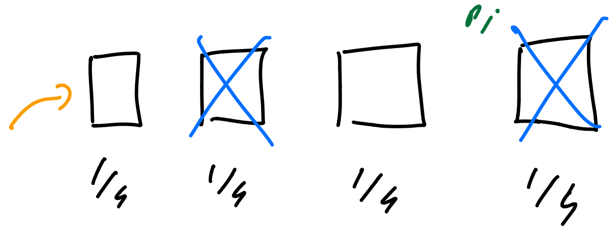
$$-\sum_i p_i \log p_i \quad + (\text{constraints})$$



$$S = \log_2 4 = -\frac{1}{4}\log_2\frac{1}{4} - \frac{1}{4}\log_2\frac{1}{4} - \frac{1}{4}\log_2\frac{1}{4} - \frac{1}{4}\log_2\frac{1}{4}$$

$$-\frac{1}{4}\log_2\frac{1}{4} - \frac{3}{4}\log_2\frac{3}{4}$$

Atoms! $\quad E = \varepsilon_{tr} + \varepsilon_{el} + \varepsilon_{nuc.}$

$$Z = \sum_i e^{-\beta E_i} \qquad \varepsilon_n^{(\text{tra})} = \frac{n^2 h^2}{8 m L^2}$$

$$z = \int_0^\infty e^{-\beta \frac{n^2 h^2}{8 m L^2}}\, dn$$

$n,\ n+1 \qquad L >> 1 \qquad m = 10^{-12} g$

$$\Delta \varepsilon_n \sim \frac{2(n+1)\, h^2}{8 m L^2} \qquad L = 10 cm$$

$$\Delta \varepsilon_n \sim 10^{-20}$$

$$\int_0^{+\infty} e^{-ax^2}\, dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$$

$$z = \frac{1}{2}\left(\frac{8 m L^2 k_B T}{h^2}\right)^{1/2} = \left(\frac{2 m k_B T}{h^2}\right)^{1/2} \cdot L$$

$$q = z^3 = \left(\frac{2 m k_B T}{h^2}\right)^{3/2} V = \frac{V}{\lambda^3}$$

$$\lambda = \frac{h}{(2 m k_B T)^{1/2}} \qquad \frac{p^2}{2m} \quad \lambda \quad h/\lambda$$

thermal wave length

$\lambda \simeq 0.7 \mathring{A}$

$H_2 \quad T = 300K \qquad L = V^{1/3} >> \lambda$

$$Z = \frac{z^N}{N!} \qquad N! = \left(\frac{N}{e}\right)^N$$

$$A = -k_B T \log Z = -N k_B T \log\left[\frac{(2\pi m k_B T)^{3/2}}{h^2}\,\frac{Ve}{N}\right]$$

$$E = \frac{\partial \log Z}{\partial(-\beta)} = \frac{3}{2} N k_B T$$

$$P = -\frac{\partial A}{\partial V} = \frac{N k_B T}{V}$$

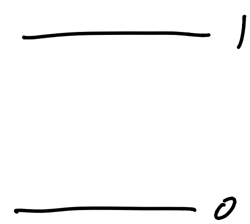
$$A = E - TS$$

$$S = \frac{E - A}{T}$$

$$S' = \frac{3}{2} N k_B + N k_B \log\left[\frac{(2\pi m k_B T)^{3/2}}{h^2}\,\frac{Ve}{N}\right]$$

$$\mu = \frac{\partial A}{\partial N} = -k_B T \log \frac{Z}{N} = -k_B T \log\left[\frac{(2\pi m k_B T)^{3/2}}{h^2} kT\right] + k_B T \log P$$

$$\mu = \mu_0(T) + k_B T \log P$$



$$Z_{el} = \sum e^{-\varepsilon/k_B T} = g_0 + g_1 e^{-\varepsilon_{10}/k_B T}$$

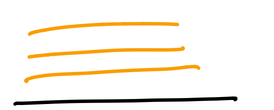
$S_{1/2}$ $\quad P_1$

$2J+1$

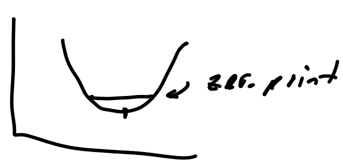
Molecules

$$E = E^{(trans)} + E^{(rot)} + E^{(vib)} + E^{(el)} + E^{(nuc)}$$

$$Z = z^{tran} \cdot z^{rot} \cdot z^{vib} \cdot z^{el} \cdot z^{nuc}$$



$$Z = \sum_{v=0}^{\infty} e^{-\beta v h \nu}$$



$E_v = \left(\frac{1}{2} + v\right) h\nu$

$$Z_{vib} = \frac{1}{1 - e^{-h\nu/k_B T}}$$

$k_B T >> h\nu$

$$Z_{vib} \approx \frac{k_B T}{h\nu} = \frac{T}{\theta_{vib}}$$

$\theta_{vib} = 2274\ K$

$T = 300 K$

$$E_J = J(J+1)\frac{\hbar^2}{2I} \qquad Z = \sum_{j=0}^{\infty} (2J+1)\, e^{-E_j/k_B T}$$

