Partition functions for non-interacting molecular gas systems

For indistinguishable molecules:
$$Q(N,V,T) = \frac{1}{N!} q_{molecule}(V,T)^N$$

The energy (Hamiltonian) of molecules can be decomposing into independent parts related to different molecular degrees of freedom:

$$\hat{H}_{molecule} = \hat{H}_{CM}(\mathbf{R}_{CM}) + \hat{H}_{rot}(\theta,\phi) + \hat{H}_{vib}(r_{rel}) + \hat{H}_{elec} + \hat{H}_{nuc}$$

In the simplest approximation, the energy of the molecule is decomposed into independent contributions from the degrees of freedon:

$$\varepsilon_{molecule} = \varepsilon_{translational} + \varepsilon_{rotational} + \varepsilon_{vibrational} + \varepsilon_{electronic} + \varepsilon_{nuclear\ spin}$$

The one-molecule canonical ensemble partition function decomposes to partition functions for different degrees of freedom:

$$q_{molecule}(V,T) = q_{trans} q_{rot} q_{vib} q_{elec} q_{nuc}$$

Molecular motion: Diatomic molecules

The total energy for the two atom system is

$$E = T + U = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 + U(\mathbf{r}_1, \mathbf{r}_2)$$
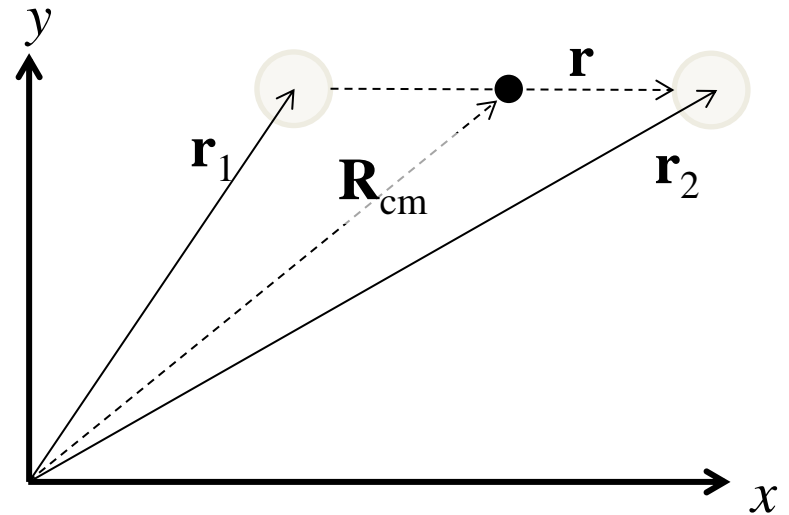
Consider atoms 1 and 2 interacting with a force which is a function of the distance between the two atoms, $\mathbf{F}(|\mathbf{r}_1 - \mathbf{r}_2|) = \mathbf{F}(r)$

$$\begin{cases} m_1 \dfrac{d^2 \mathbf{r}_1}{dt^2} = F_{12}(|\mathbf{r}_1 - \mathbf{r}_2|) \\ m_2 \dfrac{d^2 \mathbf{r}_2}{dt^2} = F_{21}(|\mathbf{r}_1 - \mathbf{r}_2|) = -F_{12}(|\mathbf{r}_1 - \mathbf{r}_2|) \end{cases}$$

Define
- center of mass position, $\mathbf{R}_{cm}$,
- relative coordinates, $\mathbf{r}$, as,

$$\begin{cases} \mathbf{R}_{cm} = \dfrac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \\ \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \end{cases}$$

In terms of these coordinates, the position vectors of the two particles can therefore be written as,

$$\begin{cases} \mathbf{r}_1 = \mathbf{R}_{cm} + \dfrac{m_2}{m_1 + m_2} \mathbf{r} \\ \mathbf{r}_2 = \mathbf{R}_{cm} - \dfrac{m_1}{m_1 + m_2} \mathbf{r} \end{cases}$$

The second time derivatives of $\mathbf{r}_1$ and $\mathbf{r}_2$ can be written in terms of time derivatives of $\mathbf{R}_{cm}$ and $\mathbf{r}$

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Molecular motion: Diatomic molecules, separating motions

Substituting into the equations motion gives new equations for the center of mass and relative motion:

$$\begin{cases} (m_1 + m_2)\dfrac{d^2\mathbf{R}_{cm}}{dt^2} = 0 \\[2em] \dfrac{m_1 m_2}{m_1 + m_2}\dfrac{d^2\mathbf{r}}{dt^2} = \mu_{12}\dfrac{d^2\mathbf{r}}{dt^2} = \mathbf{F}(r) \end{cases}$$

In the new coordinate system,
- Motions of the center of mass and relative coordinates are not coupled
- The center of mass moves as a free particle subject to no force
- The relative motion is described by a particle of mass μ_{12} moving under a force $\mathbf{F}(r)$.

Rather than Cartesian coordinates $\mathbf{r} \equiv \{x, y, z\}$, the relative motion is described in the polar coordinate system

$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$$
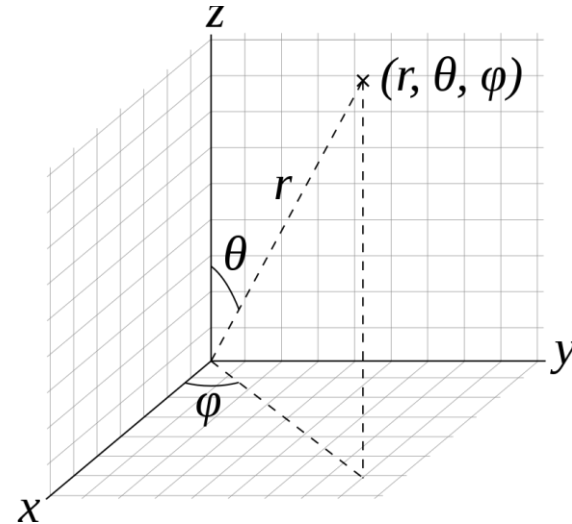
Showing time derivatives with the "dot" notation introduced by Newton: $\implies$

$$\dot{x} = \frac{dx}{dt}$$

$$\begin{cases} \dot{x} = \dot{r}\sin\theta\cos\phi + r\cos\theta\dot{\theta}\cos\phi - r\cos\theta\sin\phi\dot{\phi} \\ \dot{y} = \dot{r}\sin\theta\sin\phi + r\cos\theta\dot{\theta}\sin\phi - r\cos\theta\cos\phi\dot{\phi} \\ \dot{z} = \dot{r}\cos\theta - r\sin\theta\dot{\theta} \end{cases}$$

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Molecular motion: Diatomic molecules, separating motions

The total energy in the center of mass and relative position frame becomes

$$E = T + U = \frac{1}{2}(m_1 + m_2)v_{cm}^2 + \frac{1}{2}\mu_{12}v_{\mathbf{r}}^2 + U(|\mathbf{r}|)$$

Changing the relative position to polar coordinates allows separation of:
- Center of mass motion (involving changing R_{cm})
- Vibrational motion (involving changing r)
- Rotational motion (involving change of θ and ϕ)

$$E = \frac{1}{2}(m_1 + m_2)\dot{R}_{cm}^2 + \frac{1}{2}\mu_{12}\dot{r}^2 + U(r) + \frac{1}{2}\mu_{12}r^2\dot{\theta}^2 + \frac{1}{2}\mu_{12}r^2\sin^2\theta\dot{\phi}^2$$

$$= E_{trans} + E_{vib} + E_{rot}$$

The energy is broken down to independent contributions from translation of the "molecule" as a whole, and "intramolecular" rotations and vibrations.

A procedure is carried out to show that for polyatomic molecules, the mechanical energy is separated into translational motion of the center of mass and rotational - vibrational intermolecular motions (Wilson, Decius, Cross: Molecular Vibrations: The theory of Infrared and Raman Vibrational Spectra)

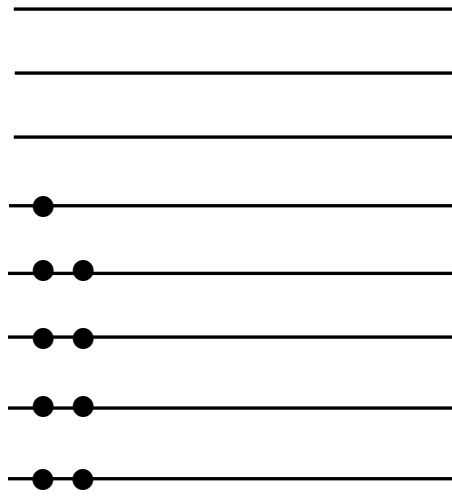# The Pauli Exclusion Principle and Distributing Molecules Among States
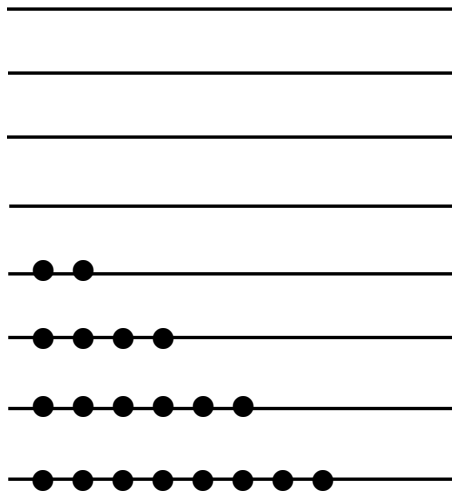
Bosons
(integer spin)

$$W = N! \Big/ \prod_j a_j!$$

$$a_j = 0, 1, 2, \ldots$$

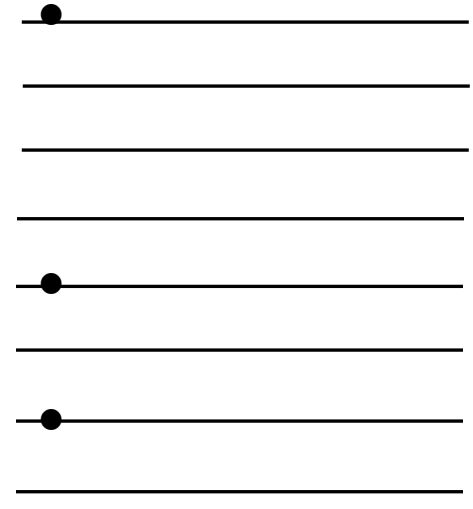Wave functions are symmetric wrt exchange

Fermions
(half-integer spin)

$$W = N! \Big/ \prod_j a_j!$$

$$a_j = 0, 1$$

Wave functions are antisymmetric wrt exchange

Boltzmann Statistics
(Available states much greater than number of particles)

$$W = \frac{N!}{1!1!1!\cdots1!} = N!$$

Classical mechanics can describe the system

When calculating the partition function, the proper symmetry of the wavefunction and its implications on distributions among levels must be considered

Calculating Partition Functions: How large are energy gaps between states?

