

Chapter 24

Quantum Statistical Thermodynamics

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Counting Microstates in Quantum Mechanics

- **Microcanonical ensemble:** Number of quantum microstates, $\Omega(E, V, N)$, with N particles confined to finite volume, V , with fixed energy E is number of discrete eigenstates obtained from solving time-independent Schrödinger equation,

$$\hat{H}(\hat{q}_1, \dots, \hat{q}_n, \hat{p}_1, \dots, \hat{p}_n)\psi_\gamma(q_1, \dots, q_n) = E\psi_\gamma(q_1, \dots, q_n).$$

Assume each quantum microstate in microcanonical ensemble is equally probable, i.e.,

$$\mathbb{P}_\gamma = \begin{cases} \frac{1}{\Omega(E, V, N)} & \text{if } E_\gamma = E, \\ 0 & \text{if } E_\gamma \neq E, \end{cases}$$

with ensemble average given by

$$\langle\langle Y \rangle\rangle = \sum_{\gamma=1}^{\Omega(E, V, N)} \mathbb{P}_\gamma \left[\int \psi_\gamma^*(q_1, \dots, q_n) \hat{Y} \psi_\gamma(q_1, \dots, q_n) d\tau \right]$$

Counting Microstates in Quantum Mechanics

- **Canonical partition function:**

$$p(E_i) = \frac{\Omega(E_i, V, N) \exp \{-E_i/(k_B T)\}}{Q(T, V, N)}$$

where

$$Q(T, V, N) = \sum_i \Omega(E_i, V, N) \exp \{-E_i/(k_B T)\}$$

- Non-interacting molecules:

$$Q(T, V, N) = \frac{q(T, V)^N}{\sigma_V}$$

- **Molecular canonical partition function:** $q(T, V)$ is sum over microstates over discrete energy levels in μ -space,

$$q(T, V) = \sum_i g(\epsilon_i, V) \exp \{-\epsilon_i/(k_B T)\}$$

Ideal Gas of Molecules - Non-Interacting Particles Approximation

- Consider gas of N identical molecules with X atoms.
- Energy of molecule can be approximated as sum of contributions,

$$\epsilon \approx \epsilon_{\text{trans}} + \epsilon_{\text{vib}} + \epsilon_{\text{rot}} + \epsilon_{\text{el}} + \epsilon_{\text{nuc}}$$

- Molecular partition function can be approximated as product of contributions,

$$q_{\text{mol}}(T, V) \approx q_{\text{trans}}(T, V) q_{\text{rot}}(T) q_{\text{vib}}(T) q_{\text{el}}(T) q_{\text{nuc}}(T).$$

- Canonical partition function for gas of N non-interacting molecules is

$$Q(T, V, N) = Q_{\text{trans}}(T, V, N) Q_{\text{rot}}(T, N) Q_{\text{vib}}(T, N) Q_{\text{el}}(T, N) Q_{\text{nuc}}(T, N)$$

- All thermodynamic functions are derived from natural logarithm of $Q(T, V, N)$

$$\ln Q(T, V, N) = \ln Q_{\text{trans}}(T, V) + \ln Q_{\text{rot}}(T) + \ln Q_{\text{vib}}(T) + \ln Q_{\text{el}}(T) + \ln Q_{\text{nuc}}(T)$$

- Examine each molecular partition function contribution separately.

Nuclear Molecular Partition Function : q_{nuc}

- Assume nuclei are stable and remain in nuclear ground states.
- Nuclear ground state has degeneracy of $g_{\text{nuc},1} = 2I + 1$.
- Redefine nuclear ground state energy as zero, making q_{nuc} independent of temperature. It does not contribute to thermodynamic energy and heat capacity but will contribute to entropy.
- Take nuclear partition function as

$$q_{\text{nuc}} \approx \prod_{\alpha=1}^X 2I_{\alpha} + 1$$

where I_{α} is nuclear spin quantum number of α th nucleus in molecule.

- q_{nuc} is usually omitted in statistical calculations of thermochemical properties and processes.
- However, when molecule has identical nuclei, symmetries of nuclear ground state wavefunctions must be considered along with rotational and electronic state wavefunctions when counting microstates in combined molecular partition function.

Translational Molecular Partition Function : $q_{\text{trans}}(T, V)$

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- Translational energy of a quantum particle of mass m trapped in a 3D well of volume $V = L^3$ is

$$\epsilon_{n_x, n_y, n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2), \quad n_x, n_y, n_z = 1, 2, \dots,$$

- Characteristic temperature for quantized translational motion is

$$\Theta_{\text{trans}} = \frac{\Delta\epsilon_{\text{trans}}}{k_B} = \frac{1}{k_B} \frac{h^2(n+1)^2}{8mL^2} - \frac{1}{k_B} \frac{h^2n^2}{8mL^2} = \frac{1}{k_B} \frac{h^2(2n+1)}{8mL^2} \sim 10^{-16} \text{ to } 10^{-8} \text{ K}$$

- Can use classical limit to evaluate translational partition function

$$q_{\text{trans}}(T, V) = \int_0^\infty \underbrace{\left[\frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} V \sqrt{\epsilon_{\text{trans}}} \right]}_{\bar{g}(\epsilon_{\text{trans}})} \exp \{ -\epsilon_{\text{trans}} / (k_B T) \} d\epsilon_{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

- Define *thermal De Broglie wavelength*, i.e., average de Broglie wavelength for ideal gas molecule,

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \quad \text{and obtain} \quad q_{\text{trans}}(T, V) = \frac{V}{\Lambda^3}$$

Translational Molecular Partition Function : $q_{\text{trans}}(T, V)$

$$q_{\text{trans}}(T, V) = \frac{V}{\Lambda^3} \quad \text{where} \quad \Lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

