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5.62 Physical Chemistry II
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5.62 Lecture #14: Low and High-T Limits for q_{rot} and q_{vib}

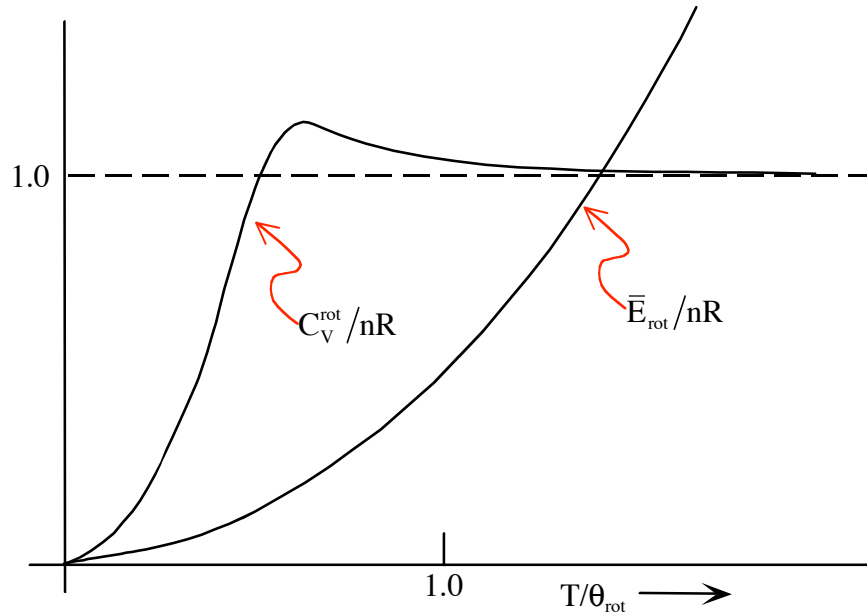
Reading: Hill, pp. 153-159, Maczek pp. 51-53

TEMPERATURE DEPENDENCE OF E_{rot} AND C_V^{rot}

Low T limit of E_{rot} :

$$\lim_{T \rightarrow 0} E_{\text{rot}} = \lim_{T \rightarrow 0} (6Nk\theta_r e^{-2\theta_r/T}) = 0$$

$$\lim_{T \rightarrow 0} C_V^{\text{rot}} = \lim_{T \rightarrow 0} \left(\frac{12Nk\theta_r^2}{T^2} e^{-2\theta_r/T} \right) = 0$$



