0.1 Ideal Gas Model

From (McQuarrie, Statistical mechanics, 2000) the ideal gas method (IGM) for calculating an absolute free energy is outlined below.

$$G = H - TS \tag{1}$$

$$H = U + RT \tag{2}$$

$$U = E_{\text{pot}} + E_{\text{ZPE}} + E_{\text{trns}} + E_{\text{rot}} + E_{\text{vib}} \tag{3}$$

$$S = S_{\text{trns}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}} \tag{4}$$

where T is temperature, R the ideal gas constant and S_{elec} is taken to be zero for all molecules. The internal energy components are then

$$E_{\text{ZPE}} = \frac{N_a}{2} \sum_i h\nu_i \tag{5}$$

$$E_{\text{trns}} = \frac{3}{2} RT \tag{6}$$

$$E_{\text{rot}} = \begin{cases} 0 & \text{if } N = 1 \\ RT & \text{if linear} \\ \frac{3}{2}RT & \text{otherwise} \end{cases} \tag{7}$$

$$E_{\text{vib}} = R \sum_i \frac{\theta_i}{e^{\theta_i/T} - 1} \quad , \quad \theta_i = h\nu_i/k_B \tag{8}$$

where N_a is Avogadro's's constant, N is the number of atoms in the molecule, k_B Boltzmann's constant, ν_i the i-th harmonic frequency and h is Planks constant. The entropic components are

$$S_{\text{trns}} = R \ln(q_{\text{trns}}) + \frac{5}{2} R \tag{9}$$

$$S_{\text{rot}} = \begin{cases} 0 & \text{if } N = 1 \\ R \ln(q_{\text{rot}}) + R & \text{if linear} \\ R \ln(q_{\text{rot}}) + \frac{3}{2}R & \text{otherwise} \end{cases} \tag{10}$$

$$S_{\text{vib}}^{\text{HO}} = R \sum_i \frac{\theta_i}{T(e^{\theta_i/T} - 1)} - \ln(1 - e^{-\theta_i/T}) \tag{11}$$

$$q_{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V_{\text{eff}} \quad , \quad V_{\text{eff}} = \begin{cases} k_B T/p^\circ & \text{if 1 atm standard state} \\ 1/c^\circ N_a & \text{if 1 M standard state} \end{cases} \tag{12}$$

$$q_{\text{rot}} = \frac{T^{3/2}}{\sigma_r} \sqrt{\frac{\pi}{\omega_r}} \quad , \quad \omega_r = \prod_k \frac{h^2}{8\pi^2 k_B I_k} \tag{13}$$

where q are molecular partition functions, p° is the standard pressure (1 atm) and c° the standard concentration (1 mol dm^{-3}), σ_r is the rotational symmetry number for the molecule and I_k a diagonal element of the moment of inertia matrix.

Due to the vibrational entropy contribution being overestimated for low frequency modes Thrular proposed a correction, which instead of summing over frequencies in $S_{\text{vib}}^{\text{HO}}$ does so over $\max(\nu_{\text{thresh}},\ \nu_i)$ to shift all low frequencies to a threshold value (*J. Phys. Chem. B* 2011, **115**, 14556). An alternative method from Grimme (*Chem. Eur. J.*, 2012, **18**, 9955) uses an interpolation between a harmonic oscillator and rigid rotor to scale down the contribution from the low frequency modes as

$$S_{\text{vib}}^{\text{Grimme}} = \sum_i w_i S_{\text{vib}}^{\text{HO}}(i) + (1 - w_i)\left(R\ln\left(\sqrt{\frac{8\pi^3 \mu_i' k_B T}{h^2}}\right) + \frac{R}{2} \right) \qquad (14)$$

$$\mu_i' = \frac{\mu_i \bar{B}}{\mu_i + \bar{B}} \quad , \quad \mu_i = \frac{h}{8\pi^2 \nu_i} \quad , \quad \bar{B} = \text{Tr}[I]/3 \qquad (15)$$

$$w_i = \frac{1}{1 + (\omega_0/\nu_i)^\alpha} \qquad (16)$$

where ω_0 and α are adjustable parameters.