# 7. Ideal molecular gasses with internal degrees of freedom

We begin our discussion of ideal *molecular* gasses with the case of diatomic molecules. Such systems have the additional internal degrees of motion involving *vibration* along the line joining the atoms and *rotation* about an axis perpendicular to the line passing through the center of mass as depicted in Fig. 7.1.
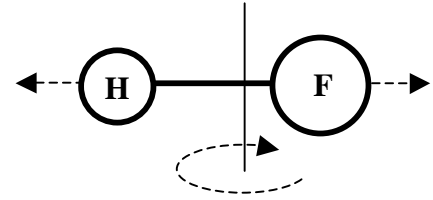
7.1. Rotation and vibration in a diatomic molecule

From elementary quantum mechanics we recall the energy levels of a harmonic oscillator

$$\varepsilon_\upsilon = (\upsilon + 1/2)\hbar\omega \qquad (7.1)$$

where υ is the vibrational quantum number and ω is the vibrational angular frequency. Likewise the energy levels of a rigid rotator are

$$\varepsilon_K = \frac{\hbar^2 K(K+1)}{2I} \qquad (7.2)$$

where I is the moment of inertia, $I = m_r a^2$, with a the fixed distance between its two mass points 1 and 2, and $m_r = m_1 m_2 / (m_1 + m_2)$ is the reduced mass[1]. Referring to Eq. (6.50) we see that there will be additional contributions to Z_{total} associated with both vibration and rotation and so we write

$$Z_{vib} = \sum_\upsilon e^{-\beta(\upsilon+1/2)\hbar\omega} \qquad (7.3)$$

and

$$Z_{rot} = \sum_K (2K+1) e^{-\beta\hbar^2 K(K+1)/2I} . \qquad (7.4)$$

where we included the degeneracy factor $g_K = 2K+1$ of the rotational levels associated with the projection of the angular momentum along some arbitrary axis.

7.1. Rotational levels for diatomic molecules with unlike atoms

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[1] Here we will ignore the interaction between the rotational and vibrational degrees of freedom that is present in rapidly rotating molecules.

We start with the case where our molecules consists of *unlike* atoms examples being HF or HCl. The spacing between the rotational levels, $\Delta\varepsilon_K = \varepsilon_{K+1} - \varepsilon_K = \hbar^2 K / I$, is generally much smaller than that between vibrational levels, and when it is small compared to $k_B T$ we can treat this degree of freedom classically. For a rotational angular momentum of $\mathbf{M}$ the classical kinetic energy is $M^2 / 2I$. For a diatomic molecule there is no angular momentum along the axis of the molecule for our point atoms[2] which we label ζ; i.e., $M_\zeta = 0$. Denoting the remaining two components as M_ξ and M_η the two dimensional quasi-classical volume element is

$$dp^s dq^s / (2\pi\hbar)^s \rightarrow dM_\xi dM_\eta d\phi_\xi d\phi_\eta / (2\pi\hbar)^2$$

where $d\phi_\xi$ and $d\phi_\eta$ are infinitesimal rotations about the ξ and η axes and $d\phi_\xi d\phi_\eta = d\Omega$, the differential solid angle. Eq. (7.4) then takes the form

$$Z_{rot} = \int \frac{dM_\xi dM_\eta d\Omega}{(2\pi\hbar)^2} e^{-\beta(M_\xi^2 + M_\eta^2)/2I}$$

$$= \frac{4\pi}{(2\pi\hbar)^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dM_\xi dM_\eta \, e^{-\beta(M_\xi^2 + M_\eta^2)/2I} = \frac{2k_B T}{\hbar^2} I. \qquad (7.5)$$

