Statistical Thermodynamics I, 23915

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Aim

- Your most valuable asset is your learning ability.
- This course is a practice in learning and specially improves your deduction skills.
- This course provides you with tools applicable in understanding many natural, societal or financial phenomena.
- End of semester objective: You should become able to calculate any equilibrium thermodynamic property of a system given intermolecular interactions in that system.

Aim

- Statistical mechanics is about deducing macroscopic properties of a system from microscopic properties of the constituents of that same system (molecules).
- Equilibrium statistical mechanics aims at calculating equilibrium properties of the system, e.g., energy, entropy and free energy.
- Non-equilibrium statistical mechanics aims at calculating non-equilibrium (transport) properties of the system, e.g., electrical conduction, heat conduction, absorption spectra and viscosity.
- This course will cover equilibrium statistical mechanics and leaves non-equilibrium statistical mechanics to another course.

References

- Statistical Mechanics by Donald A. McQuarrie
- Statistical Thermodynamics by Donald A. McQuarrie
- Statistical Thermodynamics, Theories and Applications by G. A. Parsafar (In Farsi)

Course structure

Midterm exam	16 Ordibehesht 11 AM	Ch. 1-4	35%
Final exam	12 Tir 3:30 pm	Ch. 5 - 8	45%
Class presentation	15 Tir-22 Tir		20%

- Raise your question and concern as it might be the question or concern of your classmates.
- Always remember that equations are the language of science but they never do suffice.

Topics

- Preamble
- Ensembles
- Classical and quantum statistics
- Monatomic and diatomic gases
- Classical statistical mechanics
- Polyatomic gases
- Chemical equilibrium
- Crystals

Classical Mechanics-Newton formalism

- In the absence of external forces, motion will continue with a constant speed. $\vec{F} = m\vec{a}$. If body A exert a force on body B, then B exerts the same force in the opposite direction on A.
- Two dimensional motion under coulombic attraction to a fixed center.
- $\vec{F} = -k\vec{r}/r^3$, break down into components.
- $m\ddot{x} = F_x = -\frac{Kx}{(x^2+y^2)^{3/2}}$ and $m\ddot{y} = F_y = -\frac{Ky}{(x^2+y^2)^{3/2}}$
- Use polar coordinate system $x = r\cos\theta$ and $y = r\sin\theta$ to derive.
- $mr^2\dot{\theta} =$ constant and $m\ddot{r} = -\frac{k}{r^2} + \frac{l^2}{mr^3}$

Classical Mechanics-Lagrangian

- Joseph-Louis Lagrange (1736-1813) was an Italian enlightenment era mathematician and astronomer with significant contributions to analysis, number theory, and both classical and celestial mechanics.
- Lagrange succeeded Euler as the director of mathematics at the Prussian Academy of Sciences in Berlin, where he stayed for over twenty years, producing volumes of work and winning several prizes of the French Academy of Sciences.
- Lagrange's treatise on analytical mechanics offered the most comprehensive treatment of classical mechanics since Newton and formed a basis for the development of mathematical physics in the nineteenth century.
- Lagrangian, $L \equiv K - U$, where $K = \sum_i \frac{m_i}{2} \dot{x}_i^2$.
- Lagrangian dynamics: $\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_j} = \frac{\partial L}{\partial q_j}$, the form of this equation is invariant under the change of coordinates.
- Two dimensional motion under coulombic attraction to a fixed center.

Classical Mechanics-Hamiltonian

- Sir William Rowan Hamilton (1805–1865) was an Irish mathematician, astronomer, and mathematical physicist, who made important contributions to classical mechanics, optics, and algebra.
- His studies of mechanical and optical systems led him to discover new mathematical concepts and techniques.
- His reformulation of Newtonian mechanics, now called Hamiltonian mechanics has proven central to the modern study of classical field theories such as electromagnetism, and to the development of quantum mechanics.
- Momentum, $p_j = \frac{\partial L}{\partial \dot{q}_j}$.
- Hamiltonian, $H = \sum_j p_j \dot{q}_j - L$.
- Kinetic energy, $K = \sum_j a_j(q) \dot{q}_j^2$. Total energy of the system, $H = K + V$.
- Hamilton's equations of motion, $\frac{\partial H}{\partial p_j} = \dot{q}_j, \qquad \frac{\partial H}{\partial q_j} = -\dot{p}_j$.

Classical Mechanics-Liouvillian

- Classical mechanics occurs in phase space which consists of one dimension (axe) for each coordinate and each momenta.
- The state of a system is determined by a single point in its phase space.
- Joseph Liouville (1809–1882) was a French mathematician.
- Liouville became a member of the Constituting Assembly in 1848. However, after his defeat in the legislative elections in 1849, he turned away from politics.
- Every property, f, of the system is a function of coordinates, r, and momenta, p.
- Dynamics: $\frac{\partial f}{\partial t} = \{f, H\}$
- Poisson bracket: $\{f, g\} = \sum_i (\frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i})$

Quantum Mechanics-preamble

- From the late 19th century people started to patch classical physics to justify some observations including photoelectric effect and black body radiation.
- Quantum mechanics was formally formulated in the 1920s.
- Quantum mechanics lives in the Hilbert space where there is no hole. A hole in a space occurs when the limit of a series cannot be found in that space.
- A vector, C, is denoted by a ket $|C\rangle$. Complex conjugate of such a vector, $C^\dagger$, is denoted by a bra $\langle C|$.
- bra * ket = bracket, $\langle D|C\rangle$.
- ket * bra = operator, $|C\rangle\langle D|$.
- Operator acts on a vector to produce another vector
- Every observable in quantum mechanics is represented by an operator. If we require that the expectation value of an operator $\hat{A}$ is real, then $\hat{A}$ must be a Hermitian operator.

Quantum Mechanics-operators

Observable Name	Observable Symbol	Operator Symbol	Operator Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiply by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$
Angular	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
momentum	l_y	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	l_z	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

Quantum Mechanics

- A density matrix is a matrix that describes the statistical state of a system in quantum mechanics. The probability for any outcome of any well-defined measurement upon a system can be calculated from the density matrix for that system.
- The extreme points in the set of density matrices are the pure states, which can also be written as state vectors or wavefunctions. Density matrices that are not pure states are mixed states.
- Any mixed state can be represented as a convex combination of pure states, and so density matrices are helpful for dealing with statistical ensembles of different possible preparations of a quantum system, or situations where a precise preparation is not known, as in quantum statistical mechanics.
- given a finite number of points $x_1, x_2, \ldots, x_n$ in a real vector space, a convex combination of these points is a point of the form $\alpha_1 x_1 + \alpha_2 x_2 + \cdots + \alpha_n x_n$ where the real numbers α_i satisfy $\alpha_i \geq 0$ and $\alpha_1 + \alpha_2 + \cdots + \alpha_n = 1$.

Quantum Mechanics

- Density matrix, $\hat{\rho}$, contains all information that can be known about a system.
- For a pure state, $\hat{\rho} = |\psi\rangle\langle\psi|$ in general $\hat{\rho} = \sum_i c_i |\psi_i\rangle\langle\psi_i|$
- Quantum Liouville equation determines quantum dynamics as $\frac{\partial \hat{\rho}(t)}{\partial t} = \frac{i}{\hbar}[\hat{\rho}(t), \hat{H}]$.
- $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.
- $\{\cdot, \cdot\} \leftrightarrow \frac{i}{\hbar}[\cdot, \cdot]$.
- Formal solution: $\hat{\rho}(t) = e^{-i\hat{H}t/\hbar}\hat{\rho}(0)e^{i\hat{H}t/\hbar}$.
- Every linear operator has a matrix representation.
- Schrodinger equation for pure states: $i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle$
- $\langle x|\psi\rangle = \psi(x, t)$
- For a time independent Hamiltonian assume $\psi(x, t) = \phi(x)\theta(t), \qquad \theta = e^{iEt/\hbar}, \qquad \hat{H}\phi = E\phi.$

Quantum Mechanics

- Wave function or state function, has the important property that $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau$ is the probability that the particle lies in the volume element $d\tau$ located at $\mathbf{r}$ at time t.
- For the case of a single particle, the probability of finding it somewhere is 1, we have the normalization condition $\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau = 1$.
- The wavefunction must also be single-valued, continuous, and finite.
- In any measurement of the observable associated with operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a, which satisfy the eigenvalue equation $\hat{A}\Psi = a\Psi$.
- The values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues).
- If the system is in an eigenstate of $\hat{A}$ with eigenvalue a, then any measurement of the quantity A will yield a.

Quantum Mechanics

- Although measurements must always yield an eigenvalue, the state does not have to be an eigenstate of $\hat{A}$ initially. An arbitrary state can be expanded in the complete set of eigenvectors of $\hat{A}$ ($\hat{A}\Psi_i = a_i \Psi_i$) as $\Psi = \sum_i^n c_i \Psi_i$
- We only know that the measurement of A will yield one of the values a_i, but we don't know which one. However, we do know the probability that eigenvalue a_i will occur–it is the absolute value squared of the coefficient, $|c_i|^2$.
- After measurement of A on Ψ yields some eigenvalue a_i, the wavefunction immediately "collapses" into the corresponding eigenstate Ψ_i (in the case that a_i is degenerate, then Ψ is projected onto the degenerate subspace of a_i). Thus, measurement affects the state of the system.

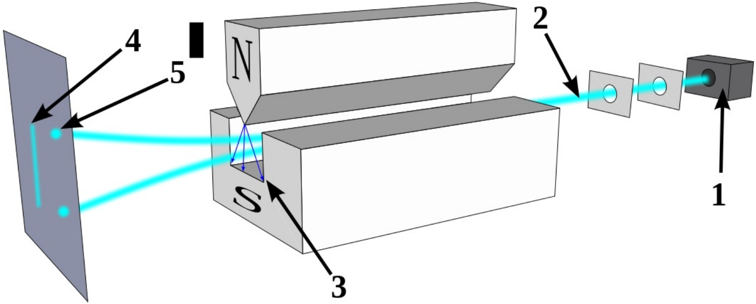
Stern-Gerlach experiment and Spin

- Magnetic moment is a quantity that represents the magnetic strength and orientation of a magnet.
- Loops of electric current (such as electromagnets), permanent magnets, elementary particles (such as electrons), various molecules, and many astronomical objects poses magnetic dipole moment.
- The magnetic dipole moment of an object is readily defined in terms of the torque that object experiences in a given magnetic field. $\boldsymbol{\tau} = \mathbf{m} \times \mathbf{B}$
- The direction of the magnetic moment points from the south to north pole of the magnet (inside the magnet).
- A magnetic moment in an externally produced magnetic field has a potential energy $U = -\mathbf{m} \cdot \mathbf{B}$.

Stern-Gerlach experiment and Spin

- $\mathbf{m} = -\hat{\mathbf{x}}\frac{\partial U_{\mathrm{int}}}{\partial B_x} - \hat{\mathbf{y}}\frac{\partial U_{\mathrm{int}}}{\partial B_y} - \hat{\mathbf{z}}\frac{\partial U_{\mathrm{int}}}{\partial B_z}$.
- $\mathbf{m} = I\boldsymbol{S}$, $\mathbf{m} = NI\mathbf{S}$.
- $\mathbf{m} = \frac{1}{2}\iiint_V \mathbf{r} \times \mathbf{j}\,\mathrm{d}V$,
- Since the particles creating the current (by rotating around the loop) have charge and mass, both the magnetic moment and the angular momentum increase with the rate of rotation. The ratio of the two is called the gyromagnetic ratio or γ so that: $\mathbf{m} = \gamma\mathbf{L}$
- The Stern–Gerlach experiment demonstrated that the spatial orientation of angular momentum is quantized.

Stern-Gerlach experiment and Spin



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- Silver atoms were sent through a spatially varying magnetic field, which deflected them before they struck a detector screen, such as a glass slide.

Stern-Gerlach experiment and Spin

- Particles with non-zero magnetic moment are deflected, due to the magnetic field gradient, from a straight path.
- The screen reveals discrete points of accumulation, rather than a continuous distribution, owing to their quantized spin.
- Spin is an intrinsic angular momentum of subatomic particles that is closely analogous to the angular momentum of a classically spinning object, but that takes only certain quantized values.
  $\hat{S}_z\psi_{z+} = \frac{\hbar}{2}\psi_{z+} \qquad \hat{S}_z\psi_{z-} = -\frac{\hbar}{2}\psi_{z-}$
- Only one component of a particle's spin can be measured at one time, meaning that the measurement of the spin along the z-axis destroys information about a particle's spin along the x and y axis.
- Particles with half integral spin are called fermions while those with integral spin are called bosons.

Quantum Mechanics

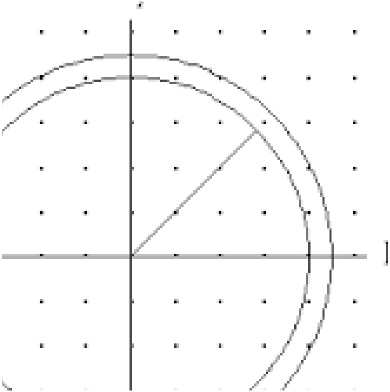
- Thus an atomic-scale system was shown to have intrinsically quantum properties.
- This experiment was decisive in convincing physicists of the reality of angular-momentum quantization in all atomic-scale systems.
- Particle in a box: $\begin{cases} U(x) = 0 & 0 < x < a, \\ U(x) = \infty & \text{otherwise.} \end{cases}$ $\epsilon_n = \frac{h^2}{8ma^2} n^2$
- If $H = H_1 + H_2$ then $\psi = \psi_1 \psi_2$ and $E = E_1 + E_2$.

Quantum Mechanics

- Harmonic oscillator is one of the few quantum-mechanical systems for which an exact, analytical solution is known: $U(x) = \frac{1}{2}kx^2, \qquad \hat{H} = \dfrac{\hat{p}^2}{2m} + \dfrac{1}{2}k\hat{x}^2 = \dfrac{\hat{p}^2}{2m} + \dfrac{1}{2}m\omega^2\hat{x}^2\,, \qquad \epsilon_n = (n+\frac{1}{2})\hbar\omega, \qquad \omega = \sqrt{k/m}.$
- $\psi_n(x) = N_n e^{-\beta^2 x^2/2} H_n(\beta x)\,,\ \ n = 0, 1, 2, 3, \ldots,\ \beta = \sqrt{m\,\omega/\hbar},$
- $$H_0(y) = 1 \qquad H_1(y) = 2y$$
  $$H_2(y) = 4y^2 - 2$$
  $$H_3(y) = 8y^3 - 12y.$$
- $\psi_0 = (\frac{\alpha}{\pi})^{1/4} e^{-y^2/2} \quad \psi_1 = (\frac{\alpha}{\pi})^{1/4}\sqrt{2}ye^{-y^2/2}$
- Rigid rotor: $H = -\frac{\hbar^2}{2I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}, \qquad \epsilon_j = \frac{J(J+1)\hbar^2}{2I}, \qquad \omega_j = 2j+1.$

Particle in a box degeneracy

- For a single particle in 2-D, $E = \frac{h^2}{8ma^2}(n_x^2 + n_y^2)$,



- Convince yourself that the number of states with energy smaller than ϵ is the area of circle of radius $r^2 = \frac{8ma^2}{h^2}\epsilon$ in the first quadrant.

Particle in a box degeneracy

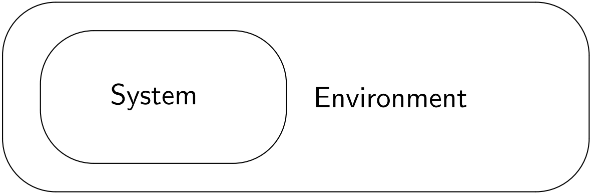
- In 3-D, number of states with energy between ϵ and $\epsilon + \Delta\epsilon$, $\omega(\epsilon, \Delta\epsilon) = \frac{\pi}{4}(\frac{8ma^2}{h^2})^{3/2}\epsilon^{0.5}\Delta\epsilon + O((\Delta\epsilon)^2)$
- N non-interacting particle: $E = \frac{h^2}{8ma^2}\sum_{j=1}^{3N} n_j^2$.
- We may define a coordinate system in an n-D space which is analogous to the spherical coordinate system defined for 3-dimensional Euclidean space, in which the coordinates consist of a radial coordinate r, and n-1 angular coordinates $\phi_1, \phi_2, \cdots, \phi_{n-1}$, where the angles $\phi_1, \phi_2, \cdots, \phi_{n-2}$ range over $[0, \pi]$ radians and ϕ_{n-1} ranges over $[0, 2\pi)$ radians.
- $x_1 = r\cos\phi_1, \qquad x_2 = r\sin\phi_1\cos\phi_2, \qquad x_3 = r\sin\phi_1\sin\phi_2\cos\phi_3, \cdots, x_n = r\sin\phi_1\cdots\sin\phi_{n-1}$.
- $V_n = \int_{Sphere} d\tau = \int_0^a h_r dr \int_0^\pi h_1 d\phi_1 \cdots \int_0^{2\pi} h_{n-1} d\phi_{n-1} = \int_0^a S_n r^{n-1} dr$.
- $\int_{angles} dx_1 \cdots dx_n = r^{n-1} S_n dr$

Particle in a box degeneracy

- $I_n = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(x_1^2+x_2^2+\cdots+x_n^2)} dx_1 \cdots dx_n = (\int_{-\infty}^{\infty} e^{-x^2} dx)^n = \pi^{n/2}$.
- $I_n = \int_0^{\infty} e^{-r^2} r^{n-1} S_n dr = S_n \Gamma(n/2)/2$.
- $\Gamma(x) = \int_0^{\infty} e^{-t} t^{x-1} dt$, show that $\Gamma(n+1) = n!$, show that $\Gamma(n+\frac{1}{2}) = \frac{(2n)!}{2^{2n} n!}\sqrt{\pi}$.
- $V_n = \frac{\pi^{n/2}}{\Gamma(n/2+1)} a^n$
- $\omega(E, \Delta E) = \frac{1}{\Gamma(n+1)\Gamma(3n/2)} (\frac{2\pi m a^2}{h^2})^{3n/2} E^{3n/2-1} \Delta E$
- Partitionable Hamiltonian. $H = H_1 + H_2 + \cdots$, $\psi = \psi_1 \psi_2 \cdots$
- Parity operator.

