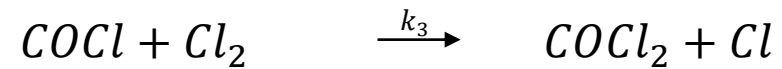
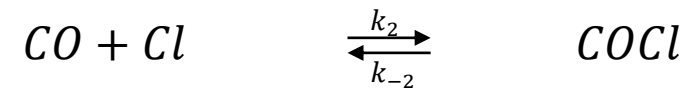
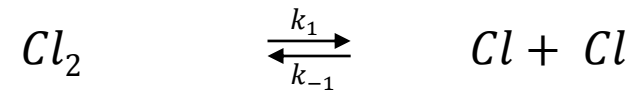
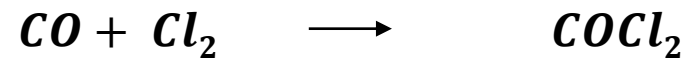


Klausur am 01.08.2019 9-12 Uhr in OSZ/H2

Zusammengesetzte Reaktionen



$$[\text{Cl}] = \sqrt{K_1[\text{Cl}_2]}$$

$$[\text{COCl}] = K_2[\text{Cl}][\text{CO}]$$

$$[\text{COCl}_2]' = k_3\sqrt{K_1}K_2[\text{Cl}_2]^{3/2}[\text{CO}]$$

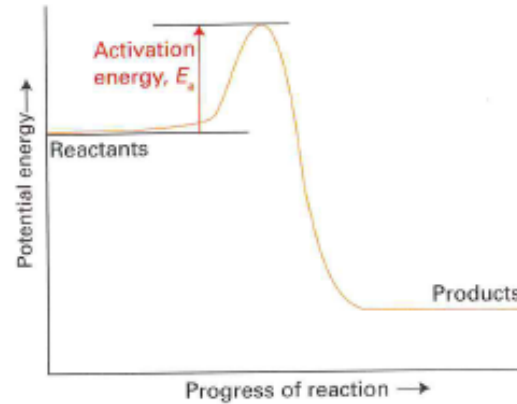
$$[\text{COCl}_2]' = k_3\sqrt{K_1} \frac{k_2}{(k_{-2} + k_3[\text{Cl}_2])} [\text{Cl}_2]^{3/2}[\text{CO}]$$

Arrhenius-Gleichung

$$k(T) = Ae^{-E_A/RT}$$

bzw.

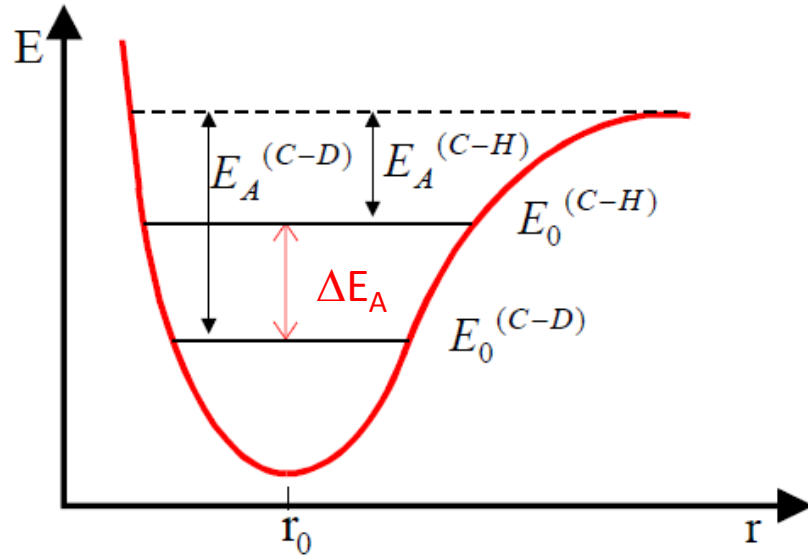
$$\left(\frac{d \ln k}{dT}\right)_p = \frac{E_A}{RT^2}$$



