

Thermodynamics and Internal Degrees of Freedom

per mole internal	Rotation	Vibration	High temperature or $h\nu_o \ll kT$
q	$q_r = \frac{kT}{\sigma \tilde{B}hc}$	$q_v = \frac{1}{1 - e^{-h\nu_o/kT}}$ $q_v = \frac{1}{1 - e^{-\beta h\nu_o}}$	$e^{-h\nu_o/kT} = 1 - \frac{h\nu_o}{kT}$ $q_v = \frac{kT}{h\nu_o}$
$U - U(0)$ $= \frac{RT^2}{q} \left(\frac{\partial q}{\partial T} \right)_V$ $= \frac{-N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V$	$\frac{RT^2}{\left(\frac{kT}{\sigma \tilde{B}hc} \right)} \left(\frac{k}{\sigma \tilde{B}hc} \right)$ $= RT$	$*$ $\frac{Nh\nu_o e^{-h\nu_o/kT}}{1 - e^{-h\nu_o/kT}}$	$\frac{RT^2}{\left(\frac{kT}{h\nu_o} \right)} \left(\frac{k}{h\nu_o} \right)$ $= RT$
$G - G(0)$ $= -RT \ln q$ at 298.15 K	$-RT \ln \left(\frac{kT}{\sigma \tilde{B}hc} \right)$ $-RT \ln \left(\frac{207.2 \text{ cm}^{-1}}{\sigma \tilde{B}} \right)$	$RT \ln(1 - e^{-h\nu_o/kT})$ $RT \ln(1 - e^{-\tilde{\nu}_o/207.2 \text{ cm}^{-1}})$	$-RT \ln \left(\frac{kT}{h\nu_o} \right)$ $-RT \ln \left(\frac{207.2 \text{ cm}^{-1}}{\tilde{\nu}_o} \right)$

* U – U(0) and Vibration

$$\left(\frac{\partial q}{\partial \beta} \right)_V = \frac{-1}{(1 - e^{-\beta h\nu_o})^2} (h\nu_o e^{-\beta h\nu_o})$$

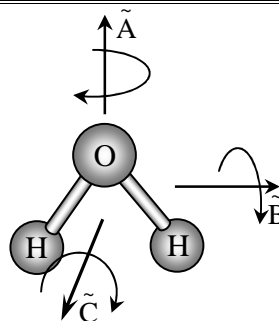
$$U - U(0) = - \frac{N \left(\frac{\partial q}{\partial \beta} \right)_V}{q} = - \left(\frac{1}{1 - e^{-\beta h\nu_o}} \right) \frac{-h\nu_o e^{-\beta h\nu_o}}{(1 - e^{-\beta h\nu_o})^2}$$

$$U - U(0) = \frac{Nh\nu_o e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}}$$

Non-linear Molecules and Rotation

$$q_r = \frac{\sqrt{\pi}}{\sigma} \left(\frac{kT}{\tilde{A}hc} \right)^{1/2} \left(\frac{kT}{\tilde{B}hc} \right)^{1/2} \left(\frac{kT}{\tilde{C}hc} \right)^{1/2}$$

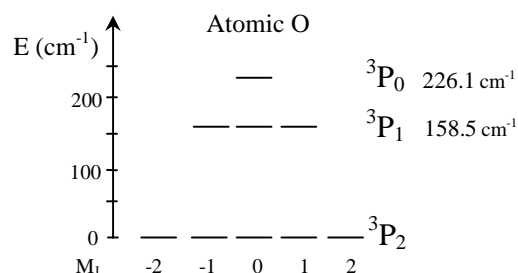
$$G - G(0) = -RT \ln \left[\frac{\sqrt{\pi}}{\sigma} \left(\frac{kT}{\tilde{A}hc} \right)^{1/2} \left(\frac{kT}{\tilde{B}hc} \right)^{1/2} \left(\frac{kT}{\tilde{C}hc} \right)^{1/2} \right]$$



Electronic Degree of Freedom

$$q_e = \sum_{\text{all energy levels}} g_i e^{-E_i/kT}$$

with $E_{gs} = 0$ as the reference energy



Ground State Atomic Terms, Low Lying Excited States, and Degeneracies (g_i).

Element	H	B	C	N	O	F	P	S	Cl	Br
Term	$^2S_{1/2}$	$^2P_{1/2}$	3P_0	$^4S_{3/2}$	3P_2	$^2P_{3/2}$	$^4S_{3/2}$	3P_2	$^2P_{3/2}$	$^2P_{3/2}$
g_{gs}	2	2	1	4	5	4	4	5	4	4
Excited states										
$E \text{ (cm}^{-1}\text{)}$		15.254	16.4		158.5	404		396.8	881	
g_{ex}		4	3		3	2		3	2	
$E \text{ (cm}^{-1}\text{)}$			43.5		226.1			573.6		
g_{ex}			5		1			1		
$q_e \text{ at } 298.15 \text{ K}$	2	5.71615	7.82505	4	6.73212	4.28470	4	5.50495	4.02850	4

Example: ground state O: $2p^4$: $\boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow}$
 $2s$ $2p$

$^3P_2 \quad J = 2 \quad M_J = -2, -1, 0, 1, 2 \quad g_{gs} = 5$

$$q_e = 5 + 3 e^{-158.5/207.2} + 1 e^{-226.1/207.2} = 5 + 1.39404 + 0.33581 = 6.72984$$

For almost all molecules the energy of the first excited state is $\gg kT$ above the ground state, only the ground state contributes and the partition function is well approximated by the ground state degeneracy at 298.2 K, $q_e \cong g_{gs}$

O_2 : $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*2} \quad ^3\Sigma_g^-, \quad g_{gs} = 3 \quad q_e = 3$

$^1\Delta_g, g_{ex} = 2 \text{ at } 7918.1 \text{ cm}^{-1} \quad \text{and} \quad ^1\Sigma_g^+, g_{ex} = 1 \text{ at } 13195.1 \text{ cm}^{-1}$

Molecular Exception: NO: $1\sigma^2 1\sigma^{*2} 2\sigma^2 3\sigma^{*2} 2\sigma^2 1\pi^4 1\pi^{*1}$

$^2\Pi_{1/2}, g_{gs} = 2 \quad \text{and} \quad ^2\Pi_{3/2}, g_{ex} = 2 \text{ at } 119.8 \text{ cm}^{-1} \quad q_e = 2 + 2 e^{-119.8/207.2} = 3.156$

Total Molecular Angular Momentum: $\Omega = \Lambda + \Sigma, |\Lambda - \Sigma|$

for NO, $\Lambda = 1$ with $M_\Lambda = +1, -1$ and $\Sigma = 1/2$ with $M_\Sigma = +1/2, -1/2 \rightarrow$ two terms $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$

