

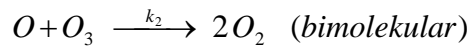
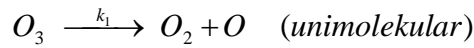
Übungsaufgaben zur Vorlesung Physikalische Chemie I – Kinetik

Musterlösung

Blatt 3

WS 2012/13

1.)



für [O] soll Quasistationarität angenommen werden, d. h. $\frac{d[O]}{dt} \approx 0$

$$\frac{d[O_3]}{dt} = -k_1[O_3] - k_2[O][O_3]$$

$$\frac{d[O_2]}{dt} = k_1[O_3] + 2k_2[O][O_3]$$

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O][O_3] \approx 0$$

daraus ergibt sich:

$$[O]_{QS} = \frac{k_1[O_3]}{k_2[O_3]} = \frac{k_1}{k_2}$$

und damit

$$\begin{aligned} \frac{d[O_3]}{dt} &= -k_1[O_3] - k_2[O]_{QS}[O_3] \\ &= -k_1[O_3] - k_2 \frac{k_1}{k_2} [O_3] \\ &= -2k_1[O_3] \end{aligned}$$

Integrieren führt auf

$$\begin{aligned} \int_{[O_3]_0}^{[O_3]} \frac{d[O_3]}{[O_3]} &= -2 \int_0^t k_1 dt \\ \ln \frac{[O_3]}{[O_3]_0} &= -2k_1 t \\ [O_3] &= [O_3]_0 \cdot \exp(-2k_1 t) \end{aligned}$$

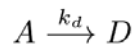
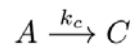
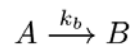
für [O₂] ergibt sich analog

$$\begin{aligned} \frac{d[O_2]}{dt} &= k_1[O_3] + 2k_2[O]_{QS}[O_3] \\ &= k_1[O_3] + 2k_2 \frac{k_1}{k_2} [O_3] \\ &= 3k_1[O_3] \\ &= 3k_1[O_3]_0 \cdot \exp(-2k_1 t) \end{aligned}$$

Integrieren führt auf

$$\begin{aligned} [O_2] &= \int_0^t 3k_1 [O_3]_0 \cdot \exp(-2k_1 t) dt \\ &= \left[-\frac{3}{2} [O_3]_0 \cdot \exp(-2k_1 t) \right]_0^t \\ &= \frac{3}{2} [O_3]_0 (1 - \exp(-2k_1 t)) \end{aligned}$$

2.)



$$\frac{d[A]}{dt} = -(k_b + k_c + k_d)[A]$$

$$\Rightarrow [A] = [A]_0 e^{-(k_b + k_c + k_d)t}$$

$$\frac{d[B]}{dt} = k_b[A]$$

$$\int_0^{[B]} d[B] = k_b[A] \int_0^t e^{-(k_b + k_c + k_d)t} dt$$

$$[B] = \frac{k_b[A]}{k_b + k_c + k_d} \left(1 - e^{-(k_b + k_c + k_d)t} \right)$$

Ausbeute von B :

$$\lim_{t \rightarrow \infty} \frac{[B]}{[A]_0} = \frac{k_b}{k_b + k_c + k_d}$$

C und D analog

mit den gegebenen Werten von k_b , k_c und k_d ergibt sich:

$$B_{Ausb} = 0,067$$

Die Summe aller Ausbeuten muss (per Definition) gleich 1 sein.

3.)

$$r_V = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{1}{5} \frac{d[D]}{dt}$$

$$\frac{d[A]}{dt} = -k_1[A][B]^2 + k_{-1}[C]^3[D]^5$$

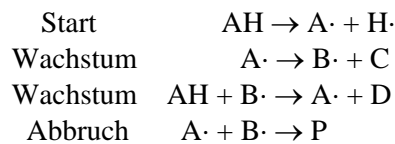
$$\frac{d[B]}{dt} = -2k_1[A][B]^2 + 2k_{-1}[C]^3[D]^5$$

$$\frac{d[C]}{dt} = 3k_1[A][B]^2 - 3k_{-1}[C]^3[D]^5$$

$$\frac{d[D]}{dt} = 5k_1[A][B]^2 - 5k_{-1}[C]^3[D]^5$$

4.)

a) Kettenreaktion



Daraus ergibt sich:

$$\frac{d[AH]}{dt} = -k_1[AH] - k_3[AH][B] = -(k_1 + k_3[B])[AH]$$

d. h., wenn $[B] = \text{const.}$, ist dies der Ausdruck für eine Reaktion 1. Ordnung

