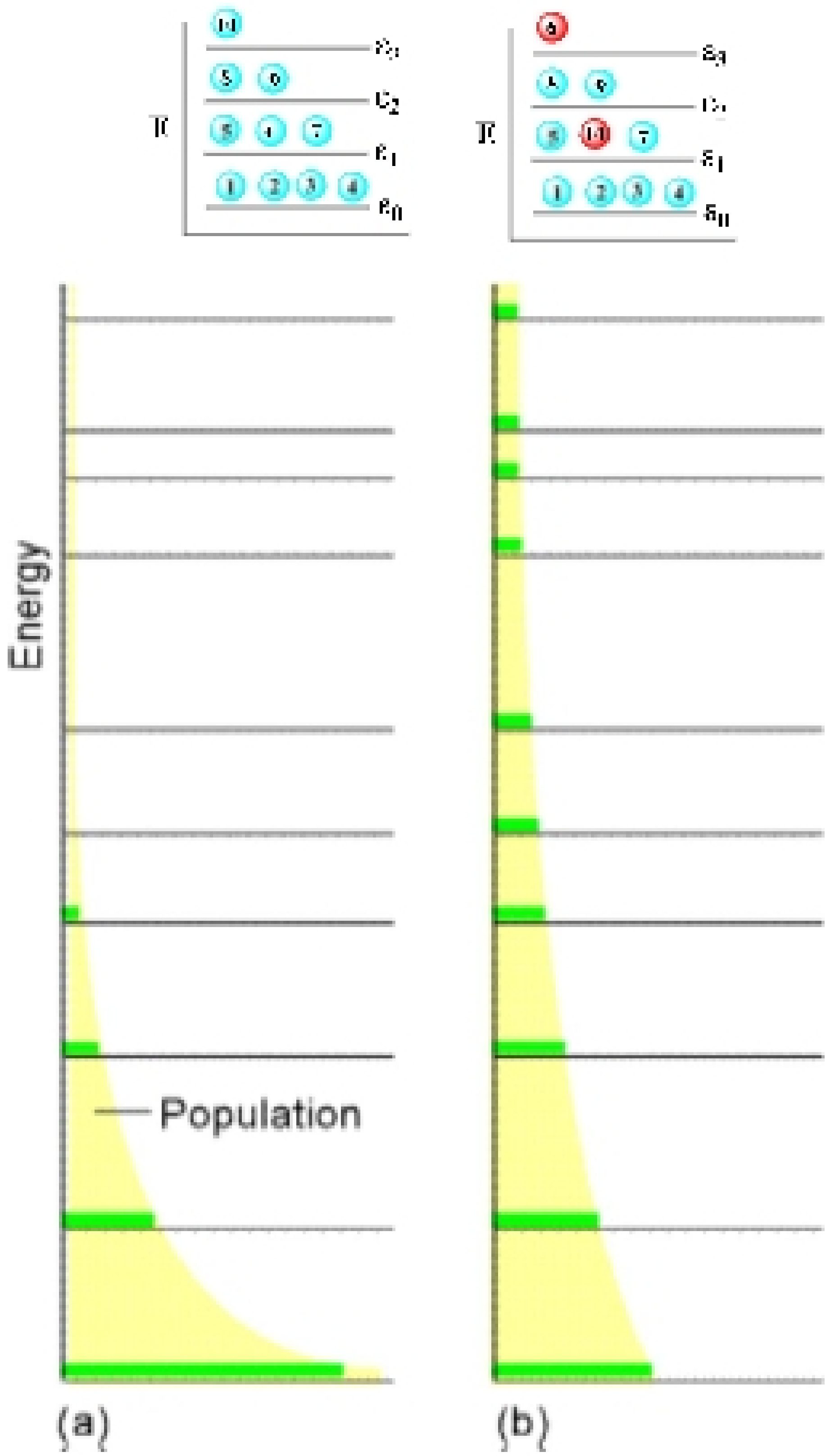
CBE 310: Molecular Concepts and Applications

Rotational Electronic and complete Partition Function

2014 10 20

1) Quick review of vibrational and translational q's
2) Rotational Partition functions
3) Electronic Partition functions
4) Total Partition functions
*5) Entropy

Boltzmann Distribution: the most probable configuration of a system



The Boltzmann distribution describes the distribution of particles into energy states with the highest statistical weight. The function itself describes either the probability that a particle will be in a particular state or the population of a particular state N_j in relation to the ground state population.

$$\frac{N_j}{N_0} = e^{-\varepsilon_j / kT} \qquad N_j = N_0 e^{-\varepsilon_j / kT}$$

$$\boxed{\frac{n_i}{N} = \frac{1}{\sum_i e^{-\beta\varepsilon_i}} e^{-\beta\varepsilon_i}}$$

Finding the configuration of greatest weight

$$d\ln W = \sum_i \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i = 0$$

the change in ln W is the sum of the changes in ln W due to changes in the n_i

But the distribution is subject to the constraints :

(1) That the total number of particles does not change, that is for every increase in one level there must be a decrease in another.

(2) That all of the configurations for a particular state must have the same total energy. These constraints can be written as below

$$\sum_i dn_i = 0 \qquad\qquad \sum_i \varepsilon_i dn_i = 0$$

Lagrange's method of undetermined multipliers involves adding the restraints times some "unknown multipliers" to the equation for the function of interest and solving the function as if the variables are independent. The unknown multipliers are then determined in relation to a problem with a known solution.

$$d\ln W = \sum_i \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i + \alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i$$