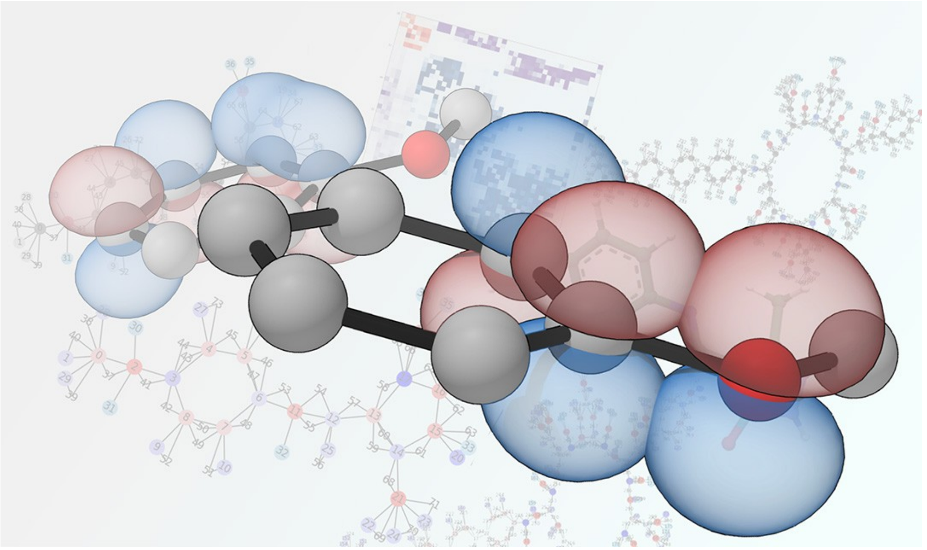
Aula 03 – Termodinâmica Molecular



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$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$$

$$|\Psi\rangle = |\psi\rangle e^{-iEt/\hbar}$$

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

Ensemble Canônico

Função de partição canônica

$$Q(N,V,T) = \sum_i e^{-\beta E_i} \quad \text{com} \quad \beta = \frac{1}{k_B T}$$

