V12
2.7.2019

Note Title

MB

$$N_j = \boxed{e^{-\alpha}} \cdot e^{-\varepsilon_j \beta} \qquad \beta = 1/kT$$

$$p_j = N_j/N = \frac{g_j \cdot e^{-\varepsilon_j\beta}}{\underbrace{\sum g_i\, e^{-\varepsilon_i\beta}}_{=:q}}$$

$$\bar{N}_j = N_j/g_j = \boxed{e^{-\alpha}} \cdot e^{-\varepsilon_j\beta} = \boxed{\frac{N}{q}} \cdot e^{-\varepsilon_j\beta}$$

$$\boxed{e^{-\alpha} = \frac{N}{q}} \ll 1 \Rightarrow \text{klassische Statistik!}$$

Bsp.: $q_{trans,3D}(O_2, V=1l, 298K) \sim 10^{29}$, $N = \sim 10^{22} \Rightarrow \frac{N}{q} \sim 10^{-7}$

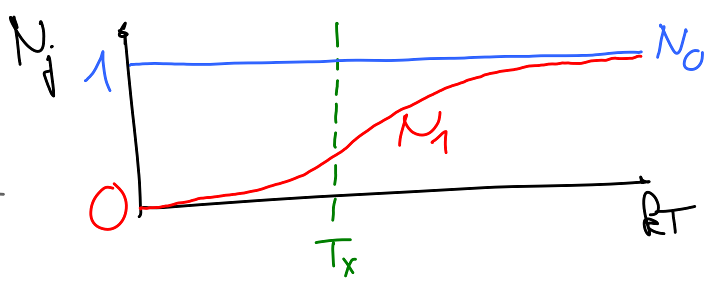
Quantenstatistiken: FD, BE allg. bei $T\downarrow$, $m\downarrow$, $V\downarrow$

Zustandssumme

$$\boxed{q = \sum_i g_i\, e^{-\varepsilon_i\beta}} \qquad (\varepsilon_0 \stackrel{!}{:=} 0)$$

2-Niveau: $q = 1 + e^{-\varepsilon/kT}$

	N_0	N_1	q	P_0	P_1
$T \to 0$	1	0	1	1	0
$T \to \infty$	1	1	2	1/2	1/2



Ergänzung:

$$\boxed{q_{trans,3D} = \frac{(2\pi m kT)^{3/2}}{h^3}} \checkmark \qquad [N\cdot s]^3 \quad [J\cdot s]^3$$

$\varepsilon_{ges} = \varepsilon_x + \varepsilon_y + \varepsilon_z$

$\Rightarrow q_{ges} = q_x \cdot q_y \cdot q_z$

$\to$ vgl. $\lambda = \frac{h}{p}$ (de Broglie)

$\Rightarrow$ thermische Wellenlänge: $\Lambda = \frac{h}{\sqrt{2\pi m kT}} \sim \frac{1}{\sqrt{T}}$ $\quad [\Lambda] = m$

Klassische Vergleichsgröße: $\delta = \frac{kT}{\sqrt{2}\,\sigma p} \sim T$

$$\boxed{q_{trans,3D} = \frac{V}{\Lambda^3}}$$

$(O_2, V = 1\,l, 298\,K, p = 1\,bar)$ $\quad \delta = 10^{-7}\,m$, $\Lambda = 1.7 \cdot 10^{-11}\,m$

„Übergang" von MB $\longrightarrow$ FD/BE : $T \downarrow$ $(m \downarrow)$

Anwendung von q_{trans}

$$\langle \varepsilon \rangle = \frac{E}{N} = \frac{\sum \varepsilon_i N_i}{\sum N_i} = \frac{\sum \varepsilon_i \cdot e^{-\alpha} \cdot e^{-\varepsilon_i \beta}}{\sum e^{-\alpha} \cdot e^{-\varepsilon_i \beta}} = \frac{\sum \varepsilon_i \cdot e^{-\varepsilon_i \beta}}{q}$$

