18. Partition Function and Ideal Gases

Boltzmann factor: describes a probability that a system in a state of energy E_j.

$$p_j \propto \exp\left[-\frac{E_j}{k_B T}\right]$$ k_B: Boltzmann constant

Partition function Q: $p_j = \frac{1}{Q}\exp\left[-\frac{E_j}{k_B T}\right]$, where $Q = \sum_j \exp\left[-\frac{E_j}{k_B T}\right]$

Boltzmann statistics defines: $Q(N,V,T) = \dfrac{[q(V,T)]^N}{N!}$

$$q(V,T) = \sum_j \exp\left[-\frac{\varepsilon_j}{k_B T}\right]$$

Average energy $\langle \varepsilon \rangle = k_B T^2 \left(\dfrac{\partial \ln q}{\partial T}\right)_V$

18-1 The Translational Partition Function of Monoatomic Ideal Gas is $(2\pi mk_B T/h^2)^{3/2} V$.

Atomic energy of monoatomic ideal gas:

$$\varepsilon_{atomic} = \varepsilon_{trans} + \varepsilon_{elec}$$

$$q(V,T) = q_{trans}(V,T) + q_{elec}(T)$$

Translational energy state in a cubic container:

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \qquad n_x, n_y, n_z = 1, 2, \cdots$$

$$q_{trans} = \sum_{n_x, n_y, n_z = 1}^{\infty} \exp\left[-\beta \varepsilon_{n_x n_y n_z}\right] = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[-\frac{\beta h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)\right]$$

$$= \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right)\right]^3 \cong \left[\int_0^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) dn\right]^3$$

$$= \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V$$

Average energy

$$\langle \varepsilon_{trans} \rangle = k_B T^2 \left(\frac{\partial \ln q_{trans}}{\partial T}\right)_V = \cdots = \frac{3}{2}k_B T$$

18-2 Most of Atoms are in the Ground Electronic State at Room Temperature.

Electronic partition function: $q_{elec} = \sum_i q_{ei} \exp(-\beta\varepsilon_{ei})$

$$q_{elec}(T) = q_{e1} + q_{e2}\exp(-\beta\varepsilon_{e2}) + \cdots$$

Normally... $\beta\varepsilon_{ei} = \dfrac{10000\,\text{cm}^{-1}}{0.6950\,\text{cm}^{-1}\,\text{K}}\dfrac{1}{T} \cong \dfrac{10^4\,\text{K}}{T}$ $\Rightarrow$ second or later terms are (often) negligible.

ex.) Ratio of helium atoms in $^3S_1$ state (1s2s) $\quad ^3S_1 - {}^1S_0 = 159850.318\ \text{cm}^{-1}$

$$f_2 = \frac{3\exp(-\beta\varepsilon_{e2})}{1 + 3\exp(-\beta\varepsilon_{e2}) + \exp(-\beta\varepsilon_{e3})} = \begin{cases} 10^{-334} & (T = 300\,\text{K}) \\ 10^{-33} & (T = 3000\,\text{K}) \end{cases}$$

Average energy $\quad U = k_B T^2 \left(\dfrac{\partial \ln Q}{\partial T}\right)_{N,V} = \dfrac{3}{2}k_B T + \dfrac{N g_{e2}\varepsilon_{e2}\exp(-\beta\varepsilon_{e2})}{q_{elec}} + \cdots$

Heat capacity $\quad \overline{C}_V = \left(\dfrac{dU}{dT}\right)_{N,V} = \dfrac{3}{2}R$

Pressure $\quad P = k_B T \left(\dfrac{\partial \ln Q}{\partial V}\right)_{N,T} = \dfrac{N k_B T}{V}$ $\quad$ (state equation of ideal gas)

18-3 The energy of a Diatomic Molecule can be Approximated as a Sum of Separate Terms.

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}}$$

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

$$q_{\text{trans}} = \left[\frac{2\pi(m_1 + m_2)k_{\text{B}}T}{h^2}\right]^{3/2}$$

baseline of $q_{\text{rot}} \Rightarrow J = 0$

baseline of $q_{\text{vib}} \Rightarrow \upsilon = 0$, bottom of potential

baseline of $q_{\text{elec}} \Rightarrow$ bottom of potential

18-4 Most Molecules are in the Ground Vibrational State.

Harmonic oscillator approximation:

$$\varepsilon_\upsilon = \left(\upsilon + \frac{1}{2}\right)h\nu$$

$$q_{\text{vib}}(T) = \sum_\upsilon \exp\left(-\beta\varepsilon_\upsilon\right) = \sum_\upsilon^\infty \exp\left[-\beta\left(\upsilon + \frac{1}{2}\right)h\nu\right]$$

$$= \exp\left(-\beta\frac{h\nu}{2}\right)\sum_\upsilon^\infty \exp\left(-\beta h\nu\upsilon\right) = \frac{\exp\left(-\beta\frac{h\nu}{2}\right)}{1 - \exp\left(-\beta h\nu\right)}$$

18-4 Most Molecules are in the Ground Vibrational State. (cont.)