Is the thermal energy ($\approx kT$) small or large compared to the difference between energy levels?

The relative magnitude of the thermal energy and the gaps between energy levels determines the procedure used to evaluate the partition function.
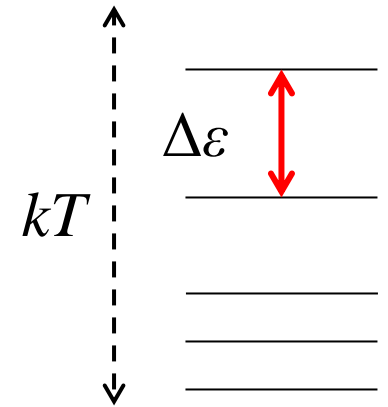
$kT \ll \Delta E$

- Low temperature limit;
- Discrete energy levels are used
- Sum over energy levels

$$Q(N,V,T) = \sum_j e^{-E_j/kT}$$

$kT \gg \Delta E$

- High temperature limit;
- Energy levels treated as continuous (semiclassical approximation)
- Integrate over energy levels

$$Q = \frac{1}{N!h^{3N}} \int \cdots \int e^{-H(\{\mathbf{p},\mathbf{q}\})/kT} \, d\mathbf{p}_1 d\mathbf{q}_1 \cdots d\mathbf{p}_N d\mathbf{q}_N$$

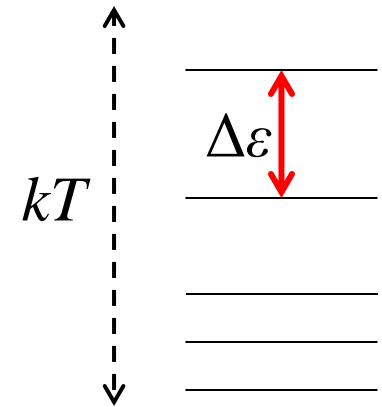It is useful to express energy separations in terms of temperature units kT; $\Delta\varepsilon = kT$ is an energy separation equivalent to an average thermal (kinetic) energy

High and low temperature limits

Energy level separations are expressed as "characteristic temperatures": $\Theta = \Delta\varepsilon / k$

Low T limit: $T \ll \Theta$
High T limit: $T \gg \Theta$

1 eV = 11,600 K = 96.485 kJ/mol   1/40 eV = 300 K (room temperature)

1 cm^{-1} = 1.44 K

$$\hat{H} = \hat{H}_{CM}(\mathbf{R}_{CM}) + \hat{H}_{rot}(\theta, \phi) + \hat{H}_{vib}(r_{rel}) + \hat{H}_{elec} + \hat{H}_{nuc}$$

Translational states: $3h^2/8mL^2 \approx 10^{-17}$ K (always high T limit)

Rotational states: Usually $\Theta_{rot} < 2$ K (most gases in the high T limit)

Vibrational states: $h\nu_0 \sim 0.025$ to 0.5 eV (200 to 4000 cm^{-1})

                    (300 K is low T for molecules, high T for solids)

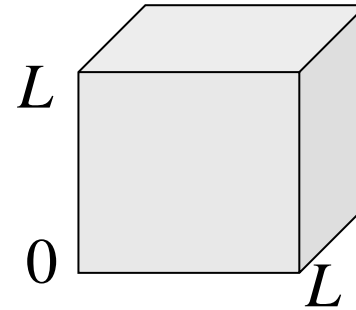Electronic state: $\Delta\varepsilon \sim 0.05$ - 20 eV (always low T limit)

Nuclear spin states: $\Delta\varepsilon = 0$ in the absence of magnetic field

Ideal gas: Translational degrees of freedom for center of mass motion

The particle in a cube is used to represent a simple gas of monatomic molecules

$$U(x, y, z) = \begin{cases} = 0 & for\ 0 \le x < L;\ \ 0 \le y < L;\ \ 0 \le z < L \\ = \infty & elsewhere \end{cases}$$

$$\varepsilon_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

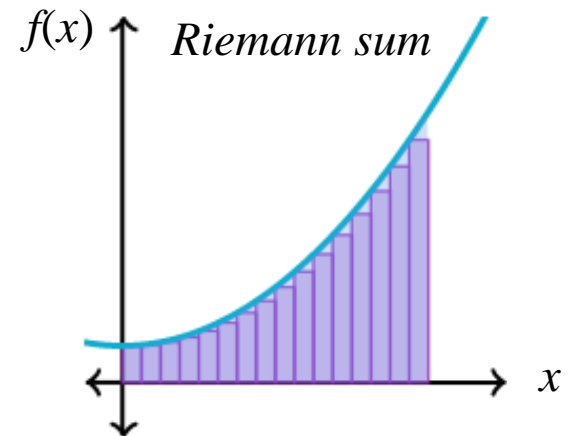The translational partition function for each independent molecule

$$q_{trans}(T) = \sum_i e^{-\varepsilon_i/kT} = \sum_{n_x} e^{-h^2 n_x^2/8mV^{2/3}kT} \sum_{n_y} e^{-h^2 n_y^2/8mV^{2/3}kT} \sum_{n_z} e^{-h^2 n_z^2/8mV^{2/3}kT}$$

The ratio of $h^2/8mkT$ is very small so the sum is approximated by an integral:

$$q_{trans}(T) = \sum_i e^{-\varepsilon_i/kT} = \left[\sum_{n_i} e^{-n_i^2 h^2/8mV^{2/3}kT}\right]^3$$

$$\approx \left(\int_0^\infty e^{-n^2 h^2/8mV^{2/3}kT}\,dn\right)^3 = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

Use this standard integral: $\quad I_0 = \int_{-\infty}^\infty e^{-\alpha x^2}\,dx = \left(\frac{\pi}{\alpha}\right)^{1/2}$

$f(x)$ *Riemann sum*

Ideal gas: Thermodynamic variables from the translational partition function

The partition function of the system of N indistinguishable molecules

$$Q = \frac{q_{molecule}^N}{N!} = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \frac{V^N}{N!}$$

Thermodynamic variables

$$A(N,V,T) = -kT \ln Q(N,V,T) = -NkT \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{Ve}{N}\right]$$

$$\langle E(N,V,T)\rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3}{2}NkT \quad \longleftarrow \quad \text{Same expression as classical mechanics}$$

$$\langle P\rangle = kT \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{NkT}{V} \quad \longleftarrow \quad \text{Ideal gas equation of state!}$$

$$S = kT \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q = \frac{3}{2}Nk + Nk \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{Ve}{N}\right]$$

Sackur-Tetrode equation

Determining the chemical potential from the partition function

Chemical potential of an ideal gas

- The chemical potential is the free energy change if a molecule is added or removed from the system

$$\langle \mu \rangle = -kT \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T} = -kT \ln \frac{q}{N}$$

$$= -kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} \right]$$

$$= -kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{\langle P \rangle} \right]$$

$$= -kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} kT \right] + kT \ln \langle P \rangle$$

$$= \mu_0(T) + kT \ln \langle P \rangle$$

Effect of electronic states on the monatomic ideal gas partition function

The analysis above is for an ideal gas where atoms / molecules are in the ground electronic state in the absence of a magnetic field.
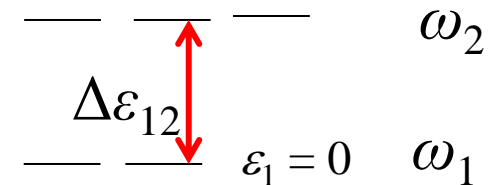
At high temperatures, some atoms may have accessible electronically excited levels.
- The electronic levels are independent of the translational motion of the atoms

$$q_{molecule}(V,T) = q_{trans}(V,T)\, q_{nuc}(T) q_{elec}(T)$$

Electronic levels usually have energy gaps between 0.05 - 20 eV

1 eV $\leftrightarrow$ 38.94 kT $\leftrightarrow$ 12,000 K

$$\omega_2$$

$$\Delta\varepsilon_{12}$$

$$\varepsilon_1 = 0 \quad \omega_1$$

Usually only a few excited electronic levels have energies low enough to be accessible at $T < 1000$ K. Only one to two terms in the expansion of the partition function contribute significantly:

$$q_{elec}(T) = \sum_{elec} \omega_{elec} e^{-\varepsilon_{elec}/kT}$$

$$= \omega_{elec,1} e^{-0/kT} + \omega_{elec,2} e^{-\Delta\varepsilon_{12}/kT} + \omega_{elec,3} e^{-\Delta\varepsilon_{13}/kT}$$

Determine the contributions of electronic degree of freedom to thermodynamic variables

Electronic states of gas phase atomic species

Atom	Electronic configuration	Term symbol / $^{(2S+1)}L_J$	Degeneracy	Energy / eV
H	$1s^1$ $2p^1, 2s^1, 2p^1$	$^2S_{1/2}$ $^2P_{1/2}, {}^2S_{1/2}, {}^2P_{3/2}$	2 2, 2, 4	0 10.20, ~10.20, ~10.20
He	$1s^2$ $1s^1 2s^1$	$^1S_0$ $^3S_1$	1 3	0 19.82
Li	$1s^2 2s^1$ $1s^2 2p^1$	$^2S_{1/2}$ $^2P_{1/2}$	2 2	0 1.85
O	$1s^2 2s^2 2p^4$ $1s^2 2s^2 2p^4$ $1s^2 2s^2 2p^4$ $1s^2 2s^2 2p^4$	$^3P_2$ $^3P_1$ $^3P_0$ $^1D_2$	5 3 1 5	0 0.02 0.03 1.97
F	$1s^2 2s^2 2p^5$ $1s^2 2s^2 2p^5$	$^2P_{3/2}$ $^2P_{1/2}$	4 2	0 0.05