In this same limit where the levels are close together relative to $k_B T$ we can convert the sum in (7.4) into an integral

$$Z_{rot} = \sum_K (2K+1) e^{-\beta\hbar^2 K(K+1)/2I} \rightarrow \int_0^\infty 2K dK \, e^{-\beta\hbar^2 K^2/2I}$$

$$= \frac{2k_B T}{\hbar^2} I. \qquad (7.6)$$

The rotational contribution to the free energy, F_{rot}, can now be evaluated as

$$F_{rot} = -Nk_B T \ln Z_{rot} = -Nk_B T \ln\left(\frac{2k_B T}{\hbar^2} I\right)$$

$$= -Nk_B T \ln(k_B T) - Nk_B T \ln(2I / \hbar^2). \qquad (7.7)$$

These two terms result in the following contribution to the heat capacity,

$$c_V \rightarrow \frac{3}{2} k_B + k_B = \frac{5}{2} k_B, \qquad (7.8)$$

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[2] A contribution from quantum mechanical electron spin or angular momentum will be accounted for separately.

and the chemical constant,

$$\zeta_{rot} = l\,n(2I/\hbar). \tag{7.9}$$

At low temperatures where $k_BT << \hbar^2/2I$ we can expand (7.4) as.

$$Z_{rot} = 1 + 3e^{-\beta\hbar^2/I} + \cdots. \tag{7.10}$$

The free energy is then

$$F_{rot} \cong -Nk_BTl\,n\left(1 + 3e^{-\hbar^2/Ik_BT}\right)$$

$$\cong -3Nk_BTe^{-\hbar^2/Ik_BT}. \tag{7.11}$$

The associated entropy $S = -(\partial F/\partial T)_V$ is

$$S_{rot} \cong \frac{3N\hbar^2}{IT}e^{-\hbar^2/Ik_BT}\left(1 + \frac{Ik_BT}{\hbar^2}\right) \tag{7.12}$$

while the heat capacity $C_v = T(\partial S/\partial T)_V$ is

$$C_{rot} \cong 3Nk_B\left(\frac{\hbar^2}{Ik_BT}\right)^2 e^{-\hbar^2/Ik_BT}. \tag{7.13}$$

7.2. Rotational levels for diatomic molecules with identical atoms

Diatomic molecules consisting of identical atoms, examples being H_2, O_2, and N_2, require additional considerations. The first consideration is that at high temperatures, where we take the system to be classical, we must divide the partition function by the $2! = 2$ permutations of the atoms which, rather than having $\zeta_{rot} = l\,n(2I/\hbar^2)$ as in (7.9), the chemical constant is

$$\zeta_{rot} = l\,n(I/\hbar^2). \tag{7.14}$$

The molecule must also have the correct symmetry under exchange of the nuclei: The overall nuclear wave function must be odd for fermions (e.g., ^1H) and even for bosons (e.g., ^{16}O). For a diatomic molecule exchanging the atoms is *equivalent to inversion*, which is governed by parity operator. For the rotational coordinates this is $(-1)^K$.

Consider the case of the hydrogen nucleus which has a spin $i = 1/2$. The total nuclear wave functions of the H_2 molecule with a total spin of either $I = 0$ or 1 has the form

$$\text{Singlet: } \chi_s = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow); \quad I_z = I = 0; \quad (2I+1) = 1 \tag{7.15}$$

and

$$\text{Triplet: } \chi_t = \begin{cases} (\uparrow\uparrow) & I_z = +1 \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) & I_z = 0; \\ (\downarrow\downarrow) & I_z = -1 \end{cases} \quad (2I+1) = 3 \tag{7.16a-c}$$

The *singlet* nuclear spin state is *antisymmetric*. Therefore to insure the *overall* wavefunction, $\psi_{\text{nuclear}} \cdot \psi_{\text{rotational}}$, is *antisymmetric* this requires that $K = \text{even}$. On the other hand the *triplet* states are even which then requires $K = \text{odd}$. Thus we must form *two separate sums*[3]