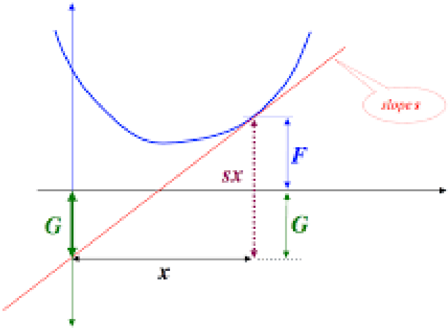
Thermodynamics

- Universe:



- Zeroth law of thermodynamics, first law of thermodynamics, Second law of thermodynamics.
- State functions vs. path functions
- $dU = dq + dw = TdS - pdV \qquad U = U(S, V)$
- $T = (\frac{\partial U}{\partial S})_V, \quad p = -(\frac{\partial U}{\partial V})_S.$

Thermodynamics



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- Legendre transformation: $F = F(x), \quad s = \frac{F-G}{x-0} \quad G(s) = F - sx$. Generally, $G(s) = F - \sum_j s_j x_j$.
- $U(S,V), \quad H(S,p) = ?, \quad A(T,V) = U - (\frac{\partial U}{\partial S})_V S = U - TS, \quad G(T,p) = ?$
- A thermodynamic potential is a scalar quantity used to represent the thermodynamic state of a system.

Thermodynamics

- The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Josiah Willard Gibbs in his papers used the term fundamental functions.
- Internal energy U is the energy of configuration of a given system of conservative forces and only has meaning with respect to a defined set of references.
- Expressions for all other thermodynamic energy potentials are derivable via Legendre transforms from an expression for U.
- For an open quantum system $dU = TdS - pdV + \mu dn$ where $\mu = (\frac{\partial U}{\partial n})_{S,V}$.
- Grand potential or Landau free energy is defined by $\Phi_G(T, V, \mu) \overset{\text{def}}{=} \Omega \ \overset{\text{def}}{=} \ F - \mu N = \ U - TS - \mu N$
- Fundamental equation: $d\Phi_G = dU - TdS - SdT - \mu dN - Nd\mu = -PdV - SdT - Nd\mu$
- When the system is in thermodynamic equilibrium, Φ_G is a minimum.

Thermodynamics

- For homogeneous systems, one obtains $\Omega = -PV$.
- Internal energy (U) is the capacity to do work plus the capacity to release heat.
- Gibbs energy (G) is the capacity to do non-mechanical work.
- Enthalpy (H) is the capacity to do non-mechanical work plus the capacity to release heat.
- Helmholtz energy (F) is the capacity to do mechanical plus non-mechanical work.
- ΔU is the energy added to the system, ΔF is the total work done on it, ΔG is the non-mechanical work done on it, and ΔH is the sum of non-mechanical work done on the system and the heat given to it.
- The principle of minimum energy follows from the first and second laws of thermodynamics.
- When the entropy S and "external parameters" (e.g. volume) of a closed system are held constant, the internal energy U decreases and reaches a minimum value at equilibrium.

Thermodynamics

- The following three statements are directly derivable from this principle.
- When the temperature T and external parameters of a closed system are held constant, the Helmholtz free energy F decreases and reaches a minimum value at equilibrium.
- When the pressure p and external parameters of a closed system are held constant, the enthalpy H decreases and reaches a minimum value at equilibrium.
- When the temperature T, pressure p and external parameters of a closed system are held constant, the Gibbs free energy G decreases and reaches a minimum value at equilibrium.
- The variables that are held constant in this process are termed the natural variables of that potential

Thermodynamics

- If a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be found by taking partial derivatives of that potential with respect to its natural variables and this is true for no other combination of variables.
- If there are D dimensions to the thermodynamic space, then there are 2^{D} unique thermodynamic potentials.
- $U[\mu_j] = U - \mu_j N_j$, $F[\mu_j] = U - TS - \mu_j N_j$, $H[\mu_j] = U + pV - \mu_j N_j$ and $G[\mu_j] = U + pV - TS - \mu_j N_j$.
- Fundamental equations: $dH =$ $dA =$ $dG =$
- If the system has more external variables than just the volume that can change, the fundamental thermodynamic relation generalizes to: $dU = T\,dS - \sum_i X_i\,dx_i + \sum_j \mu_j\,dN_j$, X_i are the generalized forces corresponding to the external variables x_i.
- Maxwell relations, e.g., using dA=-pdV-SdT to derive $(\frac{\partial S}{\partial V})_T = (\frac{\partial p}{\partial T})_V$.

Thermodynamics

- Extensive vs. intensive.
- Fundamental relation can be written as, $\frac{dU}{dV} = T(\frac{dS}{dV}) - p$, imposing the constant temperature condition and using a Maxwell relation yields $(\frac{\partial U}{\partial V})_{N,T} - T(\frac{\partial p}{\partial T})_{N,V} = -p$.
- U=U(V,T), thus $dU = [T(\frac{\partial p}{\partial T})_V - p]dV + C_V dT$.
- $C_V = (\frac{\partial U}{\partial T})_V = T(\frac{\partial S}{\partial T})_V$ and $C_p = (\frac{\partial H}{\partial T})_p = T(\frac{\partial S}{\partial T})_p$.
- Thus, $C_p - C_v = [p + (\frac{\partial U}{\partial V})_T](\frac{\partial V}{\partial T})_p$
- Chemical potential, $\mu_j = (\frac{\partial U}{\partial N_j})_{S,V,\ldots} = (\frac{\partial H}{\partial N_j})_{S,p,\ldots} = (\frac{\partial A}{\partial N_j})_{V,T,\ldots} = (\frac{\partial G}{\partial N_j})_{p,T,\ldots}$.
- Homogeneous of degree n, $f(\lambda x_1, \cdots, \lambda x_N) = \lambda^n f(x_1, \cdots, x_N)$
- Euler's theorem: If f is a homogeneous function of degree n, $nf(x_1, \cdots, x_N) = x_1\frac{\partial f}{\partial x_1} + x_2\frac{\partial f}{\partial x_2} + \cdots + x_N\frac{\partial f}{\partial x_N}$
- $n(n-1)f(x_1, \cdots, x_N) = \sum_{i,j=1}^{N} x_i x_j (\frac{\partial^2 f}{\partial x_i \partial x_j})$
- $G(T, p, N_i) = \sum_j N_j(\frac{\partial G}{\partial N_j})_{T,p,\cdots} = \sum_j N_j \mu_j$

Thermodynamics

- Find expressions for other thermodynamic potentials.
- Gibbs-Duhem equation: $\sum_j N_j d\mu_j = 0$
- For a chemical reaction $aA + bB \rightleftarrows cC + dD$, which can be represented by $\sum_j \nu_j A_j = 0$, $dG = \sum_j \mu_j dN_j = (\sum_j \mu_j \nu_j) d\lambda$.
- At equilibrium: $\sum_j \mu_j \nu_j = 0$
- Phase equilibrium
- $\mu_j = \mu_j^0 + RT \ln \frac{p_j}{p^0} = \mu_j^0 + RT \ln p_j'$
- $\Delta\mu_0 = -RT \ln[\frac{(P_c')^{\nu_c}(P_d')^{\nu_d}}{(P_a')^{\nu_a}(P_b')^{\nu_b}}] = -RT \ln K_p$

Ensembles

- An experimenter repeating an experiment under the same macroscopic conditions is unable to control microscopic details, thus he might expect a range of outcomes.
- A large number of identical (on a macroscopic level) systems constitute an ensemble.
- An ensemble is a collection of systems sharing one or more macroscopic characteristics but each being in a unique microstate.
- The complete ensemble is specified by giving all systems or microstates consistent with the common macroscopic characteristics of the ensemble.
- The system may be specified by N, V, E, or N, V, T, while the ensemble has $\mathcal{A}$ identical systems.
- There is an enormous number of microstates, $\mathrm{O}(10^N)$, consistent with the systems specifications.
- System properties depend on the microstate of the system.
- Time independent Schrodinger equation determines allowed energy levels E_j and their corresponding degeneracies $\Omega(E_j)$.

Canonical Ensemble: Definition

- Ensemble average of the mechanical property B, $\bar{B} = \frac{1}{\mathcal{A}} \sum_{i=1}^{\mathcal{A}} B_i$ where $B_i = \int \psi_i^* \hat{B} \psi_i d\tau$.
- Ergodic hypothesis states that time average of a mechanical property equals ensemble average of the same thermodynamic property.
- Make a large collection of systems each having walls impermeable to matter but heat conducting. Bring this collection in contact with a heat bath of temperature T. After equilibration isolate the ensemble.
- Each system is specified by N, V, T while the ensemble is specified by $\mathcal{A}$N, $\mathcal{A}$V, and ϵ.
- Solve Schrodinger equation for the system specified by N V. Specify states $E_1, E_2, E_3, \cdots$ such that $E_i \leq E_{i+1}$. The number of systems occupying each state, respectively, is $a_1, a_2, a_3, \cdots$. Set of occupation numbers $a_1, a_2, a_3, \cdots$ is called a distribution.
- Energy time uncertainty relation: $\Delta E \Delta t \geq \frac{\hbar}{2}$
- The principle of equal a priori probabilities.

Canonical Ensemble: Averages

- The number of ways the systems can take this distribution, distribution multiplicity, is $W(a_1, a_2, \cdots) = \frac{\mathcal{A}!}{\Pi_i a_i!}$ where $\sum_i a_i = \mathcal{A} \qquad \sum_i a_i E_i = \epsilon$.
- $\bar{a}_j = \frac{\sum_a a_j W(a)}{\sum_a W(a)}$
- $P_j = \frac{\bar{a}_j}{\mathcal{A}} = \frac{\sum_a a_j W(a)}{\mathcal{A} \sum_a W(a)}$
- $\bar{M} = \sum_j M_j P_j$
- What are unjustified assumptions in this treatment?
- Noting that $W(a)$ is a multinomial distribution, and letting $\mathcal{A} \to \infty \qquad P_j = \frac{\bar{a}_j}{\mathcal{A}} = \frac{\sum_a a_j W(a)}{\mathcal{A} \sum_a W(a)} = \frac{a_j^* W(a^*)}{\mathcal{A} W(a^*)} = \frac{a_j^*}{\mathcal{A}}$
- $\frac{\partial}{\partial a_j} W(a) - \alpha \frac{\partial}{\partial a_j}(\mathcal{A} - \sum_i a_i) - \beta \frac{\partial}{\partial a_j}(\epsilon - \sum_i a_i E_i) = 0$
- $\frac{\partial}{\partial a_j} \ln \frac{\mathcal{A}!}{\Pi_i a_i!} - \alpha \frac{\partial}{\partial a_j}(\mathcal{A} - \sum_i a_i) - \beta \frac{\partial}{\partial a_j}(\epsilon - \sum_i a_i E_i) = 0$
- $\frac{\partial}{\partial a_j}[\mathcal{A} \ln \mathcal{A} - \mathcal{A} - \Sigma_i (a_i \ln a_i - a_i)] + \alpha(\sum_i \delta_{ij}) + \beta(\sum_i \delta_{ij} E_i) = 0$
- $\ln a_j^* + \alpha + \beta E_j = 0 \to a_j^* = e^{-\alpha - \beta E_j}$. Thus $P_j = \frac{a_j^*}{\mathcal{A}} = \frac{e^{-\alpha} e^{-\beta E_j}}{\mathcal{A}}$.
- Using the normalization of probabilities $P_j = \frac{e^{-\beta E_j}}{\sum_i e^{-\beta E_i}}$.

Canonical Ensemble: Partition function

- Canonical ensemble partition function, $Q = \sum_i e^{-\beta E_i}$, is a bridge between quantum mechanical energy levels and thermodynamic functions.
- $\bar{E} = \sum_j E_j \frac{e^{-\beta E_j}}{Q} = -\frac{(\partial Q/\partial \beta)_{N,V}}{Q} = -(\frac{\partial \ln Q}{\partial \beta})_{N,V}$
- Adiabatic process, PV work only $dE_j = -p_j dV,\ p_j = -(\frac{\partial E_j}{\partial V})_N$
- $\bar{p} = \sum_j p_j P_j = -\frac{\sum_j (\frac{\partial E_j}{\partial V})_N e^{-\beta E_j}}{Q} = \frac{1}{\beta Q}(\frac{\partial Q}{\partial V})_{N,\beta} = \frac{1}{\beta}(\frac{\partial \ln Q}{\partial V})_{N,\beta}$
- Ensemble postulate of Gibbs. $E = \bar{E} \qquad p = \bar{p}$
- $(\frac{\partial \bar{E}}{\partial V})_{\beta,N} = (\frac{\partial (\frac{E_j e^{-\beta E_j}}{Q})}{\partial V})_{\beta,N} = -\bar{p} + \beta \overline{Ep} - \beta \bar{E}\bar{p}$
- $(\frac{\partial \bar{p}}{\partial \beta})_{N,v} = -\frac{\partial}{\partial \beta} \frac{(\frac{\partial E_j}{\partial V})_N e^{-\beta E_j}}{Q} = \bar{E}\bar{p} - \overline{Ep}$
- $(\frac{\partial \bar{E}}{\partial V})_{\beta,N} + \beta(\frac{\partial \bar{p}}{\partial \beta})_{N,V} = -\bar{p}$
- $(\frac{\partial E}{\partial V})_{T,N} - T(\frac{\partial p}{\partial T})_{N,V} = -p$ or $(\frac{\partial E}{\partial V})_{T,N} + \frac{1}{T}(\frac{\partial p}{\partial (1/T)})_{N,V} = -p$

Canonical Ensemble: Value of β

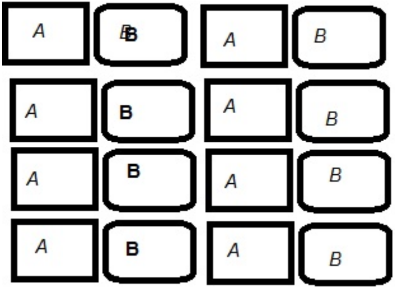
- $\beta = \frac{1}{kT}$
- To prove the universality of k, construct an ensemble composed of systems A and B paired, with number of particles and volume, N_A, V_A and N_B, V_B, respectively.
- 

Figure: A composite ensemble consisting of A and B systems.

Canonical Ensemble: Value of β

- The number of possible system distributions resulting in the composite ensemble state ab, $W(a,b) = \frac{\mathcal{A}!}{\Pi_j a_j!}\frac{\mathcal{B}!}{\Pi_k b_k!}$
- $\sum_j a_j = \mathcal{A},\ \sum_j b_j = \mathcal{B},\ \sum_j (a_j E_{jA} + b_j E_{jB}) = \mathcal{E}$
- $P_{ij} = \frac{\bar{a}_i}{\mathcal{A}}\frac{\bar{b}_j}{\mathcal{B}} = \frac{\sum_{ab} a_i W(a,b)}{\mathcal{A}\sum_{ab} W(a,b)}\frac{\sum_{ab} b_j W(a,b)}{\mathcal{B}\sum_{ab} W(a,b)}$
- Using maximum term method: $P_{ij} = \frac{a_i^*}{\mathcal{A}}\frac{b_j^*}{\mathcal{B}}$
- $\frac{\partial}{\partial a_l}\ln W(a,b) - \alpha_1\frac{\partial}{\partial a_l}(\mathcal{A} - \sum_j a_j) - \alpha_2\frac{\partial}{\partial a_l}(\mathcal{B} - \sum_j b_j) - \beta\frac{\partial}{\partial a_l}(\mathcal{E} - \sum_j (a_j E_{jA} + b_j E_{jB})) = 0 \qquad \frac{\partial}{\partial b_l}\ln W(a,b) - \alpha_1\frac{\partial}{\partial b_l}(\mathcal{A} - \sum_j a_j) - \alpha_2\frac{\partial}{\partial b_l}(\mathcal{B} - \sum_j b_j) - \beta\frac{\partial}{\partial b_l}(\mathcal{E} - \sum_j (a_j E_{jA} + b_j E_{jB})) = 0$
- Using the normalization condition $P_{ij} = \frac{e^{-\beta E_{iA}}}{Q_A}\frac{e^{-\beta E_{jB}}}{Q_B} = P_{iA}P_{jB}$
- Thus two arbitrary systems in thermal contact have the same value of β. Since $\beta = \frac{1}{kT}$ they must have the same value of k.
- k can be determined for any system including an ideal gas.

