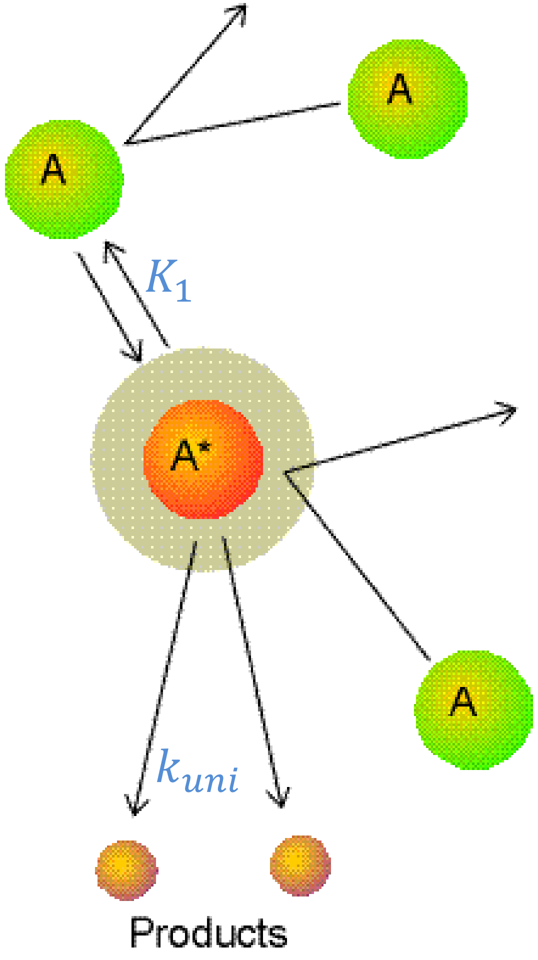
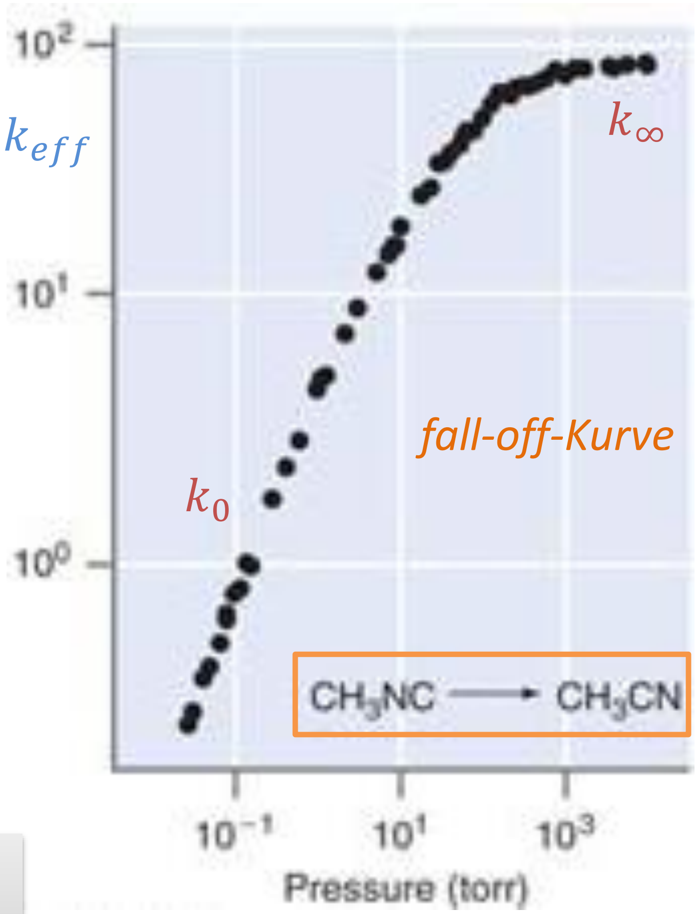
Theorie unimolekularer Reaktionen: Lindemann-Hinshelwood-Mechanismus



