactions



This reaction is ten times faster than a typical diffusion controlled reaction, because H^+ transfer is a concerted process (Grotthus mechanism, see Fig. 11.4)!

► **Figure 11.4:** Structures involved in fast H^+ transfer processes in liquid water.



11.3 Activation controlled reactions

The rate constant for an activation controlled reaction is

$$k = k_r K_{\{AB\}} \quad (11.34)$$

- ▶ **Estimation of $K_{\{AB\}}$:** We can estimate the equilibrium constant $K_{\{AB\}}$ using simple arguments based on the coordination number. Accordingly, the concentration of the encounter complex is

$$[\{AB\}] = [A] \times (\text{probability of finding } B \text{ next to } A) \quad (11.35)$$

$$= [A] \times \frac{n[B]}{[S]} \quad (11.36)$$

where $[S]$ is the solvent concentration and n is the coordination number. ↗

$$K_{\{AB\}} = \frac{[\{AB\}]}{[A][B]} = \frac{n}{[S]} \quad (11.37)$$

For H_2O at $T = 298 \text{ K}$, $[S] = 55.5 \text{ mol l}^{-1}$. Thus, taking for example $n = 8$, we find that

$$K_{\{AB\}} = 0.141 \text{ mol l}^{-1} \quad (11.38)$$

- ▶ **Application of thermodynamic TST:** TST can be applied in two ways:

- (1) Considering the overall reaction, we can write

$$k = \kappa \frac{k_B T}{h} \exp(-\Delta G^\ddagger / RT) \quad (11.39)$$

where ΔG^\ddagger is the *overall* Gibbs free enthalpy for the reaction.

- (2) We can also separate the effects from k_r and $K_{\{AB\}}$ by writing

$$K_{\{AB\}} = \exp(-\Delta G_{\{AB\}}^\ominus / RT) \quad (11.40)$$

and

$$k_r = \kappa \frac{k_B T}{h} \exp(-\Delta G^+ / RT) \quad (11.41)$$

$\Delta G_{\{AB\}}^\ominus$ is the Gibbs free enthalpy change for the formation of the encounter complex, and ΔG^+ is the Gibbs free enthalpy of activation from the encounter complex. Thus,

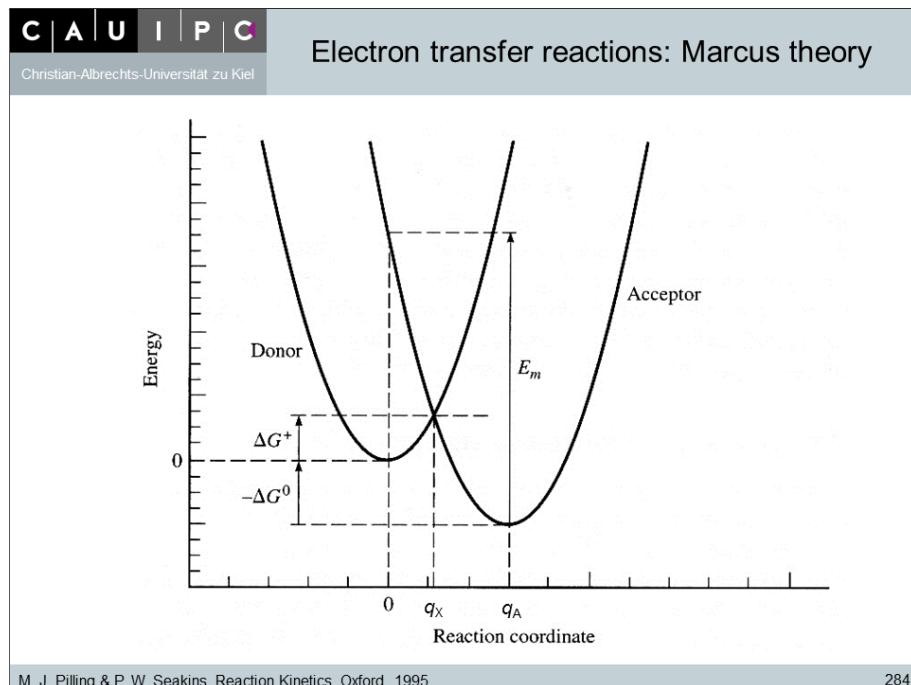
$$k = \kappa \frac{k_B T}{h} \exp\left(-\left(\Delta G_{\{AB\}}^\ominus + \Delta G^+\right) / RT\right) \quad (11.42)$$

- ▶ **Pressure dependence of the rate constant:** ⇒ See section 7.3.5.

11.4 Electron transfer reactions (Marcus theory)

Electron transfer is what happens in oxidation-reduction reactions. Hence, electron transfer reactions are extremely important. They are strongly affected by the solvent because the change of the charge distribution results in a large reorganization energy.

► **Figure 11.5:**



► **Marcus theory:** For a simplified derivation of $k_{ET}(T)$, we refer to Fig. 11.5.

- (1) The energy of the donor and acceptor molecules will generally depend on all $3N-6$ internal coordinates. We consider the dependence on an effective coordinate q , which describes the minimum energy path from reactant to product (Fig. 11.5).
- (2) The exergonicity of the ET reaction ΔG^\ominus is negative for an exergonic reaction (convention; cf. Fig. 11.5).
- (3) For the donor (D) and the acceptor (A), the Gibbs energy profiles $G_D(q)$ and $G_A(q)$ shall be of parabolic form, which we may write as

$$G_D(q) = q^2 \quad (11.43)$$

and

$$G_A(q) = (q - q_A)^2 + \Delta G^\ominus. \quad (11.44)$$

The origin $q = 0$ has been placed at the minimum of the donor; the acceptor has its minimum at $q = q_A$.⁵⁰

⁵⁰ We assume that $G \propto q^2$, taking any proportionality constant into account by proper rescaling of the abscissa.

(4) The ET rate constant is described by TST as

$$k_{ET} = \frac{k_B T}{h} \exp \left(-\Delta G^+ / RT \right) \quad (11.45)$$

The Gibbs free energy of activation

$$\Delta G^+ = q_X^2 \quad (11.46)$$

is the difference from the donor minimum to the TS at the donor/acceptor curve crossing at point q_X .

(5) In order to relate ΔG^+ to the G potential curves, we define the “**reorganization energy**” E_m as the energy that the acceptor would have at the equilibrium geometry of the donor. This is the energy of the acceptor parabola $G_A(q)$ at $q = 0$.

If we count E_m from the minimum of the acceptor parabola $G_A(q)$, we have

$$E_m = (-q_A)^2 = q_A^2 \quad (11.47)$$

(6) We now determine the energy of the intersection point q_X of the two parabolas from the condition

$$G_D(q_X) = G_A(q_X) . \quad (11.48)$$

Inserting q_X into Eqs. 11.43 and 11.44 yields, and using Eq. 11.47, yields

$$q_X^2 = (q_X - q_A)^2 + \Delta G^\ominus \quad (11.49)$$

$$= q_X^2 - 2 q_X q_A + q_A^2 + \Delta G^\ominus \quad (11.50)$$

$$= q_X^2 - 2 q_X q_A + E_m + \Delta G^\ominus \quad (11.51)$$

↷

$$2 q_X q_A = E_m + \Delta G^\ominus \quad (11.52)$$

↷

$$q_X = \frac{E_m + \Delta G^\ominus}{2 q_A} \quad (11.53)$$

↷

$$\Delta G^+ = q_X^2 = \frac{(E_m + \Delta G^\ominus)^2}{4 q_A^2} = \frac{(E_m + \Delta G^\ominus)^2}{4 E_m} \quad (11.54)$$

↷

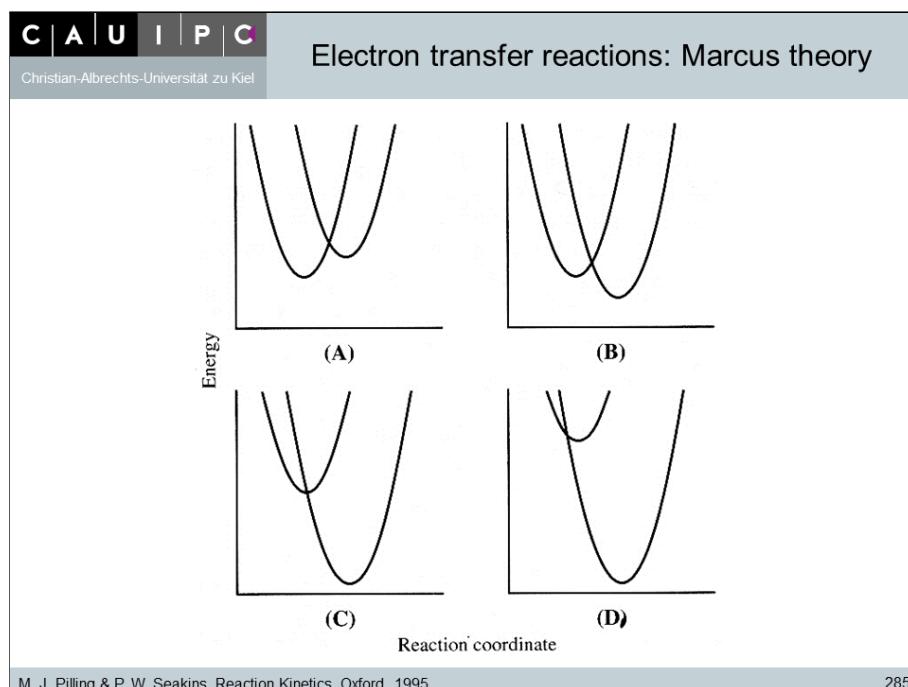
$$k_{ET}(T) = \kappa \frac{k_B T}{h} \exp \left(-\frac{(E_m + \Delta G^\ominus)^2}{4 E_m RT} \right) \quad (11.55)$$

(7) Limiting cases: We can distinguish between

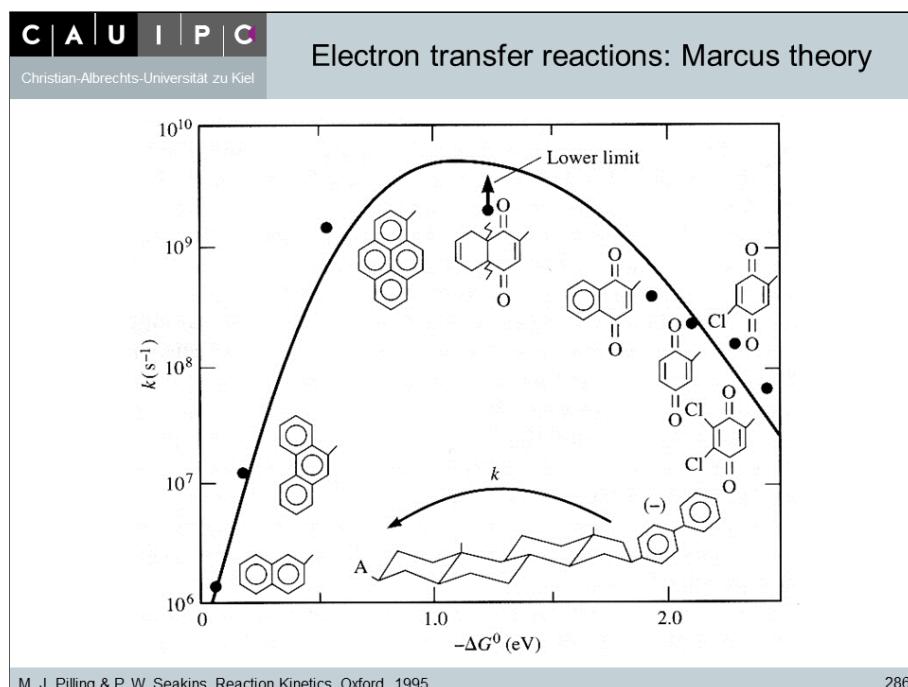
- $-\Delta G^\ominus < E_m$: Regular region — the reaction becomes faster, the more exergonic the reaction becomes.
- $-\Delta G^\ominus = E_m$: turning point
- $-\Delta G^\ominus > E_m$: Inverted region — the reaction becomes slower, the more exergonic the reaction becomes.

► **Conclusion:** Equation 11.55 predicts the ET rate constant to increase with increasing exoergicity ($-\Delta G^\ominus$) of the reaction. However, once $-\Delta G^\ominus > E_m$, the rate constant is predicted to decrease again (see Figs. 11.6D and 11.7). The prediction of this unexpected **inverted Marcus regime** before any experimental data were available is the hallmark of Marcus theory.

► **Figure 11.6:**



► **Figure 11.7:**



11.5 Reactions of ions in solutions

Reactions of ionic species in liquids are one exception to the rule that reactions in the liquid phase usually have similar rates as in the gas phase (the other exception being electron transfer reactions). The reason is that the charged species are very sensitive to their environment, in particular solvation. Changes of the charge distribution are accompanied by correspondingly large solvation shell rearrangements.

11.5.1 Effect of the ionic strength of the solution

The main effect arises from the stabilization of shielding every ion in solution by the oppositely charged "ionic atmosphere" or "ion cloud" (\Rightarrow Debye-Hückel theory, Appendix ??).

► **Equilibrium constant for $[AB^\ddagger]$:**

$$K^\ddagger = \frac{a_{AB}^\ddagger}{a_A a_B} = \frac{\gamma_{AB}^\ddagger}{\gamma_A \gamma_B} \frac{[AB^\ddagger]}{[A] [B]} \quad (11.56)$$

► **Activity coefficient from Debye-Hückel theory:**

$$\log \gamma_i = -A z_i^2 I_c^{1/2} \quad (11.57)$$

with (for water at $T = 298$ K, according to Debye-Hückel theory)

$$A = 0.509 \text{ l}^{1/2} \text{ mol}^{-1/2} \quad (11.58)$$

► **Ionic strength:**

$$I_c = \frac{1}{2} \sum_i c_i z_i^2 \quad (11.59)$$

11.5.2 Kinetic salt effect

► **TST rate constant:**

$$\frac{d[P]}{dt} = \nu^\ddagger [AB^\ddagger] = \nu^\ddagger \frac{\gamma_A \gamma_B}{\gamma_{AB}^\ddagger} K^\ddagger [A] [B] \quad (11.60)$$

Defining k_0 as the rate constant for the ideal solution, where all $\gamma_i = 1$, this becomes

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_{AB}^\ddagger} \quad (11.61)$$

► **Dependence of the rate constant on the ionic strength:**

$$\log k = \log k_0 - A \left(z_A^2 + z_B^2 - z_{AB}^{\ddagger 2} \right) I_c^{1/2} \quad (11.62)$$

with $z_{AB}^{\ddagger} = z_A + z_B$.

Inserting $z_{AB}^{\ddagger} = z_A + z_B$, we obtain

$$\log k = \log k_0 - A \left(z_A^2 + z_B^2 - (z_A + z_B)^2 \right) I_c^{1/2} \quad (11.63)$$

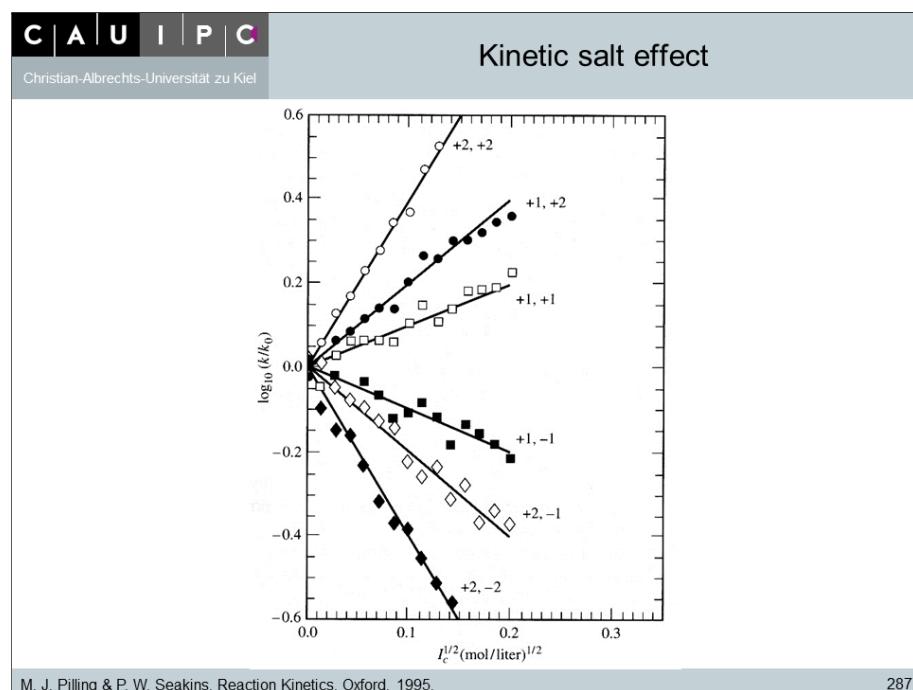
↷

$$\log \frac{k}{k_0} = +2A z_A z_B I_c^{1/2} \quad (11.64)$$

► **Conclusions:**

- If z_A and z_B have the same sign, then k will increase with increasing I , because the repulsion is reduced by the shielding effect of the ion cloud.
- If z_A and z_B have opposite sign, then k will decrease with increasing I , because the attraction is reduced by the shielding effect of the ion cloud.

► **Figure 11.8:** Kinetic salt effect for reactions of ions in solution.



11.6 References

Eigen 1954a M. Eigen, Disc. Faraday Soc. **17**, 194 (1954).

Eigen 1954b M. Eigen Z. Physik. Chem. NF **1**, 176 (1954).

12. Photochemical reactions

12.1 Radiative processes in a two-level system; Einstein coefficients

► **Three fundamental radiative processes (Einstein):**

- absorption,
- spontaneous emission,
- stimulated emission:

► **Rate equation using Einstein coefficients:**

$$\frac{dN_2}{dt} = -\frac{dN_1}{dt} = B_{12}\rho(\nu)N_1 - B_{21}\rho(\nu)N_2 - A_{21}N_2 \quad (12.1)$$

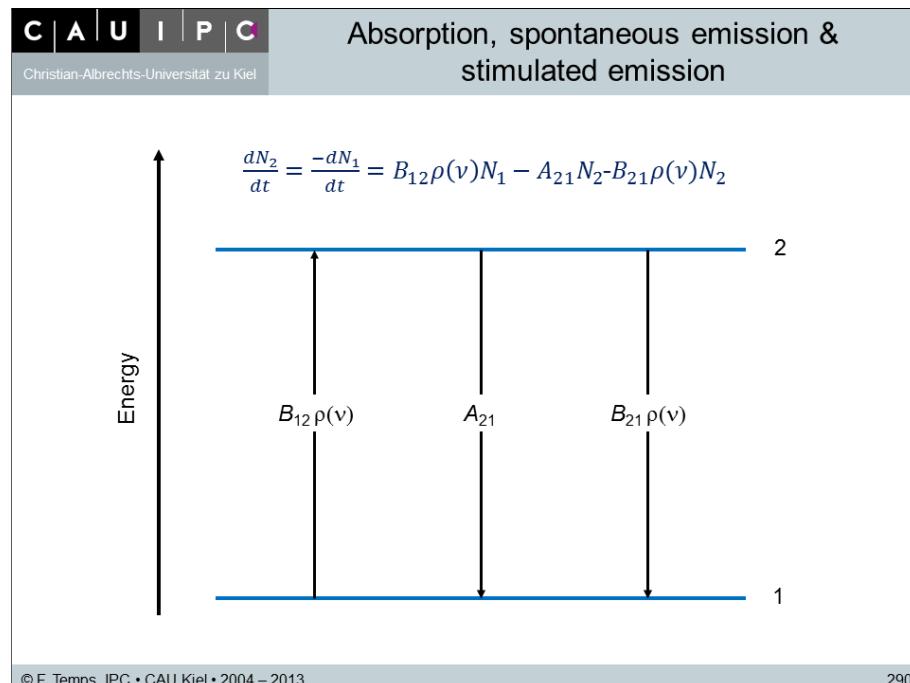
with

$$A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21} \quad (12.2)$$

and (for a true two-level system, with $g_1 = g_2$)

$$B_{12} = B_{21} \quad (12.3)$$

► **Figure 12.1:** Absorption, stimulated emission, and spontaneous emission.