$$Z_g = \sum_{K=0,2,\cdots} (2K+1)e^{-\hbar^2 K(K+1)/2Ik_BT} \tag{7.17a}$$

and

$$Z_u = \sum_{K=1,3,\cdots} (2K+1)e^{-\hbar^2 K(K+1)/2Ik_BT} . \tag{7.17b}$$

To account for the multiplicity of the nuclear spin states we must also weight these sums by accompanying *degeneracy factors*; i.e., $Z_g \to g_g Z_g$ and $Z_u \to g_u Z_u$ associated with the nuclear spin. We now give the expressions for these factors for the case of arbitrary nuclear spin. Note these factors differ for nuclei with integral and half-integral i as follows:

$$\text{half integral: } \quad g_g = \frac{i}{2i+1}; \quad g_u = \frac{i+1}{2i+1}, \tag{7.18a}$$

and

$$\text{integral: } \quad g_g = \frac{i+1}{2i+1}; \quad g_u = \frac{i}{2i+1} . \tag{7.18b}$$

The normalization here is such that $g_g + g_u = 1$. For the case of hydrogen with nuclear spin $i = 1/2$ discussed above we have $g_g = 1/4$; $g_u = 3/4$. Also of interest is the case of deuterium which has nuclear spin $i = 1$ with degeneracy factors $g_g = 2/3$; $g_u = 1/3$.

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[3] In german g = grad denotes even and u = ungrad denotes even.

Note the total number of nuclear states will be $(2i+1)^2$ leading to an additional nuclear entropy[4] $k_B l n(2i+1)^2 = 2k_B l n(2i+1)$ which would only freeze out at exceedingly low (essentially unachievable) temperatures.

The total rotational partition function can now be written

$$Z_{rot} = \left(g_g Z_g + g_u Z_u\right); \tag{7.19}$$

the corresponding free energy is then given by

$$F_{rot} = -Nk_B T l n\left(g_g Z_g + g_u Z_u\right). \tag{7.20}$$

At high temperatures we have the following

$$Z_g = Z_u = \frac{Z_{rot}}{2} = \frac{I k_B T}{\hbar^2}; \qquad T \to \infty, \tag{7.21}$$

(see Eq. (7.6)). In the opposite limit for our example of the H_2 molecule we have

$$Z_g = 1; \qquad Z_u = 3e^{-\hbar^2/I k_B T}; \qquad T \to 0. \tag{7.22}$$

For molecules with either identical or non-identical atoms the higher rotational states should freeze out as T approaches zero; i.e., the equilibrium state would be the $K = 0$ state. For the case of hydrogen this would be an $I = 0$ state, so as to be compatible with the anti-symmetric behavior of Fermi particles (the protons) on interchange. The $I = 0$ state is called *para-hydrogen* while the $I = 1$ state is called *ortho-hydrogen*. The above statement assumed the system actually *achieves* thermal equilibrium which further assumes the protons in the triplet state at high temperatures are able to "flip" into the singlet state so as to achieve thermal equilibrium on cooling. In practice this process is slow, although it can be speeded up with an appropriate catalyst. If equilibrium is not achieved the system will involve a mixture of the $K = 0$ and the $K = 1$ states at low temperatures. One then regards the $K = 0$ and $K = 1$ states as *independent chemical species* that do not inter convert; each is taken as being in the *ground state*. The ratio would be what ever value is "frozen in" by the cooling process (with the upper limit of the singlet to triplet ratio being one to three, that being the limiting ratio at high temperatures).

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[4] With our choice of the normalization of the degeneracy factors g_g and g_u in Eq. (7.18a,b) the corrections to the chemical constant arising Eq. (7.19) are measured relative to the contribution $2k_B l n(2i+1)$.

The nucleus of O^{16} has $i = 0$ and hence it is a boson; this then requires $K = even$; hence odd K values *are not present*, as is observed experimentally. This example dramatically proves the importance of wave function symmetry.