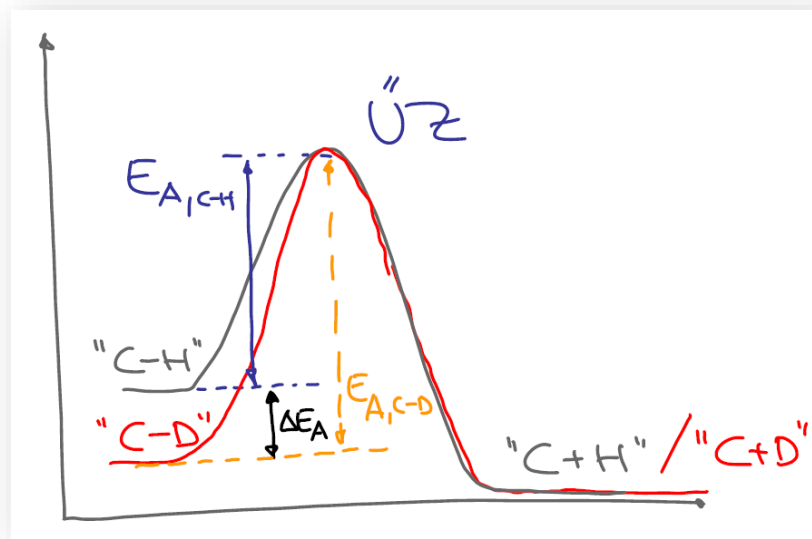
Svante Arrhenius (1859-1927)

- für $T = 298\text{K}$: $E_A = RT = 2.5 \text{ kJ/mol}$
- E_A bei zusammengesetzte Reaktionen
- Dreikörpereffekt und negative E_A

