PC III 08.07.

8.6 Gleichgewichtskonstante

zunächst: Statist. Beschreibung des chemischen Potentials

$$A = U - TS$$
$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$
$$S = kT \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q$$

$$\hookrightarrow \boxed{A = -kT \ln Q}$$ freie Energie in Abhängigkeit von der Zustandssumme

$$dA = \underbrace{\left(\frac{\partial A}{\partial V}\right)_{T,N}} dV + \underbrace{\left(\frac{\partial A}{\partial T}\right)_{N,V}} dT + \left(\frac{\partial A}{\partial N}\right)_{V,T} dN$$

$$dA = -p \; dV - S \; dT + \underbrace{\left(\frac{\partial A}{\partial n}\right)_{,-}}_{?} dn$$

Guggenheim:
$$\begin{array}{ccc} -S & U & V \\ H & & A \\ -p & G & T \end{array}$$
$dA = -pdV - SdT$

$$G = H - TS = U + pV - TS = A + pV$$

$$dG = dA + d(pV) = dA + pdV + Vdp$$
$$= Vdp - SdT + \left(\frac{\partial A}{\partial n}\right)_{V,T} dn$$

$$dG = \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n}} dp + \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n}} dT + \underbrace{\left(\frac{\partial G}{\partial n}\right)_{p,T}} dn$$
$$= V \; dp - S \; dT + \mu \; dn$$

durch Vergleich: $\boxed{\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T} = \left(\frac{\partial A}{\partial n}\right)_{V,T}}$

$$\boxed{\mu = -kT \left(\frac{\partial \ln Q}{\partial n}\right)_{V,T} = -RT \left(\frac{\partial \ln Q}{\partial N}\right)_{V,T}}$$ chem. Potential in Abhängigkeit von Zustandssumme

<u>Bsp.:</u> id. Gas

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

$$\ln Q = N \ln q - \ln N! = N \ln q - N \ln N + N \quad \text{(Stirling)}$$

$$\hookrightarrow \mu = -RT(\ln q - \ln N - 1 + 1)$$

$$\boxed{\mu = -RT \ln \frac{q}{N}}$$ chem. Pot. id. Gas

Gasphasenreaktion: $\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g)$

V, T const.: $dA = \sum_i \mu_i dn_i = \sum_i \mu_i \underbrace{\nu_i \, d\xi}_{dn_i}$

$$\Delta_r A = \left(\frac{\partial A}{\partial \xi}\right)_{T,V} = \sum_i \nu_i \mu_i$$

Gleichgewicht: $\Delta_r A = 0 = \nu_A \mu_A + \nu_B \mu_B - \nu_Y \mu_Y - \nu_Z \mu_Z$

$$= \nu_A \ln\left(\frac{q_A}{N_A}\right) + \nu_B \ln\left(\frac{q_B}{N_B}\right) - \nu_Y \ln\left(\frac{q_Y}{N_Y}\right) - \nu_Z \ln\left(\frac{q_Z}{N_Z}\right)$$

$$= \ln\left(\frac{q_A}{N_A}\right)^{\nu_A} + \ln\left(\frac{q_B}{N_B}\right)^{\nu_B} \ldots$$

$$= \ln q_A^{\nu_A} + \ln q_B^{\nu_B} \ldots - \ln N_A^{\nu_A} - \ln N_B^{\nu_B} \ldots$$

$$\prod_i q_i^{\nu_i} = \prod_i N_i^{\nu_i} \quad \| : V^{\nu_i}$$

$$\boxed{k_c(T) = \prod_i \frac{q_i^{\nu_i}}{V^{\nu_i}} = \prod \left(\frac{N_i}{V}\right)^{\nu_i} = \prod \rho_i^{\nu_i}}$$ mit $\rho_i = \frac{N_i}{V}$