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

$p \uparrow: k_{eff} \rightarrow K_1 k_{uni}$

$p \downarrow: k_{eff} \rightarrow k_1[M]$

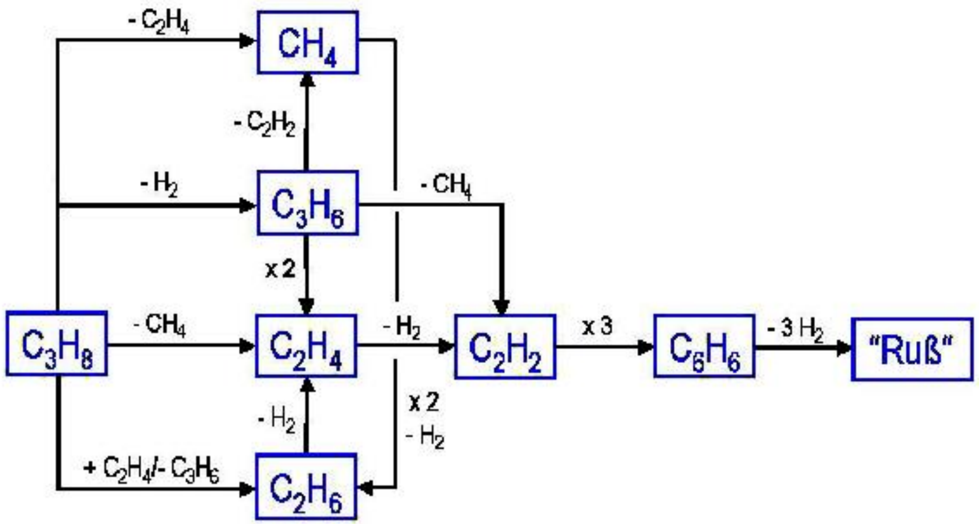


- LH bei Zerfall/Rekombination
- E_A für $k_0/[M]$ und k_∞
- RRK(M)-Erweiterung

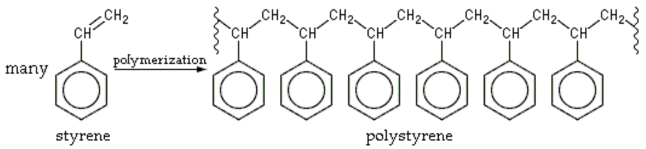
Atkins, Physical Chemistry, 8th Ed.