Total angular momentum
$J = L + S, L + S - 1, …, | L - S|$

S Spin angular momentum
L Orbital angular momentum

Spin - orbital coupling affects the electronic energy

Diatomic ideal gas: The rotational – vibrational degrees of freedom

The six degrees of freedom for a diatomic molecule in Cartesian coordinates: $\{x_1, y_1, z_1, x_2, y_2, z_2\}$

$$H = \frac{1}{2m}\left(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 \right) + U(x_1, y_1, z_1, x_2, y_2, z_2)$$

$$U(x_1, y_1, z_1, x_2, y_2, z_2) = \frac{1}{2}k\left[\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} - r_0 \right]^2$$

In the simplest approximation, the motion is described in terms of independent motions:

- Translational motion of the center of mass: $\{R_{cm,x}, R_{cm,y}, R_{cm,z}\}$
- Rotational motion of the molecule: $\{\theta, \phi\}$
- Vibrational motion of the two atoms with respect to each other: $\{r_{rel}\}$

Statistical Mechanics of Diatomic Ideal Gas

The Hamiltonian can be separated into different contributions:

$$\hat{H}_{molecule} = \hat{H}_{CM}(\mathbf{R}_{CM}) + \hat{H}_{rot}(\theta,\phi) + \hat{H}_{vib}(r_{rel})$$
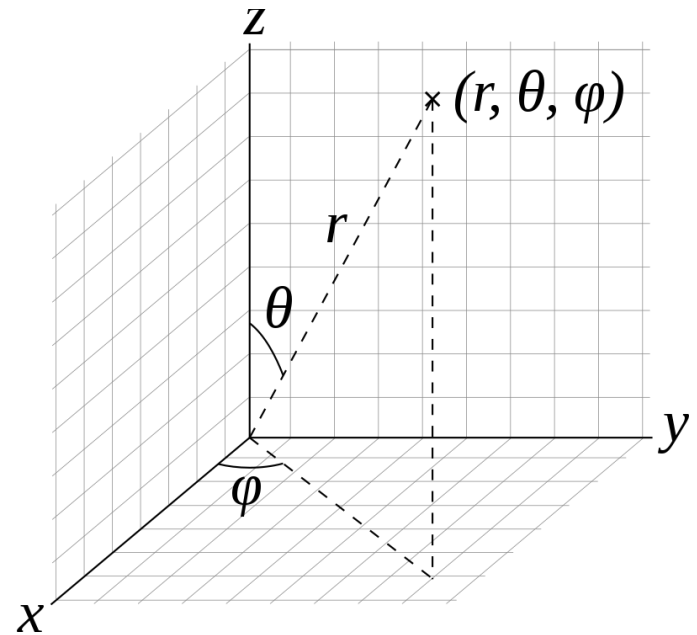
We assume the range of the vibrations are small and this gives the rigid rotor – harmonic oscillator approximation

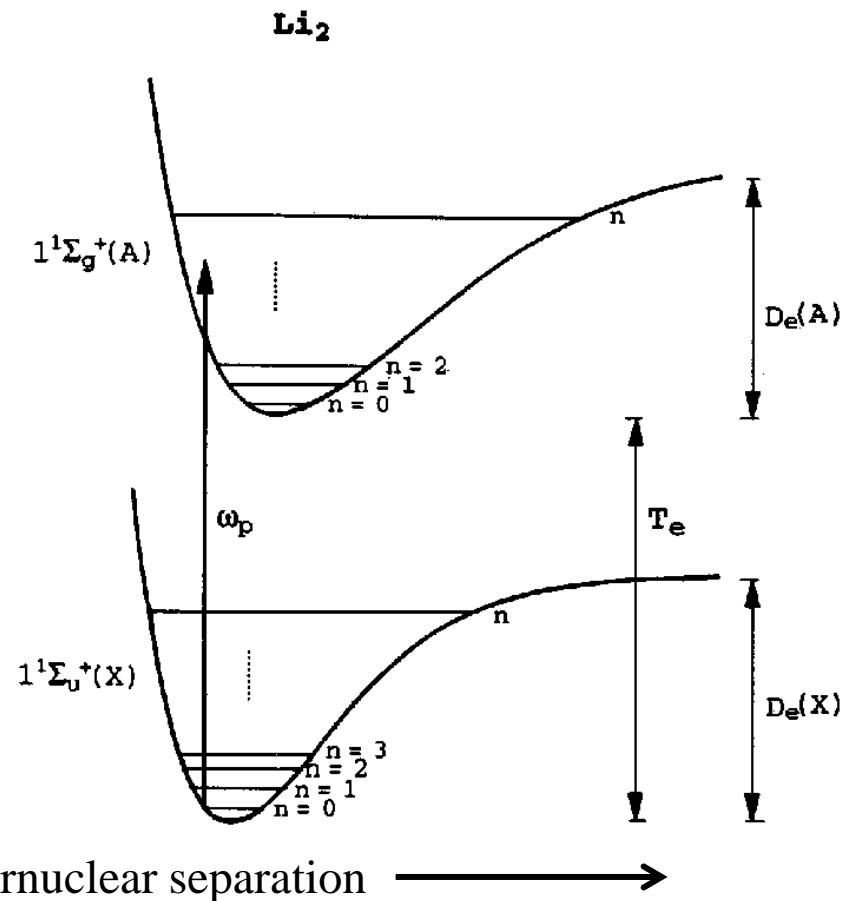# Electronic Partition Function for Diatomic Molecules

Solution of the Schrödinger equation gives a set of energy levels for any atom / molecule which have large energy gaps.

For molecules, the electronic energy of the ground electronic state is measured with respect to the sum of the electronic energies of the separate atoms
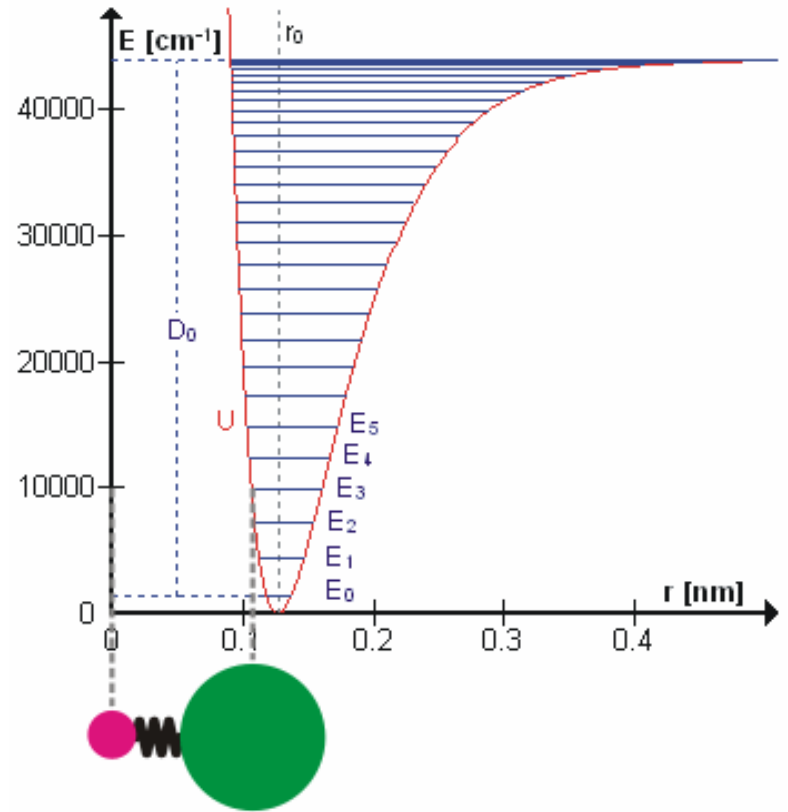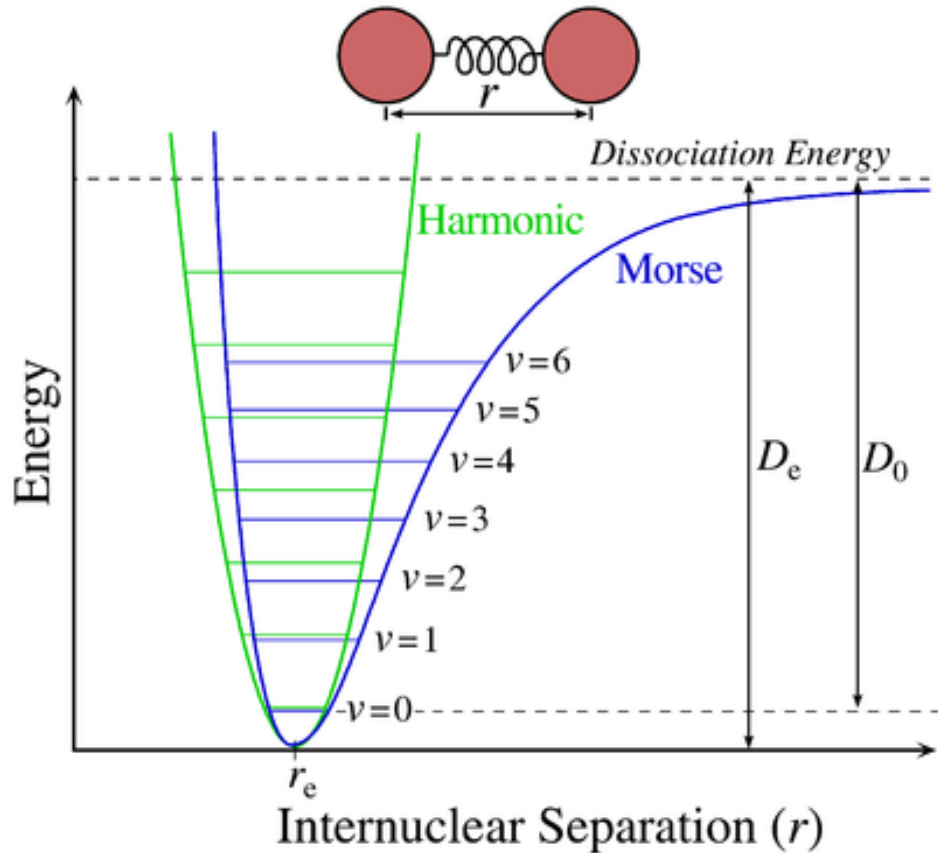
$$q_{elec}(T) = \omega_{e_1} e^{D_e/kT} + \omega_{e_2} e^{-\varepsilon_2/kT} + \cdots$$

Degeneracy of ground molecular state

Orbital angular momentum of molecular electronic states are shown with capital Greek letters in the molecular term symbol.

