Useful Results from Statistical Thermodynamics

$$U = kT\left(\frac{\partial \ln Q}{\partial \ln T}\right)_{V,N} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

$$S = k\left[\ln Q + \left(\frac{\partial \ln Q}{\partial \ln T}\right)_{V,N}\right]$$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

Ideal Gas

Consider translational, rotational, vibrational, and electronic parts. Treat electronic parts on a case-by-case basis. Often, molecules are electronically in their ground states. Otherwise, we need to know the energy levels corresponding to other states.

Partition Function:

$$q_t = \left[\frac{2\pi kT\sum m_i}{h^2}\right]^{3/2} V$$

polyatomic: $q_r = \dfrac{\pi^{1/2}}{\sigma}\left(\dfrac{8\pi^2 kT}{h^2}\right)^{3/2}\left(I_A I_B I_c\right)^{1/2}$

diatomic: $q_r = \dfrac{8\pi^2 IkT}{\sigma h^2}$

$$q_v = \prod_{i=1}^{n'} \frac{\exp\left(-\Theta_{v,i} / 2T\right)}{1-\exp\left(-\Theta_{v,i} / T\right)}$$

n'=3n-5 (linear or diatomic) or 3n-6 (non-linear)

$$\Theta_{v,i} = h\nu_i / k$$

Internal Energy:

$$E_t = \frac{3}{2}NkT$$

$E_r = NkT$, linear or diatomic $\quad E_r = \dfrac{3}{2}NkT$, non-linear

$$E_\nu = Nk\sum_{i=1}^{n'}\left(\frac{\Theta_{\nu,i}}{2} + \frac{\Theta_{\nu,i}}{\left(\exp(\Theta_{\nu,i}/T)-1\right)}\right),$$ n'=3n-5 (linear or diatomic) or 3n-6 (non-linear)

$$\Theta_{\nu,i} = h\nu_i / k$$

Heat Capacity:

$$C_{V,t} = \frac{3}{2}Nk$$

$C_{V,r} = Nk$, linear or diatomic $\qquad C_{V,r} = \frac{3}{2}Nk$, non-linear

$$C_{V,\nu} = Nk\sum_{i=1}^{n'}\left[\left(\frac{\Theta_{\nu,i}}{T}\right)^2 \frac{\exp(\Theta_{\nu,i}/T)}{\left(\exp(\Theta_{\nu,i}/T)-1\right)^2}\right],$$ n'=3n-5 (linear or diatomic) or 3n-6 (non-linear)

Entropy:

$$S_t = Nk\left[\frac{5}{2} + \ln\left[\left(\frac{2\pi kT\sum m_i}{h^2}\right)^{3/2}\frac{V}{N}\right]\right]$$

diatomic:

$$S_r = Nk\left(1 + \ln\frac{T}{\sigma\Theta_r}\right)$$

$$\Theta_r = h^2 / 8\pi^2 Ik$$

polyatomic:

$$S_r = Nk\left[\frac{3}{2} + \ln\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right]$$

$$\Theta_A\Theta_B\Theta_C = h^6 / [(8\pi^2 k)^3 I_x I_y I_z]$$

$$S_\nu = Nk\sum_{i=1}^{n'}\left[\frac{h\nu_i / kT}{e^{h\nu_i/kT} - 1} - \ln\left(1 - e^{-h\nu_i/kT}\right)\right],$$ n'=3n-5 (linear or diatomic) or 3n-6 (non-linear)