

a) Hydrogen is a diatomic homonuclear molecule and the nuclear part of its wavefunction must obey the Pauli exclusion principle since the protons obey Fermi-Dirac statistics.

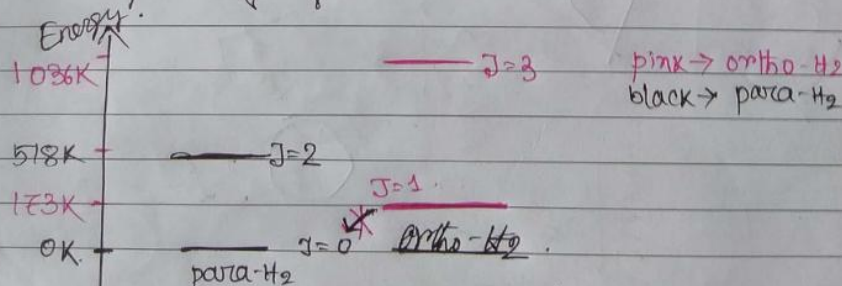
The Pauli principle implies that, the space behaviour of the wave function for the nuclear motion in the molecule has the opposite symmetry from the spin part, e.g., in Orthohydrogen where the spins are aligned and the spin wave function is symmetric, the wave function for the nuclear motion in the molecule must be anti-symmetric under the exchange of the two protons whereas, in parahydrogen the wave function must be symmetric. Hence, ortho-hydrogen and parahydrogen have space wave functions of opposite symmetry character and therefore entirely different energy levels.

Due to symmetry reasons, the rotational ground state of hydrogen can only be occupied by parahydrogen molecule, while the lowest possible state for ortho hydrogen is the first excited rotational state.

$$\psi \rightarrow (-1)^L$$

if, $L = \text{odd} \Rightarrow \psi \rightarrow -1 \Rightarrow$ anti-symmetric wavefunction (ortho-H)
 if, $L = \text{even} \Rightarrow \psi \rightarrow +1 \Rightarrow$ symmetric wavefunction (para-H)

So, only odd and even L values are allowed in the ortho and para hydrogen case.



b) Given that energy, $E(L) = \frac{\hbar^2}{2I} (L(L+1))$.
 So, conventionally rotational partition function can be written as,

$$\tilde{Z}_{rot} = \sum_{L=0}^{\infty} g_L e^{-E_L/k_B T}$$

However as long as these two isomers are not in equilibrium. So,

$$\tilde{Z}_{para} = \sum_{\text{even } L} (2L+1) e^{-L(L+1)\hbar^2/2IK_B T}$$

$$\tilde{Z}_{ortho} = 3 \sum_{\text{odd } L} (2L+1) e^{-L(L+1)\hbar^2/2IK_B T}$$

* The '3' factor in the partition function for orthohydrogen accounts for the spin degeneracy associated with +1 spin state.

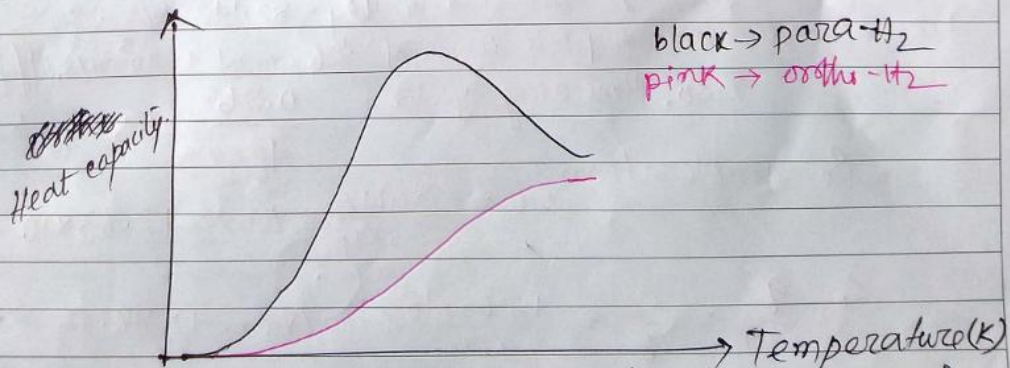
$$U_{rot} = RT^2 \left(\frac{\partial \ln \tilde{Z}_{rot}}{\partial T} \right) \quad \& \quad C_{v,rot} = \frac{\partial U_{rot}}{\partial T}$$

$$U_{para} = RT^2 \frac{\partial}{\partial T} \left(\ln \left[\sum_{\text{even } L} (2L+1) e^{-L(L+1)\hbar^2/2IK_B T} \right] \right)$$

$$C_{v,para} = \frac{\partial U_{para}}{\partial T} = \frac{\partial}{\partial T} \left[RT^2 \frac{\partial}{\partial T} \ln \left[\sum_{L=\text{even}} (2L+1) e^{-L(L+1)\hbar^2/2IK_B T} \right] \right]$$

Similarly for ortho we can calculate it.

$C_{v,para}$ & $C_{v,ortho}$ are shown in the following figure.



* At low temp^s para-H₂ exists and high temp^s ortho-H₂ exists.