Primärer kinetischer Isotopeneffekt

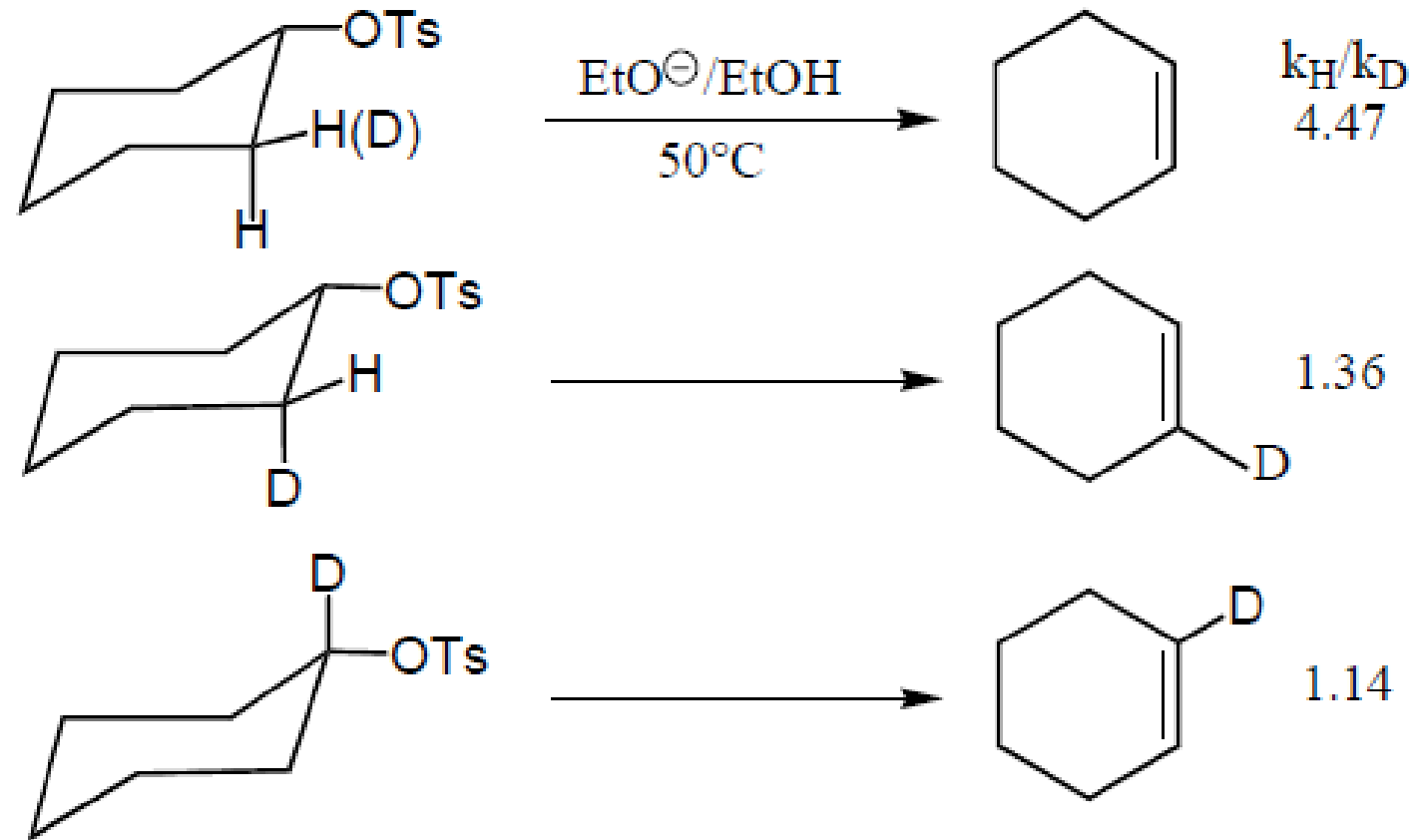


$$\begin{aligned} \frac{k_{C-H}}{k_{C-D}} &= \left(\frac{A_{C-H}}{A_{C-D}} \right) \exp \left(-\frac{1}{RT} (E_{A,C-H} - E_{A,C-D}) \right) \\ &= \left(\frac{A_{C-H}}{A_{C-D}} \right) \exp \left(+\frac{1}{RT} (E_{0,C-H} - E_{0,C-D}) \right) \\ &= \exp \left(+\frac{1}{RT} N_A h c \tilde{\nu} \left(1 - \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}} \right) \right) \end{aligned}$$

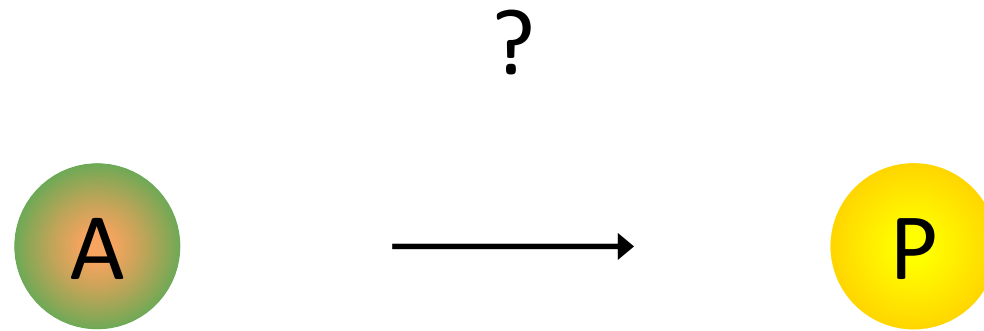


Nuclide	$k_{\text{light}} / k_{\text{heavy}}$ (at 25°C)
C-H/C-D	6 - 8
C-H/C-T	15 - 16
$^{12}\text{C} / ^{13}\text{C}$	1.04
$^{12}\text{C} / ^{14}\text{C}$	1.07
$^{14}\text{N} / ^{15}\text{N}$	1.03
$^{16}\text{O} / ^{18}\text{O}$	1.02
$^{32}\text{S} / ^{34}\text{S}$	1.01
$^{35}\text{Cl} / ^{37}\text{Cl}$	1.01

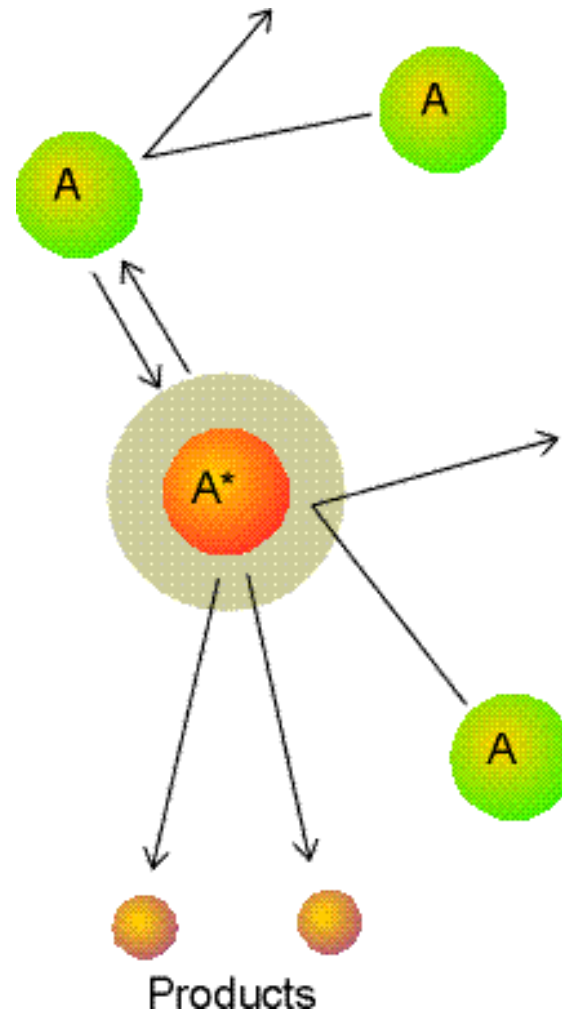
Kinetischer Isotopeneffekt zur Aufklärung von Reaktionsmechanismen