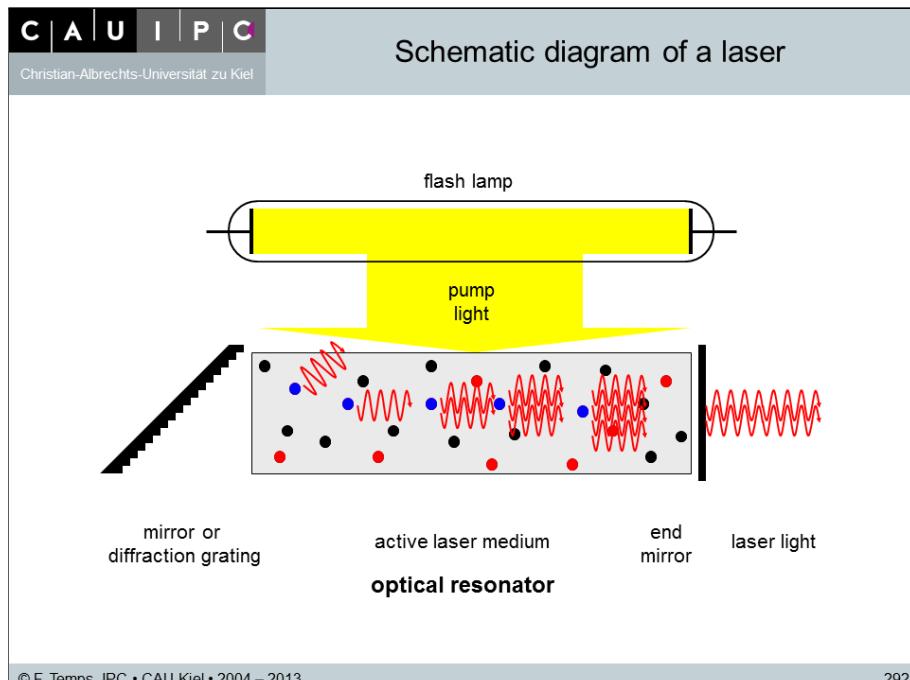


12.2 Light amplification by stimulated emission of radiation (LASER)

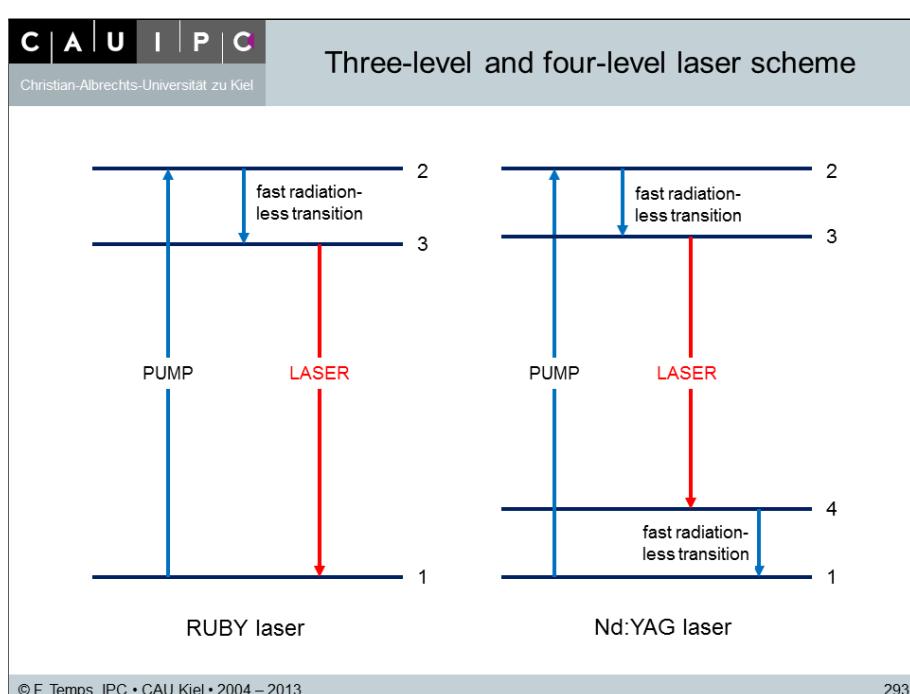
► Requirements for a laser:

- Optical medium with population inversion,
- pump source to achieve population inversion,
- optical resonator for feedback.

► Figure 12.2: Light amplification by stimulated emission of radiation (LASER).

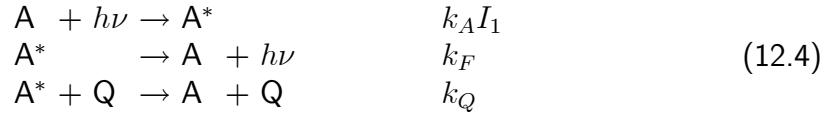


► Figure 12.3: Three-level and four-level laser.



12.3 Fluorescence quenching (Stern-Volmer equation)

► **Kinetic model:**



If any other radiationless processes can be neglected, we find

$$[A^*]_{ss} = \frac{k_A I_1 [A]}{k_F + k_Q [Q]} \quad (12.5)$$

► **Fluorescence intensity $I_{F,0}$ in the absence of the quencher Q:**

$$I_{F,0} \propto k_F [A^*]_{ss} = k_A I_1 [A] \quad (12.6)$$

► **Fluorescence intensity I_F in the presence of the quencher Q:**

$$I_F \propto k_F [A^*]_{ss} = k_F \frac{k_A I_1 [A]}{k_F + k_Q [Q]} \quad (12.7)$$

► **Stern-Volmer equation:**

$$\frac{I_{F,0}}{I_F} = k_A I_1 [A] \times \frac{k_F + k_Q [Q]}{k_F k_A I_1 [A]} = \frac{k_F + k_Q [Q]}{k_F} \quad (12.8)$$

↷

$$\boxed{\frac{I_{F,0}}{I_F} = 1 + k_Q \tau_0 [Q]} \quad (12.9)$$

with the

► **Radiative lifetime:**

$$\tau_0 = \frac{1}{k_F} \quad (12.10)$$

► **Figure 12.4:** Stern-Volmer plot.

A plot of $I_{F,0}/I_F$ vs. $[Q]$ should give a straight line with intercept 1 and slope $k_Q \tau_0 [Q]$.

12.4 The radiative lifetime τ_0 and the fluorescence quantum yield Φ_F

- **Determination of the radiative lifetime τ_0 :** Assuming that there are no competing nonradiative processes, we can determine the radiative lifetime τ_0 by

- (1) time-resolved measurements of the (exponential) fluorescence decay after pulsed excitation,
- (2) high-resolution measurement of the natural (Lorentzian) linewidth according to

$$\Delta E \Delta t = \hbar \quad (12.11)$$

↷

$$\boxed{\tau_0 = \frac{1}{2\pi \Delta\nu_0}} \quad (12.12)$$

- (3) evaluation from the molar absorption coefficient (Lambert-Beer) using the relationship between the Einstein coefficients A_{21} and B_{21} ,⁵¹

$$\boxed{A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}} \quad (12.13)$$

- (4) calculation from first principles of the value of

$$|\mu_{if}|^2 \propto A_{21} \propto B_{21} \propto B_{12} \propto I. \quad (12.14)$$

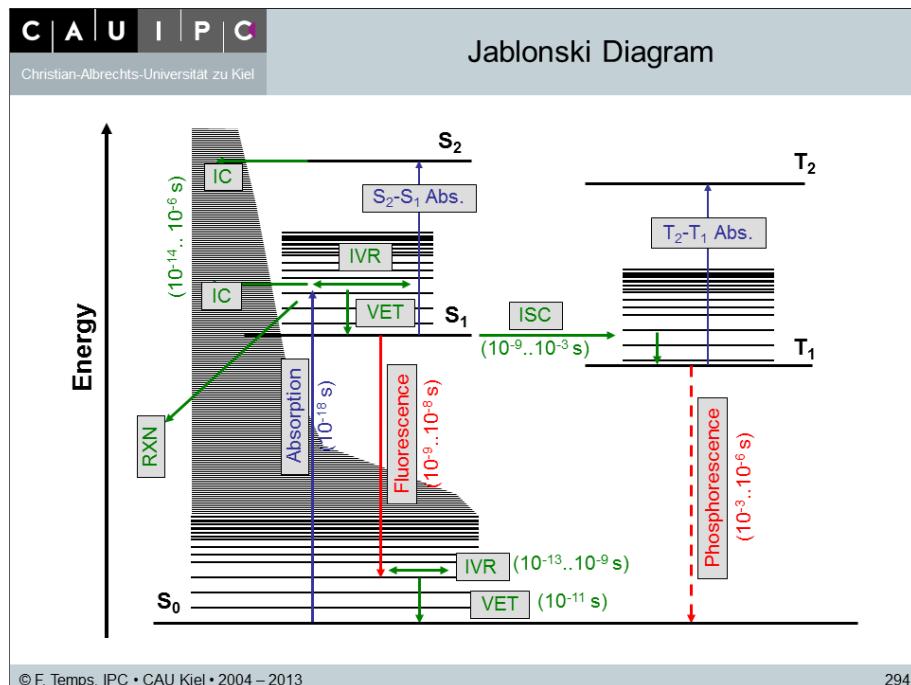
- **Fluorescence quantum yield:** Apart from quenching, the fluorescence is reduced by other radiationless processes (IC, ISC, R, ...). The experimentally measured fluorescence lifetime τ is therefore smaller (often much smaller) than the radiative lifetime τ_0 . The ratio is the fluorescence quantum yield:

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_R + k_{ISC} + k_Q [Q] + \dots} = \frac{\tau}{\tau_0} \quad (12.15)$$

⁵¹ The actual procedure, which involves integration over the absorption band, corrects for the influence of the refraction index of the solvent, etc., is called the Strickler-Berg analysis.

12.5 Radiationless processes in photoexcited molecules

► **Figure 12.5:** Jablonski Diagram.



► **Primary photochemical processes:**

- Absorption of a photon (depends on transition dipole moment $|\mu_{if}|^2$),
- Intramolecular processes:
 - fluorescence (\equiv spontaneous emission of a photon, FLUO),
 - stimulated emission (SE), \Rightarrow Einstein coefficients
 - intramolecular vibrational (energy) redistribution (IVR),
 - internal conversion (IC),
 - chemical reaction in the excited state (RXN),
 - intersystem crossing (ISC),
 - phosphorescence (PHOS).
- Intermolecular (i.e., collisional) processes:
 - electronic deactivation (quenching, Q),
 - * may affect fluorescence as well as phosphorescence,
 - vibrational energy transfer (VET),
 - rotational energy transfer (RET),
 - collision-induced intersystem crossing (CIISC).

12.5.1 The Born-Oppenheimer approximation and its breakdown

a) The full Hamiltonian

We consider a non-moving, non-rotating molecule in the laboratory framework. The molecule is described by the Schrödinger equation (SE)

$$\hat{H}\psi(\mathbf{r}, \mathbf{R}) = \varepsilon\psi(\mathbf{r}, \mathbf{R}) \quad (12.16)$$

or

$$(\hat{H} - \varepsilon)\psi(\mathbf{r}, \mathbf{R}) = 0 \quad (12.17)$$

with ε being the energy eigenvalue associated with the wavefunction $\psi(\mathbf{r}, \mathbf{R})$ as function of the electronic (e) coordinates \mathbf{r} and the nuclear (N) coordinates \mathbf{R} .

The Hamilton operator \hat{H} appearing in the SE can be written as

$$\hat{H} = \hat{T} + \hat{V} = \hat{T}_e(\mathbf{r}) + \hat{T}_N(\mathbf{R}) + V(\mathbf{r}, \mathbf{R}) \quad (12.18)$$

where

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla_i^2 \quad (12.19)$$

$$\hat{T}_N = -\frac{\hbar^2}{2M_k} \sum_{k=1}^{N_N} \nabla_k^2 \quad (12.20)$$

and

$$V(\mathbf{r}, \mathbf{R}) = V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}) \quad (12.21)$$

with

$$V_{NN} = +\frac{e^2}{4\pi\epsilon_0} \sum_{k>k'} \sum_{k'=1}^{N_N} \frac{Z_k Z_{k'}}{R_{k,k'}} \quad (12.22)$$

$$V_{eN} = -\frac{e^2}{4\pi\epsilon_0} \sum_{k=1}^{N_N} \sum_{i=1}^{N_e} \frac{Z_k}{r_{i,k}} \quad (12.23)$$

$$V_{ee} = +\frac{e^2}{4\pi\epsilon_0} \sum_{i>i'} \sum_{i'=1}^{N_e} \frac{1}{r_{i,i'}} \quad (12.24)$$

Electronic spin, spin-orbit interaction, and nuclear spins are neglected here. Further, we have left aside the so-called electronic mass and electronic nuclear cross polarization terms, which appear in the case of a moving molecule as result of the separation of the center-of-mass.

b) Adiabatic separation of nuclear and electronic motion

We now want to separate the *slow* motion of the nuclei from the the *fast* motion of the electrons. This separation can be made because the fast electrons can be assumed

to very rapidly follow the slow nuclei. The kinetic energy of the nuclei is assumed to be small compared to the electronic energy.

Thus, for every *nuclear* configuration \mathbf{R} , there is an electronic wavefunction $\phi_n^{\text{el}}(\mathbf{r}, \mathbf{R})$ belonging to the electronic state $|n\rangle$ specified by quantum number n . This $\phi_n^{\text{el}}(\mathbf{r}, \mathbf{R})$ depends on the nuclear coordinates \mathbf{R} , but only very little on the nuclear velocities.

We say that the electrons *adiabatically* follow the periodic vibrational motion of the nuclei. This approximation is therefore called *adiabatic approximation*.

► **Ansatz for \hat{H} :**

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (12.25)$$

with

$$\hat{H}_0 = \hat{T}_e + V(\mathbf{r}, \mathbf{R}) = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla_i^2 + V(\mathbf{r}, \mathbf{R}) \quad (12.26)$$

$$\hat{H}' = \hat{T}_N = -\frac{\hbar^2}{2M_k} \sum_{k=1}^{N_N} \nabla_k^2 \quad (12.27)$$

► **The zero-order Hamiltonian \hat{H}_0 :**

- The *zero-order Hamiltonian* \hat{H}_0 depends only on the electron kinetic energy operator \hat{T}_e and the potential energy V and describes the *rigid* molecule (all \mathbf{R} are fixed!) via the unperturbed SE

$$\hat{H}_0 \phi^{\text{el}}(\mathbf{r}; \mathbf{R}) = E^{(0)}(\mathbf{R}) \phi^{\text{el}}(\mathbf{r}; \mathbf{R}) \quad (12.28)$$

- The *zero-order electronic wave functions* $\phi_n^{\text{el}}(\mathbf{r}; \mathbf{R})$ describe the electrons and their distribution $|\phi_n^{\text{el}}(\mathbf{r}; \mathbf{R})|^2$ for the case of *fixed* nuclei in the electronic state $|n\rangle$ with the electronic energy E_n^{el} .
- The $\phi_n^{\text{el}}(\mathbf{r}; \mathbf{R})$ depend on \mathbf{R} only as a parameter, not as a variable (we do not differentiate or integrate with respect to the R_k in the zero-order SE).
- The $\phi_n^{\text{el}}(\mathbf{r}; \mathbf{R})$ form a complete orthonormal system.
- The eigenvalues $E^{(0)}(\mathbf{R})$ of the electronic SE are what we have come to know as the molecular potential energy functions (or hypersurfaces) $V(\mathbf{R})$ of the molecule with all nuclei at rest.

► **The perturbation \hat{H}' :**

- The *perturbation* \hat{H}' is the *nuclear kinetic energy operator* \hat{T}_N .

c) Solution of the complete SE

- To solve the complete SE

$$\left(\hat{H}_0 + \hat{H}' - \varepsilon \right) \psi(\mathbf{r}, \mathbf{R}) = 0 \quad (12.29)$$

we use the ansatz

$$\psi(\mathbf{r}, \mathbf{R}) = \sum_m \chi_m(\mathbf{R}) \phi_m^{\text{el}}(\mathbf{r}; \mathbf{R}) \quad (12.30)$$

with the expansion coefficients $\chi = \chi(\mathbf{R})$ depending only on \mathbf{R} but not on \mathbf{r} .

- Inserting the ansatz 12.30 into the complete SE,

$$\left(\hat{H}^0 + \hat{H}' - \varepsilon \right) \sum_m \chi_m(\mathbf{R}) \phi_m^{\text{el}}(\mathbf{r}; \mathbf{R}) = 0 \quad (12.31)$$

and doing some algebraic manipulation, we arrive at a

- *system of coupled equations* for the electronic wavefunctions $\phi_m^{\text{el}}(\mathbf{r}; \mathbf{R})$ for the electronic state $\phi_n^{\text{el}}(\mathbf{r}; \mathbf{R})$ and the nuclear wavefunctions $\chi(\mathbf{R})$:

$$\hat{H}_0 \phi_n^{\text{el}}(\mathbf{r}; \mathbf{R}) = E_n^{(0)}(\mathbf{R}) \phi_n^{\text{el}}(\mathbf{r}; \mathbf{R}) \quad (12.32)$$

and

$$\hat{H}' \chi_n(\mathbf{R}) + \sum_m c_{nm}(\mathbf{R}) \chi_m(\mathbf{R}) = (\varepsilon - E_n^{(0)}(\mathbf{R})) \chi_n(\mathbf{R}) \quad (12.33)$$

with the *coupling coefficients*

$$\begin{aligned} c_{nm}(\mathbf{R}) &= \int_{\mathbf{r}} \phi_n^*(\mathbf{r}; \mathbf{R}) \hat{H}' \phi_m(\mathbf{r}; \mathbf{R}) d\mathbf{r} \\ &= -\hbar^2 \int_{\mathbf{r}} \phi_n^*(\mathbf{r}; \mathbf{R}) \sum_k \frac{1}{M_k} \frac{\partial}{\partial R_k} \phi_m(\mathbf{r}; \mathbf{R}) d\mathbf{r} \frac{\partial}{\partial R_k} \quad (12.34) \end{aligned}$$

- We interpret these Eqs. as follows:

- (1) $E_n^{(0)}(\mathbf{R})$ can be interpreted as the *zero-order potential functions* of the n th zero-order electronic state that is given by the solution of the electronic SE (Eq. 12.28) for *fixed* nuclei \mathbf{R} .
- (2) Without the $c_{nm}(\mathbf{R})$, Eq. 12.33 describes the kinetic energy of the nuclei in the potential $E_n^{(0)}(\mathbf{R})$.⁵² Eq. 12.33 is thus simply the *vibrational SE* for the electronic potential $E_n^{(0)}(\mathbf{R})$.
- (3) The coefficients $c_{nm}(\mathbf{R})$ defined by Eq. 12.34 are *coupling terms* that connect (i.e., mix) the electronic states ϕ_n and ϕ_m . They describe how the different electronic states ϕ_n and ϕ_m are coupled by the nuclear motion (the two terms on the RHS resulting from the *nuclear* kinetic energy operator \hat{T}_N ; see Eq. 12.34).

⁵² We usually denote these potential energy functions as $V_n(\mathbf{R})$.

d) Born-Oppenheimer approximation

The *Born-Oppenheimer (BO) approximation* completely neglects the coupling coefficients c_{nm} . The complete SE is therefore reduced to two uncoupled equations, which we denote as electronic SE

$$\hat{H}_0 \phi_n^{\text{el}}(\mathbf{r}) = E_n^{(0)}(\mathbf{R}) \phi_n^{\text{el}}(\mathbf{r}) \quad (12.35)$$

and nuclear (vibrational) SE

$$\left[\hat{T}_N + E_n^{(0)} \right] \chi_n(\mathbf{R}) = E_{n,i} \chi_n(\mathbf{R}) \quad (12.36)$$

which describe, respectively, the electronic wavefunction ϕ_n^{el} for fixed nuclear coordinates \mathbf{R} in the electronic state ϕ_n^{el} and the set of nuclear wavefunctions $\chi_{n,i}(\mathbf{R})$ for the energy state i of the nuclei in the electronic state ϕ_n^{el} .

e) Breakdown of the Born-Oppenheimer approximation

When two (or more) electronic states $\phi_n^{\text{el}}(\mathbf{R})$, $\phi_m^{\text{el}}(\mathbf{R})$ become nearly isoenergetic or, at a crossing, even degenerate, the coupling matrix element $c_{nm}(\mathbf{R})$ may no longer be neglected, because through the $c_{nm}(\mathbf{R})$, the *nuclear motion leads to a mixing between the different electronic BO-states*.

► **This breakdown of the BO approximation leads to non-adiabatic coupling of electronic states:**

- For a diatomic molecule, the coupling leads to an *avoided crossing* of the two electronic potential curves.
- For polyatomic molecules, the coupling can lead to a *conical intersection* (CI) between the two electronic potential energy hypersurfaces.