Li$_2$

$1^1\Sigma_g^+(A)$

$D_e(A)$

n = 2
n = 1
n = 0

ω_p

T_e

n

$1^1\Sigma_u^+(X)$

$D_e(X)$

n = 3
n = 2
n = 1
n = 0

Internuclear separation

Quantum mechanics of diatomic electronic - vibrational – rotational states

$$U_{Morse}(r_{rel}) = D_0 \left\{ 1 - \exp\left[-\alpha(r_{rel} - r_0)\right] \right\}^2$$

Bond energies are accurately represented by the anharmonic Morse potential with dissociation energy, D_e.

The vibrational levels of the Morse potential converge to a continuum at high energies.

The vibrational states of a diatomic molecule

- Dissociation energies (D_e) are large and at normal temperatures diatomic molecules remain bound to each other

- At normal temperatures, the molecules are confined near the potential minimum

- The harmonic oscillator is a good approximation at low energies

$$\varepsilon_{harm,n} = \left(n + \frac{1}{2}\right)h\nu = \varepsilon_0 + nh\nu$$

- At low energies, the range of vibrations are small relative to the bond length

- Under these conditions, the rigid-rotor is a good approximation for the rotational motion of the molecule
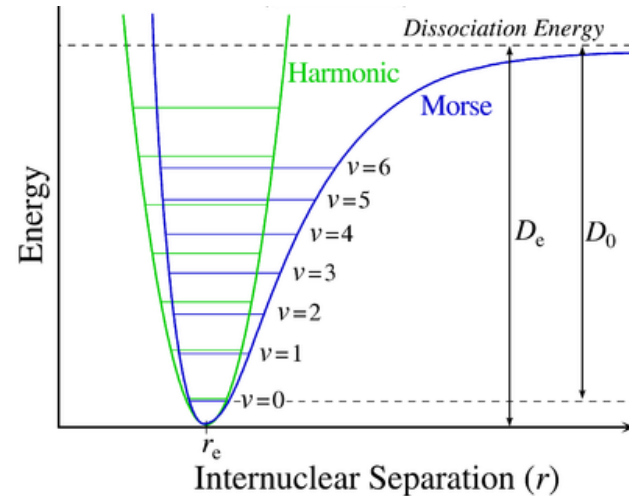
Rigid rotor – harmonic oscillator approximation for the partition function of a diatomic molecule

$$q_{molecule}(V,T) = \sum_i e^{-\varepsilon_{i,trans}/kT} \sum_j e^{-\varepsilon_{j,rot}/kT} \sum_k e^{-\varepsilon_{k,vib}/kT} \sum_\ell e^{-\varepsilon_{\ell,elec}/kT} \sum_s e^{-\varepsilon_{s,nuc}/kT}$$

$$= q_{trans}q_{rot}q_{vib}q_{elec}q_{nuc}$$

Vibrational Partition Function for the Harmonic Oscillator

Substitute the quantized energy levels of the harmonic oscillator in the partition function

$$q_{vib}(T) = \sum_n e^{-\varepsilon_{n,vib}/kT} = \sum_{n=0}^{\infty} e^{-(n+1/2)h\nu/kT} = e^{-h\nu/2kT} \sum_{n=0}^{\infty} e^{-nh\nu/kT}$$

The geometric series for $x < 1$

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

The partition function

$$q_{vib}(T) = \frac{e^{-h\nu/2kT}}{1-e^{-h\nu/kT}} = \frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}$$
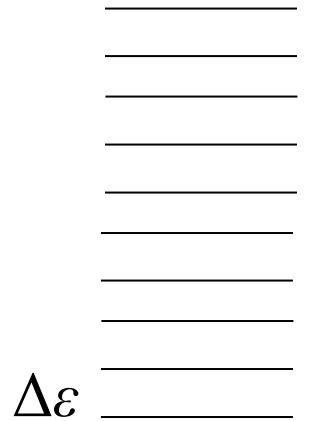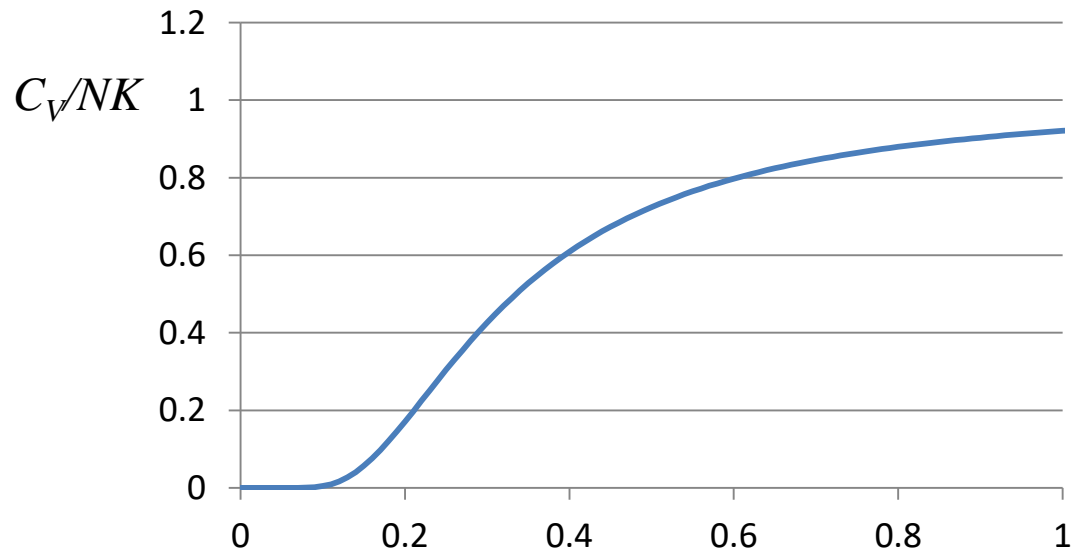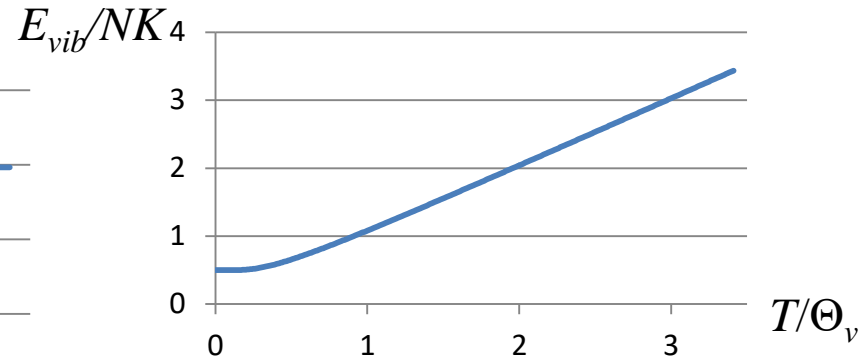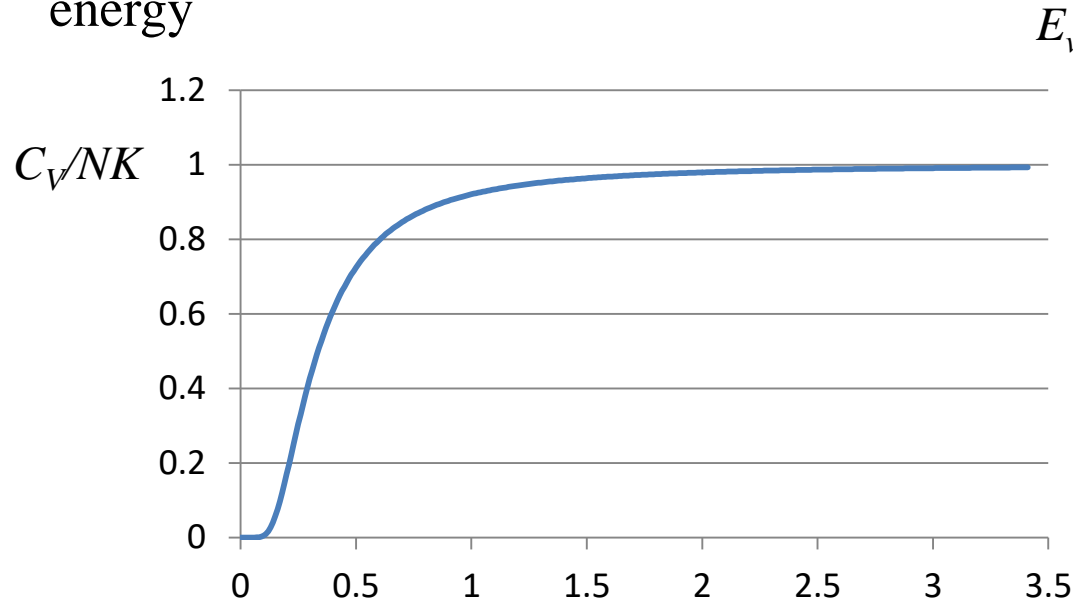
High temperature limit of the partition function

$$\lim_{T\to\infty} q_{vib}(T) = \frac{kT}{h\nu} = \frac{T}{\Theta_v}$$

$$\left\langle E_{vib}(N,T) \right\rangle = NkT^2 \left(\frac{\partial \ln q_{vib}}{\partial T} \right)_{N,V} = Nk \left(\frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T}-1} \right)$$

$$C_{v,vib} = \frac{dE_{vib}}{dT} = \frac{\left(\Theta_v/T \right)^2 e^{\Theta_v/T}}{\left(e^{\Theta_v/T} - 1 \right)^2}$$