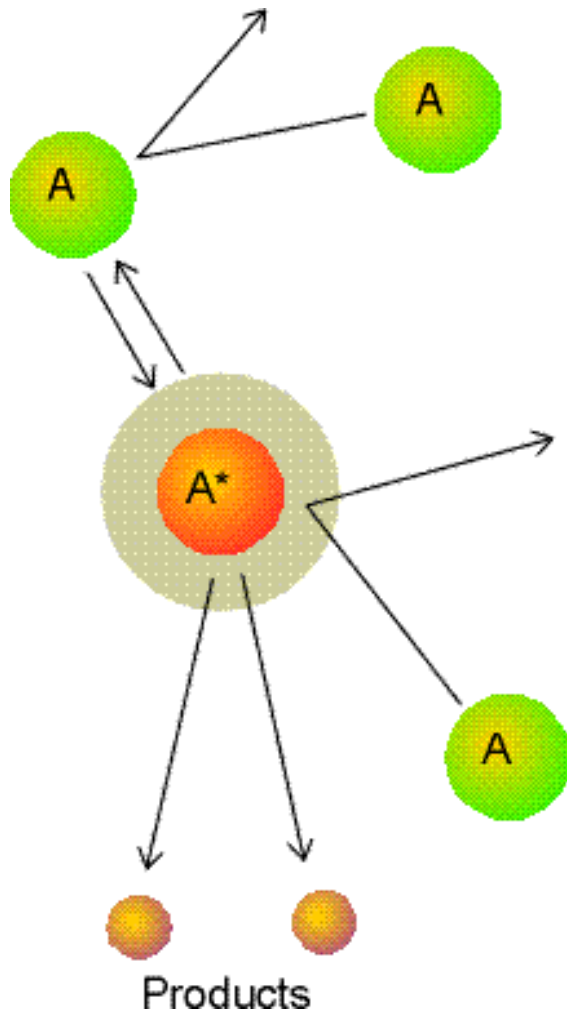
Theorie unimolekularer Reaktionen



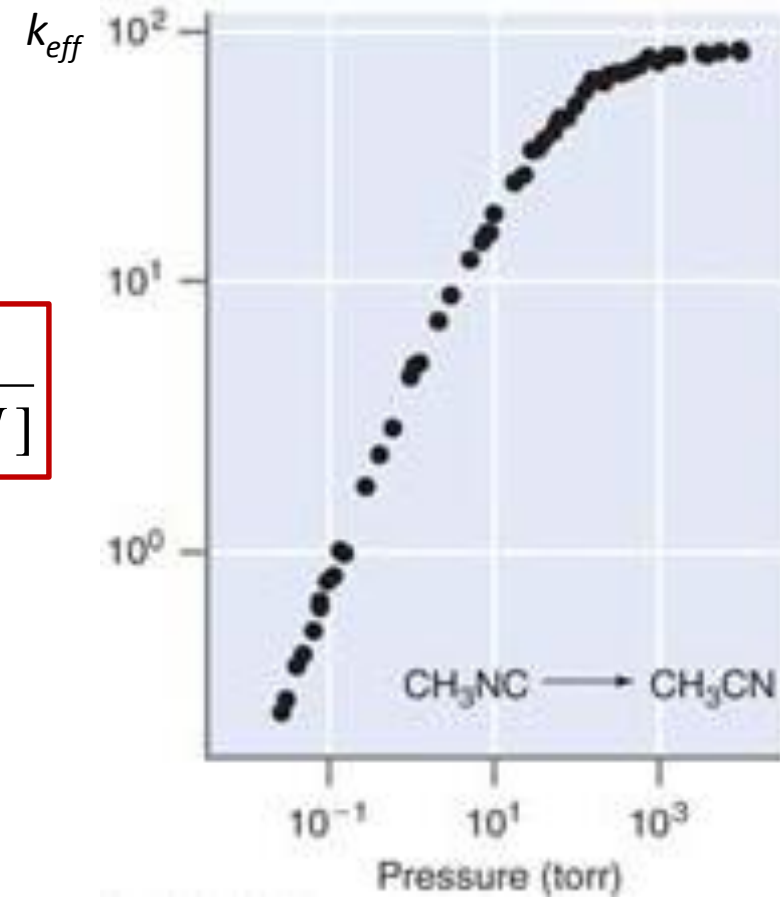
Theorie unimolekularer Reaktionen: Lindemann-Hinshelwood-Mechanismus