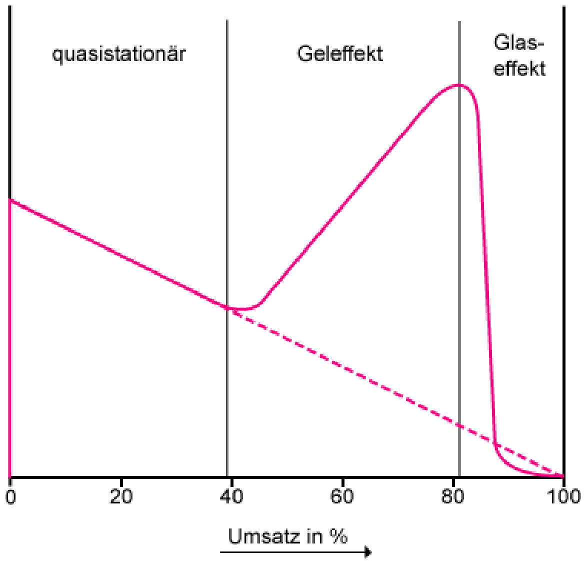
Engel & Reid, Thermodynamics

Kettenreaktionen

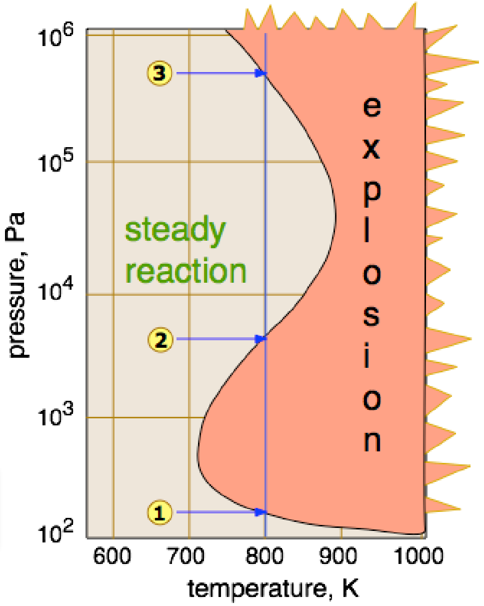


Pyrolyse



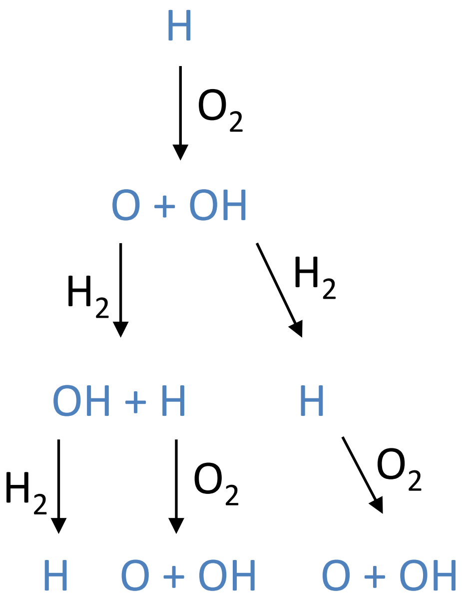


Polymerisation

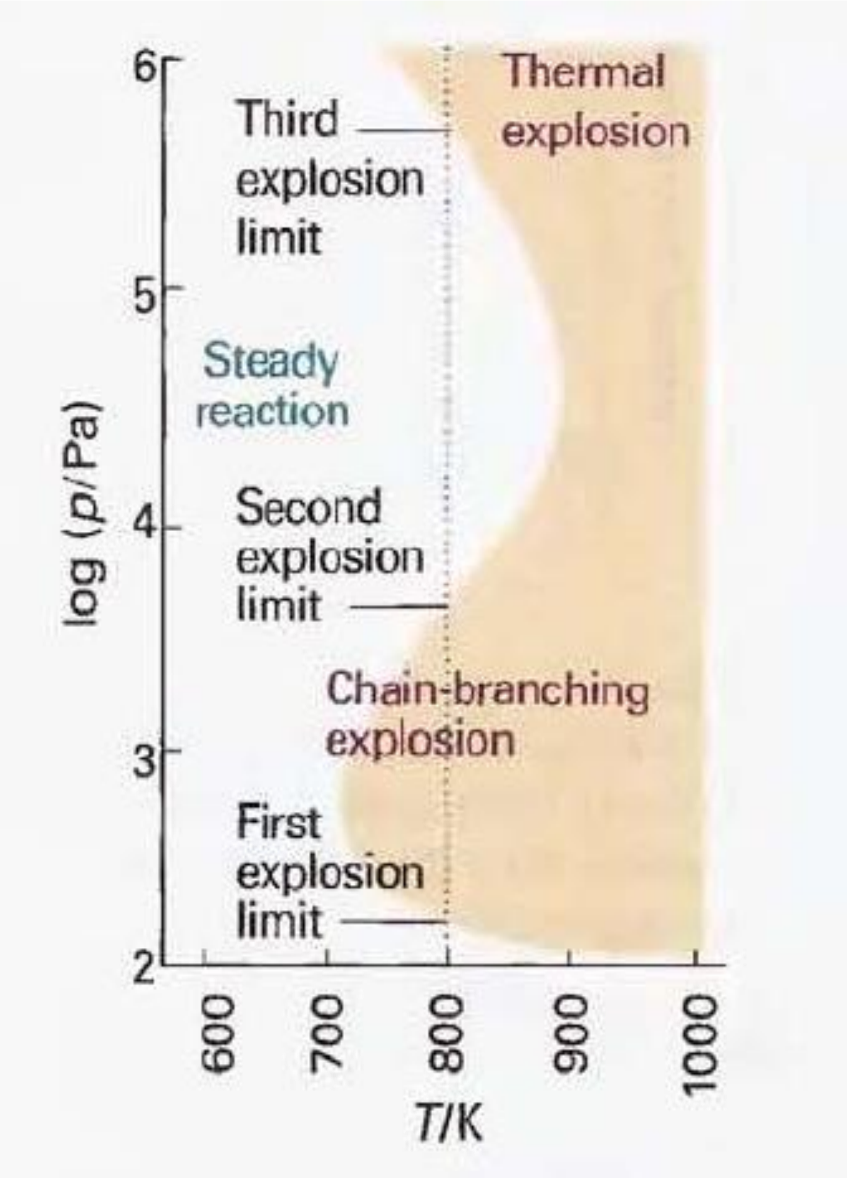


Explosion

Explosionen

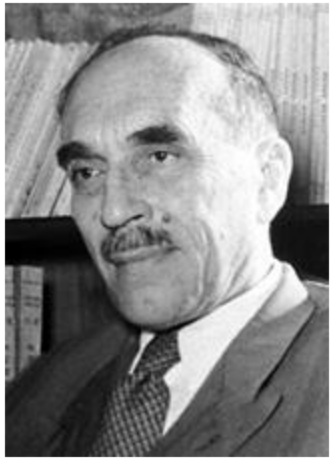


H, O, OH = Kettenträger



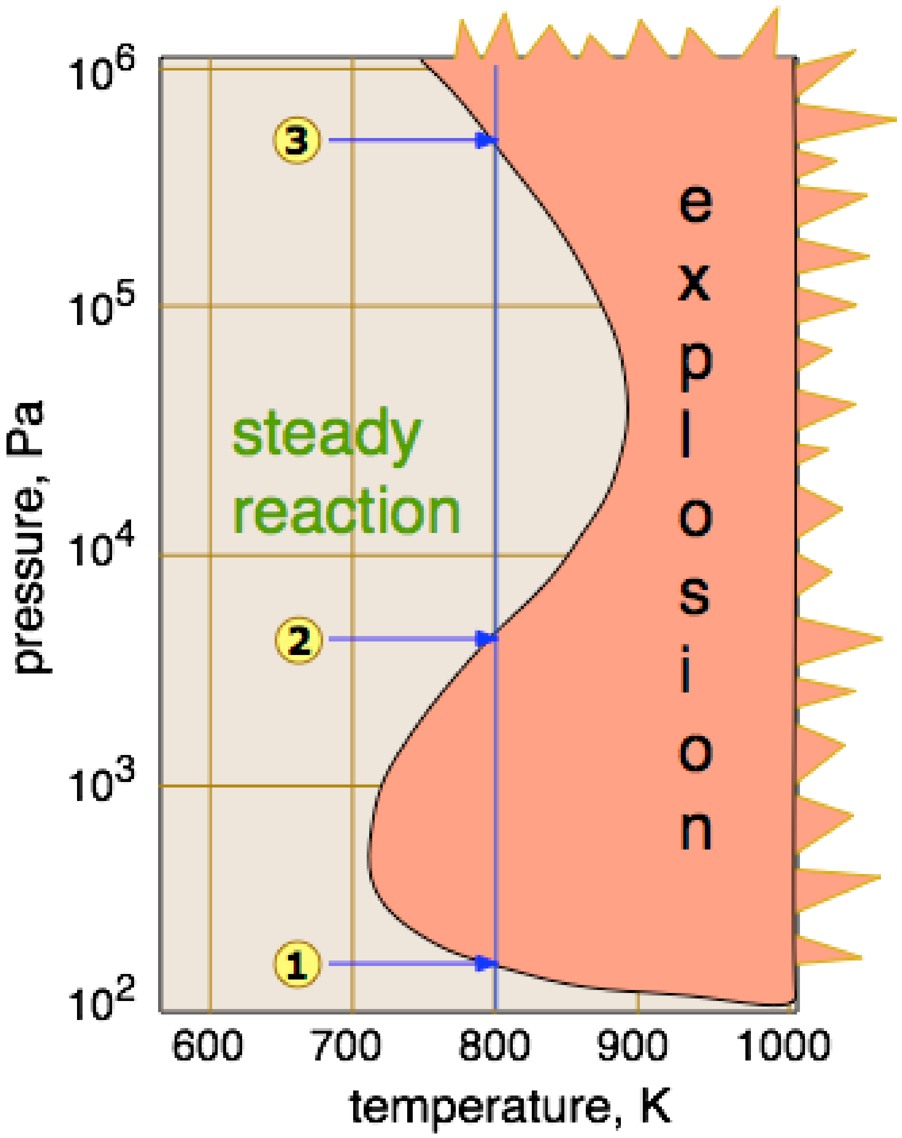
NP für Chemie, 1956

Sir Cyril Hinshelwood
(1897-1967)



Nikolay Semjonow
(1896-1986)

Explosionsgrenzen der Knallgasreaktion



Start

$$H_2 \rightarrow H + H$$

$$H_2 + O_2 + W \rightarrow OH + OH + W$$

Fortpflanzung

$$H_2 + OH \rightarrow H_2O + H$$

Verzweigung

$$O_2 + H \rightarrow O + OH$$

$$H_2 + O \rightarrow OH + H$$

gleichzeitig

Abbruch ($p \downarrow$)

$$H + W \rightarrow \frac{1}{2} H_2 + W \quad (linear)$$

Bei $p \uparrow$:

$$H + O_2 + M \rightarrow HO_2 + M \quad (Abbruch)$$ > (2) und < (3)

$$HO_2 + H_2 \rightarrow H_2O_2 + H \quad (Verzweigung)$$ > (3)

