Thermodynamics: Classical to Statistical
Prof. Sandip Paul
Department of Chemistry
Indian Institute of Technology Guwahati
Lecture - 30
Nuclear spin statistics; Ortho and para hydrogens

Nuclear Spins Statistics

Quantum Mechanics requires that the total wave function be either symmetric (for bosons) or antisymmetric (for fermions) with respect to exchange of any two identical nuclei. The total wave function ψ_{total} must be symmetric if nuclei have integer spins (bosons) or antisymmetric if nuclei have half integer spins (fermions).

Homonuclear diatomic oxygen molecule

We will discuss elaborately about nuclear spins statistics for homonuclear diatomic molecule like oxygen. T

The ^{16}O nuclei have spin I = 0, so these are bosons.

Therefore, ψ_{total} for O_2 molecule is symmetric and this is an even function.

Now, we know, ψ_{total} consists of five different degrees of freedoms.

$$\psi_{total} = \psi_{trans}\ \psi_{rot}\ \psi_{vib}\ \psi_{elec}\ \psi_{nucl}$$

We need to examine symmetry of each one of these wave functions for oxygen molecule upon exchange of two ^{16}O nuclei. (Note that we are permutating nuclei not atoms.)

1. ψ_{trans} depends only on the center of mass coordinate of the molecule. So, this function is not affected by exchange of two ^{16}O nuclei. We will not consider this as it will not affect ψ_{total}.

2. ψ_{vib} depends only on distance between two ^{16}O nuclei so this coordinate is not affected by exchange of two ^{16}O nuclei. So, we will not consider this also.

3. The ground electronic state of O_2 is $^3\sum_g^-$. This term symbol suggests that the electronic wave function is antisymmetric, so this is odd function with respect to exchange of two ^{16}O nuclei.

4. For ψ_{rot}, we consider rigid rotor model, where the rotational wave functions are spherical harmonics with rotational quantum number J.

- ψ_{rot} (J=0, 2, 4, 6, …) is symmetric with respect to exchange of two ^{16}O nuclei. Hence this is even function.
- ψ_{rot} (J=1, 3, 5, 7, …) is antisymmetric with respect to exchange of two ^{16}O nuclei.

5. Since ^{16}O nucleus has nuclear spin, I = 0, ^{16}O nuclei are bosons.

   The number of nuclear spin states is

- (2I +1)(I + 1) for symmetric (even) nuclear spin states and they are termed as “ortho”
- (2I +1) I for antisymmetric (odd) nuclear spin states and we call them “para”.

So when I = 0, we get

- 1 symmetric nuclear spin states state or ortho
- 0 antisymmetric nuclear spin state or para.

Only ortho oxygen is possible. Therefore, ψ_{nucl}, for oxygen is even, because there is no antisymmetric nuclear spins state for O_2 molecule.

Now,

$$\psi_{total} = \psi_{elec} \times \psi_{rot} \times \psi_{nucl}$$

$$\text{Even} = \text{odd} \times \text{odd} \times \text{even}$$

In order to make ψ_{total} even, ψ_{rot} has to be odd, which suggests J =1, 3, 5 are possible. So only in ground state of oxygen molecule only odd rotational levels are possible.

Therefore, for O_2 molecule in ground electronic state,

$$q_{rot} = \sum_{J=1,3,5,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

$$q_{rot} = \frac{1}{2}\int_{J=0}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}} dJ$$

(2J + 1) is the degeneracy factor) and the half term appears due to symmetry number.

Ortho and para hydrogen

The molecules of hydrogen can exist in two forms depending on the spins on the two hydrogen nuclei. If both the nuclear spins are parallel, the molecule is called ortho hydrogen and if the spins are antiparallel, it is referred to as para hydrogen.

This nomenclature comes from the di-substituted benzene. If we consider a ortho di-substituted benzene, both spins are parallel, while for para di-substituted benzene, the spins are antiparallel.

The spin on hydrogen nucleus, I = 1/2.