Theorie unimolekularer Reaktionen: Lindemann-Hinshelwood-Mechanismus

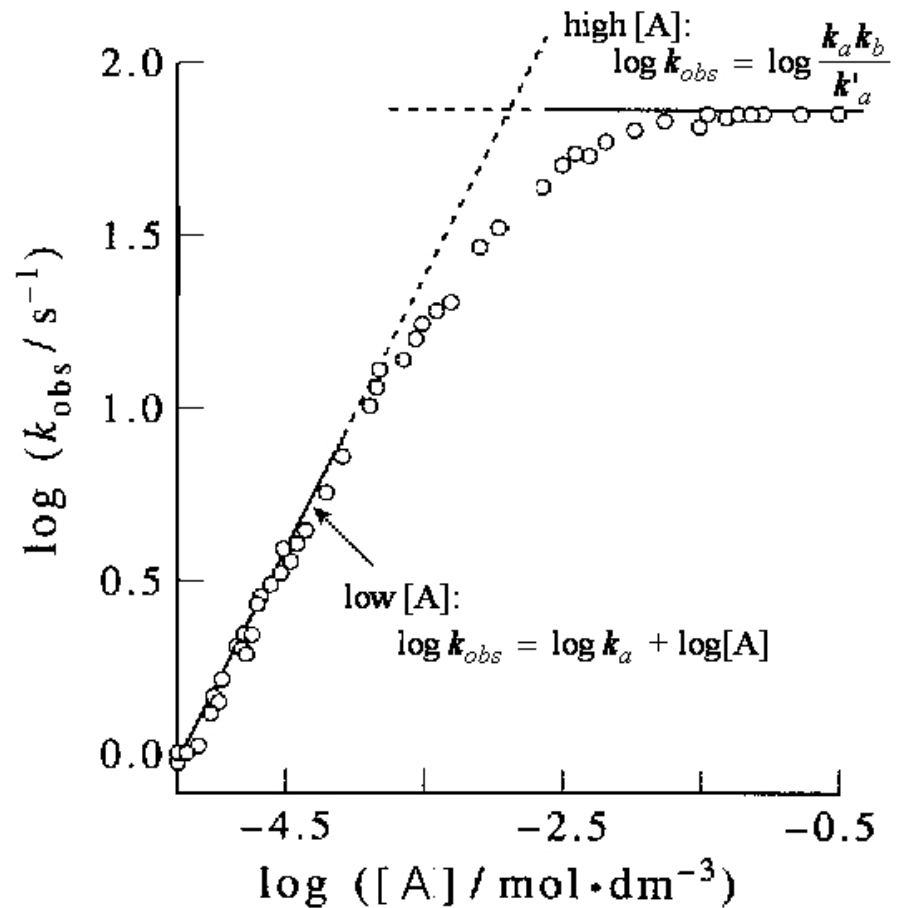


$$k_{eff} = \frac{k_{uni} k_1 [M]}{k_{uni} + k_{-1} [M]}$$



Engel & Reid, Thermodynamics

Theorie unimolekularer Reaktionen: Lindemann-Hinshelwood-Mechanismus



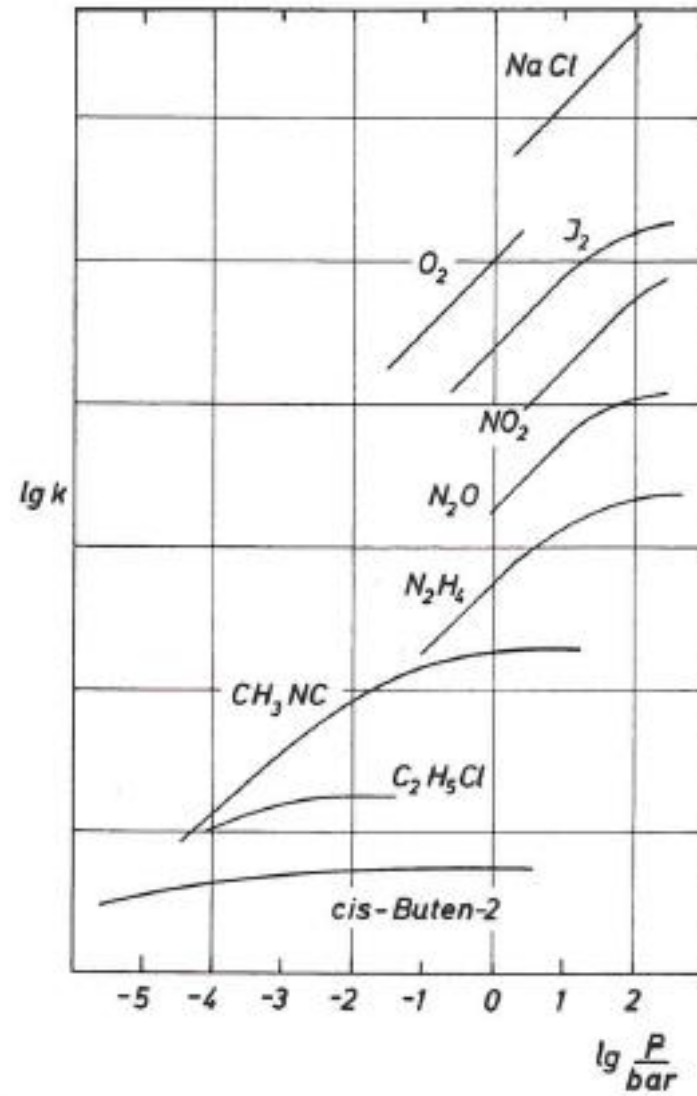


Abb. 28. „Fall-off“-Kurven für den unimolekularen Zerfall bzw. die Isomerisation (CH_3NC , cis-Buten-2) verschiedener Moleküle⁴⁹⁾:

Tab. 3. Geschwindigkeitskonstanten k_0 und k_∞ thermischer unimolekularer Reaktionen

Reaktion	Dissoziationsenergie D_0 bzw. Reaktionsenthalpie h_0 kJ mol^{-1}	T K	$\frac{k_0}{c_{\text{Ar}}}$ in $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ E_a in kJ mol^{-1}	k_∞ in s^{-1} E_a in kJ mol^{-1}
$\text{NaCl} \rightarrow \text{Na} + \text{Cl}$	408	2300–4800	$5 \cdot 10^{14} \exp\left(-\frac{335}{RT}\right)$	
$\text{O}_2 \rightarrow 2\text{O}$	494	5000–18000	$1,7 \cdot 10^{14} \exp\left(-\frac{460}{RT}\right)$ $k(\text{Ar:Kr:Xe:O}_2:\text{O}) \approx 1:2:6:20:60$	
$\text{J}_2 \rightarrow 2\text{J}$	149	1000–1600	$9,8 \cdot 10^{13} \exp\left(-\frac{127}{RT}\right)$ $k(\text{Ar:He:O}_2:\text{CO}_2) = 1:0,5:1,2:1,6$	$\approx 8 \cdot 10^{11} \exp\left(-\frac{149}{RT}\right)$