Kinetik der Knallgasreaktion

$H_2 + OH \rightarrow H_2O + H$ (1)

$O_2 + H \rightarrow O + OH$ (2)

$H_2 + O \rightarrow OH + H$ (3)

$H + W \rightarrow \frac{1}{2}H_2 + W$ (4)

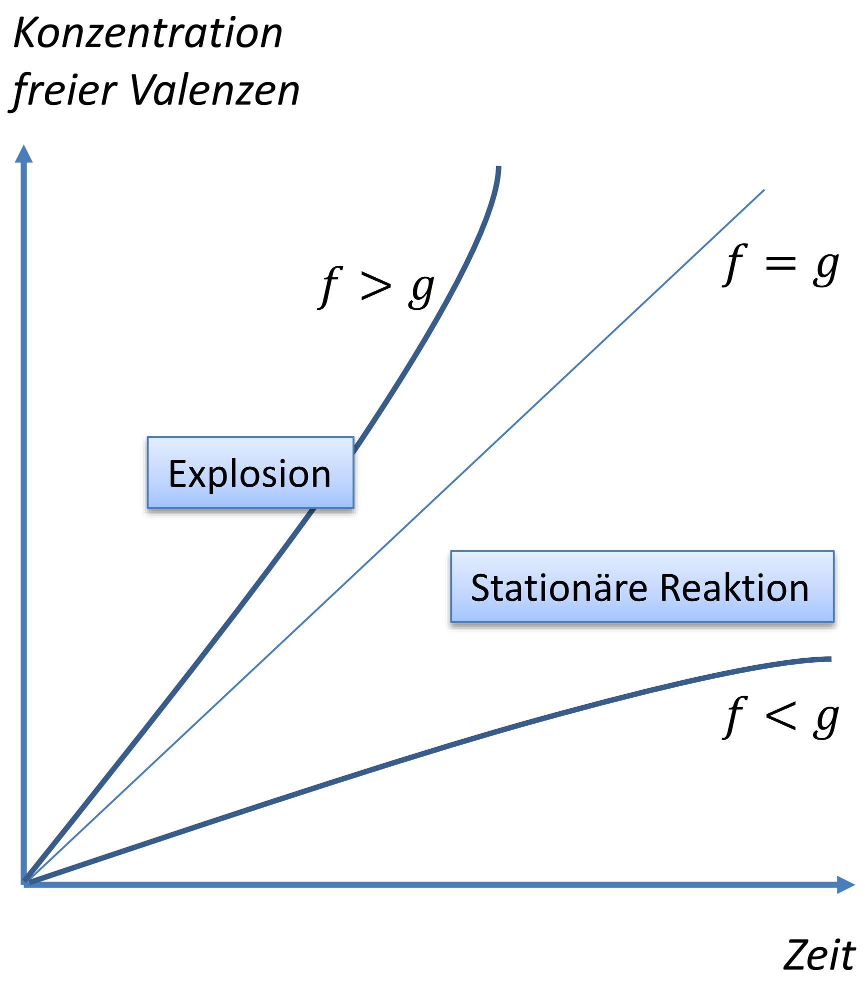
$(Abbruch, Wandreaktion, linear)$

$H + O_2 + M \rightarrow HO_2 + M$ (5)

$(Abbruch, Gasphasenreaktion)$

$$c_n' = v_S + (f - g)c_n$$

$f = 2k_2[O_2], \quad g = k_4 + k_5[O_2][M]$



Radikalische Polymerisation

$$\frac{dR_1}{dt} = v_S - k_W[R_1][\mathrm{M}] - k_A[R_1]\sum_i [R_i]$$

$$\frac{dR_2}{dt} = k_W[R_1][\mathrm{M}] - k_W [R_2][\mathrm{M}] - k_A[R_2]\sum_i [R_i]$$

$$\frac{dR_3}{dt} = k_W[R_2][\mathrm{M}] - k_W [R_3][\mathrm{M}] - k_A[R_3]\sum_i [R_i]$$

