VIBRATIONAL PARTITION FUNCTION

HO − QM

$$E_n = hc\bar{\nu}\left(\frac{1}{2} + n\right) \quad n = 0, 1, \ldots$$

$$q_V = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\frac{\beta hc\bar{\nu}}{2}} \sum_{n=0}^{\infty} e^{-\beta hc\bar{\nu} n}$$

$$= e^{-\beta\frac{hc\bar{\nu}}{2}} \sum_{n=0}^{\infty} \left[e^{-\beta hc\bar{\nu}}\right]^n$$

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \simeq 1 - x + \ldots$$

$$q_R = \frac{e^{-\beta\frac{hc\bar{\nu}}{2}}}{1 - e^{-\beta hc\bar{\nu}}} \longrightarrow \frac{1}{1 - e^{-\beta hc\bar{\nu}}}$$

$\downarrow$ $E_0 \neq 0$

$\downarrow$ ENERGY SHIFT $\Rightarrow E_0 = 0$

POLYATOMIC MOL

N ATOMS $\Rightarrow$ 3N DEGREES OF FREEDOM

3 $\rightarrow$ TRANSLATIONAL DEGREES OF FREEDOM

2 ROT D.F. LINEAR MOL
3 ROT D.F. NON LINEAR MOL

$\Rightarrow$

$$N_V \begin{Bmatrix} 3N-5 \\ 3N-6 \end{Bmatrix}$$ VIBRATIONAL DEGREES OF FREEDOM

$$q_V = \prod_{i=1}^{N_V} q_{V_i}$$

$$\Theta_V \equiv \frac{hc\bar{\nu}}{k}$$ VIBRATIONAL TEMP

$$q_v = \frac{1}{1 - e^{-\Theta_v/T}}$$

$$e^{-x} = 1 - x \Rightarrow x << 1$$

SO $\frac{\Theta_v}{T} << 1$ OR $\Theta_v << T$

HIGH TEMP

$$\boxed{q_v \longrightarrow \frac{T}{\Theta_v} \quad \text{AT HIGH TEMP}}$$

COMPARE HIGH TEMP APPROXIMATION
VS
EXACT

DEGENERACY g_v

$$q_v = \prod_{i=1}^{N_v} \left(q_{v_i}\right)^{g_i}$$

ELECTRONIC PARTITION FUNCTION

$$q_E = \sum_{i=0} g_i \, e^{-\beta E_i}$$

FOR PRACTICAL $T \rightarrow k_B T << E_0$

THE q_E is DOMINATED BY THE GROUND STATE!

$$q_E = \sum_{i=0} g_i \, e^{-\beta E_i} \longrightarrow g_0$$

(shift the energy $\rightarrow$ ZERO).

$$\boxed{q_{mol} = \frac{V}{\Lambda^3} \frac{T}{\Theta_{Rot}} \frac{1}{1-e^{-\Theta_v/T}} g_0}$$

PARTITION FUNCTION

$$q = \sum_i e^{-\beta \varepsilon_i} \quad ; \quad P_i = \frac{e^{-\beta \varepsilon_i}}{q}$$

$$\bar{u} = \sum \varepsilon_i P_i = \sum \varepsilon_i \frac{n_i}{N}$$ AVERAGE ENERGY

$$\frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{q}$$

TOTAL ENERGY $\quad U = N\bar{u}$

$$\bar{u} = \sum_i \varepsilon_i \frac{e^{-\beta \varepsilon_i}}{q}$$

CONSIDER $\ln q$

$$\left(\frac{\partial}{\partial \beta} \ln q\right)_V = \frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -\frac{1}{q}\sum_i \varepsilon_i e^{-\beta \varepsilon_i}$$

$$= -\bar{u}$$

$$\bar{u} = -\left(\frac{\partial}{\partial \beta} \ln q\right)_V$$

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

$$\frac{\partial}{\partial\beta} = \frac{\partial T}{\partial\beta}\frac{\partial}{\partial T} = \frac{1}{\frac{\partial\beta}{\partial T}}\frac{\partial}{\partial T} = -k_BT^2\frac{\partial}{\partial T}$$

$$\frac{\partial\beta}{\partial T} = \frac{\partial}{\partial T}\frac{1}{k_BT} = -\frac{1}{k_B}\frac{1}{T^2}$$

$$\boxed{\frac{\partial}{\partial\beta} = -k_BT^2\frac{\partial}{\partial T}}$$

$$\boxed{U = Nk_BT^2\left(\frac{\partial}{\partial T}\ln q\right)_V}$$

NOTICE

$$-\left(\frac{\partial}{\partial\beta}\ln q\right)_V = k_BT^2\left(\frac{\partial}{\partial T}\ln q\right)_V$$

$$Q = \frac{q^N}{N!}$$

$$\ln Q = N \ln q - \ln N!$$

$$\left(\frac{\partial}{\partial \beta} \ln Q\right)_V = N \left(\frac{\partial}{\partial \beta} \ln q\right)_V$$