The presence of nuclear spins leads to very interesting consequences for the populations of the rotational states and on a macroscopic scale, has consequences on measured entropies and heat capacities as well.

The total partition function for H_2 can be written

$$q_{total} = q_{trans}\ q_{rot}\ q_{vib}\ q_{elec}\ q_{nucl}$$

and from here we get,

$$\psi_{total} = \psi_{trans}\ \psi_{rot}\ \psi_{vib}\ \psi_{elec}\ \psi_{nucl}$$

As we have discussed that we can neglect ψ_{trans} and ψ_{vib}, so

$$\psi_{total} = \psi_{elec} \times \psi_{rot} \times \psi_{nucl}$$

The ground electronic state for H_2 is ${}^1\sum_g^+$ which is an even function.

Since each nuclei has 1/2 integral spin, ψ_{total} is an odd function.

Now, ψ_{rot} can be even or can be odd, so there are two possibilities,

$$\psi_{total} = \psi_{elec} \times \psi_{rot} \times \psi_{nucl}$$

$$\text{odd} = \text{even} \times \text{odd} \times \text{even}$$

$$\text{odd} = \text{even} \times \text{even} \times \text{odd}$$

Combining the nuclear spin and the rotational parts, we see that, the product $\psi_{rot} \times \psi_{nucl}$ must be antisymmetric with respect to exchange of two ${}^1H$ nuclei. To accomplish this, the singlet nuclear states (para), which is antisymmetric, must be combined with the even rotational function and the triplet nuclear (ortho) must be combined with the odd rotational states.

So, the rotational partition functions for ortho and para hydrogens are,

$$q_{ortho} = 3 \sum_{J=1,3,5,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

$$q_{para} = \sum_{J=0,2,4,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

where θ_{rot} is the rotational temperature.

The total partition function consisting of ortho and para hydrogens,

$$q_{rot,nucl} = \sum_{J=0,2,4,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}} + 3 \sum_{J=1,3,5,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

Thus, the ratio of ortho to para hydrogens at thermal equilibrium,

$$\frac{N_{ortho}}{N_{para}} = \frac{3 \sum_{J=1,3,5,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}}{\sum_{J=0,2,4,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}}$$

At high temperature , the two summations in the above expression are equal,

$$\frac{N_{ortho}}{N_{para}} = 3$$

Hence, at high temperature we have 3 times more number of ortho hydrogen than para hydrogen. At low temperature, we get

$$\frac{N_{ortho}}{N_{para}} \rightarrow 0 \text{ as } T \rightarrow 0$$

A good experimental verification of the above analysis is a comparison between the calculated rotational heat capacities at constant volume ($((C_V)_{rot,nucl})$). From the partition function expression, we get the average energy and if we differentiate average energy with respect to temperature at constant volume, we get ($((C_V)_{rot,nucl})$). The plot of heat capacity as a function of temperature is shown below,

In the above plot, the curve marked "Exp" gives the variation of C_v as temperature changes. The curve "eq" represents the data for an equilibrated mixture of ortho and para hydrogen. The curves ortho and para refer to the heat capacities of pure ortho and pure para hydrogens respectively .

Initially, it was a puzzle as to why the experimental heat capacity values of hydrogen molecule differ from the calculated value. In fact, the experimental data agree very well with the below equation.

$$(C_v)_{rot,nucl} = \frac{3}{4}(C_v)_{rot,nucl}\,(ortho) + \frac{1}{4}(C_v)_{rot,nucl}\,(para)$$

The reason for this is that, when H_2 molecule is cooled down from a high temperature, the ortho/para ratio continues to remain 0.75/0.25 (the high temperature value) because the ortho-para inter conversion rate is very very small and we do not reach equilibrium composition unless a catalyst such as activated charcoal is added to the mixture.

The above expression of C_v corresponds to a "frozen high temperature mixture" of ortho and para hydrogen. In the presence of the catalyst, the experiments also give the curve labelled as eq in the above plot.

This is indeed a nice case, where the experiments support not only the methods of statistical thermodynamics but also the antisymmetry principle of bosons and fermions.