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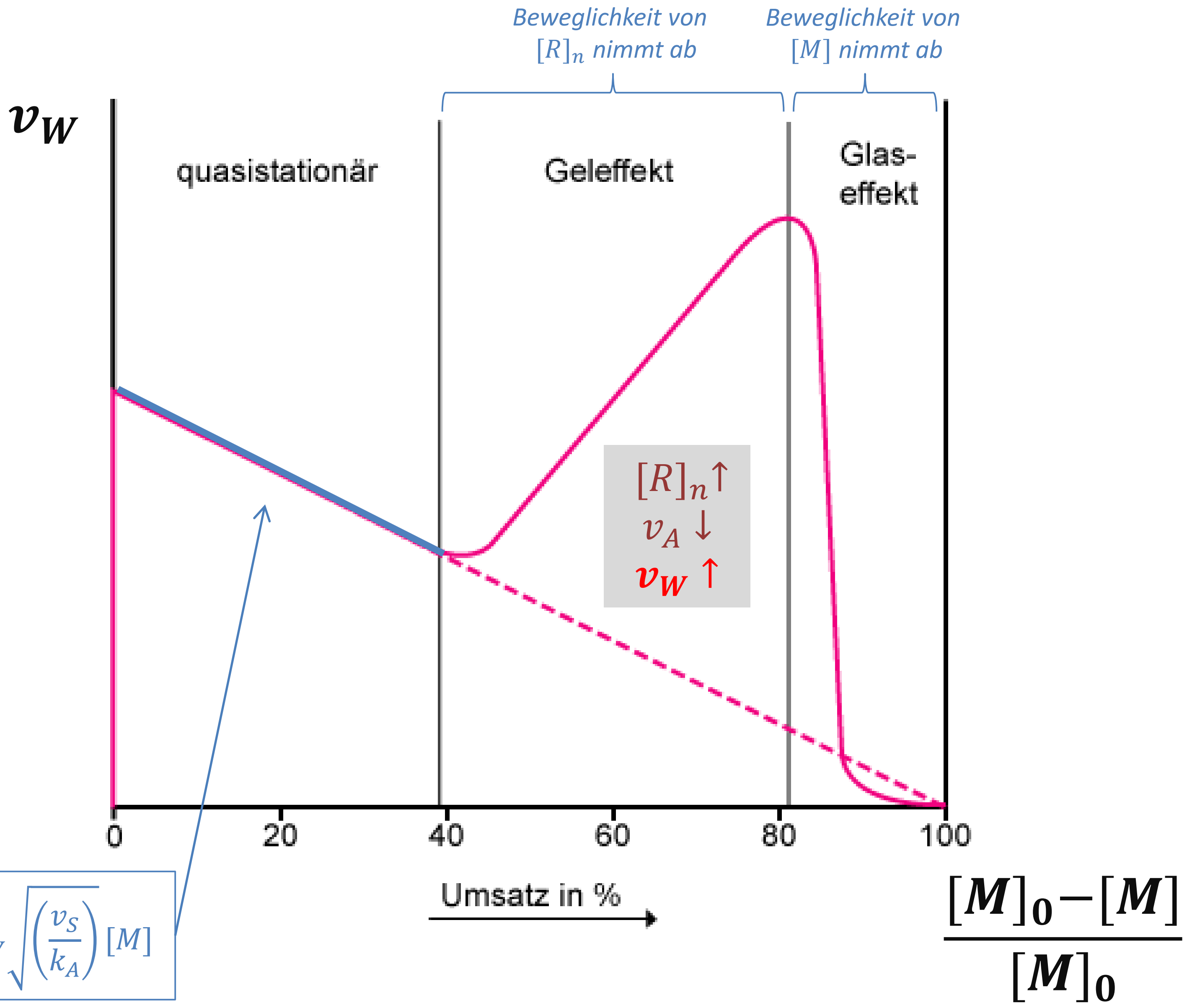
$$\frac{dR_n}{dt} = k_W[R_{n-1}][\mathrm{M}] - k_A[R_n]\sum_i [R_i]$$

$$0 \approx v_S - k_A \sum_j [R_j] \sum_i [R_i]$$

$$(v_S = v_A)$$

Radikalische Polymerisation: Trommsdorf-Norrish-Effekt



$$v_W = \frac{-d[M]}{dt} = k_W \sqrt{\left(\frac{v_S}{k_A}\right)}[M]$$

Schrittweise Polymerisation

Polymerisationsgrad

$$f = \frac{c_0 - c}{c_0}$$

Mittlere Kettenlänge:

$$< n > = \frac{c_0}{c} = \frac{1}{1-f} = 1 + c_0 kt$$

Konzentration des n-mers:

$$[M_n] = [M]_0 f^{n-1}(1-f)^2$$