$\text{NO}_2 \rightarrow \text{NO} + \text{O}$	300,8	1450–2000	$1,1 \cdot 10^{16} \exp\left(-\frac{270}{RT}\right)$	$\approx 2 \cdot 10^{14} \exp\left(-\frac{301}{RT}\right)$
$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(^3\text{P})$	263 ¹⁾	1500–2500	$5 \cdot 10^{14} \exp\left(-\frac{243}{RT}\right)$	$1,3 \cdot 10^{11} \exp\left(-\frac{249}{RT}\right)$
$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$	207	950–1450	$2 \cdot 10^{16} \exp\left(-\frac{180}{RT}\right)$	$\geq 8 \cdot 10^{13} \exp\left(-\frac{200}{RT}\right)$
$\text{N}_2\text{H}_4 \rightarrow \text{NH}_3 + \text{NH}$	≈ 232	1280–1550	$4 \cdot 10^{15} \exp\left(-\frac{171}{RT}\right)$	$8 \cdot 10^{13} \exp\left(-\frac{232}{RT}\right)$
$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	161 ²⁾	673–773	$6,8 \cdot 10^{17} \exp\left(-\frac{133}{RT}\right)^3$	$\approx 2,7 \cdot 10^{14} \exp\left(-\frac{170}{RT}\right)$
$n\text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	110 ²⁾	533–573		$\approx 3,7 \cdot 10^{13} \exp\left(-\frac{131}{RT}\right)$
$\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$	$-70^2)$	473–533	$1 \cdot 10^{18} \exp\left(-\frac{152}{RT}\right)$ $k(\text{Ar:He:H}_2:\text{CH}_3\text{NC}) = 1:1,1:2,2:9,1$	$4 \cdot 10^{13} \exp\left(-\frac{161}{RT}\right)$