As will be outlined in the following, the existence of conical intersections between different excited electronic potential energy hypersurfaces and between an excited and the ground electronic potential energy hypersurface has dramatic consequences for the dynamics of photochemical reactions.⁵³

12.5.2 Avoided crossings of two potential curves of a diatomic molecule

► **Illustration of an avoided crossing using two diabatic model potential functions + coupling term:**

$$V_1(R) = D_1 [1 - \exp[-\beta_1(r - r_1)]]^2 \quad (12.37)$$

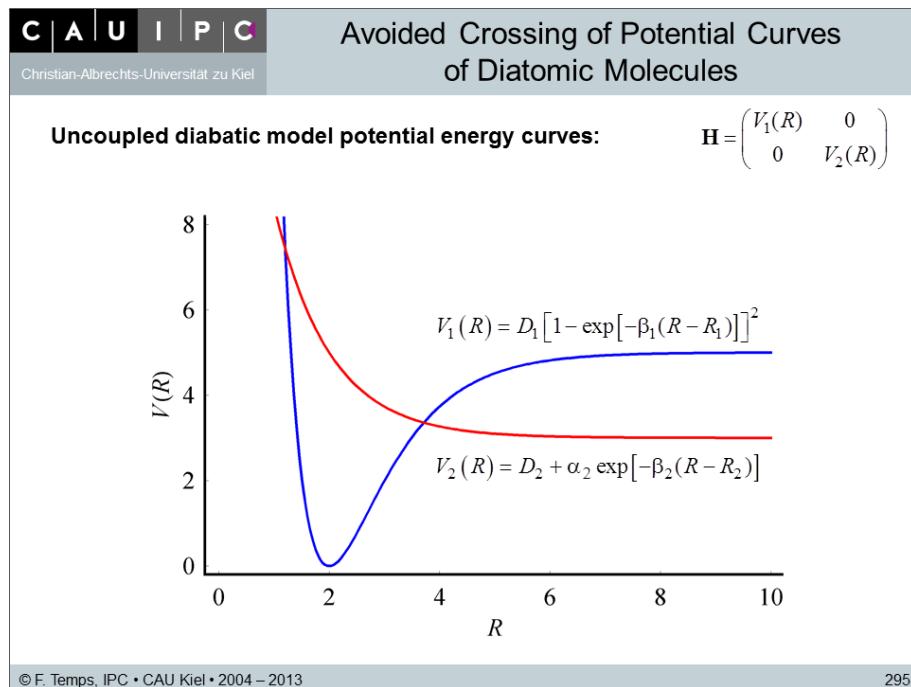
$$V_2(R) = D_2 + \alpha \exp[-\beta_2(r - r_2)] \quad (12.38)$$

$$W_{12}(R) = \lambda_1 [1 + \tanh[-\lambda_2(r - r_{12})]] \quad (12.39)$$

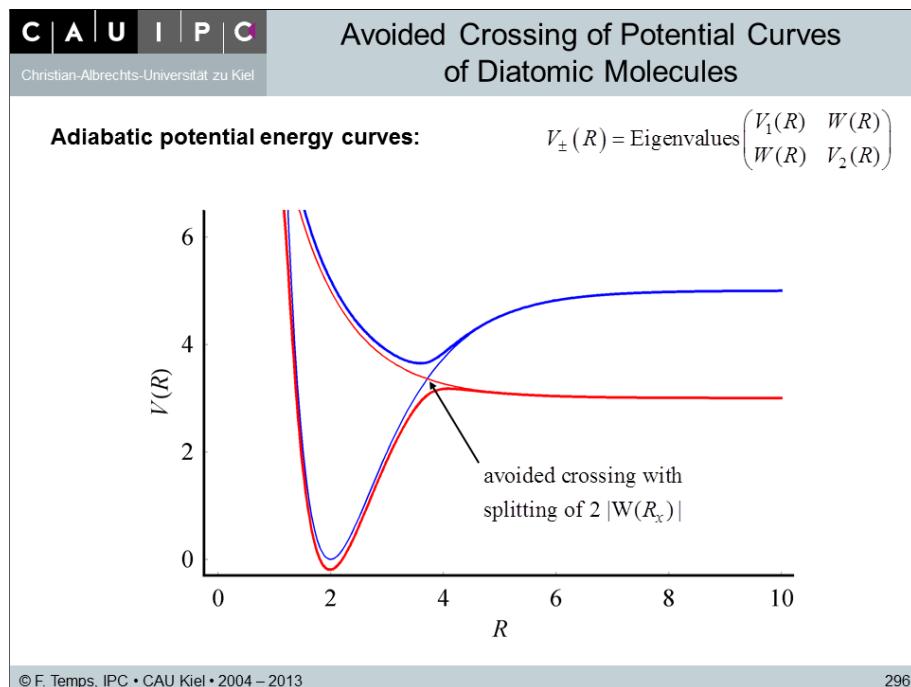
$W_{12}(R)$ is just a convenient model function with the physically correct behavior $W_{12}(R) \rightarrow 0$ for $R \rightarrow \infty$.

⁵³ The recognition since about the years 2000 - 2005 that conical intersections in polyatomic molecules are the rule rather than the exception has indeed revolutionized our understanding of photochemical reactions.

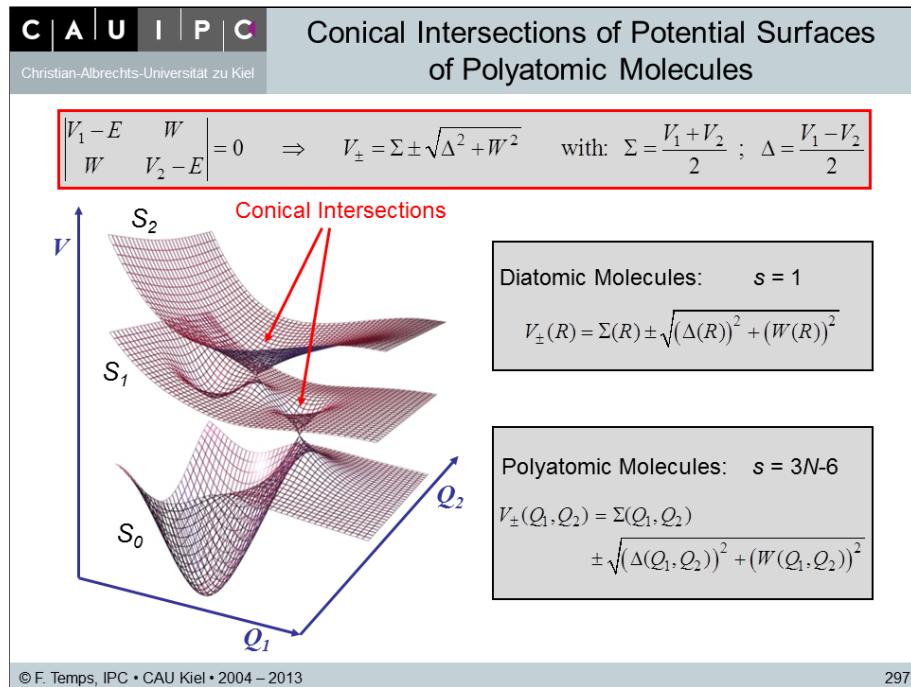
- **Figure 12.6:** Diabatic model potential curves for a diatomic molecule.



- **Figure 12.7:** Avoided crossing of two potential curves of a diatomic molecule.



- **Figure 12.8:** Conical intersection of potential energy surfaces of a polyatomic molecule.



12.5.3 Quantum mechanical treatment of a coupled 2×2 system

We can easily verify the “avoided crossing” of two coupled potential energy curves as follows:

- **Schrödinger equation:**

$$(H - \varepsilon) |\psi\rangle = 0 \quad (12.40)$$

- **Hamilton-Operator:**

$$H = H^{(0)} + H^{(1)} \quad (12.41)$$

- **Ansatz:**

$$|\psi\rangle = c_1 |\varphi_1\rangle + c_2 |\varphi_2\rangle \quad (12.42)$$

with orthonormal basis vectors that are eigenvectors of $H^{(0)}$, i.e.,

$$\langle \varphi_j | \varphi_i \rangle = \delta_{ji} = \begin{cases} 1 & \text{for } j = i \\ 0 & \text{for } j \neq i \end{cases} \quad (12.43)$$

and the zero-order energies

$$H^{(0)} |\varphi_1\rangle = E_1^{(0)} |\varphi_1\rangle \quad (12.44)$$

$$H^{(0)} |\varphi_2\rangle = E_2^{(0)} |\varphi_2\rangle \quad (12.45)$$

- **Solution of the Schrödinger equation:** Insertion of the ansatz (Eq. 12.42) into the SE and multiplication from the left by either $\langle \varphi_1 |$ or by $\langle \varphi_2 |$ gives the two equations:

$$c_1 \langle \varphi_1 | (H - \varepsilon) | \varphi_1 \rangle + c_2 \langle \varphi_1 | (H - \varepsilon) | \varphi_2 \rangle = 0 \quad (12.46)$$

$$c_1 \langle \varphi_2 | (H - \varepsilon) | \varphi_1 \rangle + c_2 \langle \varphi_2 | (H - \varepsilon) | \varphi_2 \rangle = 0 \quad (12.47)$$

This is a system of coupled linear equations ("secular equations"):

$$c_1 (H_{11} - \varepsilon) + c_2 H_{12} = 0 \quad (12.48)$$

$$c_1 H_{21} + c_2 (H_{22} - \varepsilon) = 0 \quad (12.49)$$

with the "matrix elements" (integrals over all \mathbf{r} resp. \mathbf{R}):

$$H_{mn} = \langle \varphi_m | H | \varphi_n \rangle \quad (12.50)$$

$$= \langle \varphi_m | H^{(0)} + H^{(1)} | \varphi_n \rangle \quad (12.51)$$

$$= \langle \varphi_m | H^{(0)} | \varphi_n \rangle + \langle \varphi_m | H^{(1)} | \varphi_n \rangle \quad (12.52)$$

Specifically, we have

$$H_{11} = \langle \varphi_1 | H^{(0)} | \varphi_1 \rangle = E_1^{(0)} \quad (12.53)$$

$$H_{22} = \langle \varphi_2 | H^{(0)} | \varphi_2 \rangle = E_2^{(0)} \quad (12.54)$$

and

$$H_{12} = \langle \varphi_1 | H^{(1)} | \varphi_2 \rangle = \langle \varphi_2 | H^{(1)} | \varphi_1 \rangle = H_{21} \quad (12.55)$$

Therefore, we obtain the secular equations as follows:

- **Secular equations:**

$$c_1 (E_1^{(0)} - \varepsilon) + c_2 H_{12} = 0 \quad (12.56)$$

$$c_1 H_{21} + c_2 (E_2^{(0)} - \varepsilon) = 0 \quad (12.57)$$

- **Secular determinant:** A non-trivial solution for the secular equations requires that

$$\begin{vmatrix} E_1^{(0)} - \varepsilon & H_{12} \\ H_{21} & E_2^{(0)} - \varepsilon \end{vmatrix} = 0 \quad (12.58)$$

- **Eigenvalues:**

$$0 = (E_1^{(0)} - \varepsilon) (E_2^{(0)} - \varepsilon) - |H_{12}|^2 \quad (12.59)$$

$$= E_1^{(0)} E_2^{(0)} - \varepsilon (E_1^{(0)} + E_2^{(0)}) + \varepsilon^2 - |H_{12}|^2 \quad (12.60)$$

with

$$|H_{12}|^2 = H_{12} H_{21} \quad (12.61)$$

because $H^{(1)}$ is Hermitian.

With some rewriting⁵⁴, we obtain

$$\varepsilon_{\pm} = \frac{1}{2} \left(E_1^{(0)} + E_2^{(0)} \right) \pm \frac{1}{2} \sqrt{\left(E_1^{(0)} + E_2^{(0)} \right)^2 - 4E_1^{(0)}E_2^{(0)} + 4|H_{12}|^2} \quad (12.62)$$

↷

$$\boxed{\varepsilon_{\pm} = \frac{1}{2} \left(E_1^{(0)} + E_2^{(0)} \right) \pm \frac{1}{2} \sqrt{\left(E_1^{(0)} - E_2^{(0)} \right)^2 + 4|H_{12}|^2}} \quad (12.63)$$

► **Shorthand form:** Using the abbreviations

$$V_{\pm}(\mathbf{R}) = \varepsilon_{\pm} \quad (12.64)$$

$$V_1(\mathbf{R}) = E_1^{(0)} \quad (12.65)$$

$$V_2(\mathbf{R}) = E_2^{(0)} \quad (12.66)$$

$$W^2(\mathbf{R}) = |H_{12}|^2 \quad (12.67)$$

$$\Sigma(\mathbf{R}) = \frac{1}{2} (V_1(\mathbf{R}) + V_2(\mathbf{R})) \quad (12.68)$$

$$\Delta(\mathbf{R}) = \frac{1}{2} (V_1(\mathbf{R}) - V_2(\mathbf{R})) \quad (12.69)$$

we can rewrite the solution for the eigenvalues V_+ and V_- in a compact form as

$$\boxed{V_{\pm}(\mathbf{R}) = \Sigma(\mathbf{R}) \pm \sqrt{(\Delta(\mathbf{R}))^2 + (W(\mathbf{R}))^2}} \quad (12.70)$$

12.5.4 Radiationless processes in polyatomic molecules: Conical intersections

► **“Traditional” view on the cis-trans isomerization of C_2H_4 :**

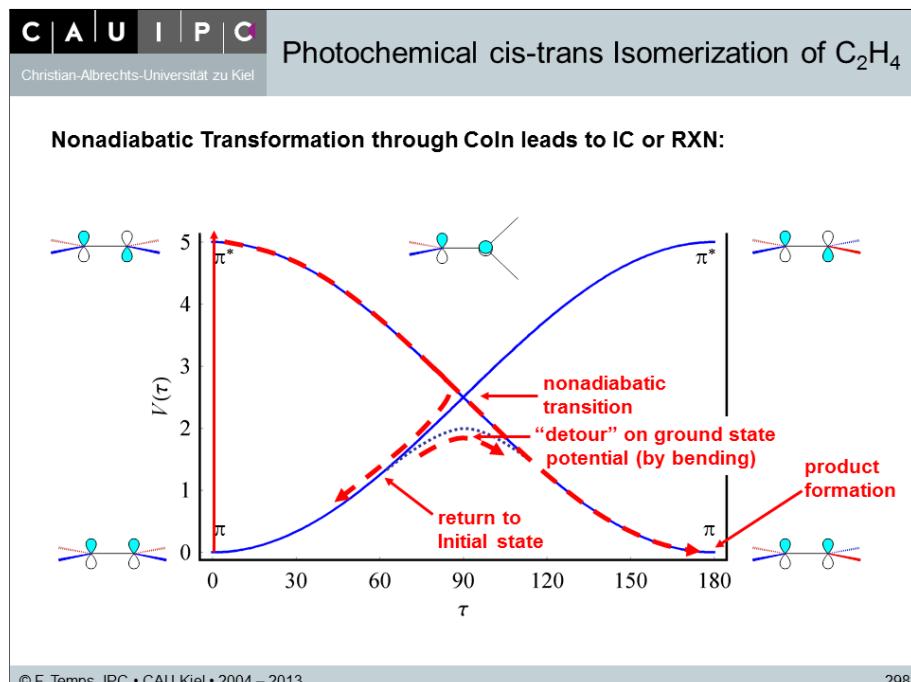
- Reaction coordinate can be approximated by torsion angle τ ($0 \leq \tau \leq 180^\circ$).
- Reaction proceeds *via* a perpendicular transition state ($\tau = 90^\circ$), in which the C atoms are connected by a single bond.
- Correlation diagram shows that the π orbital of the *trans*-isomer transforms into the π^* orbital of the *cis*-isomer and *vice versa*.
- Crossing of the two diabatic states corresponds to an *avoided crossing* of the adiabatic states.

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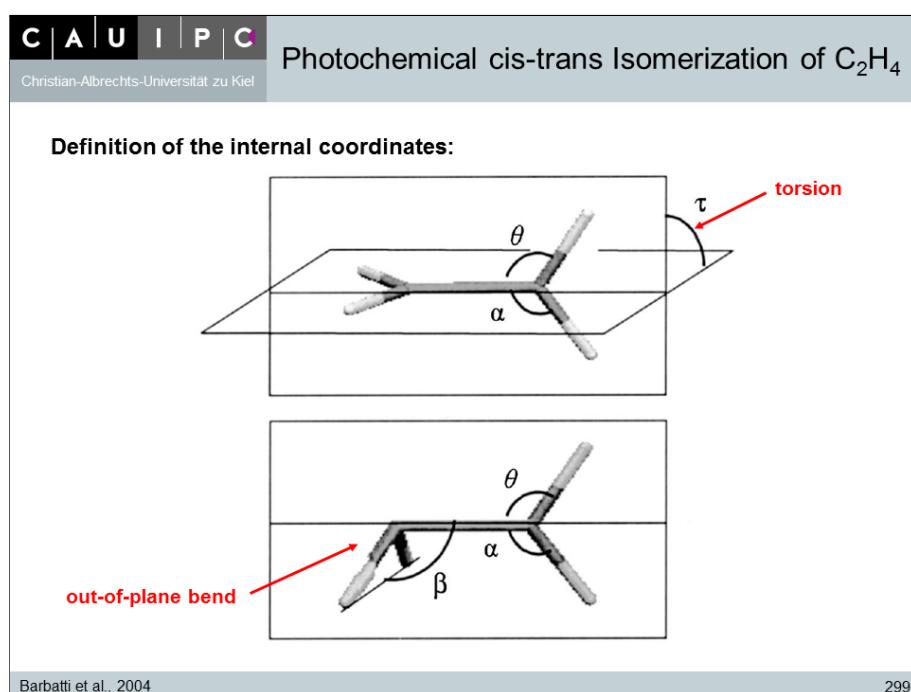
$$\begin{aligned} \left(E_1^{(0)} + E_2^{(0)} \right)^2 - 4E_1^{(0)}E_2^{(0)} &= \left(E_1^{(0)} \right)^2 + \left(E_2^{(0)} \right)^2 + 2E_1^{(0)}E_2^{(0)} - 4E_1^{(0)}E_2^{(0)} \\ &= \left(E_1^{(0)} \right)^2 + \left(E_2^{(0)} \right)^2 - 2E_1^{(0)}E_2^{(0)} = \left(E_1^{(0)} - E_2^{(0)} \right)^2 \end{aligned}$$

- The reaction is thus *thermally forbidden* because of the high energy barrier at the avoided crossing between the *trans* and *cis* isomers on the left and right.
- The reaction is *photochemically allowed* because of the barrierless adiabatic correlation between the $\pi\pi^*$ states on the left and right.

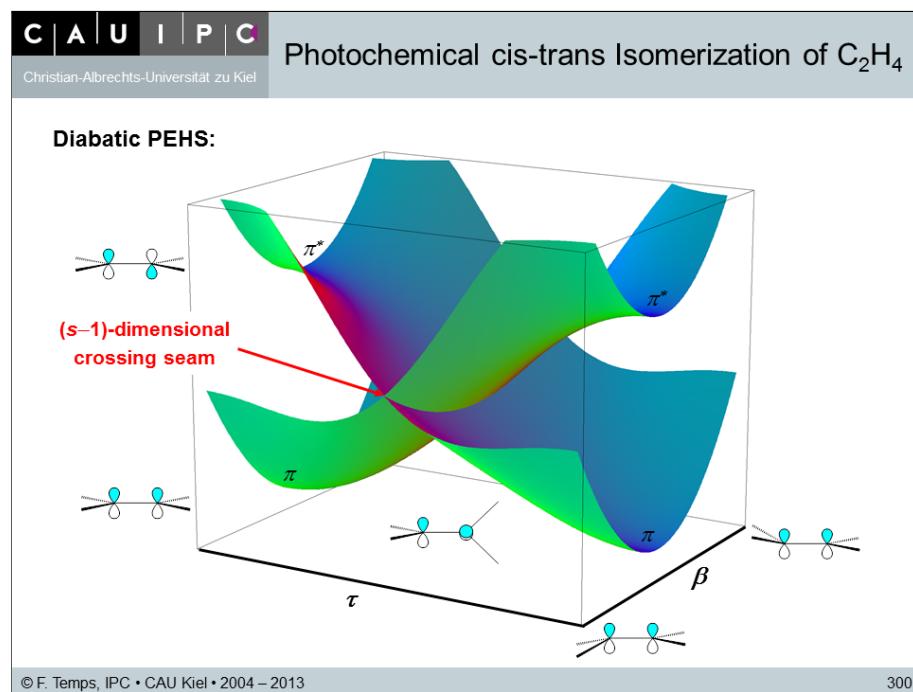
- **Figure 12.9:** *Cis-trans* isomerization of C_2H_4 : HMO picture with transformation of π and π^* orbitals and conical intersection.



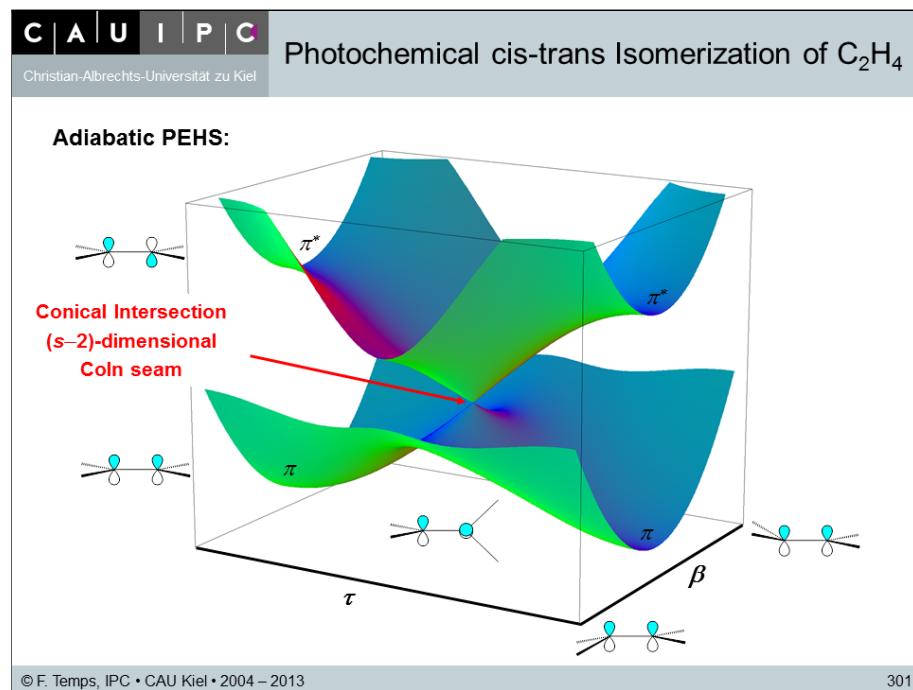
- **Figure 12.10:** Internal coordinates relevant for the *cis-trans* isomerization of C_2H_4 . The out-of-plane bending angle β plays a role as coupling mode leading to a CI; the angles θ and α play a role in the isomerization to H_3CCH (also by a CI).