Canonical Ensemble: Value of β

- If the external parameters of the system remain constant then the interaction is termed a purely thermal interaction. It is the distribution of the systems in the ensemble over the various microstates which is modified.
- Suppose that the system A is thermally insulated from its environment. The system A is still capable of interacting with its environment via its external parameters. This type of interaction is termed mechanical interaction, and any change in the average energy of the system is attributed to work done on it by its surroundings.
- On a microscopic level, the energy of the system changes because the energies of the individual microstates are functions of the external parameters. Thus, if the external parameters are changed then, in general, the energies of all of the systems in the ensemble are modified (since each is in a specific microstate).
- Consider $f(\beta, E_1, E_2, \cdots) = \ln Q$,
  $df = (\frac{\partial f}{\partial \beta})_{E_j} d\beta + \sum_k (\frac{\partial f}{\partial E_k})_{\beta, E_{i \neq k}} dE_k = -\bar{E} d\beta - \beta \sum_k P_k dE_k$

Canonical Ensemble: interpretation of work and heat

- $d(f + \beta \bar{E}) = \beta(d\bar{E} - \sum_k P_k dE_k)$
- Molecular interpretation of reversible work is a change in the energy of levels without an accompanying change in the population of levels.
- Since $d\bar{E} = \sum_j E_j dP_j + \sum_j P_j dE_j = \delta q_{rev} + \delta w_{rev}$
- $\delta q_{rev} = \sum_j E_j dP_j$
- $\sum_k P_k dE_k$ is the ensemble average of the reversible work done by the system.
- $d(f + \beta \bar{E}) = \beta \delta q_{rev}$ is derivative of a state function.
- β is an integrating factor of δq_{rev}.
- According to the second law, integrating factor of δq_{rev} is constant/T.
- $\frac{dS}{k} = d(f + \beta \bar{E})$. Thus $S = \frac{\bar{E}}{T} + k \ln Q + constant = k \ln \sum_j e^{-E_j/kT} + \frac{1}{T} \frac{\sum_j E_j e^{-E_j/kT}}{\sum_j e^{-E_j/kT}} + constant$

Canonical Ensemble: Thermodynamic connection

- Partition function in terms of levels: $Q(N,V,T) = \sum_E \Omega(N,V,E) e^{-E(N,V)/kT}$
- By setting $E_0 = 0$, $\lim_{T\to 0} S = \lim_{T\to 0}(k \ln \sum_E \Omega(N,V,E) e^{-E/kT} + \frac{1}{T}\frac{\sum_E \Omega(N,V,E) E e^{-E/kT}}{\sum_E \Omega(N,V,E) e^{-E/kT}}) = k \ln \Omega(N,V,E_0)$ which is very small. Thus $S = \frac{\bar{E}}{T} + k \ln Q$.
- $E = kT^2 (\frac{\partial \ln Q}{\partial T})_{N,V}$ and $p = kT(\frac{\partial \ln Q}{\partial V})_{N,T}$
- $S = kT(\frac{\partial \ln Q}{\partial T})_{N,V} + k \ln Q$
- $A(N,V,T) = E - TS = -kT \ln Q(N,V,T)$
- To derive the second law
- consider spontaneous process of going from state 1 to state 2 involves removal of a constraint or barrier. Thus for an isolated system $\Omega_2(N,V,E) \geq \Omega_1(N,V,E)$.

Second law

- E.g., expansion of an ideal gas where $\Omega(E, \Delta E) = \frac{1}{\Gamma(N+1)\Gamma(3N/2)}(\frac{2\pi M}{h^2})^{3N/2} E^{3N/2-1} V^N \Delta E$.
- Or addition of a catalyst to a kinetically stable non-equilibrium mixture.
- $Q_2 - Q_1 = \sum_E (\Omega_2(N, V, E) - \Omega_1(N, V, E)) e^{-E(N,V)/kT}$.
- Thus, $\Delta A = -kT \ln(\frac{Q_2}{Q_1}) < 0$ for an spontaneous process, at constant volume and temperature.

Grand Canonical Ensemble

- Walls are heat conducting and permeable to the passage of molecules. Each system is specified by V, T and μ.
- For each value of N the system has energy states $\{E_{Nj}(V)\}$. a_{Nj} is the number of systems in the ensemble with N particles and in energy state j.
- The number of ways to achieve any distribution, $W(\{a_{Nj}\}) = \frac{\mathcal{A}!}{\Pi_N \Pi_j a_{Nj}!}$.
- $P_{Nj} = \frac{\bar{a}_{Nj}}{\mathcal{A}} = \frac{\sum_a a_{Nj} W(\{a_{Nj}\})}{\mathcal{A} \sum_a W(\{a_{Nj}\})} = \frac{a^*_{Nj} W(\{a_{Nj}\})^*}{\mathcal{A} W(\{a_{Nj}\})^*}$
- Recourse to the maximum term method, W(a) should be maximized subject to constraints $\sum_N \sum_j a_{Nj} = \mathcal{A}$, $\sum_N \sum_j a_{Nj} E_{Nj} = \mathcal{E}$ and $\sum_N \sum_j a_{Nj} N = \mathcal{N}$.
- $a^*_{NJ} = e^{-\alpha} e^{-\beta E_{Nj}(V)} e^{-\gamma N}$
- $P_{Nj}(V, \beta, \gamma) = \frac{a^*_{Nj}}{\mathcal{A}} = \frac{e^{-\beta E_{Nj}(V)} e^{-\gamma N}}{\sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}}$
- $\Xi(V, \beta, \gamma) = \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$

Grand Canonical Ensemble

- $\bar{E}(V,\beta,\gamma) = \frac{1}{\Xi}\sum_N \sum_j E_{Nj}(V) e^{-\beta E_{Nj}(V)} e^{-\gamma N} = -(\frac{\partial \ln \Xi}{\partial \beta})_{V,\gamma}$
- $\bar{p}(V,\beta,\gamma) = \frac{1}{\Xi}\sum_N \sum_j (-\frac{\partial E_{Nj}(V)}{\partial V}) e^{-\beta E_{Nj}(V)} e^{-\gamma N} = \frac{1}{\beta}(\frac{\partial \ln \Xi}{\partial V})_{\beta,\gamma}$
- $\bar{N}(V,\beta,\gamma) = \frac{1}{\Xi}\sum_N \sum_j N e^{-\beta E_{Nj}(V)} e^{-\gamma N} = -(\frac{\partial \ln \Xi}{\partial \gamma})_{\beta,V}$
- Make the walls impermeable to molecules to derive a collection of canonical ensembles. For all these ensembles $\beta = \frac{1}{kT}$.
- $f(\beta,\gamma,\{E_{Nj}(V)\}) = \ln \Xi = \ln \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$
- $df = (\frac{\partial f}{\partial \beta})_{\gamma,\{E_j\}} d\beta + (\frac{\partial f}{\partial \gamma})_{\beta,\{E_j\}} d\gamma + \sum_N \sum_j (\frac{\partial f}{\partial E_{Nj}})_{\beta,\gamma,\{E_{s\neq j}\}} dE_{Nj}$
- $df = -\bar{E} d\beta - \bar{N} d\gamma - \beta \sum_N \sum_j P_{Nj} dE_{Nj}$
- Ensemble average reversible work is $\sum_N \sum_j P_{Nj} dE_{Nj}$
- Assuming only PV work $df = -\bar{E} d\beta - \bar{N} d\gamma + \beta \bar{p} dV$
- $d(f + \beta \bar{E} + \gamma \bar{N}) = \beta d\bar{E} + \beta \bar{p} dV + \gamma d\bar{N}$

Grand Canonical Ensemble

- $\frac{d(f+\beta\bar{E}+\gamma\bar{N})}{\beta} = d\bar{E} + \bar{p}dV + \frac{\gamma}{\beta}d\bar{N}$
- $TdS = dE + pdV - \mu dN$
- $\gamma = \frac{-\mu}{kT}, \quad S = \frac{\bar{E}}{T} - \frac{\bar{N}\mu}{T} + k\ln\Xi$
- Grand canonical partition function $\Xi(V,T,\mu) = \sum_N \sum_j e^{-E_{Nj}(V)/kT} e^{\mu N/kT}$
- Absolute activity, $\lambda = e^{\mu/kT}$.
- The relative activity of a species i: $a_i = e^{\frac{\mu_i - \mu_i^{\ominus}}{RT}}$.
- $\Xi(V,T,\mu) = \sum_{N=0}^{\infty} Q(N,V,T)\lambda^N$.
- $G = \mu N = E + pV - TS \rightarrow S = \frac{E}{T} + \frac{pV}{T} - \frac{N\mu}{T}$.
- By equating statistical and thermodynamic entropies: $pV = kT\ln\Xi(V,T,\mu)$.
- In cases where the constant N constraint make calculation of Q awkward, one resorts to the calculation of Ξ.

Isothermal-Isobaric Ensemble

- Walls are flexible and heat permeable, while particles cannot pass them (N,T,p).
- Most chemical reactions are performed under these conditions.
- $W(\{a_{Vj}\}) = \frac{\mathcal{A}!}{\Pi_V \Pi_j a_{Vj}!}$ shall be maximized constrained by $\sum_V \sum_j a_{Vj} = \mathcal{A}$, $\sum_V \sum_j a_{Vj} E_{Vj} = \mathcal{E}$ and $\sum_V \sum_j a_{Vj} V = \mathcal{V}$.
- Every partition function can be constructed from $\Omega(N, V, E)$ multiplied by the appropriate exponential and summed over the quantities which can pass through the walls of each system.
- Isothermal-isobaric partition function $\Delta = \sum_E \sum_V \Omega(N, V, E) e^{-E/kT} e^{-pV/kT} = \int \frac{dV}{V_0} e^{-pV/kT} \sum_E \Omega(N, V, E) e^{-E/kT} = \int \frac{dV}{V_0} e^{-pV/kT} Q(N, V, T)$.
- $P_{Vj} = \frac{e^{-\beta E_j - \beta PV}}{\Delta}$
- $G(N, T, p) = -kT \ln \Delta(N, T, p)$
- $dG = -SdT + VdP + \mu dN$

Micro-canonical Ensemble

- An isolated system, $\Omega(N, V, E)$.
- The whole of a grand canonical ensemble is a microcanonical system.
- $$\begin{aligned} S_{GC} &= k(\beta\bar{E} + \gamma\bar{N} + \ln\Xi) \\ &= k\ln\Xi + k\left(\sum_{N,j}\beta E_{N,j}\frac{e^{-\beta E_{Nj}(V)}e^{-\gamma N}}{\Xi} + \sum_{N,j}\gamma N\frac{e^{-\beta E_{Nj}(V)}e^{-\gamma N}}{\Xi}\right) \\ &= k\ln\Xi + k\sum_{N,j}(\beta E_{N,j} + \gamma N)\frac{e^{-\beta E_{Nj}(V)}e^{-\gamma N}}{\Xi} \end{aligned}$$
- Using $P_{Nj}(V,\beta,\gamma) = \frac{a^*_{Nj}}{\mathcal{A}} = \frac{e^{-\beta E_{Nj}(V)}e^{-\gamma N}}{\sum_N\sum_j e^{-\beta E_{Nj}(V)}e^{-\gamma N}}$
- $S_{GC} = k\ln\Xi - k\sum_{N,j}(\ln a^*_{Nj} + \ln\Xi - \ln\mathcal{A})\frac{a^*_{Nj}}{\mathcal{A}} = -\frac{k}{\mathcal{A}}\sum_{N,j}a^*_{N,j}\ln a^*_{N,j} + k\ln\mathcal{A}$
- $S_{MC} = \mathcal{A}S = k\ln W(a^*_{Nj})$

Micro-canonical Ensemble

- $S = k \ln \Omega(N, V, E)$ for an spontaneous process
  $\Delta S = k \ln(\Omega_2(N, V, E)/\Omega_1(N, V, E))$
- Second law for a system at constant volume and energy.
- For an ideal gas $S = Nk \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve^{5/2}}{N}]$
- Since $dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$ we have $\frac{p}{T} = (\frac{\partial S}{\partial V})_{N,E}$
- pV=NkT, thus $k = R/N_A$.

Fluctuation Theory: Canonical ensemble

- Deviation of a mechanical property from its mean is called fluctuation, investigation of such deviations is called fluctuation theory.
- In the thermodynamic limit the possibility of observing any value other than the mean value is extremely remote.
- All ensembles are equivalent for all practical purposes.
- $\sigma_E^2 = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2 = \sum_j E_j^2 P_j - \bar{E}^2$
- $\sum_j E_j^2 P_j = \frac{1}{Q} \sum_j E_j^2 e^{-\beta E_j} = -\frac{1}{Q} \frac{\partial}{\partial \beta} \sum_j E_j e^{-\beta E_j} = -\frac{1}{Q} \frac{\partial}{\partial \beta} (\bar{E} Q) = -\frac{\partial \bar{E}}{\partial \beta} - \bar{E} \frac{\partial \ln Q}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} + \bar{E}^2$
- $\sigma_E^2 = kT^2 (\frac{\partial \bar{E}}{\partial T})_{N,V} = kT^2 C_v$
- $\frac{\sigma_E}{\bar{E}} = \frac{(kT^2 C_v)^{1/2}}{\bar{E}}$
- For an ideal gas $\frac{\sigma_E}{\bar{E}} = O(N^{-1/2})$ thus $\bar{E} \approx E^*$

Fluctuation Theory: Canonical ensemble

- $P(E) = c\Omega(E)e^{-E/kT}$
- $(\frac{\partial \ln P}{\partial E})_{E=E^*} = (\frac{\partial \ln \Omega}{\partial E})_{E=E^*} - \beta = 0$
- $(\frac{\partial^2 \ln P}{\partial E^2}) = (\frac{\partial^2 \ln \Omega}{\partial E^2})$ at $E = E^*$, $(\frac{\partial^2 \ln \Omega}{\partial E^2}) = (\frac{\partial \beta}{\partial E^*}) = \frac{-1}{kT^2 C_v}$
- $\ln P(E) = \ln P(\bar{E}) - \frac{(E-\bar{E})^2}{2kT^2 C_v} + \cdots$
- $P(E) = P(\bar{E}) \exp[-\frac{(E-\bar{E})^2}{2kT^2 C_v}]$
- $\sigma_p^2 = \overline{p^2} - \bar{p}^2$
- $\overline{p^2} = \sum_j p_j^2 \frac{e^{-\beta E_j}}{Q} = \frac{1}{Q}\sum_j(-\frac{\partial E_j}{\partial V})^2 e^{-\beta E_j} =$
  $\frac{1}{Q}[\frac{1}{\beta}\frac{\partial}{\partial V}\sum_j((\frac{-\partial E_j}{\partial V})e^{-\beta E_j}) + \frac{1}{\beta}\sum_j(\frac{\partial^2 E_j}{\partial V^2})e^{-\beta E_j}] =$
  $\frac{kT}{Q}(\frac{\partial}{\partial V}(\bar{p}Q) - (\sum_j(\frac{\partial p_j}{\partial V})e^{-E_j/kT})) = kT(\frac{\partial \bar{p}}{\partial V} + \bar{p}\frac{\partial \ln Q}{\partial V} - \overline{\frac{\partial p}{\partial V}})$
- $\sigma_p^2 = kT(\frac{\partial \bar{p}}{\partial V} - \overline{\frac{\partial p}{\partial V}})$
- Calculate $\frac{\sigma_p}{\bar{p}}$ for an ideal gas?

Fluctuation Theory: Grand canonical ensemble

- $\sigma_N^2 = \overline{N^2} - \bar{N}^2 = \sum_{N,j} N^2 P_{Nj} - \bar{N}^2$
- $\sum_{N,j} N^2 P_{Nj} = \frac{1}{\Xi} \sum_{N,j} N^2 e^{-\beta E_{Nj}} e^{-\gamma N} = \frac{-1}{\Xi} \frac{\partial}{\partial \gamma} \sum_{N,j} N e^{-\beta E_{Nj}} e^{-\gamma N} = \frac{-1}{\Xi} \frac{\partial}{\partial \gamma} (\bar{N}\Xi) = -\frac{\partial \bar{N}}{\partial \gamma} - \bar{N} \frac{\partial \ln \Xi}{\partial \gamma} = kT(\frac{\partial \bar{N}}{\partial \mu}) + \bar{N}^2$
- $\sigma_N^2 = kT(\frac{\partial \bar{N}}{\partial \mu})$
- A is homogeneous of degree one, $A(T, \lambda V, \lambda N) = \lambda A(T, V, N)$
- According to Euler's theorem, $N(\frac{\partial A}{\partial N}) + V(\frac{\partial A}{\partial V}) = A$ (1)
- Further, $N^2(\frac{\partial^2 A}{\partial N^2}) + 2NV(\frac{\partial^2 A}{\partial N \partial V}) + V^2(\frac{\partial^2 A}{\partial V^2}) = 0$ (2)
- (1) $\rightarrow NV(\frac{\partial^2 A}{\partial N \partial V}) + V^2(\frac{\partial^2 A}{\partial V^2}) = 0$
- (1) $\rightarrow N^2(\frac{\partial^2 A}{\partial N^2}) + NV(\frac{\partial^2 A}{\partial N \partial V}) = 0$
- $N^2(\frac{\partial^2 A}{\partial N^2}) = V^2(\frac{\partial^2 A}{\partial V^2})$
- $-V^2(\frac{\partial p}{\partial V})_{T,N} = N^2(\frac{\partial \mu}{\partial N})_{T,V}$

Fluctuation Theory: Grand canonical ensemble

- $(\frac{\partial \mu}{\partial \bar{N}})_{V,T} = -\frac{V^2}{N^2}(\frac{\partial p}{\partial V})_{N,T}$. Thus $\sigma_N^2 = \frac{\bar{N}^2 kT\kappa}{V}$.
- Isothermal compressibility, $\kappa = \frac{-1}{V}(\frac{\partial V}{\partial p})_{N,T}$
- $\frac{\sigma_N}{\bar{N}} = (\frac{kT\kappa}{V})^{1/2}$
- Typical fluctuations in statistical thermodynamics are $O(N^{-1/2})$.
- $\frac{\sigma_\rho}{\bar{\rho}} = \frac{\sigma_N}{\bar{N}} = (\frac{kT\kappa}{V})^{1/2}$
- $P(N) = CQ(N, V, T)e^{\beta\mu N}$
- $(\frac{\partial \ln P}{\partial N})_{N=N^*} = (\frac{\partial \ln Q}{\partial N})_{N=N^*} + \beta\mu = 0$
- $(\frac{\partial^2 \ln P}{\partial N^2})_{N=N^*} = (\frac{\partial^2 \ln Q}{\partial N^2})_{N=N^*} = -(\frac{\partial \beta\mu}{\partial N})_{N=N^*} = -\frac{1}{kT(\partial \bar{N}/\partial\mu)_{V,T}}$
- $P(N) = P(\bar{N})\exp[\frac{-(N-\bar{N})^2}{2kT(\partial\bar{N}/\partial\mu)_{V,T}}]$

Equivalence of various ensembles

- $Q(N, V, T) = \sum_E \Omega(N, V, E) e^{-E/kT} = \Omega(N, V, \bar{E}) e^{-\bar{E}/kT}$.
- $A = -kT \ln Q = \bar{E} - kT \ln \Omega(N, V, \bar{E})$. Thus $S = k \ln \Omega(N, V, \bar{E})$.
- $\Xi = \sum_N Q(N, V, T) e^{\beta\mu N} = \sum_{E,N} \Omega(N, V, E) e^{-\beta E} e^{\beta\mu N}$
- $\Xi = Q(\bar{N}, V, T) e^{\beta\mu\bar{N}} = \Omega(\bar{N}, V, \bar{E}) e^{-\beta\bar{E}} e^{\beta\mu\bar{N}}$
- $kT \ln \Xi = kT \ln Q + \mu\bar{N} = kT \ln \Omega - \bar{E} + \mu\bar{N}$
- $kT \ln \Xi = -A + G = TS - \bar{E} + G = pV$

Ideal gas

- $Q(N,V,T) = \sum_\alpha e^{-E_\alpha/kT} = \sum_{i,j,k,\cdots} e^{-(\epsilon_i^a+\epsilon_j^b+\epsilon_k^c+\cdots)/kT} = \sum_i e^{-\epsilon_i^a/kT} \sum_j e^{-\epsilon_j^b/kT} \sum_k e^{-\epsilon_k^c/kT} \cdots = q_a q_b q_c \cdots$ where molecular partition function $q(V,T) = \sum_i e^{-\epsilon_i/kT}$
- For N distinguishable identical particles $Q(N,V,T) = [q(v,T)]^N$, e.g., sites in a solid crystal are distinguishable.
- Partitioning of the molecular Hamiltonian, $H = H_{trans} + H_{rota} + H_{vibr} + H_{elect}$, lead to the division of molecular partition function. $q_{molecula} = q_{translational} q_{rotational} q_{vibration} q_{electronic}$
- The unrestricted sum for partition function is not valid for fermions as it allows repeated indices, i.e., more than one particle in the same energy state.
- The unrestricted sum for partition function is not valid for Bosons as it over-counts states with repeated indices, i.e., states where more than one particle is in the same energy state.