Lindemann-Hinshelwood-Mechanismus bei hohen Drücken

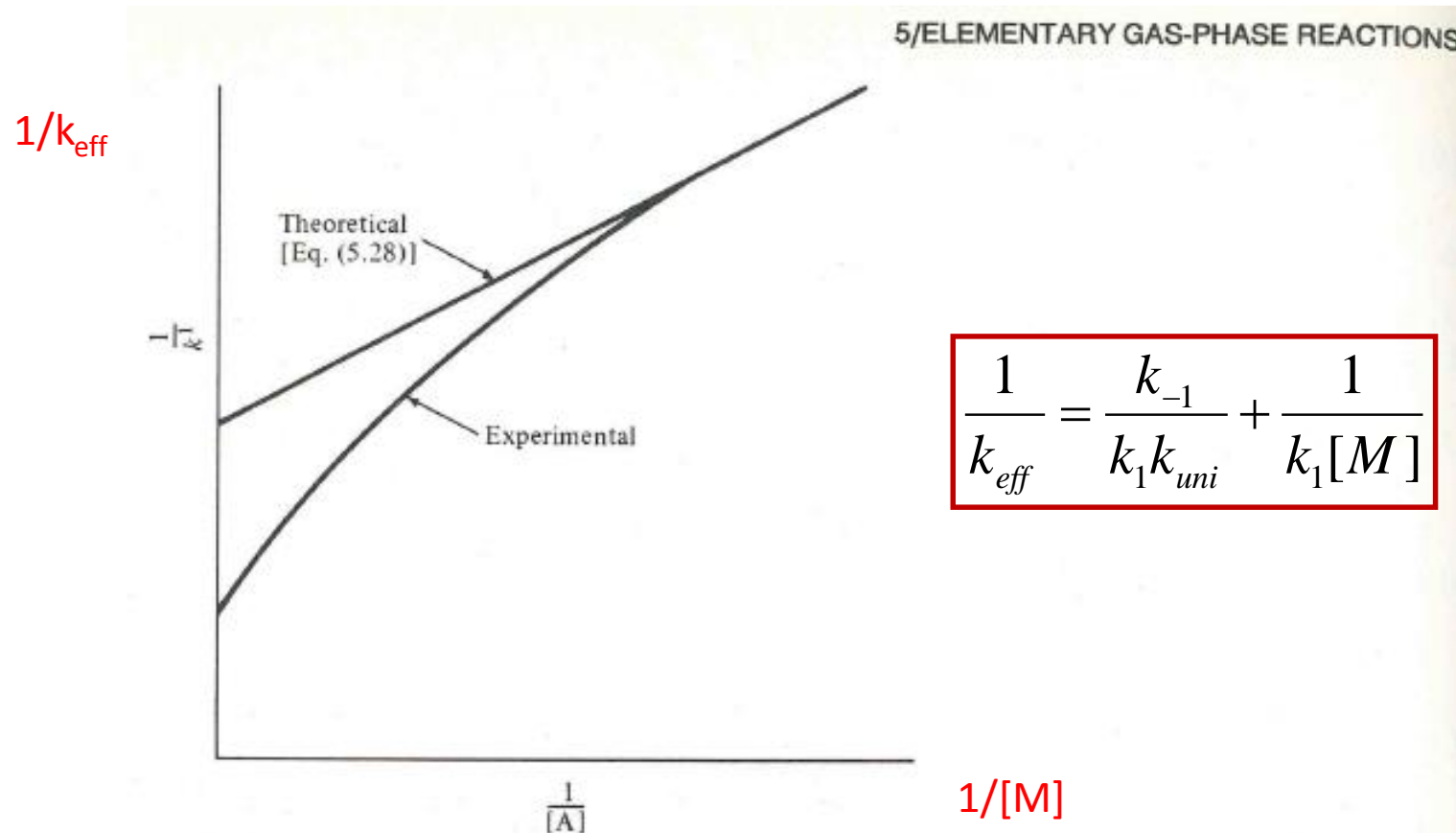
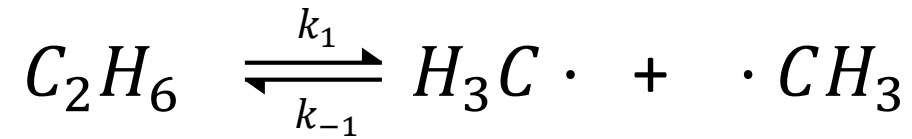


Figure 5.6 Schematic plots of $1/k^1$ versus $1/[A]$.