$$\boxed{U = -\left(\frac{\partial}{\partial \beta} \ln Q\right)_V}$$

$$\boxed{U = k_B T^2 \left(\frac{\partial}{\partial T} \ln Q\right)_V}$$

$$U = -\left(\frac{\partial}{\partial\beta}\ln Q\right)_V$$

$$= -N\left(\frac{\partial}{\partial\beta}\ln q_m\right)_V$$

$$= -N\left(\frac{\partial}{\partial\beta}\left\{\ln q_T + \ln q_R + \ln q_V + \ln q_E\right\}\right)_V$$

$$= -N\left\{\left(\frac{\partial}{\partial\beta}\ln q_T\right)_V + \left(\frac{\partial}{\partial\beta}\ln q_R\right)_V + \left(\frac{\partial}{\partial\beta}\ln q_V\right)_V + \left(\frac{\partial}{\partial\beta}\ln q_E\right)_V\right\}$$

$$\boxed{U = U_T + U_R + U_V + U_E}$$

$$q_T = \frac{V}{\Lambda^3} \qquad \Lambda \equiv \sqrt{\frac{h^2\beta}{2\pi m}}$$

$$q_R = \frac{T}{\sigma\Theta_R} \qquad \Theta_R = \frac{hcB}{k_B}$$ LINEAR

$$= \frac{\sqrt{\pi}}{\sigma}\frac{T^{3/2}\, k_B^{3/2}}{\sqrt{(hc)^3 B_A B_B B_C}}$$ Non linear

$$q_v = \prod_{n}^{n_{\neq}} (q_{vn})^{g_n}$$

$$q_{vn} = \frac{1}{1 - e^{-\beta h c \bar{\nu}_n}}$$

$$n_{\neq} = 3N - 6 \quad \text{nonlinear}$$
$$= 3N - 5 \quad \text{linear}$$

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a) U_T

$$q_T = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \frac{V}{\beta^{3/2}}\left(\frac{2\pi m}{h^2}\right)^{3/2}$$

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

$$\ln q_T = \ln V + \frac{3}{2}\ln T + \ln(\text{Const})$$

$$\left(\frac{\partial}{\partial T}\ln q_T\right)_V = \frac{3}{2}\frac{1}{T}$$

$$\boxed{U_T = N k_B \frac{3}{2} T = \frac{3}{2} n R T}$$

b) U_R

$$\ln q_R = \frac{3}{2} \ln T + \ln(\text{Const})$$

$$\left(\frac{\partial}{\partial T} \ln q_R\right)_V = \frac{3}{2T}$$

$$\boxed{U_R = N k_B \frac{3}{2} T = \frac{3}{2} nRT}$$ Nonlinear

or $U_R^L = nRT$ linear

Vibrational Partition Function

$$q_V = \prod_{i}^{n_t} (q_{V_i})^{g_i}$$

$$\ln q_V = \sum_{i}^{n_t} g_i \ln(q_{Vi})$$

$$\left(\frac{\partial}{\partial T} \ln q_V\right)_V = \sum_{i}^{n_t} g_i \frac{1}{q_{V_i}} \left(\frac{\partial q_{Vi}}{\partial T}\right)_V$$

$$\left(\frac{\partial q_{Vi}}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} \frac{1}{1 - e^{-\beta h c \bar{\nu}_i}}\right)_V$$

$$= -\frac{1}{(1 - e^{-\beta h c \bar{\nu}_i})^2} \left(- e^{-\beta h c \bar{\nu}_i} (-h c \bar{\nu}_i) \left(\frac{\partial \beta}{\partial T}\right)_V \right)$$

$$\left(\frac{\partial q_{Vi}}{\partial T}\right)_V = \frac{h c \bar{\nu}_i}{k_B T^2} \frac{e^{-\beta h c \nu_i}}{(1 - e^{-\beta h c \nu_i})^2}$$

$$U_V = N \cancel{k_B T^2} \frac{hc\bar{\nu}_i}{\cancel{k_B T^2}} \frac{g_i\, e^{-\beta hc\bar{\nu}_i}}{q_{v_i}\left(1 - e^{-\beta hc\bar{\nu}_i}\right)^2}$$

For $g_i = 1$

$$U_V = \frac{N hc\bar{\nu}_i\, e^{-\beta hc\bar{\nu}_i}}{\left(1 - e^{-\beta hc\bar{\nu}_i}\right)}$$

$$\boxed{U_V = \frac{N hc\bar{\nu}_i}{\left(e^{\beta hc\bar{\nu}_i} - 1\right)}} \xrightarrow[T \to \infty]{} \frac{N hc\bar{\nu}_i}{\beta hc\bar{\nu}_i} = N k_B T$$

PER VIBRATIONAL MODEL

$$= nRT$$

$$U = \frac{3}{2} nRT + n_R\, nRT + \underbrace{n_V\, nRT}_{\text{HIGH TEMP}}$$

<u>Linear</u> $n_R = 1$ $n_V = 3N - 5$

<u>Nonlinear</u> $n_R = \frac{3}{2}$ $n_V = 3N - 6$