<u>Beziehung zu $k_p(T)$ und $k_c(T)$?</u>

$$k_p(T) = \prod_i \left(\frac{p_i}{p^0}\right)^{\nu_i}$$

$$pV = nRT$$

$$p = cRT$$

$$k_p(T) = k_c(T) \left(\frac{RTc^0}{p^0}\right)^{\sum_i \nu_i}$$

einheitenlos

$$\frac{\cancel{\text{bar}}\ \cancel{L}}{\cancel{K}\ \text{mol}} \cdot \cancel{K} \cdot \frac{1}{\cancel{L}} \Big/ \cancel{\text{bar}} \cdot \frac{1}{\cancel{\text{mol}}}$$

Bsp. 1: $CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2} O_2(g)$

$$k_c(T) = \frac{\left(\frac{q_{CO}}{V}\right)\left(\frac{q_{O_2}}{V}\right)^{1/2}}{\frac{q_{CO_2}}{V}}$$

$$\frac{q_{CO}}{V} = \left(\frac{2\pi m_{CO} kT}{h^2}\right)^{3/2} \cdot \left(\frac{T}{\theta_{rot}^{CO} \cdot \underset{\overset{\shortparallel}{1}}{\sigma}}\right) \cdot \left(\frac{e^{-\frac{\theta_{vib}^{CO}}{2T}}}{1 - e^{\frac{-\theta_{vib}^{CO}}{T}}}\right) \cdot e^{\frac{D_e^{CO}}{RT}} \underset{\overset{\shortparallel}{1}}{g_{e1}}$$

$$-\frac{\theta_{vib}^{CO}}{2T} + \frac{D_e}{RT} = \frac{1}{T}\left(-\frac{\theta_{vib}^{CO}}{2} + \frac{D_e^{CO}}{R}\right) \qquad \boxed{\theta_{vib} = \frac{h\nu}{k}}$$

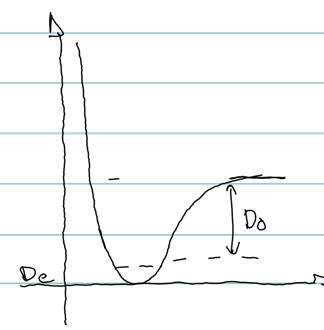
$$D_e^{CO} - \frac{1}{2} h\nu^{CO} N_L = D_0^{CO}$$

$$\left(\frac{q_{CO}}{V}\right) = \left(\frac{2\pi m_{CO} kT}{h^2}\right)^{3/2} \left(\frac{T}{\theta_{rot}^{CO}}\right) \left(1 - e^{-\frac{\theta_{vib}}{T}}\right)^{-1} e^{\frac{D_0^{CO}}{RT}}$$

$$\left(\frac{q_{O_2}}{V}\right) = \left(\frac{2\pi m_{O_2} kT}{h^2}\right)^{3/2} \left(\frac{T}{\underset{\overset{\shortparallel}{2}}{\sigma}\, \theta_{rot}^{O_2}}\right) \left(1 - e^{-\frac{\theta_{vib}^{O_2}}{T}}\right)^{-1} e^{\frac{D_0^{O_2}}{RT}} \underset{\overset{\shortparallel}{3}}{g_{e1}}$$

$2S+1) \to S = 1$

$\hat{=} \sum g$



$D_e = D_0 + \frac{1}{2} h\nu$

$$\left(\frac{q_{CO_2}}{V}\right) = \left(\frac{2\pi m_{CO_2} kT}{h^2}\right)^{3/2} \left(\frac{T}{\sigma\, \theta_{rot}^{CO_2}}\right) \prod_i^4 \left(1 - e^{-\frac{\theta_{vib,i}^{CO_2}}{T}}\right)^{-1} e^{\frac{D_0^{CO_2}}{RT}} \underset{\overset{\shortparallel}{1}}{g_{e1}}$$

lin. Molekül: $3N - 5 = 9 - 5 = 4$

Werte aus Tabellen (→ ÜB 7)

$\hookrightarrow k_p(2000\,K) = k_c(2000\,K) \left(\frac{RTc^\circ}{p^\circ N_L}\right)^{1/2} = 1{,}468 \cdot 10^{-3}$

