5. Canonical Statistics

5.1 Statistical thermodynamics

⟨Translational contribution⟩

$$\frac{{}^{\mathrm{m}}U_{\mathrm{trans}}}{RT} = \frac{3}{2} \tag{A.1}$$

$$\frac{{}^{\mathrm{m}}S_{\mathrm{trans}}}{R} = \frac{5}{2} + \ln q^{\circ}_{\mathrm{trans}} - \ln \frac{p}{k_{\mathrm{B}}T} \tag{A.2a}$$

$$\text{or} \quad \frac{{}^{\mathrm{m}}S_{\mathrm{trans}}}{R} = \frac{3}{2}\ln\frac{m}{\mathrm{amu}} + \frac{5}{2}\ln\frac{T}{\mathrm{K}} - \ln\frac{p}{\mathrm{bar}} - 1.151704822 \tag{A.2b}$$

$$\frac{{}^{\mathrm{m}}C_{V,\mathrm{trans}}}{R} = \frac{3}{2} \tag{A.3}$$

⟨Rotational contribution⟩

$$\frac{{}^{\mathrm{m}}U_{\mathrm{rot}}}{RT} = \frac{r}{2} \tag{A.4}$$

$$\frac{{}^{\mathrm{m}}S_{\mathrm{rot}}}{R} = \frac{r}{2} + \ln q_{\mathrm{rot}} \tag{A.5}$$

$$\frac{{}^{\mathrm{m}}C_{V,\mathrm{rot}}}{R} = \frac{r}{2} \tag{A.6}$$

r: dimension of rotation

⟨Vibrational contribution⟩

by using $\tilde{q}_{\mathrm{vib}}(T)$ in (4.5')

$$\frac{{}^{\mathrm{m}}U_{\mathrm{vib}}}{RT} = \frac{x}{e^{x}-1} \tag{A.7}$$

$$\frac{{}^{\mathrm{m}}S_{\mathrm{vib}}}{R} = \frac{x}{e^{x}-1} - \ln(1-e^{-x}) \tag{A.8}$$

$$\frac{{}^{\mathrm{m}}C_{V,\mathrm{vib}}}{R} = \frac{x^2 e^{x}}{(e^{x}-1)^2} \tag{A.9}$$

where $x = h\nu\beta = h\nu / k_{\mathrm{B}}T$

classical limit:

$$q^{\mathrm{cl}}_{\mathrm{vib}}(T) = \frac{k_{\mathrm{B}}T}{h\nu} \tag{4.16}$$

$$\frac{{}^{\mathrm{m}}U^{\mathrm{cl}}_{\mathrm{vib}}}{RT} = 1 \tag{A.10}$$

$$\frac{{}^{\mathrm{m}}S^{\mathrm{cl}}_{\mathrm{vib}}}{R} = 1 - \ln x \tag{A.11}$$

$$\frac{{}^{\mathrm{m}}C^{\mathrm{cl}}_{V,\mathrm{vib}}}{R} = 1 \tag{A.12}$$

⟨Contribution of intramolecular rotations⟩

· Free rotor

→ (A.4)~(A.6) with $r = 1$

· Sinusoidally hindered rotor

$$q_{\mathrm{SinHR}}(T) \cong q^{\mathrm{cl}}_{\mathrm{SinHR}}(T)\frac{q_{\mathrm{vib}}(T)}{q^{\mathrm{cl}}_{\mathrm{vib}}(T)} \qquad (4.14)$$

$${}^{\mathrm{m}}U_{\mathrm{SinHR}} = {}^{\mathrm{m}}U^{\mathrm{cl}}_{\mathrm{SinHR}} + {}^{\mathrm{m}}U_{\mathrm{vib}} - {}^{\mathrm{m}}U^{\mathrm{cl}}_{\mathrm{vib}} \qquad (A.13)$$

$${}^{\mathrm{m}}S_{\mathrm{SinHR}} = {}^{\mathrm{m}}S^{\mathrm{cl}}_{\mathrm{SinHR}} + {}^{\mathrm{m}}S_{\mathrm{vib}} - {}^{\mathrm{m}}S^{\mathrm{cl}}_{\mathrm{vib}} \qquad (A.14)$$

$${}^{\mathrm{m}}C_{V,\mathrm{SinHR}} = {}^{\mathrm{m}}C^{\mathrm{cl}}_{V,\mathrm{SinHR}} + {}^{\mathrm{m}}C_{V,\mathrm{vib}} - {}^{\mathrm{m}}C^{\mathrm{cl}}_{V,\mathrm{vib}} \qquad (A.15)$$

$$q^{\mathrm{cl}}_{\mathrm{SinHR}}(T) = q^{(1\mathrm{D})}_{\mathrm{rot}}(T)\exp\left(-\frac{V_0}{2k_{\mathrm{B}}T}\right)I_0\left(\frac{V_0}{2k_{\mathrm{B}}T}\right) \qquad (4.15)$$

$$\frac{{}^{\mathrm{m}}U^{\mathrm{cl}}_{\mathrm{SinHR}}}{RT} = \frac{1}{2} + y\left[1 - \frac{I_1(y)}{I_0(y)}\right] \qquad (A.16)$$

$$\frac{{}^{\mathrm{m}}S^{\mathrm{cl}}_{\mathrm{SinHR}}}{R} = \frac{1}{2} + y\left[1 - \frac{I_1(y)}{I_0(y)}\right] + \ln q^{\mathrm{cl}}_{\mathrm{SinHR}} \qquad (A.17)$$

$$\frac{{}^{\mathrm{m}}C^{\mathrm{cl}}_{V,\mathrm{SinHR}}}{R} = \frac{1}{2} + y^2\,\frac{I_2(y)I_0(y) + y^{-1}I_1(y)I_0(y) - I_1^2(y)}{I_0^2(y)} \qquad (A.18)$$

where $y = \dfrac{V_0}{2k_{\mathrm{B}}T} = \dfrac{V_0}{2}\beta$

⟨Electronic contribution⟩

$$q_{\mathrm{elec}} = g_{\mathrm{elec}} \qquad (A.19)$$

$$\frac{{}^{\mathrm{m}}S_{\mathrm{elec}}}{R} = \ln g_{\mathrm{elec}} \qquad (A.20)$$