NR: $\partial q / \partial T = \partial / \partial T \left(\sum_i e^{-\varepsilon_i / kT} \right) = \sum_i \left(+ \frac{\varepsilon_i}{kT^2} \cdot e^{-\varepsilon_i / kT} \right) = \frac{1}{kT^2} \sum_i \varepsilon_i \cdot e^{-\varepsilon_i / kT}$

$$\Longrightarrow \boxed{\langle \varepsilon \rangle = kT^2 \frac{\partial q / \partial T}{q} = kT^2 \frac{\partial \ln q}{\partial T}} \qquad q \overset{!}{\Longrightarrow} \langle \varepsilon \rangle$$

Bsp. Translation (3D): $\langle \varepsilon \rangle = kT^2 \left(\partial / \partial T \left(\ln \frac{(2\pi m k)^{3/2}}{h^3} + \ln T^{3/2} - \ln V \right) \right)$

$$= kT^2 \cdot \left(\frac{3}{2T} \right) = \underline{\underline{3/2\, kT}}$$

$\Longrightarrow$ Gleichverteilungssatz, $1/2\, kT$ pro FG

ZS der Rotation

QM: starrer Rotator, 2-atomig : $\varepsilon_{rot} = J(J+1) hcB$

$g_J = 2J + 1$ $\qquad J = 0, 1 \ldots$ $\qquad [cm^{-1}]$, $B = \frac{\hbar}{4\pi c I}$

$$\boxed{q_{rot} = \sum_{J=0}^{\infty} (2J+1) \cdot e^{-J(J+1) hcB / kT}} \qquad (\varepsilon_{J=0} = 0)$$

Definition: $\Theta_{rot} = \frac{hcB}{k}$

$\rightarrow \varepsilon_{rot} = J(J+1) \Theta_{rot} k$

Abschätzung Θ_{rot}: (298K) $\qquad \Theta_{rot} = \underbrace{\left(\frac{hc}{kT} \right)}_{1/200\,cm^{-1}} \cdot T \cdot \underset{\sim 1\,cm^{-1}}{B} \approx 1.5\,K$

$T \gg \Theta_{rot}$

$$q_{rot} \approx \int_{J=0}^{\infty} (2J+1) \cdot e^{-J(J+1) \frac{\Theta_{rot}}{T}} dJ = \ldots = \frac{T}{\Theta_{rot}}$$

ABER! Pauli-Prinzip beachten

$\Rightarrow$ Rotationssymmetriezahl σ

Bsp. Boranen: $\langle O=C=O \rangle$, $\Psi_T(\psi)$ muß erhalten bleiben

$\Longrightarrow \boxed{\sigma = 2}$ $\Rightarrow J = 0, 2, 4 \ldots$

$$\hookrightarrow \boxed{q_{rot} = \frac{T}{\Theta_{rot} \cdot \sigma}} \quad (T \gg \Theta_{rot})$$

Ergänzungen: $I_x, I_y, I_z \Rightarrow q_{rot} = \left(\frac{8\pi^2 kT}{h^2}\right)^{3/2} \cdot \frac{(\pi I_x I_y I_z)^{1/2}}{\sigma}$

$\langle \varepsilon_{rot} \rangle_{(H-Ce)} = kT$ $\left(\text{aus } \langle \varepsilon \rangle = \frac{1}{kT^2} \frac{\partial \ln q}{\partial T}\right)$ $\left(\text{in 3D}: \frac{3}{2} kT\right)$

Jeder $(J \to J+1)$-System $\Rightarrow$ 2-Niveau-System

ZS Schwingung

QM: harm. Osz., $\varepsilon_n = (n+\frac{1}{2})h\nu = (n+\frac{1}{2})hc\tilde{\nu}$ $[\tilde{\nu}] = cm^{-1}$

