[Rekommenderad uppg. 21.1 – 21.6]

# Statistisk Termodynamik för ideala gaser

$$\mathcal{Z} = \sum_{j=1}^{\infty} \exp(-\epsilon_j / kT)$$

där $k = \frac{R}{N_A}$

tillstånds-summa (stort Zäta!)

~ alla kanttillstånd!

└ Boltzmann's konst.

$$\mathcal{Z} = \mathcal{Z}(V, T, N_B)$$

~ sammansättning

{$N_B$ - N partiklar av typ B}

$$P = kT \left(\frac{\partial \ln \mathcal{Z}}{\partial V}\right)_{T, N_B}$$

tryck

$$U = kT^2 \left(\frac{\partial \ln \mathcal{Z}}{\partial T}\right)_{V, N_B}$$

inre energi

$$S = UT^{-1} + k \ln \mathcal{Z}$$

entropi

$$A = -kT \ln \mathcal{Z} \qquad \{A = U - TS\}$$

Helmholtz

Antag $\mathcal{Z}$ för en ideal gas {ideal gas - icke växelverkande partiklar!}

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \ldots + \hat{h}_N$$

{$\hat{h}_N$ = Hamiltonoperatorn för partikel N}

Hamilton-operatorn för systemet (av icke-växelverk. part.)

$$E_j = \epsilon_{1,r} + \epsilon_{2,s} + \ldots + \epsilon_{N,w}$$

~~Om identiska molekyler: $E_j = (\epsilon_{1,r} + \epsilon_{1,s} + \ldots + \epsilon_{1,w})$~~

$$\mathcal{Z} = \sum_j \exp(-\beta E_j) = \sum_j \exp\left(-\beta(\varepsilon_{1,r} + \varepsilon_{2,s} + \ldots + \varepsilon_{N,w})\right) =$$

$$= \sum_r \exp(-\beta \varepsilon_{1,r}) \cdot \sum \exp(-\beta \varepsilon_{2,s}) \ldots$$

molekylär tillst. summa för part 1

molekyler tillst. summa för part. 2 ...

$$z = \sum \exp\left(-\frac{\varepsilon_r}{kT}\right)$$ Molekylär tillståndssumma

(lilla zäta)

$$\mathcal{Z} = z^N \quad \{\text{identiska, urskiljbara, icke-växelverkande molekyler}\}$$

↳ $1_{(s)}2_{(r)}$ samma som $1_{(r)}2_{(s)}$ !

* Om icke-urskiljbara → måste dela på antal permutationer!

$$\mathcal{Z} = \frac{z^N}{N!} \quad \{\text{identiska, icke-urskiljbara, icke-växelverkande molekyler}\}$$

↳ gäller för ideal gas vid normala förhållanden!

$$U = kT^2 \left(\frac{\partial \ln \mathcal{Z}}{\partial T}\right)_{V,N_B}$$

Obs! $\ln \mathcal{Z} = N \ln z - \ln N!$

N part. av typ. B ~ $N_B = n \cdot N_A$ ~ avogadro

$N_B \cdot k = n \cdot N_A \cdot k = n \cdot R$ ~ antal mol

$$U = nRT^2 \left(\frac{\partial \ln z}{\partial T}\right)_{V,n}$$

→ $S = \frac{U}{T} + nR \ln z - k \ln N_B!$

Stirlings approx. för stora N: $\ln N! = N\ln N - N =$

$= N(\ln N - 1)$

Ger:

$$S = \frac{U}{T} + nR\ln z - k\ln N_B! =$$

$$= \frac{U}{T} + nR\ln z - nR(\ln N_A + \ln n - 1)$$

$R = 8.314\ \frac{J}{mol\cdot K}$

$\ln N_A = 54.755$

$$\varepsilon_r = \varepsilon_{tr,s} + \varepsilon_{rot,t} + \varepsilon_{vib,v} + \varepsilon_{el,v}$$

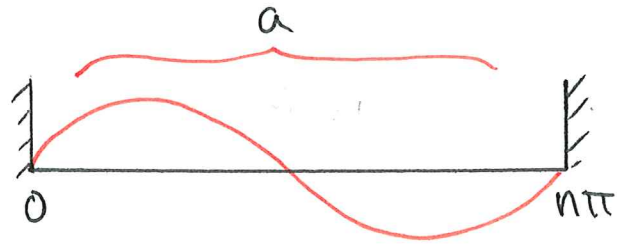
kärnornas vågfunktion; elektronernas vågfunktion