Vibrational Temperature: $\Theta_{vib} = \dfrac{h\nu}{k_B}$

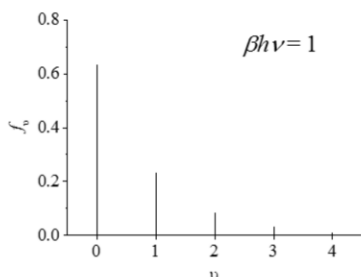$$q_{vib}(T) = \frac{\exp\left(-\Theta_{vib}/2T\right)}{1 - \exp\left(-\Theta_{vib}/T\right)}$$

Energy
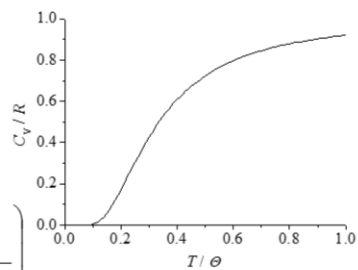
$$\langle E_{vib} \rangle = Nk_B T^2 \frac{d\ln q_{vib}}{dT} = Nk_B \left(\frac{\Theta_{vib}}{2} + \frac{\Theta_{vib}}{\exp\left(-\Theta_{vib}/T\right) - 1} \right)$$

Heat Capacity

$$C_{V,vib} = \frac{d\langle E_{vib} \rangle}{dT} = R\left(\frac{\Theta_{vib}}{T}\right)^2 \frac{\exp\left(-\Theta_{vib}/2T\right)}{\left[1 - \exp\left(-\Theta_{vib}/T\right)\right]^2}$$

Probability of vibrational excitation

$$f_\upsilon = \frac{\exp\left(-\beta h\nu\left(\upsilon + \frac{1}{2}\right)\right)}{q_{vib}}$$

$\beta h\nu = 1$

18-5 Most Molecules are in Excited Rotational States.

Energy level of rigid rotater: $\varepsilon_J = \dfrac{\hbar^2 J(J+1)}{2I}$ $(J = 0,1,2,\cdots)$

degeneracy
$g_J = 2J+1$

Partition function: $q_{\text{rot}}(T) = \displaystyle\sum_{J=0}^{\infty} (2J+1)\exp\left[-\beta\dfrac{\hbar^2 J(J+1)}{2I}\right]$

Rotation Temperature: $\Theta_{\text{rot}} = \dfrac{\hbar^2}{2Ik_B} = \dfrac{hB}{k_B}$ $q_{\text{rot}}(T) = \displaystyle\sum_{J=0}^{\infty} (2J+1)\exp\left[-\Theta_{\text{rot}}\dfrac{J(J+1)}{T}\right]$
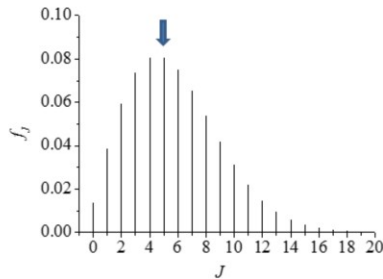
At ambient temperature, Θ_{rot}/T is small.

$q_{\text{rot}}(T) = \displaystyle\int_0^{\infty} (2J+1)\exp\left[-\Theta_{\text{rot}}\dfrac{J(J+1)}{T}\right] dJ$ (high temperature approximation)

$= \dfrac{T}{\Theta_{\text{rot}}} = \dfrac{8\pi^2 I k_B T}{h^2}$

Average rotational energy:

$\langle E_{\text{rot}} \rangle = Nk_B T^2 \dfrac{d\ln q_{\text{rot}}}{dT} = Nk_B T$ (rigid rotator
$\Rightarrow$ degree of freedom is 2)

18-5 Most Molecules are in Excited Rotational States. (cont.)

most probable value $\sim \left(\dfrac{T}{\Theta_{rot}}\right)^{1/2} - \dfrac{1}{2}$

$J = 7$ for CO at 300 K

This determines the profile of P- and R-branches of rotational spectrum.

18-6 Rotational Partition Functions Contain a Symmetry Number.

Homonuclear diatomic molecule $q_{rot}(T) = \dfrac{T}{2\Theta_{rot}}$

Heteronuclear diatomic molecule $q_{rot}(T) = \dfrac{T}{\Theta_{rot}}$

In summary $q(V,T) = q_{trans} q_{rot} q_{vib} q_{elec}$

$$= \left[\dfrac{2\pi M k_B T}{h^2}\right]^{3/2} V \dfrac{T}{\sigma \Theta_{rot}} \dfrac{\exp[-\Theta_{vib}/2T]}{1 - \exp[-\Theta_{vib}/T]} g_{el} \exp[-D_e/k_B T]$$

18-7 The Vibrational Partition Function of a Polyatomic Molecule is a Product of Harmonic Oscillator Partition Functions for Each Normal Coordinate.

