

Canonical Ensemble II [tsc12]

This module presents further applications of the canonical ensemble to systems of noninteracting degrees of freedom. Surprisingly diverse physical phenomena can be inferred from the canonical partition function.

Vibrational heat capacities of solids:

The lowest-energy configuration of a macroscopic system of N identical atoms or molecules is a perfect lattice. This is the equilibrium state at $T = 0$. It has zero entropy.

Heat input $dQ = CdT$ causes lattice vibrations. In the following we study vibrational heat capacities C in successively improved approximations.¹

There are many other contributions to the heat capacity of solids originating in the magnetism of electrons or the motion of electrons in conductors, for example, which will be discussed in due course.

Theory of Dulong and Petit:

Considers an array of N classical 3D harmonic oscillators with identical frequencies, representing atoms bound to a rigid lattice by a harmonic force. The Dulong-Petit result for the vibrational heat capacity,

$$C = 3Nk_B,$$

is T -independent and is calculated in [tex74] in the microcanonical ensemble and in [tex78] in the canonical ensemble.

The main insufficiency of the Dulong-Petit result is that C does not approach zero in the low-temperature limit, in violation of the third law and in contradiction to empirical evidence.

Theory of Einstein:

Considers instead an array of N quantum 3D harmonic oscillators with identical frequencies, again representing atoms bound to a rigid lattice by a harmonic force. The Einstein result for the vibrational heat capacity,

$$C = \left(\frac{\Theta_E}{T}\right)^2 \frac{3Nk_B e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}, \quad k_B \Theta_E = \hbar\omega,$$

¹What is measured in solids, for the most part, is C_p rather than C_V , with p being the ambient air pressure. It is common to drop the subscript p in this context.

approaches zero exponentially in the low- T limit, $C \sim e^{-\Theta_E/T}$, and connects with the Dulong-Petit result, $C = 3Nk_B$, at high T .

Einstein's result is worked out in [tex75] for the microcanonical ensemble and in [tex82] for the canonical ensemble. Its main insufficiency is that it contradicts experimental evidence, which suggests $C \sim T^3$ at low T .

Atoms interacting via harmonic forces:

Harmonic interaction forces are bilinear in the atomic positions q_i .

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{ij} A_{ij} q_i q_j = \sum_{i=1}^{3N} \left[\frac{P_i^2}{2m} + \frac{1}{2} m \omega_i^2 Q_i^2 \right].$$

The coupling constants are elements of what is called the dynamical matrix $\{A_{ij}\}$, which is real and symmetric.

The second equation results from a (diagonalizing) transformation to normal-mode coordinates. In this context the normal modes are named phonons.

At this stage, we have arrived at a classical theory which has the same flaws as that of Dulong and Petit. Quantization of $3N$ independent oscillators of arbitrary normal-mode frequencies ω_i is straightforward:

$$H = \sum_{i=1}^{3N} \hbar \omega_i \left(n_i + \frac{1}{2} \right), \quad n_i = 0, 1, 2, \dots$$

The Helmholtz free energy (in generalization of the result in [tex82]) reads:

$$A = \frac{1}{2} \sum_{i=1}^{3N} \hbar \omega_i + k_B T \sum_{i=1}^{3N} \ln (1 - e^{-\beta \hbar \omega_i}).$$

Theory of Debye:

The normal modes consist, in general, of multiple bands of (acoustic and optical) phonons.²

In Debye's theory, the normal modes are replaced by a single branch of sound waves with linear dispersion, $\omega = ck$, as is expected in a continuous isotropic elastic medium.

²Optical phonons have nonzero frequencies in the the long-wavelength limit. Their role in low-temperature heat capacities is insignificant.

- Total number of modes: $3N$ (as in original lattice model).
- Density of modes in k -space: $\frac{V}{(2\pi)^3}$.
- Number of polarizations: 3 (2 transverse, 1 longitudinal).
- Number of modes in interval $d\omega = cdk$ (use $d^3k = 4\pi k^2 dk$):

$$n(\omega)d\omega = (3)\frac{V}{(2\pi)^3}(4\pi)\frac{\omega^2}{c^2}\frac{d\omega}{c} = \frac{3V}{2\pi^2c^3}\omega^2d\omega.$$

- Cutoff at Debye frequency ensures $3N$ modes:

$$\frac{3V}{2\pi^2c^3}\int_0^{\omega_D}d\omega\omega^2 = 3N \Rightarrow \omega_D^3 = \frac{6N\pi^2c^3}{V}.$$

