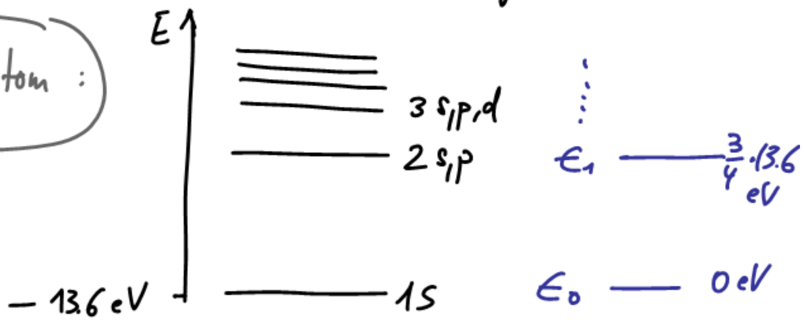
Zustandsumme für elektronische Anregung

H-Atom:



$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \cdot \frac{1}{n^2}$$

$$q_e = \sum_i g_i \, e^{-\epsilon_i/kT}$$

$$= \underbrace{g_0}_{2} \cdot 1 + \underbrace{g_1}_{8} \cdot e^{\overbrace{-\epsilon_1/kT}^{*}} + \ldots$$

mit Spinquantenzahl

$*$ $T = 300\,K \rightarrow kT = 4\cdot 10^{-21}\,J \approx 2\,meV$

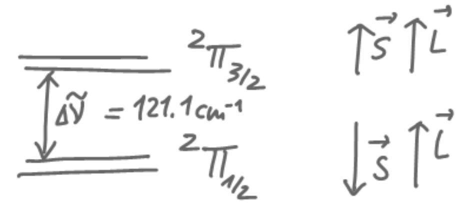
$\epsilon_1 = 5\cdot 10^{-19}\,J$

$\hookrightarrow e^{-\epsilon_1/kT} \approx e^{-100} \approx 4\cdot 10^{-44}$

angeregte Niveaus 2s, 2p tragen normalerweise nicht bei!

$\theta_E = \frac{\epsilon_1}{k}$ char. T für elektr. Anregung

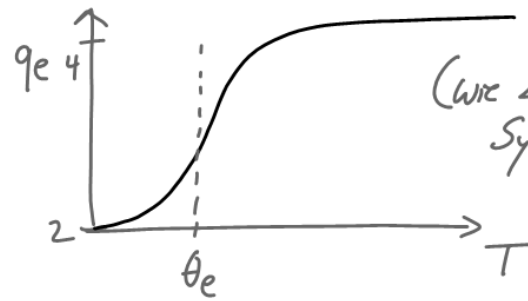
NO $[N_2]\,\pi^1$ 4 Zustände



$\Delta E = \epsilon_1 = h\cdot c\cdot \Delta\tilde{\nu} = 2.4\cdot 10^{-21}\,J$

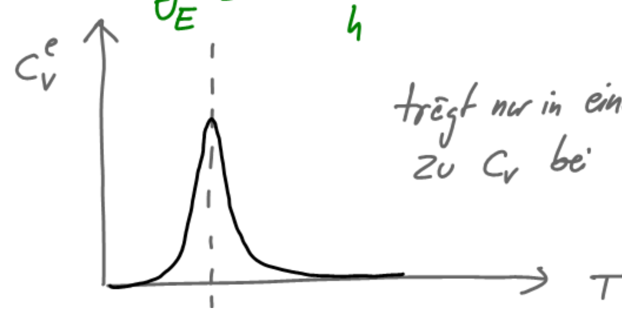
$T = 300\,K$: $e^{-\epsilon_1/kT} \approx 0.55$!

$$q_e = 2 + 2\cdot 0.55 \approx 3.1$$



(wie 2 Niveau-System)

$\theta_E = \frac{E_{LUMO} - E_{HOMO}}{k}$ für Moleküle



trägt nur in einem T-Bereich zu C_V bei

Zusammenfassung aller Terme

Translation

$$q_T = q_{Tx} \cdot q_{Ty} \cdot q_{Tz}$$

$$\left\{ q_{Tx} = \frac{L_x}{\Lambda}, \quad \Lambda = \frac{h}{\sqrt{2\pi m k T}} \right\}$$

$$q_T = \frac{V}{\Lambda^3} = \left(\frac{T}{\Theta_T}\right)^{3/2}$$

$\Theta_T = \frac{\sqrt{h}}{2\pi V m}$ char. T für Translation $\quad \Theta_T \ll T$ typischerweise

$\Rightarrow U_T^m = \frac{3}{2} RT, \quad C_{VT}^m = \frac{3}{2} R$

Rotation

$$q_R = \frac{\sqrt{\pi}}{\sigma} \frac{(kT)^{3/2}}{B_x \cdot B_y \cdot B_z}, \quad (\text{für } \Theta_R \ll T$$

$\Theta_R = \frac{B}{k}$ char. T der Rotation

$\Rightarrow U_R^m = \frac{3}{2} RT \quad$ (RT für lin. Mol.)

$C_{VR}^m = \frac{3}{2} R \quad$ (R für lin. Mol.)

