

Delta-G

$$dG^m = \underbrace{\left(\frac{\partial G^m}{\partial T}\right)}_{-S^m} dT + \underbrace{\left(\frac{\partial G^m}{\partial p}\right)}_{V^m} dp + \sum_i \underbrace{\frac{\partial G^m}{\partial n_i}}_{\mu_i} dn_i$$

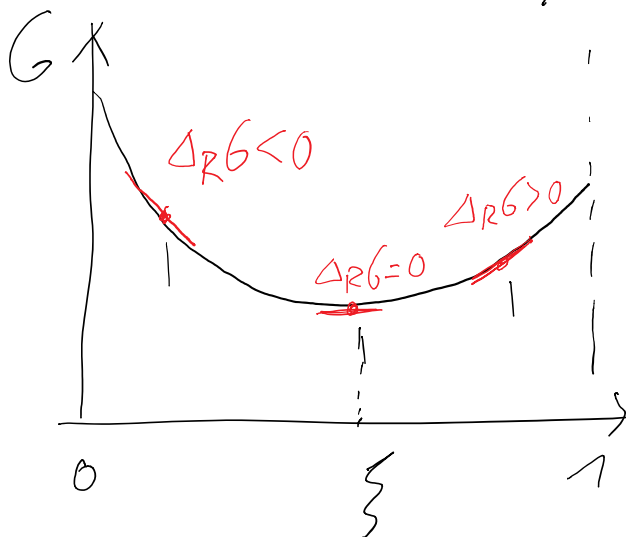
bei konstantem Druck p und konst. Temperatur T :

$$dG^m = \sum_i \mu_i dn_i$$

$$\left(\frac{dn_i}{d\xi} = \nu_i \quad \text{Stöchiometrie} \right)$$

$$dG^m = \sum_i \nu_i \mu_i d\xi$$

$$\Delta_R G = \frac{dG^m}{d\xi}$$



$\Delta_R G < 0 \rightarrow$ Hinreaktion
läuft spontan

$\Delta_R G = 0 \rightarrow$ TD-Gleichgewicht

$\Delta_R G > 0 \rightarrow$ Rückreaktion
läuft spontan



$$\Delta_R G = \sum_i \nu_i \mu_i$$

$$\mu_i = \mu_i^* + RT \ln a_i$$

$$\Delta_R G = \underbrace{\sum_i \nu_i \mu_i^*}_{\Delta_R G^0} + RT \sum_i \nu_i \ln a_i$$

im TD-Gleichgewicht

$$\left[\begin{array}{l} \ln a + \ln b = \ln a \cdot b \\ n_1 \cdot \ln a = \ln a^{n_1} \end{array} \right]$$

$$0 \stackrel{!}{=} \Delta_R G^0 + RT \ln \prod_i a_i^{\nu_i}$$

$$\ln \prod_i a_i^{\nu_i} = -\frac{\Delta_R G^0}{RT}$$

$$\prod_i a_i^{\nu_i} = \exp \left\{ -\frac{\Delta_R G^0}{RT} \right\}$$

Gasreaktion



$$\prod_i a_i^{\nu_i} = \exp \left\{ - \frac{\Delta_R G^\circ}{RT} \right\}$$

$$\frac{a_{\text{NH}_3}}{a_{\text{N}_2}^{1/2} \cdot a_{\text{H}_2}^{3/2}} = \exp \left\{ - \frac{\Delta_R G^\circ}{RT} \right\}$$

$$\begin{aligned} \Delta_R G^\circ &= \sum_i \nu_i \underbrace{G_i^\circ}_{G_i^m} \\ &= G_{\text{NH}_3}^\circ - \frac{1}{2} G_{\text{N}_2}^\circ - \frac{3}{2} G_{\text{H}_2}^\circ \end{aligned}$$

ideale Gase $f_i = 1$

$$X_i = \frac{P_i}{P} = \frac{P_i}{P_0}$$

$$K \equiv \frac{\frac{P_{\text{NH}_3}}{P_0}}{\left(\frac{P_{\text{N}_2}}{P_0} \right)^{1/2} \cdot \left(\frac{P_{\text{H}_2}}{P_0} \right)^{3/2}} = \frac{P_{\text{NH}_3} \cdot (P_0)}{P_{\text{N}_2}^{1/2} \cdot P_{\text{H}_2}^{3/2}} = \exp \left\{ - \frac{\Delta G^\circ}{RT} \right\}$$

dimensionslose

Gleichgewichtskonstante

$$K_P = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} \cdot P_{\text{H}_2}^{3/2}}$$

$$K = (p_0)^{-\sum \nu_i} \cdot \prod_i f_i^{\nu_i} \cdot K_p$$

TD - Gleichgewichtskonstante

Druck-Gleichgewichtskonst.