- Density of modes rewritten: $n(\omega) = \frac{9N}{\omega_D^3}\omega^2$.
- Integral expression for Helmholtz potential:

$$A(T, N) = \frac{9N\hbar}{2\omega_D^3}\int_0^{\omega_D}d\omega\omega^3 + \frac{9Nk_B T}{\omega_D^3}\int_0^{\omega_D}d\omega\omega^2\ln(1 - e^{-\beta\hbar\omega}).$$

The resulting vibrational heat capacity is calculated in [tex83] and does show the experimentally observed $\sim T^3$ behavior as $T \rightarrow 0$ (see [tsl29]):

$$C = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{\Theta_D/T}dx\frac{x^4e^x}{(e^x - 1)^2}, \quad \Theta_D = \hbar\omega_D/k_B.$$

Paramagnetism of localized magnetic dipoles:

Paramagnetic salts contain localized ions with permanent magnetic dipole moments associated with unpaired electron spins.

No interaction potential energy and no kinetic energy is associated with the magnetic dipole moments. Hence the internal energy vanishes identically, $U \equiv 0$, which implies that $C_M \equiv 0$.

The microstate of a system of magnetic dipoles,

$$\mathbf{m}_i, \quad i = 1, \dots, N,$$

is specified by their orientation relative to an external magnetic field \mathbf{H} . The Hamiltonian expressing the interaction between moments and field,

$$\mathcal{H} = -\sum_{i=1}^N \mathbf{m}_i \cdot \mathbf{H} = -H \sum_{i=1}^N m_i^z,$$

produces the co-called the Zeeman energy. It favors alignment of the magnetic moments with the magnetic field.

The localized moments can be treated as distinguishable particles. They do not need to have a definite permutation symmetry.

The canonical partition function, in this case leads to the Gibbs potential:

$$Z_N = \text{Tr} e^{-\beta \mathcal{H}}, \quad G(T, H, N) = -k_B T \ln Z_N.$$

Macroscopic equilibrium states in the canonical ensemble are characterized by magnetization,

$$M(T, H, N) \doteq \sum_{i=1}^N \langle \mathbf{m}_i \rangle = \sum_{i=1}^N \langle m_i^z \rangle = - \left(\frac{\partial G}{\partial H} \right)_{T, N}.$$

The thermodynamic equation of state, $M = M(T, H, N)$, in combination with the caloric equations of state, $C_M \equiv 0$, inferred from empirical information, can be used to reconstruct the Gibbs free energy (see [tsc4]).

Langevin paramagnetism:

The magnetic moment is described as a 3-component vector of unit length:

$$\mathbf{m}_i = (m_i^x, m_i^y, m_i^z) = (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i).$$

Each \mathbf{m}_i represents one degree of freedom described by one pair of canonical coordinates $q_i = \phi_i$, $p_i = \cos \theta_i$.

- Partition function evaluated in spherical coordinates:

$$Z_N = \left(4\pi \frac{\sinh(\beta H)}{\beta H} \right)^N.$$

- Gibbs free energy: $G(T, H, N) = -k_B T \ln Z_N$.

- Magnetization: $M \doteq - \left(\frac{\partial G}{\partial H} \right)_{T, N} = NL(y)$, $y \doteq \beta H$.

- Langevin function: $L(y) \doteq \coth(y) - \frac{1}{y}$.

- A more systematic and complete analysis, which includes the isothermal susceptibility χ_T and the heat capacity C_H , is worked out in [tex84].

Two-level system:

The magnetic moment originates from a single electron spin. This is a two-level system: $E_{\pm} = \pm \frac{1}{2}H$ (in scaled units). Two-level systems have many applications unrelated to paramagnetism.

- Partition function: $Z_N = \left[2 \cosh \left(\frac{1}{2} \beta H \right) \right]^N$.
- Gibbs free energy: $G(T, H, N) = -k_B T \ln Z_N$.
- Magnetization: $M \doteq - \left(\frac{\partial G}{\partial H} \right)_{T,N} = \frac{N}{2} \tanh \left(\frac{1}{2} \beta H \right)$.
- A more systematic and complete analysis, which includes the isothermal susceptibility χ_T and the heat capacity C_H , is worked out in [tex85].

Brillouin paramagnetism:

The magnetic moment in this case originates from an effective spin of quantum number $s = \frac{1}{2}, 1, \frac{3}{2}, \dots$. The magnetic moment in appropriate units is quantized as follows:

$$m_i^z = -s, -s + 1, \dots, s - 1, s.$$

The canonical partition function is calculated in exercise [tex86].