7.3. Vibrational contributions to diatomic molecules

The vibrational partition function associated with the motion along the axis joining the two atoms with energy levels given by (7.1) is

$$Z_{vib} = \sum_{v=0}^{\infty} e^{-v\beta\hbar\omega} \qquad (7.23)$$

where we have included the zero point contribution $\hbar\omega/2$ in the ground state energy. This sum has the form of a geometric series (see the discussion preceding Eq. (5.56)) and results in the following expression

$$Z_{vib} = \frac{1}{1 - e^{-\beta\hbar\omega}} . \qquad (7.24)$$

The corresponding free energy is then

$$F_{vib} = Nk_BT l n(1 - e^{-\hbar\omega/k_BT}) \qquad (7.25)$$

from which the entropy $S = -(\partial F/\partial T)_V$ follows as

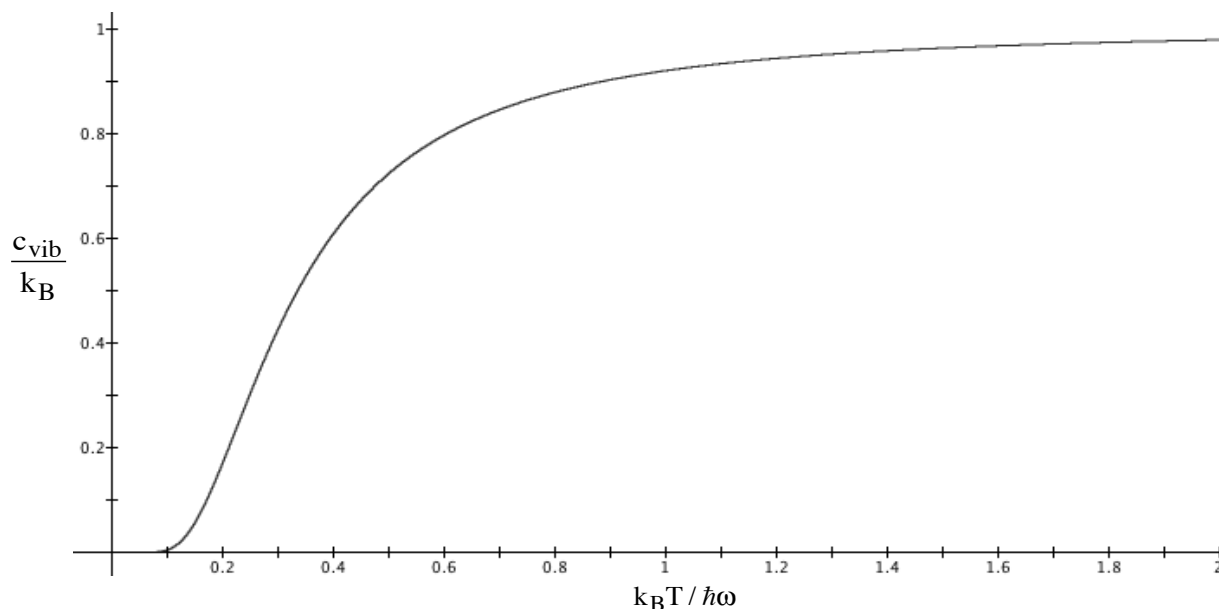$$S_{vib} = -Nk_B l n(1 - e^{-\hbar\omega/k_BT}) - \frac{N\hbar\omega}{T}(1 - e^{-\hbar\omega/k_BT}) . \qquad (7.26)$$

Figure 7.2 A plot of c_{vib}/k_B vs. $k_BT/\hbar\omega$.

The energy is given by (see Eq. (5.56))

$$E_{vib} = \frac{N\hbar\omega}{e^{\hbar\omega/k_BT} - 1} \qquad (7.27)$$

from which the heat capacity $C_V = (\partial E / \partial T)_V$ follows; on a per atom basis this is given by

$$c_{vib} = k_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT} - 1)^2} . \qquad (7.28)$$

This function is plotted in Fig. 7.3.

