Lecture:Chem383

Physical Significance of Partition Function

- Partition function is a dimensionless quantity and summarizes in convenient mathematical form, the way in which energy of a system of molecules is partitioned among the different energy states
- Its value depends on the molecular weight, molecular volume, temperature, inter nuclear distance, the inter molecular motion and inter molecular forces

- Partition function provides the most convenient way for linking the microscopic properties of individual molecules with macroscopic properties of the system
- Reflects the diversity of energy states of molecules of a system
- The energy of a molecule is the sum of contributions from its different modes of motion:
- $\varepsilon_i = \varepsilon_i^T + \varepsilon_i^R + \varepsilon_i^V + \varepsilon_i^E$
- where T denotes translation, R rotation, V vibration, and E the electronic contribution.

- Maxwell’s Boltzmann Distribution Equation

$$\frac{n_i}{N} = \frac{g_i \exp\left(-\frac{\epsilon_i}{kT}\right)}{z}.$$

Where g_i =degeneracy of the energy state(statistical weight factor)

E_i=the energy levels

- Over here the lower term, that is

$$z = \sum g_i \exp\left(-\frac{\varepsilon_i}{kT}\right).$$

This term is called the partition function and given by a scientist name Fowler.

- The ratio of number of particles in any state of energy E_i relative to that in state of energy E_0

follows from above equation

$$\frac{n_i}{n_o} = \frac{g_i\, e^{-\epsilon_i/kT}}{g_o\, e^{-\epsilon_o/kT}}$$

or

$$\frac{n_i}{n_o} = \frac{g_i}{g_o}\, e^{-(\epsilon_i - \epsilon_o)/kT}$$

For computational purposes, it is convenient to consider E_0 =0, and to take all E_i values relative to this ground state. On this basis the above equation becomes

$$\frac{n_i}{n_o} = \frac{g_i}{g_o}\, e^{-\epsilon_i/kT}$$

or

$$n_i = \frac{n_o}{g_o}\, g_i\, e^{-\epsilon_i/kT}$$

- Where ni is the number of molecules in the ith state, n_0, the number of molecules in the zero energy level, g_i & g_0 represent the degeneracies in the ith and zero levels respectively

When $E_0=0$, then $g_0=1$, therefore it can be written as

$$\frac{n_i}{n_o} = g_i\, e^{-\epsilon_i/kT}$$

or $$n_i = n_o\, g_i\, e^{-\epsilon_i/kT}$$

Now $$N = \Sigma\, n_i$$

$$N = \Sigma\, n_0\, g_i\, e^{-\epsilon_i/kT}$$

or $$N = n_0\, g_0\, e^0 + n_0\, g_1\, e^{-\epsilon_1/kT} + n_0\, g_2\, e^{-\epsilon_2/kT} + \ldots$$

or $$N = n_0\, [g_0 + g_1\, e^{-\epsilon_1/kT} + g_2\, e^{-\epsilon_2/kT} + \ldots]$$

or $$N = n_0\, \Sigma\, g_i\, e^{-\epsilon_i/kT} \qquad (g_0 = 1)$$

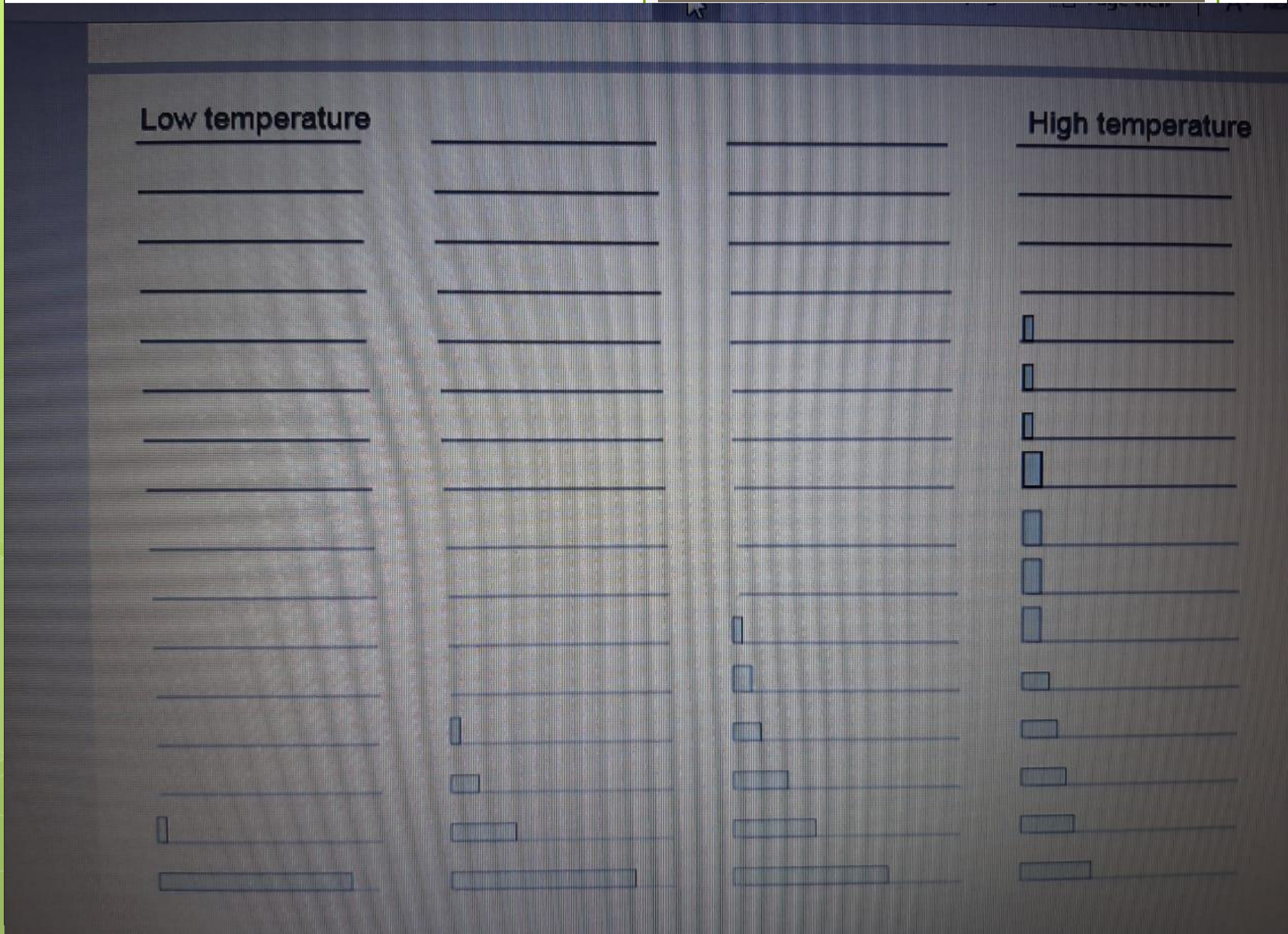
or $$N = n_0\, Q$$

or $$Q = N/n_0$$

- From the above equation, it follows that the partition function is defined as the number of particles or molecules in the ith levels to that of zero level
- At absolute zero,

	N	→	n_0
And	Q=q	→	1
As	T	→	0

Hence, the value of partition function increases with temperature.


Low temperature
High temperature

- As the temperature is raised, there are more molecules in the highest energy levels and few no.of molecules in zero energy level.
- Therefore, the partition function is larger at higher temperature