Energia de Helmholtz

$$F = -k_B \ln Q$$

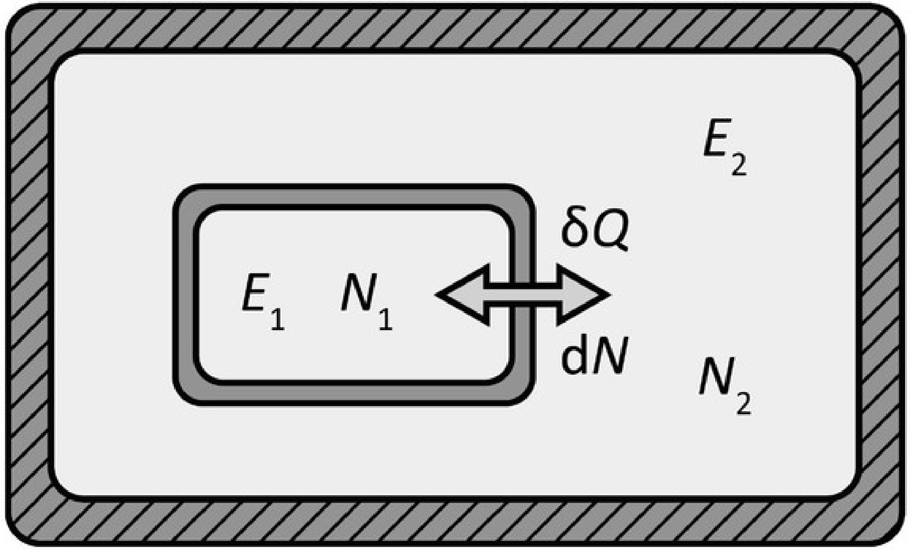
Quantidades Termodinâmicas

$$U = k_B T^2 \left(\frac{\ln Q}{T} \right)_{N,V}$$

$$S = k_B \ln Q + k_B T \left(\frac{\ln Q}{T} \right)_{N,V}$$

$$H = U + PV$$

$$G = H - TS$$

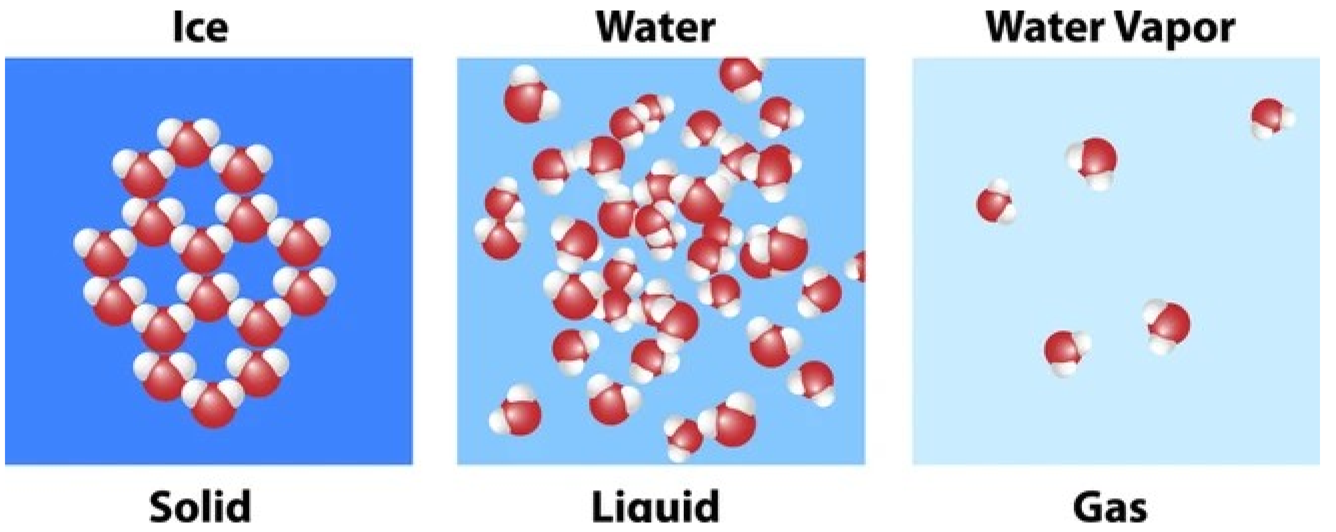


Aproximação de Gás Ideal

Moléculas não interagem entre si

$$Q(N,V,T) = \frac{1}{N!}\sum_i e^{-\beta[\epsilon_1+\epsilon_2+\cdots+\epsilon_N]_i}$$

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



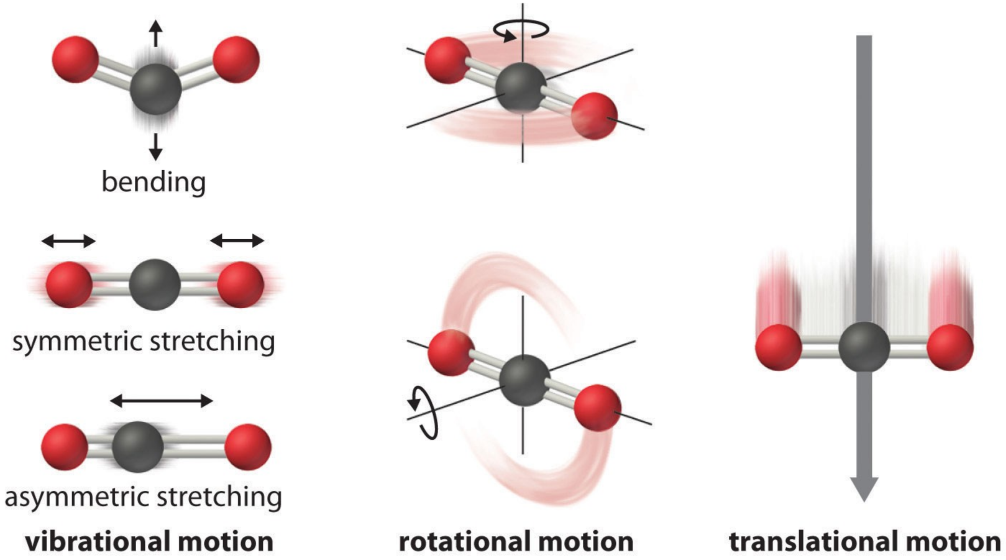
Função de partição molecular

$$q(V,T) = \sum_i e^{-\beta\epsilon_i}$$

Separando Energias

$$q(V,T) = \sum_{\mu}^{\text{energias}} e^{-\beta[\epsilon_{\text{trans}}+\epsilon_{\text{rot}}+\epsilon_{\text{vib}}+\epsilon_{\text{elec}}]_\mu}$$

Separação em auto-estados de energia



$$q(V,T) = \left[\sum_{i}^{\text{trans}} e^{-\beta\epsilon_i}\right]\left[\sum_{j}^{\text{rot}} e^{-\beta\epsilon_j}\right]\left[\sum_{k}^{\text{vib}} e^{-\beta\epsilon_k}\right]\left[\sum_{l}^{\text{elec}} e^{-\beta\epsilon_l}\right]$$