$$q_{vib} = \prod_{j=1}^{\alpha} \frac{\exp[-\Theta_{vib,j}/2T]}{1 - \exp[-\Theta_{vib,j}/T]}$$

eigenfrequency temperature

$$\Theta_{vib,j} = \frac{h\nu_j}{k_B}$$

$$E_{vib} = Nk_B \sum_j^{\alpha} \left(\frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j}}{\exp\left(-\Theta_{vib,j}/T\right) - 1} \right)$$

$$C_{V,vib} = Nk_B \sum_j^{\alpha} \left(\left(\frac{\Theta_{vib,j}}{2}\right)^2 \frac{\exp\left(-\Theta_{vib,j}/T\right)}{\left[\exp\left(-\Theta_{vib,j}/T\right) - 1\right]^2} \right)$$

18-8 The Form of the Rotational Partition Function of a polyatomic Molecule Depends Upon the Shape of the Molecule.

$$q_{rot}(T) = \frac{8\pi^2 I k_B T}{\sigma h^2} = \frac{\sqrt{\pi T}}{\sigma \Theta_{rot}}$$
  σ : symmetry number

$$\Theta_{rot,j} = \frac{\hbar^2}{2 I_j k_B}$$
  $j = A, B, C$: eigenrotational temperature

$$q_{rot}(T) = \begin{cases} \dfrac{\sqrt{\pi}}{\sigma}\left(\dfrac{T}{\Theta_{rot}}\right)^{3/2} & \text{spherical top} \quad (I_A = I_B = I_C) \\[3ex] \dfrac{\sqrt{\pi}}{\sigma}\left(\dfrac{T}{\Theta_{rot,A}}\right)\left(\dfrac{T}{\Theta_{rot,C}}\right)^{1/2} & \text{symmetrical top} \quad (I_A = I_B < I_C) \\[3ex] \dfrac{\sqrt{\pi}}{\sigma}\left(\dfrac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}\right)^{1/2} & \text{asymmetrical top} \quad (I_A < I_B < I_C) \end{cases}$$

Average molar rotational energy
$$U_{rot} = N_A k_B T^2 \frac{d\ln q_{rot}(T)}{dT} = \frac{3RT}{2}$$

Heat capacity
$$\overline{C}_{V,rot} = \frac{3R}{2}$$

18-9 Calculated Molar Heat Capacities are in Very Good Agreement with Experimental Data.

Linear polyatomic molecule (ideal gas)

$$q(V,T) = \left[\frac{2\pi M k_B T}{h^2}\right]^{3/2} V \frac{T}{\sigma \Theta_{rot}} \left(\prod_{j}^{3N-5} \frac{\exp[-\Theta_{vib,j}/2T]}{1-\exp[-\Theta_{vib,j}/T]}\right) g_{el} \exp\left[-\frac{D_e}{k_B T}\right]$$

$$\frac{U}{N k_B T} = \frac{3}{2} + \frac{2}{2} + \sum_{j}^{3N-5}\left(\frac{\Theta_{vib,j}}{2T} + \frac{\Theta_{vib,j}/T}{\exp\left(-\Theta_{vib,j}/T\right)-1}\right) - \frac{D_e}{k_B T}$$

$$\frac{C_V}{N k_B} = \frac{3}{2} + \frac{2}{2} + \sum_{j}^{3N-5}\left(\left(\frac{\Theta_{vib,j}}{2}\right)^2 \frac{\exp\left(-\Theta_{vib,j}/T\right)}{\left[\exp\left(-\Theta_{vib,j}/T\right)-1\right]^2}\right)$$

18-9 Calculated Molar Heat Capacities are in Very Good Agreement with Experimental Data. (cont.)

Non-linear polyatomic molecule (ideal gas)

$$q(V,T) = \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} V \frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_{rot,A} \Theta_{rot,B} \Theta_{rot,C}} \right)^{1/2}$$

$$\times \left(\prod_{j=1}^{3N-6} \frac{\exp[-\Theta_{vib,j}/2T]}{1-\exp[-\Theta_{vib,j}/T]} \right) g_{el} \exp\left[-\frac{D_e}{k_B T} \right]$$

$$\frac{U}{Nk_B T} = \frac{3}{2} + \frac{3}{2} + \sum_{j}^{3N-6} \left(\frac{\Theta_{vib,j}}{2T} + \frac{\Theta_{vib,j}/T}{\exp\left(-\Theta_{vib,j}/T \right) - 1} \right) - \frac{D_e}{k_B T}$$

$$\frac{C_V}{Nk_B} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3N-6} \left(\frac{\Theta_{vib,j}}{2} \right)^2 \frac{\exp\left(-\Theta_{vib,j}/T \right)}{\left[\exp\left(-\Theta_{vib,j}/T \right) - 1 \right]^2}$$

Molar heat capacity (300 K)

	C_V/R calcd.	C_V/R exptl.
CO_2	3.49	3.46
CH_4	3.30	3.29
H_2O	3.03	3.01