- Fermion/Boson behavior can be ignored if Λ is much smaller than $(V/N)^{1/3}$.
- Using approximation $\ln N! \approx N \ln(N/e)$

$$\ln Q_{\text{trans}}(T, V, N) = \ln \frac{[q_{\text{trans}}]^N}{N!} = N \ln q_{\text{trans}} - \ln N! = N \ln \left[\frac{q_{\text{trans}} e}{N} \right] = N \ln \left[\frac{Ve}{\Lambda^3 N} \right]$$

- Helmholtz energy: $F_{\text{trans}} = -k_B T \ln Q_{\text{trans}}(T, V, N) = -Nk_B T \ln \left[\frac{Ve}{\Lambda^3 N} \right]$

- Pressure: $p = k_B T \left(\frac{\partial \ln Q_{\text{trans}}(T, V, N)}{\partial V} \right)_{N, T} = \frac{Nk_B T}{V}$

matches ideal gas equation-of-state function. Applies to ideal polyatomic gas molecules since only translational molecular partition function depends on volume.

Translational Molecular Partition Function : $q_{\text{trans}}(T, V)$

$$\ln Q_{\text{trans}}(T, V, N) = N \ln \left[\frac{Ve}{\Lambda^3 N} \right] \quad \text{where} \quad q_{\text{trans}}(T, V) = \frac{V}{\Lambda^3} \quad \text{and} \quad \Lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

- Internal energy: $U_{\text{trans}} = k_B T^2 \left(\frac{\partial \ln Q_{\text{trans}}(T, V, N)}{\partial T} \right)_{V, N} = \frac{3}{2} N k_B T,$

- Heat Capacity: $C_{V, \text{trans}} = \left(\frac{\partial U_{\text{trans}}}{\partial T} \right)_{V, N} = \frac{3}{2} N k_B,$

both agree with equipartition of energy theorem

- Entropy:

$$S_{\text{trans}} = \frac{U}{T} + k_B \ln Q(T, V, N) = \frac{3}{2} N k_B + N k_B \ln \left[\frac{Ve}{\Lambda^3 N} \right]$$

Translational Molecular Partition Function : $q_{\text{trans}}(T, V)$

Example

For 1.00 millimole of H_2O vapor in 1.00 liter at 400.0 K, Calculate translational molecular partition function and translational contribution to its entropy.

Calculate thermal de Broglie wavelength using water molecule mass, $m = 18.01528 \text{ u}$,

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} = \left(\frac{h^2}{2\pi (18.01528 \text{ u}) k_B (400 \text{ K})} \right)^{1/2} = 20.57 \text{ pm}$$

which is smaller than average nearest-neighbor distance between molecules

$$(V/N)^{1/3} = (1 \text{ L}/((1.00 \text{ mmol})N_A))^{1/3} = 1.184 \times 10^4 \text{ pm} \gg 20.57 \text{ pm}$$

Translational molecular partition function :

$$q_{\text{trans}}(T, V) = V/\Lambda^3 = 1 \text{ L}/(20.57 \text{ pm})^3 = 1.15 \times 10^{29}$$

Entropy:

$$S_{\text{trans}} = \frac{3}{2} (1.00 \text{ mmol}) R + (1.00 \text{ mmol}) R \ln \left[\frac{(1.150 \times 10^{29})e}{(1.00 \text{ mmol})N_A} \right] = 0.1793 \text{ J/K}$$

Rotational Molecular Partition Function : $q_{\text{rot}}(T)$

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- Hamiltonian for rotational motion of asymmetric molecule

$$\hat{h}_{\text{rot}}(J_a, J_b, J_c) = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} = \frac{2\pi c_0}{\hbar} [\tilde{A}_e \hat{J}_a^2 + \tilde{B}_e \hat{J}_b^2 + \tilde{C}_e \hat{J}_c^2],$$

- Hamiltonian for rotational motion of linear molecule, where $I_a = 0$ and $I_b = I_c = I$,

$$\hat{h}_{\text{rot}} = \frac{\hat{J}_b^2 + \hat{J}_c^2}{2I} = \frac{\hat{J}^2}{2I} = \frac{2\pi c_0}{\hbar} \tilde{B}_e \hat{J}^2, \quad (\text{linear}).$$

- Characteristic temperatures for rotation around molecular principal component axes

$$\Theta_A = \frac{hc_0}{k_B} \tilde{A}_e, \quad \Theta_B = \frac{hc_0}{k_B} \tilde{B}_e, \quad \text{and} \quad \Theta_C = \frac{hc_0}{k_B} \tilde{C}_e.$$

Characteristic Temperatures for Rotation of Asymmetric Molecules

Molecule	$\tilde{A}_e/\text{cm}^{-1}$	$\tilde{B}_e/\text{cm}^{-1}$	$\tilde{C}_e/\text{cm}^{-1}$	Θ_A/K	Θ_B/K	Θ_C/K	$\tilde{\nu}_k/\text{cm}^{-1}$	$g_{\text{vib},k}$	$\Theta_{\text{vib},k}/\text{K}$
H ₂ O	27.33	14.58	9.50	39.32	20.98	13.67	$\tilde{\nu}_1 = 3651.7$	1	5254.0
							$\tilde{\nu}_2 = 1595.0$	1	2294.8
							$\tilde{\nu}_3 = 3755.8$	1	5403.8
H ₂ S	10.393	9.040	4.723	14.953	13.01	6.795	$\tilde{\nu}_1 = 2610.8$	1	3756.4
							$\tilde{\nu}_2 = 1290$	1	1856.0
							$\tilde{\nu}_3 = 2684$	1	3861.7
ClO ₂	1.738	0.332	0.278	2.50	0.478	0.400	$\tilde{\nu}_1 = 945.25$	1	1360
							$\tilde{\nu}_2 = 444.8$	1	640
							$\tilde{\nu}_3 = 1112.1$	1	1600
H ₂ O ₂	10.056	0.859	0.791	14.468	1.24	1.14	$\tilde{\nu}_1 = 2869$	1	4127.9
							$\tilde{\nu}_2 = 1435$	1	2064.6
							$\tilde{\nu}_3 = 1408$	1	2025.8
							$\tilde{\nu}_4 = 870$	1	1251.7
							$\tilde{\nu}_5 = 3417$	1	4916.3
							$\tilde{\nu}_6 = 1370$	1	1971.1

