WHAT DO WE KNOW?

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

$$q = q_T \, q_R \, q_V \, q_E \, q_N$$

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

$$q_R = \frac{T}{\Theta_R} \quad \text{or} \quad T^{3/2} \frac{\sqrt{\pi}}{\sigma} \left(\frac{k_B}{hcB_A} \right)^{1/2} \left(\frac{k_B}{hcB_B} \right)^{1/2} \left(\frac{k_B}{hcB_C} \right)^{1/2}$$

$$q_V = \prod_n (q_{vni})^{g_n} \; ; \; q_{vni} = \frac{1}{1 - e^{-\beta hc\bar{\nu}_n}}$$

$$q_E = g_0$$

$$q_N = 1$$

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

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

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

$$\boxed{U = \frac{3}{2} N k_B + n_R N k_B + \sum_{n=1}^{n_v} \frac{N h c \bar{\nu}_n}{e^{hc\bar{\nu}_n \beta} - 1}}$$

$$n_R = \begin{cases} 1 & \text{linear} \\ \frac{3}{2} & \text{nonlinear} \end{cases}$$

$$n_v = \begin{cases} 3N-5 & \text{linear} \\ 3N-6 & \text{nonlinear} \end{cases}$$

HEAT CAPACITY C_V

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

$$U = \frac{3}{2} nRT + n_R\, nRT$$

$$+ \sum_i \frac{N h c \bar{\nu}_i}{\left(e^{\beta h c \bar{\nu}_i} - 1\right)}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} \cancel{N} R + n_R \cancel{N} R - \sum_i \frac{N h c \bar{\nu}_i\, e^{\beta h c \bar{\nu}_i} (h c \bar{\nu}_i)}{\left(e^{\beta h c \bar{\nu}_i} - 1\right)^2} \left(\frac{\partial \beta}{\partial T}\right)$$

$$\boxed{C_V = \frac{3}{2} nR + n_R\, nR + \frac{N (hc)^2}{k_B T^2} \sum \frac{\bar{\nu}_i^2 e^{\beta h c \bar{\nu}_i}}{\left(e^{+\beta h c \bar{\nu}_i} - 1\right)^2}}$$

$$\Theta_{v_i} = \frac{h c \bar{\nu}_i}{k_B} \; ; \; N k_B = nR$$

$$C_V = \left(\frac{3}{2} + n_R\right) \cancel{N} R + N k_B \sum_i \frac{\left(\frac{\Theta_{v_i}}{T}\right)^2 e^{\Theta_{v_i}/T}}{\left(e^{\Theta_{v_i}/T} - 1\right)^2}$$

NOW WE CAN CALCULATE

$$C_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V = -k_B \beta^2 \left(\frac{\partial U}{\partial \beta}\right)_V$$

WE HAVE 3 CONTRIBUTIONS

$$C_V = \frac{3}{2} N k_B + n_R N k_B + \sum_n \frac{N k_B \beta^2 (hc\bar{\nu})^2 e^{\beta hc\bar{\nu}}}{\left(e^{\beta hc\bar{\nu}_n} - 1\right)^2}$$

- AT HIGH TEMPERATURE

$$\boxed{C_V = \frac{3}{2} N k_B + n_R N k_B + N n_V k_B}$$

Dulong-Petite

At low temperatures the vibration contribution becomes very important

Einstein Solid

Residual Entropy

IN THE CRYSTALLINE FORM, SOMETIMES MOLECULES HAVE EQUIVALENT ORIENTATIONS

SO AT T=0K AND TWO ORIENTATIONS

$$W = 2^N$$

$$\boxed{S = k \ln W} = kN \ln 2$$

HELMHOLTZ ENERGY

$$A \equiv U - TS$$

$$= U - T\left\{\frac{U}{T} + k_B \ln Q\right\}$$

$$\boxed{A = -k_B T \ln Q}$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$\boxed{P = k_B T\left(\frac{\partial}{\partial V}\ln Q\right)_T}$$

ENTHALPY

$$H = U + PV$$

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

$$\boxed{H = -\left(\frac{\partial}{\partial \beta} \ln Q\right)_V + V k_B T \left(\frac{\partial}{\partial V} \ln Q\right)_T}$$

$$\boxed{H = T\left[k_B T \left(\frac{\partial}{\partial T} \ln Q\right) + k_B V \left(\frac{\partial}{\partial V} \ln Q\right)_T\right]}$$

GIBBS ENERGY

$$G = A + PV$$

$$= -k_B T \ln Q + V k_B T \left(\frac{\partial}{\partial V} \ln Q\right)_T$$

$$\boxed{G = -kT\left[\ln Q - V\left(\frac{\partial}{\partial V} \ln Q\right)_T\right]}$$

ENTROPY

$$S = -Nk_B \sum_i P_i \ln P_i$$

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

$$\ln P_i = -\beta \varepsilon_i - \ln q$$

$$S = -Nk_B \left\{ -\beta \sum_i \varepsilon_i P_i - \ln q \sum_i P_i \right\}$$

$$S = +\frac{N \cancel{k_B}}{\cancel{k_B} T} \bar{u} + k_B \ln q^N$$

$$\boxed{S = \frac{U}{T} + k_B \ln Q}$$

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

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