Low T Limit

$$\frac{C_V^{\text{rot}}}{nR} \cong \frac{12\theta_r^2}{T^2} e^{-2\theta_r/T}$$

$$\frac{E_{\text{rot}}}{nR} \cong 6\theta_r e^{-2\theta_r/T}$$

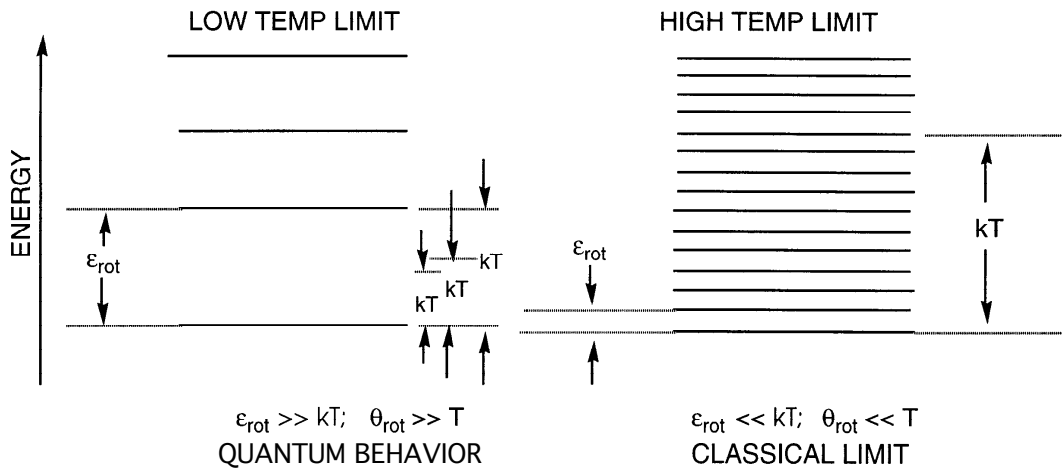
High T Limit

$$\frac{C_V^{\text{rot}}}{nR} \cong 1$$

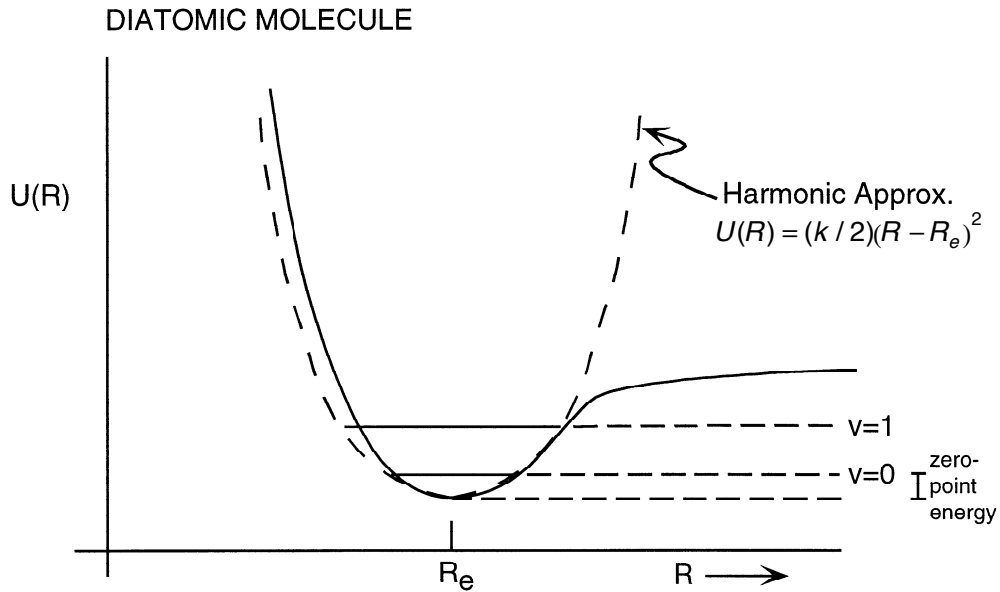
$$\frac{E_{\text{rot}}}{nR} \cong T$$

Note maximum in $\frac{C_V}{R} \cong 1.624$ at $\frac{T}{\theta_{\text{rot}}} = 1.0$ if we retain the **two-term** formula for the low-T limit. Actual maximum, **derived from the full q_{rot}** , is $C_V/nR = 1.098$ at $T/\theta_{\text{rot}} = 0.8$. [Rapid

change in C_V is a signal of a gap in the level spacing measured in units of kT . What gap would be relevant here? At what value of T/θ_{rot} would you expect the most rapid change in C_V ?



VIBRATIONAL MOLECULAR PARTITION FUNCTION q_{vib}



Using harmonic approximation:

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

zero point energy — when $v = 0$

$$\epsilon(v = 0) = \frac{1}{2} h\nu$$

Calculate q_{vib}

$$q_{\text{vib}} = \sum_{v=0}^{\infty} e^{-\epsilon(v)/kT} = \sum_{v=0}^{\infty} e^{-hc\omega_e(v+1/2)/kT}$$

Define $\theta_{\text{vib}} = \frac{hc\omega_e}{k}$ “vibrational temperature” [K]

$$q_{\text{vib}} = \sum_{v=0}^{\infty} e^{-(v+1/2)\theta_{\text{vib}}/T}$$

For vibration, $\theta_{\text{vib}} > T$ almost always. Must sum over each vibrational level.

$$q_{\text{vib}} = e^{-\theta_{\text{vib}}/2T} \sum_{v=0}^{\infty} e^{-v\theta_{\text{vib}}/T} \quad \text{pull zero point energy out of sum}$$

Let $x = e^{-\theta_{\text{vib}}/T}$

$$q_{\text{vib}} = x^{1/2} \sum_{v=0}^{\infty} x^v$$

Now $\sum_{v=0}^{\infty} x^v = 1 + x + x^2 + \dots = \frac{1}{1-x}$ converges for $|x| < 1$, but $0 \leq e^{-\theta_{\text{vib}}/T} < 1$ for all T , thus we have q_{vib} valid for all T .

$$q_{\text{vib}} = \frac{x^{1/2}}{1-x} = \frac{e^{-\theta_{\text{vib}}/2T}}{1-e^{-\theta_{\text{vib}}/T}}$$

Molecular Vibrational Partition Function
Zero of E_{vib} is set at minimum of potential energy curve

Define q_{vib}^*

$$q_{\text{vib}} = e^{-\theta_{\text{vib}}/2T} \underbrace{\sum_{v=0}^{\infty} e^{-\theta_{\text{vib}}/T}}_{q_{\text{vib}}^*}$$

$$\text{So } q_{\text{vib}}^* = \sum_{v=0}^{\infty} \exp[-(\epsilon(v) - \epsilon(v=0))/kT]$$

$$q_{\text{vib}}^* = \sum_{v=0}^{\infty} e^{-v\theta_{\text{vib}}/T} = \sum_{v=0}^{\infty} x^v = \frac{1}{1-x}$$

$$q_{\text{vib}}^* = \frac{1}{1 - e^{-\theta_{\text{vib}}/T}}$$

all values of θ_{vib}/T

Put this result aside. We will see how it is useful later in redefining our zeros of energy. q_{vib}^* effectively shifts the zero of E_{vib} to the energy of the $v = 0$ level.