translation rotation vibration

$$z = z_{tr}\cdot z_{rot}\cdot z_{vib}\cdot z_{el}$$

$$\ln z = \ln z_{tr} + \ln z_{rot} + \ln z_{vib} + \ln z_{el}$$

En-dimensionell låda



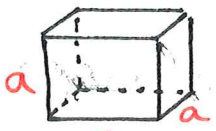

$$\hat{H} = \frac{\hbar^2}{2m}\cdot\frac{d^2\psi(x)}{dx^2} = E_n\psi(x)$$

$$\Rightarrow \psi = A\sin\left(\frac{n\pi x}{a}\right)$$

$$E_n = \frac{h^2}{8m}\left(\frac{n^2}{a^2}\right) \qquad n = 1,2,3,\ldots$$

energi-nivåer för part. i en 1D-låda {Partikeln i lådan}

Tre-dimensionell låda:




$$\varepsilon_{tr,s} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad n_x, n_y, n_z = 1, 2, 3, \ldots$$

$$z_{tr} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left(-\frac{1}{kT}\frac{h}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)\right) =$$

$$= \sum_{n_x=1}^{\infty} \exp\left(-\frac{1}{kT}\frac{h}{8ma^2} n_x^2\right) \cdot \sum_{n_y=1}^{\infty} \ldots\ldots$$

$$z_{tr,x} = z_{tr,y} = z_{tr,z} \longrightarrow z_{tr} = z_{tr,x}^3$$

$$z_{tr,x} \approx \int_0^{\infty} \exp\left(-\frac{1}{kT}\frac{h^2}{8ma^2} n^2\right) dn = \left\{c = \frac{1}{kT}\frac{h^2}{8m}\right\}$$

det "är ett integral ett tecken!!!"

$$= \int_0^{\infty} \exp\left(-\frac{c}{a^2} n^2\right) dn =$$

$$= \frac{1}{2}\left(\pi a^2 c^{-1}\right)^{\frac{1}{2}} = \frac{1}{2}\left(\frac{\pi}{c}\right)^{\frac{1}{2}} a$$

$$z_{tr} = \left(\frac{\pi \cdot 2mkT}{h^2}\right)^{\frac{3}{2}} \cdot V \qquad \{V = a^3\}$$

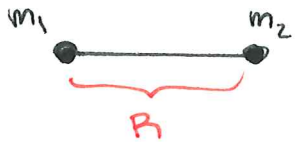
$$\ln z_{tr} = \frac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\right) + \frac{3}{2}\ln T + \ln V$$

## $z_{rot}$

~~Diatom~~ Diatomär molekyl med stel rotor (approx.)

$$\varepsilon_{rot} = \left(\frac{\hbar}{2I}\right) J(J+1) \qquad J = 0, 1, 2, \ldots \quad \text{rot. kvanttal}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} R^2$$



$(2J+1)$ olika kvanttillstånd!

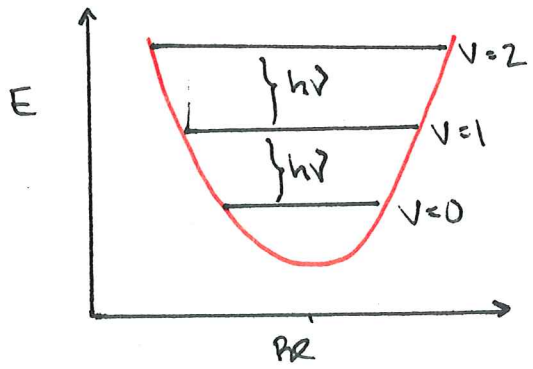
$$z_{rot} = \int_0^\infty \cdot \exp\left(-\frac{\Theta}{T} W\right) dW \qquad \begin{cases} W = J(J+1) \\ dW = 2J+1 \end{cases}$$

Integral

$$\rightarrow z_{rot} = \frac{I}{\sigma \cdot \Theta_{rot}} \qquad \begin{cases} \sigma = 1 & \text{hetero} \\ \sigma = 2 & \text{homo} \end{cases} \Big\} \text{nukleära}$$

$$\hookrightarrow \Theta_{rot} = \left(\frac{\hbar^2}{2Ik}\right)$$

## $z_{vib}$




$\nu$ - karaktäristisk vibrations-frekvens

$$\varepsilon_{vib} = \left(v + \frac{1}{2}\right) h\nu \rightarrow \varepsilon_{vib} = v h\nu \qquad v = 0, 1, 2, \ldots$$

$$\{\varepsilon_{vib,0} = 0\} \rightarrow \text{dvs } \varepsilon_{vib} = \frac{1}{2} h\nu = 0 \ldots$$

$$z_{vib} = \sum_{V=0}^{\infty} \exp(-\beta h\nu \cdot v) = \sum_{V=0}^{\infty} \exp\left(-\frac{h\nu}{kT}\right)^V$$

$$= \frac{1}{1 - \exp\left(-\frac{kT}{h\nu}\right)}$$

Obs!

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

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad H = U + PV$$

$$C_p = C_V + R$$