Vibration

$$q_V = \frac{1}{1 - e^{-h\nu/kT}}$$

$$\approx \frac{kT}{h\nu} \quad (\text{für } \Theta_V < T)$$

$\Theta_V = \frac{h\nu}{k}$ char. T der Vibration

($\Theta_V > T$ typischerweise)

$\Rightarrow U_V^m = n \cdot R \cdot T \quad$ ($n = 3N-6$ Schwingungsfreiheitsgrade)

$C_{VV}^m = n \cdot R$

elektronische Anregung

$$q_e = g_0 \left(+ g_1 e^{-\epsilon_1/kT}\right)$$

insgesamt:

$$q_{Gesamt} = q_T \cdot q_R \cdot q_V \cdot q_e$$

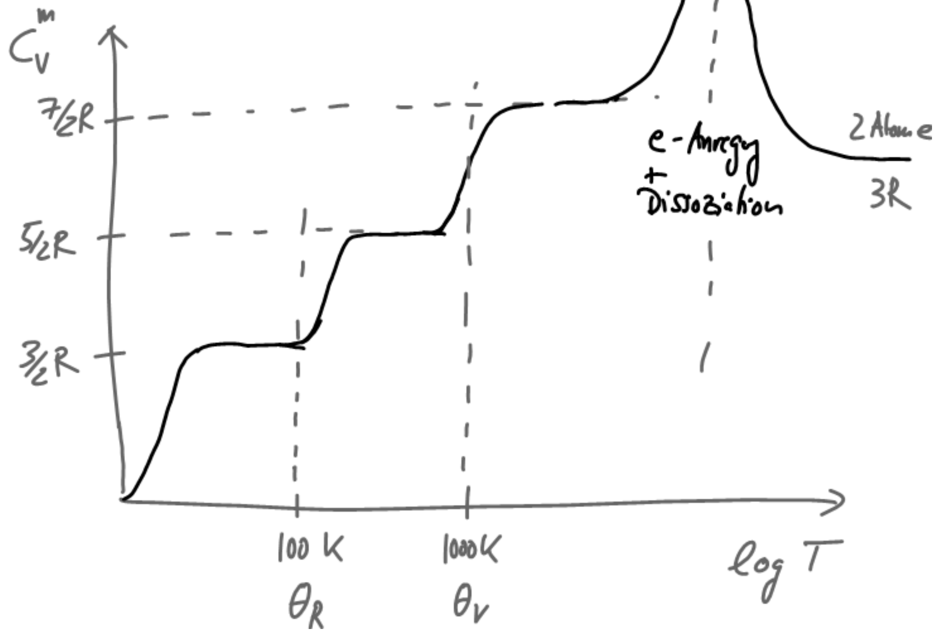
$$\ln q_{Gesamt} = \ln q_T + \ln q_R + \ln q_V + \ln q_e$$

$$U_{Gesamt} = U_T + U_R + U_V + U_e$$

im Allgemeinen $\quad \Theta_T \ll \Theta_R < T < \Theta_V \ll \Theta_e$

Beispiel: HCl (2-atomiges Molekül):

$$q_{Gesamt} = \left(\frac{T}{\theta_T}\right)^{3/2} \cdot \left(\frac{T}{\sigma\, \theta_R}\right) \cdot \left(\frac{1}{1-e^{-T/\theta_V}}\right) \cdot g_0^e$$



Berechnung von U, c_V, S aus numerischen Zustandsummen

$$q = \sum_i g_i\, e^{-\beta\epsilon_i}$$

$$\dot{q} = \sum_i g_i(\beta\epsilon_i)\, e^{-\beta\epsilon_i}$$

$$\ddot{q} = \sum_i g_i(\beta\epsilon_i)^2\, e^{-\beta\epsilon_i}$$

} Hilfs-Summen

$$U-U_0 = -\frac{N}{q}\left(\frac{\partial q}{\partial\beta}\right)$$

$$= -\frac{N}{q}\sum_i \frac{\partial}{\partial\beta}\left(g_i\, e^{-\beta\epsilon_i}\right)$$

$$= -\frac{N}{q}\sum_i g_i\,(-\epsilon_i)\, e^{-\beta\epsilon_i}$$

$$= \frac{N}{q}\,\frac{1}{\beta}\sum_i g_i\,(\beta\epsilon_i)\, e^{-\beta\epsilon_i}$$

$$\Rightarrow \boxed{U-U_0 = \frac{NkT}{q}\cdot \dot{q}}$$

$$\boxed{S_m = \frac{U^m-U_0^m}{T} + R\ln\left(\frac{q}{N_L}\right) + R = R\left(\frac{\dot{q}}{q} + \ln\left(\frac{e\cdot q}{N_L}\right)\right)}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial \beta}{\partial T}\left(\frac{\partial U}{\partial \beta}\right)_V$$

$$= -\frac{1}{kT^2}\frac{\partial}{\partial \beta}\left(\frac{N}{q}\sum_i g_i \epsilon_i e^{-\beta\epsilon_i}\right)$$

$$= -\frac{N}{kT^2}\left\{-\frac{1}{q^2}\left(\frac{\partial q}{\partial \beta}\right)\sum_j g_i \epsilon_i e^{-\beta\epsilon_i} - \frac{1}{q}\sum_i g_i \epsilon_i^2 e^{-\beta\epsilon_i}\right\}$$

$$= \frac{N}{kT^2}\left\{\frac{1}{q^2}\left(-\sum_i g_i \epsilon_i e^{-\beta\epsilon_i}\right)\left(\sum_i g_i \epsilon_i e^{-\beta\epsilon_i}\right) + \frac{1}{q}\sum_i g_i \epsilon_i^2 e^{-\beta\epsilon_i}\right\}$$

$$= \frac{N}{kT^2}\left\{-\frac{1}{q^2}\frac{1}{\beta^2}\dot{q}^2 + \frac{1}{q}\cdot\frac{1}{\beta^2}\ddot{q}\right\}$$

$$= Nk\left\{-\frac{\dot{q}^2}{q^2} + \frac{\ddot{q}}{q}\right\}$$

$$\Rightarrow \boxed{C_V^m = R\left\{-\left(\frac{\dot{q}}{q}\right)^2 + \frac{\ddot{q}}{q}\right\}}$$