In the low temperature limit $\hbar\omega \gg k_BT$, F_{vib} and c_{vib} have the limiting forms

$$F_{vib} = -Nk_BTln\,e^{-\hbar\omega/k_BT} \qquad (7.29)$$

and

$$c_{vib} = k_B\left(\frac{\hbar\omega}{k_BT}\right)^2 e^{-\hbar\omega/k_BT} \qquad (7.30)$$

while at high temperatures we have[5]

$$F_{vib} = -Nk_BT\,ln\,(k_BT) + Nk_BT\,ln\,(\hbar\omega) - N\frac{\hbar\omega}{2} \qquad (7.31)$$

and

$$c_{vib} = k_B \qquad (7.32)$$

resulting in a total heat capacity of

$$c_V = c_{trans} + c_{rot} + c_{vib}$$
$$= (3/2 + 1 + 1)k_B = (7/2)k_B \qquad (7.33)$$

Note that at temperatures where the vibrational heat capacity is fully classical many molecules would dissociate.

7.4. Ideal gasses of polyatomic molecules

As the number of atoms in the molecules making up a gas increases so does the number of degrees of freedom and with it the heat capacity per molecule.

7.4.1. Rotational degrees of freedom in polyatomic molecules

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[5] Typical diatomic molecules have very high vibration frequencies so the classical region is reached only at very high temperatures. The quantity $\hbar\omega / k_BT$ is 6100^oK for H_2, 3340° for N_2, and 2230° for O_2.

The generally large size of polyatomic molecules together with their relatively high condensation temperatures results in the three rotational motions of their gas phase being *largely classical* and we will only treat that case. The kinetic energy associated with such motion is

$$\varepsilon_{rot} = \frac{1}{2}\boldsymbol{\Omega}\cdot\mathbf{I}\cdot\boldsymbol{\Omega} \qquad (7.34)$$

where $\boldsymbol{\Omega}$ is the angular velocity vector and $\mathbf{I}$ is the moment of inertia tensor of the molecule considered as a rigid body. The angular momentum is given by $\mathbf{M} = \mathbf{I}\cdot\boldsymbol{\Omega}$ in terms of which we can write (7.34) as

$$\varepsilon_{rot} = \frac{1}{2}\mathbf{M}\cdot\mathbf{I}^{-1}\cdot\mathbf{M} \qquad (7.35)$$

which on diagonalizing can be written

$$\varepsilon_{rot} = \frac{1}{2}\left(\frac{M_\xi^2}{I_1} + \frac{M_\eta^2}{I_2} + \frac{M_\zeta^2}{I_2} \right) . \qquad (7.36)$$

Our semiclassical partition function is then

$$Z_{rot} = \int \frac{dM_\xi dM_\eta dM_\zeta d\phi_\xi d\phi_\eta d\phi_\zeta}{(2\pi\hbar)^3} \exp(-\beta\varepsilon_{rot}) \qquad (7.37)$$

where ϕ_ξ, ϕ_η and ϕ_ζ are the angles conjugate to M_ξ, M_η and M_ζ and the integral is to be carried out only over *physically distinct* angular ranges, as we now discuss. If the molecule has no symmetry at all we can take of the two angular integrations, here taken as $d\phi_\xi$ and $d\phi_\eta$, as being over all solid angles; this yields a factor 4π. Integration over the remaining angle $d\phi_\zeta$ produces an additional factor of 2π for an overall factor of $8\pi^2$. Suppose now that the molecule has an *axis of symmetry*, which we choose as ζ. Rotations by discrete angles about this axis cause the molecule to reproduce itself and hence the physically distinct angular range is reduced by some integer factor. Additional rotations about other axes may also cause the molecule to reproduce itself, further reducing the physically distinct angular range. We designate the *over all*

restriction on the angular integration range in Eq. (7.37) by the integer σ; i.e., $8\pi^2 \rightarrow 8\pi^2/\sigma$.[6]

