Übungen zur Physikalischen Chemie für Mikrosystemtechnik WS2007/2008

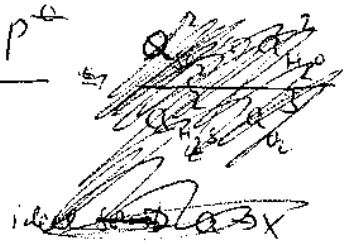
Übungsblatt 11 – Lösungen

A 11.1:

(7)

$$2\,H_2S\,(g) + 3\,O_2\,(g) \longrightarrow 2\,SO_2\,(g) + 2\,H_2O\,(g)$$

$$Q = \frac{(P_{SO_2}/p^\ominus)^2 \cdot (P_{H_2O}/p^\ominus)^2}{(P_{H_2S}/p^\ominus)^2\,(P_{O_2}/p^\ominus)^3} = \frac{P_{SO_2}^2 \cdot P_{H_2O}^2 \cdot p^\ominus}{P_{H_2S}^2 \cdot P_{O_2}^3}$$



nicht ideal Partialdruck → Fugazität

P_{SO_2} → f_{SO_2} etc.

b) $\Delta G_R^\ominus = -RT \ln K$

$$\Delta G_R^\ominus = 2\,\Delta G_B^\ominus(SO_2, g) + 2\,\Delta G_B^\ominus(H_2O, g) -$$

$$- 2\,\Delta G_B^\ominus(H_2S, g) - 3\,\Delta G_B^\ominus(O_2, g) =$$

$$= [2 \times (-300.19) + 2 \times (-228.57) - 2 \times (-33.56) - 3 \times (0)] = \text{kJ mol}^{-1}$$

$$= -990.4\ \text{kJ mol}^{-1}$$

$$\ln K = -\frac{-990.4 \cdot 10^3\ \text{J mol}^{-1}}{8.314 \cdot 298\ \text{J K}^{-1}\text{mol}^{-1} \cdot \text{K}} = +399.75$$

$$\Rightarrow K = e^{400} = 4.05 \cdot 10^{173}$$

c) $x_{SO_2} = x_{H_2O} = x_{O_2} = x_{H_2O} = 0.25$

Dalton: $x_{SO_2} = \frac{p_{SO_2}}{p^\ominus}$ etc $\Rightarrow$ $Q = \frac{x_{SO_2}^2 \cdot x_{H_2O}^2}{x_{H_2S}^2 \cdot x_{O_2}^3} = \frac{(0.25)^4 \cdot (0.25)^2}{(0.25)^2 (0.25)^3} = (0.25)^{-1} = 4$

$\Delta G_R = \Delta G_R^\ominus + RT \ln Q = -990.4\,kJ\,mol^{-1} + \underbrace{2.48 \cdot 1.44}_{3.44}$

$= -987.0\,kJ\,mol^{-1}$

A 11.2: $CH_4(g) + 3Cl_2(g) \rightarrow CHCl_3(l) + 3HCl(g)$

a) $\Delta G_R^\ominus = -RT \ln K$

$\Delta G_R^\ominus = \sum \nu_i G_{B,i}^\ominus (Prod) - \sum \nu_i G_{B,i}^\ominus (Ed) =$

$= (-73.66 - 3 \times 95.3 + 50.52 + 0)\,kJ\,mol^{-1}$

$\Delta G_B^\ominus (Element) = 0$

$= -309\,kJ\,mol^{-1}$

$K = e^{-\Delta G_R^\ominus / RT}$ $\qquad \frac{\Delta G_R^\ominus}{RT} = \frac{-309 \cdot 10^3\,J\,mol^{-1}}{8.314 \cdot 298\,J\,K^{-1}\,mol^{-1}\,K} = -124.7$

$K = e^{124.7} = 1.48 \cdot 10^{54}$

b) $\ln K_2 = \ln K_1 - \frac{\Delta H_R^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\Delta H_R^\ominus = \sum \nu_i \Delta H_{B,i}^\ominus (Prod) - \sum \nu_i \Delta H_{B,i}^\ominus (Ed) =$

$= (-134.47 - 3 \times 92.31 + 74.81)\,kJ\,mol^{-1}$

$= -336.6\ kJ\ mol^{-1}$

$$\ln k_2 = 124.7 + \underbrace{\frac{+336.6\cdot10^3}{8.314}}_{10.5}\left(\frac{1}{323.15} - \frac{1}{298.15}\right) = 114.2$$

$$K = e^{114.2} = 3.93\cdot10^{49}$$ (2)

$$\Delta G_R^\ominus = -RT\ln K = -8.314\cdot323.15\cdot114.2\ J\,mol^{-1} = -306.82\ kJ\,mol^{-1}$$

Das GG liegt in beiden Fälle auf der Produktseite

Entropie betrachtet (für 25°C)

$$-\frac{\Delta G_R^\ominus}{T} = \underbrace{-\frac{\Delta H_R^\ominus}{T}}_{\Delta S_u} + \underbrace{\Delta S_R^\ominus}_{\Delta S_s}$$

$$\Delta S_u = \frac{+336.6\cdot10^3}{298} = 1013\ J\,K^{-1}\,mol^{-1}$$

$$\Delta S_s = \frac{\Delta G_R^\ominus - \Delta H_R^\ominus}{T} = \frac{(-309 + 336.6)\cdot10^3}{298}\ J\,K^{-1}\,mol^{-1} = -93\ J\,K^{-1}\,mol^{-1}$$

$\Rightarrow$ Zunahme der Umgebungsentropie ist Triebkraft.

A 11.3:

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

$\alpha = 0.201$ für 298 K, 1 bar

a) $\alpha = 0.5$ $\quad T = ?$

$\alpha = 0.201$: $K = \frac{4\alpha^2}{1-\alpha^2}\frac{p}{p^\ominus} = \frac{4\alpha^2}{1-\alpha^2} = \frac{4\cdot(0.2)^2}{1-(0.2)^2} = 0.167$ $\quad$ 298 K, 1 bar

$\alpha = 0.5$: $K = \frac{4\cdot(0.5)^2}{1-(0.5)^2} = 1.33$

$$\ln K_2 = \ln K_1 - \frac{\Delta H_R^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Rightarrow -\ln(K_2/K_1)\frac{R}{\Delta H_R^\ominus} = \frac{1}{T_2} - \frac{1}{T_1}$$

$$\Rightarrow \frac{1}{T_2} = \frac{1}{T_1} - \ln\left(\frac{K_2}{K_1}\right)\frac{R}{\Delta H_R^\ominus} = \left(\frac{1}{298.15} - \underbrace{\left(\ln\frac{1.33}{0.167}\right)}_{2.077}\cdot\underbrace{\frac{8.314}{57.2\cdot10^3}}_{1.453\cdot10^{-4}}\right) K^{-1} =$$

$$= \left(\frac{1}{298.15} - 3.018\cdot10^{-4}\right) K^{-1} = 3.052\cdot10^{-3}\,K^{-1}$$

$$\Rightarrow T_2 = 327.6\,K$$

b) $\Delta G_R^\ominus = -RT\ln K = (-8.314\cdot327.6\cdot\ln 1.333)\,J\,mol^{-1} =$

$= 0.783\,kJ\,mol^{-1}$

c) $\Delta G_R = 0$ das GG kennzeichnet!