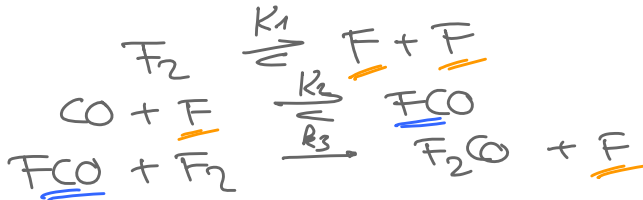




(1) Elementarreaktion  $\rightarrow$  Spektroskopie



(2) Intermediäre

$$[FCO]' = +R_2[CO][F] - R_{-2}[FCO] - R_3[FCO][F_2] \approx 0$$

$$[F]' = 2R_1[F_2] - 2R_{-1}[F]^2 - R_2[CO][F] + R_{-2}[FCO] + R_3[FCO][F_2] \approx 0$$

$$\rightarrow [F] = \sqrt{K_1[F_2]} \approx 0 \quad (= -[FCO]')$$

$$(3) [F_2CO]' = R_3[FCO][F_2] = \sqrt{K_1} R_2 R_3 \frac{[CO][F_2]^{3/2}}{R_{-2} + R_3[F_2]}$$

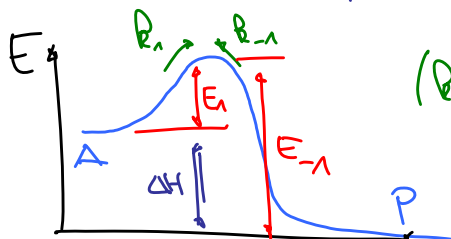
Schnelles GG  $K_2$ :  $[F_2CO]' = \sqrt{K_1} K_2 R_3 [CO][F_2]^{3/2}$

### J. Arrhenius

van't Hoff:

$$\left( \frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta H}{RT^2} \quad K = \frac{R_{f1}}{R_{r1}}$$

$$\Rightarrow \left( \frac{\partial \ln R_{f1}}{\partial T} \right)_p - \left( \frac{\partial \ln R_{r1}}{\partial T} \right)_p = \frac{E_{f1}}{RT^2} - \frac{E_{r1}}{RT^2} \quad \Delta H = E_{f1} - E_{r1}$$

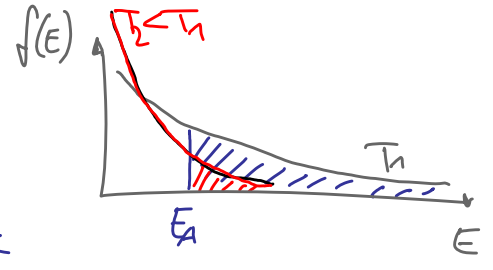


$\Rightarrow E_{f1}, E_{r1} :=$  Aktivierungsenergie

wil  $\left( \frac{\partial \ln R_{f1}}{\partial T} \right)_p = \frac{E_{f1}}{RT^2} \Rightarrow \ln R_{f1} + C = -\frac{E_{f1}}{RT}$

$$R_{f1} = \underbrace{e^{-C}}_A \cdot e^{-E_{f1}/RT}$$

$\Rightarrow R(T) = A \cdot e^{-E_A/RT}$   
 Stoßfaktor  
 Frequenzfaktor  
 Moleküle mit  
 ausreichend Energie  
 ( $E_A \sim 50-250 \text{ kJ/mol}$ )



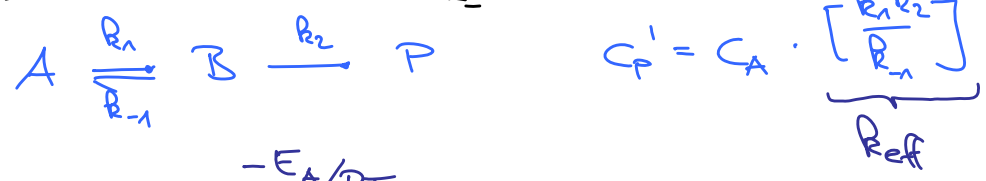
$\Rightarrow E_A(T)?$

$\frac{\partial \ln k}{\partial T} = \frac{E_A}{RT^2}$ ,  $k = A' \cdot T^m \cdot e^{-E_0/RT}$

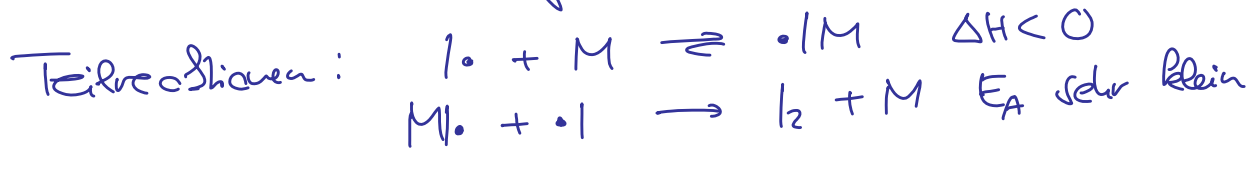
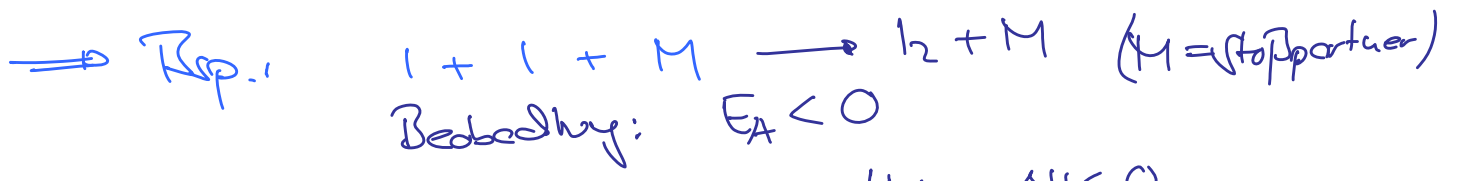
$\Rightarrow \frac{\partial}{\partial T} (\ln A' + m \ln T - E_0/RT) = \frac{m}{T} + \frac{E_0}{RT^2} = \frac{E_A}{RT^2}$