Interpretation of the heat capacity

Heat capacity shows the transfer between kinetic energy (temperature) and potential energy

C_V/NK

T/Θ_v

E_{vib}/NK

T/Θ_v

C_V/NK

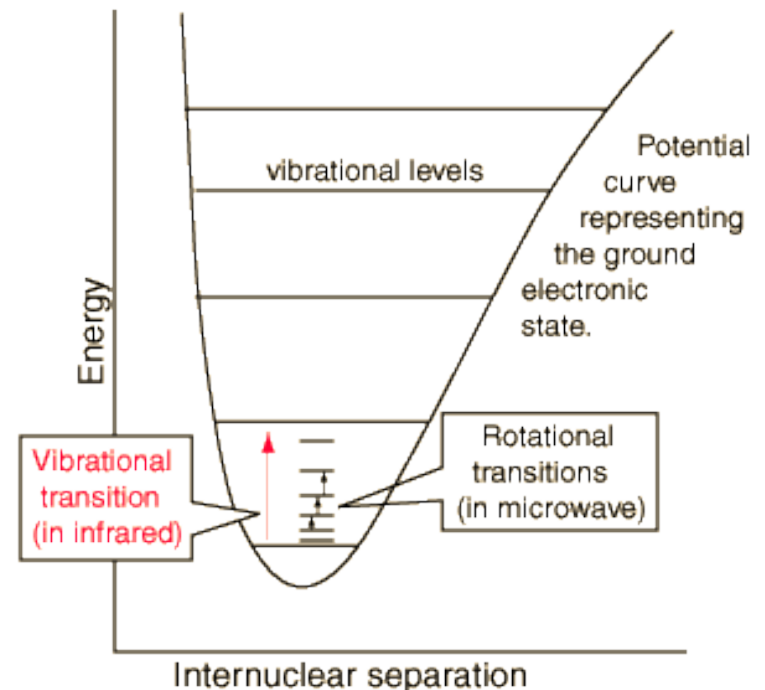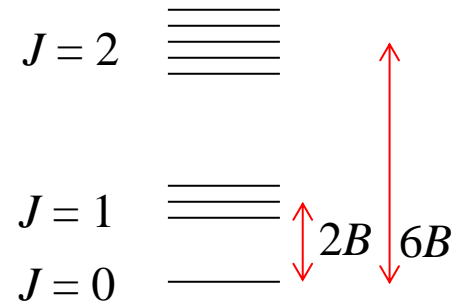T/Θ_v

$\Delta\varepsilon$

As the thermal energy becomes larger than the energy gap, heat capacity becomes a constant value

Statistical mechanics of rotational degrees of freedom: Rigid rotor

Energy levels of the rigid rotor

$$\varepsilon_{rot,J} = J(J+1)\frac{h^2}{8\pi^2 I} = J(J+1)B$$

- J is the rotational quantum number
- I is the moment of inertia of the molecule with respect to the center of mass ($I = m_1 r_1^2 + m_2 r_2^2$)
- B is the rotational constant
- The rotational state wave functions correspond to the spherical harmonics (see H atom in quantum chemistry)
- The wave functions have even and odd symmetry (S, P, D, F, … orbital angular dependences)
- Degeneracy of each energy level is $2J + 1$

$J = 2$

$J = 1$

$J = 0$

$2B$ $6B$

Energy

vibrational levels

Potential curve representing the ground electronic state.

Vibrational transition (in infrared)

Rotational transitions (in microwave)

Internuclear separation

The Pauli Exclusion Principle

General Chemistry:

- No two electrons in orbitals can have the same four quantum numbers.

- Electrons in the same atomic or molecular orbitals must have opposite spins

Physical / Quantum Chemistry:

- The wave function for an atomic or molecular system must be anti-symmetric with respect to exchange of any pair of electrons (Fock – Slater determinant). This guaranties that each orbital only contains two electrons.

$$\psi_{spin}^{symm}(1) = \alpha(1)\alpha(2)$$

$$\psi_{spin}^{symm}(2) = \beta(1)\beta(2)$$

$$\psi_{spin}^{anti-symm} = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$\psi_{spin}^{symm}(3) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$

For example, for the He atom: $\psi_0 = 1s(1)1s(2)\cdot\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$

The Pauli Exclusion Principle

More general form:

- The wave function for a homo-nuclear diatomic molecule must be anti-symmetric with respect to exchange of any pair of Fermions (particles with half-integer spin ½, 3/2, …), including unpaired electrons and nuclei;

- The wave function for a homo-nuclear diatomic molecule must be symmetric with respect to exchange of any pair of Bosons (particles with 0 or integer spin 1, 2, …), including nuclei;

- Closed shells of electrons have a net 0 spin and have symmetric wave functions

- Examples: Total wave function for exchange of ^1H nuclei in the H_2 molecule

Symmetry of wave functions for diatomic molecules (3)

The exchange of nuclei in a diatomic (polyatomic) molecule is performed by a two-step process
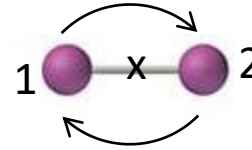
1) Electrons and nuclei are inverted through the center of symmetry of the molecule
2) The electrons alone are inverted back through the center of symmetry

$$\Psi_{molecule} = \Psi_{elec}\Psi_{vib}\Psi_{rot}\Psi_{nuc}$$

Symm: J even (S, D, …, spherical harmonics)

Antisymm: J odd (P, F, …, spherical harmonics)

Symmetric for both steps for most ground electronic states (in closed-shell species)

Symmetric under inversion

				$J = 0$
				$J = 1$
				$J = 2$
				$J = 3$
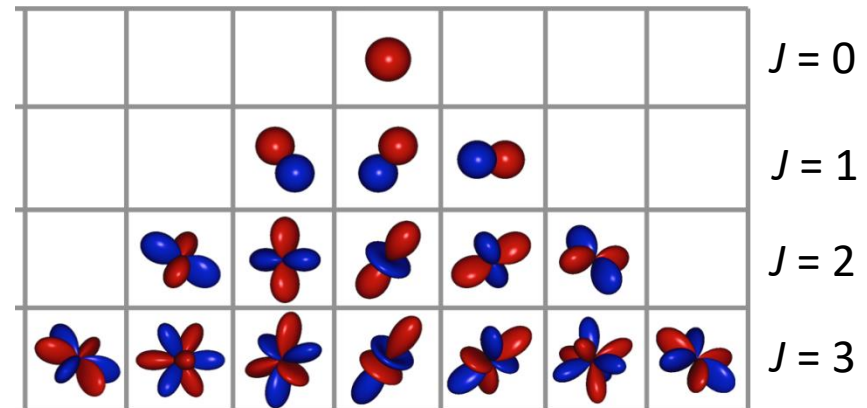
The symmetry of ψ_{nuc} is chosen to give $\psi_{molecule}$ the correct symmetry

Symmetry of nuclear wave function

1) Nuclei are Fermions (protons ^1H, ^{13}C) and $\psi_{molecule}$ is antisymmetric wrt nucleus exchange:

   a) If the rotational wave function is anti-symmetric (J is odd)

   ψ_{nuc} is symmetric wrt nucleus exchange (three states, slide 21)

   b) If the rotational wave function is symmetric (J is even)

   ψ_{nuc} is antisymmetric wrt nucleus exchange (one state, slide 21)

In ortho-H_2 ($\uparrow\uparrow$) the nuclear spin wave function is symmetric

In para-H_2 ($\uparrow\downarrow - \downarrow\uparrow$) the nuclear spin wave function is anti-symmetric

2) Nuclei are Bosons (^{12}C, ^2H, …) and $\psi_{molecule}$ is symmetric wrt nucleus exchange:

   a) If the nuclear spin is 0 (symmetric wave function)

   Only symmetric rotational states (J even) are allowed

   b) If the nuclear spin is integer

   I=1 spins, 9 nuclear spin functions of which 6 are symmetric (ortho), and 3 antisymmetric (para) to exchange can be written

Rotation - Nuclear Spin Partition Function

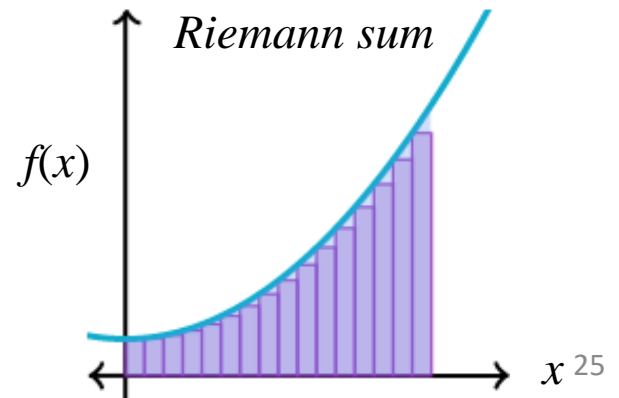For spin ½ nuclei (H_2) at low temperatures

$$q_{rot,nuc}(T) = 1 \times \sum_{J\ \text{even}}^{\infty} (2J+1)e^{-J(J+1)B/kT} + 3 \times \sum_{J\ \text{odd}}^{\infty} (2J+1)e^{-J(J+1)B/kT}$$

For spin 0 nuclei at low temperatures

$$q_{rot,nuc}(T) = 1 \times \sum_{J\ \text{even}}^{\infty} (2J+1)e^{-J(J+1)B/kT} + 0 \times \sum_{J\ \text{odd}}^{\infty} (2J+1)e^{-J(J+1)B/kT}$$

In the high temperature limit many rotational states are accessible:

$$\sum_{J\ \text{even}}^{\infty} (2J+1)e^{-J(J+1)\Theta_r/T} \approx \sum_{J\ \text{odd}}^{\infty} (2J+1)e^{-J(J+1)\Theta_r/T} \approx \frac{1}{2} \sum_{J\ \text{all}}^{\infty} (2J+1)e^{-J(J+1)\Theta_r/T}$$

$$\approx \frac{1}{2} \int_0^{\infty} (2J+1)e^{-J(J+1)\Theta_r/T}\,dJ = \frac{T}{2\Theta_r}$$