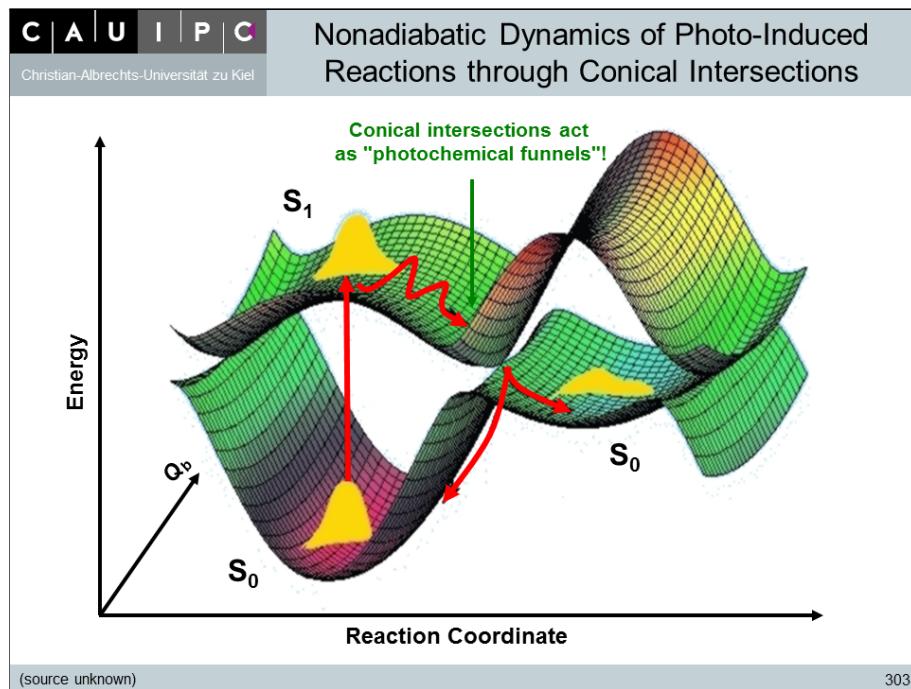
► **Figure 12.11:** Diabatic model PES's for C_2H_4 .



► **Figure 12.12:** Adiabatic model PES's for C_2H_4 with the conical intersection at $\tau = 90^\circ$.

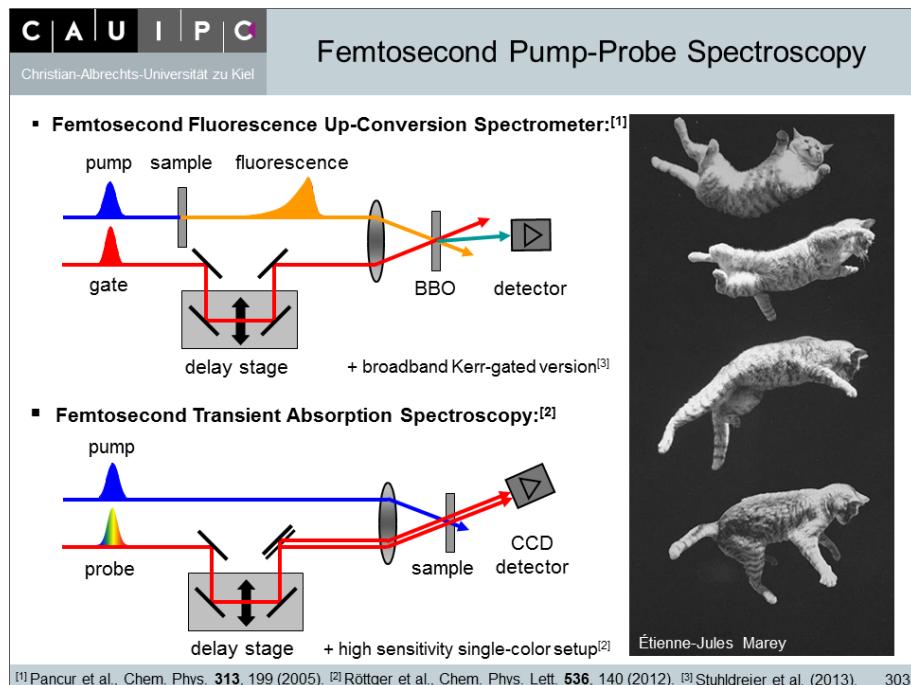


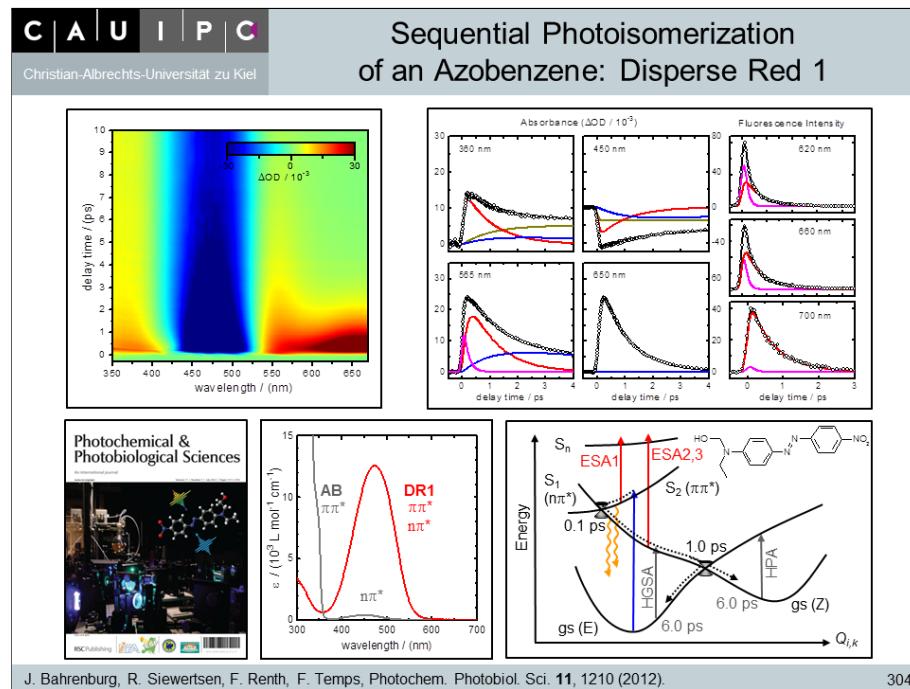
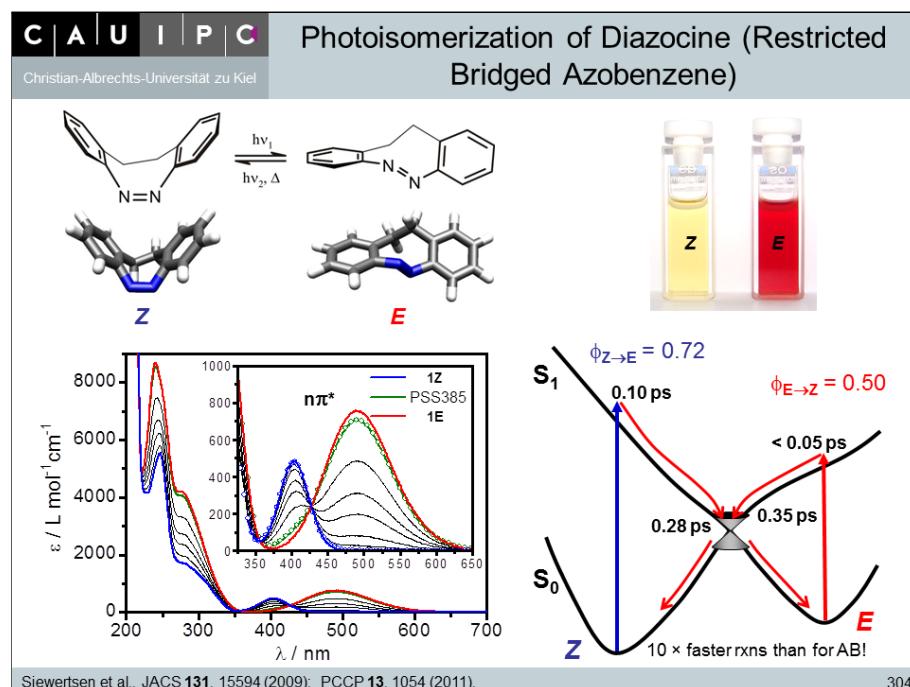
- **Figure 12.13:** Wave packet motion in a complex photo-induced reaction.



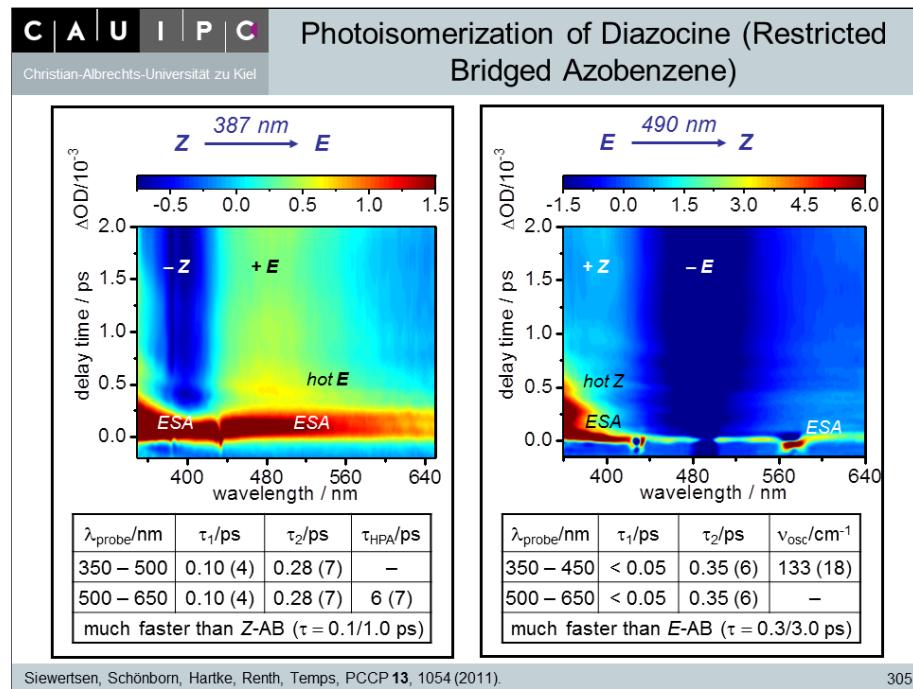
12.5.5 Femtosecond Time-Resolved Experiments

- **Figure 12.14:**

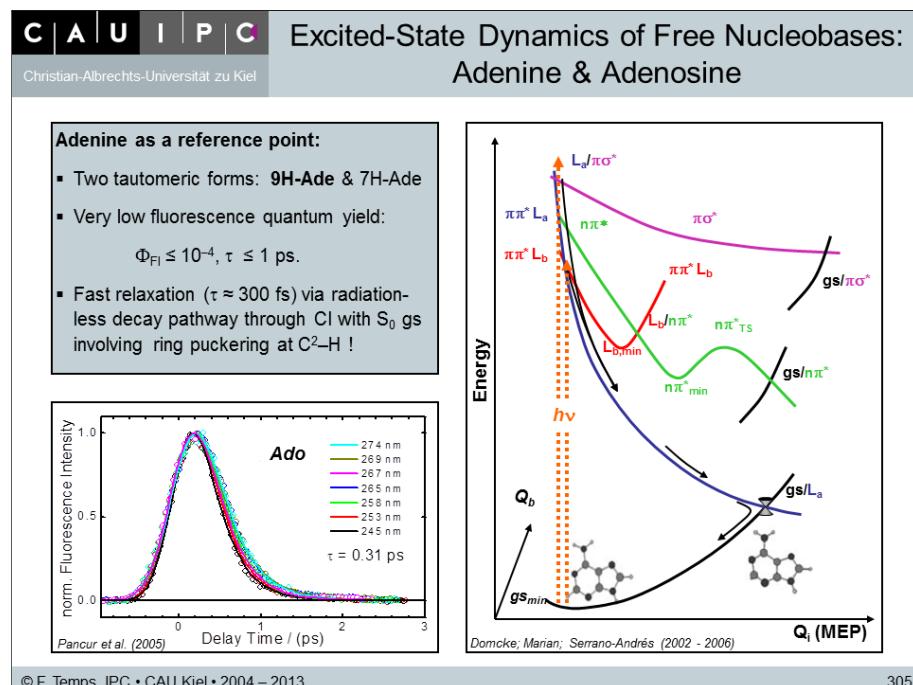


► **Figure 12.15:**► **Figure 12.16:**

► Figure 12.17:



► Figure 12.18:



13. Atmospheric chemistry*

(skipped for lack of time in the semester)

14. Combustion chemistry*

(skipped for lack of time in the semester)

15. Astrochemistry*

(skipped for lack of time in the semester)

16. Energy transfer processes*

(See lecture in M.Sc. course.)

17. Reaction dynamics*

(See lecture in M.Sc. course.)

18. Electrochemical kinetics*

(skipped for lack of time in the semester)

Appendix A: Useful physicochemical constants

► **Table A.1:** List of useful physical constants (Cohen 1986).

physical constant	symbol	value
Loschmidt (or Avogadro) number	N_L	$N_L = 6.0221367 \times 10^{23} \text{ mol}^{-1}$
gas constant	R	$R = 8.314511 \text{ J mol}^{-1} \text{ K}^{-1}$
Boltzmann constant	k_B	$k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1}$
electron charge	e	$e_{el} = 1.60217733 \times 10^{-19} \text{ C}$
Faraday constant	F	$F = 96485.309 \text{ C mol}^{-1}$
speed of light	c	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$
Planck's constant	h	$h = 6.6260755 \times 10^{-34} \text{ J s}$
	\hbar	$\hbar = 1.0547266 \times 10^{-34} \text{ J s}$
electron mass	m_e	$m_{el} = 9.1093897 \times 10^{-31} \text{ kg}$
proton mass	m_p	$m_p = 1.6726231 \times 10^{-27} \text{ kg}$
neutron mass	m_n	$m_n = 1.6749286 \times 10^{-27} \text{ kg}$
atomic mass unit	m_{au}	$m_{au} = 1.6605402 \times 10^{-27} \text{ kg}$
Rydberg constant	\tilde{R}	$\tilde{R} = 1.0973731534 \times 10^7 \text{ m}^{-1}$
Bohr radius	a_0	$a_0 = 5.29177249 \times 10^{-11} \text{ m}$
electric field constant	ϵ_0	$\epsilon_0 = 1/(\mu_0 c^2)$ $\epsilon_0 = 8.854187817 \times 10^{-12} \text{ F m}^{-1}$
magnetic field constant	μ_0	$\mu_0 = 4\pi \times 10^{-7} \text{ N A}^{-2}$ $\mu_0 = 1.25664 \times 10^{-6} \text{ N A}^{-2}$

► **References:**

Cohen 1986 E. R. Cohen and B. N. Taylor, The 1986 Adjustment of the Fundamental Constants, *CODATA Bull.* **63**, 1 (1986). An updated list is contained in every August issue of *Physics Today*.

Appendix B: The Marquardt-Levenberg non-linear least-squares fitting algorithm

With the omnipresence of the computer, the Marquardt-Levenberg algorithm (Bevington 1992, Press 1992) has become an extremely important data analysis tool. It is generally the method of choice in cases where it is not possible to make simple linear plots to determine rate constants.

- **Problem:** Experimentally, we measure the values of some quantity f_i at the points x_i, y_i, \dots . Suppose we take n measurements. Now suppose we would like to describe our n data points f_i by some model. Towards these ends, we take a physically reasonable model function

$$f = f(x, y, \dots; (a_1, \dots, a_m)) \quad (\text{B.1})$$

which we would like to fit to our data in such a way that $f(\dots)$ describes the data points f_i in “the best possible way”. The model function f depends directly on the variables x, y, \dots , and it also depends parametrically on m nonlinear parameters a_j . In kinetics, for example, f is usually some concentration, e.g. c_A , which depends on time t , i.e., $c_A = c_A(t)$. The parameters a_j may be the rate constants k (or decay times τ) and the initial concentration c_0 . Our job is to adjust and optimize these m parameters by somehow “fitting” them. The method of choice is, of course, “least-squares fitting”:

We start by defining the so-called **figure-of-merit** or **goodness-of-fit function**⁵⁵

$$\chi^2 = \sum_{i=1}^n \left[\frac{[f_i - f(x_i, y_i, \dots)]^2}{\sigma_i^2} \right] \quad (\text{B.2})$$

Here, the f_i and the independent variables x_i, y_i, \dots are the measured quantities, the σ_i are the experimental uncertainties of the f_i , and $f(x_i, y_i, \dots)$ is the calculated value of the model fit function f at the point $\{x_i, y_i, \dots\}$ (the parameters a_1, \dots, a_m are omitted here in f). What we have to do is to adjust the m parameters a_j in the model function such that χ^2 reaches a minimum, i.e. we have to search the m -dimensional parameter space for the (global) minimum of χ^2 .

- **Solution:** The Marquardt-Levenberg algorithm is a method to determine this minimum of χ^2 as function of the fit parameters a_j in the model fit function f .

The minimum of χ^2 as function of the fit parameters a_j is defined by the conditions

$$\frac{\partial \chi^2}{\partial a_j} = \frac{\partial}{\partial a_j} \sum_{i=1}^n \left[\frac{[f_i - f(x_i, y_i, \dots)]^2}{\sigma_i^2} \right] = 0 \quad (\text{B.3})$$

$$= -2 \sum_{i=1}^n \left[\frac{[f_i - f(x_i, y_i, \dots)]}{\sigma_i^2} \frac{\partial f(x_i, y_i, \dots)}{\partial a_j} \right] \quad (\text{B.4})$$

Thus, taking the partial derivatives of χ^2 with respect to each of the m parameters a_j , we obtain a set of m coupled equations in the m unknown parameters a_j . These equations are, in general, nonlinear in the a_j .

⁵⁵ Deutsch: Fehlerquadratsumme.

The Marquardt-Levenberg algorithm gives a recipe for finding the minimum of χ^2 using a combination of the method of steepest descent (following the gradient of the hypersurface defined by χ^2 as a function of the parameters a_1, \dots, a_m and, near the minimum of χ^2 , a parabolic Taylor series expansion of the fitting function f around the minimum).

At the end of a fit, we shall usually report the a_j ($\pm 2\sigma$ standard deviations), the standard deviation of the c_i 's, and the so-called reduced- χ^2 , which is χ^2 divided by the number of degrees of freedom, $\nu = n - m$, i.e.,

$$\chi_{red}^2 = \frac{1}{n - m} \sum_{i=1}^n \left[\frac{[f_i - f(x_i, y_i, \dots)]^2}{\sigma_i^2} \right] \quad (\text{B.5})$$

- **Example 1: Exponential decay.** Suppose we measure the time dependent concentration $c(t)$ of a molecule in some quantum state, which is populated at some time t_0 by a laser pulse and then decays monoexponentially. As a model fit function, we use the expression

$$c(t) = a_1 \exp[-a_2(t - a_3)] + a_4 + a_5 t \quad (\text{B.6})$$

The parameters we are interested in are a_2 (the decay rate coefficient) and a_1 (the initial amplitude or initial concentration). The parameter a_3 just describes the trigger delay time ($= t_0$). We have also added the parameters a_4 and a_5 to describe a constant background term (due to some offset of our experimental signal) and a linear drift in this background term (perhaps due to some experimental instability, such as a gradual temperature increase in the lab). Our figure of merit is then

$$\chi^2 = \sum_{i=1}^n \left[\frac{[c_i - c(t)]^2}{\sigma_i^2} \right] \quad (\text{B.7})$$

The m (in general nonlinear) conditions for the minimum of χ^2 , from which we determine the parameters a_j , are

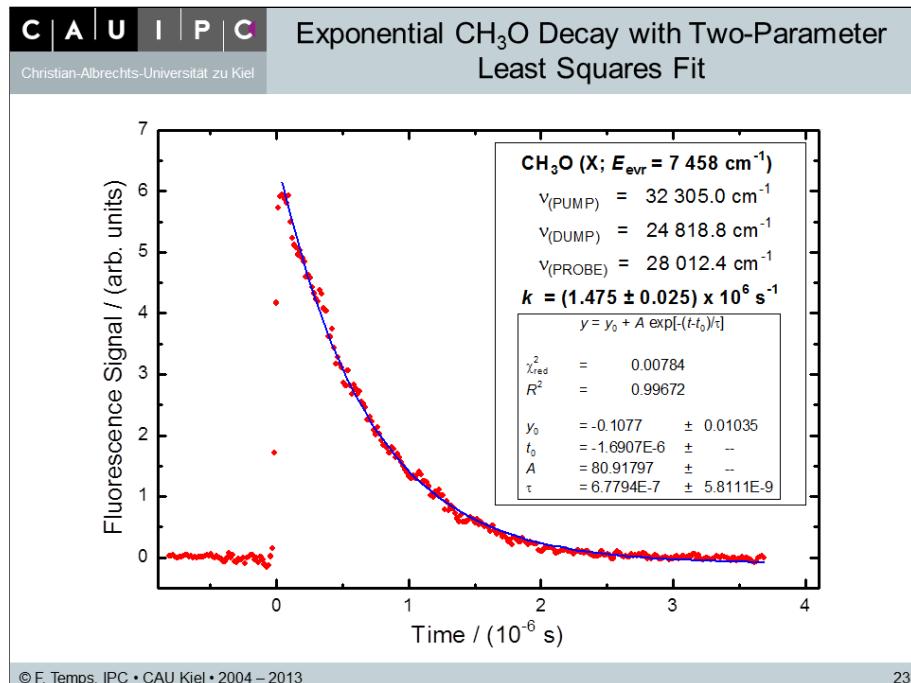
$$\frac{\partial \chi^2}{\partial a_1} = \frac{\partial}{\partial a_1} \sum_{i=1}^n \left[\frac{[c_i - c(t)]^2}{\sigma_i^2} \right] = -2 \sum_{i=1}^n \left[\frac{[c_i - c(t)]}{\sigma_i^2} \frac{\partial c(t)}{\partial a_1} \right] = 0 \quad (\text{B.8})$$

$$\frac{\partial \chi^2}{\partial a_2} = \dots \quad (\text{B.9})$$

$$\dots \quad (\text{B.10})$$

Figure B.1 below shows a simple two-parameter fit (parameters $A1$ and $t1$) to such a signal.