$g_n = 1$, $\hookrightarrow \varepsilon_0 = \frac{1}{2}h\nu$

$$q_{vib} = \sum_{n=0}^{\infty} e^{-nh\nu/kT} = \sum \underbrace{\left(e^{-h\nu/kT}\right)^n}_{<1} = \boxed{\frac{1}{1-e^{-h\nu/kT}}}$$

(geometr. Summe)

DEF.: $\Theta_{vib} = \frac{hc\tilde{\nu}}{k}$, Abschätzung: $\Theta_{vib} = \left(\frac{hc}{kT}\right) \cdot T \cdot \tilde{\nu} = 1500\,K$

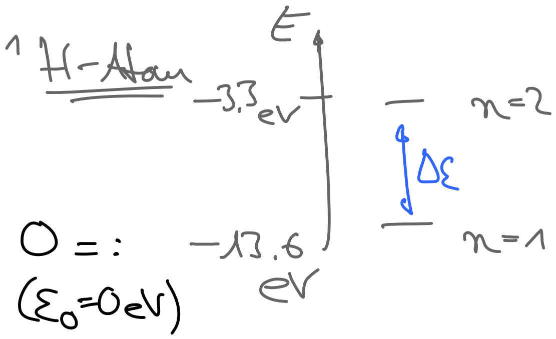
$\sim 1000\ cm^{-1}$

$\longrightarrow$ (mit Θ) $\boxed{q_{vib} = \frac{1}{1-e^{-\Theta/T}}}$, häufig $q_{vib} \approx 1$

$\underset{\circ}{?}$ oft mehre FG der Schwingung: $\boxed{q_{vib,ges} = \prod_i q_{vib,i}}$

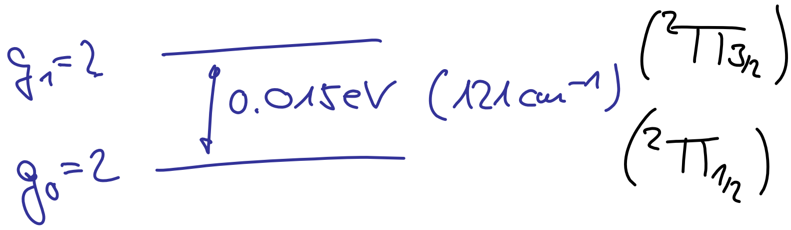
Elektronische ZS

$q_{el} = g_0$ $\qquad (g_{0,\text{Radikal}} = 2)$



$$q_{el} = 2\cdot e^{0} + 8\cdot e^{-\Delta\varepsilon/kT}$$

<u>el. Anregung in NO:</u>



$$\Longrightarrow q_{el}(300K) = 3.1$$

Molekulare Zustandssumme

$$q_{mol}(T,V) = q_{el}\cdot q_{vib}\cdot q_{rot}\cdot q_{trans}$$

$$\boxed{q_{mol} = g_{0,el}\cdot\frac{1}{1-e^{-\Theta_{vib}/T}}\cdot\frac{T}{\sigma\cdot\Theta_{rot}}\cdot\frac{V}{\Lambda^3}}$$

<u>Anwendungen</u>

$$\langle\varepsilon\rangle = \frac{1}{kT^2}\,\frac{\partial \ln q}{\partial T} \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(U(0)+E(T)\right)$$

$$\longrightarrow \boxed{C_V = \partial/\partial T\,\langle\varepsilon\rangle = \partial/\partial T\left(\frac{1}{kT^2}\,\frac{\partial \ln q}{\partial T}\right)}$$

$$\langle\varepsilon\rangle_{trans} = 3/2\,kT, \quad \langle\varepsilon\rangle_{rot,linear} = kT$$

$$\langle\varepsilon_{vib}\rangle = \frac{k\Theta}{e^{\Theta/T}-1} \Longrightarrow C_V(T)_{vib}$$