- Partition function: $Z_N = \left[\frac{\sinh \left(\left(s + \frac{1}{2} \right) x \right)}{\sinh \left(\frac{1}{2} x \right)} \right]^N$, $x \doteq \frac{H}{k_B T}$.
- Gibbs free energy: $G(T, H, N) = -k_B T \ln Z_N$.
- Magnetization: $M \doteq - \left(\frac{\partial G}{\partial H} \right)_{T,N} = M_{\text{sat}} B_s(y)$, $y = sx$.
Saturation value: $M_{\text{sat}} = Ns$.
Rescaled magnetization: $\tilde{M} \doteq \frac{M_{\text{sat}}}{s} B_s(y)$.
- Brillouin function: $B_s(y) \doteq \frac{2s + 1}{2J} \coth \left(\frac{2s + 1}{2s} y \right) - \frac{1}{2s} \coth \left(\frac{y}{2s} \right)$.
Quantum limit: $B_{\frac{1}{2}}(y) = \tanh(y)$.
Classical limit: $B_{\infty}(y) = \coth(y) - \frac{1}{y}$.
- A more systematic and complete analysis is worked out in [tex86].

Fluctuations in a magnetic system:

Consider a system of N interacting magnetic moments with components m_i in the direction of an external magnetic field of magnitude H .

Hamiltonian: $\mathcal{H} = \mathcal{H}_{int} - HM$.

Canonical partition function: $Z_N = \text{Tr} e^{-\beta\mathcal{H}}$.

Gibbs free energy: $G(T, H, N) = -k_B T \ln Z_N$.

Magnetisation: $M = \sum_{i=1}^N \langle m_i \rangle = \frac{1}{Z_N} \text{Tr} [M e^{-\beta\mathcal{H}}] = \beta^{-1} \frac{\partial}{\partial H} \ln Z_N$.

Enthalpy: $E = U - HM = \langle \mathcal{H} \rangle = \frac{1}{Z_N} \text{Tr} [\mathcal{H} e^{-\beta\mathcal{H}}] = -\frac{\partial}{\partial \beta} \ln Z_N$.

Energy fluctuations and heat capacity [tex109]:

$$\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Z_N = k_B T^2 C_H.$$

Magnetisation fluctuations and susceptibility [tex109]:

$$\langle M^2 \rangle - \langle M \rangle^2 = \beta^{-2} \frac{\partial^2}{\partial H^2} \ln Z_N = k_B T \chi_T.$$

Gases with internal degrees of freedom

Dilute molecular gases are still very well approximated by the classical ideal gas regarding their translational motion, but their internal degrees of freedom (rotations and vibrations) must be taken into account.

It is reasonable to assume that translational (T), rotational (R), and vibrational (V) degrees of freedom are independent of each other.³

$$H = \sum_{i=1}^N \left[H_T^{(i)} + H_R^{(i)} + H_V^{(i)} \right] \Rightarrow Z_N = \frac{1}{N!} \tilde{Z}^N, \quad \tilde{Z} = \tilde{Z}_T \tilde{Z}_R \tilde{Z}_V.$$

Quantum effects in the rotational and vibrational degrees of freedom are attributes of individual molecules and will be analyzed here in what follows.

Quantum effects in the translational degrees of freedom are related to the permutation symmetry of particles. They will be analyzed later and separately for bosons and fermion.

³The justification is, in part, based on the empirical evidence that in most molecules rotational degrees of freedom are thermally activated at much lower temperatures than vibrational degrees of freedom.

Translational motion (classical):

A summary statement of results derived previously reads as follows [tex76]:

$$H_T^{(i)} = \frac{p_i^2}{2m}, \quad \tilde{Z}_T = \frac{V}{\lambda_T^3}, \quad \lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}, \quad C_V^{(T)} = \frac{3}{2} N k_B.$$

Quantum statistics comes into play when the average distance between molecules, $\sim (V/N)^{1/3}$, is comparable to the thermal wavelength λ_T .

Rotational motion (classical):

Here we use resources from classical mechanics (rigid-body dynamics). We start with the Hamiltonian for a symmetric top, representing a molecule with one symmetry axis that is at least threefold.