Termodinâmica

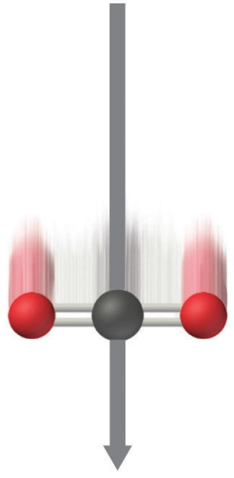
$$\ln[Q(N,V,T)] = \ln\{\frac{[q_{\text{trans}}(V,T)q_{\text{rot}}(V,T)q_{\text{vib}}(V,T)q_{\text{elec}}(V,T)]}{N!}\}$$

$$\ln[Q(N,V,T)] \approx N\ln[q_{\text{trans}}(V,T)] + N\ln[q_{\text{rot}}(V,T)] + N\ln[q_{\text{vib}}(V,T)] + N\ln[q_{\text{elec}}(V,T)] - N\ln N + N$$

Função de Partição de Translação

$$q_{\text{trans}}(V,T) = \sum_i^{\text{trans}} e^{-\beta\epsilon_i}$$

$$= \frac{1}{h^3} \iint e^{-\beta \boldsymbol{p}^2/2M} \mathrm{d}\boldsymbol{p}\mathrm{d}\boldsymbol{x}$$



$$q_{\text{trans}}(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V$$

$$E_{\text{trans}} = \frac{3}{2} N k_B T$$

$$S_{\text{trans}} = N k_B \left[\ln q_{\text{trans}} + \frac{3}{2}\right]$$

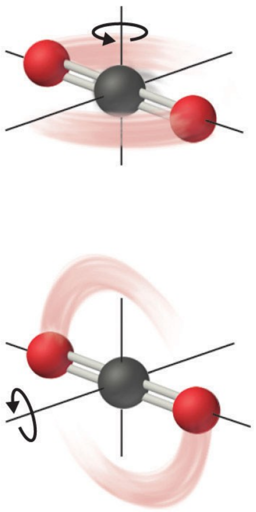
Função de Partição de Rotação

$$q_{\text{rot}}(V,T) = \sum_{j}^{\text{rot}} e^{-\beta\epsilon_j}$$

$$= \sum_{j=0}^{\infty} g_j e^{-\beta \frac{\hbar^2 j(j+1)}{I_{\text{eff}}}}$$

degenerescência

$$g_j = 2j+1$$



$$q_{\text{rot}}(V,T) = \pi^{1/2}\left(\frac{8\pi^2 k_B T I_{\text{eff}}}{h^2}\right)^{3/2}$$

$$E_{\text{rot}} = \frac{d_{\text{rot}}}{2} N k_B T$$

$$S_{\text{rot}} = N k_B \left[\ln q_{\text{rot}} + \frac{d_{\text{rot}}}{2}\right]$$

$$I_{\text{eff}} = \frac{(I_A I_B I_C)^{1/3}}{\sigma}$$

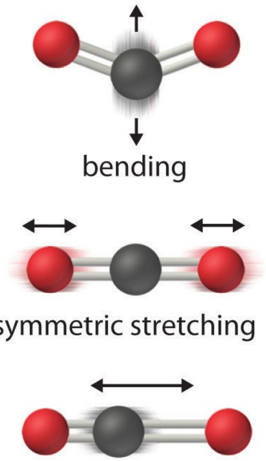
Mom. De inércia eixos principais

Número de simetria rotacional
(Table 10.1 - Cramer)

Função de Partição de Vibração

$$q_{\text{vib}}(V,T) = \sum_k^{\text{vib}} e^{-\beta\epsilon_k}$$

$$= \prod_{k=0}^{3M-6} \sum_{n_k=0}^{\infty} e^{-\beta\hbar(n_k+\frac{1}{2})\omega_k}$$



$$q_{\text{vib}}(V,T) = \prod_{k=0}^{3M-6} \frac{1}{(1-e^{-\beta\hbar\omega_k})}$$

$$E_{\text{vib}} = N \sum_k^{3M-6} \frac{\hbar\omega_k e^{-\beta\hbar\omega_k}}{(1-e^{-\beta\hbar\omega_k})}$$

$$S_{\text{vib}} = N \sum_k^{3M-6} \left[\frac{1}{T}\frac{\hbar\omega_k e^{-\beta\hbar\omega_k}}{(1-e^{-\beta\hbar\omega_k})} - \ln(1-e^{-\beta\hbar\omega_k})\right]$$

Função de Partição Eletrônica

$$q_{\text{ele}}(V,T) = \sum_{l}^{\text{ele}} e^{-\beta \epsilon_l}$$