Ideal gas

- Number of quantum states with energy $\leq \epsilon$,
  $\Phi(\epsilon) = \frac{\pi}{6}(\frac{8ma^2\epsilon}{h^2})^{3/2} = \frac{\pi}{6}(\frac{8m\epsilon}{h^2})^{3/2} V$
- If the number of available molecular states is much greater than the number of molecules in the system, two molecules in the same state is a rare event.
- Thus the only problem with $Q(N, V, T) = q^N$ is indistinguishability of molecules, partition function can be corrected as:
  $Q(N, V, T) = q^N / N!$.
- Valid when $\Phi(\epsilon) \gg N \rightarrow \frac{\pi}{6}(\frac{12mkT}{h^2})^{3/2} \gg \frac{N}{V}$
- Boltzmann statistics or classical limit become a better approximation by increasing mass or temperature or decreasing density.
- $E = kT^2(\frac{\partial \ln Q}{\partial T})_{N,V} = NkT^2(\frac{\partial \ln q}{\partial T}) = N \sum_j \epsilon_j \frac{e^{-\epsilon_j/kT}}{q} = N\bar{\epsilon}$
- $\bar{\epsilon} = \sum_j \epsilon_j \frac{e^{-\epsilon_j/kT}}{q}$
- Probability of a molecule being in the j'th energy state $\pi_j = \frac{e^{-\epsilon_j/kT}}{q}$

Ideal gas

- For a non-interacting gas one can consider the container to be an ensemble and each molecule to be a system.
- Label each molecular state with $1, 2, 3, \cdots$ such that $\epsilon_i \leq \epsilon_{i+1}$.
- Consider N as the total number of molecules and n_i as the number of molecules in the state i.
- Derive probability of state occupation similar to the last section by maximizing ways of distributing molecules over energy states $W(\{n_j\}) = \frac{N!}{\Pi_i n_i!}$ subject to $\sum_i n_i = N$ and $\sum_i n_i \epsilon_i = E$.
- $\pi_i = \frac{\bar{n}_i}{N} = \frac{n_i^*}{N} = \frac{e^{-\epsilon_i/kT}}{q}$ in the Boltzmann statistics.
- Exact partition function for fermions is $Q(N, V, T) = \sum^*_{i \neq j \neq k \neq \cdots} e^{-(\epsilon_i^a + \epsilon_j^b + \epsilon_k^c + \cdots)/kT}$ where * denotes that $\epsilon_i + \epsilon_j + \cdots = E$.
- For bosons $Q(N, V, T) = \sum^*_{i,j,k,\cdots} e^{-(\epsilon_i^a + \epsilon_j^b + \epsilon_k^c + \cdots)/kT}$ where * also denotes that any term with repeated indices is counted just once.

Fermi-Dirac and Bose-Einstein statistics

- $E_j = \sum_k \epsilon_k n_k$ and $N = \sum_k n_k$.
- $Q(N,V,T) = \sum_j e^{-\beta E_j} = \sum^*_{\{n_k\}} e^{-\beta \sum_i \epsilon_i n_i}$ where $*$ signifies $\sum_k n_k = N$.
- Due to difficulty of performing this sum, we turn to the grand canonical partition function:
- $\Xi(V,T,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Q(N,V,T) = \sum_{N=0}^{\infty} \lambda^N \sum^*_{\{n_k\}} e^{-\beta\sum_i \epsilon_i n_i} = \sum_{N=0}^{\infty} \sum^*_{\{n_k\}} \lambda^{\sum n_i} e^{-\beta \sum_j \epsilon_j n_j} = \sum_{N=0}^{\infty} \sum^*_{\{n_k\}} \prod_{k=1}^{\infty} (\lambda e^{-\beta\epsilon_k})^{n_k} = \sum_{n_1=0}^{n_1^{max}} \sum_{n_2=0}^{n_2^{max}} \cdots \prod_{k=1}^{\infty} (\lambda e^{-\beta\epsilon_k})^{n_k}$
- $\Xi(V,T,\mu) = \sum_{n_1=0}^{n_1^{max}} (\lambda e^{-\beta\epsilon_1})^{n_1} \sum_{n_2=0}^{n_2^{max}} (\lambda e^{-\beta\epsilon_2})^{n_2} \cdots = \prod_{k=1}^{\infty} \sum_{n_k=0}^{n_k^{max}} (\lambda e^{-\beta\epsilon_k})^{n_k}$
- $\Xi_{FD} = \prod_{k=1}^{\infty} (1 + \lambda e^{-\beta\epsilon_k})$
- $\Xi_{BE} = \prod_{k=1}^{\infty} (\sum_{n_k=0}^{\infty} (\lambda e^{-\beta\epsilon_k})^{n_k}) = \prod_{k=1}^{\infty} ((1 - \lambda e^{-\beta\epsilon_k})^{-1}), \quad \lambda e^{-\beta\epsilon_k} < 1, \quad e^{\beta(\mu-\epsilon_k)} < 1, \quad (\mu - \epsilon_k) < 0 \rightarrow \mu < \epsilon_0.$

Fermi-Dirac and Bose-Einstein statistics

- $\Xi_{BE}^{FD} = \Pi_{k=1}^{\infty}(1 \pm \lambda e^{-\beta\epsilon_k})^{\pm 1}$
- $\bar{N} = N = kT(\frac{\partial \ln \Xi}{\partial \mu})_{V,T} = \lambda(\frac{\partial \ln \Xi}{\partial \lambda})_{V,T} = \sum_k \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}} = \sum_k \bar{n}_k$
- $\bar{n}_k = \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$
- $\bar{E} = \sum_k \bar{n}_k \epsilon_k = \sum_k \frac{\lambda \epsilon_k e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$
- $pV = kT \ln \Xi = \pm kT \sum_k \ln[1 \pm \lambda e^{-\beta\epsilon_k}]$
- In quantum statistics even non-interacting particles are not independent (through symmetry requirement), thus molecular partition function q is irrelevant.
- In the limit of classical statistics $\bar{n}_k \to 0$. This requires $\lambda \to 0$ meaning $N/V \to 0$ for constant T or $T \to \infty$ for constant N/V.

Fermi-Dirac and Bose-Einstein statistics

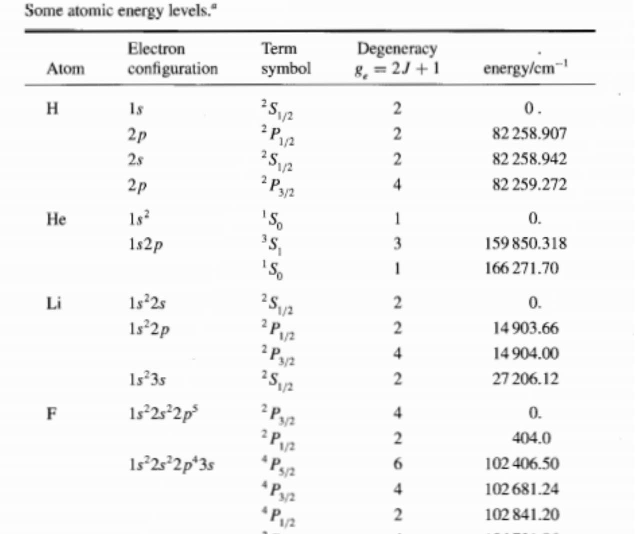
- For small λ $\quad \bar{n}_k = \lambda e^{-\beta\epsilon_k} \rightarrow \bar{N} = \lambda q$
- $\frac{\bar{n}_k}{\bar{N}} = \frac{e^{-\beta\epsilon_k}}{q}$
- $\bar{E} \rightarrow \sum_j \lambda \epsilon_j e^{-\beta\epsilon_j}$
- $\bar{\epsilon} = \frac{\bar{E}}{\bar{N}} = \frac{\sum_j \epsilon_j e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}}$
- $pV = \pm kT \sum_k \ln[1 \pm \lambda e^{-\beta\epsilon_k}] = (\pm kT)(\pm\lambda \sum_j e^{-\beta\epsilon_j}) = \lambda kTq$
- $\beta pV = \ln \Xi = \lambda q = \bar{N}$
- $\Xi = e^{\lambda q} = \sum_{N=0}^{\infty} \frac{(\lambda q)^N}{N!}$ thus $Q(N, V, T) = \frac{q^N}{N!}$.
- Thus Boltzmann statistics is valid in the limit of small λ.

Ideal monatomic gas

- $q(V,T) = q_{trans} q_{elect} q_{nucl}$
- Translational energy
  $\epsilon_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, 3, \cdots$
- $q_{trans} = \sum_{n_x,n_y,n_z=1}^{\infty} e^{-\beta\epsilon_{n_x,n_y,n_z}} = \sum_{n_x,n_y,n_z=1}^{\infty} e^{-\beta\frac{h^2}{8ma^2}(n_x^2+n_y^2+n_z^2)} = \sum_{n_x=1}^{\infty} e^{-\frac{\beta h^2 n_x^2}{8ma^2}} \sum_{n_y=1}^{\infty} e^{-\frac{\beta h^2 n_y^2}{8ma^2}} \sum_{n_z=1}^{\infty} e^{-\frac{\beta h^2 n_z^2}{8ma^2}} = (\sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}})^3$
- $q_{trans}(V,T) = (\int_0^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}} dn)^3 = (\frac{2\pi mkT}{h^2})^{3/2} V$
- $q_{trans} = \int_0^{\infty} \omega(\epsilon) e^{-\beta\epsilon} d\epsilon$ where $\omega(\epsilon) d\epsilon = \frac{\pi}{4}(\frac{8ma^2}{h^2})^{3/2} \epsilon^{1/2} d\epsilon$
- $q_{trans} = \frac{\pi}{4}(\frac{8ma^2}{h^2})^{3/2} \int_0^{\infty} \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon = (\frac{2\pi mkT}{h^2})^{3/2} V = \frac{V}{\Lambda^3}$
- $\bar{\epsilon}_{trans} = kT^2(\frac{\partial \ln q_{trans}}{\partial T}) = \frac{3}{2}kT = \frac{\overline{p^2}}{2m}$
- Λ is the thermal De Broglie wavelength of the particle.

Ideal monatomic gas

- Condition for applicability of classical or Boltzmann statistics $\Lambda^3/V \ll 1$
- $q_{elect} = \sum_i \omega_{ei} e^{-\beta\epsilon_i} = \omega_{e1} + \omega_{e2} e^{-\beta\Delta\epsilon_{e12}} + \cdots$



Some atomic energy levels.[a]

Atom	Electron configuration	Term symbol	Degeneracy $g_e = 2J+1$	energy/cm^{-1}
H	$1s$	$^2S_{1/2}$	2	0.
	$2p$	$^2P_{1/2}$	2	82 258.907
	$2s$	$^2S_{1/2}$	2	82 258.942
	$2p$	$^2P_{3/2}$	4	82 259.272
He	$1s^2$	$^1S_0$	1	0.
	$1s2p$	$^3S_1$	3	159 850.318
		$^1S_0$	1	166 271.70
Li	$1s^22s$	$^2S_{1/2}$	2	0.
	$1s^22p$	$^2P_{1/2}$	2	14 903.66
		$^2P_{3/2}$	4	14 904.00
	$1s^23s$	$^2S_{1/2}$	2	27 206.12
F	$1s^22s^22p^5$	$^2P_{3/2}$	4	0.
		$^2P_{1/2}$	2	404.0
	$1s^22s^22p^43s$	$^4P_{5/2}$	6	102 406.50
		$^4P_{3/2}$	4	102 681.24
		$^4P_{1/2}$	2	102 841.20

Ideal monatomic gas thermodynamic functions

- k=0.695 cm^{-1}/deg-molecule, 1 eV=8065.73 cm^{-1}.
- Nuclear levels are separated by millions of eV's. Nuclear states do not contribute in thermodynamic change.
- $q_{nucl} = \sum_i \omega_{ni} e^{-\beta\epsilon_i} = \omega_{n1} + \omega_{n2} e^{-\beta\Delta\epsilon_{n12}} + \cdots$
- $A = -kT \ln Q = -NkT \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve}{N}] - NkT \ln(\omega_{e1} + \omega_{e2} e^{-\beta\Delta\epsilon_{12}})$
- $E = kT^2(\frac{\partial \ln Q}{\partial T})_{N,V} = \frac{3}{2} NkT + \frac{N\omega_{e2}\Delta\epsilon_{e12} e^{-\beta\Delta\epsilon_{e12}}}{q_{elect}}$
- $p = kT(\frac{\partial \ln Q}{\partial V})_{N,T} = \frac{NkT}{V}$
- $S = \frac{3}{2} Nk + Nk \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve}{N}] + Nk \ln(\omega_{e1} + \omega_{e2} e^{-\beta\Delta\epsilon_{12}}) + \frac{Nk\omega_{e2}\beta\Delta\epsilon_{12} e^{-\beta\Delta\epsilon_{12}}}{q_{elect}} = Nk \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve^{5/2}}{N}] + S_{elect}$, which is the Sackur-Tetrode equation.
- $\mu(T,p) = -kT(\frac{\partial \ln Q}{\partial N})_{V,T} = -kT \ln \frac{q}{N} = -kT \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{V}{N}] - kT \ln q_e q_n = -kT \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{kT}{p}] - kT \ln q_e q_n = -kT \ln[(\frac{2\pi mkT}{h^2})^{3/2} kT] - kT \ln q_e q_n + kT \ln p = \mu_0(T) + kT \ln p$
- $\mu_0(T) = -kT \ln[(\frac{2\pi mkT}{h^2})^{3/2} kT] - kT \ln q_e q_n$

Atomic term symbols

- Term symbol is an abbreviated description of the angular momentum quantum numbers in a multi-electron atom.
- Each energy level of an atom with a given electron configuration is described by not only the electron configuration but also its own term symbol, as the energy level also depends on the total angular momentum including spin.
- The usual atomic term symbols assume LS coupling (also known as Russell-Saunders coupling or spin-orbit coupling). The ground state term symbol is predicted by Hund's rules.
- Hund's rule of maximum multiplicity states that the electron configuration maximizing spin multiplicity is more stable.
- Multielectron atomic Hamiltonian, $\hat{H} = -\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_j \frac{Ze^2}{r_j} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_j \zeta(r_j) l_j \cdot s_j = H_0 + H_{ee} + H_{so}$
- H_{so} represent the interaction between the magnetic moment associated with an electrons spin with the magnetic field generated by its own orbital motion.

Atomic term symbols

- Russell-Saunders or L-S coupling: For $Z < 40$, $\hat{H}_{so}$ can be treated as a small perturbation. Then $[\hat{H}_0 + \hat{H}_{ee}, \hat{L}] = [\hat{H}_0 + \hat{H}_{ee}, \hat{S}] = 0$. So S and L are good quantum numbers.
- $\hat{L}^2\psi = L(L+1)\hbar^2\psi \qquad \hat{S}^2\psi = S(S+1)\hbar^2\psi$
- L and S are the vector sums of l_j and s_j respectively. For electrons, $L = l_1 + l_2, l_1 + l_2 - 1, \cdots, |l_1 - l_2|$ and $S = s_1 + s_2, s_1 + s_2 - 1, \cdots, |s_1 - s_2|$
- Terms with $L = 0, 1, 2, \cdots$ are denoted by S, P, D, ...
- When $\hat{H}_{so}$ is taken into account only $[\hat{H}, \hat{J}] = 0$. Only $\hat{J} = \hat{L} + \hat{S}$ is conserved. Eigenvalues of $\hat{J}^2 = (\hat{L} + \hat{S})^2$ are $J(J+1)\hbar^2$ with $\omega_j = 2J + 1$ corresponding to 2J+1 eigenvalues of $\hat{J}_z$ which are $J\hbar, (J-1)\hbar, \cdots, -J\hbar$
- Allowed values of J are $L + S, L + S - 1, \cdots, |L - S|$. Term symbol is written as ${}^{2S+1}L_J$.

Atomic term symbols

- For heavier atoms j-j coupling is used. Total angular momenta for each electron is defined as $j_i = s_i + l_i$. Total angular momentum, J, is derived by coupling the j's. Term symbol is written as $^{2S+1}L_J$.
- For molecules, Greek letters are used to designate the component of orbital angular momenta along the molecular axis.
- For a given electron configuration:
- The combination of an S value and an L value is called a term, and has a statistical weight (i.e., number of possible microstates) equal to (2S+1)(2L+1);
- A combination of S, L and J is called a level. A given level has a statistical weight of (2J+1), which is the number of microstates associated with this level in the corresponding term;
- A combination of S, L, J and M_J determines a single state.

