Statistical Thermodynamics: Part-1 (Microstates and ensembles)

- Microstates and ensembles
- Thermodynamic probability
- Partition functions

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Statistical Thermodynamics: Part-1

- **Statistical Thermodynamics:** Statistical mechanics provides the means of predicting the properties of chemical systems from knowledge of its constituent particles and the interactions between the particles. We cannot predict the behaviour of a given particle in a collection of a large mutually interacting particles, it is possible to predict average properties, which are often what are measured in experiments anyway.

As an example: It is not possible to predict every interaction e.g., collision between particles in a gas stored inside a container but as an average, we can always predict the average pressure (force per unit area) of the total gas stored.

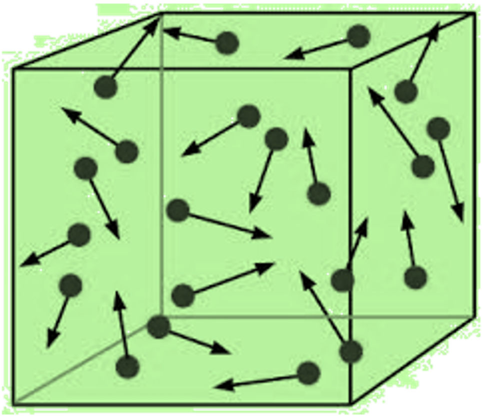

Figure: Gaseous molecules in a container

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- **Microstates and ensembles:** Consider a system of particles in a fixed volume (e.g., a gas stored inside a container); this is quite common chemical situation. According to the quantum mechanics at any given moment, the system is in a superposition of distinct quantum states called microstates. An ensemble on the other and is the collection of all possible microstates consistent with the externally controlled macroscopic parameter.

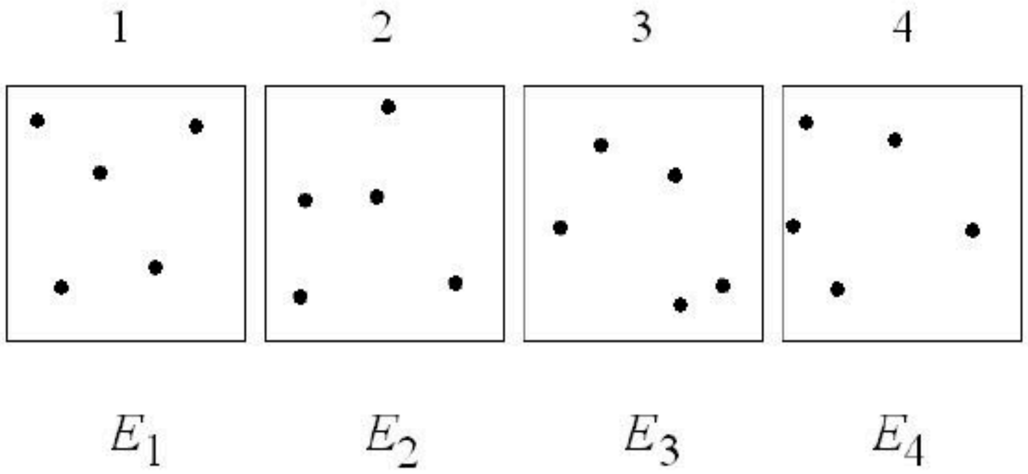

Figure: A part of an ensemble of four microstates (E1 to E4)

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- **Canonical ensembles:** A canonical ensemble is the ensemble that represents the possible states of a system in thermal equilibrium with a heat bath at a fixed T. The system can exchange energy with the heat bath, so that the states differ in total energy (E). A canonical ensemble is the ensemble of all microstates corresponding to a system with number of particles (N), volume (V), and temperature (T). It is also often called the **NVT ensemble**.

N: Number of particles
V: Volume of the system
E: Energy of the system

- **Microcanonical ensemble:** A micro-canonical ensemble is the ensemble that represents the possible states of a system with an exactly specified total energy. The system is isolated and cannot exchange energy or particles with its surroundings. Thus by the conservation of energy the energy of the system remains always same. This ensemble is also often called the **NVE ensemble**, as each of these three quantities is a constant of the ensemble.

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- **Grand Canonical ensemble:** It is the ensemble that is used to represent the possible states of a mechanical system of particles that are in thermodynamic equilibrium with a reservoir. The system is therefore an open system which can exchange energy and particles with a reservoir. The ensemble is also termed as **μVT ensemble** as the thermodynamic variables of the ensemble are chemical potential (μ), Volume (V) and absolute temperature (T).

