Diatomic gases

\((\text{CO}, \text{NO}, \ldots)\)

Consider a molecule consisting of 2 different atoms.

In this case, additional rotational and vibrational degrees of freedom must be taken into account. The energy level of a diatomic molecule is

\[ \varepsilon_{\text{mol}} = \varepsilon_0 + 2\hbar \omega \left( \nu + \frac{1}{2} \right) + \frac{\hbar^2}{2I} K(K+1) \]

- \(\varepsilon_0\) - electronic energy
- \(\hbar \omega\) - quantum of vibrational energy
- \(\nu\) - vibrational quantum number
- \(K\) - rotational quantum number
- \(I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = M r_0^2\) - momentum of inertia of the molecule
- \(m = \frac{m_1 m_2}{m_1 + m_2}\) - the reduced mass

Note: Diatomic gases should be considered at temperatures \(T \leq T_{\text{dissociation}}\). Thus, only the lowest electronic state of the molecule need to be considered in \(Z\).
The partition function of diatomic gas

\[ Z = \sum_{n} e^{-E_{\text{mol}}/T} = e^{-\varepsilon_0/T} Z_{\text{rot}} Z_{\text{vib}} Z_{\text{trans}} \]

\[ Z_{\text{rot}} = \sum_{k=0}^{\infty} \frac{(2k+1)e^{-\hbar^2k(k+1)/2IT}}{k!} \]

\[ Z_{\text{vib}} = \sum_{v=0}^{\infty} \frac{e^{-\hbar\omega_0(v+\frac{1}{2})/T}}{v!} = \sum_{v=0}^{\infty} e^{-\beta\hbar\omega_0(v+\frac{1}{2})} \]

\[ Z_{\text{trans}} = \frac{1}{N!} \left( \sum_{p=1}^{\infty} e^{-\frac{p^2}{2\hbar^2}} \right)^N = \frac{1}{N!} \left( \sum_{p=1}^{\infty} e^{-\beta \frac{p^2}{2\hbar^2}} \right)^N \]

Let us first consider the case of large temperatures \( T \gg \hbar^2/2I \).

Let us compute the "rotational" free energy

\[ Z_{\text{rot}} = \sum_{k=0}^{\infty} (2k+1) e^{-\hbar^2k(k+1)/2IT} \]

Only the largest \( k \) will give significant contribution.
to 2rot. For large values of $k$, the rotation of the molecule is quasi-classical. In this case the summation can be replaced by integration and

$$Z_{\text{rot}} = \int_{0}^{\infty} 2k e^{-\frac{k^{2}t}{2I}} \frac{1}{I} dk = \frac{2\pi I}{k^{2}}$$

we first substitute $x = -\frac{k^{2}t}{2I}$ and compute the integrated

$$\int_{0}^{\frac{2\pi I}{k^{2}}} e^{-x} dx = \frac{2\pi I}{k^{2}}$$

The same result can be obtained simply using the kinetic energy of rotation as

$$Z_{\text{rot}} = \int e^{-\frac{\varepsilon(\vec{M})}{T}} d\tau_{\text{rot}}$$

$$\varepsilon(\vec{M}) = \left(\frac{M_{\xi}^{2} + M_{\eta}^{2}}{2I}\right)$$

$$d\tau_{\text{rot}} = \frac{dM_{\xi} dM_{\eta}}{(2\pi h)^{2}} d\varphi_{\xi} d\varphi_{\eta}$$

$M_{\xi} = [\hat{p} \times \vec{r}_{0}] \cdot \hat{\xi}$

$M_{\eta} = [\hat{p} \times \vec{r}_{0}] \cdot \hat{\eta}$

$d\varphi_{\xi}$ and $d\varphi_{\eta}$ are "generalized" coordinates corresponding to $M_{\xi}, M_{\eta}$ (i.e. the infinitesimal angles of rotation about $\xi$ and $\eta$ axes).
\[
Z_{\text{rot}} = \frac{4\pi}{(2\pi \hbar)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2\hbar I} (M_x^2 + M_y^2)\right) dM_x dM_y = \frac{2\pi I}{\hbar^2}
\]

\[
\Rightarrow \text{Free energy is}
\]

\[
F_{\text{rot}} = -NT \ln\left(\frac{2\pi I}{\hbar^2}\right) = -NT \ln T - NT \ln \left(\frac{2I}{\hbar^2}\right)
\]

The rotational part of the specific heat

\[
C_V^{\text{rot}} = -T \frac{\partial^2 F_{\text{rot}}}{\partial T^2}. \frac{1}{N} \quad \text{(per particle)}
\]

\[
\frac{\partial F_{\text{rot}}}{\partial T} = \frac{2}{\partial T} \left( -NT \ln T - NT \ln \left(\frac{2I}{\hbar^2}\right) \right) = -N \ln T - N \ln \frac{2I}{\hbar^2}
\]

\[
\frac{\partial^2 F_{\text{rot}}}{\partial T^2} = -\frac{N}{T}
\]

\[
\Rightarrow C_V^{\text{rot}} = -T \left( -\frac{N}{T}\right) \frac{1}{N} = 1
\]

- in agreement with our estimates from counting degrees of freedom.
Thus, if temperature is rather high, \( T \gg \frac{\hbar^2}{2I} \), then the rotational part of the specific heat is constant, \( C_{\text{rot}} = 4 \).