- **Figure B.1:** Exponential decay curve of a particular vibration-rotation state of the CH_3O radical resulting from the unimolecular dissociation reaction of the radical according to $\text{CH}_3\text{O} \rightarrow \text{H} + \text{H}_2\text{CO}$ (Dertinger 1995). The small box is the output box from a fit using the ORIGIN program.



- **Example 2: Multiexponential decay.** In femtosecond spectroscopy, we often observe ultrafast multiexponential decays of laser-excited molecules. The laser prepares an excited wavepacket, which usually does not decay single-exponentially. Further, we need to take into account the final duration of the pump laser pulse (by deconvolution, or by forward convolution).

- Model function to be fitted to measured data:

$$I(t) = \sum_j a_j \exp(-t/\tau_j) \quad (\text{B.11})$$

with adjustable parameters a_j and τ_j .

- Instrument response function (IRF): Often represented by a Gaussian centered at time t_0

$$G(t) = \frac{1}{\sigma_{\text{IRF}} \sqrt{2\pi}} \exp\left(-\frac{(t-t_0)^2}{2\sigma_{\text{IRF}}^2}\right) \quad (\text{B.12})$$

with width parameter σ_{IRF} related to the full width at half maximum (FWHM) of the IRF by

$$\text{FWHM} = \sqrt{8 \ln 2} \approx 2.355 \sigma_{\text{IRF}} \quad (\text{B.13})$$

- Convolution of the molecular intensity $I(t)$ and $G(t)$ gives the signal function

$$S(t) = \int_{-\infty}^{+\infty} I(t') G(t - t') dt' = \int_{-\infty}^{+\infty} I(t - t') G(t') dt' = I(t) \otimes G(t) \quad (\text{B.14})$$

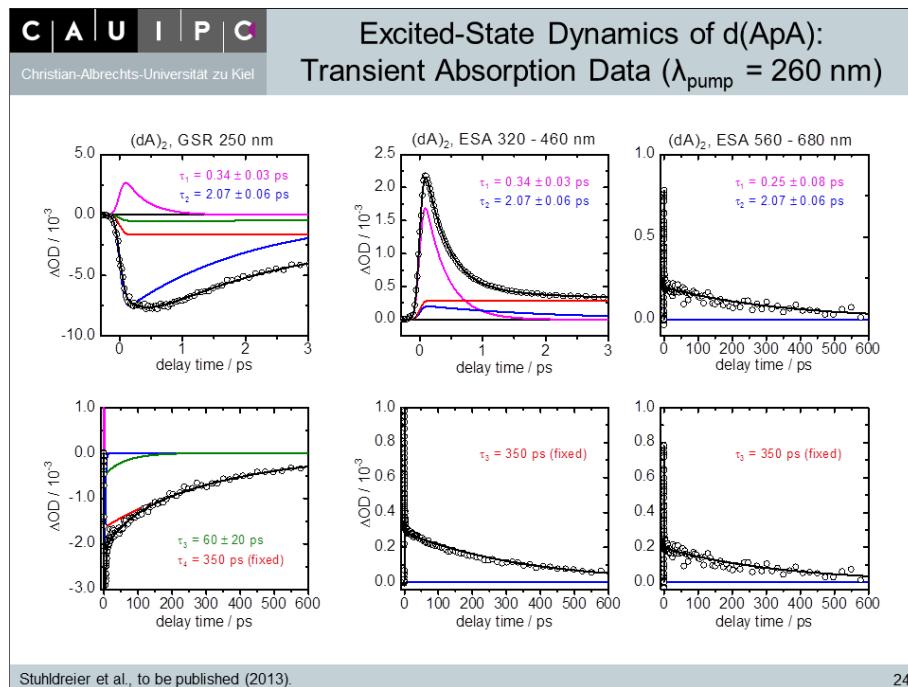
where \otimes denotes the convolution.

- Resulting model function to be fitted to the data:

$$S(t) = \frac{1}{2} \sum_j a_j \exp \left[\frac{1}{2} \frac{\sigma_{\text{IRF}}^2}{\tau_j^2} - \frac{(t - t_0)}{\tau_j} \right] \left[1 + \text{erf} \left(\frac{(t - t_0) \tau_j - \sigma_{\text{IRF}}^2}{\sqrt{2} \sigma_{\text{IRF}} \tau_j} \right) \right] + b \quad (\text{B.15})$$

where $\text{erf}()$ is the error function and b is a simple constant background term (can be replaced by background + drift $b + mt$).

- **Figure B.2:** Excited-state relaxation dynamics of the adenine dinucleotide after UV photoexcitation.



- **References:**

- Bevington 1992** P. R. Bevington, D. K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, Boston, 1992.
- Dertinger 1995** S. Dertinger, A. Geers, J. Kappert, F. Temps, J. W. Wiebrecht, Rotation-Vibration State Resolved Unimolecular Dynamics of Highly vibrationally Excited CH₃O (²E): III. State Specific Dissociation Rates from Spectroscopic Line Profiles and Time Resolved Measurements, *Faraday Discuss. Roy. Soc.* **102**, 31 (1995).
- Press 1992** W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in Fortran*, Cambridge University Press, Cambridge, 1992. Versions are also available for C and Pascal.

Appendix C: Solution of inhomogeneous differential equations

C.1 General method

An inhomogeneous DE is a DE of the type

$$y' + f(x) \times y = g(x) \quad (\text{C.1})$$

In order to solve Eq. C.1, we first find a solution y_H of the homogeneous DE

$$y' + f(x) \times y = 0 \quad (\text{C.2})$$

and then determine a particular solution y_P of the inhomogeneous DE:

- Solution of the homogeneous DE by separation of variables:

$$y_H' + f(x) \times y_H = 0 \quad (\text{C.3})$$

$$y_H' = -f(x) \times y_H \quad (\text{C.4})$$

$$\frac{d \ln y_H}{dt} = -f(x) dx \quad (\text{C.5})$$

↷

$$y_H = C \times e^{-\int f(x) dx} \quad (\text{C.6})$$

- Determination of a particular solution of the inhomogeneous DE by variation of constant:

$$C \rightarrow C(x) \quad (\text{C.7})$$

$$C'(x) = \dots \quad (\text{C.8})$$

Insertion of $C(x)$ and $C'(x)$ into Eq. C.1 and integration gives

$$y_P = \dots \quad (\text{C.9})$$

The general solution of Eq. C.1 is then given by

$$y = y_H + y_P \quad (\text{C.10})$$

C.2 Application to two consecutive first-order reactions

Consider the reaction system



which is described by the following rate equations

$$\frac{d[A]}{dt} = -k_1 [A] \quad (C.13)$$

$$\frac{d[B]}{dt} = +k_1 [A] - k_2 [B] \quad (C.14)$$

$$\frac{d[C]}{dt} = +k_2 [B] \quad (C.15)$$

The solution for Eq. C.13 is

$$[A] = [A]_0 e^{-k_1 t} \quad (C.16)$$

Thus we have to find the solution of the inhomogeneous DE for [B] (Eq. C.14)

$$\frac{d[B]}{dt} + k_2 [B] = k_1 [A]_0 e^{-k_1 t} \quad (C.17)$$

- Solution of the homogeneous DE by separation of variables:

$$\frac{d[B]}{dt} = -k_2 [B] \quad (C.18)$$

↷

$$[B]_H = C \times e^{-k_2 t} \quad (C.19)$$

- Determination of a particular solution by variation of constant:

$$C = C(t) \quad (C.20)$$

↷

$$[B]_P = C(t) \times e^{-k_2 t} \quad (C.21)$$

$$\frac{d[B]_P}{dt} = \frac{dC(t)}{dt} \times e^{-k_2 t} - C(t) \times k_2 e^{-k_2 t} \quad (C.22)$$

Insertion of $[B]_P$ and $\frac{d[B]_P}{dt}$ into Eq. C.17 gives

$$\frac{dC(t)}{dt} \times e^{-k_2 t} - C(t) \times k_2 e^{-k_2 t} + C(t) \times k_2 e^{-k_2 t} = k_1 [A]_0 e^{-k_1 t} \quad (C.23)$$

which simplifies to

$$\frac{dC(t)}{dt} = k_1 [A]_0 e^{(k_2 - k_1)t} \quad (C.24)$$

This DE is easily integrated to obtain $C(t)$:

– If $k_1 \neq k_2$ we obtain

$$C(t) = \frac{k_1 [A]_0}{k_2 - k_1} e^{(k_2 - k_1)t} \quad (C.25)$$

and thus

$$[B]_P = C(t) e^{-k_2 t} \quad (C.26)$$

$$= \frac{k_1 [A]_0}{k_2 - k_1} e^{(k_2 - k_1)t} e^{-k_2 t} \quad (C.27)$$

$$= \frac{k_1 [A]_0}{k_2 - k_1} e^{-k_1 t} \quad (C.28)$$

– If $k_1 = k_2$ we obtain

$$\frac{dC(t)}{dt} = k_1 [A]_0 e^{(k_2 - k_1)t} \quad (C.29)$$

$$= k_1 [A]_0 \quad (C.30)$$

↷

$$C(t) = k_1 [A]_0 t \quad (C.31)$$

↷

$$[B]_P = C(t) e^{-k_2 t} \quad (C.32)$$

$$= k_1 [A]_0 t e^{-k_2 t} \quad (C.33)$$

• General solution:

$$[B] = [B]_H + [B]_P \quad (C.34)$$

↷

$$[B] = \begin{cases} C \times e^{-k_2 t} + \frac{k_1 [A]_0}{k_2 - k_1} e^{-k_1 t} & \text{if } k_1 \neq k_2 \\ C \times e^{-k_2 t} + k_1 [A]_0 t e^{-k_2 t} & \text{if } k_1 = k_2 \end{cases} \quad (C.35)$$

Initial value condition at $t = 0$:

$$[B(t = 0)] = 0 \quad (C.36)$$

↷

$$C = \begin{cases} -\frac{k_1 [A]_0}{k_2 - k_1} & \text{if } k_1 \neq k_2 \\ 0 & \text{if } k_1 = k_2 \end{cases} \quad (C.37)$$

Final solutions for $[B(t)]$:

$$[B(t)] = \begin{cases} \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) & \text{if } k_1 \neq k_2 \\ k_1 [A]_0 t e^{-k_2 t} & \text{if } k_1 = k_2 \end{cases} \quad (C.38)$$

C.3 Application to parallel and consecutive first-order reactions

Consider the reaction system



which is described by the following rate equations

$$\frac{d[A]}{dt} = -(k_{1a} + k_{1b})[A] = -k_1[A] \quad (C.41)$$

$$\frac{d[B]}{dt} = +k_{1b}[A] - k_2[B] \quad (C.42)$$

$$\frac{d[P]}{dt} = +k_{1a}[A] + k_2[B] \quad (C.43)$$

with $k_1 = (k_{1a} + k_{1b})$.⁵⁶

The solution for Eq. C.41 is

$$[A] = [A]_0 e^{-(k_{1a} + k_{1b})t} = [A]_0 e^{-k_1 t} \quad (C.44)$$

Thus we have to find the solution of the inhomogeneous DE for [B] (Eq. C.42)

$$\frac{d[B]}{dt} + k_2[B] = +k_{1b}[A]_0 e^{-k_1 t} \quad (C.45)$$

using the above standard procedure:

- Solution of the homogeneous DE by separation of variables:

$$\frac{d[B]}{dt} = -k_2[B] \quad (C.46)$$

↷

$$[B]_H = C \times e^{-k_2 t} \quad (C.47)$$

- Determination of a particular solution by variation of constant:

$$C = C(t) \quad (C.48)$$

↷

$$[B]_P = C(t) \times e^{-k_2 t} \quad (C.49)$$

$$\frac{d[B]_P}{dt} = \frac{dC(t)}{dt} \times e^{-k_2 t} - C(t) \times k_2 e^{-k_2 t} \quad (C.50)$$

⁵⁶ An example is the radiationless deactivation of a $\pi\pi^*$ electronically excited molecule A directly to the ground state P or via an intermediate optically dark $n\pi^*$ state B, which decays to the ground state more slowly.

Insertion of $[B]_P$ and $\frac{d[B]_P}{dt}$ into Eq. C.45 gives

$$\frac{dC(t)}{dt} \times e^{-k_2 t} - C(t) k_2 e^{-k_2 t} + k_2 C(t) e^{-k_2 t} = k_{1b} [A]_0 e^{-k_1 t} \quad (\text{C.51})$$

The terms with $\pm C(t) k_2 e^{-k_2 t}$ cancel, so that

$$\frac{dC(t)}{dt} \times e^{-k_2 t} = k_{1b} [A]_0 e^{-k_1 t} \quad (\text{C.52})$$

which we rewrite in order to solve $C(t)$ as

$$\frac{dC(t)}{dt} = k_{1b} [A]_0 e^{-k_1 t} \times e^{+k_2 t} \quad (\text{C.53})$$

or

$$\frac{dC(t)}{dt} = k_{1b} [A]_0 e^{(k_2 - k_1)t} \quad (\text{C.54})$$

This DE is easily integrated to obtain $C(t)$:

- If $k_2 \neq k_1 = (k_{1a} + k_{1b})$ we obtain

$$C(t) = \frac{k_{1b} [A]_0}{k_2 - k_1} e^{(k_2 - k_1)t} \quad (\text{C.55})$$

and thus

$$[B]_P = C(t) e^{-k_2 t} \quad (\text{C.56})$$

$$= \frac{k_{1b} [A]_0}{k_2 - k_1} e^{(k_2 - k_1)t} e^{-k_2 t} \quad (\text{C.57})$$

$$= \frac{k_{1b} [A]_0}{k_2 - k_1} e^{-k_1 t} \quad (\text{C.58})$$

- The case $k_2 = k_1$ does not interest us here, as the $n\pi^*$ state B should be a longer-lived one.

- General solution for $k_2 \neq k_1$:

$$[B] = [B]_H + [B]_P \quad (\text{C.59})$$

↷

$$[B] = C \times e^{-k_2 t} + \frac{k_{1b} [A]_0}{k_2 - k_1} e^{-k_1 t} \quad (\text{C.60})$$

Initial value condition at $t = 0$:

$$[B(t = 0)] = 0 \quad (\text{C.61})$$

↷

$$C = -\frac{k_{1b} [A]_0}{k_2 - k_1} \quad (\text{C.62})$$

Final solutions for $[B(t)]$:

$$[B(t)] = -\frac{k_{1b}[A]_0}{k_2 - k_1} \times e^{-k_2 t} + \frac{k_{1b}[A]_0}{k_2 - k_1} e^{-k_1 t} \quad (C.63)$$

$$= \frac{k_{1b}[A]_0}{k_2 - k_1} e^{-k_1 t} - \frac{k_{1b}[A]_0}{k_2 - k_1} \times e^{-k_2 t} \quad (C.64)$$

i.e.

$$[B(t)] = \frac{k_{1b}[A]_0}{k_1 - k_2} \times (e^{-k_2 t} - e^{-k_1 t}) \quad (C.65)$$

- In the time-resolved fluorescence measurements, we observe

$$F(t) \propto [A(t)] + \beta [B(t)] \quad (C.66)$$

with some unknown factor β accounting for the (lower) transition probability of state B, i.e., the fluorescence-time profile $F(t)$ is

$$F(t) = [A]_0 e^{-k_1 t} + \beta \frac{k_{1b}[A]_0}{k_1 - k_2} \times (e^{-k_2 t} - e^{-k_1 t}) \quad (C.67)$$

$$= [A]_0 e^{-k_1 t} + \beta \frac{k_{1b}[A]_0}{k_1 - k_2} \times e^{-k_2 t} - \beta \frac{k_{1b}[A]_0}{k_1 - k_2} \times e^{-k_1 t} \quad (C.68)$$

$$= \beta \frac{k_{1b}[A]_0}{k_1 - k_2} \times e^{-k_2 t} + \left([A]_0 - \beta \frac{k_{1b}[A]_0}{k_1 - k_2} \right) \times e^{-k_1 t} \quad (C.69)$$

$$= a_2 \times e^{-k_2 t} + a_1 \times e^{-k_1 t} \quad (C.70)$$

This is the same result as would be obtained by a fit to a sum of two exponentials with the rate constants $k_1 = k_{1a} + k_{1b}$ and k_2 , i.e., time constants $\tau_1 = (k_{1a} + k_{1b})^{-1}$ and $\tau_2 = k_2$.

Appendix D: Matrix methods

This appendix has been taken from the “Introduction to Molecular Spectroscopy” script, not all subsections apply to chemical kinetics.

D.1 Definition

- **Matrices:** A matrix is a rectangular, $m \times n$ dimensional array of numbers A_{ij} :

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} & A_{13} & \dots & A_{1n} \\ A_{21} & A_{22} & A_{23} & \dots & A_{2n} \\ \vdots & \vdots & \vdots & \dots & \vdots \\ A_{m1} & A_{m2} & A_{m3} & \dots & A_{mn} \end{pmatrix} \quad (\text{D.1})$$

The A_{ij} are called the matrix elements.

We will need to consider only $n \times n$ dimensional square matrices, which we can think of as a collection of column vectors \mathbf{a}_n :

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & A_{2n} \\ \vdots & \vdots & \dots & \vdots \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{pmatrix} \quad (\text{D.2})$$

- **Notation:** Matrices will be denoted by bold symbols:

$$\mathbf{A} \quad (\text{D.3})$$

- **Matrix manipulation by computer programs:** Matrix manipulations are carried out efficiently using computer programs (see, e.g., Press1992) or with symbolic algebra programs.⁵⁷

⁵⁷ The most common symbolic math programs are *MathCad*, *MuPad*, *Maple*, and *Mathematica*. *MathCad* and *Mathematica* are available in the PC lab.