Atomic term symbols

- The product (2S+1)(2L+1) as the number of possible microstates $|S, m_S, L, m_L\rangle$ with given S and L is also the number of basis states in the uncoupled representation, where S, m$_S$, L, m$_L$ are good quantum numbers whose corresponding operators mutually commute.
- With given S and L, the eigenstates $|S, m_S, L, m_L\rangle$ in this representation span function space of dimension (2S+1)(2L+1).
- In the coupled representation where total angular momentum is treated, the associated microstates are $|J, M_J, S, L\rangle$ and these states span the function space with dimension of $\sum_{J=J_{min}=|L-S|}^{J_{max}=L+S} (2J+1)$ as $M_J = J, J-1, \ldots - J+1, -J$.

Adiabatic approximation

- Adiabatic, Born-Oppenheimer approximation.
- Adiabatic means not passing through and in thermodynamics refers to a condition imposed on a system that prevents any passage of heat into or out of the system.
- In quantum dynamics, adiabatic refers to an inherent property of a process, i.e., its tendency to occur without any change in quantum state.
- Ehrenfest showed that when the parameters of a system in a particular quantum state are changed slowly, the system remains in the same quantum state (adiabatic theorem).

Adiabatic approximation

- Now, adiabatic implies that there are two sets of variables which describe the system of interest and the system can be characterized by the eigenstates defined at each fixed value of one set of variables, which change slowly compared to the other set.
- In the first step of the adiabatic approximation, the electronic Schrodinger equation is solved, yielding the wave-function $\psi_{\text{electronic}}$ depending on electrons only.
- During this solution the nuclei are fixed in a certain configuration, very often the equilibrium configuration.
- In the second step of the BO approximation this function serves as a potential in a Schrodinger equation containing only the nuclei.
- The success of the BO approximation is due to the difference between nuclear and electronic masses.

Adiabatic approximation

- Molecular Hamiltonian, $\hat{H} = \sum_{I=1}^{N_n} \frac{\hat{P}_I^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\hat{p}_i^2}{2m_e} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{I<J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|} = \hat{T}_n + \hat{T}_e + V_e + V_n + V_{ne}$
- $\left[\hat{T}_{\mathrm{n}} + \hat{T}_{\mathrm{e}} + V_e + V_n + V_{en}\right] \Psi(r, R) = E\Psi(r, R)$
- $\Psi(r, R) = \phi(r; R)\chi(R)$,
- where $\chi(R)$ is a nuclear wave function and $\phi(r; R)$ is an electronic wave function that depends parametrically on the nuclear positions.
- The difference in the nuclear and electronic mass also results in a difference in their momenta, i.e., nuclear momenta are greater, which in turn causes the nuclear wave function (coordinate amplitude) to change more steeply than the electronic wave function.
- $\nabla_I \chi(R) \gg \nabla_I \phi(r; R)$

Adiabatic approximation

- $\hat{T}_{\mathrm{n}}\big(\phi(r;R)\chi(R)\big) = -\frac{\hbar^2}{2}\sum_I \frac{1}{M_I}\Big[\phi(r;R)\nabla_I^2\chi(R) + 2\nabla_I\phi(r;R)\cdot \nabla_I\chi(R) + \chi(R)\nabla_I^2\phi(r;R)\Big] \approx -\frac{\hbar^2}{2}\sum_I \frac{1}{M_I}\phi(r;R)\nabla_I^2\chi(R)$
- $\Big[\hat{T}_{\mathrm{n}} + \hat{T}_{\mathrm{e}} + V_e + V_n + V_{en}\Big]\phi(r;R)\chi(R) = E\phi(r;R)\chi(R)$
- $\frac{\big[\hat{T}_{\mathrm{e}}+V_{\mathrm{e}}(r)+V_{\mathrm{en}}(R,r)\big]\phi(r;R)}{\phi(r;R)} = E - \frac{\big[\hat{T}_n+V_{\mathrm{n}}(R)\big]\chi(R)}{\chi(R)}$.
- $\Big[\hat{T}_{\mathrm{e}} + V_{\mathrm{e}}(r) + V_{\mathrm{en}}(r,R)\Big]\phi(r;R) = \varepsilon(R)\phi(r;R)$
- $\Big[\hat{T}_{\mathrm{n}} + V_{\mathrm{n}}(R) + \varepsilon_i(R)\Big]\chi(R) = E\chi(R)$.
- The physical interpretation is that the electrons respond instantaneously to the nuclear motion, therefore, it is sufficient to obtain a set of instantaneous electronic eigenvalues and eigenfunctions at each nuclear configuration, R (hence the parametric dependence of $\phi_i(r;R)$ and $\varepsilon_i(R)$ on R)

Distance dependent potential

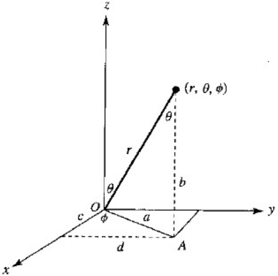
- $\left[\hat{T}_{\mathrm{n}} + V_{\mathrm{n}}(R) + \varepsilon_i(R)\right]\chi(R,t) = i\hbar\frac{\partial}{\partial t}\chi(R,t).$
- $\varepsilon_i(R)$ give rise to BO hypersurfaces.
- This equation describes the nuclear dynamics and vibronic states.
- Breaking down the motion of nuclei:
- In 2D consider two particles with a distance dependent potential. $E = \frac{m_1}{2}(\dot{x}_1^2 + \dot{y}_1^2) + \frac{m_2}{2}(\dot{x}_2^2 + \dot{y}_2^2) + U(x_1 - x_2, y_1 - y_2)$
- Center of mass and relative coordinates are defined as $X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \quad Y = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2} \qquad x_{12} = x_1 - x_2 \quad y_{12} = y_1 - y_2$
- $x_1 = X + \frac{m_2}{m_1+m_2}x_{12} \quad y_1 = Y + \frac{m_2}{m_1+m_2}y_{12} \qquad x_2 = X - \frac{m_1}{m_1+m_2}x_{12} \quad y_2 = Y - \frac{m_1}{m_1+m_2}y_{12}$
- $E = \frac{m_1+m_2}{2}(\dot{X}^2 + \dot{Y}^2) + \frac{m_1 m_2}{2(m_1+m_2)}(\dot{x}_{12}^2 + \dot{y}_{12}^2) + U(x_{12}, y_{12}) = \frac{M}{2}(\dot{X}^2 + \dot{Y}^2) + \frac{\mu}{2}(\dot{x}_{12}^2 + \dot{y}_{12}^2) + U(x_{12}, y_{12}) = E_{cm} + E_{rel}$

Distance dependent potential

- Thus the center of mass motion can be separated from relative motion of a two particle system.
- Mapping the relative motion into polar coordinates r and θ where $x_{12} = r\cos\theta \quad y_{12} = r\sin\theta \quad \dot{x}_{12} = \dot{r}\cos\theta - r\dot{\theta}\sin\theta \quad \dot{y}_{12} = \dot{r}\sin\theta + r\dot{\theta}\cos\theta$:
  $E_{rel} = \frac{\mu}{2}(\dot{r}^2 + r^2\dot{\theta}^2) + U(r) = \frac{\mu}{2}\dot{r}^2 + U(r) + \frac{\mu}{2}r^2\dot{\theta}^2 = E_{vib} + E_{rot}$
- Similarly in 3D consider two particles with a distance dependent potential.
  $E = \frac{m_1}{2}(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) + \frac{m_2}{2}(\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) + U(x_1 - x_2, y_1 - y_2, z_1 - z_2)$
- Center of mass and relative coordinates are defined as $X = \frac{m_1x_1 + m_2x_2}{m_1+m_2} \quad Y = \frac{m_1y_1 + m_2y_2}{m_1+m_2} \quad Z = \frac{m_1z_1 + m_2z_2}{m_1+m_2} \qquad x_{12} = x_1 - x_2 \quad y_{12} = y_1 - y_2 \quad z_{12} = z_1 - z_2$
- $x_1 = X + \frac{m_2}{m_1+m_2}x_{12} \quad y_1 = Y + \frac{m_2}{m_1+m_2}y_{12} \qquad z_1 = Z + \frac{m_2}{m_1+m_2}z_{12} \qquad x_2 = X - \frac{m_1}{m_1+m_2}x_{12} \quad y_2 = Y - \frac{m_1}{m_1+m_2}y_{12} \quad z_2 = Z - \frac{m_1}{m_1+m_2}z_{12}$

Distance dependent potential

- $\frac{m_1\dot{x}_1^2+m_2\dot{x}_2^2}{2} = \frac{(m_1+m_2)}{2}\dot{X}^2 + \frac{m_1 m_2}{m_1+m_2}\dot{x}_{12}^2$
- $E = \frac{M}{2}(\dot{X}^2+\dot{Y}^2+\dot{Z}^2)+\frac{\mu}{2}(\dot{x}_{12}^2+\dot{y}_{12}^2+\dot{z}_{12}^2)+U(x_{12},y_{12},z_{12}) = E_{cm}+E_{rel}$
- Finally transform the relative coordinates into spherical polar coordinates.



- $\dot{x}_{12} = \dot{r}\sin\theta\cos\phi + r\dot{\theta}\cos\theta\cos\phi - r\dot{\phi}\sin\theta\sin\phi$ $\quad \dot{y}_{12} = \dot{r}\sin\theta\sin\phi + r\dot{\theta}\cos\theta\sin\phi + r\dot{\phi}\sin\theta\cos\phi$ $\quad \dot{z}_{12} = \dot{r}\cos\theta - r\dot{\theta}\sin\theta$
- $\dot{x}_{12}^2 + \dot{y}_{12}^2 + \dot{z}_{12}^2 = \dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2\sin^2\theta$

Diatomic molecule

- $E_{rel} = \frac{\mu}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2 \sin^2\theta) + U(r)$
- $E_{vib} = \frac{\mu}{2}\dot{r}^2 + U(r) \qquad E_{rot} = \frac{\mu}{2}(r^2\dot{\theta}^2 + r^2\dot{\phi}^2 \sin^2\theta)$
- $H_n = H_{trans} + H_{Int}$, $\epsilon_n = \epsilon_{trans} + \epsilon_{int}$, $q_n = q_{trans} q_{int}$
- $q_{trans} = [\frac{2\pi MkT}{h^2}]^{3/2} V$, $Q(N, V, T) = \frac{q_{trans}^N q_{int}^N}{N!}$
- Relative motion of the two nuclei consists of rotary motion about the center of mass and vibratory motion about the equilibrium internuclear distance r_e.
- Small amplitude of the vibratory motion allows treatment of the rotary motion as the rotation of a rigid dumbbell.
- $U(r) = U(r_e) + (r - r_e)(\frac{dU}{dr})_{r=r_e} + \frac{1}{2}(r - r_e)^2(\frac{d^2U}{dr^2})_{r=r_e} + \cdots = u(r_e) + \frac{1}{2}k(r - r_e)^2 + \cdots$
- Rigid rotor-Harmonic oscillator approximation: $H_{rot,vib} = H_{rot} + H_{vib}$, $\epsilon_{rot,vib} = \epsilon_{rot} + \epsilon_{vib}$, $q_{rot,vib} = q_{rot} q_{vib}$

Diatomic molecule

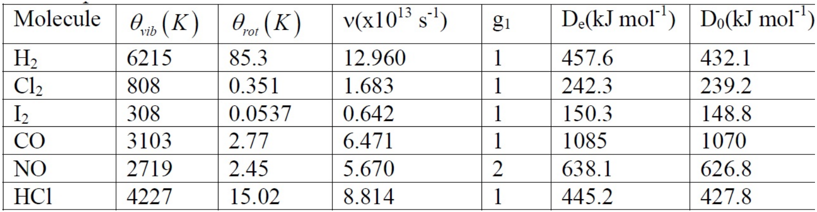
- For a rigid rotor,
  $\epsilon_J = \frac{\hbar^2 J(J+1)}{2I} \quad J = 0, 1, 2, \cdots \qquad \omega_J = 2J+1 \qquad I = \mu r_e^2$
- For a harmonic oscillator
  $\epsilon_{vib} = h\nu(n+1/2) \quad n = 0, 1, 2, \cdots \qquad \omega_n = 1 \qquad \nu = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}$
- Selection rule for radiation induced rotational transition: 1) Possession of permanent dipole moment. 2) $\Delta J = \pm 1$
- $\nu = \frac{\epsilon_{j+1} - \epsilon_j}{h} = \frac{h}{4\pi^2 I}(J+1) \quad J = 0, 1, 2, \cdots$
- $\bar{B} = \frac{h}{8\pi^2 Ic}$, $\bar{\epsilon}_J(cm^{-1}) = \bar{B}J(J+1)$
- Selection rule for radiation induced vibrational transition: 1) Change of dipole moment by the respective vibration. 2) $\Delta n = \pm 1$
- $\nu = \frac{\epsilon_{j+1} - \epsilon_j}{h} = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}$
- Assume: $H = H_{trans} + H_{rot} + H_{vib} + H_{elec} + H_{nucl}$; thus
  $\epsilon = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec} + \epsilon_{nucl}$.

Diatomic molecule: vibrational partition function

- $q = q_{trans} q_{rot} q_{vib} q_{elec} q_{nucl}$, $Q(N, V, T) = \frac{(q_{trans} q_{rot} q_{vib} q_{elec} q_{nucl})^N}{N!}$
- Zero of rotational energy taken as the energy of $J = 0$ state.
- Zero of vibrational energy taken as the bottom of the internuclear potential well of ground electronic state.
- Zero of the electronic energy is separated ground state atoms.
- $q_{elec} = \Omega_{e1} e^{D_e/kT} + \Omega_{e2} e^{-\epsilon_2/kT} + \cdots$
- $q_{vib}(T) = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu n} = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}$
- If $kT \gg h\nu$ $\qquad q_{vib}(T) = e^{-\beta h\nu/2} \int_0^{\infty} e^{-\beta h\nu n} dn = \frac{kT}{h\nu} e^{-\beta h\nu/2}$
- $E_\nu = NkT^2 \frac{d \ln q_v}{dT} = Nk(\frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1})$ in terms of vibrational temperature.
- $C_{V,vib} = (\frac{\partial E_v}{\partial T})_N = Nk(\frac{\theta_\nu}{T})^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}$

Diatomic molecule: vibrational partition function

- $f_n = \frac{e^{-\beta h\nu(n+1/2)}}{q_{vib}} = (1 - e^{-\beta h\nu})e^{-\beta h\nu n}$



Molecule	$\theta_{vib}(K)$	$\theta_{rot}(K)$	ν(x10^{13} s^{-1})	g_1	D_e(kJ mol^{-1})	D_0(kJ mol^{-1})
H_2	6215	85.3	12.960	1	457.6	432.1
Cl_2	808	0.351	1.683	1	242.3	239.2
I_2	308	0.0537	0.642	1	150.3	148.8
CO	3103	2.77	6.471	1	1085	1070
NO	2719	2.45	5.670	2	638.1	626.8
HCl	4227	15.02	8.814	1	445.2	427.8

- $q_{rot}(T) = \sum_{J=0}^{\infty}(2J+1)e^{-\beta\bar{B}J(J+1)}$
- Characteristic temperature of rotation $\theta_r = \bar{B}/k$

Diatomic molecule: rotational partition function

- $q_{rot}(T) = \int_0^\infty (2J+1)e^{-\theta_r J(J+1)/T} dJ = \int_0^\infty e^{-\theta_r J(J+1)/T} dJ(J+1) = \frac{T}{\theta_r} = \frac{8\pi^2 IkT}{h^2} \quad \theta_r \ll T$
- At small temperatures $q_{rot}(T) = 1 + 3e^{-2\theta_r/T} + 5e^{-6\theta_r/T} + \cdots$
- For intermediate temperatures Euler-MacLaurin summation formula: $\sum_{n=a}^{b} f(n) =$ $\int_a^b f(n)dn + \frac{1}{2}\{f(b)+f(a)\} + \sum_{j=1}^{\infty}(-1)^j \frac{B_j}{(2j)!}\{f^{(2j-1)}(a) - f^{(2j-1)}(b)\}$
- The formula was discovered independently by Leonhard Euler and Colin Maclaurin around 1735 (and later generalized as Darboux's formula). Euler needed it to compute slowly converging infinite series while Maclaurin used it to calculate integrals.
- Bernoulli numbers, $B_1 = 1/6, B_2 = 1/30, B_3 = 1/42, \cdots$
- Use to calculate $\sum_{j=0}^{\infty} e^{-\alpha j}$.
- Euler-MacLaurin formula is applied to $q_{rot}(T)$ with $f(J) = (2J+1)e^{-\frac{\Theta_r}{T}J(J+1)}, \quad a = 0, \quad b = \infty$

Diatomic molecule: rotational partition function

- $q_{rot}(T) = \frac{T}{\theta_r}\{1 + \frac{1}{3}(\frac{\theta_r}{T}) + \frac{1}{15}(\frac{\theta_r}{T})^2 + \frac{4}{315}(\frac{\theta_r}{T})^3 + \cdots\}$
- $\ln q_{rot}(T) = \ln\frac{T}{\theta_r} + \ln\{1 + \frac{1}{3}(\frac{\theta_r}{T}) + \frac{1}{15}(\frac{\theta_r}{T})^2 + \frac{4}{315}(\frac{\theta_r}{T})^3 + \cdots\}$
- $E_{rot} = NkT^2(\frac{\partial \ln q_{rot}}{\partial T}) = NkT + \cdots$
- $\frac{N_j}{N} = \frac{(2J+1)e^{-\theta_r J(J+1)/T}}{q_{rot}(T)}$.
- $J_{max} = (\frac{kT}{2\bar{B}})^{1/2} - 1/2 \approx (\frac{T}{2\theta_r})^{1/2}$.
- If the nuclei have integer spin they are Bosons and the molecular wavefunction must be symmetric with respect to interchange of the two nuclei.
- If the nuclei have half odd integer spin they are Fermions and the molecular wavefunction must be antisymmetric with respect to interchange of the two nuclei.
- For a homonuclear diatomic molecule symmetry requirement most be considered.
- If temperature is fairly large
  $q_{rot}(T) = \frac{T}{\sigma\theta_r}\{1 + \frac{1}{3}(\frac{\theta_r}{T}) + \frac{1}{15}(\frac{\theta_r}{T})^2 + \frac{4}{315}(\frac{\theta_r}{T})^3 + \cdots\}$

Diatomic molecule: rotational partition function

- Symmetry number σ is the number of indistinguishable orientations of a molecule.
- Exclusive of the nuclear part $\psi'_{total} = \psi_{trans}\psi_{rot}\psi_{vib}\psi_{elec}$
- Consider the interchange of nuclei as first inverting the molecule followed by an inversion of only electrons.
- Translational partition function is unaffected by inversion.
- Vibrational partition function is unaffected by inversion.
- Most molecules electronic ground state is Σ_g^+ which is symmetric under both inverting the molecule and an inversion of only electrons.
- Thus rotational wavefunction controls the symmetry of ψ'_{total}
- Rigid rotor wavefunctions are the same functions as the angular functions of the hydrogen atom.