In the opposite limit, at low-\( T \), only two first terms with \( k = 0 \) and \( k = 1 \) contribute to the specific-heat partition function:

\[ Z_{\text{rot}} = \sum_{k=0}^{\infty} (2k+1) e^{-\frac{\hbar^2}{2IT}} = 
\]

\[ = 1 + 3 e^{-\frac{\hbar^2}{IT}} \]

\[ \Rightarrow F_{\text{rot}} = -3kT e^{-\frac{\hbar^2}{IT}} \]

\[ C_{\text{rot}}^v = -T \frac{\partial^2 E}{\partial T^2} \frac{L}{N} = 3 \left( \frac{\hbar^2}{IT} \right)^2 e^{-\frac{\hbar^2}{IT}} \]

Thus, the rotational specific heat tends to zero exponentially as \( T \to 0 \). Diatomic gas behaves as monoatomic gas.

![Graph showing specific heat as a function of temperature](image)

In the case of arbitrary temperature, a diatomic gas \( C_v \) should be calculated numerically. The result is that \( C_{\text{rot}}^v(\text{max}) = 1.1 \) at \( T = 0.81 \left( \frac{\hbar^2}{2IT} \right) \) and then asymptotically tends to 1.
Vibrational degree of freedom

The vibrational part of the thermodynamic quantities for a gas becomes important at considerably larger temperatures than the rotational part, because the intervals in the vibrational structure of the terms are large compared with those in rotational structure.

\[ \frac{h \omega_0}{k_B} \approx \begin{cases} 6000 \text{ K} & \text{for H}_2 \\ 3000 \text{ K} & \text{for N}_2 \\ 2000 \text{ K} & \text{for O}_2 \end{cases} \]

\[ Z_{vib} = \sum_{v=0}^{\infty} e^{-\frac{h \omega_0 (v + \frac{1}{2})}{k_B} T} = \frac{1}{1 - e^{-\frac{h \omega_0}{k_B} T}} \]

\[ \text{direct summation of geometric series} \]

\[ F_{vib} = -T \ln Z_{vib} = N T \ln \left( 1 - e^{-\frac{h \omega_0}{k_B} T} \right) \]

\[ S_{vib} = -N \ln \left( 1 - e^{-\frac{h \omega_0}{k_B} T} \right) + N \frac{h \omega_0}{k_B} T \left( e^{\frac{h \omega_0}{k_B T}} - 1 \right) \]

\[ C_{vib} = -T \frac{\partial^2 F_{vib}}{\partial T^2} = \left( \frac{h \omega_0}{k_B} \right)^2 \frac{e^{\frac{h \omega_0}{k_B T}}}{\left( e^{\frac{h \omega_0}{k_B T}} - 1 \right)^2} \]
When $T \ll \hbar \omega_0$, $C_v^{\text{vib}} \to 0$ as $C_v = \left(\frac{\hbar \omega_0}{T}\right)^2 e^{-\frac{\hbar \omega_0}{T}}$.

When $T \gg \hbar \omega_0$, $C_v^{\text{vib}} \to 1$.

Finally, let see what are contributions of different degrees of freedom to $C_v$ at different $T$.

- $C_v = \frac{3}{2}$
- $C_v = \frac{5}{2}$
- $C_v = \frac{7}{2}$

At sufficiently high temperatures, when vibrations with large $V$ are excited, the anharmonicity of the vibrations and their interaction with the rotation of the molecule become important.
In order to take into account the anharmonicity of vibrations and their interaction with rotation, we write the potential energy as

\[ u(r) = U(0) + \frac{1}{2} m \omega^2 r_0^2 \left( \xi^2 - \alpha \xi^3 + \beta \xi^4 \right) , \]

where \( U(0) = U_0 \) is the potential energy at equilibrium distance between particles.

\[ \xi = \frac{r}{r_0} - 1 \]

\( \alpha, \beta \) are some "small" constants.

Then, we expand \( e^{-u(r)/T} \), which enter into definition of partition function \( Z = \int e^{-u(r)/T} \, dV \) in powers of \( \xi \), separating the factor \( \exp \left( - \left( U_0 + \frac{1}{2} m \omega^2 r_0^2 \xi^2 / T \right) \right) \), corresponding to harmonic oscillations.

In the expansion, only those terms need be retained which after integration give the highest and next highest powers of \( T \). The zeroth order gives the usual value of the partition function, and remaining terms give corrections.
\[ F_{anh} = -N\frac{1}{2Iw^2} (1 + 3d - \frac{3}{2} \beta + \frac{15}{8} \alpha^2) \]