Characteristic Temperatures for Rotation of Diatomic Molecules

Molecule	T_{fus}/K	$\tilde{B}_e/\text{cm}^{-1}$	Θ_B/K	$\tilde{\nu}_e/\text{cm}^{-1}$	$\Theta_{\text{vib}}/\text{K}$
H ₂	13.99	60.853	87.6	4401.21	6332
D ₂	18.72	30.444	43.8	3115.50	4483
H ¹⁹ F	189.6	2150	30.2	4138.39	5954
H ³⁵ Cl	158.93	531.94	15.2	2990.92	4303
H ⁸¹ Br	186.2	345.8	12.2	2648.97	3811
H ¹²⁷ I	222.35	206.9	9.2	2309.01	3322
¹⁹ F ₂	53.48	3.3	1.3	916.93	1319
³⁵ Cl ₂	171.6	0.186	0.35	559.75	805
¹²⁷ I ₂	386.85	0.0043	0.054	214.50	309
¹⁴ N ₂	63.23	5.737	2.9	2358.56	3393
¹⁴ N ¹⁶ O	109	0.5	2.4	1903.68	2740
¹⁴ N ¹⁶ O	109	0.5	2.4	1904.03	2740
¹² C ¹⁶ O	68.13	6.1216	2.8	2169.81	3122
¹⁶ O ₂	54.36	4.839	2.1	1580.19	2274

Rotational Molecular Partition Function : $q_{\text{rot}}(T)$

- When $T \gg \Theta_A, \Theta_B, \Theta_C$, approximate the rotational partition function using classical limit.

$$q_{\text{rot}}(T) = \frac{1}{\sigma h^3} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\chi \int_{-\infty}^{\infty} dJ_a \int_{-\infty}^{\infty} dJ_b \int_{-\infty}^{\infty} dJ_c e^{-h_{\text{rot}}(J_a, J_b, J_c)/(k_B T)} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2}$$

- Symmetry number, σ , avoids overcounting indistinguishable orientations of molecule.
- Higher symmetry molecules:

$$\underbrace{q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B^2} \right)^{1/2}}_{\text{Prolate Symmetric, } (I_A < I_B = I_C)}, \quad \underbrace{q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_B^2 \Theta_C} \right)^{1/2}}_{\text{Oblate Symmetric, } (I_A = I_B < I_C)}, \quad \underbrace{q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_B^3} \right)^{1/2}}_{\text{Spherically Symmetric, } (I_A = I_B = I_C)}$$

- In linear molecule case, where $(I_A = 0, I_B = I_C)$, we integrate

$$q_{\text{rot}}(T) = \frac{1}{\sigma h^3} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dJ_b \int_{-\infty}^{\infty} dJ_c e^{-h_{\text{rot}}(J_b, J_c)/(k_B T)} = \underbrace{\frac{1}{\sigma} \frac{T}{\Theta_B}}_{\text{Linear}}$$

Rotational Molecular Partition Function : $q_{\text{rot}}(T)$

$$\ln Q_{\text{rot}}(T, N) = \ln[q_{\text{rot}}(T)]^N = N \ln \left\{ \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right\},$$

- Helmholtz energy: $F_{\text{rot}} = G_{\text{rot}} = -Nk_B T \ln q_{\text{rot}}(T) = -Nk_B T \ln \left\{ \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right\}$

- Pressure: $p_{\text{rot}} = k_B T \left(\frac{\partial \ln Q_{\text{rot}}(T, N)}{\partial V} \right)_{N, T} = 0$

$p_{\text{rot}} = 0$ because $Q_{\text{rot}}(T, N)$ is independent of volume. Also, explains why rotational contribution to Helmholtz and Gibbs energy is equal, i.e., $G = U - TS + \overset{0}{p} V = F + \overset{0}{p} V$.

- Internal energy and Heat Capacity: $U_{\text{rot}} = \frac{3}{2} Nk_B T$, and $C_{V, \text{rot}} = \frac{3}{2} Nk_B$,

- Entropy:

$$S_{\text{rot}} = \frac{3}{2} Nk_B + Nk_B \ln q_{\text{rot}}(T) = \frac{3}{2} Nk_B + Nk_B \ln \left\{ \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right\}$$

Rotational Molecular Partition Function : $q_{\text{rot}}(T)$

Example

Calculate the rotational molecular partition function for 1.00 millimole of H₂O vapor at 400.0 K, and the rotational contribution to its entropy.