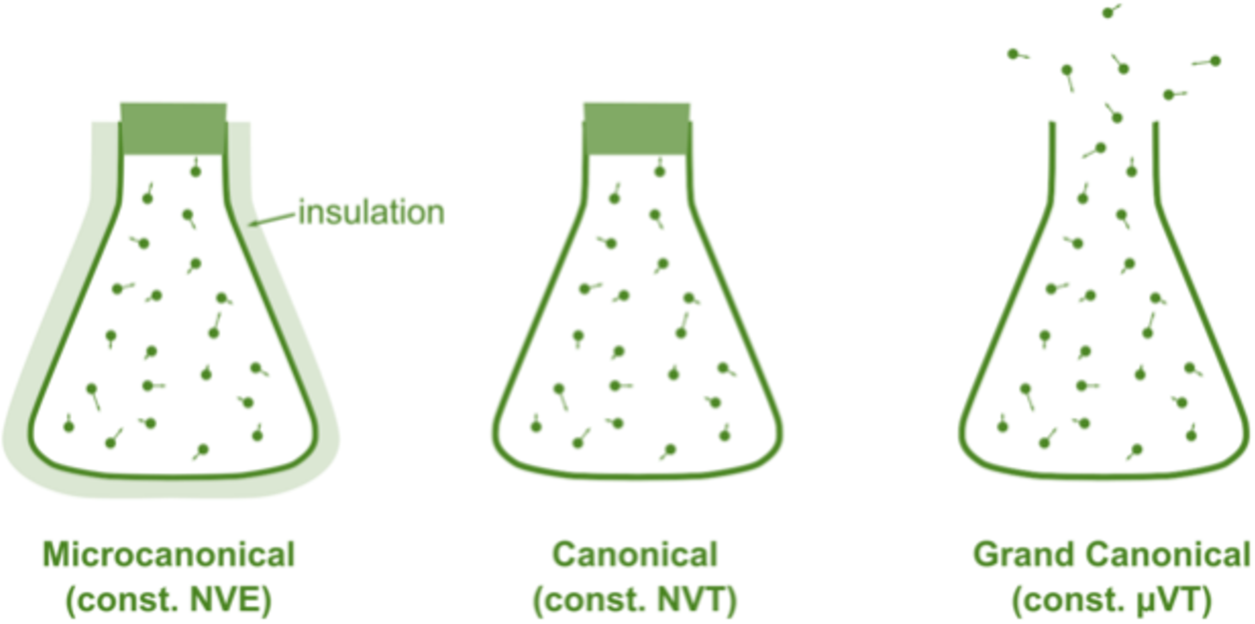

Figure: Three different types of emsembles

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Thermodynamic Probability:

I order to know if a chemical change is spontaneous or not, we must find some general way of determining whether the final state is more probable than the initial state. This can be done using a number Ω, called the thermodynamic probability. Ω is defined as the number of alternative microscopic arrangements which correspond to the same macroscopic state.
Under specified conditions, the number of equally likely states in which a substance may exist; the thermodynamic probability Ω is related to the entropy S by $S = k \ln \Omega$, where k is Boltzmann's constant.

Boltzmann's constant relates the average relative kinetic energy of particles in a gas with the temperature of the gas.

$$S = k \ln \Omega$$

$k = 1.38 \times 10^{-23}$ J/K
or 8.617 x 10-5 eV/K
or 1.38 x 10-16 erg/K

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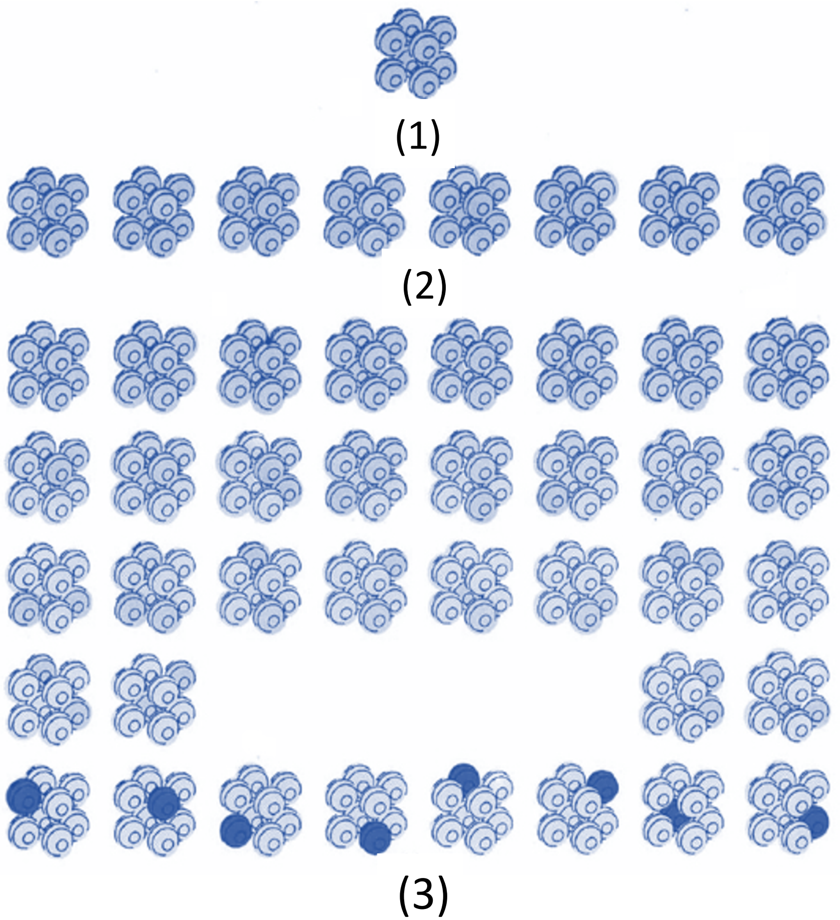

Figure. The thermodynamic probability Ω of a crystal with eight atoms at three different temperatures.