für Konzentrationen

$$x_i = \frac{p_i}{p} \quad p_i = \frac{n_i}{V} \cdot RT$$

$$f_i = 1, \quad p_i = c_i RT$$

$$K = \prod_i a_i^{\nu_i} = \prod_i \left(\frac{p_i}{p} \right)^{\nu_i} = \prod_i \left(\frac{c_i RT}{p} \right)^{\nu_i}$$

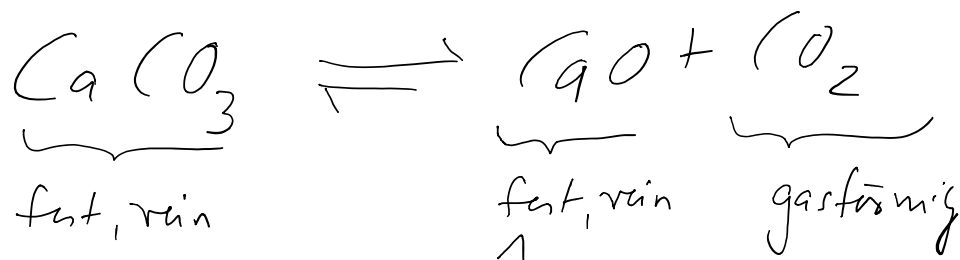
$$= \underbrace{\prod_i \left(\frac{RT}{p} \right)^{\nu_i}}_{\left(\frac{RT}{p} \right)^{\sum \nu_i}} \cdot \underbrace{\prod_i c_i^{\nu_i}}_{K_c}$$

$$K = \left(\frac{RT}{p} \right)^{\sum \nu_i} \cdot K_c$$

in Flüssig-Phasen:

$$K = \prod_i a_i^{\nu_i} = (c_i^0)^{-\sum \nu_i} \cdot \prod_i f_i^{\nu_i} \cdot K_c$$

Heterogene Reaktionen mit reinen Phasen



$$K = \frac{a(\text{CaO}) \cdot a(\text{CO}_2)}{a(\text{CaCO}_3)} \rightarrow \frac{p(\text{CO}_2)}{p^\circ}$$

↙ ↘
↑ ↓
1 1

$$K = \frac{p(\text{CO}_2)}{p^\circ}$$

$$K_p = p(\text{CO}_2)$$

T-Abhängigkeit

$$\ln K = - \frac{\Delta_R G^\circ}{RT}$$

$$\frac{d \ln K}{dT} = - \frac{1}{R} \frac{d}{dT} \left(\frac{\Delta_R G^\circ}{T} \right)$$

Gibbs-Helmholtz-Gleichung $\frac{d}{dT} \left(\frac{\Delta G}{T} \right) = - \frac{\Delta H}{T^2}$

$$\frac{d \ln K}{dT} = \frac{1}{R} \frac{\Delta_R H^\circ}{T^2}$$

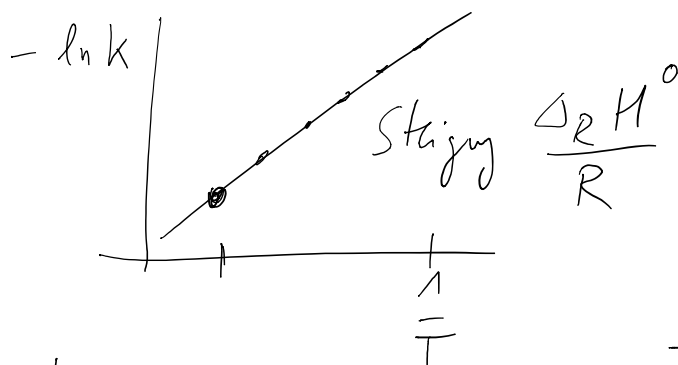
 Van't Hoffsche
Rechenweise
 $p = \text{konst.}$

$\int \rightarrow$ $\Delta_R H^\circ \neq f(T)$

$$d \ln K = \frac{\Delta_R H^\circ}{RT^2} dT$$

$$\ln K(T_2) - \ln K(T_1) = \frac{\Delta_R H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Wie Clausius-Clapeyron



ansonsten:

$$\Delta H(T) = \Delta H(T_0) + \int \Delta C_p dT \quad \text{Kirchhoff}$$

$$\Delta H(T) = \Delta H(T_0) + \int_{T_0}^T \Delta c_p dT \quad \text{Kirchhoff}$$

$$\frac{d \ln K}{dT} = \frac{1}{RT^2} \left\{ \Delta H^{\circ}(T_0) + \int_{T_0}^T \Delta c_p^{\circ} dT \right\}$$

$$c_{p_i} = a_i + b_i(T - T_0) + c_i(T - T_0)^2 + \dots$$

$$\Delta c_p^{\circ} = A + B(T - T_0) + C(T - T_0)^2$$

$$\frac{d \ln K}{dT} = \frac{1}{RT^2} \left\{ \Delta H^{\circ}(T_0) + A(T - T_0) + \frac{B}{2}(T - T_0)^2 \right\}$$

$$\int_{T_0}^T d \ln K = \int_{T_0}^T \frac{1}{RT^2} \left\{ \Delta H^{\circ}(T_0) + A(T - T_0) + \frac{B}{2}(T - T_0)^2 \right\} dT$$