- Characteristic temperatures for H₂O are $\Theta_A = 39.32$ K, $\Theta_B = 20.98$ K, and $\Theta_C = 13.67$ K.
- Symmetry number for H₂O, i.e., number of indistinguishable orientations, is $\sigma = 2$.
- Since H₂O is asymmetric molecule, calculate molecular partition function with

$$q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} = \frac{\pi^{1/2}}{2} \left(\frac{(400.0 \text{ K})^3}{(39.32 \text{ K})(20.98 \text{ K})(13.67 \text{ K})} \right)^{1/2} = 66.76$$

- Entropy is

$$S_{\text{rot}} = \frac{3}{2} N k_B + N k_B \ln q_{\text{rot}}(T)$$

and substituting $nN_A k_B = nR$ and numerical values gives

$$S_{\text{rot}} = \frac{3}{2} (1.00 \text{ mmol}) R + (1.00 \text{ mmol}) R \ln(66.76) = 47.40 \text{ mJ/K}$$

Rotational Molecular Partition Function : $q_{\text{rot}}(T)$ at Low Temperatures

- Most substances are solids well before temperature reaches Θ_{rot} . Therefore, we consider low-temperature limit only for diatomics.
- Substitute $\epsilon_J = hc_0\tilde{B}eJ(J+1)$ with $g_{\text{rot},J} = 2J+1$ into molecular canonical partition function

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp \left\{ -hc_0\tilde{B}eJ(J+1)/(k_B T) \right\} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\Theta_B/T}$$

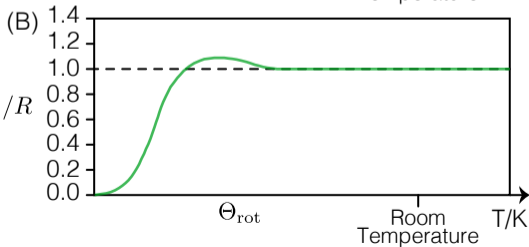
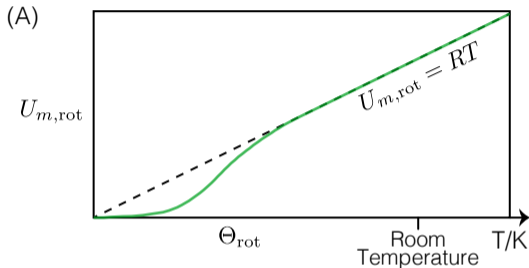
- At very low-temperature limit ($T < 1.5\Theta_B$), approximate with 1st few terms in summation

$$q_{\text{rot}} \approx 1 + 3e^{-2\Theta_B/T} + 5e^{-6\Theta_B/T} + 7e^{-8\Theta_B/T} + \dots, \quad (T < 1.5\Theta_B)$$

- Useful expansion below high-temperature limit ($T > 1.5\Theta_B$) is

$$q_{\text{rot}} \approx \frac{T}{\Theta_B} \left(1 + \frac{1}{3} \left(\frac{\Theta_B}{T} \right) + \frac{1}{15} \left(\frac{\Theta_B}{T} \right)^2 + \frac{4}{315} \left(\frac{\Theta_B}{T} \right)^3 + \dots \right), \quad (T > 1.5\Theta_B)$$

$U_{m,\text{rot}}$ and $C_{V,m,\text{rot}}$ contributions as function of T for ideal diatomic gas.



- Both molar energy and heat capacity contributions agree with classical limit (dashed line) when $T > \Theta_{\text{rot}}$.
- Molar energy rotational contribution falls below classical limit prediction at $T < \Theta_B$.
- Heat capacity falls below classical limit prediction below Θ_B and goes through a small hump around $T \sim \Theta_B$ before leveling off at classical limit value of R .

Nuclear statistics in molecules with identical nuclei - para-H₂ and ortho-H₂

- Para-H₂ and ortho-H₂ forms are associated with even J and odd J rotational states, respectively.
- Nuclear degeneracies of para-H₂ and ortho-H₂ are 1 and 3, respectively.
- Must count nuclear and rotational states in combined nuclear-rotation molecular partition function

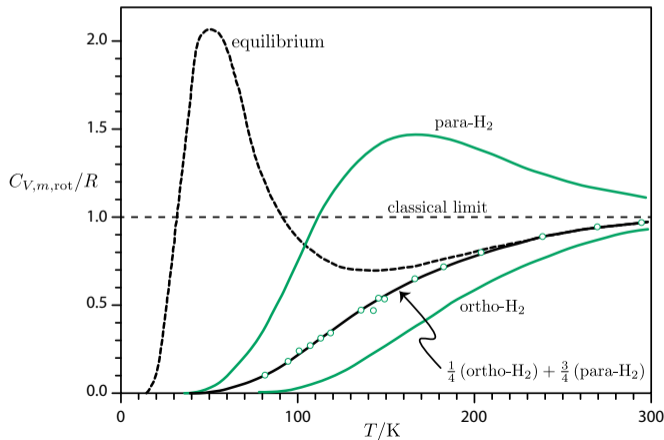
$$q_{\text{H}_2} = \sum_{\text{even } J=0}^{\infty} (2J+1)e^{-J(J+1)\Theta_{\text{rot}}/T} + 3 \sum_{\text{odd } J=1}^{\infty} (2J+1)e^{-J(J+1)\Theta_{\text{rot}}/T}$$

- At high temperatures or in presence of a catalyst, where two forms can interconvert, this partition function leads to nuclear-rotational contribution to heat capacity

$$C_{V,\text{rot}} = \frac{1}{4}C_{V,\text{para}} + \frac{3}{4}C_{V,\text{ortho}}$$

Nuclear-rotational contribution to $C_{V,m,rot}$ of H_2 as function of T

- Might expect only $J = 0$ ground state will be populated at $T \ll \Theta_B$.
- Without interconversion between 2 forms, odd to even ratio of J state populations get “locked in”
- As temperature is lowered, heat capacity continues as if it was mixture of 2 different gases.



- Dashed line represents expected heat capacity of equilibrium mixture, assuming no restriction of ortho-para conversion.
- Small circles represent experimental heat capacity values after subtraction of translational contribution R
- Vibrational contribution for H_2 is negligible in temperature range considered.