$\Rightarrow E_A = E_0 + mRT$  ( $E_0 \hat{=} \text{Akt.energie für } T \rightarrow 0K$ )

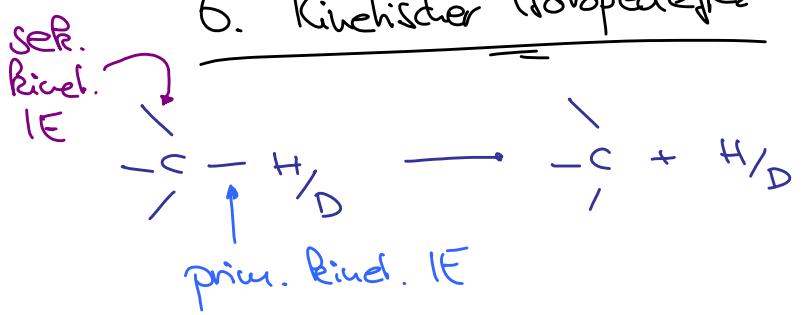
$E_A$  bei zusammengeordneten Reaktionen



$k_{\text{eff}} = A \cdot e^{-E_A/RT} = \frac{(A_1 \cdot e^{-E_1/RT}) (A_2 \cdot e^{-E_2/RT})}{(A_{-1} \cdot e^{-E_{-1}/RT})} = A \cdot e^{-1/RT (E_1 + E_2 - E_{-1})}$   
 $\Delta H_1 + E_2$



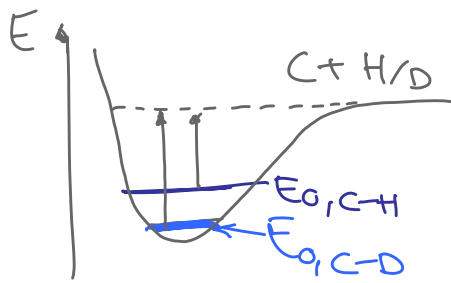
6. Kinetischer Isotopeneffekt



$k_{C-H} > k_{C-D}$

① Nullpunktenergie

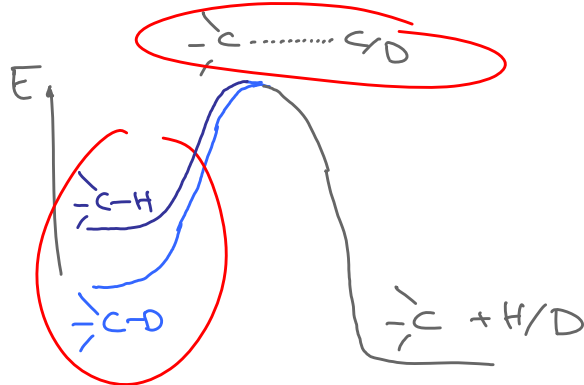
$$\mu = \frac{m_1 m_2}{m_1 + m_2} \begin{array}{l} \nearrow \text{C-H} \quad \frac{12}{13} \\ \searrow \text{C-D} \quad \frac{14}{14} \end{array}$$



$$E = \hbar \omega \left( v + \frac{1}{2} \right)$$

↑  
 $\sqrt{\frac{k}{\mu}}$  ← Federkonstante

② Übergangszustand



$$\mu_{C-D} > \mu_{C-H}$$

$$E_{0, C-D} < E_{0, C-H}$$

$$E_{A, C-D} > E_{A, C-H}$$

$$\Rightarrow \Delta E_A = E_{A, C-D} - E_{A, C-H} = E_{0, C-H} - E_{0, C-D}$$

$$= \frac{1}{2} \hbar \omega (\omega_{C-H} - \omega_{C-D}) \cdot N_A \quad \left| \begin{array}{l} \text{Spektroskopie} \\ \text{liefert } \omega_C, \omega_D \end{array} \right.$$

$$= \frac{1}{2} h c (\tilde{\nu}_{C-H} - \tilde{\nu}_{C-D}) \cdot N_A$$

$$\Rightarrow \Delta E_A = \frac{1}{2} h c N_A \tilde{\nu}_{C-H} \left( 1 - \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}} \right)$$

wit:  $\frac{\tilde{\nu}_{C-D}}{\tilde{\nu}_{C-H}} = \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}}$  →

$$\frac{k_{C-H}}{k_{C-D}} = \left( \frac{A_{C-H}}{A_{C-D}} \right) \cdot e^{-\frac{1}{RT} \left( \frac{1}{2} h c N_A \tilde{\nu}_{C-H} \left( 1 - \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}} \right) \right)}$$

mit Arrhenius

bei  $T = 298 K \Rightarrow \frac{k_{C-H}}{k_{C-D}} \sim 7$

bei  $T \uparrow \Rightarrow$  prim. kin. IE nimmt ab  
 (↳ bei  $T \uparrow \Rightarrow$  angeregte Schwingungsniveaus)

Sek. kin. IE  
 $\sim 0.5 \dots 1.5$   
 keine T-Abh.