$$Z_{rot} = \frac{8\pi^2 I k_B T}{h^2} = \frac{T}{\theta_{rot}}$$

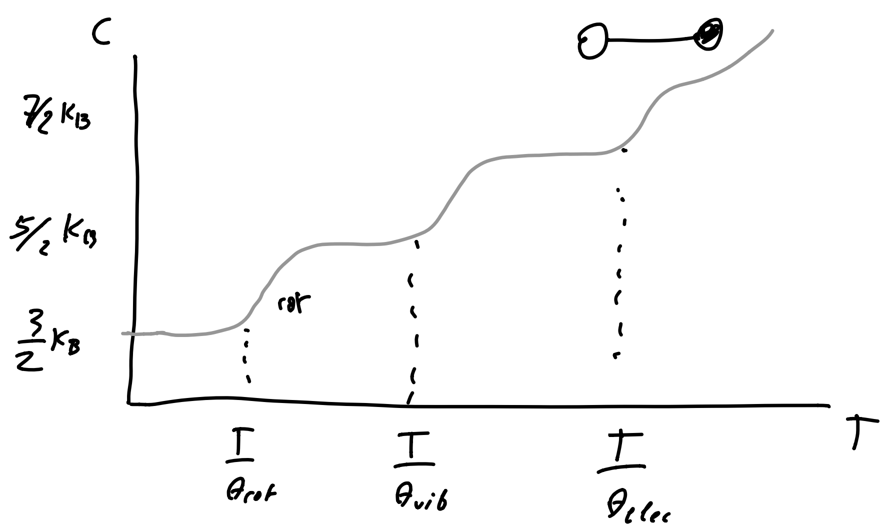
$\theta_{rot} = 2.08\ K$

$T = 300 K$

symmetry fix $\frac{T}{\sigma \theta_{rot}}$

$\sigma = 2$ homonuclear, $\sigma = 2$ H_2O, $\sigma = 12$ CH_4

$$Z = \underbrace{g_0}_{\text{deg elec}} \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V}_{\text{translational}} \left(\frac{8\pi^2 I k_B T}{\sigma h^2}\right) \left(\frac{1}{1 - e^{-h\nu/k_B T}}\right)$$



$P, T = \text{const} \qquad dG = -SdT + Vdp + \sum \mu_i dN_i$

$$dG = \sum_i{}' \mu_i \, dN_i$$

$$A \rightleftarrows B \qquad N_A + N_B = N$$

$$dN_A = -dN_B$$

$$(\mu_A - \mu_B)\, dN_B = 0$$

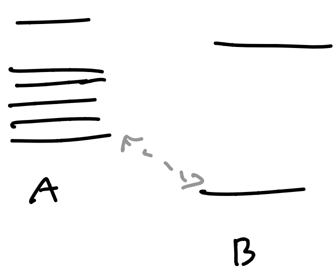
$$\mu_A = \mu_B$$

$$\mu_A = -k_B T \log \frac{Z_A}{N_A} \qquad \mu_B = -k_B T \log \frac{Z_B}{N_B}$$

$$K = \frac{N_B}{N_A} \qquad \mu_A = \mu_B$$

$$\frac{Z_A}{N_A} = \frac{Z_B}{N_B}$$

$$K = \frac{Z_B}{Z_A} = \frac{Z_B'}{Z_A'} e^{-(\varepsilon_{0B} - \varepsilon_{0A})/k_B T}$$



$$aA + bB \longrightarrow cC + dD$$

$$\mu_A dN_A + \mu_B dN_B = \mu_C dN_C + \mu_D dN_D$$

$$\sum_i{}' \mu_i \nu_i \, dX = 0$$

progress coord

$$(-a\mu_A - b\mu_B + c\mu_C + d\mu_D) = 0$$

$$a\left[-k_B T \log \frac{Z_A}{N_A}\right] + b\left[-k_B T \log \frac{Z_B}{N_B}\right] = c\left[-k_B T \log \frac{Z_C}{N_C}\right] + \ldots$$

$$K = \frac{N_C^c \, N_D^d}{\ldots} = \frac{Z_c^c \, Z_d^d}{\ldots} e^{-(\varepsilon_{0C} + \varepsilon_{0D} - \varepsilon_{0A} - \varepsilon_{0B})}$$

$$\frac{}{N_A^a \; N_B^b} = \frac{}{z_A^a \; z_B^b} \qquad k_B T$$

$$H_2 + D_2 \longrightarrow 2HD$$

$$K_t = \frac{z_{HD}^2}{z_{H_2} \, z_{D_2}} = \frac{m_{HD}^2}{m_{H_2} \, m_{D_2}} = 1.19$$

$$K_r = \frac{z_{HD}^{rot\,2}}{z_{H_2}^{rot} \, z_{D_2}^{rot}} = \frac{\sigma_{H_2} \, \sigma_{D_2}}{\sigma_{HD}^2} \cdot \frac{I_{HD}^2}{I_{H_2} \, I_{D_2}} = 4 \cdot (\,\cdot\,\cdot\,) = 3.56$$

$$K_v = \frac{\left(1 - e^{-h\nu_{HD}/k_B T}\right)^{-2}}{\left(1 - e^{-h\nu_{H_2}/k_B T}\right)^{-1} \left(1 - e^{-h\nu_{D_2}/k_B T}\right)^{-1}} \simeq 1$$