Spherical harmonics

- $l = 0, m_l = 0 \rightarrow Y_{0,0} = \frac{1}{\sqrt{4\pi}}$
- $l = 1, m_l = 1, 0, -1 \rightarrow \begin{cases} Y_{P_x} = (\frac{3}{4\pi})^{1/2} \sin\theta\cos\phi \\ Y_{P_y} = (\frac{3}{4\pi})^{1/2} \sin\theta\sin\phi \\ Y_{P_z} = (\frac{3}{4\pi})^{1/2} \cos\theta \end{cases}$
- $l = 2, m_l = 2, 1, 0, -1, -2 \rightarrow \begin{cases} Y_{d_{z^2}} = (\frac{5}{16\pi})^{1/2}(3\cos^2\theta - 1) \\ Y_{d_{xz}} = (\frac{15}{4\pi})^{1/2}(\sin\theta\cos\theta\cos\phi) \\ Y_{d_{yz}} = (\frac{15}{4\pi})^{1/2}(\sin\theta\cos\theta\sin\phi) \\ Y_{d_{xy}} = (\frac{15}{16\pi})^{1/2}(\sin\theta\sin 2\phi) \\ Y_{d_{x^2-y^2}} = (\frac{15}{16\pi})^{1/2}(\sin\theta\cos 2\phi) \end{cases}$

Diatomic molecule: rotational partition function

- Effect of inversion on the orientation of the diatomic molecule is $(\theta, \phi) \rightarrow (\pi - \theta, \phi + \pi)$
- ψ'_{total} remains unchanged for even J and changes sign for odd J.
- Symmetric spin wavefunctions for spin-1/2 nuclei are $\alpha\alpha$, $\beta\beta$ and $2^{-1/2}(\alpha\beta + \beta\alpha)$
- Antisymmetric spin wavefunctions for spin-1/2 nuclei is $2^{-1/2}(\alpha\beta - \beta\alpha)$
- Odd J levels have a statistical weight of 3 compared to a statistical weight of 1 for even J levels.
- Nuclei of spin I has 2I+1 spin states with eigenfunctions $\alpha_1, \alpha_2, \cdots, \alpha_{2I+1}$
- There are $(2I+1)^2$ nuclear wavefunctions.
- $(2I+1)I$ antisymmetric spin functions are $\alpha_i(1)\alpha_j(2) - \alpha_i(2)\alpha_j(1),\ 1 \leq i, j \leq 2I+1$
- Remaining $(2I+1)^2 - (2I+1)I = (2I+1)(I+1)$ are symmetric nuclear functions.

Diatomic molecule: rotational partition function

- For Σ_g^+ states and integral spin
- (2I+1)I antisymmetric nuclear spin functions couple with odd J
- (2I+1)(I+1) symmetric nuclear spin functions couple with even J
- For Σ_g^+ states and half integral spin
- (2I+1)I antisymmetric nuclear spin functions couple with even J
- (2I+1)(I+1) symmetric nuclear spin functions couple with odd J
- These results apply to polyatomic linear molecules as well.
- Homonuclear diatomic molecule with integral spin: $q_{rot,nucl}(T) = (I+1)(2I+1)\sum_{\text{J even}}(2J+1)e^{-\Theta_r J(J+1)/T} + I(2I+1)\sum_{\text{J odd}}(2J+1)e^{-\Theta_r J(J+1)/T}$
- Homonuclear diatomic molecule with half integer spin: $q_{rot,nucl}(T) = I(2I+1)\sum_{\text{J even}}(2J+1)e^{-\Theta_r J(J+1)/T} + (I+1)(2I+1)\sum_{\text{J odd}}(2J+1)e^{-\Theta_r J(J+1)/T}$

Diatomic molecule: rotational partition function

- If $\Theta_r \ll T \rightarrow \sum_{\text{J odd}}(2J+1)e^{-\Theta_r J(J+1)/T} \approx \sum_{\text{J even}}(2J+1)e^{-\Theta_r J(J+1)/T} \approx 1/2\sum_J(2J+1)e^{-\Theta_r J(J+1)/T} \approx 1/2\int_0^\infty(2J+1)e^{-\Theta_r J(J+1)/T}dJ = \frac{T}{2\Theta_r}$
- $q_{rot,nucl}(T) = \frac{(2I+1)^2T}{2\Theta_r} = q_{rot}(T)q_{nucl}$ where $q_{rot}(T) = \frac{T}{2\Theta_r}$ and $q_{nucl} = (2I+1)^2$
- $q_{rot}(T) \approx \frac{8\pi^2IkT}{\sigma h^2} \approx \frac{1}{\sigma}\sum_{J=0}^\infty(2J+1)e^{-\beta\bar{B}J(J+1)} \quad \Theta_r \ll T$
- Spin isomers of hydrogen
- Hydrogen with opposite nuclear spins, singlet hydrogen, is called para-Hydrogen.
- Hydrogen with parallel nuclear spins, triplet, is called ortho-Hydrogen.
- The para form is more stable than the ortho form by 1.06 kJ/mol.
- For $H_2 \quad q_{\text{nuc,rot}} = \sum_{\text{J even}}(2J+1)e^{-\Theta_r J(J+1)/T} + 3\sum_{\text{J odd}}(2J+1)e^{-\Theta_r J(J+1)/T}$

Diatomic molecule: rotational partition function

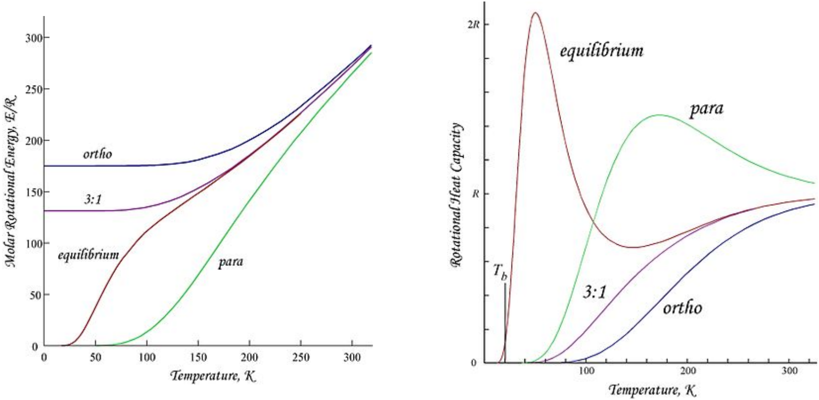
- For H_2 $\quad q_{\text{nuc,rot}} = \sum_{\text{J even}}(2J+1)e^{-\Theta_r J(J+1)/T} + e^{-1060J/molk/RT}3\sum_{\text{J odd}}(2J+1)e^{-\Theta_r J(J+1)/T}$
- The conversion between ortho and para hydrogen in the absence of a catalyst (e.g., Fe^{III} or activated charcoal) is very slow.
- $\frac{N_{ortho}}{N_{para}} = e^{-1060J/molk/RT}\frac{3\sum_{\text{J odd}}(2J+1)e^{-\Theta_r J(J+1)/T}}{\sum_{\text{J even}}(2J+1)e^{-\Theta_r J(J+1)/T}}$
- 

Figure: Energy and heat capacity for spin isomers of hydrogen taken from

Diatomic molecule: Thermodynamic functions

- Predict the H_2 heat capacity at very low temperatures.
- Try the same analysis on D_2.
- $E_{rot} = NkT[1 - \frac{\Theta_r}{3T} - \frac{1}{45}(\frac{\Theta_r}{T})^2 + \cdots]$
- $C_{V,rot} = Nk[1 + \frac{1}{45}(\frac{\Theta_r}{T})^2 + \cdots]$
- $S_{rot} = kT(\frac{\partial \ln q_{rot}}{\partial T})_{N,V} + k \ln q_{rot} = Nk[1 - \ln(\frac{\sigma\Theta_r}{T}) - \frac{1}{90}(\frac{\Theta_r}{T})^2 + \cdots]$
- Harmonic oscillator-rigid rotor approximation: $q(T) = (\frac{2\pi MkT}{h^2})^{3/2} V \frac{8\pi^2 IkT}{\sigma h^2} e^{-\beta h\nu/2}(1 - e^{-\beta h\nu})^{-1}\omega_{e1} e^{D_e/kT}$
- $\ln q(T) =$ $\frac{3}{2}\ln(\frac{2\pi MkT}{h^2}) + \ln V + \ln \frac{8\pi^2 IkT}{\sigma h^2} - \frac{h\nu}{2kT} - \ln(1 - e^{-\beta h\nu}) + \ln \omega_{e1} + D_e/kT$
- $\frac{E}{NkT} = \frac{5}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT}-1} - \frac{D_e}{kT}$
- $\frac{C_v}{Nk} = \frac{5}{2} + (\frac{h\nu}{kT})^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}$
- $\frac{S}{Nk} = \ln[\frac{2\pi MkT}{h^2}]^{3/2} \frac{Ve^{5/2}}{N} + \ln \frac{8\pi^2 IkTe}{\sigma h^2} + \frac{\frac{h\nu}{kT}}{e^{h\nu/kT}-1} - \ln(1 - e^{-h\nu/kT}) + \ln \omega_e$

Diatomic molecule: Thermodynamic functions

- $p = -NkT(\frac{\partial \ln q}{\partial V}) \rightarrow pV = NkT$
- $\mu = (\frac{\partial A}{\partial N})_{T,V} = -kT(\frac{\partial \ln Q}{\partial N})_{T,V} = -kT \ln \frac{q}{N} \rightarrow \frac{\mu^0(T)}{kT} = -\ln[\frac{2\pi MkT}{h^2}]^{3/2} - \ln \frac{kT}{P^0} - \ln \frac{8\pi^2 IkT}{\sigma h^2} + \frac{h\nu}{2kT} + \ln(1 - e^{-h\nu/kT}) - \frac{D_e}{kT}$
- Centrifugal distortion effects, anharmonic effects can be included.
- Σ state has zero total angular momentum. In other cases electronic and rotational angular momentum must be coupled. I.e., the electronic and rotational partition functions do not separate.
- At $T \gg \Theta_r$ electronic and rotational partition functions separate.

Classical statistical mechanics

- $q = \sum e^{-\beta(energy)} \to q_{class} \sim \int \cdots \int e^{-\beta H(p,q)} dpdq$
- Available (effective) number of states vs. available (effective) volume of phase space.
- For a monatomic ideal gas $H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$. Thus $q_{class} \sim \int \cdots \int e^{-\beta \frac{(p_x^2+p_y^2+p_z^2)}{2m}} dp_x dq_x dp_y dq_y dp_z dq_z = V[\int_0^\infty e^{-\beta p^2/2m} dp]^3 = (2\pi mkT)^{3/2} V$
- Compare with $q_{trans}(V,T) = (\frac{2\pi mkT}{h^2})^{3/2} V$
- For a linear rigid rotor $H = \frac{1}{2I}(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta})$
- $q_{rot} \sim \int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\phi \int_0^{2\pi} d\phi \int_0^{\pi} d\theta e^{-\frac{\beta}{2I}(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta})} = 8\pi^2 IkT$
- Compare with $q_{rot}(T) = \frac{T}{\theta_r} = \frac{8\pi^2 IkT}{h^2}$

Classical statistical mechanics

- For a harmonic oscillator $H = \frac{p^2}{2\mu} + \frac{k}{2}x^2$
- $q_{vib} \sim \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx e^{-\beta(\frac{p^2}{2\mu} + \frac{k}{2}x^2)} = \frac{kT}{\nu}$ where $\nu = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}$
- Compare with the high temperature limit $q_{vib}(T) = e^{-\beta h\nu/2} \int_0^{\infty} e^{-\beta h\nu n} dn = \frac{kT}{h\nu}$
- Conjecture: $q = \frac{1}{h^s} \int \cdots \int e^{-\beta H} \prod_{j=1}^{s} dp_j dq_j$
- A weighted area of h in phase space is equivalent to one weighted quantum mechanical state.
- This seem to be intimately related to space-momentum uncertainty relation, $\Delta x \Delta p \geq \frac{\hbar}{2}$. And to the Wigner transform

$$A_w(Q, P) = \int dZ \langle Q - \frac{Z}{2} | \hat{A} | Q + \frac{Z}{2} \rangle e^{iPZ/\hbar}$$

.

Classical statistical mechanics

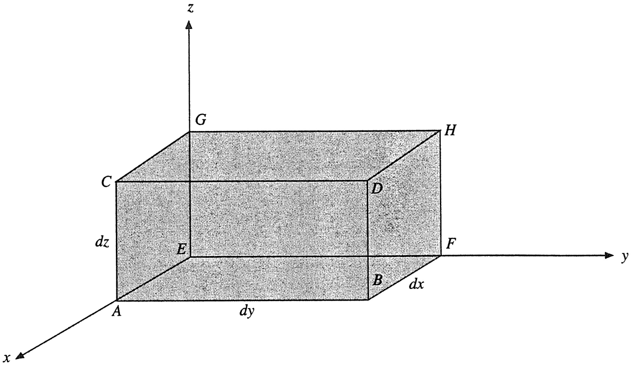
- $Q = \frac{q^N}{N!} = \frac{1}{N!}\prod_{j=1}^{N} \frac{1}{h^s} \int \cdots \int e^{-\beta H_j} \prod_{i=1}^{s} dp_{ji} dq_{ji}$
- $Q = \frac{1}{N! h^{sN}} \int \cdots \int e^{-\beta \sum_j H_j} \prod_{i=1}^{sN} dp_i dq_i = \frac{1}{N! h^{sN}} \int \cdots \int e^{-\beta H} \prod_{i=1}^{sN} dp_i dq_i$
- Conjecture: $Q = \frac{1}{N! h^{sN}} \int \cdots \int e^{-\beta H(p,q)} dpdq$
- For monatomic gas $H(p,q) = \frac{1}{2m} \sum_{j=1}^{N} (p_{xj}^2 + p_{yj}^2 + p_{zj}^2) + U(x_1, y_1, z_1, \cdots, x_N, y_N, z_N)$
- Thus $Q_{clas} = \frac{1}{N!} (\frac{2\pi mkT}{h^2})^{3N/2} Z_N$ where the classical configuration integral $Z_N = \int_V e^{-U(x_1, \cdots, z_N)/kT} dx_1 \cdots dz_N$
- For a molecule $H = H_{class} + H_{quant} \rightarrow q = q_{class} q_{quant}$ where $q_{class} = \frac{1}{h^s} \int e^{-H_{class}(p,q)/kT} dp_1 dq_1 \cdots dp_s dq_s$
- For entire system $H = H_{class} + H_{quant} \rightarrow Q = Q_{class} Q_{quant} = \frac{Q_{quant}}{h^{sN}} \int e^{-H_{class}(p,q)/kT} dp_{class} dq_{class}$

Phase space and the Liouville equation

- Each system is represented by a phase point in the phase space and a microcanonical ensemble is represented by a cloud of phase points in the phase space.
- Each phase point evolves according to $\dot{q}_j = \frac{\partial H}{\partial p_j}$ and $\dot{p}_j = -\frac{\partial H}{\partial q_j} \quad j = 1, 2, \cdots, l = sN$
- The postulate of equal a priori probabilities states that the density of points is uniform over the constant energy hyper surface.
- Number of systems that have phase point in dpdq about the point p, q at time t is f(p,q,t)dpdq. $\int \cdots \int f(p, q, t) dpdq = \mathcal{A}$
- Ensemble average of a function of coordinate and momenta, $\bar{\phi} = \frac{1}{\mathcal{A}} \int \cdots \int \phi(p, q) f(p, q, t) dpdq$
- Gibbs postulate equates $\bar{\phi}$ with the corresponding thermodynamic function.

