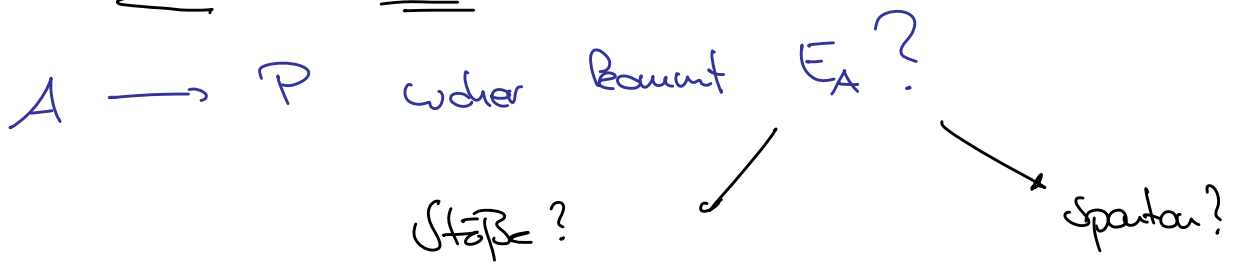


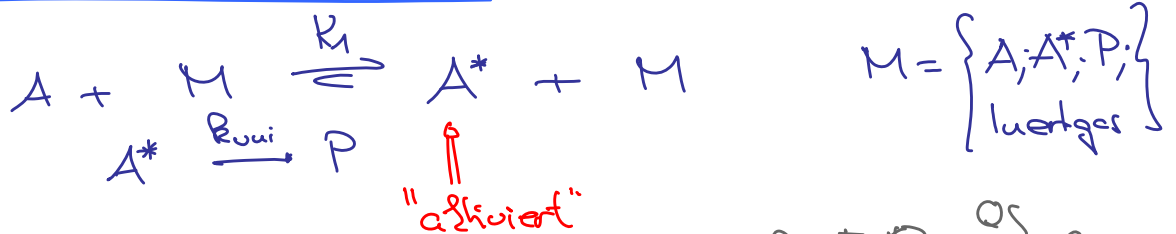
Intermediate: $\text{NO}_3, \text{NO} \Rightarrow R' = \frac{2k_1 k_2}{k_{-1} + k_2}$

7. Unimolekulare Reaktionen



Erinnerung: $Z_{AA} = \frac{1}{2} \sigma \cdot c \cdot \sqrt{2} \cdot (N_A \cdot [A])^2 \Rightarrow Z_{AA} \sim [A]^2 \sim p^2$

Modell: Lindemann, Christiansen (1921, Faraday-Meeting)



$$\Rightarrow [A^*]' = k_1 [A][M] - k_{-1} [A^*][M] - k_{\text{uni}} [A^*] \stackrel{0 \approx 0}{\approx} 0$$

$$\Rightarrow [A^*] = \frac{k_1 [A][M]}{k_{-1} [M] + k_{\text{uni}}}$$

$$[P]' = \frac{k_{\text{uni}} k_1 [M]}{k_{-1} [M] + k_{\text{uni}}} \cdot [A]$$

$=: R_{\text{eff}}$

$p \downarrow$ ($[M] \downarrow$)

$$\Rightarrow R_{\text{eff}} = k_1 [M] = \boxed{R_0}$$

geschwindigkeitsbest.