P Abhängigkeit

$$\ln K = - \frac{1}{RT} \Delta_R G^\circ$$

$$\left(\frac{\partial \ln K}{\partial p} \right)_T = - \frac{1}{RT} \left(\frac{\partial \Delta_R G^\circ}{\partial p} \right)_T$$

$$\Delta_R V^\circ = \sum_i \nu_i V_i^m$$

kondensierte Phasen $\Delta_R V^\circ \sim 10^{-6} \frac{\text{m}^3}{\text{mol}}$

$$T = 300 \text{ K} \quad \sim 10^{-9} \text{ Pa}^{-1} = 10^{-4} \text{ bar}^{-1}$$

$$\Delta p = 1 \text{ bar} \quad \Delta \ln K \approx 10^{-4} \rightarrow \text{schwache Abhängigkeit der Konstante von } p$$

$$\Delta V^\circ \text{ in Gasphase } 10^{-2} \frac{\text{m}^3}{\text{mol}}$$

ist 10^4 x stärker

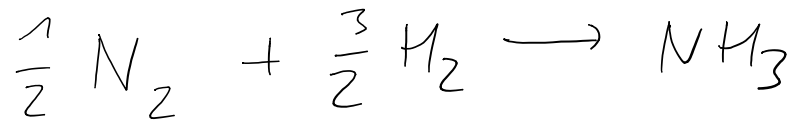
$$\left(\frac{\partial \ln K}{\partial p} \right)_T = - \frac{\Delta_R V^\circ}{RT}$$

$$\left[\begin{array}{l} \text{also:} \\ \text{bei } \Delta_R V^\circ > 0 \\ \hookrightarrow \left(\frac{\partial \ln K}{\partial p} \right) < 0 \end{array} \right]$$

gilt für K (und K_x)

$$\hookrightarrow \left(\frac{\partial \ln K_p}{\partial p} \right)_T = 0$$

Berechnung der Ausbeute



$$n_0(H_2) = 3n_0(N_2)$$

Ausbeute $\gamma = n(NH_3)$ im TD-Gleichgewicht

$$n(N_2) = n_0(N_2) - \frac{1}{2}\gamma$$

$$n(H_2) = 3n_0(N_2) - \frac{3}{2}\gamma$$

$$n = \sum_i n_i = \gamma + n_0(N_2) - \frac{1}{2}\gamma + 3n_0(N_2) - \frac{3}{2}\gamma$$

$$= 4n_0(N_2) - \gamma$$

ideales Gas $\varphi_i = 1$, $x_i = \frac{n_i}{n}$

$$K = \frac{\gamma}{n}$$

$$\frac{\gamma}{\left(\frac{n_0(N_2) - \frac{1}{2}\gamma}{n}\right)^{1/2} \left(\frac{3n_0(N_2) - \frac{3}{2}\gamma}{n}\right)^{3/2}}$$

$$= \frac{\gamma (4n_0(N_2) - \gamma)}{\left(n_0(N_2) - \frac{1}{2}\gamma\right)^{1/2} \left(3n_0(N_2) - \frac{3}{2}\gamma\right)^{3/2}}$$

$$\left[z = \frac{\gamma}{n_0(N_2)} \right]$$

$$K = \frac{\frac{y}{n_0} \cdot n_0^2 (4-z)}{\left(\frac{n_0}{z}\right)^{1/2} (2-z)^{1/2} \left(\frac{n_0}{z}\right)^{3/2} (2-z)^{3/2}}$$

$$K = \frac{z(4-z) \cancel{n_0^2} 4}{(2-z)^2 \cancel{n_0} (3)^{3/2}}$$

$$K = \frac{z(4-z) 4}{(2-z)^2 (3)^{3/2}}$$

$$K_p = p^{\sum v_i} \cdot K = p^{-1} \cdot K$$

$$\boxed{K_p} = \frac{4z(4-z)}{p^0 \cdot 3^{3/2} (2-z)^2}$$

K_p ist definiert bei Standarddruck und damit nicht explizit p -Abhängig

$$z \ll 1 \quad K_p \approx \frac{4z \cdot 4}{p \cdot 3^{3/2} \cdot 4} \neq f(p)$$



$$z \approx 1.3 \cdot p \cdot K_p(T)$$

annähernd lineare Zunahme
der Ausbeute z bei Erhöhung
von p