Phase space and the Liouville equation

- The number of phase points inside the volume element $\delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l$ about the point $p_1, \cdots, p_l, q_1, \cdots, q_l$ is $\delta N = f(p_1, \cdots, p_l, q_1, \cdots, q_l, t)\delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l$
- Remember divergence: The flow going through a differential volume



per unit time is:

Phase space and the Liouville equation

- Consider a hyper rectangular differential volume $\delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l$ around the point $p_1, \cdots, p_l, q_1, \cdots, q_l$
- Number of phase points entering through the face perpendicular to the q_1 axis and located at q_1 is $f \dot{q}_1 \delta p_1 \cdots \delta p_l \delta q_2 \cdots \delta q_l$
- The number passing through the opposite face is $f(p_1, \cdots, p_l, q_1 + \delta q_1, \cdots, q_l, t)\dot{q}_1(p_1, \cdots, p_l, q_1 + \delta q_1, q_2, \cdots, q_l)\delta p_1 \cdots \delta p_l \delta q_2 \cdots \delta q_l =$ $(f + \frac{\partial f}{\partial q_1}\delta q_1)(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\delta q_1)\delta p_1 \cdots \delta p_l \delta q_2 \cdots \delta q_l$
- net flow in the q_1 direction $-(\frac{\partial f}{\partial q_1}\dot{q}_1 + f\frac{\partial \dot{q}_1}{\partial q_1})\delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l + \cdots$

Phase space and the Liouville equation

- Similarly, net flow in the p_1 direction is $-(\frac{\partial f}{\partial p_1}\dot{p}_1 + f\frac{\partial \dot{p}_1}{\partial p_1})\delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l + \cdots$
- Thus total flow of phase points is $-\sum_{j=1}^{l}(\frac{\partial f}{\partial q_j}\dot{q}_j + f\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial f}{\partial p_j}\dot{p}_j + f\frac{\partial \dot{p}_j}{\partial p_j})\delta p_1 \cdots \delta p_l \delta q_1 \cdots \delta q_l = \frac{d(\delta N)}{dt}$
- $\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} = 0$
- $\frac{\partial f}{\partial t} = -\sum_{j=1}^{l}(\frac{\partial f}{\partial q_j}\dot{q}_j + \frac{\partial f}{\partial p_j}\dot{p}_j) = -\sum_{j=1}^{l}(\frac{\partial f}{\partial q_j}\frac{\partial H}{\partial p_j} - \frac{\partial f}{\partial p_j}\frac{\partial H}{\partial q_j})$
- In terms of Poisson bracket, $\{A, B\} = \sum_{j=1}^{l}(\frac{\partial A}{\partial q_j}\frac{\partial B}{\partial p_j} - \frac{\partial B}{\partial q_j}\frac{\partial A}{\partial p_j})$, $\frac{\partial f}{\partial t} + \{f, H\} = 0$
- In terms of the Liouville operator, $\frac{\partial f}{\partial t} + iLf = 0$.
- Equivalent to Hamiltonian equations of motion.
- $\frac{\partial f}{\partial t} + \sum_{j=1}^{N}\frac{\vec{P}_j}{m_j}\cdot\nabla_{r_j} f + \sum_{j=1}^{N}\vec{F}_j\cdot\nabla_{p_j} f = 0.$

Phase space and the Liouville equation

- Liouville equation is equivalent to $\frac{df}{dt} = 0$.
- Principle of the conservation of density in phase space: density in the neighborhood of any moving phase point is a constant along the trajectory of that point. Implies that $f(p, q; t) = f(p_0, q_0; t_0)$.
- $p = p(p_0, q_0; t)$ and $q = q(p_0, q_0; t)$.
- The existence and uniqueness theorem implies that no two trajectories can pass through the same point, i.e. they never cross.
- Conservation of extension in phase space: $\delta p \delta q = \delta p_0 \delta q_0$ or Jacobian of (p,q) to (p_0, q_0) is unity.
- In general if we are given two sets of momenta and their conjugate coordinate $dq_1 dq_2 \cdots dq_{3n} dp_1 \cdots dp_{3n} = dQ_1 \cdots dQ_{3n} dP_1 \cdots dP_{3n}$ e.g., $dp_x dp_y dp_z dxdydz = dp_r dp_\theta dp_\phi dr d\theta d\phi$. This is a reason for using momenta and not velocities for describing classical systems.

Equipartition of energy

- $\bar{\epsilon} = \frac{\int\cdots\int He^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s}{\int\cdots\int e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s}$
- $H(p_1, p_2, \cdots, q_s) = \sum_{j=1}^{m} a_j p_j^2 + \sum_{j=1}^{n} b_j q_j^2 + H(p_{m+1}, \cdots, p_s, q_{n+1}, \cdots, q_s)$
- $\bar{\epsilon} = \frac{\int\cdots\int(\sum_{j=1}^{m} a_j p_j^2 + \sum_{j=1}^{n} b_j q_j^2 + H(p_{m+1}, \cdots, p_s, q_{n+1}, \cdots, q_s)e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s}{\int\cdots\int e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s} = \frac{\sum_{j=1}^{m} a_j \int\cdots\int p_j^2 e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s + \sum_{j=1}^{n} b_j \int\cdots\int q_j^2 e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s}{\int\cdots\int e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s} + \frac{\int\cdots\int H(p_{m+1}, \cdots, p_s, q_{n+1}, \cdots, q_s)e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s}{\int\cdots\int e^{-\beta H} dq_1\cdots dq_s dp_1\cdots dp_s}$
- Principle of the equipartition of energy state that each of the quadratic terms contribute kT/2 to the energy and k/2 to the heat capacity.
- E.g., for monatomic ideal gas
  $H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \quad E = 3kT/2 \quad C_v = 3k/2$
- a_j and b_j can be functions of the variables not involved in the quadratic terms, i.e., $p_{m+1}, \cdots, p_s; q_{n+1}, \cdots, q_s$.
- E.g., for a linear rigid rotor $H = \frac{1}{2I}(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}), \quad E = kT, \quad C_v = k.$

Equipartition of energy

- Equipartition is a classical concept thus a small $\Delta\epsilon/kT$ between levels is required for its validity.
- For a diatomic molecule $C_v = \frac{5}{2}Nk + \frac{Nk(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T}-1)^2}$
- The most general form of the equipartition theorem states that under suitable assumptions, for a physical system with Hamiltonian energy function H and degrees of freedom $\mathrm{x_n}$, the following equipartition formula holds in thermal equilibrium for all indices m and n: $\left\langle x_m \frac{\partial H}{\partial x_n} \right\rangle = \delta_{mn} k_B T$.
- The general equipartition theorem is an extension of the virial theorem, which states that $\left\langle \sum_k q_k \frac{\partial H}{\partial q_k} \right\rangle = \left\langle \sum_k p_k \frac{\partial H}{\partial p_k} \right\rangle = \left\langle \sum_k p_k \frac{dq_k}{dt} \right\rangle = -\left\langle \sum_k q_k \frac{dp_k}{dt} \right\rangle$

Ideal polyatomic gas

- Start by applying the adiabatic or Born-Oppenheimer approximation thus separating electronic and nuclear degrees of freedom.
- Then $H_{nuc} = H_{trans} + H_{int} \quad \epsilon_{nuc} = \epsilon_{trans} + \epsilon_{int} \quad q_{nuc} = q_{trans} q_{int}$ where $q_{trans} = [\frac{2\pi MkT}{h^2}]^{3/2} V$
- $Q(N, V, T) = \frac{q_{trans}^N q_{int}^N}{N!}$
- 3n coordinates are required to specify the location of all atoms. 3 coordinates are to specify the center of mass while 2 or 3 (for linear or non-linear molecule) are needed to specify its orientation. The remaining 3n -5 or 3n-6 internal coordinates are needed for specifying the relative position of the nuclei.
- Use a rigid rotor-harmonic oscillator approximation to write $Q(N, V, T) = \frac{(q_{trans} q_{rot} q_{vib} q_{elec} q_{nucl})^N}{N!}$
- Consider all atoms separated in their ground electronic state as the zero of energy

Vibrational partition function

- Potential energy of the molecule is a function of $\alpha = 3n - 6$ $(3n-5)$ relative coordinate. At equilibrium configuration its gradient is zero.
- $U(\vec{r}) = U(\vec{r_0}) + \sum_{i,j=1}^{\alpha} \frac{1}{2}(r_i - r_{i_0})(\frac{\partial^2 U}{\partial r_i \partial r_j})_{r_0}(r_j - r_{j_0}) + \cdots$
- $\frac{\partial^2 U}{\partial r_i \partial r_j}$ are elements of a matrix called Hessian which at the point r_0 equals k_{ij}.
- If the Hessian is positive definite at x, then U attains an isolated local minimum at x. If the Hessian is negative definite at x, then U attains an isolated local maximum at x. If the Hessian has both positive and negative eigenvalues then x is a saddle point for U. Otherwise the test is inconclusive.
- Assuming molecular vibrations to be small we truncate this expansion at the third term.
- $U(\vec{r}) = \sum_{i,j=1}^{\alpha} \frac{k_{ij}}{2}(r_i - r_{i_0})(r_j - r_{j_0})$.
- The problem is α coupled harmonic oscillators.

Vibrational partition function

- To practically deal with this problem assume all molecular motions as vibrations and write $M\frac{d^2}{dt^2}X = -KX$ where $X = \begin{bmatrix} x_1 \\ \vdots \\ x_{3n} \end{bmatrix}$, $M = \begin{bmatrix} m_1 & \cdots & 0 \\ 0 & \ddots & 0 \\ 0 & \cdots & m_{3n} \end{bmatrix}$, $K = \begin{bmatrix} k_{1,1} & \cdots & k_{1,3n} \\ \vdots & \ddots & \vdots \\ k_{3n,1} & \cdots & k_{3n,3n} \end{bmatrix}$.
- To solve this equation, we put it into complex form: $\frac{d^2}{dt^2}Z = -M^{-1}KZ$
- Try solutions of the form $Z^{(j)} = A^{(j)}e^{i\omega^{(j)}t}$.
- Yields eigenvalue equation $M^{-1}KA^{(j)} = (\omega^{(j)})^2A^{(j)}$.
- $M^{-1/2}KM^{-1/2}(M^{1/2}A^{(j)}) = (\omega^{(j)})^2(M^{1/2}A^{(j)})$
- A real symmetric $3n \times 3n$ matrix has $3n$ real eigenvalues and correspondingly $3n$ real orthogonal eigenvectors.

Vibrational partition function

- Thus there are $3n$ eigenmodes characterized by eigenfrequency $\omega^{(j)}$ and eigenvector $M^{1/2}A^{(j)}$, where $(A^{(k)})^T M A^{(j)} = \delta_{kj}$.
- This is the origin of mass weighted coordinate in computational chemistry.
- Each molecular position can be described as $Q_j M^{1/2} A^{(j)}$
- Coordinate corresponding to the set of smallest frequencies represent center of mass motion while the next set of small frequencies represent rotational motion.
- $H_{vib} = -\sum_{j=1}^{\alpha} \frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_j^2} + \sum_{j=1}^{\alpha} \frac{k_j}{2} Q_j^2$
- $\epsilon = \sum_{j=1}^{\alpha} (n_j + 1/2) h\nu_j \quad n_j = 0, 1, 2, \cdots$, where $\nu_j = \frac{1}{2\pi}(k_j)^{1/2}$
- $q_{vib} = \Pi_{j=1}^{\alpha} \frac{e^{-\Theta_{\nu j}/2T}}{(1-e^{-\Theta_{\nu j}/T})}$, where $\Theta_{\nu j} = \frac{h\nu_j}{k_B}$
- $E_{vib} = Nk \sum_{j=1}^{\alpha} (\Theta_{\nu j}/2 + \frac{\Theta_{\nu j} e^{-\Theta_{\nu j}/T}}{(1-e^{-\Theta_{\nu j}/T})})$
- $C_{V,vib} = Nk \sum_{j=1}^{\alpha} [(\frac{\Theta_{\nu j}}{T})^2 \frac{e^{-\Theta_{\nu j}/T}}{(1-e^{-\Theta_{\nu j}/T})^2}]$

Rotational partition function

- For linear molecules $\epsilon_j = \frac{J(J+1)h^2}{8\pi^2 I} \quad \omega_J = 2J+1 \quad J = 0, 1, 2, \cdots$
  where moment of inertia $I = \sum_{j=1}^{n} m_j d_j^2$
- $q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{T}{\sigma \Theta_r}$
-

$$I_{xx} = \sum_{j=1}^{\alpha} m_j[(y_j - y_{cm})^2 + (z_j - z_{cm})^2]$$

$$I_{yy} = \sum_{j=1}^{\alpha} m_j[(x_j - x_{cm})^2 + (z_j - z_{cm})^2]$$

$$I_{zz} = \sum_{j=1}^{\alpha} m_j[(x_j - x_{cm})^2 + (y_j - y_{cm})^2]$$

- Also $I_{xz} = \sum_{j=1}^{\alpha} m_j[(x_j - x_{cm})(z_j - z_{cm})]$

Rotational partition function

- There is a particular set of coordinates called the principal axes passing through the center of mass of the body such that the inertia matrix become diagonal.
- Moments of inertia about these axes I_{XX}, I_{YY}, I_{ZZ} are called the principal moments of inertia. They are customarily denoted by I_A, I_B, I_C
- principal axes often coincide with molecular axis of symmetry.
- Moments of inertia about principal axes are often found experimentally and tabulated in terms of rotational constants as $\bar{A} = \frac{h}{8\pi I_A c} \quad \bar{B} = \frac{h}{8\pi I_B c} \quad \bar{C} = \frac{h}{8\pi I_C c}$ in units of cm^{-1}.
- $I_A = I_B = I_C$: Spherical top, e.g., CH_4, CCl_4.
- $I_A = I_B \neq I_C$: Symmetric top, e.g., CH_3Cl, NH_3.
- $I_A \neq I_B \neq I_C$: Asymmetric top, e.g., H_2O, NO_2.

Rotational partition function

- For a spherical top: $\epsilon_j = \frac{J(J+1)\hbar^2}{2I} \quad \omega_J = (2J+1)^2 \quad J = 0, 1, 2, \cdots$
- $q_{rot} = \frac{1}{\sigma} \int_0^\infty (2J+1)^2 e^{-J(J+1)\hbar^2/2IkT} dJ$
- Symmetry number σ is the number of ways a molecule can be rotated into itself. For H_2O, $\sigma = 2$, for NH_3 $\sigma = 3$, for CH_4 $\sigma = 12$, for C_2H_4 $\sigma = 4$ and for C_6H_6 $\sigma = 12$.
- Symmetry number avoids over counting indistinguishable configurations in phase space.
- σ is the number of pure rotational elements in the point group of a nonlinear molecule.
- $q_{rot} = \frac{1}{\sigma} \int_0^\infty 4J^2 e^{-J^2\hbar^2/2IkT} dJ = \frac{\pi^{1/2}}{\sigma} (\frac{8\pi^2 IkT}{h^2})^{3/2}$
- Any molecule with an $n \geq 3$-fold axis of symmetry is at least a symmetric top.

Rotational partition function

- For a symmetric top $\epsilon_{JK} = \frac{\hbar^2}{2}\{\frac{J(J+1)}{I_A} + K^2(\frac{1}{I_C} - \frac{1}{I_A})\} \quad J = 0, 1, 2, \cdots ; \; K = -J, -J+1, \cdots, J-1, J \quad \omega_{JK} = 2J+1.$
- J is a measure of total rotational angular momentum of the molecule.
- K is component of rotational angular momentum along the axes C of symmetric top.
- $q_{rot} = \frac{1}{\sigma}\Sigma_{j=0}^{\infty}(2J+1)e^{-J(J+1)\alpha_A}\Sigma_{K=-J}^{J}e^{-(\alpha_C-\alpha_A)K^2} \quad \alpha_j = \frac{\hbar^2}{2I_j kT}.$
- $q_{rot} = \frac{\pi^{1/2}}{\sigma}(\frac{8\pi^2 I_A kT}{h^2})(\frac{8\pi^2 I_C kT}{h^2})^{1/2}$
- For a symmetric top: $K = \frac{p_\theta^2}{2I_A} + \frac{(p_\phi - p_\psi\cos\theta)^2}{2I_A\sin^2\theta} + \frac{p_\psi^2}{2I_c}$
- Asymmetric top is the most common type of molecule.
- Hamiltonian for an asymmetric top $H = \frac{1}{2I_A\sin^2\theta}[(p_\phi - p_\psi\cos\theta)\cos\psi - p_\theta\sin\theta\sin\psi]^2 + \frac{1}{2I_B\sin^2\theta}[(p_\phi - p_\psi\cos\theta)\sin\psi + p_\theta\sin\theta\cos\psi]^2 + \frac{1}{2I_c}p_\psi^2$
- $0 \le \theta \le \pi \qquad 0 \le \phi \le 2\pi \qquad 0 \le \psi \le 2\pi$ are Euler angles.

Polyatomic thermodynamic functions

- For asymmetric top
  $$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_B kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_C kT}{h^2}\right)^{1/2} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}$$
- $E_{rot} = \frac{3}{2}NkT \quad C_{V,rot} = \frac{3}{2}Nk \quad S_{rot} = Nk\ln[\frac{\pi^{1/2}}{\sigma}(\frac{T^3e^3}{\Theta_A\Theta_B\Theta_C})^{1/2}]$
- Linear polyatomic molecule:
  $$q = \left(\frac{2\pi MkT}{h^2}\right)^{3/2} V\frac{T}{\sigma\Theta_r}\left\{\prod_{J=1}^{\alpha}\frac{e^{-\Theta_{\nu j}/2T}}{1-e^{-\Theta_{\nu j}/T}}\right\}\omega_{e1}e^{D_e/kT}$$
- $$-\frac{A}{NkT} = \ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] + \ln\left(\frac{T}{\sigma\Theta_r}\right) - \sum_{j=1}^{\alpha}\left[\frac{\Theta_{\nu j}}{2T} + \ln(1-e^{-\Theta_{\nu j}/T})\right] + \frac{D_e}{kT} + \ln\omega_{e1}$$
- $$\frac{E}{NkT} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{\alpha}\left[\frac{\Theta_{\nu j}}{2T} + \frac{\Theta_{\nu j}/T}{e^{\Theta_{\nu j}/T}-1}\right] - \frac{D_e}{kT}$$
- $$\frac{C_v}{Nk} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{\alpha}(\Theta_{\nu j}/T)^2\frac{e^{\frac{\Theta_{\nu j}}{T}}}{(1-e^{\Theta_{\nu j}/T})^2}$$
- $$\frac{S}{Nk} = \ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right] + \ln\left(\frac{Te}{\sigma\Theta_r}\right) + \sum_{j=1}^{\alpha}\left[\frac{\Theta_{\nu j}/T}{e^{\Theta_{\nu j}/T}-1} - \ln(1-e^{-\Theta_{\nu j}/T})\right] + \ln\omega_{e1}$$
- pV=NkT

Polyatomic thermodynamic functions

- For nonlinear polyatomic molecules:
  $q = (\frac{2\pi MkT}{h^2})^{3/2} V \frac{\pi^{1/2}}{\sigma}(\frac{T^3}{\Theta_A\Theta_B\Theta_C})^{1/2}\{\Pi_{J=1}^{\alpha}\frac{e^{-\Theta_{\nu j}/2T}}{1-e^{-\Theta_{\nu j}/T}}\}\omega_{e1}e^{D_e/kT}$
- $-\frac{A}{NkT} = \ln[(\frac{2\pi MkT}{h^2})^{3/2}\frac{Ve}{N}] + \ln(\frac{\pi^{1/2}}{\sigma}(\frac{T^3}{\Theta_A\Theta_B\Theta_C})^{1/2}) - \Sigma_{j=1}^{\alpha}[\frac{\Theta_{\nu j}}{2T} + \ln(1-e^{-\Theta_{\nu j}/T})] + \frac{D_e}{kT} + \ln\omega_{e1}$
- $\frac{E}{NkT} = \frac{3}{2}+\frac{3}{2}+\Sigma_{j=1}^{\alpha}[\frac{\Theta_{\nu j}}{2T}+\frac{\Theta_{\nu j}/T}{e^{\Theta_{\nu j}/T}-1}] - \frac{D_e}{kT}$
- $\frac{C_v}{Nk} = \frac{3}{2}+\frac{3}{2}+\Sigma_{j=1}^{\alpha}(\Theta_{\nu j}/T)^2\frac{e^{\frac{\Theta_{\nu j}}{T}}}{(1-e^{\Theta_{\nu j}/T})^2}$
- $\frac{S}{Nk} = \ln[(\frac{2\pi MkT}{h^2})^{3/2}\frac{Ve^{5/2}}{N}] + \ln(\frac{\pi^{1/2}e^{3/2}}{\sigma}(\frac{T^3}{\Theta_A\Theta_B\Theta_C})^{1/2}) + \Sigma_{j=1}^{\alpha}[\frac{\Theta_{\nu j}/T}{e^{\Theta_{\nu j}/T}-1} - \ln(1-e^{-\Theta_{\nu j}/T})] + \ln\omega_{e1}$
- pV=NkT
- $D_0 = D_e - \Sigma_j\frac{1}{2}h\nu_j$
- Residual entropy for CO and CH_3D.

