Lecture 3: Boltzmann Factor, Partition Function

Boltzmann Factor, Partition Function

Setting the Stage

- Quantum Mechanics: Microscopic view, particles in energy levels
- Statistical Mechanics: Macroscopic view, thermodynamic properties like pressure, heat capacity, energy
- Quantum mechanics is probabilistic, $|\psi(x)|^2$ works for small systems but not macroscopic systems that chemists are interested in
- Key Idea: Apply statistics at the microscopic level to arrive at macroscopic thermodynamic properties

Probability of Energy

From quantum mechanics, we know the energy of translational, rotational, vibrational movement of particles

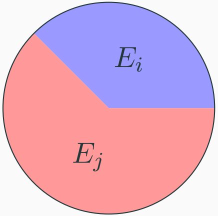
Consider two independent events:

- $P(E_i)$: Probability particle is in state i with energy E_i
- $P(E_j)$: Probability particle is in state j with energy E_j

What is the probability that both of these events occurring?

$$P_{ij}(E_i + E_j) = P_i(E_i) \times P_j(E_j)$$

$E_i + E_j$ is the total energy



Boltzmann Factor

What function does this resemble?

$$P_{ij}(E_i + E_j) = P_i(E_i) \times P_j(E_j)$$
$$f(a+b) = f(a) \times f(b)$$
$$e^{a+b} = e^a \times e^b$$

Boltzmann Factor

Probability that a system has energy E_i at given temperature T

$$P_i(E_i) \propto e^{-\beta E_i} \qquad \beta = \frac{1}{k_B T} \text{ (inverse temperature)}$$

where k_B is Boltzmann's constant: 1.38×10^{-23} J/K

Applying our Physical Intuition

Boltzmann's Factor:

$$P_i(E_i) \propto e^{-\beta E_i} \qquad \beta = \frac{1}{k_B T}$$

Low energy states are more probable than high energy states

$$E_i \uparrow \quad P_i(E_i) \downarrow$$

Higher temperature causes more molecules in high energy states

$$T \uparrow \quad \beta \downarrow \quad P_i(E_i) \uparrow$$

Exponentials and Logarithms are unitless quantities

$$P_i(E_i) \propto e^{-\beta E_i} = e^{-\frac{E_i}{k_B T}} = e^{-\frac{\mathrm{J}}{\mathrm{J/K \cdot K}}} = e^{-\frac{\mathrm{J}}{\mathrm{J}}} = \text{unitless}$$

Boltzmann Factor hiding in the Arrhenius Equation

Boltzmann's Factor:

$$P_i(E_i) \propto e^{-\beta E_i} \qquad \beta = \frac{1}{k_B T}$$

Only molecules with energy at least activation energy E_a can react:

$$\text{fraction with energy} \geq E_a \ \propto \ \exp\left(-\frac{E_a}{k_B T}\right)$$

Can see the similarities to the Arrhenius Equation:

$$\boxed{k = A\exp\left(-\frac{E_a}{RT}\right) \qquad k_B = \frac{R}{N_A}}$$

Normalization Condition

Assign a constant a for proportionality:

$$P_i(E_i) \propto e^{-\beta E_i} \implies P_i(E_i) = a e^{-\beta E_i}$$

Recall normalization means:

$$\sum_i P_i = 1$$

Rearrange and solve for a:

$$\sum_i a e^{-\beta E_i} = 1$$

$$a \sum_i e^{-\beta E_i} = 1$$

$$a = \frac{1}{\sum_i e^{-\beta E_i}} = \frac{1}{Q}$$

Partition Function

Partition Function (Q)

Mathematical quantity that contains a system's thermodynamic information

$$Q = \sum_i e^{-\beta E_i}$$

It is a sum over all possible microstates (a configuration of particles in a system) that normalizes the probability to be 1.

Probability of being in state i :

$$P_i = \frac{e^{-\beta E_i}}{Q} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Factors that affect Q

Partition function Q depends $Q(N, V, \beta) = \sum_i e^{-\beta E_i(N,V)}$

- Number of Particles (N)
- Volume (V)
  $E_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \quad V = a^3$
- Inverse Temperature ($\beta = \frac{1}{k_B T}$)

Why is E not a variable that affects Q?

$$Q(N, V, \beta) = \sum_i e^{-\beta E_i(N,V)}$$

- $E_i(N, V)$ are energies eigenvalues with N and V dependance
- Temperature (T) does *not* change the energy levels, it only changes the distribution of probabilities among them
- Recall Kinetic Molecular Theory: higher T increases the probability that particles occupy higher energy states, but does not change the energies ‘

Example: Partition Function

For stat mech, if you don't know where to start a problem, start by writing the partition function.

A system consisting of a single particle can occupy one of 3 energy levels: $E_0 = 0, E_1 = \varepsilon, E_2 = 3\varepsilon$. What is the probability you are in the ground state?

$$Q = \sum_i e^{-\beta E_i} = e^{-\beta \cdot 0} + e^{-\beta\varepsilon} + e^{-\beta \cdot 3\varepsilon}$$
$$= 1 + e^{-\beta\varepsilon} + e^{-3\beta\varepsilon}$$

$$P_0 = \frac{e^{-\beta E_0}}{Q} = \boxed{\frac{1}{1 + e^{-\beta\varepsilon} + e^{-3\beta\varepsilon}}}$$