Näherung des stationären Zustandes:

$$\frac{d[A]}{dt} = k_1[AH] - k_2[A] + k_3[AH][B] - k_4[A][B] = 0 \quad (1)$$

$$\frac{d[B]}{dt} = k_2[A] - k_3[AH][B] - k_4[A][B] = 0 \quad (2)$$

(1) + (2):

$$k_1[AH] - 2k_4[A][B] = 0$$

$$\frac{k_1}{2k_4}[AH] = [A][B] \quad (3)$$

(1) - (2):

$$k_1[AH] - 2k_2[A] + 2k_3[AH][B] = 0$$

$$\left(\frac{k_1 + 2k_3[B]}{2k_2} \right) [AH] = [A] \quad (4)$$

(4) in (3):

$$\frac{k_1}{2k_4} [AH] = \left(\frac{k_1 + 2k_3[B]}{2k_2} \right) [AH][B]$$

$$\frac{k_1}{2k_4} = \left(\frac{k_1 + 2k_3[B]}{2k_2} \right) [B] = \frac{k_1}{2k_2} [B] + \frac{k_3}{k_2} [B]^2$$

$$\frac{k_1}{2k_2} [B] + \frac{k_3}{k_2} [B]^2 - \frac{k_1}{2k_4} = 0$$

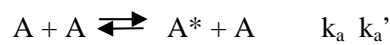
$$[B]^2 + \frac{k_1}{2k_3} [B] - \frac{k_1 k_2}{2k_4 k_3} = 0$$

$$[B] = \frac{k_1}{4k_3} \pm \sqrt{\left(\frac{k_1}{4k_3} \right)^2 + \frac{k_1 k_2}{2k_4 k_3}}$$

$$[B] = \frac{k_1}{4k_3} + \sqrt{\left(\frac{k_1}{4k_3} \right)^2 + \frac{k_1 k_2}{2k_4 k_3}} = \text{const.}$$

5.)

Lindemann-Hinshelwood:



Es gilt zudem:

$$\frac{dP}{dt} = \frac{k_a k_b [A]^2}{k_b + k_a' [A]} = k_{eff} [A]$$

$$k_{eff} = \frac{k_a k_b [A]}{k_b + k_a' [A]}$$

aus idealem Gasgesetz folgt $c_i = \frac{n_i}{V} = \frac{P_i}{RT}$ und damit

$$k_{eff} = \frac{k_a k_b \frac{P}{RT}}{k_b + k_a' \frac{P}{RT}}$$

$$\frac{1}{k_{eff}} = \frac{RT}{k_a P} + \frac{k_a'}{k_a k_b}$$

$$\frac{1}{k_{eff}(p_1)} = \frac{RT}{k_a p_1} + \frac{k_a'}{k_a k_b} \quad (1)$$

$$\frac{1}{k_{eff}(p_2)} = \frac{RT}{k_a p_2} + \frac{k_a'}{k_a k_b} \quad (2)$$

aus (1) – (2) folgt:

$$\frac{1}{k_{eff}(p_1)} - \frac{1}{k_{eff}(p_2)} = \frac{RT}{k_a p_1} - \frac{RT}{k_a p_2} = \frac{RT}{k_a} \left(\frac{1}{p_1} - \frac{1}{p_2} \right)$$

$$k_a = \frac{RT \left(\frac{1}{p_1} - \frac{1}{p_2} \right)}{\frac{1}{k_{eff}(p_1)} - \frac{1}{k_{eff}(p_2)}}$$

$$k_a = \frac{8,206 \cdot 10^{-2} \text{ l atm K}^{-1} \text{ mol}^{-1} \cdot 423 \text{ K} \left(\frac{1}{1,30 \text{ kPa}} - \frac{1}{0,012 \text{ kPa}} \right) \cdot \frac{101,325 \text{ kPa}}{\text{ atm}}}{\frac{1}{2,5 \cdot 10^{-4} \text{ s}^{-1}} - \frac{1}{2,1 \cdot 10^{-5} \text{ s}^{-1}}}$$

$$= 6,65 \frac{\text{ l}}{\text{ s mol}}$$

Oder Näherung für niedrige Drücke ($k_a[A] \ll k_b$):

$$k_a = \frac{RT k_{eff}(p_2)}{p_2}$$

$$k_a = 6,15 \frac{\text{ l}}{\text{ s mol}}$$