

Orthohydrogen and parahydrogen [tln81]

Molecular hydrogen (H_2) comes in two (nuclear) spin isomers.

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 much higher energies.

Nuclear wave functions with symmetric spin part and antisymmetric space part or vice versa are energetically close to each other. The space part is described by rotational modes with orbital quantum numbers $l = 0, 1, 2, \dots$. Vibrational modes have much higher energies.

- **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.

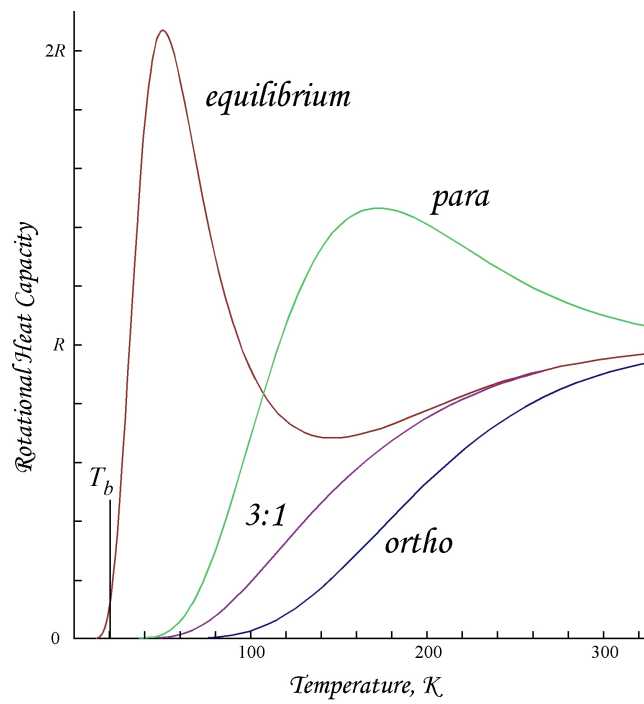
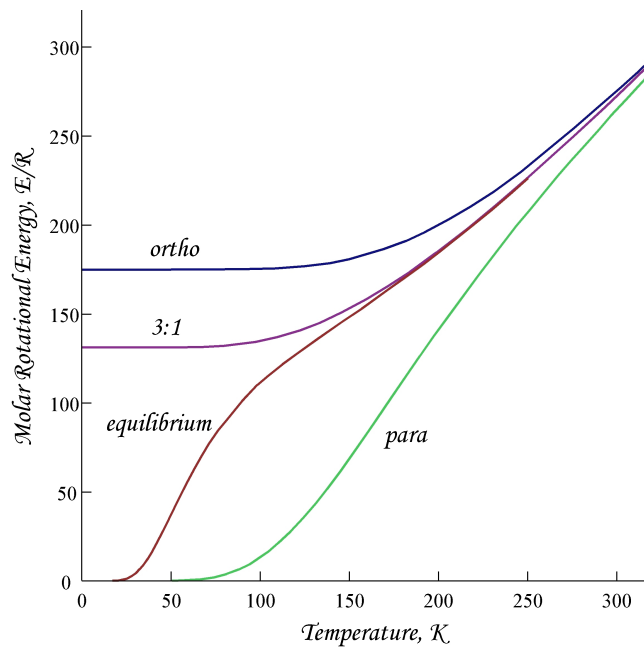
The lowest parahydrogen level is lower than the lowest orthohydrogen level by $\Delta E/k_B = \hbar^2/k_B I \simeq 175\text{K}$. Conversion is slow in the absence of catalysts. Cooling and condensing hydrogen may leave the majority of molecules in a metastable state. The transition to equilibrium at low T releases significant amounts of energy.

Rotational factors of canonical partition function under two conditions:

- {eq} Slow temperature variation with catalysts present.
- {3:1} More rapid temperature reduction with catalysts absent.

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

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



[from Wikipedia]