Partition Functions

$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e$

$q/N_A = (q_t/N_A)\, q_r\, q_v\, q_e$

$q_t \cong 10^{28} - 10^{29}$ V/L

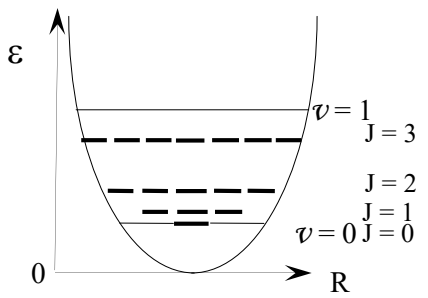
$q^\circ_t/N_A \cong 10^6 - 10^7$

$q_r \cong 10 - 100$

$q_v \cong 1 - 10$

$\varepsilon_r = \tilde{B}\, hc\, J(J+1)$ $\qquad g_J = 2J+1$

$\varepsilon_v = h\nu_o(v+1/2)$



Vibration: $q_v = \sum_{v=0}^{\infty} e^{-h\nu_o(v+1/2)/kT} = e^{-h\nu_o/2kT} \sum_{v=0}^{\infty} e^{-h\nu_o v/kT}$

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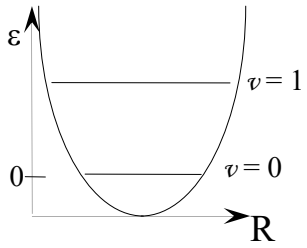
let $a = e^{-h\nu_o/kT}$ $\qquad$ then $e^{-h\nu_o v/kT} = a^v$

$1 + a + a^2 + a^3 + \ldots = \dfrac{1}{1-a}$

$q_v = \dfrac{e^{-h\nu_o/2kT}}{1 - e^{-h\nu_o/kT}}$ $\qquad q_v = q_{mode1}\, q_{mode2}\, q_{mode3}\ldots$



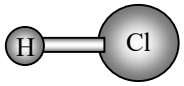
$q_v = \dfrac{1}{1 - e^{-h\nu_o/kT}} = \dfrac{1}{1 - e^{-hc\tilde{\nu}_o/kT}}$

at T $\dfrac{kT}{hc} = 207.2\ \text{cm}^{-1}$ $\quad q_v = \dfrac{1}{1 - e^{-\tilde{\nu}_o/207.2\ \text{cm}^{-1}}}$

Rotation: $q_r = \sum_{J=0}^{\infty} (2J+1)\, e^{-\tilde{B}hc\, J(J+1)/kT}$ $\qquad \tilde{B} = \dfrac{h}{8\pi^2 Ic}$

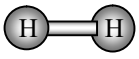
$q_r = \int_0^{\infty} (2J+1)\, e^{-\tilde{B}hc\, J(J+1)/kT}\, dJ = -\dfrac{kT}{\tilde{B}hc} \int_0^{\infty} \dfrac{d\,(e^{-\tilde{B}hc\, J(J+1)/kT})}{dJ}\, dJ$

$q_r = -\dfrac{kT}{\tilde{B}hc}\, e^{-\tilde{B}hc\, J(J+1)/kT}\Big|_0^{\infty} = \dfrac{kT}{\tilde{B}hc}$

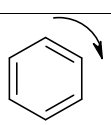


$\sigma = 1$

$q_r = \dfrac{kT}{\sigma \tilde{B}hc}$ $\qquad$ at T $\quad q_r = \dfrac{207.2\ \text{cm}^{-1}}{\sigma \tilde{B}}$



$\sigma = 2$



$\sigma = 12$