High Temp Limit of q_{vib}^* $\theta_{\text{vib}} \ll T$ or $\epsilon_{\text{vib}} \ll kT$

$$q_{\text{vib}}^* = \frac{1}{1 - e^{-\theta_{\text{vib}}/T}}$$

If $\theta_{\text{vib}} \ll T$, then $e^{-\theta_{\text{vib}}/T} \sim +1 - \frac{\theta_{\text{vib}}}{T} + \frac{\theta_{\text{vib}}^2}{2T^2} - \dots$

So $q_{\text{vib}}^* = \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} \approx \frac{1}{1 - [1 - \theta_{\text{vib}}/T + \theta_{\text{vib}}^2/2T^2]}$

$$q_{\text{vib}}^* \approx \frac{T}{\theta_{\text{vib}}} = \frac{kT}{hc\omega_e} \text{ high temperature limit}$$

When is high temperature limit form useful? For molecules, not often ...

MOLECULE	$\theta_{\text{vib}}[\text{K}]$	EXACT $q^*(T=300\text{K})$	$(300/\theta_{\text{vib}})$	EXACT $q^*(3000\text{K})$	$(3000/\theta_{\text{vib}})$
H ₂	6328	$1 + 7 \times 10^{-10}$	0.0474	1.138	0.474
HCl	4302	$1 + 6 \times 10^{-7}$	0.0697	1.313	0.697
CO	3124	$1 + 3 \times 10^{-5}$	0.0961	1.546	0.961
Br ₂	465	1.269	0.645	6.964	6.45
I ₂	309	1.556	1.029	10.22	10.29
Cs ₂	60.4	5.481	4.926	50.14	49.64

1% error

Only for very heavy molecules at very high T is the high temperature limit form for q_{vib}^* useful.

VIBRATIONAL CONTRIBUTIONS TO THERMODYNAMIC FUNCTIONS

$$q_{\text{VIB}} = \frac{e^{-\theta_{\text{vib}}/2T}}{1 - e^{-\theta_{\text{vib}}/T}} = e^{-\theta_{\text{vib}}/2T} q_{\text{vib}}^*$$

$$Q_{\text{VIB}} = q_{\text{vib}}^N = e^{-N\theta_{\text{vib}}/2T} q_{\text{vib}}^{*N}$$

$$\ln Q_{\text{VIB}} = -N\theta_{\text{vib}}/2T + N \ln q_{\text{vib}}^*$$

$$\begin{aligned} E_{\text{vib}} &= kT^2 \left(\frac{\partial \ln Q_{\text{vib}}}{\partial T} \right)_{N,V} = kT^2 \left[\frac{\partial(-N\theta_{\text{v}}/2T)}{\partial T} + \frac{N\partial \ln q_{\text{vib}}^*}{\partial T} \right] \\ &= \frac{NkT^2\theta_{\text{vib}}}{2T^2} + NkT^2 \left[\frac{\partial \ln(1 - e^{-\theta_{\text{v}}/T})^{-1}}{\partial T} \right] \\ &= \frac{Nk}{2} \theta_{\text{vib}} + NkT^2 (1 - e^{-\theta_{\text{v}}/T}) \left[\frac{\partial(1 - e^{-\theta_{\text{v}}/T})^{-1}}{\partial T} \right] \end{aligned}$$

$$E_{\text{vib}} = \frac{Nk}{2} \theta_{\text{vib}} + NkT^2 (1 - e^{-\theta_{\text{v}}/T}) \frac{\theta_{\text{vib}}}{T^2} \frac{e^{-\theta_{\text{v}}/T}}{(1 - e^{-\theta_{\text{v}}/T})^2}$$

$$(E - E_0)_{\text{vib}} = \frac{Nk\theta_{\text{vib}} e^{-\theta_{\text{v}}/T}}{1 - e^{-\theta_{\text{v}}/T}} = \frac{Nk\theta_{\text{vib}}}{e^{\theta_{\text{v}}/T} - 1}$$

↑

zero point energy (energy of $v = 0$ above minimum of potential curve)

$$E_0 = \frac{Nk}{2} \theta_{\text{vib}} = \frac{Nhc\omega_e}{2} \quad \text{reference all energies with respect to zero point energy}$$

$$\text{Define } x \equiv \theta_{\text{vib}}/T \quad (E - E_0)_{\text{vib}} = \frac{NkTx}{e^x - 1}$$

$$\boxed{\frac{(E - E_0)_{\text{vib}}}{RT} = \frac{x}{e^x - 1}}$$

Einstein Function
plotted vs. x in handout