Electronic Partition function

$$q_{elec} = \sum w_{ei} e^{-\beta \varepsilon_i}$$

where w_{ei} is the degeneracy, and ε_i is the energy of the i^{th} electronic level. ε_1 is taken to be zero i.e. all the electronic energies are measured relative to the ground state. Now,

$$q_{elec} = w_{e1} + w_{e2} e^{-\beta \Delta \varepsilon_{12}} + w_{e3} e^{-\beta \Delta \varepsilon_{13}} + \ldots$$

where $\Delta \varepsilon_{1j}$ is the energy of the j^{th} electronic level relative to the ground state.

$\Delta \varepsilon_{ij}$ are typically of the order of electron volts. Thus $\beta \Delta \varepsilon$ is a high value at ordinary temperatures. So the exponential term becomes smaller and smaller. Thus, it is generally convenient to neglect terms higher than the third term.

Examples for rare gases

Term symbol → $^1S_0$ (singlet Ground state)

Difference between G.S. and 1st excited state is of the order of 10 eV.

Alkali metals

$^2S_{1/2}$ (G.S) Diff. b/w G.S and 1st E.S is of order 1eV

Halogens

$^2P_{3/2}$ ↓ G.S. $^2P_{1/2}$ ↓ E.S. Diff. b/w G.S and E.S. = 0.1eV

Thus, at ordinary temperatures, the electronic partition function of the rare gases is unity, alkali metals is 2 and of halogens consists of two terms.

Nuclear Partition function

The nuclear partition function is similar in form to the electronic partition function.

$$q_{nuc} = \sum w_{ni} e^{-\beta E_{ni}}$$

Nuclear energy levels are separated by millions of eV. So it requires very high temperature ($\geq 10^{10}$ K) to produce excited nuclei.

So we consider only the first term i.e. the degeneracy of the ground nuclear state, w_{ni}.

$$\therefore q_{nuclear} = w_{n_1}$$

The q_{nuc} contributes only a multiplicative constant to the Q and it only affects the entropy and free energy by a constant additive factor.

Since the nuclear state is rarely altered in any chemical process, it does not contribute to thermodynamic changes and so it is not usually included in Q. Same explaination is not valid for q_{elec} as electron states change in many chemical processes.

Although, nuclear partition function is not always equal to unity, it is usually omitted from calculating thermodynamic properties.