V14

16.7.2019

Note Title

Nullpunktsentropie

TD: $S - S(0K) = \int_0^T \frac{1}{T} C_V \, dT = \int_0^T \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT$

$= \int_0^T \frac{1}{T} \frac{\partial}{\partial T} \Big(\underbrace{U(0)}_{=0} + kT^2 \left(\frac{\partial \ln Q}{dT}\right)_V \Big) dT = \int_0^T \frac{1}{T} \left(2kT \left(\frac{\partial \ln Q}{\partial T}\right)_V + kT^2 \left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_V \right) dT$

$\int (uv)' = \int u'v + \int uv'$

$\Rightarrow \underbrace{S}_{S(T)} - S(0K) = \underbrace{\frac{1}{T}(U - U(0)) + k \ln Q}_{S(T)} - \underbrace{k \ln Q(T=0)}_{= S(0K)}$

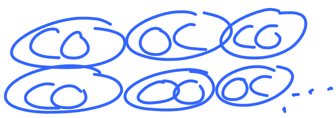
$\boxed{S(0) = k \cdot \ln q(0K)} = k \ln g_0$ || vgl. $S = k \ln \Omega$

Bsp: ideales Kristall: $g_0 = 1 \xrightarrow{N = N_A} S(0K) = N_A \cdot k \cdot \ln 1 = 0 \, \mathrm{J/mol \cdot K}$

eine Fehlstellen: $g_0 = N_A \rightarrow S(0K) = k \ln N_A$

$\sim 10^{-21} \, \mathrm{J/mol \cdot K}$

molekulare Orientierung:



"Kristall"

$\Rightarrow$ 2 Anordnungen pro Molekül: $g_0 = 2^{N_A}$

$\rightarrow S(0K) = k \cdot N_A \cdot \ln 2 \sim 5.8 \, \mathrm{J/mol \cdot K}$

(exp: $5 \, \mathrm{J/mol \cdot K}$)

$\Rightarrow S(0K)_{\text{Eis}}$? $\rightarrow \boxed{S(0) = 3.4 \, \mathrm{J/mol \cdot K}}$

($\rightarrow$ Pauling)

(ii) Entropie des einatomigen Gases

$Q = \frac{(q_{mol})^N}{N!}$; $q_{mol} = g_{0,el} \cdot \frac{V}{\Lambda^3}$ || $U - U(0) = \frac{3}{2} NkT$

$S(T) = \frac{1}{T}(U - U(0)) + k \ln Q$

$= \frac{3}{2} Nk + k \ln \left(\frac{q^N}{N!} \right) = \frac{3}{2} Nk + Nk \ln q \underbrace{- Nk \ln N + Nk}_{\text{Stirling!}}$

$= Nk \left(\frac{5}{2} + \ln g_{0,el} \cdot \frac{V}{\Lambda^3} - \ln N \right)$ / $N = n N_A$, $k N_A = R$

$$= nR\left(\tfrac{5}{2} + \ln g_{0,el}\frac{V}{\Lambda^3} - \ln n N_A\right)$$

$$\boxed{S_m = R\cdot\ln\left(\frac{e^{5/2}\cdot g_{0,el}\cdot V}{\Lambda^3\, n N_A}\right) = R\ln\left(\frac{g_{0,e}\cdot e^{5/2}\cdot kT}{p\cdot\Lambda^3}\right)} \quad \Big| \; V/n = RT/p$$

$$\Longrightarrow S_m(T) \sim \ln m^{3/2}$$

Sackur-Tetrode-Gleichung

7. Thermodynamische Funktionen

$$S(Q),\ U(Q)\ \ldots \Longrightarrow G(T),\ \Delta_R G^\ominus \ldots \sim -\ln K$$

Freie Energie:

$$A = U - TS$$
$$= (U(0) + E(T)) - T\cdot\left(\frac{1}{T}(E(T)) + k\ln Q\right)$$

(für $T \to 0$: $A(0) = U(0)$)

$$\boxed{A - A(0) = -kT\ln Q}$$

Druck:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

ideales Gas:

$$Q = \frac{q_{trans}^N}{N!} = \left(\frac{V}{\Lambda^3}\right)^N / N!$$

$$\longrightarrow p = +kT\,\partial/\partial V\left(\ln V^N - \ln \Lambda^{3N} - \ln N!\right) = \frac{kTN}{V}$$

$$\boxed{\text{mit } N = nN_A:\ pV = nRT}$$

Freie Enthalpie:

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

$$\hookrightarrow \boxed{G - G(0) = -kT\ln Q + V\cdot kT\cdot\left(\frac{\partial \ln Q}{\partial V}\right)_T}$$

Bsp.:

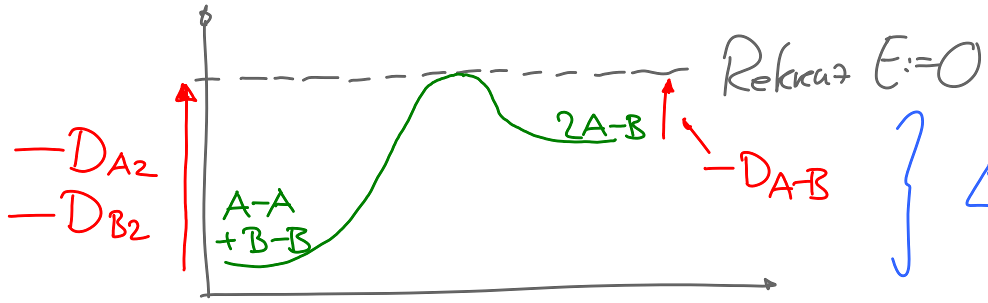
$$G - G(0) = -kT\ln\left(\frac{q^N}{N!}\right) + V\left(\frac{nRT}{V}\right)$$
$$= -NkT\ln q + kT(N\ln N - N) + nRT \quad \Big| \; N = nN_A,\ kN_A = R$$
$$= -nRT\ln q + nRT(\ln n N_A)$$

$$\Longrightarrow \boxed{G - G(0) = -nRT\ln\left(\frac{q}{n\cdot N_A}\right)} \qquad \left(\frac{q}{n} =: q_m\right)$$

GG-Konstante

$$\underbrace{\Delta_R G_m^\ominus}_{\Delta G} = -RT \ln K$$

$$= \underbrace{\sum_i \nu_i G_{m,i}^\ominus(0K)}_{\Delta G(0)} - \underline{\underline{RT}} \sum_i \nu_i \ln \underbrace{\left(\frac{q_i}{n_i N_A}\right)}_{\left(=\frac{q_{m,i}}{N_A}\right)}$$



$$\boxed{\Delta G(0) = -\sum_i \nu_i D_{i,m}^\ominus}$$

→ Tabelle

$$\rightarrow \Delta_R G_m^\ominus = \Delta G_{0,m} - RT \sum_i \nu_i \ln \frac{q_{m,i}}{N_A}$$

mit $\ln K = -\frac{\Delta_R G}{RT} = -\frac{1}{RT}\Delta G_{0,m} + \underbrace{\sum_i \nu_i \ln \frac{q_{m,i}}{N_A}}$

$$= \sum_i \ln \left(\frac{q_{m,i}}{N_A}\right)^{\nu_i}$$

$$= \ln \prod \left(\frac{q_{m,i}}{N_A}\right)^{\nu_i}$$

$$\boxed{K = \prod_i \left(\frac{q_{m,i}}{N_A}\right)^{\nu_i} \cdot e^{-\frac{\Delta_R G(0)}{RT}}}$$