Carrying out the Gaussian integrations over $dM_\xi dM_\eta dM_\zeta$ Eq. (7.37) becomes

$$Z_{rot} = \frac{8\pi^2}{\sigma(2\pi\hbar)^3}(2\pi k_B T)^{3/2}(I_1 I_2 I_3)^{1/2}$$

$$= \frac{(2k_B T)^{3/2}(\pi I_1 I_2 I_3)^{1/2}}{\sigma\hbar^3} \qquad (7.38)$$

and the free energy is

$$F_{rot} = -Nk_B T \mathit{l}n Z_{rot}$$

$$= -\frac{3}{2}Nk_B T \mathit{l}n k_B T - Nk_B T \mathit{l}n\left(\frac{(8\pi I_1 I_2 I_3)^{1/2}}{\sigma\hbar^3}\right). \qquad (7.39)$$

The heat capacity and chemical constant then follow as

$$c_{rot} = \frac{3}{2}k_B; \qquad\qquad \zeta_{rot} = \mathit{l}n\left(\frac{(8\pi I_1 I_2 I_3)^{1/2}}{\sigma\hbar^3}\right). \qquad (7.40a,b)$$

If the atoms in the molecule lie on a line (a linear molecule) the rotational properties are the same as for a diatomic molecule .

7.4.2. Vibrational degrees of freedom in polyatomic molecules

A three dimensional poly atomic molecule consisting of n atoms will have $3n-6$ vibrational modes each with its own frequency although there can be degeneracies. The normal mode Hamiltonian was given earlier as Eq. (5.62). The partition function then involves a product over the individual oscillators

$$Z_{vib} = \prod_{\alpha=1}^{3n-6} \frac{1}{1-e^{-\beta\hbar\omega_\alpha}}, \qquad (7.41)$$

and the free energy becomes a sum of terms of the form

$$F_{vib} = Nk_B T \sum_{\alpha=1}^{3n-6} \mathit{l}n\left(1-e^{-\hbar\omega_\alpha/k_B T}\right). \qquad (7.42)$$

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[6] The benzene molecule, C_6H_6, has the symmetry of a hexagon with six fold rotations about an axis perpendicular to the plane of the molecule. In addition this plane has reflection symmetry. Hence the range of $d\zeta$ is reduced by a factor 6 while the $d\xi d\eta$ integration is restricted to a single hemisphere for an over all factor $\sigma = 2 \times 6 = 12$

Eq.'s (7.26) through (7.28) can be generalized in a similar manner. In general the frequencies will differ widely and hence as the temperature falls the contribution to the energy, and with it the heat capacity, from the higher frequency modes will decrease more rapidly. For smaller molecules regions where c_{vib} is approximately constant can occur. The fully classical heat capacity per molecule would correspond to $c_{vib} = (3n - 6)k_B$.

A linear molecule has $3n - 5$ degrees of freedom and the above expressions would be modified accordingly.

Problems

7.1. You are given a gas of HD diatomic molecules where H is hydrogen with nuclear spin 1/2 and D is deuterium with nuclear spin 1.
      a) Find the first two terms in the expansion of the rotational heat capacity at low temperatures.
      b) What is the heat capacity in the classical limit including all degrees of freedom?
      c) What is the residual entropy at $T = 0$?

7.2. You are given a gas of D_2 molecules.
    a) Find the first two terms in the rotational heat capacity at low temperatures.
    b) What is the residual entropy at $T = 0$?

7.3. The individual nuclei of the $^{14}N_2$ molecule have spin $i = 1$. From the vector addition rule the total nuclear spin of the molecule, I^{total}, can have the values 0, 1, and 2. For the cases where $I^{total} = 0, 2$ the nuclear spin states are even while for the $I^{total} = 1$ they are odd.

    a) What are the degeneracies of levels for these three cases?
    b) What values of the angular momentum, K, are allowed in evaluating the partition function for these three cases?
    c) Write down the expression for the partition function for the this molecule.
    d) Calculate the first two terms in the rotational heat capacity.

7.4. Carbon dioxide, CO_2, is a linear molecule.
    a) How many vibrational frequencies does it have?
    b) Are any of them the same?
    c) Assuming the different frequencies are denoted as ω_α write down the expression for the vibrational partition function, free energy, and heat capacity.
    d) What is the heat capacity in the classical limit including all degrees of freedom?