D.2 Special matrices and matrix operations

► Identity matrix: $\mathbf{I} = \mathbf{1}$

$$\mathbf{I} = \mathbf{1} = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \vdots & \vdots & \dots & \vdots \\ 0 & 0 & \dots & 1 \end{pmatrix} \quad (\text{D.4})$$

We frequently use the **Kronecker** δ :

$$I_{ij} = \delta_{ij} \quad (\text{D.5})$$

where

$$\delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases} \quad (\text{D.6})$$

► Diagonal matrices:

$$\begin{pmatrix} A_{11} & \dots & \dots & 0 \\ 0 & A_{22} & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & A_{nn} \end{pmatrix} \quad (\text{D.7})$$

► Block diagonal matrices:

$$\begin{pmatrix} A_{11} & A_{12} & \dots & 0 \\ A_{21} & A_{22} & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & A_{nn} \end{pmatrix} \quad (\text{D.8})$$

► Complex conjugate (c.c.) of a matrix: \mathbf{A}^*

To obtain the *complex conjugate* \mathbf{A}^* of the matrix \mathbf{A} , change i to $-i$:

$$(A^*)_{ij} = (A_{ij})^* \quad (\text{D.9})$$

► Transpose of a matrix: \mathbf{A}^T

To obtain the *transpose* \mathbf{A}^T of the matrix \mathbf{A} , interchange rows and columns:

$$(A^T)_{ij} = (A_{ji}) \quad (\text{D.10})$$

► **Hermitian conjugate (“transpose conjugate”) of a matrix: $\underline{\underline{A}}^\dagger$**

To obtain the *Hermitian conjugate* (or “transpose conjugate” or “adjoint”) $\underline{\underline{A}}^\dagger$ of the matrix $\underline{\underline{A}}$, take the complex conjugate and transpose:

$$\underline{\underline{A}}^\dagger = (\underline{\underline{A}}^*)^T = (\underline{\underline{A}}^T)^* \quad (\text{D.11})$$

where

$$(\underline{\underline{A}}^\dagger)_{ij} = (A_{ji})^* \quad (\text{D.12})$$

► **Hermitian matrices:** A matrix $\underline{\underline{A}}$ is *Hermitian*, if

$$\underline{\underline{A}}^\dagger = (\underline{\underline{A}}^*)^T = \underline{\underline{A}} \quad (\text{D.13})$$

i.e.,

$$(\underline{\underline{A}}^\dagger)_{ij} = (A_{ji})^* = A_{ij} \quad (\text{D.14})$$

► **Inverse of a matrix:** $\underline{\underline{A}}^{-1}$

A matrix $\underline{\underline{A}}^{-1}$ is the *inverse* of the original matrix $\underline{\underline{A}}$, if

$$\underline{\underline{A}} \underline{\underline{A}}^{-1} = \underline{\underline{A}}^{-1} \underline{\underline{A}} = \mathbf{I} \quad (\text{D.15})$$

► **Orthogonal matrices:** A matrix $\underline{\underline{A}}$ is *orthogonal*, if the inverse of $\underline{\underline{A}}$ equals its transpose:

$$\underline{\underline{A}}^{-1} = \underline{\underline{A}}^T \quad (\text{D.16})$$

► **Unitary matrices:** A matrix \mathbf{U} is *unitary*, if the inverse of \mathbf{U} equals its transpose conjugate:

$$\mathbf{U}^{-1} = \mathbf{U}^\dagger = (\mathbf{U}^*)^T \quad (\text{D.17})$$

↷

$$\mathbf{U}^\dagger \mathbf{U} = \mathbf{I} \quad (\text{D.18})$$

► **Trace of a matrix:**

$$\text{tr}(\underline{\underline{A}}) = \sum_{i=1}^n A_{ii} \quad (\text{D.19})$$

► **Matrix addition:**

$$\mathbf{C} = \mathbf{A} + \mathbf{B} \quad (\text{D.20})$$

with

$$C_{ij} = A_{ij} + B_{ij} \quad (\text{D.21})$$

► **Multiplication by a scalar:**

$$\mathbf{C} = \lambda \mathbf{A} \quad (D.22)$$

with

$$C_{ij} = \lambda A_{ij} \quad (D.23)$$

► **Matrix multiplication:**

$$\mathbf{C} = \mathbf{A} \cdot \mathbf{B} = \mathbf{A} \mathbf{B} \quad (D.24)$$

with

$$C_{ij} = \sum_{k=1}^n A_{ik} B_{ik} \quad (D.25)$$

Example:

$$\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \begin{pmatrix} 5 & 6 \\ 7 & 8 \end{pmatrix} = \begin{pmatrix} 1 \times 5 + 2 \times 7 & 1 \times 6 + 2 \times 8 \\ 3 \times 5 + 4 \times 7 & 3 \times 6 + 4 \times 8 \end{pmatrix} \begin{pmatrix} 19 & 22 \\ 43 & 50 \end{pmatrix} \quad (D.26)$$

Notes:

(1) Matrix multiplication is defined only if the number of columns of the first matrix is identical to the number of rows of the second matrix.

(2)

$$\mathbf{A} \mathbf{B} \neq \mathbf{B} \mathbf{A} \quad (D.27)$$

► **Singular matrices:** A matrix \mathbf{A} is called *singular*, if its determinant vanishes:

$$\det(\mathbf{A}) = |\mathbf{A}| = 0 \quad (D.28)$$

D.3 Determinants

- **Determinant of a matrix:** A *determinant* of a matrix is, in general, a *number* which is evaluated according to the rule

$$\det(\mathbf{A}) = |\mathbf{A}| = \sum_{j=1}^n A_{ij} M_{ij} \quad (\text{D.29})$$

The M_{ij} are called the *co-factors* which are obtained by omitting the i 'th row and j 'th column (marked below in red) and multiplying by $(-1)^{i+j}$:

$$M_{ij} = (-1)^{i+j} \begin{vmatrix} A_{11} & \dots & \color{red}{A_{1j}} & \dots & A_{1n} \\ \vdots & \dots & \vdots & \dots & \vdots \\ \color{red}{A_{i1}} & \dots & A_{ij} & \dots & A_{in} \\ \vdots & \dots & \vdots & \dots & \vdots \\ A_{n1} & \dots & \color{red}{A_{nj}} & \dots & A_{nn} \end{vmatrix} \quad (\text{D.30})$$

- **Evaluation of simple determinants:**

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} = AD - BC \quad (\text{D.31})$$

$$\begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} = A_{11}A_{22}A_{33} + A_{12}A_{23}A_{31} + A_{13}A_{21}A_{32} - (A_{13}A_{22}A_{31} + A_{11}A_{23}A_{32} + A_{12}A_{21}A_{33}) \quad (\text{D.32})$$

where we “extended” the original determinant according to the scheme

$$\begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} \begin{vmatrix} \color{red}{A_{11}} & \color{red}{A_{12}} \\ \color{red}{A_{21}} & \color{red}{A_{22}} \\ \color{red}{A_{31}} & \color{red}{A_{32}} \end{vmatrix} \quad (\text{D.33})$$

D.4 Coordinate transformations

► Multiplication of a vector by a matrix: $\mathbf{x}' = \mathbf{A} \mathbf{x}$

The multiplication of an n -dimensional column vector \mathbf{x} by an $n \times n$ matrix \mathbf{A} gives a new vector \mathbf{x}' with components corresponding to those of \mathbf{x} in a transformed coordinate system.

► Example: Multiplication of a 2-dim vector

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad (D.34)$$

by a matrix

$$\mathbf{A} = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \quad (D.35)$$

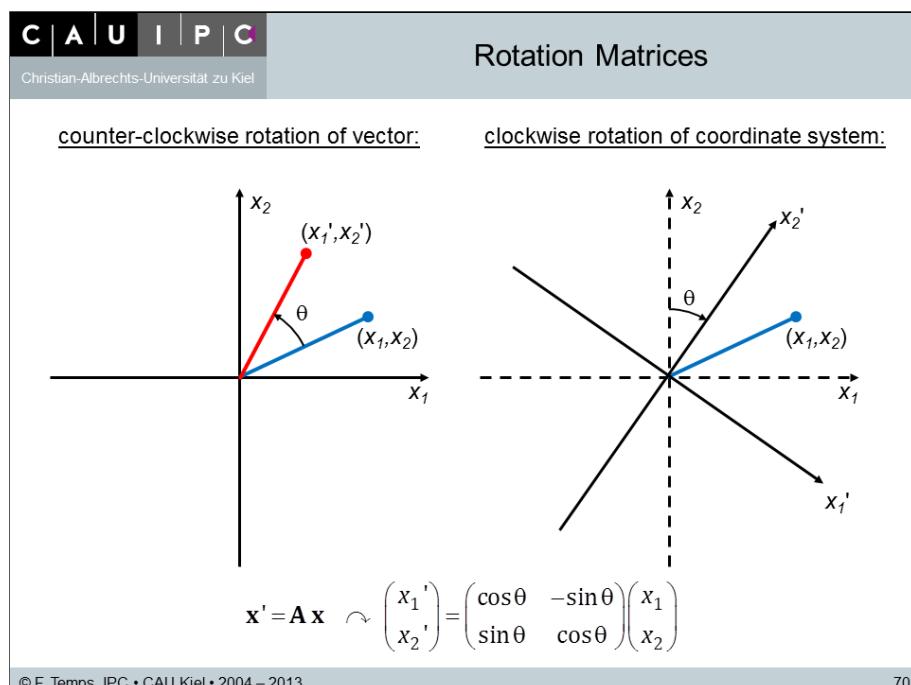
gives

$$\mathbf{A} \mathbf{x} = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad (D.36)$$

$$= \begin{pmatrix} x_1 \cos \theta - x_2 \sin \theta \\ x_1 \sin \theta + x_2 \cos \theta \end{pmatrix} \quad (D.37)$$

$$= \mathbf{x}' \quad (D.38)$$

► Figure D.1: Rotation of a coordinate system.



► **The result is a rotation:**

- In the original coordinate system, the new vector \mathbf{x}' corresponds to the result of an anti-clockwise rotation of \mathbf{x} around θ .
- Alternatively, we can say that \mathbf{x}' is given in a new coordinate system that is obtained by a clockwise rotation of the old coordinate system around θ .

- **Rotation matrices and rotation operators:** \mathbf{A} is called a *rotation matrix*. We shall also call \mathbf{A} a *rotation operator*.
- **Exercise D.1:** Show that Eqs. D.36 - D.38 does describe an anti-clockwise rotation of the vector \mathbf{x} to the new vector \mathbf{x}' and determine its coordinates using trigonometric arguments. □

D.5 Systems of linear equations

- **Solutions of linear equations (I): Cramer's rule.** Matrices and determinants can be generally used for solving systems of linear equations of the type

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + \dots a_{1n}x_n &= c_1 \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + \dots a_{2n}x_n &= c_2 \\ &\dots = \dots \\ a_{n1}x_1 + a_{n2}x_2 + a_{n3}x_3 + \dots a_{nn}x_n &= c_n \end{aligned} \quad (\text{D.39})$$

These equations can be written in matrix form:

$$\begin{pmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \quad (\text{D.40})$$

or

$$\mathbf{A} \mathbf{x} = \mathbf{c} \quad (\text{D.41})$$

Simple algebraic manipulations (see any math textbook) gives the expressions

$$|\mathbf{A}| x_i = |\mathbf{A}_i| \quad (\text{D.42})$$

where $|\mathbf{A}|$ is the determinant of the coefficient matrix \mathbf{A} and $|\mathbf{A}_i|$ is the respective determinant of $|\mathbf{A}|$ in which the i th column is replaced by the c_1, c_2, c_3, \dots , e.g.

$$|\mathbf{A}_2| = \begin{pmatrix} a_{11} & c_1 & \dots & a_{1n} \\ a_{21} & c_2 & \dots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & c_n & \dots & a_{nn} \end{pmatrix} \quad (\text{D.43})$$

Solutions for the x_i : From Eq. D.42 we obtain the non-trivial solutions for the x_i according to

$$x_i = \frac{|\mathbf{A}_i|}{|\mathbf{A}|} \quad (\text{D.44})$$

under the condition that the \mathbf{A} matrix is *not* singular, i.e., the determinant of coefficients does not vanish

$$|\mathbf{A}| \neq 0 \quad (\text{D.45})$$

(The trivial and uninteresting solutions are $x_1, x_2, x_3, \dots = 0$).

- **Solutions of linear equations (II):** In the following, we shall only consider the special linear equations of the type

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + \dots a_{1n}x_n &= 0 \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + \dots a_{2n}x_n &= 0 \\ &\dots = \dots \\ a_{n1}x_1 + a_{n2}x_2 + a_{n3}x_3 + \dots a_{nn}x_n &= 0 \end{aligned} \quad (\text{D.46})$$

or

$$\mathbf{A} \mathbf{x} = \underline{0} \quad (D.47)$$

The trivial and uninteresting solutions of this equation are $x_1, x_2, x_3, \dots = 0$.

The interesting solutions require that the matrix of coefficients \mathbf{A} is singular, i.e., the determinant of coefficients has to vanish

$$|\mathbf{A}| = 0 \quad (D.48)$$

This type of equations is encountered in *eigenvalue problems*.

D.6 Eigenvalue equations

Consider a set of linear equations as considered in the previous section which can be written in the form

$$\mathbf{A} \mathbf{x} = \lambda \mathbf{x} \quad (\text{D.49})$$

where

- (1) \mathbf{A} is an $n \times n$ -dimensional matrix,
- (2) λ is a scalar constant, called an *eigenvalue* of \mathbf{A} (λ is any one of the set of n eigenvalues of \mathbf{A}), and
- (3) \mathbf{x} is an n -dimensional column vector (which can in general be complex), called the *eigenvector* of \mathbf{A} belonging to the particular eigenvalue.

Eq. D.49 is called an *eigenvalue equation*. It has the following property: The multiplication of \mathbf{x} by λ (and hence that of \mathbf{x} by the matrix \mathbf{A}) changes the length of \mathbf{x} (by the factor λ), but not the direction.

- ▶ **Eigenvalues and eigenvectors of the molecular Hamiltonian:** The determination of eigenvalues and eigenvectors of the *molecular Hamiltonian* \mathbf{H} , i.e., the “energy matrix”, or the matrix of the Hamilton operator \hat{H} , is the most important problem in spectroscopy (in general, it is the key problem!!).
- ▶ **Secular equation and eigenvalues λ_i :** Eq. D.49 can be rewritten as

$$(\mathbf{A} - \lambda \mathbf{I}) \mathbf{x} = \mathbf{0} \quad (\text{D.50})$$

In order not to obtain the trivial solutions $x_1 = x_2 = x_3 = \dots = 0$, $\det(\mathbf{A} - \lambda \mathbf{I})$ has to vanish, i.e., $\det(\mathbf{A} - \lambda \mathbf{I}) = 0$. This is the so-called **characteristic equation** or **secular equation**:

$$|\mathbf{A} - \lambda \mathbf{I}| = \begin{vmatrix} a_{11} - \lambda & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} - \lambda & \dots & a_{2n} \\ \vdots & \vdots & \dots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} - \lambda \end{vmatrix} = 0 \quad (\text{D.51})$$

The **secular equation** has n roots

$$\{\lambda_1, \lambda_2, \dots, \lambda_n\} \quad (\text{D.52})$$

which are called the **eigenvalues**.

- **Eigenvectors \mathbf{x}_i :** For each eigenvalue λ_i , we can write an eigenvalue equation

$$\mathbf{A} \mathbf{x}_1 = \lambda_1 \mathbf{x}_1 \quad (D.53)$$

$$\mathbf{A} \mathbf{x}_2 = \lambda_2 \mathbf{x}_2 \quad (D.54)$$

$$\vdots \quad (D.55)$$

$$\mathbf{A} \mathbf{x}_n = \lambda_n \mathbf{x}_n \quad (D.56)$$

In matrix notation, this becomes

$$\mathbf{A} \mathbf{X} = \mathbf{X} \Lambda \quad (D.57)$$

with the *diagonal* eigenvalue matrix

$$\Lambda = \begin{pmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & \dots & 0 \\ \vdots & \vdots & \dots & \vdots \\ 0 & 0 & \dots & \lambda_n \end{pmatrix} \quad (D.58)$$

The different **eigenvectors** \mathbf{x}_i are usually normalized to unity, *i.e.*,

$$|\mathbf{x}| = (\mathbf{x}^\dagger \mathbf{x})^{1/2} = 1 \quad (D.59)$$

- **Matrix diagonalization:** The matrix of the eigenvectors \mathbf{X} can be determined by multiplying the equation

$$\mathbf{A} \mathbf{X} = \mathbf{X} \Lambda \quad (D.60)$$

from the left with \mathbf{X}^{-1} , which gives

$$\mathbf{X}^{-1} \mathbf{A} \mathbf{X} = \mathbf{X}^{-1} \mathbf{X} \Lambda \quad (D.61)$$

i.e.,

$$\boxed{\mathbf{X}^{-1} \mathbf{A} \mathbf{X} = \Lambda} \quad (D.62)$$

↷

The determination of the eigenvector matrix is equivalent to finding a matrix \mathbf{X} that transforms the matrix \mathbf{A} into diagonal form (Λ).

- **Example:**

$$\mathbf{A} = \begin{pmatrix} 2 & 3 \\ 3 & 10 \end{pmatrix} \quad (D.63)$$

Eigenvalue equations:

$$\mathbf{A} \mathbf{x}_i = \lambda \mathbf{x}_i \quad (D.64)$$

or in matrix form:

$$\mathbf{A} \mathbf{X} = \mathbf{X} \Lambda \quad (D.65)$$

Secular equation:

$$\det(\mathbf{A} - \lambda \mathbf{I}) = \begin{vmatrix} 2 - \lambda & 3 \\ 3 & 10 - \lambda \end{vmatrix} \quad (D.66)$$

$$= (2 - \lambda)(10 - \lambda) - 9 = 0 \quad (D.67)$$

↷

$$0 = 20 - 2\lambda - 10\lambda + \lambda^2 - 9 = \lambda^2 - 12\lambda + 11 \quad (D.68)$$

$$\lambda_{1,2} = +\frac{12}{2} \pm \sqrt{\left(\frac{12}{2}\right)^2 - 11} = 6 \pm \sqrt{36 - 11} \quad (D.69)$$

$$= 6 \pm 5 \quad (D.70)$$

↷

Eigenvalues:

$$\lambda_1 = 1 \quad (D.71)$$

$$\lambda_2 = 11 \quad (D.72)$$

Eigenvectors: Inserting the eigenvalues one by one into the eigenvalue equation yields:

(1)

$$\begin{pmatrix} 2 & 3 \\ 3 & 10 \end{pmatrix} \begin{pmatrix} x_{11} \\ x_{21} \end{pmatrix} = \lambda_1 \begin{pmatrix} x_{11} \\ x_{21} \end{pmatrix} = 11 \begin{pmatrix} x_{11} \\ x_{21} \end{pmatrix} \quad (D.73)$$

↷

$$\begin{pmatrix} -3 \\ 1 \end{pmatrix} \quad (D.74)$$

(2)

$$\begin{pmatrix} 2 & 3 \\ 3 & 10 \end{pmatrix} \begin{pmatrix} x_{12} \\ x_{22} \end{pmatrix} = \lambda_2 \begin{pmatrix} x_{12} \\ x_{22} \end{pmatrix} = 1 \begin{pmatrix} x_{12} \\ x_{22} \end{pmatrix} \quad (D.75)$$

↷

$$\begin{pmatrix} 1 \\ 3 \end{pmatrix} \quad (D.76)$$

Unnormalized eigenvalue matrix:

$$\begin{pmatrix} -3 & 1 \\ 1 & 3 \end{pmatrix} \quad (D.77)$$

Normalized eigenvalue matrix:

$$\mathbf{X} = \begin{pmatrix} \frac{-3}{\sqrt{10}} & \frac{1}{\sqrt{10}} \\ \frac{1}{\sqrt{10}} & \frac{3}{\sqrt{10}} \end{pmatrix} \quad (D.78)$$

- ▶ **Final note:** In practice, matrix manipulations such as matrix inversion, the evaluation of determinants, the determination of eigenvalues and eigenvectors, *etc.*, are carried out numerically by using computers.

- ▶ **References**

Press 1992 W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in Fortran*, Cambridge University Press, Cambridge, 1992. Versions are also available for C and Pascal.

Appendix E: Laplace transforms

The concept of Laplace and inverse Laplace transforms is extremely useful in chemical kinetics for two reasons:

- (1) They connect microscopic molecular properties and statistically averaged quantities:
 - a) $\sigma(E) \leftrightarrow k(T)$: Collision cross section *vs.* thermal rate constant for bimolecular reactions (section ??),
 - b) $k(E) \leftrightarrow k(T)$: Specific rate constant *vs.* thermal rate constant for unimolecular reactions (section 8),
 - c) $\rho(E) \leftrightarrow q(T)$: Density of states *vs.* partition function in statistical rate theories 8).
- (2) They provide a convenient method for solving of differential equations (section 3.4.2).

- **Definition E.1:** The Laplace transform $\mathcal{L}[f(t)]$ of a function $f(t)$ is defined as the integral

$$F(p) = \mathcal{L}[f(t)] = \int_0^{\infty} f(t) e^{-pt} dt \quad (\text{E.1})$$

where

- t is a real variable,
- $f(t)$ is a real function of the variable t with the property $f(t) = 0$ for $t < 0$,
- p is a complex variable,
- $F(p) = \mathcal{L}[f(t)]$ is a function of the variable p .

- **Definition E.2:** The inverse Laplace transform $\mathcal{L}^{-1}[F(p)]$ of the function $F(p)$ is defined as the integral

$$f(t) = \mathcal{L}^{-1}[F(p)] = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} F(s) e^{pt} dp \quad (\text{E.2})$$

where

- c is an arbitrary real constant.

► **Notes:**

- Since $\mathcal{L}^{-1}[F(p)]$ recovers the original function $f(t)$, the pair of functions $f(t)$ and $F(p)$ is said to form a Laplace pair.
- The properties of the Laplace and inverse Laplace transforms can be derived from those of Fourier transforms (Zachmann 1972).
- Laplace transforms can be computed using symbolic algebra computer programs (Maple, Mathematica, etc.). In favorable cases, it is also possible to obtain inverse Laplace transforms by computer programs. However, it is often more convenient to take the Laplace and inverse Laplace transforms from corresponding Tables.⁵⁸

► **Table E.1:** Table of Laplace transforms.

$f(t)$	$F(p) = \mathcal{L}[f(t)]$	$f(t)$	$F(p) = \mathcal{L}[f(t)]$
$f(t)$	$F(p) = \int_0^\infty f(t) e^{-pt} dt$		
$\frac{d f(t)}{dt}$	$p F(p) - f(t=0)$	e^{at}	$\frac{1}{p-a}$
1	$\frac{1}{p}$	$t e^{at}$	$\frac{1}{(p-a)^2}$
t	$\frac{1}{p^2}$	$\sin at$	$\frac{a}{p^2+a^2}$
$\frac{t^2}{2}$	$\frac{1}{p^3}$	$\cos at$	$\frac{p}{p^2+a^2}$
$\frac{t^{n-1}}{\Gamma(p)}$	$\frac{1}{p^n}$	$\frac{1}{(a-b)} (e^{at} - e^{bt})$	$\frac{1}{(p-a)(p-b)}$

$\Gamma(n)$ is the Gamma function. For integer n , $\Gamma(n) = (n-1)!$ (see Appendix F).