▷ NH₃ (multi-atomic molecule):

The rotational motion has 3 degrees of freedom. The canonical coordinates are the Euler angles θ, ϕ, ψ with conjugate momenta p_θ, p_ϕ, p_ψ . The inertia tensor with uniaxially symmetry has principal moments $I_1 = I_2, I_3$.

$$\text{Hamiltonian: } H_R^{(i)} = \frac{p_{i\theta}^2}{2I_1} + \frac{p_{i\psi}^2}{2I_3} + \frac{(p_{i\phi} - p_{i\psi} \cos \theta_i)^2}{2I_1 \sin^2 \theta_i}.$$

Ranges: $0 \leq \theta_i \leq \pi$, $0 \leq \phi_i, \psi_i \leq 2\pi$, $-\infty < p_{i\theta}, p_{i\phi}, p_{i\psi} < +\infty$.

$$\Rightarrow \tilde{Z}_R = \frac{1}{\pi \hbar^3} \sqrt{(2\pi I_1 k_B T)^2 (2\pi I_3 k_B T)} \Rightarrow C_V^{(R)} = \frac{3}{2} N k_B \quad [\text{tex87}].$$

▷ HCl (two-atomic heteronuclear molecule):

In this case we have $I_3 \ll I_1 = I_2$. The rotation about the molecular axis is frozen out due to a quantum effect discussed later.

$$\text{Hamiltonian: } H_R^{(i)} = \frac{p_{i\theta}^2}{2I_1} + \frac{p_{i\phi}^2}{2I_1 \sin^2 \theta_i}, \quad 0 \leq \theta_i \leq \pi, \quad 0 \leq \phi_i \leq 2\pi.$$

$$\Rightarrow \tilde{Z}_R = \frac{2I_1 k_B T}{\hbar^2} \Rightarrow C_V^{(R)} = N k_B \quad [\text{tex88}].$$

▷ N₂ (two-atomic homonuclear molecule):

The restricted range, $0 \leq \phi \leq \pi$, of one variable owing to the reflection symmetry affects the entropy, but not the heat capacity. This change does affect the entropy but not the heat capacity [tex88].

Rotational motion (quantum):

Consider a two-atomic molecule.

Angular momentum operator: \mathbf{L} .

Hamiltonian operator: $H_R = \frac{1}{2I} \mathbf{L}^2$.

Energy levels: $E_{lm} = \frac{l(l+1)\hbar^2}{2I}$; $l = 0, 1, 2, \dots$; $m = -l, -l+1, \dots, l$.

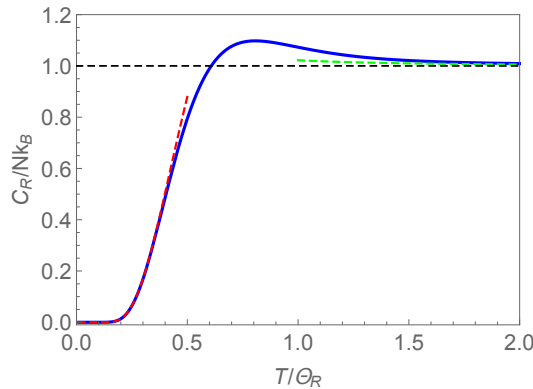
Degeneracy: $(2l+1)$ -fold.

Partition function: $\tilde{Z}_R = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} e^{-\beta E_{lm}} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)\hbar^2/2I}$.

Characteristic temperature: $k_B \Theta_R = \frac{\hbar^2}{2I}$.

Low- T heat capacity [tex89]: $C_R(T) \simeq 12Nk_B \left(\frac{\Theta_R}{T}\right)^2 e^{-2\Theta_R/T} \quad : T \ll \Theta_R$.

High- T asymptotics [tex90]: $C_R \simeq Nk_B \left[1 + \frac{1}{45} \left(\frac{\Theta_R}{T}\right)^2 + \dots \right] \quad : T \gg \Theta_R$.



Vibrational motion (quantum):

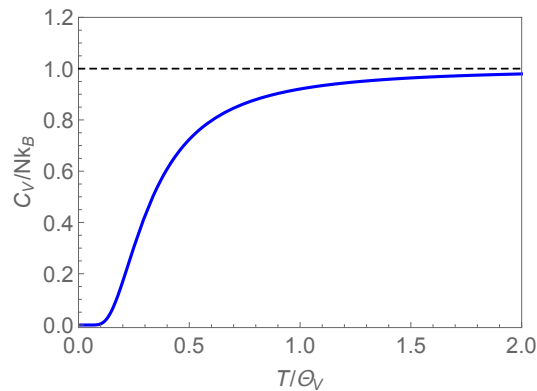
Low-amplitude vibrational modes are, by default, normal harmonic modes. Consider a molecule with f normal modes, each expressed by a pair (q_l, p_l) of canonical coordinates.