$$[P]' = k_1 [M][A]$$

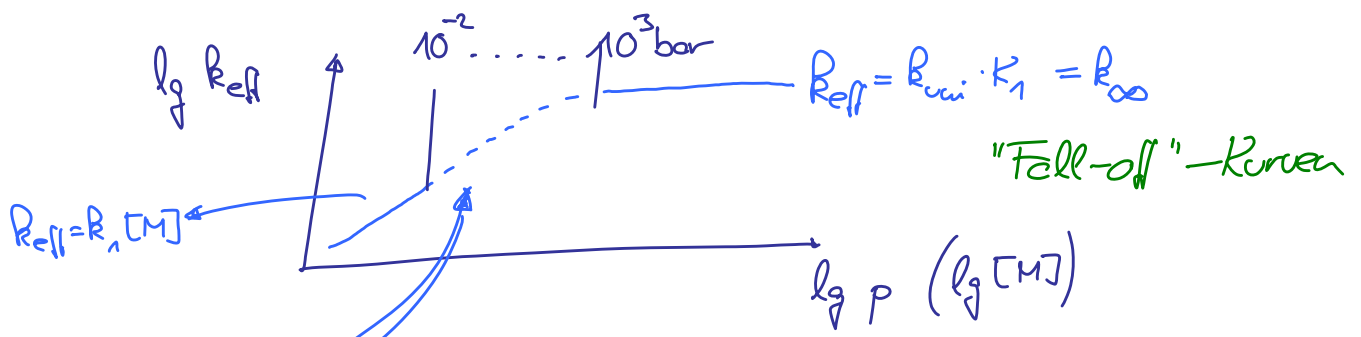
2. Ordnung

$p \uparrow$ ($[M] \uparrow$)

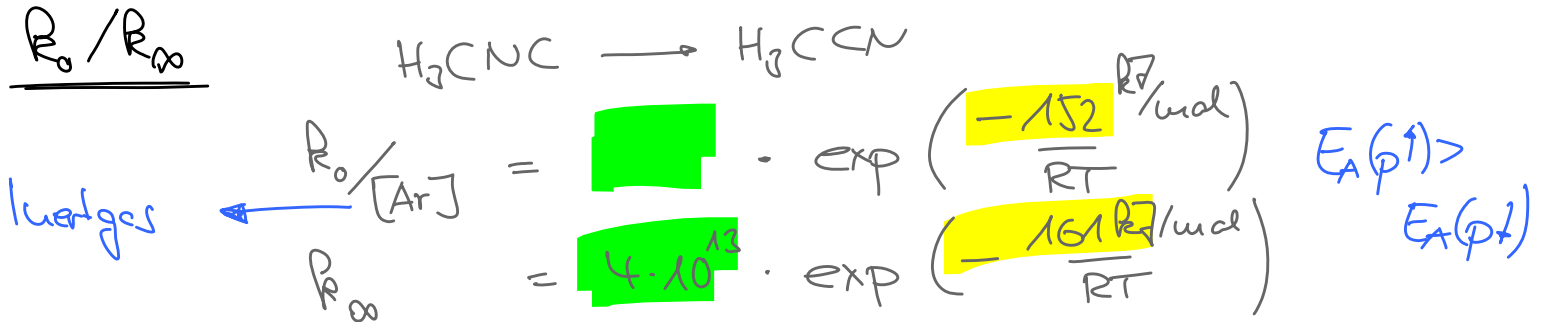
$$\Rightarrow R_{\text{eff}} = k_{\text{uni}} \cdot k_1 = \boxed{R_\infty}$$

$$[P]' = k_{\text{uni}} \cdot k_1 [A]$$

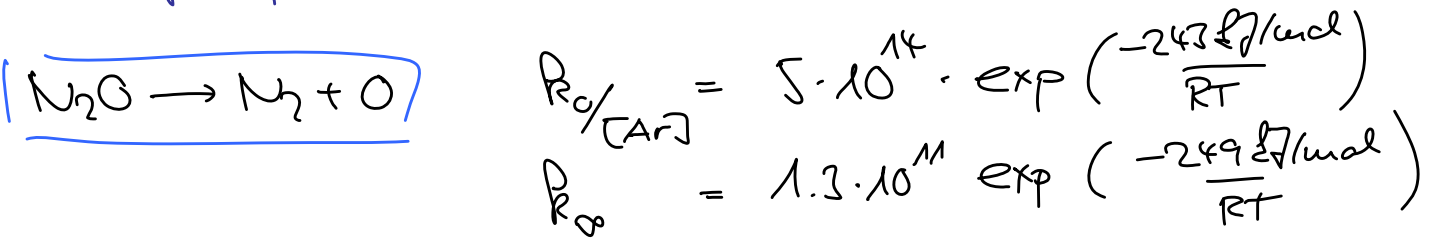
1. Ordnung



pt für große Moleküle



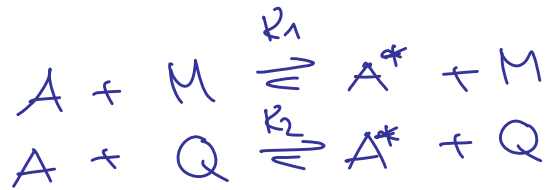
für p↓ : R_1 geschw. best. $\Rightarrow A \sim$ Stoßfaktor
 für p↑ : R_{uni} " $A \sim$ Frequenz (1350 cm^{-1})



