

Partition function

Lecture-Chem383

Physical Chemistry II

The Molecular Partition Function

The Boltzmann distribution can be written as

$$p_i = \exp(-\beta\varepsilon_i) / q$$

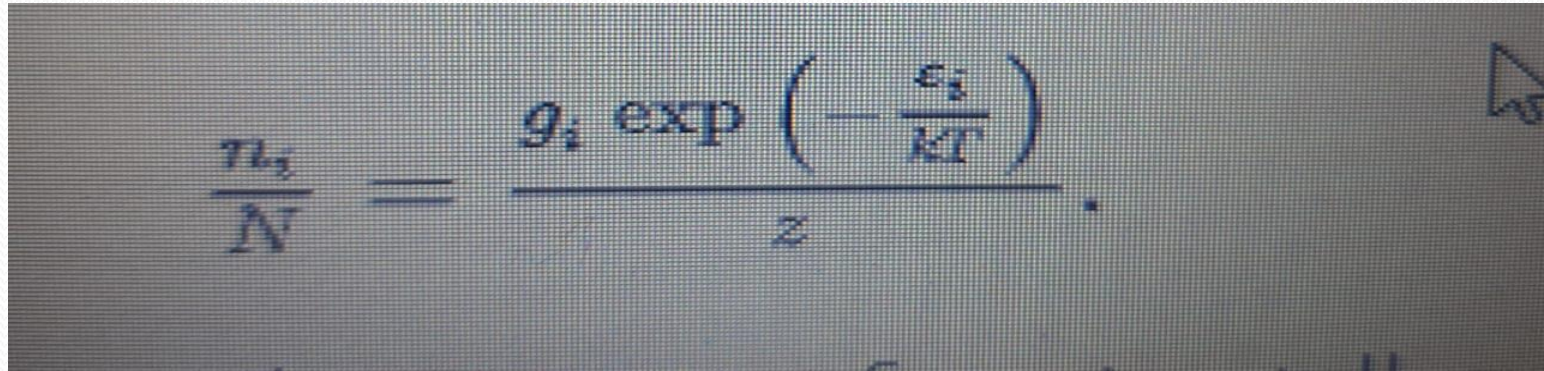
where p_i is the probability of a molecule being found in a state i with energy ε_i . q is called *the molecular partition function*,

$$q = \sum_i \exp(-\beta\varepsilon_i)$$

The summation is over all possible states (not the energy levels).

The Partition Function

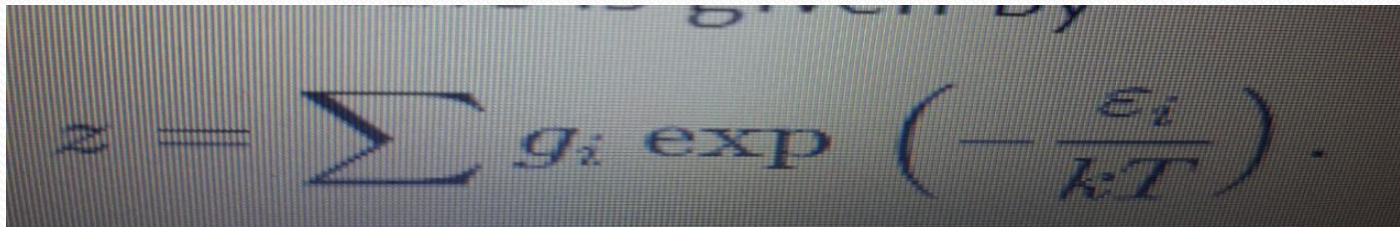
- Maxwell's Boltzmann Distribution Equation


$$\frac{n_i}{N} = \frac{g_i \exp\left(-\frac{E_i}{KT}\right)}{z}$$

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

E_i = the energy levels


- Over here the lower term, that is


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

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

- Generally it is represented either q, Q, P, z or in many books by f .
- This partition function gives the summation of energy states or all available states

- Partition function is dimensionless quantity and it depends upon molecular weight, volume, temperature and several other factors.
- The partition function for a system is simply an exponential function of the sum of all possible energies for that system.
- partition function can be represented in the form of a several other thermodynamic functions like internal energy, entropy, work function, pressure, free energy as well as heat capacity
- Quantitatively speaking it tells us how several particles are distributed among various energy levels and it is measure of available energy levels

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- So with the help of this particular term or function we can find out how several particles (suppose we have n particles) are distributed among several energy levels
 - It also provides the link between microscopic properties of individual molecules with that of macroscopic properties of the system
 - Partition function can also be defined as “ it is the sum of probability factors of various energy levels
 - If we have several number of particles, they perform different types of motion
 - Translational, Vibrational, rotational and electronic motions

- So the energy associated with or the total energy is equal to the sum of all this type of factors