Bsp. 2: $H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(g)$

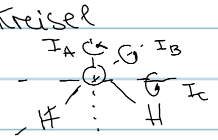
$$k_c(T) = \frac{\left(\frac{q_{H_2O}}{V}\right)}{\left(\frac{q_{H_2}}{V}\right) \cdot \left(\frac{q_{O_2}}{V}\right)^{1/2}}$$

$$\frac{q_{H_2}}{V} = \left(\frac{2\pi m_{H_2} kT}{h^2}\right)^{3/2} \left(\frac{T}{\underset{\overset{\|}{2}}{\sigma}\, \Theta_{rot}^{H_2}}\right)\left(1-e^{\frac{\Theta_{vib}^{H_2}}{T}}\right)^{-1} e^{\frac{D_0^{H_2}}{RT}} \cdot \underset{\overset{\|}{1}}{g_{e1}}$$

$$\frac{q_{O_2}}{V} = \left(\frac{2\pi m_{O_2} kT}{h^2}\right)^{3/2} \left(\frac{T}{2\,\Theta_{rot}^{O_2}}\right)\left(1-e^{\frac{\Theta_{vib}^{O_2}}{T}}\right)^{-1} e^{\frac{D_0^{H_2}}{RT}} \cdot 3$$

$$\frac{q_{H_2O}}{V} = \left(\frac{2\pi m_{H_2O} kT}{h^2}\right)^{3/2} \frac{\pi}{\underset{\overset{\|}{2}}{\sigma}} \left(\frac{T^3}{\Theta_{rot,A}^{H_2O}\,\Theta_{rot,B}^{H_2O}\,\Theta_{rot,C}^{H_2O}}\right)^{1/2} \prod_i \left(1-e^{-\frac{\Theta_{vib,i}^{H_2O}}{T}}\right)^{-1} e^{\frac{D_0^{H_2O}}{RT}}\, \underset{\overset{\|}{1}}{g_{e1}}$$

asymmetr. Kreisel



2-atom.: H_2 H—H $B \sim \frac{1}{I}$

nichtlin. Moleküle: $3N - 6 = 9 - 6 = 3$

$K_c(1500K) = 2{,}34 \cdot 10^{-7}$

$K_p(1500K) = K_c(1500K)\left(\frac{RTc_0}{p_0 N_L}\right)^{-\frac{1}{2}} = 5{,}14 \cdot 10^{5}$

$K_p(1000K) = 1{,}61 \cdot 10^{10}$

Standardreaktionsenthalpie $\Delta_r H^0$?

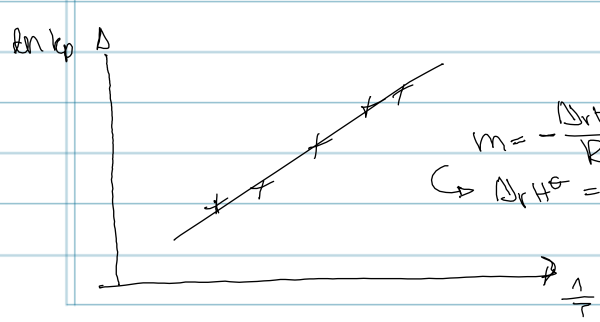
van't Hoff-Gleichung

$$\left(\frac{\partial \ln K_p}{\partial\left(\frac{1}{T}\right)}\right)_p = -\frac{\Delta_r H^\ominus}{R}$$

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$
$$-RT \ln K_p = \Delta_r H^0 - T\Delta_r S^\ominus$$
$$\ln K_p = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^0}{R}$$

ableiten nach T

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta_r H^\ominus}{RT^2}$$



$$m = -\frac{\Delta_r H^\ominus}{R}$$

$$\hookrightarrow \Delta_r H^\ominus = -mR = -\frac{\Delta \ln K_p}{\Delta\left(\frac{1}{T}\right)} = -259\ \frac{kJ}{mol}$$

KLAUSUR