Hindered rotation

- Rotation about a single bond.
- $U = \frac{1}{2} V_0 (1 - \cos 3\phi)$
- $-\frac{h^2}{8\pi^2 I_r} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{2} V_0 (1 - \cos 3\phi)\psi = \epsilon\psi$
- I_r is effective moment of inertia.
- At extremes of temperature this motion is a vibration or a rotation.
- Numerically solving Schrodinger equation for different values of V_0, one can tabulate ϵ as a function of V_0/kT.
- Partition function and thus thermodynamic properties can be derived from tables of ϵ. Comparing calculated and experimental values of thermodynamic functions one can deduce V_0.

Chemical equilibrium

- $\nu_A' A(g) + \nu_B' B(g) \rightleftarrows \nu_c' C(g) + \nu_D' D(g)$.
- $\lambda = \frac{N_{A_0} - N_A}{\nu_A'} = \frac{N_{B_0} - N_B}{\nu_B'} = \frac{N_C - N_{C_0}}{\nu_C'} = \frac{N_D - N_{D_0}}{\nu_D'}$
- $\nu_c C(g) + \nu_D D(g) + \nu_A A(g) + \nu_B B(g) = 0$
- $dN_j = \nu_j d\lambda$
- $dA = -SdT - pdV + \sum_j \mu_j dN_j$. At constant volume and temperature $dA = \sum_j \mu_j dN_j = (\sum_j \mu_j \nu_j) d\lambda$.
- At equilibrium $(\frac{\partial A}{\partial \lambda})_{T,V} = 0 = \sum_j \mu_j \nu_j = \nu_c \mu_C + \nu_D \mu_D + \nu_A \mu_A + \nu_B \mu_B$.
- $Q(N_A, N_B, N_C, N_D, V, T) = Q_A(N_A, V, T) Q_B(N_B, V, T) Q_C(N_C, V, T) Q_D(N_D, V, T) = \frac{q_A(V,T)^{N_A}}{N_A!} \frac{q_B(V,T)^{N_B}}{N_B!} \frac{q_C(V,T)^{N_C}}{N_C!} \frac{q_D(V,T)^{N_D}}{N_D!}$
- $\mu_i = -kT(\frac{\partial \ln Q}{\partial N_i})_{N_{j \neq i}, V, T} = -kT(\frac{\partial \ln Q_i}{\partial N_i})_{N_{j \neq i}, V, T} = -kT(\frac{\partial \ln(q_i^{N_i}/N_i!)}{\partial N_i})_{N_{j \neq i}, V, T} = -kT \ln \frac{q_i(V,T)}{N_i}$

Chemical equilibrium

- Derive the equilibrium constant expression.
- $\frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}}$
- $K_c(T) = \frac{\rho_C^{\nu_C} \rho_D^{\nu_D}}{\rho_A^{\nu_A} \rho_B^{\nu_B}} = \frac{(q_C/V)^{\nu_C}(q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A}(q_B/V)^{\nu_B}}$
- $p_j = \rho_j kT$ thus $K_p(T) = \frac{p_C^{\nu_C} p_D^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}} = (kT)^{\nu_C+\nu_D-\nu_A-\nu_B} K_c(T)$
- E.g., Association of alkali metal vapor,
  $2Na(g) \rightleftarrows Na_2(g) \quad K_p(T) = \frac{p_{dimer}}{p^2_{monomer}} = (kT)^{-1}\frac{(q_{Na_2}/V)}{(q_{Na}/V)^2}$
- $q_{Na}(T,V) = (\frac{2\pi m_{Na} kT}{h^2})^{3/2} V q_{elec}(T)$
  $q_{Na_2}(T,V) = (\frac{2\pi m_{Na_2} kT}{h^2})^{3/2} V \frac{8\pi^2 IkT}{2h^2} \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} \omega_{1e} e^{D_e/kT} =$
  $(\frac{2\pi m_{Na_2} kT}{h^2})^{3/2} V \frac{T}{2\Theta_r}(1-e^{-\beta h\nu})^{-1} e^{D_0/kT}$
- $\frac{q_{Na}}{V} = ? \qquad \frac{q_{Na_2}}{V} = ?$

Chemical equilibrium

- Isotopic exchange reaction, $H_2 + D_2 \rightleftarrows 2HD$. Born-Oppenheimer approximation implies that H_2, D_2, HD have the same internuclear potential, k and D_e.
- $K(T) = K_p(T) = K_c(T) = \frac{\rho_{HD}^2}{\rho_{H_2}\rho_{D_2}} = \frac{p_{HD}^2}{p_{H_2}p_{D_2}} = \frac{q_{HD}^2}{q_{H_2}q_{D_2}} =$

$$\frac{(\frac{2\pi m_{HD}kT}{h^2})^3(\frac{T}{\Theta_{r,HD}})^2(\frac{e^{-\Theta_{\nu,HD}/2T}}{1-e^{-\Theta_{\nu,HD}/T}})^2 e^{2D_e/kT}}{(\frac{2\pi m_{H_2}kT}{h^2})^{3/2}(\frac{2\pi m_{D_2}kT}{h^2})^{3/2}(\frac{T^2}{4\Theta_{r,H_2}\Theta_{r,D_2}})(\frac{e^{-\Theta_{\nu,H_2}/2T}}{1-e^{-\Theta_{\nu,H_2}/T}})(\frac{e^{-\Theta_{\nu,D_2}/2T}}{1-e^{-\Theta_{\nu,D_2}/T}})e^{2D_e/kT}} =$$

$$\frac{m_{HD}^3}{(m_{H_2}m_{D_2})^{3/2}} \frac{4\Theta_{r,H_2}\Theta_{r,D_2}}{\Theta_{r,HD}^2} \frac{(1-e^{-\Theta_{\nu,H_2}/T})(1-e^{-\Theta_{\nu,D_2}/T})}{(1-e^{-\Theta_{\nu,HD}/T})^2} e^{-(2\Theta_{\nu,HD}-\Theta_{\nu,H_2}-\Theta_{\nu,D_2})/2T}$$

- $\frac{\Theta_{\nu,HD}}{\Theta_{\nu,H_2}} = \frac{\nu_{HD}}{\nu_{H_2}} = (\frac{\mu_{H_2}}{\mu_{HD}})1/2$. Thus $\theta_{v,HD} = (\frac{3}{4})^{1/2}\theta_{v,H_2}$.
- For this reaction $K(T) = 4(1.06)exp\frac{-77.7}{T}$.

Chemical equilibrium

- For diatomic isotopic exchange reactions like ${}^{14}N_2 +{}^{15}N_2 \rightleftarrows 2{}^{14}N^{15}N$: $K(T) = 4(1+\frac{\Delta^2}{8M^2})e^{-\Delta^2\Theta_{M,vib/32M^2T}}$, where Δ is the mass difference between isotopes and M is mass of the heavier isotope
- $CH_4 + DBr \rightleftarrows CH_3D + HBr \quad K(T) = \frac{\rho_{CH_3D}\rho_{HBr}}{\rho_{CH_4}\rho_{DBr}} = \frac{q_{CH_3D}q_{HBr}}{q_{CH_4}q_{DBr}} =$

  $$\frac{\sigma_{CH_4}\sigma_{DBr}}{\sigma_{CH_3D}\sigma_{HBr}}(\frac{M_{CH_3D}M_{HBr}}{M_{CH_4}M_{DBr}})^{3/2}\frac{I_{HBr}}{I_{DBr}}\frac{(I_AI_BI_C)^{1/2}_{CH_3D}}{(I_AI_BI_C)^{1/2}_{CH_4}}\frac{q_{vib,CH_3D}q_{vib,HBr}}{q_{vib,CH_4}q_{vib,DBr}}$$

- $\frac{q_{vib,CH_3D}q_{vib,HBr}}{q_{vib,CH_4}q_{vib,DBr}} \approx \exp[-\sum_j \frac{\Theta^{CH_3D}_{\nu,j}+\Theta^{HBr}_{\nu,j}-\Theta^{CH_4}_{\nu,j}-\Theta^{DBr}_{\nu,j}}{2T}]$
- $\frac{\sigma_{CH_4}\sigma_{DBr}}{\sigma_{CH_3D}\sigma_{HBr}} = \frac{12\times 1}{3\times 1} = 4$

Chemical equilibrium

- Teller—Redlich product rule for isotopically substituted compounds: $(\frac{M'}{M})^{3/2}\frac{I'}{I} = \prod_{i=1}^{n}(\frac{m_i'}{m_i})^{3/2}\prod_{j=1}^{3n-5}\frac{\nu_j'}{\nu_j}$ for linear molecules and $(\frac{M'}{M})^{3/2}\frac{(I_A'I_B'I_C')^{1/2}}{(I_AI_BI_C)^{1/2}} = \prod_{i=1}^{n}(\frac{m_i'}{m_i})^{3/2}\prod_{j=1}^{3n-6}\frac{\nu_j'}{\nu_j}$
- Diatomic molecules: $H_2 + I_2 \rightleftarrows 2HI$
- $K(T) = \frac{(q_{HI}/V)^2}{(q_{H_2}/V)(q_{I_2/V})} = \frac{q_{HI}^2}{q_{H_2}q_{I_2}} =$ $(\frac{m_{HI}^2}{m_{H_2}m_{I_2}})^{3/2}(\frac{4\Theta_{r,H_2}\Theta_{r,I_2}}{\Theta_{r,HI}^2})\frac{(1-e^{-\Theta_{\nu,H_2}/T})(1-e^{-\Theta_{\nu,I_2}/T})}{(1-e^{-\Theta_{\nu,HI}/T})^2}\exp\frac{(2D_0^{HI}-D_0^{H_2}-D_0^{I_2})}{RT}$
- Compare with $d(\ln K) = -\frac{\Delta H}{R}d(\frac{1}{T})$
- Polyatomic molecules: $H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O \qquad K_p(T) = \frac{q_{H_2O}/V}{(kT)^{1/2}(q_{H_2}/V)(q_{O_2}/V)^{1/2}}$
- $\frac{q_{H_2}}{V} = (\frac{2\pi m_{H_2}kT}{h^2})^{3/2}(\frac{T}{2\Theta_{r,H_2}})(1-e^{-\Theta_{\nu,H_2}/T})^{-1}e^{D_{0,H_2}/RT}$

Chemical equilibrium

- $\frac{q_{O_2}}{V} = (\frac{2\pi m_{O_2} kT}{h^2})^{3/2}(\frac{T}{2\Theta_{r,O_2}})(1 - e^{-\Theta_{\nu,O_2}/T})^{-1} 3 e^{D_{0,O_2}/RT}$
- $\frac{q_{H_2O}}{V} = (\frac{2\pi m_{H_2O} kT}{h^2})^{3/2} \frac{\pi^{1/2}}{\sigma}(\frac{T^3}{\Theta_{A,H_2O}\Theta_{B,H_2O}\Theta_{C,H_2O}})\Pi_{j=1}^{3}(1 - e^{-\Theta_{\nu j,H_2O}/T})^{-1} e^{D_{0,H_2O}/RT}$
- Restricted internal rotation: Ethylene-Ethane equilibrium
- $C_2H_4 + H_2 \rightleftarrows C_2H_6$, one should find the value of V_0
- For the equilibrium $\sum_j \nu_j \mu_j = 0$ substitute $\mu(T,p) = \mu_0(T) + kT \ln p$ to get $\ln K_p = -\frac{\Delta\mu_0}{kT}$
- $\mu = -kT\ln(\frac{q}{N}) = -kT\ln[(\frac{q}{V})\frac{V}{N}] = -kT\ln[(\frac{q}{V})kT] + kT\ln p$
- $\mu_0(T) = -kT\ln[(\frac{q}{V})kT]$ depends on the unit of pressure.
- $q(V,T) = q_{trans}(V,T) q_{rot}(T) q_{vib}(T) q_{elec}(T)$

Chemical equilibrium

- Zero of energy conventions enters in calculation of $q_{elec}(T) = \omega_{e1} e^{-\epsilon_{e1}/kT} + \omega_{e2} e^{-\epsilon_{e2}/kT} + \cdots = e^{D_e/kT}(\omega_{e1} + \omega_{e2} e^{-\Delta\epsilon_{12}/kT}) = e^{D_e/kT} q^0_{elec}(T)$.
- $q(V,T) = q_{trans}(V,T) q_{rot}(T) q_{vib}(T) q^0_{elec}(T) e^{D_e/kT} = q_{trans}(V,T) q_{rot}(T) \{\prod_j (1 - e^{-\Theta_{\nu j}/T})^{-1}\} q^0_{elec}(T) e^{(D_e - 1/2 \sum_j h\nu_j)/kT} = q_{trans}(V,T) q_{rot}(T) q^0_{vib}(T) q^0_{elec}(T) e^{D_0/kT}$
- $q(V,T) = q^0(V,T) e^{D_0/kT} = q^0(V,T) e^{\epsilon^0_0/kT}$ partition as the product of an internal part $q^0(V,T)$ and a scaling factor accounting for the arbitrary zero of energy.
- $\mu - \epsilon^0_0 = -kT \ln[(\frac{q^0}{V})kT] + kT \ln p$
- $\lim_{T \to 0} \mu = \epsilon^0_0$
- Convention: Energy of an element is zero at 0°K if it is in the physical state characteristic of 25°C and 1 bar. For a molecule ϵ^0_0 represents the energy of a molecule at 0°K relative to the elements, i.e., heat of formation.

Chemical equilibrium

- $G^0 - E_0^0 = -RT \ln[(\frac{q^0}{V})kT]$ where E_0^0 is the standard free energy at 0°K.
- $E_0^0 = H_0^0 = G_0^0$
- $(G^0 - E_0^0)/T$ varies slower with T compared to $(G^0 - E_0^0)$.
- $-R \ln K_p = \frac{\Delta E_0^0}{T} + \Delta(\frac{G^0 - E_0^0}{T})$
- $S_{298}^0 = (\frac{H_{298} - E_0^0}{T}) - (\frac{G_{298}^0 - E_0^0}{T})$

Class presentations

Mr. Javadi	Crystals, 11-1:11-3	15 Tir 11 am
Mr. Hadi	Chemical Equilibrium	16 Tir 10:15 am
Mr. Moradi	Crystals, 11-4:11-6	17 Tir 10:10 am
Ms. Mirzakhani	Quantum Statistics, 10-1:10-4	19 Tir 2:45 pm
Mr. Sharbati	Quantum Statistics, 10-5:10-7	20 Tir 2:45 pm
Ms. Madadi	Simple theories of liquids	20 Tir 4 pm
Mr. Mohammadvand	Polymers	22 Tir 3 pm
Mr. Hashemi	Ideal systems in electric and magnetic fields	23 Tir 3 pm
Mr. Hajilou	Imperfect gases	24 Tir 3:15 pm
Mr. Zamani	Distribution functions in monatomic liquids	24 Tir 4:30 pm

Table of physico-chemical constants

Quantity	Symbol	Value (SI units)
atomic mass constant	$m_u = 1\ u$	$1.6605389 \times 10^{-27}$ kg
Avogadro's number	N_A, L	6.0221417×10^{23}
Boltzmann constant	$k = R/N_A$	$1.3806505 \times 10^{-23} JK^{-1}$
Faraday constant	$F = N_A e$	96485.338 Cmol^{-1}
gas constant	R	8.314472 JK^{-1}mol^{-1}, 0.08205 L atm mol^{-1}K^{-1}, 8.20573 m^3 atm mol^{-1}K^{-1}
molar Planck constant	$N_A h$	3.99031×10^{-10} J s mol^{-1}
electric constant (vacuum permittivity)	$\varepsilon_0 = 1/(\mu_0 c^2)$	$8.854187817 \times 10^{-12}$ Fm^{-1}

Table of physico-chemical constants

Quantity	Symbol	Value (SI units)
magnetic constant (vacuum permeability)	μ_0	$12.56637061 \times 10^{-7}$ NA^{-2}
Newtonian constant of gravitation	G	6.67408×10^{-11} m^{3}kg^{-1}s^{-2}
Planck constant	h	$6.626070040 \times 10^{-34}$ Js
reduced Planck constant	$\hbar$	$1.054571800 \times 10^{-34}$ Js
speed of light in vacuum	c	299792458 m/s
electronic charge	e	1.60219×10^{-19}C
electron mass	m_e	9.10956×10^{-31}Kg