Riemann sum

$f(x)$

x

Substitute the quantized energy levels of the rigid rotor in the partition function (no external magnetic field)

$$q_{rot,nuc}(T) \approx q_{nuc}q_{rot}(T) = (2S+1)^2 \frac{T}{2\Theta_r}$$

In the general case of diatomic molecules

$$q_{rot}(T) = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{T}{\sigma\Theta_r}$$

Symmetry number of molecule

(2 for homoatomics; 1 for heteroatomics)

For intermediate temperatures a more general form for the rotational partition function is:

$$q_{rot}(T) = \frac{T}{\sigma\Theta_r}\left\{1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^3 + \cdots\right\}$$

$$E_{rot}(T) = NkT\left\{1 + \frac{\Theta_r}{3T} - \frac{1}{45}\left(\frac{\Theta_r}{T}\right)^2 + \cdots\right\} \qquad C_{v,rot}(T) = Nk\left\{1 + \frac{1}{45}\left(\frac{\Theta_r}{T}\right)^2 + \cdots\right\}$$

Probability that a rotational state is occupied

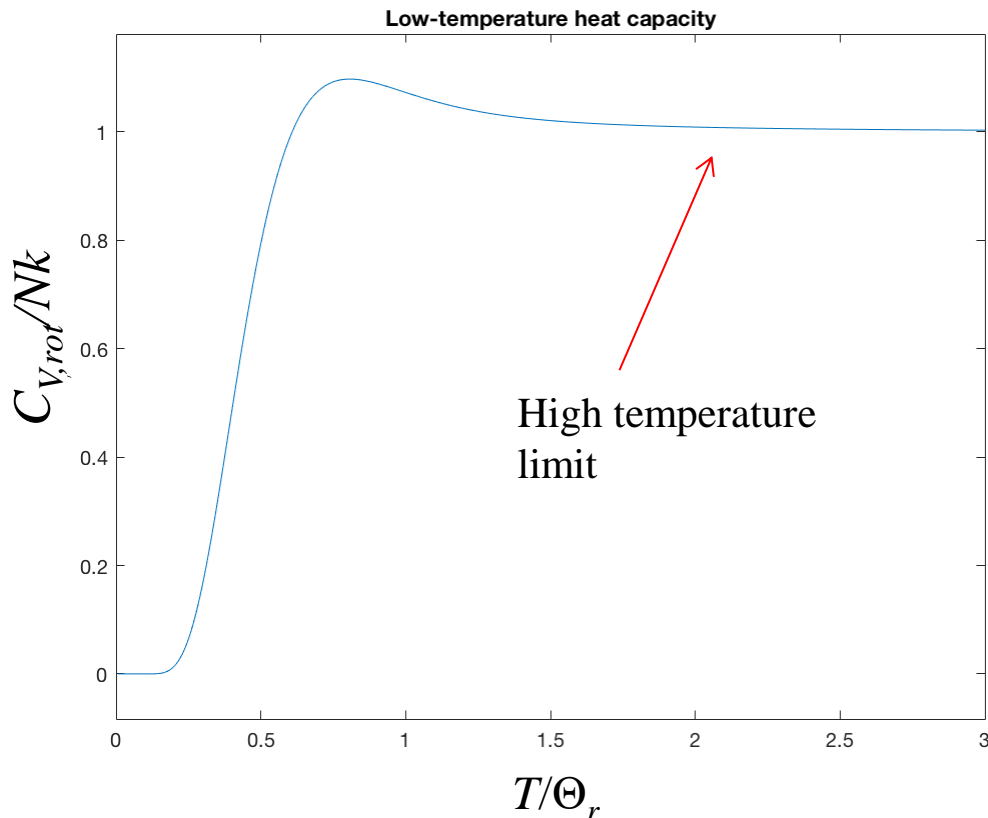$$\frac{N_J}{N} = \frac{(2J+1)e^{-J(J+1)\Theta_r/T}}{q_{rot}(T)}$$

Rotational partition function

Symmetry number σ

$$q_{rot}(T) = \frac{T}{\sigma \Theta_r} \left\{ 1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^3 + \cdots \right\}$$

$\sigma = 1$ for heteronuclear molecule (HCl)

$\sigma = 2$ for homonuclear molecule (Cl_2)

Low-temperature heat capacity

High temperature limit

Typical behavior of rotational contribution to the heat capacity at constant V

Parameters for diatomic molecules

Molecule	Electronic state	Θ_v / K	Θ_r / K	r_{eq} / Å	D_0 / eV
H_2	$^1\Sigma_g^+$	6210	85.4	0.740	4.454
N_2	$^1\Sigma_g^+$	3340	2.86	1.095	9.76
O_2	$^3\Sigma_g^-$	2230	2.07	1.204	5.08
CO	$^1\Sigma^+$	3070	2.77	1.128	9.14
NO	$^2\Pi_{1/2}$	2690	2.42	1.150	5.29
HCl	$^1\Sigma^+$	4140	15.2	1.275	4.43
HBr	$^1\Sigma^+$	3700	12.1	1.414	3.60
HI	$^1\Sigma^+$	3200	9.0	1.604	2.75
Cl_2	$^1\Sigma_g^+$	810	0.346	1.989	2.48
Br_2	$^1\Sigma_g^+$	470	0.116	2.284	1.97
I_2	$^1\Sigma_g^+$	310	0.054	2.667	1.54

- $\Theta_v = h\nu/k$. The vibrational states are mostly in the low temperature limit
- $\Theta_r = B/k$. The rotational states are mostly in the high temperature limit
- Bond breaking through kinetic energy only occurs at very high temperatures

Thermodynamic Relations for Diatomic Molecules

The partition function of the system of N indistinguishable molecules

$$q_{molecule}(V,T) = \left(\frac{2\pi(m_1+m_2)kT}{h^2} \right)^{3/2} V \frac{8\pi^2 IkT}{\sigma h^2} \frac{e^{-h\nu/2kT}}{\left(1-e^{-h\nu/kT}\right)} \omega_{e_1} e^{D_e/kT} \omega_{nuc}$$

Thermodynamic variables

$$-\frac{A}{NkT} = \ln\left(\frac{2\pi(m_1+m_2)kT}{h^2} \right)^{3/2} \frac{Ve}{N} + \ln\frac{8\pi^2 IkT}{\sigma h^2} - \ln\left(1-e^{-h\nu/kT}\right) - \frac{h\nu}{2kT} + \frac{D_e}{kT} + \ln\omega_{e_1} + \ln\omega_{nuc}$$

$$\frac{\langle E(N,V,T) \rangle}{NkT} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = \frac{3}{2} + \frac{2}{2} + \frac{h\nu/kT}{e^{h\nu/kT}-1} + \frac{h\nu}{2kT} - \frac{D_e}{kT}$$

$$\frac{C_V}{Nk} = \frac{3}{2} + \frac{2}{2} + \left(\frac{h\nu}{2kT} \right)^2 \frac{e^{h\nu/kT}}{\left(e^{h\nu/kT}-1\right)^2}$$

$$\langle P \rangle = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} = \frac{NkT}{V} \quad \longleftarrow \quad \textcolor{red}{\text{Ideal gas equation of state!}}$$

Thermodynamic Relations

Entropy

$$\frac{S}{Nk} = \ln\left[\left(\frac{2\pi(m_1+m_2)kT}{h^2}\right)^{3/2}\right]\frac{Ve^{5/2}}{N} + \ln\frac{8\pi^2 IkTe}{\sigma h^2} + \frac{h\nu/kT}{e^{h\nu/kT}-1} - \ln\left(1-e^{-h\nu/kT}\right) + \ln\omega_{e_1} + \ln\omega_{nuc}$$
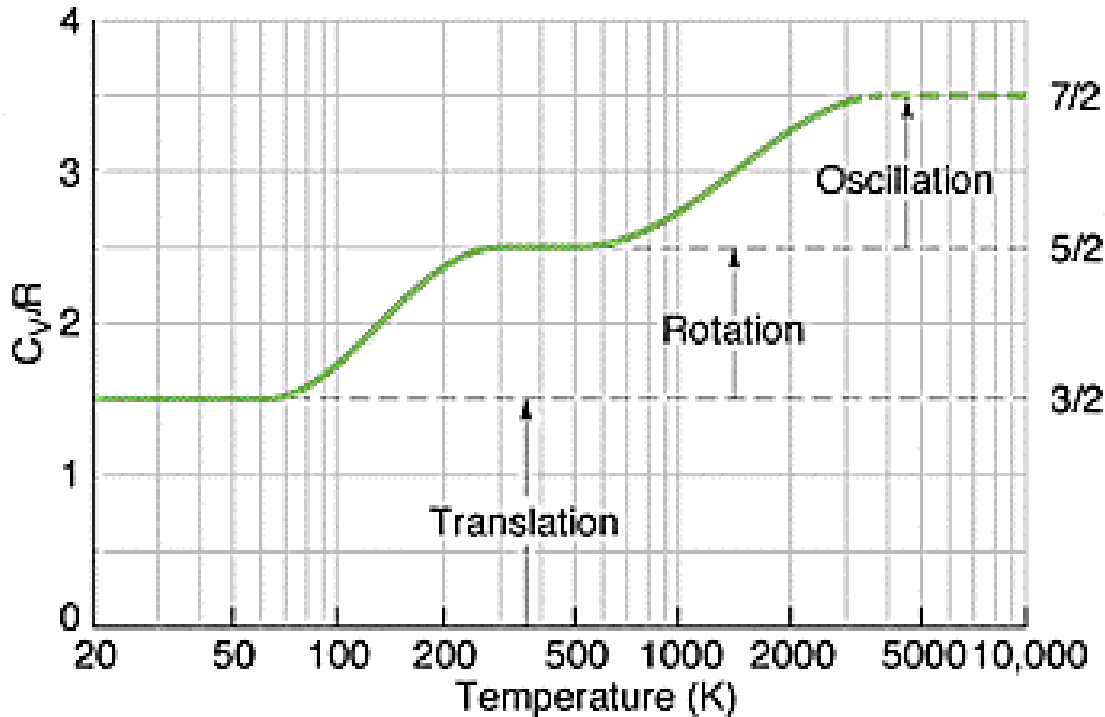
Gibbs free energy and the chemical potential

$$\frac{G}{NkT} = \frac{A}{NkT} + \frac{PV}{NkT} = \frac{\mu}{kT} = \frac{\mu^0(T)}{kT} + \ln P$$