Vibrational Molecular Partition Function : $q_{\text{vib}}(T)$

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- Molecule with X atoms has m_v vibrational normal modes

$$m_v = \begin{cases} 3X - 5, & \text{linear molecules,} \\ 3X - 6, & \text{non-linear molecules,} \end{cases}$$

- The energy eigenvalue of each normal mode is given by

$$\epsilon_{n_j} = hc_0 \tilde{\nu}_j (n_j + 1/2), \quad n_j = 0, 1, 2, \dots$$

- Define characteristic temperature for j th vibrational mode

$$\Theta_{\text{vib},j} = \frac{hc_0 \tilde{\nu}_j}{k_B}$$

- At room temperature, few vibrations are in classical limit where $T \gg \Theta_{\text{vib}}$.

Characteristic Temperatures for Vibration of Asymmetric Molecules

Molecule	$\tilde{A}_e/\text{cm}^{-1}$	$\tilde{B}_e/\text{cm}^{-1}$	$\tilde{C}_e/\text{cm}^{-1}$	Θ_A/K	Θ_B/K	Θ_C/K	$\tilde{\nu}_k/\text{cm}^{-1}$	$g_{\text{vib},k}$	$\Theta_{\text{vib},k}/\text{K}$
H_2O	27.33	14.58	9.50	39.32	20.98	13.67	$\tilde{\nu}_1 = 3651.7$	1	5254.0
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Characteristic Temperatures for Rotation of Diatomic Molecules

Molecule	T_{fus}/K	$\tilde{B}_e/\text{cm}^{-1}$	Θ_B/K	$\tilde{\nu}_e/\text{cm}^{-1}$	$\Theta_{\text{vib}}/\text{K}$
H ₂	13.99	60.853	87.6	4401.21	6332
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¹² C ¹⁶ O	68.13	6.1216	2.8	2169.81	3122
¹⁶ O ₂	54.36	4.839	2.1	1580.19	2274

Vibrational Molecular Partition Function : $q_{\text{vib}}(T)$

For molecule with X atoms with m_v vibrational normal modes

$$q_{\text{vib}}(T) = \prod_{j=1}^{m_v} \left[e^{-hc_0 \tilde{\nu}_j / (2k_B T)} \sum_{n_j=0}^{\infty} e^{-n_j hc_0 \tilde{\nu}_j / (k_B T)} \right]$$

Fortunately, this infinite sum converges to simple analytical function

$$q_{\text{vib}}(T) = \prod_{j=1}^{m_v} \frac{e^{-\Theta_{\text{vib},j}/(2T)}}{1 - e^{-\Theta_{\text{vib},j}/T}}$$

In symmetric polyatomic molecules, two or more of normal modes frequencies will be degenerate. Taking these degeneracies into account,

$$\ln Q_{\text{vib}}(T, N) = \ln [q_{\text{vib}}(T)]^N = N \sum_{k=1} g_{\text{vib},k} \ln \frac{e^{-\Theta_{\text{vib},k}/(2T)}}{1 - e^{-\Theta_{\text{vib},k}/T}}$$

where k summation is over distinct normal mode frequencies with degeneracy $g_{\text{vib},k}$.

Vibrational Molecular Partition Function : $q_{\text{vib}}(T)$

Contribution to thermodynamic properties are

- Internal Energy:

$$U_{\text{vib}} = H_{\text{vib}} = Nk_B \sum_{k=1} g_{\text{vib},k} \left[\frac{\Theta_{\text{vib},k}}{2} + \frac{\Theta_{\text{vib},k}}{e^{\Theta_{\text{vib},k}/T} - 1} \right]$$

- Heat Capacity:

$$C_{V,\text{vib}} = C_{p,\text{vib}} = Nk_B \sum_{k=1} g_{\text{vib},k} \left[\left(\frac{\Theta_{\text{vib},k}}{T} \right)^2 \frac{e^{\Theta_{\text{vib},k}/T}}{(e^{\Theta_{\text{vib},k}/T} - 1)^2} \right]$$

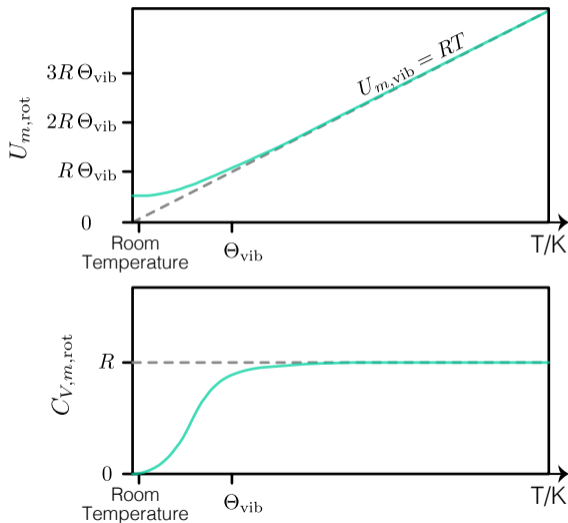
- Free Energy:

$$F_{\text{vib}} = G_{\text{vib}} = -Nk_B T \sum_{k=1} g_{\text{vib},k} \ln \frac{e^{-\Theta_{\text{vib},k}/T}}{1 - e^{-\Theta_{\text{vib},k}/(2T)}}$$

- Entropy:

$$S_{\text{vib}} = Nk_B \sum_{j=1} g_{\text{vib},k} \left[\frac{\Theta_{\text{vib},k}/T}{e^{\Theta_{\text{vib},k}/T} - 1} - \ln (1 - e^{-\Theta_{\text{vib},k}/T}) \right]$$

$U_{m,\text{vib}}$ and $C_{V,m,\text{vib}}$ contributions as function of T for ideal diatomic gas.



