Lecture 8: Diatomic Partition Functions

Rotational and Vibrational Partition Functions

Diatomic Ideal Gas

Diatomic Ideal gases have all degrees of freedom:

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vibr}} \cdot q_{\text{elec}}$$

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

Translational and Electronic partition functions behave similarity to monoatomics

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

$$\langle \varepsilon_{trans} \rangle = \frac{3}{2\beta} = \frac{3}{2} k_B T \qquad \frac{1}{2} k_B T \text{ per DOF}$$

$$q_{elec} = \sum_{i,levels} g_i e^{-\beta \varepsilon_i}$$

Virtually no contribution to ε

Vibrational Partition Function

Harmonic Oscillator:

$$\varepsilon_n = h\nu\left(n + \frac{1}{2}\right)$$

Substitute into partition function:

$$\begin{aligned} q_{\text{vib}} &= \sum_{n=0}^{\infty} e^{-\beta h\nu\left(n+\frac{1}{2}\right)} \\ &= \sum_{n=0}^{\infty} e^{-\beta h\nu n} \cdot e^{-\beta h\nu \frac{1}{2}} \end{aligned}$$

Factor out constant $e^{-\beta h\nu/2}$:

$$\begin{aligned} &= e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu n} \\ &= e^{-\beta h\nu/2} \sum_{n=0}^{\infty} \left(e^{-\beta h\nu}\right)^{n} \end{aligned}$$

Vibrational Partition Function

Vibrational partition function:

$$q_{\text{vib}} = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} \left(e^{-\beta h\nu}\right)^n$$

Recognize as a geometric series:

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r} \qquad |r| < 1$$

Where $r = e^{-\beta h\nu}$:

$$\sum_{n=0}^{\infty} \left(e^{-\beta h\nu}\right)^n = \frac{1}{1-e^{-\beta h\nu}}$$

Thus the vibrational partition function becomes:

$$q_{\text{vib}} = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}$$

What is Vibrational Temperature?

Define the vibrational temperature $\Theta_{\text{vib}} = \frac{h\nu}{k_B}$:

$$\boxed{q_{\text{vib}} = \frac{e^{-\frac{\Theta_{\text{vib}}}{2T}}}{1 - e^{-\frac{\Theta_{\text{vib}}}{T}}}}$$

Consider the probability of finding a particle in an excited state:

$$P_{excited} = 1 - P_0$$

Ground State energy:

$$\varepsilon_0 = h\nu\left(0 + \frac{1}{2}\right) = \frac{h\nu}{2}$$

Probability of being in the ground state:

$$P_0 = \frac{e^{-\beta\varepsilon_0}}{q_{\text{vib}}} = \frac{e^{-\frac{\beta h\nu}{2}}}{\left(\frac{e^{-\frac{\Theta_{\text{vib}}}{2T}}}{1-e^{-\frac{\Theta_{\text{vib}}}{T}}}\right)}$$

What is Vibrational Temperature?

Substitute vibrational temperature $\Theta_{\text{vib}} = \frac{h\nu}{k_B}$:

$$P_0 = \frac{e^{-\frac{\Theta_{\text{vib}}}{2T}}}{\left(\frac{e^{-\frac{\Theta_{\text{vib}}}{2T}}}{1-e^{-\frac{\Theta_{\text{vib}}}{T}}}\right)} = 1 - e^{-\frac{\Theta_{\text{vib}}}{T}}$$

$$\begin{aligned} P_{excited} &= 1 - P_0 \\ &= 1 - \left(1 - e^{-\frac{\Theta_{\text{vib}}}{T}}\right) = e^{-\frac{\Theta_{\text{vib}}}{T}} \end{aligned}$$

Vibrational Temperature $\Theta_{\text{vib}} = \frac{h\nu}{k_B}$

- Temperature needed to achieve substantial excited state populations.
- If $T < \Theta_{\text{vib}}$, the system is predominantly in the ground state
- If $T \gtrsim \Theta_{\text{vib}}$, there is substantial population in excited states

Example: Vibrational Temperature

At 298 K, are molecules mostly in the ground or excited vibrational state?

Molecule	Θ_{vib} (K)
H_2	6215
Cl_2	80
I_2	308

Excited-state probability:

$$P_{excited} = e^{-\Theta_{\text{vib}}/T}$$

Calculations:

$$\begin{aligned} P_{excited}(\mathrm{H_2}) &= e^{-6215/298} \approx 1.01 \times 10^{-19} && \text{Mostly ground state} \\ P_{excited}(\mathrm{Cl_2}) &= e^{-805/298} \approx 6.82 \times 10^{-2} && \text{7\% in excited state} \\ P_{excited}(\mathrm{I_2}) &= e^{-308/298} \approx 3.58 \times 10^{-1} && \text{36\% in excited state} \end{aligned}$$

Rotational Partition Function

Rigid Rotor:

$$\varepsilon_J = \frac{\hbar^2 J(J+1)}{2I} \qquad J = 0, 1, 2, \ldots$$

Each energy level has degeneracy:

$$g_J = 2J+1 \qquad m_J = -J, -J+1, \ldots, J-1, J$$

Define rotational temperature:

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$$

Partition function:

$$q_{\text{rot}} = \sum_i g e^{-\beta E_i} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{\Theta_{\text{rot}}(J(J+1))}{T}}$$

Rotational Partition Function

$$q_{\mathrm{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-\Theta_{\mathrm{rot}} J(J+1)/T}$$

Substitute $u = J(J+1)$, so $du = (2J+1)\, dJ$:

$$= \int_0^{\infty} e^{-u\Theta_{\mathrm{rot}}/T} du$$

Using the integral $\int_0^{\infty} e^{-au}\, du = \frac{1}{a}$ for $a > 0$:

$$= \frac{1}{\Theta_{\mathrm{rot}}/T}$$

$$q_{\mathrm{rot}} = \frac{T}{\Theta_{\mathrm{rot}}} \qquad T \gg \Theta_{\mathrm{rot}} \quad \text{(high T limit)}$$

What is Rotational Temperature?

