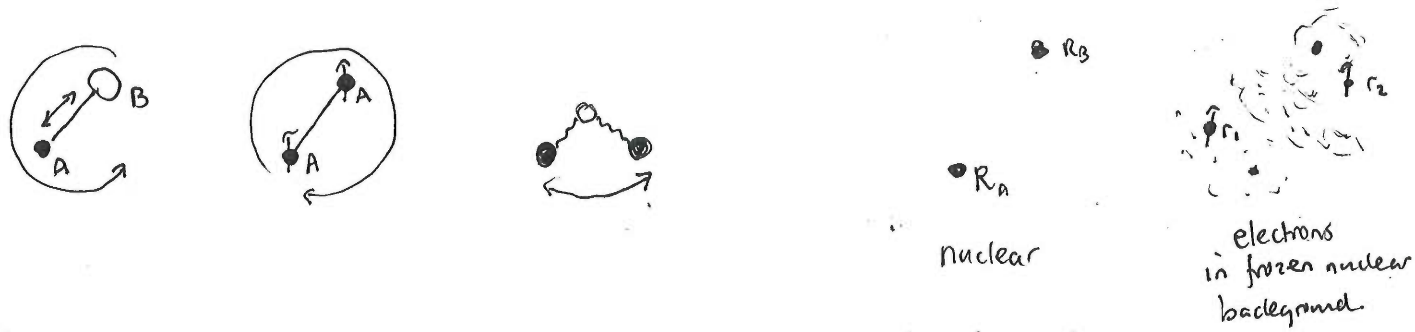
6.5 Molecules with Internal Motion (see also, Peliti section 4.6, p116).



We shall study the statistical mechanics of molecules in the limit where the translational motion is classical, i.e

$$n\lambda_T^3 = \left(\frac{\lambda_T}{a}\right)^3 \ll 1$$

Boltzmanian in its translational degrees of freedom.

Two aspects we must consider

- $\epsilon_{Rot} \sim k_B T$ We must consider the excitation of the (quantum mechanical) rotational degrees of freedom.

- Electronic & nuclear degrees of freedom become intertwined when we are dealing with identical atoms A–A molecules

$$\Psi_{\sigma_1\sigma_2}(\vec{r}) = \chi_{\sigma_1\sigma_2}\,\psi(\vec{r})$$

Fermions	+ $S=1$ − $S=0$	− l odd + l even
Bosons	+ $S=1$ − $S=0$	+ l even − l odd.

To make progress we take advantage of the BORN - OPPENHEIMER approximation: for the electrons we can consider the nuclear degrees of freedom to be frozen (R), giving rise to an electronic energy $\epsilon_n(R)$ that is a function of the nuclear co-ordinates R. This quantity then serves as an effective potential for the nuclear motions

nucleii

nuclei

$$\Psi(r, R) = \Phi_n(r, R)\, \Psi_{n\nu}(R)$$

e^-

electrons moving in frozen background of nucleii

$$\left[\hat{K}(r) + V(r) + V(\vec{R}) + V(\vec{r},\vec{R})\right] \Phi_n(\vec{r},\vec{R}) = \epsilon_n(R)\, \Phi_n(r, R)$$

$$\left[\hat{K}(R) + \epsilon_n(R)\right] \Psi_{n\nu}(R) = \epsilon_{n,\nu}\, \Psi_{n,\nu}(R)$$

electron energies become effective potential of nuclear motions.

$\nu \equiv$ vibrational + rotational.

$n \equiv$ electronic

$$Q_N(V,T) = \frac{1}{N!}\left[Q_1(V,T)\right]^N$$

$$Q_1(V,T) = \frac{V}{\lambda_T^3}\, j(T)$$

PARTITION FUNCTION OF INTERNAL DEGREES OF FREEDOM

$$j(T) = \sum g_{n\nu}\, e^{-\epsilon_{n\nu}\beta}$$

$$j(T) = \sum g_{n\sigma} \exp\left[-\frac{\epsilon_{n\sigma}}{k_B T}\right]$$

$$= g_{0,0} \exp\left[-\frac{\epsilon_{0,0}}{k_B T}\right] \sum \exp\left[-\frac{(\epsilon_{n,\nu} - \epsilon_{0,0})}{k_B T}\right]$$

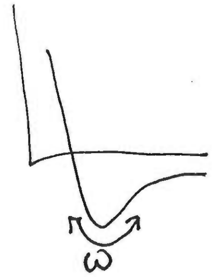
Very important to keep in mind that the differences in energy that appear in this expression are usually much larger than $k_B T$. ($1\text{eV} \sim 10^4 K$) We can ignore all but the vibrational & rotational (v) degrees of freedom.