► **References:**

- Houston 1996** P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw-Hill, Boston, 2001.
- Steinfeld 1989** J. I. Steinfeld, J. S. Francisco, W. L. Haase, *Chemical Kinetics and Dynamics*, Prentice Hall, Englewood Cliffs, 1989.
- Zachmann 1972** H. G. Zachmann, *Mathematik für Chemiker*, Verlag Chemie, Weinheim, 1972.

⁵⁸ Extensive Tables of Laplace transforms are given by (Steinfeld 1989).

Appendix F: The Gamma function $\Gamma(x)$

- If x is a positive integer, the Gamma function is

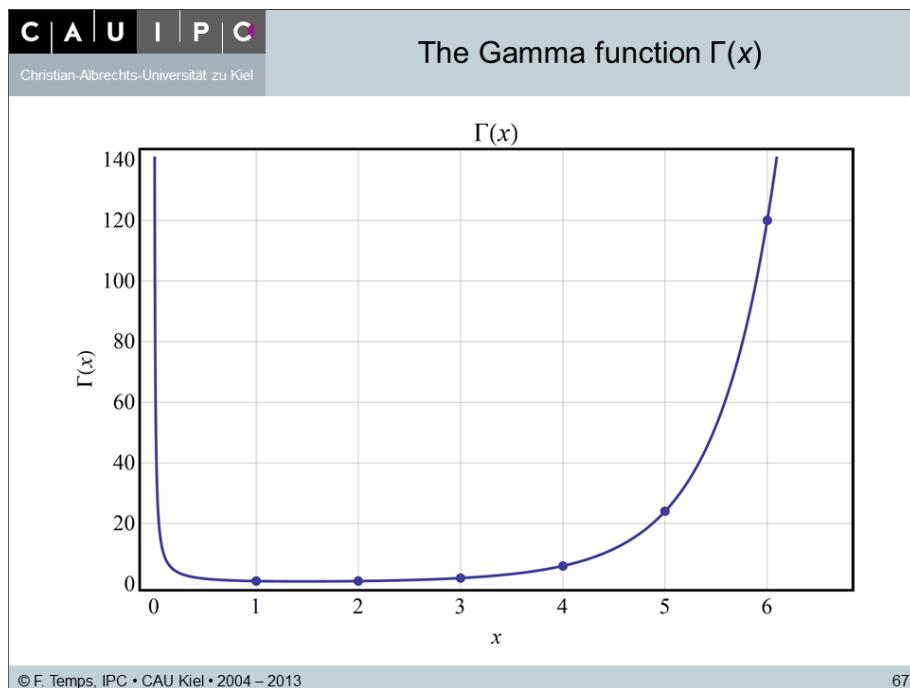
$$\Gamma(x) = (x-1)! \quad (\text{F.1})$$

- The Gamma function smoothly interpolates between all points (x, y) given by $y = (x-1)!$ for positive non-integer x (cf. Fig. F.1).
- The Gamma function is defined for all complex numbers z with a positive real part as

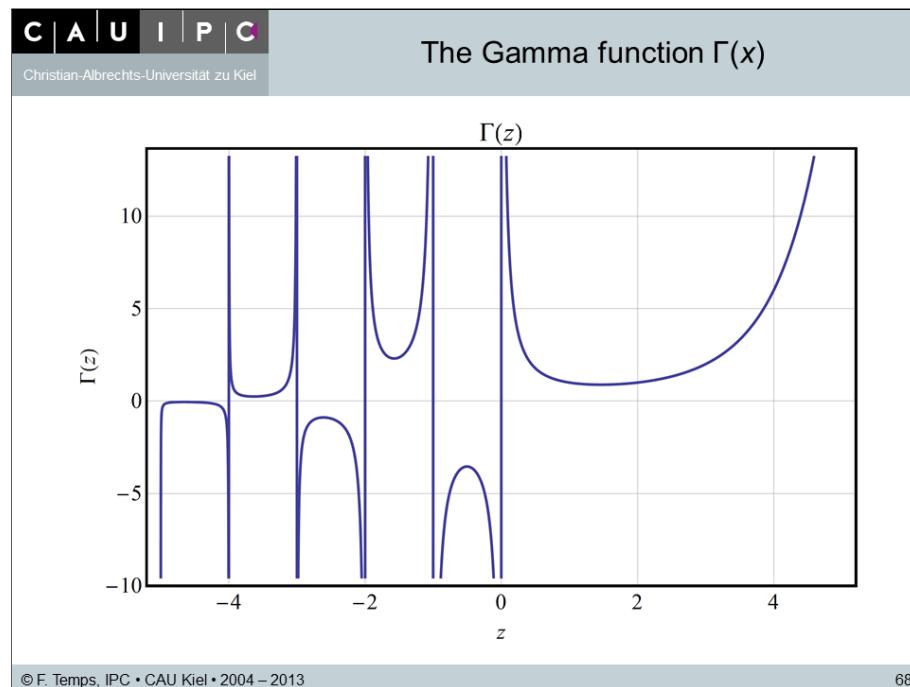
$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt \quad (\text{F.2})$$

This integral converges for complex numbers with a positive real part. It has poles for complex numbers with a negative real part (cf. Fig. F.2).

- **Figure F.1:** The Gamma function.



- **Figure F.2:** For negative arguments the Gamma function has poles (at all negative integers).



Appendix G: Ergebnisse der statistischen Thermodynamik

In diesem Kapitel sollen wichtige Ergebnisse der statistischen Thermodynamik zusammengefasst werden. Im Vordergrund steht die Berechnung der thermodynamischen Zustandsfunktionen und die Berechnung von chemischen Gleichgewichten aus *molekularen* Eigenschaften. Wir benutzen die Ergebnisse der Quantenmechanik:

- Ein Molekül kann nur bestimmte Energiezustände ϵ_i einnehmen.
- Diese Energiezustände sind im Prinzip nicht kontinuierlich sondern diskret verteilt.
- Jeder Energiezustand hat ein bestimmtes statistisches Gewicht g_i . Das statistische Gewicht gibt an, wie oft ein Zustand bei einer bestimmten Energie vorkommt.

Beispiele:

$g_i = 1$	eindimensionaler harmonischer Oszillatator	(G.1)
$g_i = 2$	isotroper zweidimensionaler harmonischer Oszillatator (z.B. Biegeschwingung von CO_2)	
$g_i = 2J + 1$	Rotation eines linearen Moleküls	

- Die Ergebnisse der statischen Thermodynamik unterscheiden sich, je nachdem ob das betrachtete System aus unterscheidbaren oder aus ununterscheidbaren Teilchen besteht:

Beispiele für unterscheidbare Teilchen:	Atome im Kristallgitter	(G.2)
Beispiele für ununterscheidbare Teilchen:	1.) Gasmoleküle 2.) Elektronen (Fermi-Statistik)	

- Die anzuwendende Statistik hängt vom Spin der Teilchen ab:

Spin gerade:	Bose-Einstein-Statistik	(G.3)
Spin ungerade:	Fermi-Dirac-Statistik	

Auf die Unterschiede zwischen der Bose-Einstein- und der Fermi-Dirac-Statistik wird an anderer Stelle eingegangen (\Rightarrow Vorlesung "Statistische Thermodynamik").

- Im Grenzfall $k_B T \gg \epsilon_i$ gilt die Boltzmann-Statistik.
- Im Folgenden werden behandelt: Elektronische Anregung, Schwingungsanregung, Rotationsanregung, Translationsanregung.

Die Translation erfordert abhängig vom Problem manchmal eine etwas andere Behandlung (klassische statistische Thermodynamik bzw. Semiklassik). Quantenmechanik und klassische Mechanik stimmen im Ergebnis für $k_B T \gg \epsilon_i$ überein.

G.1 Boltzmann-Verteilung

Die Besetzungswahrscheinlichkeit eines Zustands ϵ_i wird durch die *Boltzmann-Verteilung* angegeben. Diese ergibt sich als die *wahrscheinlichste* Verteilung aus dem Boltzmann-Ansatz für die Entropie

$$S = k_B \ln W \quad (G.4)$$

W wird als die thermodynamische Wahrscheinlichkeit bezeichnet.

Die Boltzmann-Verteilung kann hergeleitet werden, wenn man entsprechend dem 2. Hauptsatz den Maximalwert für S sucht (Methode der Lagrange'schen Multiplikatoren). Hier setzen wir die Boltzmann-Verteilung als gegeben voraus (z.B. als empirisches, experimentelles Ergebnis):

- **Boltzmann-Verteilung:** Für diskrete Energiezustände ϵ_i ist die Besetzungswahrscheinlichkeit eines Zustands proportional zu $e^{-\epsilon_i/kT}$:

$$f_i = \frac{N_i}{N} \propto e^{-\epsilon_i/kT} \quad (G.5)$$

Bei Berücksichtigung einer möglichen Entartung von Zuständen (Entartungsfaktor bzw. statistisches Gewicht g_i) und mit einer Proportionalitätskonstante C' zur Normierung gilt

$$f_i = \frac{N_i}{N} = C' \times g_i \times e^{-\epsilon_i/kT} \quad (G.6)$$

Dabei ist N_i die Zahl der Teilchen im Energiezustand ϵ_i (mit dem statistischen Gewicht g_i) und N die Gesamtzahl der Teilchen.

Die Funktion f_i gibt die Wahrscheinlichkeit der Besetzung des Zustands ϵ_i an. Die Normierungskonstante C' ergibt sich aus der Normierungsbedingung, dass die Gesamtwahrscheinlichkeit zu 1 herauskommt:

$$\frac{\sum_i N_i}{N} = \sum_i f_i = C' \times \sum_i g_i e^{-\epsilon_i/k_B T} = 1 \quad (G.7)$$

$$\leadsto C' = \frac{1}{\sum_i g_i e^{-\epsilon_i/k_B T}}. \quad (G.8)$$

↷

- **Normierte Boltzmann-Verteilungsfunktion:**

$$f_i = \frac{N_i}{N} = \frac{g_i e^{-\epsilon_i/k_B T}}{\sum_i g_i e^{-\epsilon_i/k_B T}}$$

(G.9)

- **Molekulare Zustandssumme:** Die Summe $\sum_i g_i e^{-\epsilon_i/k_B T}$ im Nenner der o.a. Gleichung wird als *molekulare Zustandssumme* bezeichnet:

$$Q = \sum_i g_i e^{-\epsilon_i/k_B T}$$

(G.10)

Die Zustandssumme Q ist die zentrale Grösse der statistischen Thermodynamik. Q ist von der Temperatur T abhängig.

► **Anschauliche Bedeutung der molekularen Zustandssumme:**

Q = Zahl der bei der Temperatur T im Mittel besetzten Energiezustände eines Molekül.

► **Boltzmann-Verteilungsfunktion für kontinuierlich verteilte Energiezustände:**

Für kontinuierlich verteilte Energiezustände ersetzt man g_i durch $\rho(\epsilon)d\epsilon$ und erhält analog eine kontinuierliche Besetzungswahrscheinlichkeit:

$$f(\epsilon)d\epsilon = \frac{dN(\epsilon)}{N} = \frac{\rho(\epsilon) \times e^{-\epsilon/k_B T} d\epsilon}{Q} \quad (\text{G.11})$$

► **Zustandsdichte:** $\rho(E)$ = Zustandsdichte (=Anzahl der Zustände pro Energie-Intervall):

$$\rho(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} \quad (\text{G.12})$$

G.2 Mittelwerte

- **Mittlere Energie $\bar{\epsilon}$:** In der Thermodynamik interessieren Mittelwerte, z.B. die mittlere Energie $\bar{\epsilon}$. Für Größen, die durch eine Verteilungsfunktion beschrieben werden, erhält man den Mittelwert nach

$$\bar{\epsilon} = \frac{\sum_i \epsilon_i f_i}{\sum_i f_i} = \frac{\sum \epsilon_i N_i}{\sum N_i} = \frac{\sum \epsilon_i N_i}{N} = \sum \epsilon_i f_i = \frac{\sum \epsilon_i f_i}{\sum f_i} \quad (G.13)$$

mit $f_i = \frac{N_i}{N}$ und $\sum f_i = 1$.

Übergang zu einer kontinuierlichen Verteilungsfunktion liefert

$$\bar{\epsilon} = \frac{\int_0^\infty \epsilon f(\epsilon) d\epsilon}{\int_0^\infty f(\epsilon) d\epsilon} \quad (G.14)$$

Diese Ausdrücke vereinfachen sich, wenn $f(\epsilon)$ auf 1 normiert ist.

- **Allgemeine Berechnung der Mittelwerts \bar{y} einer Größe $y(\epsilon)$:**

$$\bar{y} = \frac{\sum_i y_i f_i}{\sum_i f_i} \quad (G.15)$$

bzw.

$$\bar{y} = \frac{\int_0^\infty y(\epsilon) f(\epsilon) d\epsilon}{\int_0^\infty f(\epsilon) d\epsilon} \quad (G.16)$$

- **Example G.1:** Berechnung der mittleren Energie für ein 3-Niveausystem:

$$\begin{aligned} \epsilon_0 &= 0 & \epsilon_1 &= \epsilon_1 & \epsilon_2 &= 2\epsilon_1 \\ N_0 &= 3 & N_1 &= 2 & N_2 &= 1 \end{aligned} \quad (G.17)$$

$$N = \sum N_i = 6 \quad (G.18)$$

Ergebnis:

$$\bar{\epsilon} = \frac{1}{N} \sum_i N_i \epsilon_i = \sum_i \frac{N_i}{N} \epsilon_i = \sum_i f_i \quad (G.19)$$

$$= \frac{1}{6} (3\epsilon_0 + 2\epsilon_1 + 1\epsilon_2) \quad (G.20)$$

$$= \frac{1}{6} (3\epsilon_0 + 2\epsilon_1 + 2\epsilon_1) \quad (G.21)$$

$$= \frac{1}{6} (0 + 4\epsilon_1) \quad (G.22)$$

$$= \frac{4}{6} \epsilon_1 \quad (G.23)$$

$$\bar{\epsilon} = \frac{2}{3} \epsilon_1 \quad (G.24)$$

□

- **Mittlere Energie eines Moleküls:** Bei Gültigkeit der Boltzmann-Verteilung kann die mittlere Energie eines Moleküle aus der molekularen Zustandssumme berechnet werden:

$$\bar{\epsilon} = \frac{1}{N} \sum_i N_i \epsilon_i = \sum_i \frac{N_i}{N} \epsilon_i = \sum_i f_i \epsilon_i \quad (G.25)$$

$$= \frac{\sum \epsilon_i g_i e^{-\epsilon_i/k_B T}}{\sum g_i e^{-\epsilon_i/k_B T}} \quad (G.26)$$

$$= \frac{\sum \epsilon_i g_i e^{-\epsilon_i/k_B T}}{Q} \quad | \times \frac{k_B T^2}{k_B T^2} \quad (G.27)$$

$$= \frac{k_B T^2}{Q} \sum_i g_i \frac{\epsilon_i}{k_B T^2} e^{-\epsilon_i/k_B T} \quad (G.28)$$

$$= \frac{k_B T^2}{Q} \sum_i g_i \frac{d}{dT} \left(e^{-\epsilon_i/k_B T} \right) \quad |(\text{durch differenzieren zeigen}) \quad (G.29)$$

$$= \frac{k_B T^2}{Q} \frac{d}{dT} \sum_i g_i e^{-\epsilon_i/k_B T} \quad (G.30)$$

$$= \frac{k_B T^2}{Q} \frac{dQ}{dT} \quad (G.31)$$

↷

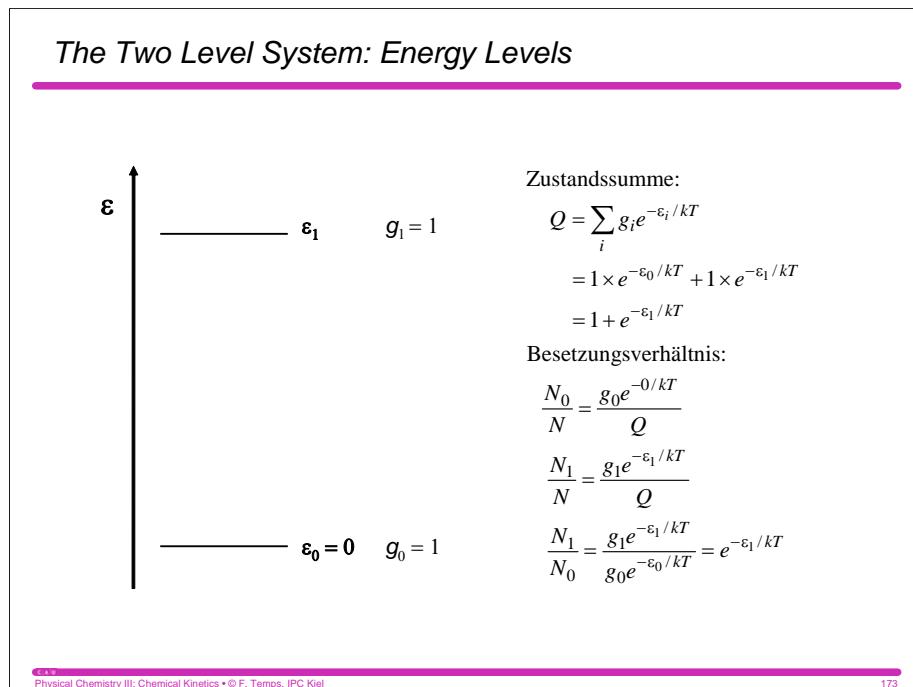
$$\bar{\epsilon} = k_B T^2 \frac{d \ln Q}{dT} \quad (G.32)$$

G.3 Anwendung auf ein Zweiniveau-System

► Chemisch relevante Beispiele für Zweiniveau-Systeme:

- Paramagnetische Atome u. Moleküle
- NMR-Spektroskopie: Atomkerne mit Kernspin. Typischer Frequenzbereich: 100 MHz.
- Molekül mit cis-trans-Isomeren oder 2 Konformeren

► Figure G.1: Zwei-Niveau-System: Energiezustände



► Besetzungsverhältnis:

$$\frac{N_1}{N} = \frac{g_1 e^{-\epsilon_1/kT}}{Q} \quad (G.33)$$

mit

$$Q = g_0 e^{-\epsilon_0/kT} + g_1 e^{-\epsilon_1/kT} \quad (G.34)$$

$$= 1 + e^{-\epsilon_1/kT} \quad (G.35)$$

(1) Grenzfall für $T \rightarrow 0$:

$$\frac{\epsilon_1}{kT} \rightarrow \infty \curvearrowright e^{-\epsilon_1/kT} \rightarrow e^{-\infty} = 0 \quad (G.36)$$

↪ Bei $T \rightarrow 0$ ist nur der tiefste Energiezustand besetzt.

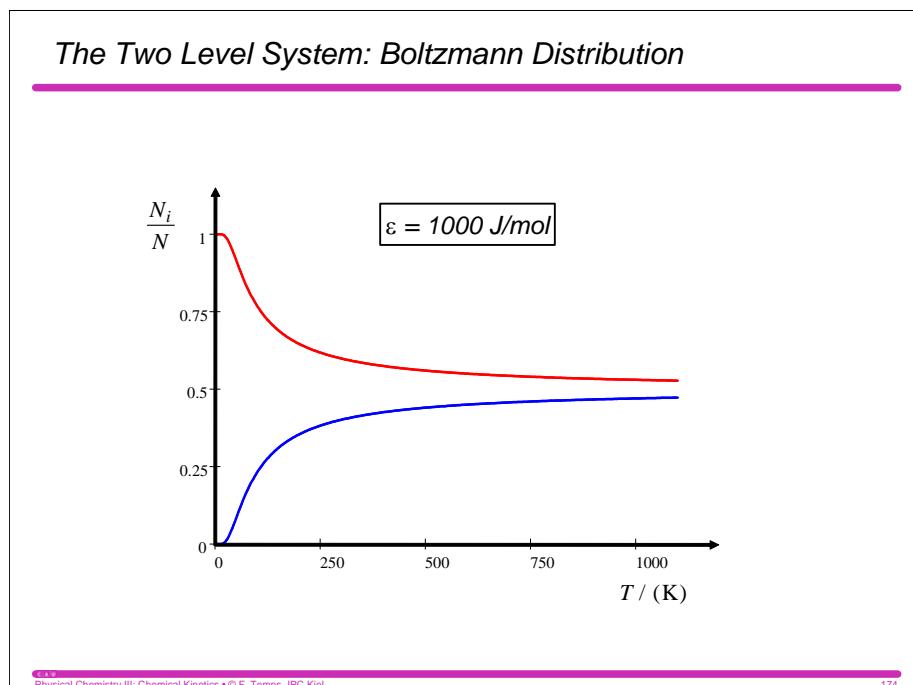
(2) Grenzfall für $T \rightarrow \infty$:

$$\frac{\epsilon_1}{kT} \rightarrow 0 \rightsquigarrow e^{-\epsilon_1/kT} \rightarrow e^{-0} = 1 \quad (G.37)$$

↪ Bei $T \rightarrow \infty$ ergibt sich eine Gleichbesetzung der Energiezustände. Dies ist die maximale Besetzung im oberen Zustand!