(1) At 0 K there is only one way in which the crystal can be arranged, so that Ω = 1.

(2) Some energy is added to make one of the atoms vibrating (color), there are eight different equally likely arrangements possible, and Ω = 8.

(3) If the energy is increased and two different atoms can vibrate simultaneously (light color) or a single atom can have all the energy (dark color). The number of equally likely arrangements is much larger than before; Ω = 36.

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- **Partition Functions:** Partition functions are used to describe the statistical properties of a system that is in thermodynamic equilibrium. Partition functions are usually a function of state variables such as Volume (V) and Temperature (T). Thermodynamic variables e.g., Pressure, Entropy, Free energy, etc can be expressed in terms of dimensionless partition functions.

- The term partition is used because it shows how probability is ***partitioned*** among all the microstates compatible with the constraints on the ensemble.

- **Some common partition functions:**

- **Canonical partition functions:** They are applied in canonical ensembles where system can exchange heat with surroundings at constant N, V, and T.

Canonical partition function is defined as $Z = \sum_i \mathrm{e}^{-\beta E_i},$

Here β is the thermodynamic quantity 1/kT (k = Boltzman's constant), E = total energy in the system in the microstate.

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- **Grand canonical partition functions:** They are applied in grand canonical ensembles where system can exchange heat as well as number of particles with surroundings at constant μ, V, and T (μ = chemical potential).

The grand canonical partition function is defined as following where $Z(\mu, V, T)$ is grand canonical partition function and N_i, E_i are total number of particles and total energy in the microstate *i*.

$$\mathcal{Z}(\mu, V, T) = \sum_i \exp\left(\frac{N_i \mu - E_i}{k_B T}\right).$$

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❖ Electronic, Vibrational, Rotational and Translational Partition Functions:

The electronic energy levels are separated in energy compared to the thermal energy *kT* at room temperature. In each electronic level, there are several vibrational levels and for each vibrational level, there are several rotational states.

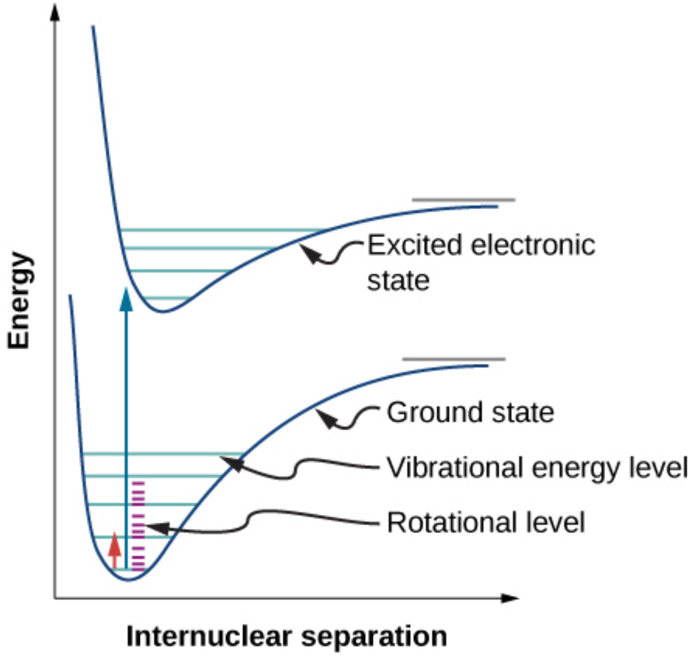
Total energy of the system is given by;

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}$$

The molecular partition functions can be given as

$$q = \sum e^{-(E_{el} + E_{vib} + E_{rot} + E_{tr})/kT}$$

$$\text{Or } q = \sum e^{-\beta E_{el}} \sum e^{-\beta E_{vib}} \sum e^{-\beta E_{rot}} \sum e^{-\beta E_{tr}}$$



Here, since the sum is over the electronic, vibrational and rotational states can be done separately since they are assumed to be independent.
Therefore, $q = q_{el}\, q_{vib}\, q_{rot}\, q_{tr}$
The molecular partition '*q*' is written as the product of electronic, vibrational, rotational and translation partition functions

Note: Students are requested to also see the following webpage for more information on partition functions
https://ether.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf
https://bit.ly/2VogsNs

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References

1) Atkins' physical chemistry

2) Statistical thermodynamics by C. L. Tien and J. H. Lienhard