Usually possible to consider the vibrational & rotational degrees of freedom as independent.

$$j(T) \approx g_0 \exp\left[-\frac{\epsilon_{00}}{k_B T}\right] \sum \exp\left[-\frac{(\epsilon_{0v} - \epsilon_{00})}{k_B T}\right]$$

$$\boxed{\Delta\epsilon_v = \epsilon_{0v} - \epsilon_{00} = \left(n+\frac{1}{2}\right)\hbar\omega + \underbrace{\ell(\ell+1)\frac{\hbar^2}{2I}}_{(2\ell+1)\text{ fold deg.}}}$$

ω is the vibration frequency around the Born-Oppenheimer minimum

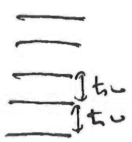


$$\boxed{\omega^2 = \left(\frac{1}{M_A} + \frac{1}{M_B}\right) \frac{\partial^2 \epsilon_0(R)}{\partial R^2}\Bigg|_{R_0}}$$

In the classical limit

$$q(T) = \frac{\overset{\substack{\text{electronic mult.}\\ \downarrow}}{g_0}}{\sigma_{AB}} \exp\left(-\frac{E_{00}}{k_BT}\right) \overbrace{(2I_A+1)(2I_B+1)}^{\text{nuclear multiplicities}} q_{vib}(T)\, q_{rot}(T)$$

$$\sigma_{AB} = \text{symmetry factor} = \begin{cases} 1. & A \neq B \\ 2. & A = B \end{cases}$$



$$q_{vib} = \sum_{n=0}^{\infty} \exp\left[-\frac{(n+\frac{1}{2})\hbar\omega}{k_BT}\right] = \exp\left[-\frac{1}{2}\frac{\hbar\omega}{k_BT}\right]\left(1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right)^{-1}$$

$$q_{rot} = \sum_{\ell=0}^{\infty} (2\ell+1) \exp\left[-\frac{\hbar^2 \ell(\ell+1)}{k_BT}\right].$$

$$\Theta_r = \hbar^2/2Ik_B$$

Approx:

$$q_{rot} \approx \int d\ell\, (2\ell+1) \exp\left[-\frac{\ell(\ell+1)\Theta_r}{T}\right] = \frac{T}{\Theta_{rot}}$$

$$-\frac{\partial \ln q_{rot}}{\partial\beta} = \frac{\partial}{\partial\beta} \ln(\beta\,\Theta_{rot} k_B) = k_BT. \qquad C_{V\,rot} = Nk_B.$$

Better

$$\sum_n f(n) \simeq \int f(x)dx + \frac{1}{2} f(0) - \frac{1}{12} f'(0) + \frac{1}{720} f'''(0) + \ldots$$

$$f(x) = (2x+1) \exp\left[-x(x+1)\Theta_r/T\right]$$

$$j_{rot}(T) = \frac{T}{\Theta_r} + \frac{1}{2} - \left[\frac{1}{6} + \frac{1}{12}\Theta/T\right] + \ldots$$

$$f'''(0) = -2(2x+1$$

$$= \frac{T}{\Theta_r} + \frac{1}{3} + \quad \frac{1}{15}\Theta_r/T + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^2 + \ldots$$

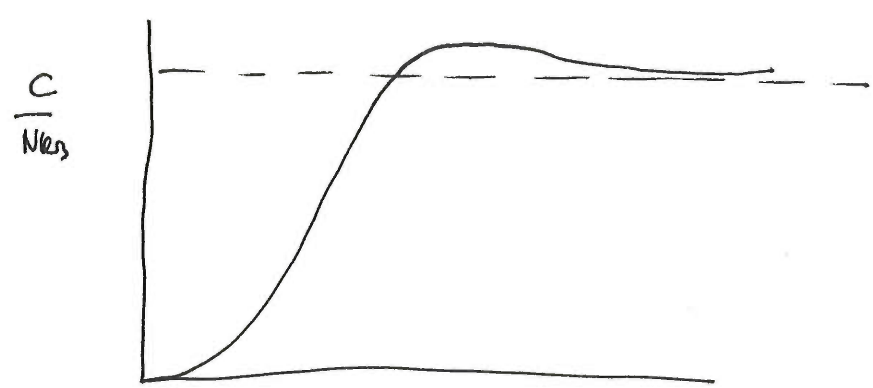
$$U = -N\frac{\partial}{\partial\beta} \ln j_{rot}(T) = N k_B T^2 \frac{\partial}{\partial T} \ln j_{rot}(T)$$