- Eine Besetzungsinversion ($N_1 > N_0$) würde formal eine negative Temperatur erfordern (→ Laser).

► **Figure G.2:** Zwei-Niveau-System: Boltzmann-Besetzung der Zustände (rot: unterer Zustand, blau: oberer Zustand).



► **Mittlere thermische Energie:**

(1) $\epsilon_1 = 12.5 \text{ kJ/mol}$ (entsprechend $\nu = 1000 \text{ cm}^{-1}$; z.B. C-C-Schwingung im IR oder Energieabstand zwischen cis-trans-Isomeren):

$$\frac{N_1}{N_0} = e^{-\epsilon_1/k_B T} = \begin{cases} 8 \times 10^{-3} & @ T = 300 \text{ K} \\ 0.23 & @ T = 1000 \text{ K} \end{cases} \quad (G.38)$$

(2) $\epsilon_1 = 0.04 \text{ kJ/mol}$ (entsprechend Energieabstand zwischen Kernspinzuständen bei 100 MHz NMR):

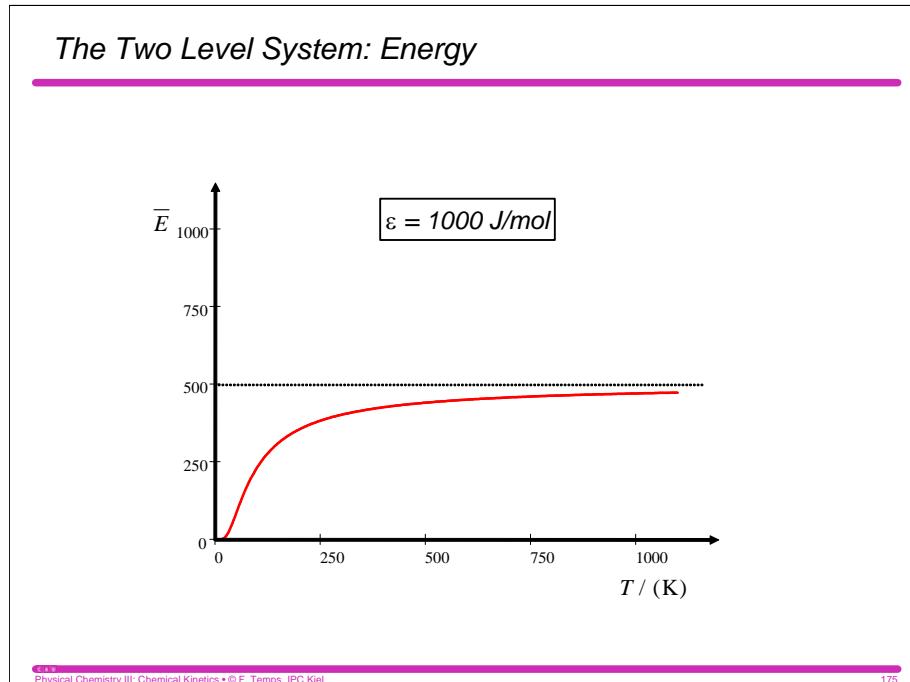
$$\frac{N_1}{N_0} = e^{-\epsilon_1/k_B T} = 0.999984 @ T = 300 \text{ K} \quad (G.39)$$

Reihenentwicklung:

$$e^{-\epsilon_1/kT} = 1 - \frac{\epsilon_1}{kT} + \dots \approx 1 - \frac{\epsilon_1}{kT} \quad (G.40)$$

↪ sehr kleiner Besetzungsunterschied ↪ Wunsch der NMR-Spektroskopiker zu immer größeren Frequenzen (Rekord heute 950 MHz).

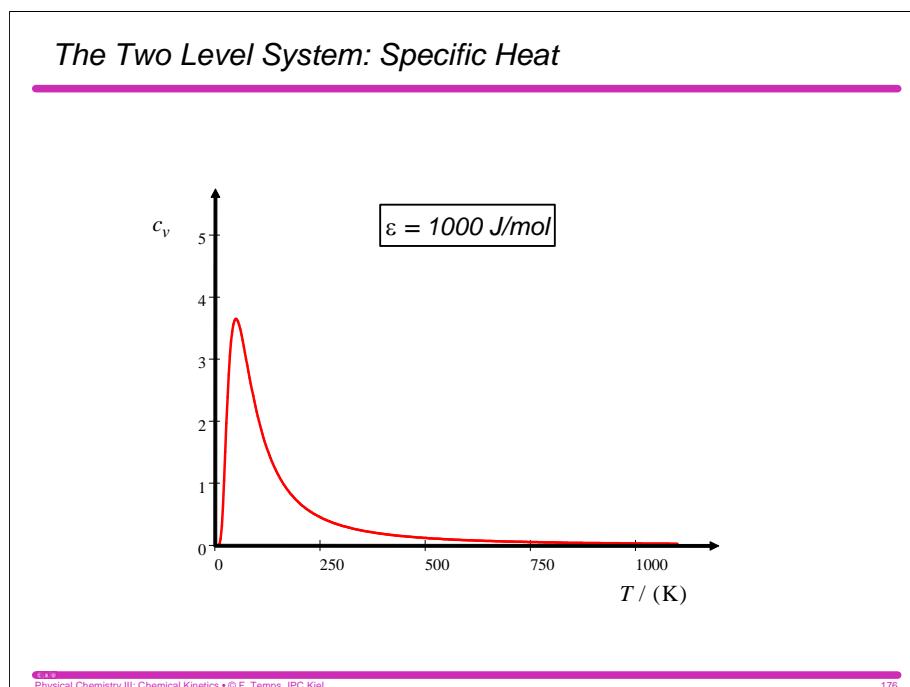
- **Figure G.3:** Zwei-Niveau-System: Mittlere thermische Energie.



- **Spezifische Wärme:**

$$c_v = \frac{\partial E}{\partial T} \quad (\text{G.41})$$

- **Figure G.4:** Zwei-Niveau-System: Spezifische Wärme.



G.4 Mikrokanonische und makrokanonische Ensembles

Die statistische Thermodynamik macht Aussagen über statistische *Ensembles* (Ansammlungen von Systemen, Molekülen). Wir betrachten verschiedene *Ensembles* von miteinander wechselwirkenden Molekülen.

- ▶ **Der Begriff des Ensembles:** Wir betrachten ein abgeschlossenes System bei konstantem Volumen, konstanter Zusammensetzung und konstanter Temperatur (bzw. bestimmter Energie (s.u.)). Ein *Ensemble* erhalten wir, wenn wir uns \mathcal{N} Replikationen dieser Systeme denken, die wir unter Einhaltung bestimmter Regeln erhalten (Regel = *Canon*). Alle Systeme in dem Ensemble sollen im thermischen Gleichgewicht miteinander (sie dürfen zwischen einander Energie austauschen).

Es werden verschiedene Sorten von Ensembles unterschieden:

- **Mikrokanonisches Ensemble:** Ensemble von N Systemen (z.B. Atomen, Molekülen) mit konstanter Teilchenzahl, konstantem Volumen, konstanter Energie.
 - **Makrokanonisches Ensemble** (kurz kanonisches Ensemble genannt): Ensemble von N Systemen (z.B. Atomen, Molekülen) mit konstanter Teilchenzahl, konstantem Volumen, konstanter Temperatur.
 - **Großkanonisches Ensemble:** Ensemble von N *offenen* Systemen (z.B. Teilchen, Molekülen) mit konstantem Volumen, konstanter Temperatur, die zwischeneinander Teilchen austauschen können.
- ▶ **Systemzustandssumme (= kanonische Zustandssumme): Molekulare Zustandssumme:**

$$Q = \sum_{\text{alle Molekülzustände}} g_i e^{-\epsilon_i/kT} \quad (G.42)$$

Systemzustandssumme (= kanonische Zustandssumme):

$$Z = \sum_{\text{alle Systemzustände}} g_i e^{-\epsilon_i/kT} \quad (G.43)$$

Innere Energie des Systems:

$$U = kT^2 \frac{d \ln Z}{dT} \quad (G.44)$$

Bei mehreren Teilchensorten (A, B, C, ...): Zustandsummen sind multiplikativ, da die Energien additiv sind, \curvearrowright

$$Z = Z_A \times Z_B \times Z_C \times \dots \quad (G.45)$$

- Systemzustandssumme für N_A unterscheidbare Teilchen der Sorte A (z.B. Kristall):

$$Z = \prod_i^{N_A} Q_A = Q_A^{N_A} \quad (G.46)$$

↪ für 1 mol:

$$U = kT^2 \frac{d \ln Z}{dT} = RT^2 \frac{d \ln Q}{dT} \quad (G.47)$$

- Systemzustandssumme für N_A nicht unterscheidbare Teilchen der Sorte A (z.B. Gas):

$$Z = \frac{Q_A^{N_A}}{N_A!} \quad (G.48)$$

↪ für 1 mol ($N_A = N_L$):

$$U = kT^2 \frac{d \ln Z}{dT} = kT^2 \frac{d}{dT} \ln \frac{Q^{N_L}}{N_L!} \quad (G.49)$$

G.5 Statistische Interpretation der thermodynamischen Zustandsgrößen

- **Innere Energie:**

$$U = kT^2 \frac{d \ln Z}{dT} \quad (G.50)$$

- **Helmholtz-Energie:**

$$\frac{A}{T} = \frac{U}{T} - S \quad (G.51)$$

$$\frac{\partial}{\partial T} \left(\frac{A}{T} \right)_V = \frac{T \left(\frac{\partial U}{\partial T} \right)_V - U}{T^2} - \left(\frac{\partial S}{\partial T} \right)_V \quad (G.52)$$

$$= \frac{T c_V - U}{T^2} - \frac{c_V}{T} = -\frac{U}{T^2} = -k \frac{d \ln Z}{dT} \quad (G.53)$$

↷

$$\frac{A}{T} = -k \ln Z \quad (G.54)$$

↷

$$A = -kT \ln Z \quad (G.55)$$

- **Entropie:**

$$S = - \left(\frac{\partial A}{\partial T} \right)_V = \frac{U - A}{T} = \dots \quad (G.56)$$

- **Druck:**

$$P = - \left(\frac{\partial A}{\partial V} \right)_T = kT \left(\frac{\partial \ln Z}{\partial V} \right)_T = \dots \quad (G.57)$$

G.6 Chemisches Gleichgewicht



$$\curvearrowleft \quad K_c = \exp \left(-\frac{\Delta_r A^\ominus}{RT} \right) \quad (G.59)$$

bzw.

$$\Delta_r A^\ominus = -RT \ln K_c \quad (G.60)$$

- **Gleichgewichtskonstante:** Wir berechnen zunächst

$$A = -kT \ln Z, \quad (G.61)$$

indem wir $Z_A = \frac{Q_A^{N_A}}{N_A!}$ etc. . . einsetzen und die Stirling'sche Näherung $\ln N! = N \ln N - N$ anwenden:

$$A = -kT [\ln Z_A + \ln Z_B + \ln Z_C] \quad (G.62)$$

$$= -kT \left[\ln \frac{Q_A^{N_A}}{N_A!} + \ln \frac{Q_B^{N_B}}{N_B!} + \ln \frac{Q_C^{N_C}}{N_C!} \right] \quad (G.63)$$

$$\begin{aligned} &= -kT [(N_A \ln Q_A - \ln N_A!) \\ &\quad + (N_B \ln Q_B - \ln N_B!) \\ &\quad + (N_C \ln Q_C - \ln N_C!)] \end{aligned} \quad (G.64)$$

$$\begin{aligned} &= -kT [(N_A \ln Q_A - N_A \ln N_A + N_A) \\ &\quad + (N_B \ln Q_B - N_B \ln N_B + N_B) \\ &\quad + (N_C \ln Q_C - N_C \ln N_C + N_C)] \end{aligned} \quad (G.65)$$

- **Gleichgewichtsbedingung:** Im chemischen Gleichgewicht muss gelten

$$\left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_j} = 0 \quad (G.66)$$

curve

$$\begin{aligned} 0 &= \frac{d}{dN_A} [(N_A \ln Q_A - N_A \ln N_A + N_A) \\ &\quad + (N_B \ln Q_B - N_B \ln N_B + N_B) \\ &\quad + (N_C \ln Q_C - N_C \ln N_C + N_C)] \end{aligned} \quad (G.67)$$

$$\begin{aligned} &= \left(\ln Q_A - N_A \frac{1}{N_A} - \ln N_A + 1 \right) \\ &\quad + \left(\ln Q_B - N_B \frac{1}{N_B} - \ln N_B + 1 \right) \\ &\quad - \left(\ln Q_C - N_C \frac{1}{N_C} - \ln N_C + 1 \right) \end{aligned} \quad (G.68)$$

$$= (\ln Q_A - \ln N_A) + (\ln Q_B - \ln N_B) - (\ln Q_C - \ln N_C) \quad (G.69)$$

$$= \ln \frac{Q_A Q_B}{Q_C} - \ln \frac{N_C}{N_A N_B} \quad (G.70)$$

↷

$$\frac{N_C}{N_A N_B} = \frac{Q_C}{Q_A Q_B} \quad (G.71)$$

Übergang auf Teilchendichten und volumenbezogenen Zustandssummen:

$$\frac{(N_C/V)}{(N_A/V)(N_B/V)} = \frac{(Q_C/V)}{(Q_A/V)(Q_B/V)} \quad (G.72)$$

↷

$$K_c = \frac{(Q_C/V)}{(Q_A/V)(Q_B/V)} = \frac{Q_C^*}{Q_A^* Q_B^*} \quad (G.73)$$

Bezug auf die getrennten molekularen Nullpunktsenergien:

$$K_c = \frac{Q'_C}{Q'_A Q'_B} \times e^{-\Delta\epsilon_0/k_B T} \quad (G.74)$$

mit $Q' =$ die auf das Volumen bezogene Molekülzustandssumme:

$$Q' = \frac{Q_{trans}}{V} \times Q_{rot} \times Q_{vib} \times Q_{el} \quad (G.75)$$

- **Endergebnis:** Die Indices * und ' wurden hier zur Klarheit benutzt. Der Einfachheit halber werden diese üblicherweise weggelassen.

↷

$$K_c = \frac{Q_C}{Q_A Q_B} \times e^{-\Delta\epsilon_0/k_B T} \quad (G.76)$$

G.7 Zustandssumme für elektronische Zustände

Die elektronische Zustandssumme muss unter Einschluss aller elektronischen Entartungen explizit berechnet werden:

$$Q_{el} = \sum_i g_i e^{-\epsilon_i/kT} \quad (G.77)$$

Speziell sind zu berücksichtigen:

- Spinentartung (Spinmultiplizität S):

$$g_s = 2S + 1 \quad (G.78)$$

- elektronischer Bahndrehimpuls (L (Atome) bzw. Λ (lin. Moleküle) bzw. Symmetrierasse E oder T für nichtlin. Moleküle):

- elektronische Feinstrukturkomponenten (Index J im Atom-Termsymbol):

$$g_J = 2J + 1 \quad (G.79)$$

Nur niedrig liegende Elektronenzustände liefern einen Beitrag. Die Zustandssumme ist explizit auszurechnen.

G.8 Zustandssumme für die Schwingungsbewegung

► **Harmonischer Oszillator:**

$$\epsilon_{vib} = h\nu v, \quad v = 0, 1, 2, \dots \quad (G.80)$$

► **Schwingungszustandssumme:**

$$Q_{vib} = \sum_{v=0}^{\infty} e^{-h\nu v/kT} = \sum_{v=0}^{\infty} e^{-x \cdot v} \text{ mit } x = \frac{h\nu}{kT} \quad (G.81)$$

$$= \{1 + e^{-x} + e^{-2x} + e^{-3x} + \dots\} \text{ mit } q = e^{-x} < 1 \quad (G.82)$$

$$= 1 + q + q^2 + q^3 + \dots \quad (G.83)$$

$$= \frac{1}{1-q} \text{ für } q < 1 \quad (G.84)$$

↷

$$Q_{vib} = \frac{1}{1 - e^{-h\nu/kT}} = \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right]^{-1} \quad (G.85)$$

► **s Oszillatoren:**

$$Q_{vib} = \prod_{i=1}^s \left[1 - \exp\left(-\frac{h\nu_i}{kT}\right) \right]^{-1} \quad (G.86)$$

► **typische Werte bei Zimmertemperatur:**

$$Q_{vib} \approx 1 \dots 10 \quad (G.87)$$

► **Grenzwert von Q_{vib} für $T \rightarrow \infty$ bzw. für $\nu \rightarrow 0$:** Für $T \rightarrow \infty$ bzw. für $\nu \rightarrow 0$ kann $\exp\left(-\frac{h\nu}{kT}\right)$ entwickelt werden:

$$\exp\left(-\frac{h\nu}{kT}\right) \approx 1 - \frac{h\nu}{kT} + \dots \quad (G.88)$$

↷

$$Q_{vib} = \frac{1}{1 - \exp\left(-\frac{h\nu}{kT}\right)} = \frac{1}{1 - \left(1 - \frac{h\nu}{kT} + \dots\right)} \quad (G.89)$$

↷

$$Q_{vib} \approx \frac{kT}{h\nu} \quad (G.90)$$

Für s klassische Oszillatoren:

$$Q_{vib} \approx \prod_{i=1}^s \frac{kT}{h\nu_i} \quad (G.91)$$

► **Abweichungen vom harmonischen Oszillator:**

- Für anharmonische Oszillatoren ist die Zustandssumme am besten durch explizite numerische Berechnung nach $\sum_{v=0}^{\infty} e^{-\epsilon_i/kT}$ zu ermitteln.
- Torsionsschwingungen können bei tiefen Temperaturen als harmonische Oszillatoren beschrieben werden, bei hohen Temperaturen als freie 1D-Rotatoren. Im Zwischenbereich muss die Zustandssumme ebenfalls explizit berechnet werden (wobei die Energiezustände für den gehinderten 1D-Rotator zugrundegelegt werden müssen).

G.9 Zustandssumme für die Rotationsbewegung

► **lineare Moleküle:**

$$\epsilon_{rot} = \frac{\hbar^2}{2I} J(J+1), \quad J = 0, 1, 2, \dots \quad (G.92)$$

$$\frac{\hbar^2}{2I} = B \quad (G.93)$$

► **Rotationszustandssumme:**

$$Q_{rot}(2D) = \frac{1}{\sigma} \sum_{J=0}^{\infty} g_{rot} e^{-\epsilon_{rot}/kT} \quad (G.94)$$

$$= \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\hbar^2 J(J+1)/2IkT} \quad (G.95)$$

$$= \frac{1}{\sigma} \int_{J=0}^{\infty} (2J+1) e^{-\hbar^2 J(J+1)/2IkT} dJ \quad (G.96)$$

↷

$$Q_{rot}(2D) = \frac{2kTI}{\sigma \hbar^2} = \frac{kT}{\sigma B} \quad (G.97)$$

► **Symmetrienzahl:**

$$\sigma \quad (G.98)$$

► **Rotationszustandssumme für nichtlineare Moleküle:** ϵ_{rot} ist nur für symmetrische Kreisel analytisch darstellbar, nicht für asymmetrische Kreisel. Für nicht zu tiefe Temperaturen ist

$$Q_{rot}(3D) = \frac{\pi^{1/2}}{\sigma} \left(\frac{2kT}{\hbar^2} \right)^{3/2} (I_x I_y I_z)^{1/2} = \frac{\pi^{1/2}}{\sigma} (kT)^{3/2} (A B C)^{-1/2} \quad (G.99)$$

► **typische Werte bei Zimmertemperatur:**

$$Q_{rot} \approx 100 \dots 1000 \quad (G.100)$$

G.10 Zustandssumme für die Translationsbewegung

► **Teilchen im 1D-Kasten:**

$$\epsilon_{trans} = \frac{h^2}{8m} \times \left(\frac{n}{L}\right)^2, \quad n = 1, 2, 3, \dots \quad (\text{G.101})$$

► **1D-Translationszustandssumme:**

$$Q_{trans} = \sum_i^{\infty} e^{-\epsilon_{trans}/kT} = \int_1^{\infty} e^{-h^2 n^2 / 8m L^2 kT} dn \quad (\text{G.102})$$

$$= \left(\frac{2\pi m k T}{h^2} \right)^{1/2} \times L \quad (\text{in cm}^{-1}) \quad (\text{G.103})$$

↷

$$\boxed{\frac{Q_{trans}}{L} = \left(\frac{2\pi m k T}{h^2} \right)^{1/2}} \quad (\text{G.104})$$

► **Teilchen im 3D-Kasten:**

$$\epsilon_{trans} = \frac{h^2}{8m} \times \left[\left(\frac{n_x}{L_x} \right)^2 + \left(\frac{n_y}{L_y} \right)^2 + \left(\frac{n_z}{L_z} \right)^2 \right] \quad (\text{G.105})$$

► **3DTranslationszustandssumme:**

$$Q_{trans} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \times V \quad (\text{in cm}^{-3}) \quad (\text{G.106})$$

↷

$$\boxed{\frac{Q_{trans}}{V} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2}} \quad (\text{G.107})$$

► **typische Werte:**

$$Q_{trans} \approx 10^{24} \times V \quad (\text{G.108})$$

↷

$$\boxed{\frac{Q_{trans}}{V} \approx 10^{24} \text{ cm}^{-3}} \quad (\text{G.109})$$