Hamiltonian: $H_V = \sum_{l=1}^f \left(\frac{p_l^2}{2m_l} + \frac{1}{2} m_l \omega_l^2 q_l^2 \right)$.

Partition functions: $\tilde{Z}_V = \prod_{l=1}^f \left[\frac{1}{e^{\beta \hbar \omega_l} - 1} \right]$.

Characteristic temperatures: $k_B \Theta_V^{(l)} = \hbar \omega_l$.

Heat capacity: $C_V = \sum_{l=1}^f N k_B \left[\frac{2T}{\Theta_V^{(l)}} \sinh \left(\frac{\Theta_V^{(l)}}{2T} \right) \right]^{-2} \xrightarrow{T \gg \Theta_V^{(l)}} f N k_B$.

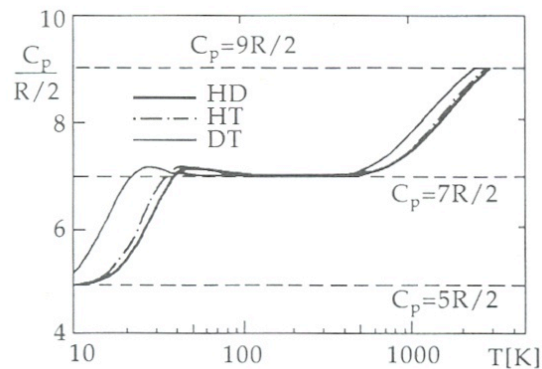


In general, vibrational modes require much higher temperatures to be activated than rotational modes.

Typically: $\Theta_R = \frac{\hbar^2}{2Ik_B} \sim 10\text{K}$, $\Theta_V = \frac{\hbar \omega_l}{k_B} \sim 1000\text{K}$

Comparison of rotational and vibrational heat capacities of hydrogen molecules with different isotopes:

H: ^1H (hydrogen), D: ^2H (deuterium), T: ^3H (tritium)



[image from Greiner et al. 1995]

Fine structure:

If the atomic ground state has zero *orbital* angular momentum ($l = 0$) and nonzero *spin* angular momentum ($s \neq 0$), the entropy acquires an additive constant, $\Delta S = Nk_B \ln(2s + 1)$. The heat capacity remains unaffected.

In the presence of an external magnetic field, this system is a paramagnetic gas. The thermodynamics of dilute paramagnetic gases are the theme of [tex22] and [tex133].

If the atomic ground state has $l \neq 0$ and $s \neq 0$, then the L - S coupling produces a fine-structure splitting of the ground-state degeneracy:

$$\tilde{Z}_{FS} = \sum_j (2j + 1)e^{-\beta\epsilon_j}, \quad |l - s| \leq j \leq l + s,$$

where j is the quantum number of the total angular momentum. If the lowest level has $j = j_0$, then the entropy of the atomic gas increases by

$$\Delta S = Nk_B \ln \frac{(2s + 1)(2l + 1)}{(2j_0 + 1)}$$

over a temperature range $0 < k_B T \lesssim \Delta E_{LS}$, where ΔE_{LS} measures the total L - S level splitting.

The contribution to the heat capacity, $C_V^{(FS)}$, is a function of T that rises from zero exponentially, exhibits a smooth maximum at $k_B T \sim \Delta E_{LS}$, and then dips back down to zero algebraically.⁴

The functional dependence of $C_V^{(FS)}$ on T is very similar to that of the heat capacity of a Langevin paramagnet as analyzed in [tex85] and [tex86].

Orthohydrogen and parahydrogen:

Molecular hydrogen H_2 consists of two pairs of identical fermions: one pair of electrons and one pair of protons. The electronic and nuclear wave functions must both be antisymmetric.

The electronic ground state has a symmetric space part and an antisymmetric spin part (spin singlet). Electronic excited states have energies high above the range considered here.

Nuclear wave functions with symmetric spin part and antisymmetric space part or vice versa are energetically close to each other.

⁴In practical reality, atomic gases with $l \neq 0, s \neq 0$ tend to form molecules or condense at temperatures far above $k_B T \sim \Delta E_{LS}$.

The energy levels of the nuclear wave function is dominated by its space part, specifically by rotational modes with orbital quantum numbers $l = 0, 1, 2, \dots$. Vibrational modes have much higher energies.

Two nuclear spin isomers of molecular hydrogen H_2 .