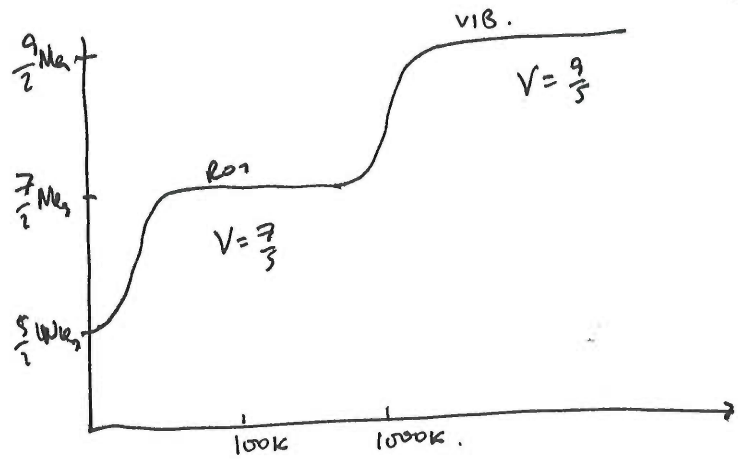
$$= N k_B \left[T - \frac{\Theta}{3} - \frac{\Theta^2}{45T} - \frac{8\Theta^3}{945T^2}\right]$$

$$C_v = \frac{\partial U}{\partial T} = N k_B \left\{1 + \frac{1}{45}\left(\frac{\Theta}{T}\right)^2 + \frac{16}{945}\left(\frac{\Theta}{T}\right)^3 + \ldots\right\}$$

When $T \ll \Theta$ $\quad j_{rot} = 1 + 3e^{-2\Theta/T} + 5e^{-6\Theta/T}$

$$C_v = 12 N k_B \left(\frac{\Theta_r}{T}\right)^2 e^{-2\Theta_r/T}.$$





e.g HD, HT, DT

Diatomic gases C_v as a fn of T.

$C_p^0 = \frac{5}{2} Nk_B$. $C_v = \frac{3}{2} Nk_B$ $\gamma = \frac{C_p}{C_v} = \frac{5}{3}$

Turn on Rotational $k_B T > \Theta_{rot}$

$C_p = \frac{7}{2} Nk_B$ $C_v = \frac{5}{2} Nk_B$ $\gamma = \frac{7}{5}$

Turn on Vib. degrees of fr

$C_p = \frac{9}{2} Nk_B$ $C_v = \frac{7}{2} Nk_B$ $\gamma = \frac{9}{7}$.

ORTHO + PARA HYDROGEN

I=1 PARA

I=0 ORTHO.

$$\Psi_{\sigma_1\sigma_2}(r) = -\Psi_{\sigma_2\sigma_1}(-r)$$

Since nuclei are fermions.

$$\Psi_{\sigma_1\sigma_2}(r) = \chi_{\sigma_1\sigma_2}\,\phi(r)$$

$$\phi(\vec{r}) = \psi(r)\,Y_{lm}(\hat{r})$$

$$\left.\begin{array}{l} Y_{lm}(\hat{r}) \longrightarrow (-1)^l\, Y_{lm}(-\hat{r}) \\ \chi_{\sigma_1\sigma_2} = \begin{cases} -\chi_{\sigma_2\sigma_1} & S=0 \\ +\chi_{\sigma_2\sigma_1} & S=1 \end{cases} \end{array}\right\} \Rightarrow \begin{array}{ll} S=0 & l=1,3,5 \\ S=1 & l=0,2,4\ldots \end{array}$$

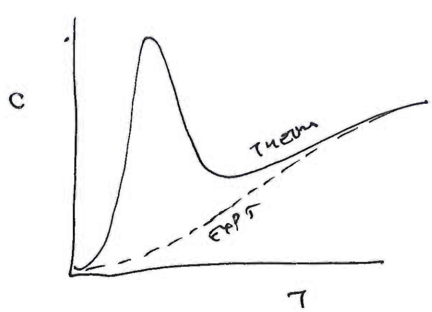
$$z_{rot} = \sum_{\ell \in \text{odd}} (2\ell+1)\, e^{-\hbar^2/2Ik_BT\;\ell(\ell+1)}$$
$$+\, 3 \sum_{\ell \in \text{even}} (2\ell+1)\, e^{-\hbar^2/2Ik_BT\;\ell(\ell+1)}$$

$$C_{rot} = N k_B T \left(\frac{\partial^2\, T \ln z}{\partial T^2} \right)$$

$$-T \ln z = A$$

$$S = -\frac{\partial A}{\partial T} = +\frac{\partial\, T \ln z}{\partial T}$$

$$NT \frac{dS}{dT} = C_v = T \frac{\partial^2\, T \ln z}{\partial T^2}$$



FAILURE!

