

**Lösungsvorschläge zu den Übungsaufgaben
der Wahlpflichtvorlesung Reaktionskinetik SS 2013**
ohne Gewähr

Blatt 3

Aufgabe 9

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_{-2}[\text{H}][\text{HBr}] - 2k_{-1}[\text{Br}]^2 = 0 \quad (\text{I})$$

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_{-2}[\text{H}][\text{HBr}] = 0 \quad (\text{II})$$

aus (II) :

$$[\text{H}]_{\text{ss}} = \frac{k_2[\text{H}_2]}{k_3[\text{Br}_2] + k_{-2}[\text{HBr}]} [\text{Br}]_{\text{ss}}$$

(I) + (II) :

$$[\text{Br}]_{\text{ss}} = \left\{ \frac{k_1}{k_{-1}} [\text{Br}_2] \right\}^{1/2}$$

$$[\text{H}]_{\text{ss}} = \frac{k_2[\text{H}_2]}{k_3[\text{Br}_2] + k_{-2}[\text{HBr}]} \left\{ \frac{k_1}{k_{-1}} [\text{Br}_2] \right\}^{1/2}$$

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + [\text{H}](k_3[\text{Br}_2] - k_{-2}[\text{HBr}])$$

$$= k_2[\text{Br}]_{\text{ss}}[\text{H}_2] + \frac{k_2[\text{H}_2]}{k_3[\text{Br}_2] + k_{-2}[\text{HBr}]} [\text{Br}]_{\text{ss}} (k_3[\text{Br}_2] - k_{-2}[\text{HBr}])$$

$$= k_2[\text{Br}]_{\text{ss}}[\text{H}_2] \left(1 + \frac{k_3[\text{Br}_2] - k_{-2}[\text{HBr}]}{k_3[\text{Br}_2] + k_{-2}[\text{HBr}]} \right)$$

$$= k_2 \left\{ \frac{k_1}{k_{-1}} [\text{Br}_2] \right\}^{1/2} [\text{H}_2] \frac{2}{1 + \frac{k_{-2}}{k_3} \frac{[\text{HBr}]}{[\text{Br}_2]}} \quad \text{entspricht formal empirischem ZG}$$

$$\Rightarrow k = 2k_2 \left\{ \frac{k_1}{k_{-1}} \right\}^{1/2}$$

$$\Rightarrow k' = \frac{k_{-2}}{k_3}$$

Aufgabe 10

$$k_{\text{beob}} = \frac{k_2 k_1 k_3}{k_{-2} k_{-1}} = \frac{A_2 A_1 A_3}{A_{-2} A_{-1}} \exp\left(-\frac{1}{RT} (E_{a,2} + E_{a,1} + E_{a,3} - E_{a,-2} - E_{a,-1})\right)$$

$$E_{a,1} - E_{a,-1} = \Delta H_{\text{assoz}}$$

$$\Rightarrow E_{a,\text{beob}} = E_{a,2} + E_{a,3} - E_{a,-2} + \Delta H_{\text{assoz}}$$

$$\Rightarrow E_{a,2} = -3,8 \text{ kcal/mol}$$