Standard chemical potential

$$\frac{\mu^0(T)}{NkT} = -\ln\left(\frac{2\pi(m_1+m_2)kT}{h^2}\right)^{3/2} kT - \ln\frac{8\pi^2 IkT}{\sigma h^2} + \frac{h\nu}{2kT} + \ln\left(1-e^{-h\nu/kT}\right) - \frac{D_e}{kT} - \ln\omega_{e_1} - \ln\omega_{nuc}$$

Significance of C_V

Shows transfer between kinetic energy (temperature) and potential energy

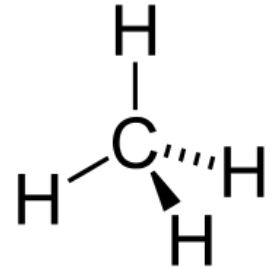Behaviour of C_V for H_2

The stepwise increase in the heat capacity is a quantum mechanical behaviour

Polyatomic molecules in the ideal gas phase

The 3N degrees of freedom for a polyatomic molecule in Cartesian coordinates:
$\{x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N\}$

$$H = \frac{1}{2m}\left[p_{1x}^2 + \cdots + p_{Nz}^2 \right] + U(x_1, y_1, z_1, x_2, y_2, z_2, \cdots, x_N, y_N, z_N)$$

Mathematical techniques used in spectroscopy show the motion of a polyatomic molecule can be broken into independent contributions of:

- Translational motion of the center of mass: $\{R_{cm,x}, R_{cm,y}, R_{cm,z}\}$

- Three rotational motions about the three principle axes of rotation (with three "Euler angles" as degrees of freedom)

- 3N – 6 normal modes of vibrational which are independent of each other. Normal modes are described by coordinates Q_1, Q_2, …Q_{3N-6} which are combinations of the motion of groups of atoms

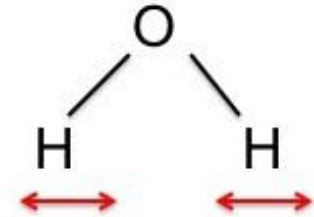# Normal vibrational modes for polyatomic molecules

Normal vibrational modes of water
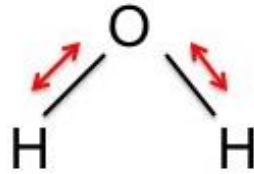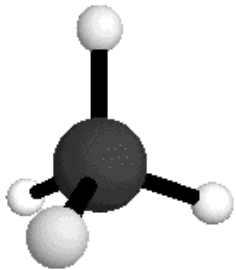
v_1 symmetric stretch
A_1 symmetry
~ 3700 cm^{-1}
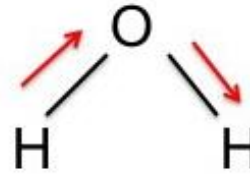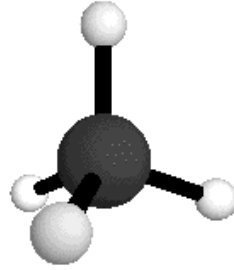
v_2 asymmetric stretch
B_1 symmetry
~ 3600 cm^{-1}
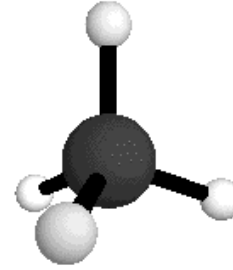
v_3 symmetric bend
A1 symmetry
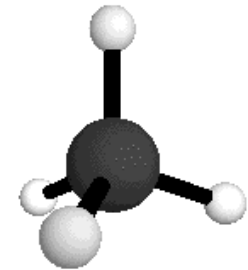~ 1600 cm^{-1}

Normal vibrational modes of methane

Symmetric stretch
A_1 symmetry
3025.5 cm^{-1}

Asymmetric stretch
F_2 symmetry
3156.8 cm^{-1}

Symmetric bend
F_2 symmetry
1367.4 cm^{-1}

Asymmetric bend
E symmetry
1582.7 cm^{-1}

Vibrational Partition Function

The Hamiltonian for normal vibrational modes for this system becomes:

$$H_{vib} = \frac{1}{2m}\left[p_{Q_1}^2 + \cdots + p_{Q_{3N-6}}^2\right] + \sum_{j=1}^{3N-6}\frac{k_j}{2}Q_j^2$$

Each normal mode is a harmonic oscillator with energy levels and frequency given by:

$$\varepsilon_{vib} = \sum_{j=1}^{3N-6}\left(n_j + \frac{1}{2}\right)h\nu_j \qquad \nu_j = \frac{1}{2\pi}\sqrt{\frac{k_j}{\mu_j}}$$
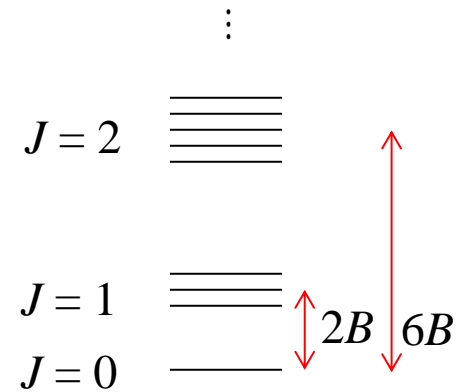
Substitute the expression for the partition function

$$q_{vib}(T) = \prod_{j=1}^{3N-6}\sum_{n_j}e^{-\varepsilon_{vib}(n_j)/kT} = \prod_{j=1}^{3N-6}\frac{e^{-\Theta_{v_j}/2T}}{1-e^{-\Theta_{v_j}/T}}$$

$$\langle E_{vib}(N,T)\rangle = Nk\sum_{j=1}^{3N-6}\left(\frac{\Theta_{v_j}}{2} + \frac{\Theta_{v_j}}{e^{\Theta_{v_j}/T}-1}\right) \qquad C_v = \sum_{j=1}^{3N-6}\left(\Theta_{v_j}/T\right)^2\frac{e^{\Theta_{v_j}/T}}{\left(e^{\Theta_{v_j}/T}-1\right)^2}$$

Rotational states of a polyatomic gas

For linear polyatomic molecules (CO_2), energy levels are the same as for the diatomic molecule

$$\varepsilon_{rot,J} = J(J+1)\frac{h^2}{8\pi^2 I} = J(J+1)B \qquad \omega_J = 2J+1$$

$J = 2$

$J = 1$

$J = 0$

$2B \quad 6B$

The moment of inertia with respect to the center of mass

$$I = \sum_{i=1}^{n} m_i r_i^2$$

For non-linear molecules, a set of Cartesian coordinates passing through the center of mass can be always chosen, called the principle axes, such that the three rotations about these axes, characterized by three Euler angles, are independent.
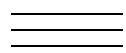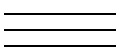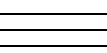
The moments of inertia about these axes are I_A, I_B, and I_C with three corresponding rotational constants,

$$A = \frac{h^2}{8\pi I_A} \qquad\qquad B = \frac{h^2}{8\pi I_B} \qquad\qquad C = \frac{h^2}{8\pi I_C}$$

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Rotational states of a polyatomic gas

For spherical top molecules, $I_A = I_B = I_C$. The quantum mechanical spherical top molecule is solvable

$J = 2$ ≡≡≡≡≡ ... 25 states

$$\varepsilon_{rot,J} = J(J+1)\frac{h^2}{8\pi^2 I} \qquad \omega_J = (2J+1)^2$$

Degeneracy of rotational state

$J = 1$

$J = 0$ —

The characteristic rotational temperature are small and the high temperature limit of the partition function can be used

$$q_{rot}(T) = \frac{1}{\sigma}\int_0^\infty (2J+1)^2 e^{-J(J+1)h^2/8\pi^2 IkT}\, dJ = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 IkT}{h^2}\right)^{3/2}$$

σ is the symmetry number of the molecule (number of pure rotational elements in the point group of the molecule in addition to the identity)

For methane $\sigma = 12$

http://symmetry.otterbein.edu/tutorial/methane.html

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Rotational states of a polyatomic gas

For symmetric top molecules, $I_A = I_B \neq I_C$. The quantum mechanical symmetric top molecule is solvable

$$\varepsilon_{rot,JK} = \frac{h^2}{8\pi^2}\left[\frac{J(J+1)}{I_A} + K^2\left(\frac{1}{I_C} - \frac{1}{I_A}\right)\right]$$

$$J = 0, 1, 2, \ldots$$
$$K = J, J-1, J-2, \ldots, -J+1, -J$$

$$\omega_{JK} = (2J+1) \longleftarrow \quad \text{Degeneracy of rotational state}$$

The characteristic rotational temperature are small and the high temperature limit of the partition function can be used

$$q_{rot}(T) = \frac{1}{\sigma}\int_0^\infty (2J+1)e^{-\alpha_A J(J+1)}dJ\int_{-J}^{J} e^{-(\alpha_C - \alpha_A)K^2}dK$$

$$= \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A kT}{h^2}\right)\left(\frac{8\pi^2 I_C kT}{h^2}\right)^{1/2}$$

For ammonia $\sigma = 3$

Rotational states of a polyatomic gas

For asymmetric top molecules, $I_A \neq I_B \neq I_C$. The quantum mechanical asymmetric top molecule is solvable numerically.