Nuclear spin & Rot degrees of freedom are not in eqm

$$C_v = N k_B T \left[\underset{\frac{1}{4}}{\frac{N_0}{N}} \frac{\partial^2\, T \ln z_0}{\partial T^2} + \underset{\frac{3}{4}}{\frac{N_1}{N}} \frac{\partial^2\, T \ln z_1}{\partial T^2} \right]$$

$$C_v = N k_B T \left[\frac{1}{4} \frac{\partial^2\, T \ln z_0}{\partial T^2} + \frac{3}{4} \frac{\partial^2\, T \ln z_1}{\partial T^2} \right]$$

CHEMICAL EQUILIBRIUM

e.g $\quad 2H_2O \rightleftharpoons H_3O^+ + OH^-$

$\quad CH_4 + 2O_2 \rightleftharpoons CO_2 + H_2O$

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

$$N_\alpha^0 \to N_\alpha^0 - \nu_\alpha \Delta N \qquad \alpha = A, B$$

$$N_\alpha^0 \to N_\alpha^0 + \nu_\alpha \Delta N \qquad \alpha = C, D$$

Choose $\quad \tilde{\nu}_\alpha = \begin{cases} -\nu_\alpha & \text{reactants} \\ +\nu_\alpha & \text{products.} \end{cases}$

$$\frac{\Delta N_\alpha}{\tilde{\nu}_\alpha} = \text{constant} = \Delta N^0$$

Fixed pressure, temperature

$$\Rightarrow \quad G = E - TS + PV = N g(T, P) = + N\mu .$$

$$dG = -S dT + V dP + \mu dN$$

$$\Delta G = \sum \Delta N_\alpha \mu_\alpha = \sum \Delta N^0 \tilde{\nu}_\alpha \mu_\alpha = 0$$

$$\Rightarrow \quad \boxed{\sum \tilde{\nu}_\alpha \mu_\alpha = \nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B = 0}$$

$$A(N, V, T) = N\epsilon + N k_B T \ln \frac{N\lambda^3}{V} - N k_B T - N k_B T \ln j(T)$$

$$\mu_A = \left(\frac{\partial A}{\partial N_A}\right)_{T,V} = \epsilon_A + k_B T \ln\left(\frac{N_A \lambda_A^3}{V}\right) - k_B T \ln j(T)$$

$$\ln\left[\prod_\alpha \left(\frac{N_\alpha}{V n_0}\right)^{\alpha}\right] + \frac{\tilde{\nu}_\alpha \mu_\alpha^{(0)}}{k_B T} = 0$$

$$\mu_\alpha^{(0)} = e_A + k_B T \ln n_0 \lambda_A^3 - k_B T \ln j(T)$$

$$\Rightarrow \quad \prod_\alpha \left(\frac{N_\alpha}{V n_0}\right)^{\tilde{\nu}_\alpha} = \prod_\alpha [\alpha]^{\tilde{\nu}_\alpha} = e^{-\Delta\mu/k_B T} = k(T)$$

$$\frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}} = k(T)$$

e.g. $\quad 2H_2O \rightleftharpoons H_3O^+ + OH^-$

$$\frac{[H_3O^+][OH^-]}{[H_2O]^2} = K(T)$$

$$\left\{\begin{array}{l} [H_3O^+][OH^-] = \underline{\underline{\text{constant}}} = 10^{-14}\ \text{mol}^2/L^3 \\ -\log_{10}[H_3O^+] = pH. \end{array}\right.$$

$L = 10^3 \text{cm}^3 = 10^{-3} m^3$

[

<u>CAR EXHAUST</u>

$$2CO + O_2 \rightleftharpoons 2CO_2$$

$$\frac{[CO_2]^2}{[CO]^2[O_2]} = k \quad \Rightarrow \quad \frac{CO}{[CO_2]} = \frac{1}{\sqrt{k[O_2]}}$$

$T = 1500K \quad k = 10^{10}$

$T = 600k \quad k \sim 10^{40} \quad \Rightarrow$ no CO!

But reaction incomplete. Reason for catalytic converters