$[E_A < D_0] \Rightarrow$ Lindemann-Hinshelwood LH (qualitativ)

LH in der Anwendung

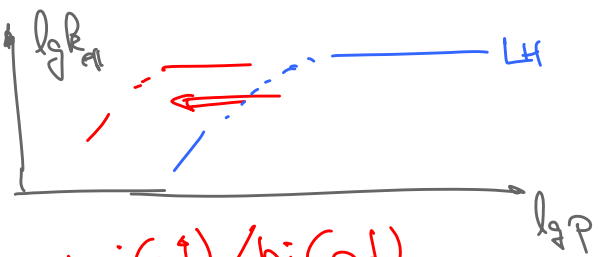
① + Luertgas



$\Rightarrow [P]' = \frac{R_{uni}(R_1[M] + R_2[Q])}{R_{uni} + R_{-1}[M] + R_{-2}[M]} \cdot [A]$

\rightarrow Energietransfer $A \leftrightarrow Q$

$\rightarrow R_{\infty}$

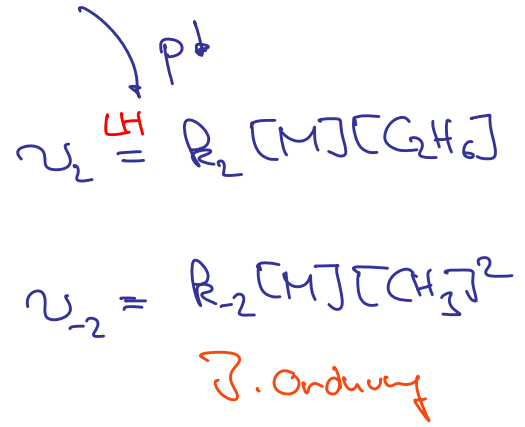
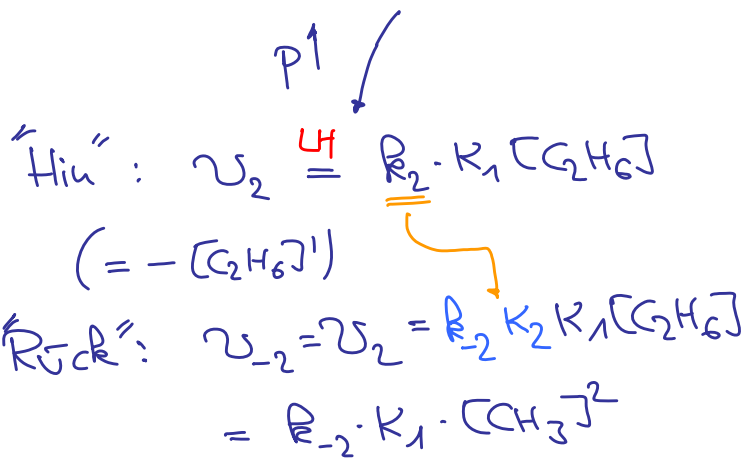


② Zerfall/radikal. Rekombination $\xrightarrow{uni(p \uparrow) / bi(p \downarrow)}$