Hence we can write

$$E = E_t + E_v + E_r + E_e$$

And value of statistical weight factor is

$$g_i = g_t + g_v + g_r + g_e$$

Independent Molecules

Consider a system which is composed of N identical molecules. We may generalize the molecular partition function q to the partition function of the system Q

$$Q = \sum_i \exp(-\beta E_i)$$

where E_i is the energy of a state i of the system, and summation is over all the states. E_i can be expressed as assuming there is no interaction among molecules,

$$E_i = \epsilon_i(1) + \epsilon_i(2) + \epsilon_i(3) + \dots + \epsilon_i(N)$$

where $\epsilon_i(j)$ is the energy of molecule j in a molecular state i

The partition function Q

$$\begin{aligned} Q &= \sum_i \exp[-\beta_{\epsilon_i}(1) - \beta_{\epsilon_i}(2) - \beta_{\epsilon_i}(3) - \dots - \beta_{\epsilon_i}(N)] \\ &= \left\{ \sum_i \exp[-\beta_{\epsilon_i}(1)] \right\} \left\{ \sum_i \exp[-\beta_{\epsilon_i}(2)] \right\} \dots \left\{ \sum_i \exp[-\beta_{\epsilon_i}(N)] \right\} \\ &= \left\{ \sum_i \exp(-\beta_{\epsilon_i}) \right\}^N \\ &= q^N \end{aligned}$$

where $q \equiv \sum_i \exp(-\beta_{\epsilon_i})$ is the molecular partition function. The second equality is satisfied because the molecules are independent of each other. The above equation applies only to molecules that are **distinguishable**, for instance, localized molecules. However, if the molecules are identical and free to move through space, we cannot distinguish them, and the above equation is to be **modified!**

Factorization of Partition Function

- One of the most important concepts of statistical mechanics involves how a specified total amount of energy E can be shared among a collection of molecules and within the internal (rotational, vibrational, electronic) and intermolecular (translational) degrees of freedom of these molecules when the molecules have a means for sharing or redistributing this energy (e.g., by collisions).
- The primary outcome of asking what is the most probable distribution of energy among a large number N of molecules within a container of volume V that is maintained in equilibrium by such energy-sharing at a specified temperature T is the most important equation in statistical mechanics.

From now on we write the Boltzmann distribution as

$$p_i = e^{-\beta \epsilon_i} / q$$

where p_i is the fraction of molecules in the state i , $p_i = n_i/N$, and q is the molecular partition function:

$$q = \sum e^{-\beta \epsilon_i}$$

The sum in q is sometimes expressed slightly differently. It may happen that several states have the same energy, and so give the same contribution to the sum. If, for example, g_i states have the same energy ϵ_i (so the level is g_i -fold degenerate), we could write

$$q = \sum g_i e^{-\beta \epsilon_i} \text{-----(1)}$$

where the sum is now over energy levels (sets of states with the same energy), not individual states.

- The energy of a molecule is the sum of contribution from the different modes of motion as **translational** (see individual particles, they are moving in a zigzag manner---they possess translational motion), **vibrational** (periodic back-and-forth motion of the particles of an elastic body or medium, commonly resulting when almost any physical system is displaced from its equilibrium condition and allowed to respond to the forces that tend to restore equilibrium), **rotational** (Rotation around a fixed axis or about a fixed axis of revolution) and **electronic** motion is due to several electronic factors,...etc.

- The energy E of a molecule is the sum of contribution from the different modes of motion such as translational, rotational, vibrational and electronic.
- Suppose that energy associated with any one mode of behaviour is independent of all other modes, then energy equal to

$$E = E_t + E_r + E_v + E_e$$

And statistical weight factor is

$$g_i = g_t + g_r + g_v + g_e$$

Where E_t , E_r , E_v and E_e are translational, rotational, vibrational and electronic contribution, respectively and g_t , g_r , g_v , g_e are degeneracy of translational, rotational, vibrational and electronic energy level, respectively.

So equation (1) can be written as;

$$q = \sum g_i e^{-\beta \epsilon_i}$$

$$q = \sum (g_t \cdot g_r \cdot g_v \cdot g_e) e^{-(E_t + E_r + E_v + E_e)/kT}$$

$$q = \sum_t g_t e^{-E_t/kT} \times \sum_r g_r e^{-E_r/kT} \times \sum_v g_v e^{-E_v/kT} \times \sum_e g_e e^{-E_e/kT}$$

Here, the summation is over the electronic, vibrational and rotational states can be done separately since they are assumed to be independent. Therefore,


$$q = q_t \cdot q_r \cdot q_v \cdot q_e \text{ -----(2)}$$

or

$$q = q_{el} \cdot q_{vib} \cdot q_{rot} \cdot q_{trans}$$

The molecular partition q function is written as the product of electronic, vibrational, rotational and partition functions.

- The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number
- Larger the value of q , larger the number of states which are available for the molecular system to occupy
- Since $E_{\text{el}} > E_{\text{vib}} > E_{\text{rot}} > E_{\text{trans}}$, there are far too many translational states available compared to the rotational, vibrational and electronic states. q_{el} is very nearly unity, q_{vib} and q_{rot} are in the range of 1 to 100 while q_{trans} can be much in excess of 10^{20} .
- We shall calculate the values of these q s and indicate how these q s are useful in calculating the equilibrium constants and also in certain cases, the rate constants

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- Equation (2) is known as multiplication theorem or factorization of partition function. So the factorization means we can investigate each contribution separately.
 - This eq (2) shows that the net partition function is equal to be the product of the separate partition function in respect of different types of energy independently associated with molecules.