- Both molar energy and heat capacity contributions agree with classical limit (dashed line) when $T > \Theta_{\text{vib}}$.
- Due to zero-point energy contribution, vibrational contribution to molar energy is higher than classical limit prediction at temperatures below Θ_B .
- Heat capacity rises to classical limit around $T \approx \Theta_B$.

Vibrational Molecular Partition Function : $q_{\text{vib}}(T)$

Example

Calculate the vibrational molecular partition function for $n = 1.00$ millimole of H_2O vapor at 400.0 K, and the vibrational contribution to its entropy and heat capacity. How does the heat capacity at this temperature compare to the classical limit prediction?

- H_2O molecule has $m_v = 3X - 6 = 3$ normal modes of vibration. Characteristic temperatures for these normal mode vibrations are $\Theta_{\text{vib},1} = 5254.0$ K, $\Theta_{\text{vib},2} = 2294.8$ K, and $\Theta_{\text{vib},3} = 5403.8$ K.
- Calculate the molecular partition function

$$\begin{aligned}q_{\text{vib}}(T) &= \prod_{j=1}^3 \frac{e^{-\Theta_{\text{vib},j}/(2T)}}{1 - e^{-\Theta_{\text{vib},j}/T}}, \\ &= \frac{e^{-5254.0 \text{ K}/(2(400.0 \text{ K}))}}{1 - e^{-5254.0 \text{ K}/(400.0 \text{ K})}} + \frac{e^{-2294.8 \text{ K}/(2(400.0 \text{ K}))}}{1 - e^{-2294.8 \text{ K}/(400.0 \text{ K})}} + \frac{e^{-5403.8 \text{ K}/(2(400.0 \text{ K}))}}{1 - e^{-5403.8 \text{ K}/(400.0 \text{ K})}}, \\ &= 0.001405 + 0.05697 + 0.001165 \\ &= 0.05954\end{aligned}$$

Vibrational Molecular Partition Function : $q_{\text{vib}}(T)$

Example

Calculate the vibrational molecular partition function for $n = 1.00$ millimole of H_2O vapor at 400.0 K, and the vibrational contribution to its entropy and heat capacity. How does the heat capacity at this temperature compare to the classical limit prediction?

- Calculate entropy contribution, with $N = nN_A$,

$$\begin{aligned} S_{\text{vib}}/(nR) &= (1.00 \text{ mmol}) \sum_{j=1} g_{\text{vib},k} \left[\frac{\Theta_{\text{vib},k}/T}{e^{\Theta_{\text{vib},k}/T} - 1} - \ln(1 - e^{-\Theta_{\text{vib},k}/T}) \right], \\ &= \frac{5254.0 \text{ K}/(400.0 \text{ K})}{e^{5254.0 \text{ K}/(400.0 \text{ K})} - 1} + \frac{2294.8 \text{ K}/(400.0 \text{ K})}{e^{2294.8 \text{ K}/(400.0 \text{ K})} - 1} + \frac{5403.8 \text{ K}/(400.0 \text{ K})}{e^{5403.8 \text{ K}/(400.0 \text{ K})} - 1} \\ &\quad - \left[\ln(1 - e^{-5254.0 \text{ K}/(400.0 \text{ K})}) + \ln(1 - e^{-2294.8 \text{ K}/(400.0 \text{ K})}) + \ln(1 - e^{-5403.8 \text{ K}/(400.0 \text{ K})}) \right], \\ &= 25.94 \times 10^{-6} + 18558 \times 10^{-6} + 18.35 \times 10^{-6} - \left[-1.975 \times 10^{-6} - 3230 \times 10^{-6} - 1.358 \times 10^{-6} \right] = 0.02182 \end{aligned}$$

and obtain $S_{\text{vib}} = 0.02182 (1 \text{ mmol}) R = 0.1814 \text{ mJ/K}$

Vibrational Molecular Partition Function : $q_{\text{vib}}(T)$

Example

Calculate the vibrational molecular partition function for $n = 1.00$ millimole of H_2O vapor at 400.0 K, and the vibrational contribution to its entropy and heat capacity. How does the heat capacity at this temperature compare to the classical limit prediction?

- To calculate heat capacity, use

$$\begin{aligned} C_{V,\text{vib}}/(nR) &= \left(\frac{5254.0 \text{ K}}{400.0 \text{ K}}\right)^2 \frac{e^{5254.0 \text{ K}/(400.0 \text{ K})}}{(e^{5254.0 \text{ K}/(400.0 \text{ K})} - 1)^2} + \left(\frac{2294.8 \text{ K}}{400.0 \text{ K}}\right)^2 \frac{e^{2294.8 \text{ K}/(400.0 \text{ K})}}{(e^{2294.8 \text{ K}/(400.0 \text{ K})} - 1)^2} \\ &\quad + \left(\frac{5403.8 \text{ K}}{400.0 \text{ K}}\right)^2 \frac{e^{5403.8 \text{ K}/(400.0 \text{ K})}}{(e^{5403.8 \text{ K}/(400.0 \text{ K})} - 1)^2}, \\ &= 0.0003407 + 0.1068 + 0.0002478 = 0.1074, \end{aligned}$$

giving

$$C_{V,\text{vib}} = 0.1074 (1 \text{ mmol}) R = 0.8930 \text{ mJ/K}.$$

Only 3.6% of classical limit prediction for water with 3 normal vibrational modes.