- *Orthohydrogen*: Nuclear spin part is symmetric (spin triplet) and nuclear space part is antisymmetric (odd l).
- *Parahydrogen*: Nuclear spin part is antisymmetric (spin singlet) and nuclear space part is symmetric (even l).

At high T , the H_2 gas at equilibrium contains 75% orthohydrogen and 25% parahydrogen. The 3:1 ratio is a reflection of the nuclear spin degeneracy.

The lowest parahydrogen level is lower than the lowest orthohydrogen level by $\Delta E/k_B = \hbar^2/k_B I \simeq 175\text{K}$. Conversion is slow in the absence of catalysts.

Cooling and condensing hydrogen may leave the majority of molecules in a metastable state. The transition to equilibrium at low T releases significant amounts of energy.

Rotational (R) factors of the canonical partition function under two distinct conditions:

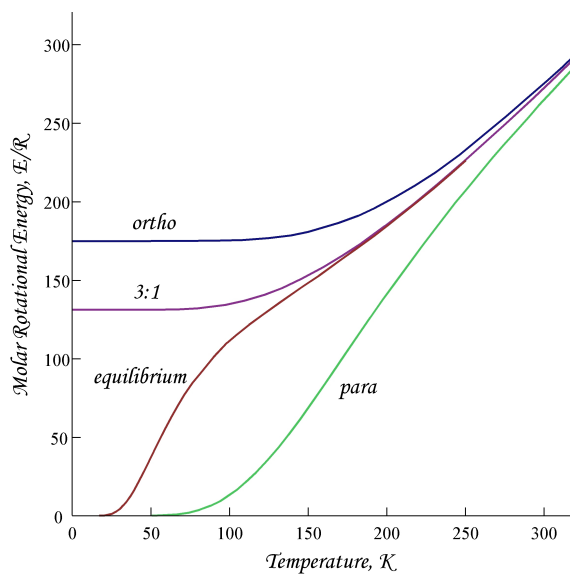
$$\tilde{Z}_R^{eq} = (\tilde{Z}_o + \tilde{Z}_p)^N, \quad \tilde{Z}_R^{3:1} = (\tilde{Z}_o)^{3N/4} (\tilde{Z}_p)^{N/4},$$

$$\tilde{Z}_o = 3 \sum_{\text{odd } l} (2l + 1) e^{-\beta l(l+1)\hbar^2/2I}, \quad \tilde{Z}_p = \sum_{\text{even } l} (2l + 1) e^{-\beta l(l+1)\hbar^2/2I}$$

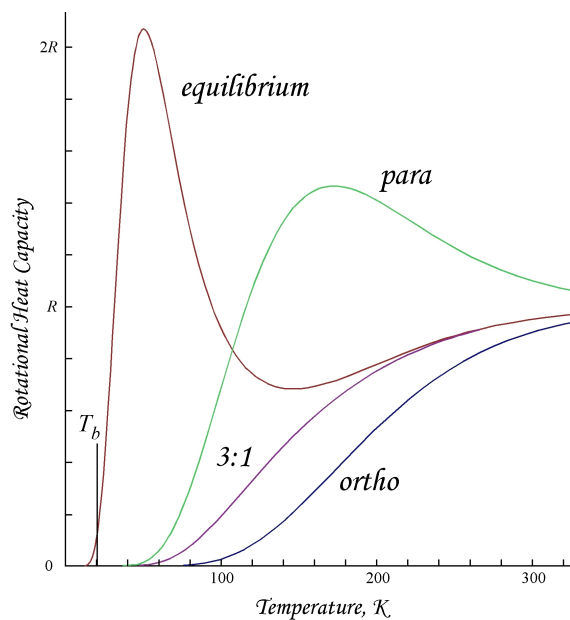
- The equilibrium expression {eq} is adequate when temperature is varied slowly and in the presence of a catalyst that facilitates conversion between isomers.
- The metastable state represented by expression {3:1} is adequate at low T when the cooling faster is than the pace of equilibration, which is very slow in the absence of a catalysts.

Storage of liquid hydrogen in the metastable is dangerous. Inadvertant conversion releases significant amounts of energy, which may increase the pressure beyond the strength of the container.

Plot of internal energy versus temperature for the two isomers separately, for the metastable {3:1} mixture, and for the stable {eq} mixture.



Plot of rotational heat capacity versus temperature for the two isomers separately, for the metastable {3:1} mixture, and for the stable {eq} mixture. The boiling temperature is marked on the lower left.



[images from Wikipedia]