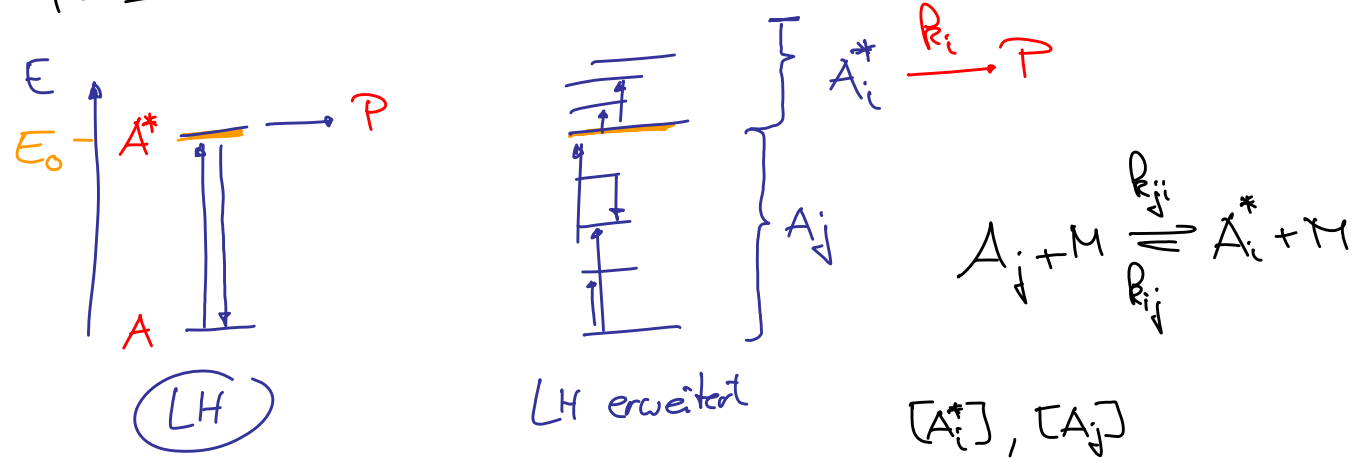


$\xleftarrow{bi(p \uparrow), ti(p \downarrow)}$

$$K_2 = \frac{[\text{CH}_3]^2}{[\text{C}_2\text{H}_6]}$$



LH "quantitativ"



Theoretische TD $\Rightarrow \nu_p = \sum R_i [A_i^*]$
 $\frac{[A_i^*]}{[A]} = q_{A_i^*}$
 Theoretische Chemie $\Rightarrow E_i^*, E_j \Rightarrow R_i$

Vernachlässigung von $A_j \Rightarrow$ GG-Modell, "harte Stoffe"

A) Modell gekoppelter Orbitale

E-Transfer zwischen Orbitalen; Annahme: gleiche Frequenz ν

$E_{ges} = n \cdot h\nu$
 Gesamtzahl der Energiequanten im Molekül

$\Rightarrow n$ verteilen auf S Orbitale: $N = \frac{(n+s-1)!}{n!(s-1)!}$ (Hollenz (ATKus))
 (=FGüb)

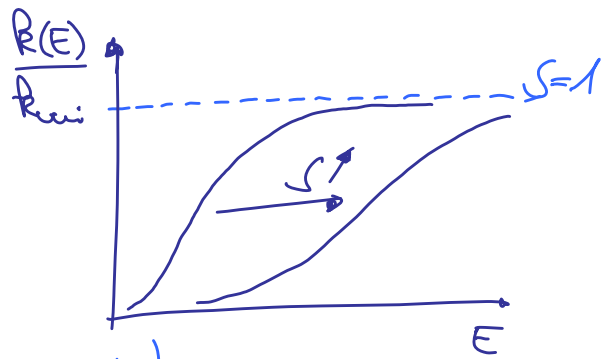
Randbedingung: $E_0 = n^* h\nu \Rightarrow$ in kritischer Mode

$(n^* \geq n)$
 \Rightarrow Besetzung $P = \frac{A^*}{A} \approx \left(\frac{n-n^*}{n}\right)^{s-1}$ | $E_{ges} = n h\nu$
 Kritische Energie

$$\Rightarrow P(E) = \left(\frac{E-E_0}{E}\right)^{s-1}$$

$$\Rightarrow R'_{uni}(E) = R_{uni} \cdot \left(\frac{E-E_0}{E}\right)^{s-1}$$

(LH)



(Jünger, Troe; \Rightarrow nicht-GG; Anharmonizität)

ⓑ Stochistische Theorie (StatTD, $\bar{U}T$)

RRKM

Rice, Ramsperger, Passel, Marcus



(Transmission)

$A \neq$ Energie in kritischer Mode

$$R'_{\infty} = \underbrace{\kappa}_{(bei\ 298K)\ 200\text{cm}^{-1}} \cdot \underbrace{\frac{R_g T}{h}}_{\text{GG-Konstante}} \cdot e^{-E_0/RT} \cdot \frac{q_{vib}^{\ddagger}}{q_{vib}^*}$$