Electronic Molecular Partition Function : $q_{\text{el}}(T)$

Electronic Molecular Partition Function : $q_{\text{el}}(T)$

- Far from classical limit, we must calculate $q_{\text{el}}(T)$ using sum over discrete energy levels,

$$q_{\text{el}}(T) = \sum_i g_{\text{el},i} \exp\{-\epsilon_{\text{el},i}/(k_B T)\}$$

- At room temperature, electronic contribution is restricted to ground electronic state except for few cases of molecules with low-lying excited electronic states.
- Use $\Delta\epsilon_{\text{el},i}$ from spectroscopic measurements, so factor out ground state energy and degeneracy

$$q_{\text{el}}(T) = g_{\text{el},1} e^{D_0/(k_B T)} \left[1 + \frac{g_{\text{el},2}}{g_{\text{el},1}} e^{-\Delta\epsilon_{\text{el},2}/(k_B T)} + \dots \right] \quad \text{where } \Delta\epsilon_{\text{el},i} = \epsilon_{\text{el},i} - D_0$$

- Applied to monatomic gases, D_0 is atomic ground electronic state energy, however,
 - ▶ Redefine absolute energy of atomic ground electronic state to $D_0 = 0$.
 - ▶ Leads to constant energy reduction in calculated thermodynamic potentials but does not affect calculated heat capacities or entropies.

Electronic Molecular Partition Function : $q_{\text{el}}(T)$

$$q_{\text{el}}(T) = g_{\text{el},1} e^{D_0/(k_B T)} \left[1 + \frac{g_{\text{el},2}}{g_{\text{el},1}} e^{-\Delta\epsilon_{\text{el},2}/(k_B T)} + \dots \right] \quad \text{where } \Delta\epsilon_{\text{el},i} = \epsilon_{\text{el},i} - D_0$$

- Applied to molecules, D_0 is molecular ground electronic state energy, however,
 - ▶ For thermochemical reaction calculations, use common D_0 for reactants and products.
 - ▶ Assign zero potential energy to separated atoms infinitely far apart and at rest at $T = 0$ K.
 - ▶ This shift corresponds to thermochemical dissociation energy of molecule at $T = 0$ K, i.e.,

$$D_0 = hc_0 D_e - \sum_{j=1}^{m_v} \frac{1}{2} hc_0 \tilde{\nu}_{e,j} = -\epsilon_{\text{el},1}$$

sum over zero-point energies of molecule's electronic ground state vibrational normal modes.

- ▶ Shifts thermodynamic potentials but not heat capacities or entropies.

Electronic Molecular Partition Function : $q_{el}(T)$

Log of electronic canonical partition function of gas

$$\ln Q_{el}(T, N) = N \ln q_{el}(T) = N \ln g_{el,1} + \frac{ND_0}{k_B T} + N \ln \left(1 + \frac{g_{el,2}}{g_{el,1}} e^{-\Delta\epsilon_{el,2}/(k_B T)} + \dots \right).$$

Using only ground and first excited state in $\ln Q_{el}(T, N)$, we obtain

$$F_{el} = G_{el} = -Nk_B T \left[\ln g_{el,1} + \frac{D_0}{k_B T} + \ln \left(1 + \frac{g_{el,2}}{g_{el,1}} e^{-\Delta\epsilon_{el,2}/(k_B T)} \right) \right],$$

$$S_{el} = k_B N \left[\ln g_{el,1} + \frac{\Delta\epsilon_{el,2}/(k_B T)}{(g_{el,1}/g_{el,2})e^{\Delta\epsilon_{el,2}/(k_B T)} + 1} + \ln \left(1 + \frac{g_{el,2}}{g_{el,1}} e^{-\Delta\epsilon_{el,2}/(k_B T)} \right) \right],$$

$$U_{el} = H_{el} = -ND_0 + \frac{N\Delta\epsilon_{el,2}}{(g_{el,1}/g_{el,2})e^{\Delta\epsilon_{el,2}/(k_B T)} + 1},$$

$$C_{V,el} = C_{p,el} = Nk_B \frac{g_{el,1}}{g_{el,2}} \frac{(\Delta\epsilon_{el,2}/(k_B T))^2 e^{\Delta\epsilon_{el,2}/(k_B T)}}{[(g_{el,1}/g_{el,2})e^{\Delta\epsilon_{el,2}/(k_B T)} + 1]^2}.$$

Electronic Molecular Partition Function : $q_{\text{el}}(T)$

When only ground electronic state is populated, electronic partition function simplifies to

$$q_{\text{el}}(T) = g_{\text{el},1} e^{D_0/(k_B T)},$$

yielding

$$F_{\text{el}} = G_{\text{el}} = -Nk_B T \ln g_{\text{el},1} - ND_0,$$

$$S_{\text{el}} = Nk_B \ln g_{\text{el},1},$$

$$U_{\text{el}} = H_{\text{el}} = -ND_0,$$

$$C_{V,\text{el}} = C_{p,\text{el}} = 0.$$

Electronic State Degeneracies

- Ground state of most stable atoms and molecules are closed shell and non-degenerate, $g_{el,1} = 1$.
- Atomic or molecular electronic state degeneracy can be obtained from spectroscopic term symbol.
- For atoms
 - ▶ Filled subshells also have $g_{el,1} = 1$.
 - ▶ States with total angular momentum J have $g_{el,i} = 2J + 1$

$$^{2S+1}\{\text{symbol}\}_J$$

- For linear molecules, states with total angular momentum along internuclear axis, $\Omega = |\Lambda + M_S|$, has $g_{el,i} = 2\Omega + 1$

$$^{2S+1}\{\text{symbol}\}_{\Lambda+M_S}$$

- For non-linear molecules, obtain degeneracy from state term symbol {letter}

$$\begin{array}{l} g_{el,i} = \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad \leftarrow \text{numerical value} \\ \{\text{letter}\} = \quad A \text{ or } B \quad E \quad T \quad G \quad H \quad \leftarrow \text{upper-case letter} \end{array}$$

Example

Ground electronic state of Cl is $^2P_{3/2}$. First electronically excited state, $^2P_{1/2}$, lies 882.35 cm^{-1} above it. Calculate electronic contribution to its entropy and heat capacity for 1 mole of Cl gas at 500 K.