Laidler, Chemical Kinetics

- Modell von Slater, Kassel (gekoppelte Oszillatoren)
- Modell von Rice, Ramsperger, Kassel & Marcus (RRKM-Theorie)
(siehe Zusatzinformation zu VL 8)

Lindemann-Hinshelwood-Mechanismus bei Zerfalls/Rekombinationsreaktionen



$$K_1 = \frac{[CH_3]^2}{[C_2H_6]}$$

p ↑

$$v_1 = k_1 [C_2H_6]$$

$$v_{-1} = v_1 = k_{-1} K_1 [C_2H_6] = k_{-1} [CH_3]^2$$

p ↓

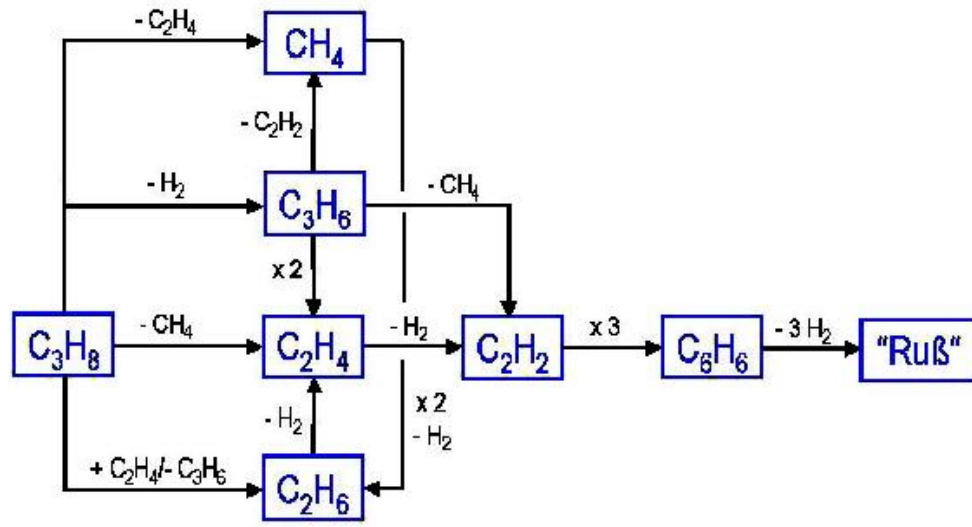
$$v_1 = k_1' [C_2H_6]^2$$

$$v_{-1} = v_1 = k_{-1}' K_1 [C_2H_6]^2 = k_{-1}' [CH_3]^2 [C_2H_6]$$

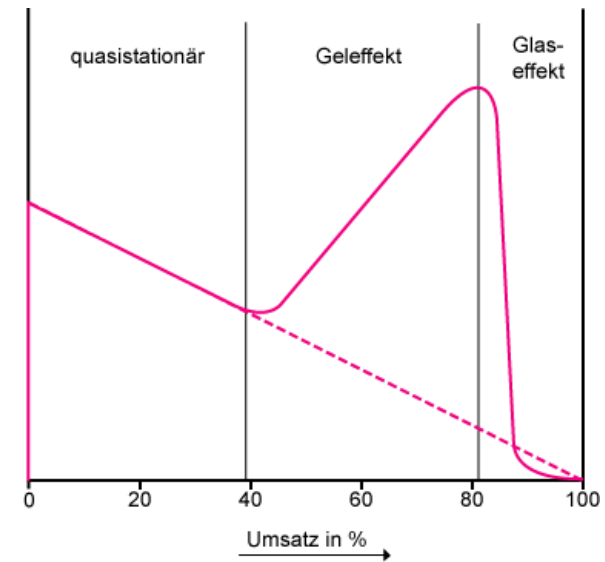
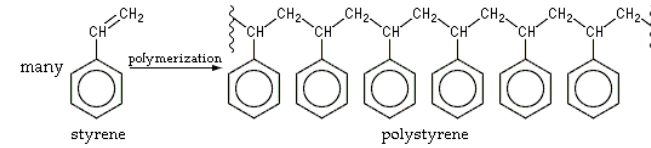


$$\alpha_{\text{Rekombination}} = \alpha_{\text{Zerfall}} + 1$$

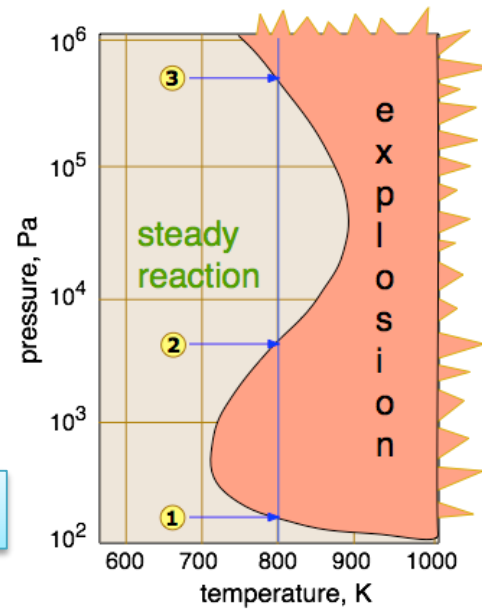
Kettenreaktionen



Pyrolyse



Polymerisation



Explosion