The characteristic rotational temperature are small and the high temperature limit of the partition function can be used

$$q_{rot}(T) = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_B kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_C kT}{h^2}\right)^{1/2} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}$$

For water $\sigma = 2$

$$\langle E_{rot}(N,T)\rangle = \frac{3}{2}Nk \qquad C_{V,rot} = \frac{3}{2}Nk$$

Thermodynamic Relations for Linear Polyatomic Molecules

The partition function of the system of N indistinguishable molecules (0 spin nuclei)

$$q_{molecule}(V,T) = \left(\frac{2\pi MkT}{h^2}\right)^{3/2} V \frac{T}{\sigma\Theta_r}\left\{\prod_{j=1}^{3N-5}\frac{e^{-\Theta_{vj}/2T}}{\left(1-e^{-\Theta_{vj}/T}\right)}\right\}\omega_{e_1}e^{D_e/kT}$$

Thermodynamic variables

$$-\frac{A}{NkT} = \ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] + \ln\frac{T}{\sigma\Theta_r} - \sum_{j=1}^{3N-5}\left[\frac{\Theta_{vj}}{2T} - \ln\left(1-e^{-\Theta_{vj}/T}\right)\right] + \frac{D_e}{kT} + \ln\omega_{e_1}$$

$$\frac{\langle E(N,V,T)\rangle}{NkT} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3N-5}\left[\frac{\Theta_{vj}}{2T} + \frac{\Theta_{vj}/T}{e^{\Theta_{vj}/T}-1}\right] - \frac{D_e}{kT}$$

$$\frac{C_V}{Nk} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3N-5}\left(\frac{\Theta_{vj}}{2T}\right)^2\frac{e^{\Theta_{vj}/T}}{\left(e^{\Theta_{vj}/T}-1\right)^2}$$

$$\langle P\rangle = kT\left(\frac{\partial\ln Q}{\partial V}\right)_{N,T} = \frac{NkT}{V} \qquad \longleftarrow \qquad \text{Ideal gas equation of state!}$$

Thermodynamic Relations for Nonlinear Polyatomic Molecules

The partition function of the system of N indistinguishable molecules

$$q_{molecule}(V,T) = \left(\frac{2\pi MkT}{h^2}\right)^{3/2} V \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\left\{\prod_{j=1}^{3N-6}\frac{e^{-\Theta_{vj}/2T}}{\left(1-e^{-\Theta_{vj}/T}\right)}\right\}\omega_{e_1}e^{D_e/kT}$$

Thermodynamic variables

$$-\frac{A}{NkT} = \ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] + \ln\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}$$

$$-\sum_{j=1}^{3N-6}\left[\frac{\Theta_{vj}}{2T} - \ln\left(1-e^{-\Theta_{vj}/T}\right)\right] + \frac{D_e}{kT} + \ln\omega_{e_1}$$

$$\frac{\langle E(N,V,T)\rangle}{NkT} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3N-6}\left[\frac{\Theta_{vj}}{2T} + \frac{\Theta_{vj}/T}{e^{\Theta_{vj}/T}-1}\right] - \frac{D_e}{kT} \qquad \frac{C_V}{Nk} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3N-6}\left(\frac{\Theta_{vj}}{2T}\right)^2\frac{e^{\Theta_{vj}/T}}{\left(e^{\Theta_{vj}/T}-1\right)^2}$$

$$\langle P\rangle = \frac{NkT}{V} \qquad \longleftarrow \qquad \text{Ideal gas equation of state!}$$

Parameters for polyatomic molecules

Molecule	Θ_v / K	Θ_r / K	D_0 / kcal/mol
CO_2	3360, 954(2), 1890	0.561	381.5
H_2O	5360, 5160, 2290	40.1, 20.9, 13.4	219.3
NH_3	4800, 1360, 4880(2), 2330(2)	13.6, 13.6, 8.92	276.8
ClO_2	1360, 640, 1600	2.50, 0.478, 0.400	90.4
SO_2	1660, 750, 1960	2.92, 0.495, 0.422	254.0
N_2O	3200, 850(2), 1840	0.603	263.8
NO_2	1900, 1980, 2330	11.5, 0.624, 0.590	221.8
CH_4	4170, 2180(2), 4320(3), 1870(3)	7.54, 7.54, 7.54	392.1
CH_3Cl	4270, 1950, 1050, 4380(2), 2140(2), 1460(2)	7.32, 0.637, 0.637	370.7
CCl_4	660, 310(2), 1120(3), 450(3)	0.0823, 0.0823, 0.0823	308.8

Chemical Equilibrium in Ideal Gas Mixtures

In general for a reaction in an the ideal gas mixture:

$$v_A A(g) + v_B B(g) \leftrightarrow v_C C(g) + v_D D(g)$$
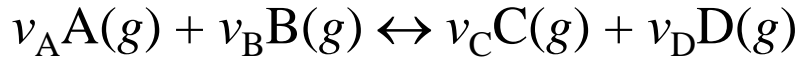
Condition for equilibrium

$$v_D \mu_D + v_C \mu_C = v_A \mu_A + v_B \mu_B$$

Partition function for the ideal gas mixture is a product of the partition functions of all the gases

$$Q(N_A, N_B, N_C, N_D, V, T) = Q(N_A, V, T) Q(N_B, V, T) Q(N_C, V, T) Q(N_D, V, T)$$

$$= \frac{q^{N_A}}{N_A!} \frac{q^{N_B}}{N_B!} \frac{q^{N_C}}{N_C!} \frac{q^{N_D}}{N_D!}$$

We know that for the chemical potential:

$$\mu_A(T) = -kT \left(\frac{\partial \ln Q}{\partial N_A} \right)_{N_j, V, T} = -kT \ln \left(\frac{q_A}{N_A} \right)$$

Substituting the expressions for the chemical potential in the condition for equilibrium

$$\frac{N_C^{v_C} N_D^{v_D}}{N_A^{v_A} N_B^{v_B}} = \frac{q_C^{v_C} q_D^{v_D}}{q_A^{v_A} q_B^{v_B}}$$

Chemical Equilibrium in Ideal Gas Mixtures

Dividing both sides by proper powers of the volume

$$\frac{\rho_C^{\nu C}\,\rho_D^{\nu D}}{\rho_A^{\nu A}\,\rho_B^{\nu B}} = \frac{\left(q_C/V\right)^{\nu C}\left(q_D/V\right)^{\nu D}}{\left(q_A/V\right)^{\nu A}\left(q_B/V\right)^{\nu B}} = K_C(T)$$
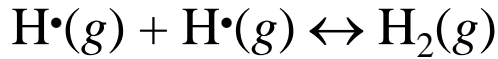
A temperature dependent constant

Using the ideal gas law we get the familiar expression for the equilibrium constant

$$\frac{P_C^{\nu C}\,P_D^{\nu D}}{P_A^{\nu A}\,P_B^{\nu B}} = K_C(T)(kT)^{\nu C + \nu D - \nu A - \nu B} = K_P(T)$$

Chemical equilibrium is probabilistic!

Chemical equilibrium in ideal gas mixtures (recombination reactions)

Example: Consider a high temperature reaction:

$H\cdot(g) + H\cdot(g) \leftrightarrow H_2(g)$

The equilibrium condition is determined by: $\quad \mu(H_2) = 2\mu(H^{\bullet})$

$$q_H(V,T) = \left(\frac{2\pi m_H kT}{h^2}\right)^{3/2} V q_{elec}$$

$$q_{H_2}(V,T) = \left(\frac{2\pi m_{H_2} kT}{h^2}\right)^{3/2} V \frac{8\pi^2 IkT}{2h^2} \frac{e^{-h\nu/2kT}}{\left(1-e^{-h\nu/kT}\right)} \omega_{e1} e^{D_e/kT}$$
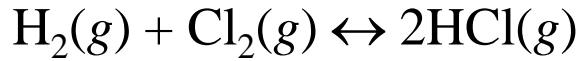
$$= \left(\frac{2\pi m_{H_2} kT}{h^2}\right)^{3/2} V \frac{T}{\Theta_r} \frac{1}{\left(1-e^{-\Theta_v/T}\right)} \omega_{e1} e^{D_0/kT}$$

$$\frac{P_{H_2}}{P_H^2} = \frac{q_{H_2}/V}{\left(q_H/V\right)^2}(kT)^{-1}$$

What are the contributing factors to the equilibrium constant?

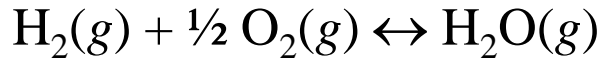# Chemical Equilibrium: Examples

Consider a high temperature reaction

$H_2(g) + Cl_2(g) \leftrightarrow 2HCl(g)$

The equilibrium condition is determined by:

$2\mu(HCl) = \mu(H_2) + \mu(Cl_2)$

$$K_P = \frac{P_{H_2} P_{Cl_2}}{P_{HCl}^2} = \frac{\left(q_{H_2}/V\right)\left(q_{Cl_2}/V\right)}{\left(q_{HCl}/V\right)^2}$$

Polyatomic reaction: Consider a high temperature reaction

$H_2(g) + \tfrac{1}{2} O_2(g) \leftrightarrow H_2O(g)$

The equilibrium condition is determined by:

$\mu(H_2O) = \mu(H_2) + \frac{1}{2}\mu(O_2)$

$$K_P(T) = \frac{\left(q_{H_2O}/V\right)}{(kT)^{1/2}\left(q_{H_2}/V\right)\left(q_{O_2}/V\right)^{1/2}}$$

Partition functions for H_2, O_2, and H_2O

$$q_{H_2}(V,T) = \left(\frac{2\pi m_{H_2}kT}{h^2}\right)^{3/2} V \frac{T}{2\Theta_{r,H_2}}\left(1-e^{-\Theta_{v,H_2}/T}\right)^{-1} e^{D_{0,H_2}/kT}$$

$$q_{O_2}(V,T) = \left(\frac{2\pi m_{O_2}kT}{h^2}\right)^{3/2} V \frac{T}{2\Theta_{r,O_2}}\left(1-e^{-\Theta_{v,O_2}/T}\right)^{-1} 3e^{D_{0,O_2}/kT}$$

$$q_{H_2O}(V,T) = \left(\frac{2\pi m_{H_2O}kT}{h^2}\right)^{3/2} V \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A^{H_2O}\Theta_B^{H_2O}\Theta_C^{H_2O}}\right)^{1/2}$$

$$\times \prod_{j=1}^{3}\left(1-e^{-\Theta_{vj,H_2O}/T}\right)^{-1} e^{D_{0,H_2O}/kT}$$

Molecule	Electronic state	Θ_v / K	Θ_r / K	r_{eq} / Å	D_0 / eV
H_2	$^1\Sigma_g^+$	6210	85.4	0.740	4.454
O_2	$^3\Sigma_g^-$	2230	2.0	1.204	5.0
H_2O		5360, 5160, 2290	40.1, 20.9, 13.4		9.51