For entropy, substituting $nN_A k_B = nR$ leads to

$$S_{\text{el}}/R = n \left[\ln g_{\text{el},1} + \frac{\Delta\epsilon_{\text{el},2}/(k_B T)}{(g_{\text{el},1}/g_{\text{el},2})e^{\Delta\epsilon_{\text{el},2}/(k_B T)} + 1} + \ln \left(1 + \frac{g_{\text{el},2}}{g_{\text{el},1}} e^{-\Delta\epsilon_{\text{el},2}/(k_B T)} \right) \right]$$

Ratio of $^2P_{3/2}$ to $^2P_{1/2}$ degeneracies is $g_{\text{el},1}/g_{\text{el},2} = 4/2 = 2$. Calculating ratio

$$\frac{\Delta\epsilon_{\text{el},2}}{k_B T} = \frac{hc_0(882.35 \text{ cm}^{-1})}{k_B(500.0 \text{ K})} = 2.539$$

and substituting into entropy expression gives

$$S_{\text{el}}/R = (1.00 \text{ mol}) \left[\ln 4 + \frac{2.539}{2e^{2.539} + 1} + \ln \left(1 + \frac{1}{2} e^{-2.539} \right) \right] = 1.52 \text{ mol},$$

and

$$S_{\text{el}} = (1.52 \text{ mol}) R = 12.6 \text{ J/K}.$$

Example

Ground electronic state of Cl is $^2P_{3/2}$. First electronically excited state, $^2P_{1/2}$, lies 882.35 cm^{-1} above it. Calculate electronic contribution to its entropy and heat capacity for 1.00 mole of Cl gas at 500.0 K.

For heat capacity,

$$C_{V,\text{el}}/R = C_{p,\text{el}}/R = n \left[\frac{g_{\text{el},1} (\Delta\epsilon_{\text{el},2}/(k_B T))^2 e^{\Delta\epsilon_{\text{el},2}/(k_B T)}}{g_{\text{el},2} [(g_{\text{el},1}/g_{\text{el},2})e^{\Delta\epsilon_{\text{el},2}/(k_B T)} + 1]^2} \right]$$

Substituting into expression gives

$$C_{V,\text{el}}/R = (1.00 \text{ mol}) \left[2 \frac{(2.539)^2 e^{2.539}}{[2e^{2.539} + 1]^2} \right] = 0.236 \text{ mol},$$

giving

$$C_{V,\text{el}} = (0.236 \text{ mol})R = 1.96 \text{ J/K}.$$

Example

NO molecule possesses an unpaired electron and has ${}^2\Pi_{1/2}$ ground state with ${}^2\Pi_{3/2}$ state lying approximately 123.8 cm^{-1} above it. Calculate electronic contribution to its entropy and heat capacity for 1.00 mole of NO gas at 400.0 K.

$$S_{\text{el}}/R = n \left[\ln g_{\text{el},1} + \frac{\Delta\epsilon_{\text{el},2}/(k_B T)}{(g_{\text{el},1}/g_{\text{el},2})e^{\Delta\epsilon_{\text{el},2}/(k_B T)} + 1} + \ln \left(1 + \frac{g_{\text{el},2}}{g_{\text{el},1}} e^{-\Delta\epsilon_{\text{el},2}/(k_B T)} \right) \right]$$

Ratio of ${}^2\Pi_{1/2}$ to ${}^2\Pi_{3/2}$ degeneracies is $g_{\text{el},1}/g_{\text{el},2} = 2/4 = 1/2$. Calculating ratio

$$\frac{\Delta\epsilon_{\text{el},2}}{k_B T} = \frac{hc_0(123.8\text{ cm}^{-1})}{k_B(400.0\text{ K})} = 0.4453$$

and substituting into entropy expression gives

$$S_{\text{el}}/R = (1.00\text{ mol}) \left[\ln 2 + \frac{0.4453}{(1/2)e^{0.4453} + 1} + \ln (1 + 2e^{-0.4453}) \right] = 1.77\text{ mol},$$

giving

$$S_{\text{vib}} = (0.272\text{ mol})R = 2.26\text{ J/K}.$$

Example

NO molecule possesses an unpaired electron and has ${}^2\Pi_{1/2}$ ground state with ${}^2\Pi_{3/2}$ state lying approximately 123.8 cm^{-1} above it. Calculate electronic contribution to its entropy and heat capacity for 1.00 mole of NO gas at 400.0 K.

$$C_{V,\text{el}}/R = C_{p,\text{el}}/R = n \left[\frac{g_{\text{el},1} (\Delta\epsilon_{\text{el},2}/(k_B T))^2 e^{\Delta\epsilon_{\text{el},2}/(k_B T)}}{g_{\text{el},2} [(g_{\text{el},1}/g_{\text{el},2})e^{\Delta\epsilon_{\text{el},2}/(k_B T)} + 1]^2} \right]$$

Substituting into expression gives

$$C_{V,\text{el}}/R = (1.00\text{ mol}) \left[2 \frac{(2.539)^2 e^{2.539}}{[2e^{2.539} + 1]^2} \right] = 0.236\text{ mol},$$

and

$$C_{V,\text{el}} = (0.236\text{ mol})R = 1.96\text{ J/K}.$$