Consider the probability of finding a particle in an excited state:

$$P_{excited} = 1 - P_0$$

Ground State energy:

$$\varepsilon_0 = \frac{\hbar^2}{2I} \cdot 0(0+1) = 0$$

Probability of being in the ground state:

$$P_0 = \frac{g_0 e^{-\beta\varepsilon_0}}{q_{\mathrm{rot}}} = \frac{1 \cdot e^0}{T/\Theta_{\mathrm{rot}}} = \frac{\Theta_{\mathrm{rot}}}{T}$$

What is Rotational Temperature?

Probability of being in excited rotational states:

$$\begin{aligned} P_{excited} &= 1 - P_0 \\ &= 1 - \frac{\Theta_{\text{rot}}}{T} \end{aligned}$$

Rotational Temperature $\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$

- Temperature needed to achieve substantial excited state populations.
- If $T < \Theta_{\text{rot}}$, the system is predominantly in the ground state
- If $T \gtrsim \Theta_{\text{rot}}$, there is substantial population in excited states

Example: Rotational Temperature

At 298 K, are molecules mostly in the ground or excited rotational state?

Molecule	Θ_{rot} (K)
H_2	87.5
CO	2.77
I_2	0.054

Excited-state probability:

$$P_{excited} = 1 - \frac{\Theta_{\text{rot}}}{T}$$

Calculations:

$$P_{excited}(\text{H}_2) = 1 - \frac{87.5}{298} \approx 0.706 \qquad 71\% \text{ in excited states}$$

$$P_{excited}(\text{CO}) = 1 - \frac{2.77}{298} \approx 0.991 \qquad 99\% \text{ in excited states}$$

$$P_{excited}(\text{I}_2) = 1 - \frac{0.054}{298} \approx 0.9998 \quad {>}99.9\% \text{ in excited states}$$

Vibrational Energy Contribution

$$
\begin{aligned}
q_{\text{vib}} &= \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} \\
\langle \varepsilon_{\text{vib}} \rangle &= -\frac{1}{q_{\text{vib}}} \frac{\partial}{\partial \beta} \left(\frac{1}{1 - e^{-\beta \hbar \omega}} \right) \\
&= -\frac{1}{q_{\text{vib}}} \frac{\partial}{\partial \beta} \left(1 - e^{-\beta \hbar \omega} \right)^{-1} \\
&= -\frac{1}{q_{\text{vib}}} (-1) \left(1 - e^{-\beta \hbar \omega} \right)^{-2} \left(-(-\hbar \omega) e^{-\beta \hbar \omega} \right) \\
&= (1 - e^{-\beta \hbar \omega}) \cdot \frac{\hbar \omega e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2}
\end{aligned}
$$

$$
\begin{aligned}
\langle \varepsilon_{\text{vib}} \rangle &= \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \\
&= \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \cdot \frac{e^{\beta \hbar \omega}}{e^{\beta \hbar \omega}} \\
&= \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \\
e^{x} &\approx 1 + x \text{ (for small x)} \\
e^{\beta \hbar \omega} &\approx 1 + \beta \hbar \omega \\
\langle \varepsilon_{\text{vib}} \rangle &\approx \frac{\hbar \omega}{\beta \hbar \omega} = k_B T
\end{aligned}
$$

$$\boxed{k_B T \text{ for each vibrational degree of freedom in diatomic, high T limit}}$$

Rotational Energy Contribution

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}}$$

$$\langle \varepsilon_{\text{rot}} \rangle = k_B T^2 \frac{1}{q_{\text{rot}}} \frac{\partial q_{\text{rot}}}{\partial T}$$

$$\frac{\partial q_{\text{rot}}}{\partial T} = \frac{\partial}{\partial T} \left(\frac{T}{\Theta_{\text{rot}}} \right) = \frac{1}{\Theta_{\text{rot}}}$$

$$\langle \varepsilon_{\text{rot}} \rangle = k_B T^2 \frac{1}{T/\Theta_{\text{rot}}} \cdot \frac{1}{\Theta_{\text{rot}}} = k_B T$$

$$\boxed{\frac{1}{2} k_B T \text{ per rotational degree of freedom in diatomic}}$$

Summary: Molecular Partition Functions

Summary Table

Mode	Partition function	Energy spacing	Population at 300 K
Trans	$q_{\text{trans}} = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$	Continuous ($k_B T \gg \Delta\varepsilon$)	More excited
Rot	$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}}$	Small ($\Theta_{\text{rot}} \sim 1{-}10$ K)	Mostly excited
Vib	$q_{\text{vib}} = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}}$	Large ($\Theta_{\text{vib}} \sim 300{-}6000$ K)	Mostly ground
Elec	$q_{\text{elec}} = \sum_i g_i e^{-\beta\varepsilon_i}$	Very large ($k_B T \ll \Delta\varepsilon$)	Ground state

$$P_{\text{vib,excited}} = e^{-\Theta_{\text{vib}}/T} \qquad P_{\text{rot,excited}} = 1 - \frac{\Theta_{\text{rot}}}{T} \qquad \Theta_{\text{vib}} = \frac{h\nu}{k_B} \qquad \Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$$

$T \gg \Theta \implies$ excited states populated $\qquad T \ll \Theta \implies$ ground state dominates