

University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 4. 1/12/15

A. Partition Function; Properties and Applications

- In the last lecture we introduced the Boltzmann Distribution Law:

$$P_i = \frac{e^{-E_i/k_B T}}{Q} \quad (4.1)$$

- In equation 4.1 Q in the denominator is called the partition function and is defined as $Q = \sum_j e^{-E_j/k_B T}$. The partition function is sometimes called the “sum over states” because it numerates that number of occupied energy states at a given temperature.

- Each system is composed of many particles. If the particles interact each energy is a multi-particle energy which contains kinetic energy terms that are functions of momentum as well as potential terms that involve inter-particle distances.

- If the particles do not interact, the system energy E_j is a sum of the particle energies: i.e. $E_j = \varepsilon_k^a + \varepsilon_l^b + \varepsilon_m^c + \dots$ where the superscripts a, b, c, etc. label the particle and the subscripts, k, l, and m label the individual particle energies.

- For simplicity suppose we have two distinguishable particles distributed over 2 energy levels. From Figure 4.1, it is clear there are four ways to distribute two distinguishable particles between two energy states. Therefore $E_j = \varepsilon_k^a + \varepsilon_l^b$, and $j=1, 2, 3, \text{ or } 4$; $k=1,2$ and $l=1,2$.

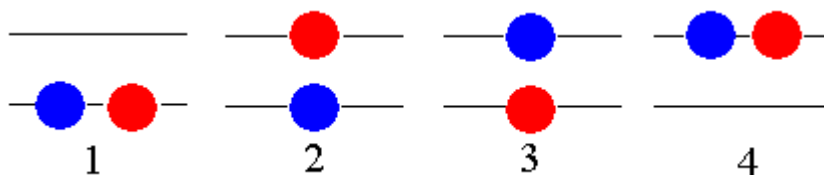


Figure 4.1 Two non-interacting particles are distinguished by color. There are four ways to distribute these particles between two energy levels.

- Using the assumption that the system energy E_j is the sum of the individual particle energies we get:

$$Q = \sum_{j=1,4} e^{-E_j/k_B T} = e^{-(\varepsilon_1^a + \varepsilon_1^b)/k_B T} + e^{-(\varepsilon_1^a + \varepsilon_2^b)/k_B T} + e^{-(\varepsilon_2^a + \varepsilon_1^b)/k_B T} + e^{-(\varepsilon_2^a + \varepsilon_2^b)/k_B T} \quad (4.2)$$

$$= \left(e^{-\varepsilon_1^a/k_B T} + e^{-\varepsilon_2^a/k_B T} \right) \left(e^{-\varepsilon_1^b/k_B T} + e^{-\varepsilon_2^b/k_B T} \right) = q_a \times q_b = q^2$$

where q is called the single particle or molecular partition function, because it sums over single particle energy states.

- a. For N molecules having the same energy levels we get

$$Q = \prod_{i=1}^N q_i = q^N \quad (4.3)$$

- b. Equation 4.2 actually over-counts the number of multi-particle states if the particles are indistinguishable. If the particles or molecules are indistinguishable, then switching two particles between energy states does not produce distinguishable states. See Figure 4.2 .

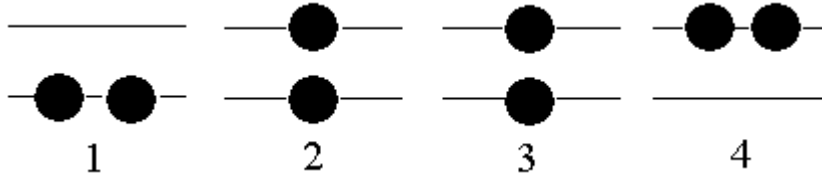


Figure 4.2;: There are only three **DISTINGUISHABLE** ways to distribute two indistinguishable particles between two energy levels.

- c. A similar situation is encountered in poker where the order in which cards are dealt does not affect the scoring of the hand. The number of ways of dealing 5 card poker hands is:

$$W_{\text{poker}} = \frac{52!}{5!47!} = \frac{52 \times 51 \times 50 \times 49 \times 48}{5!} = 2,598,960 \quad (4.4)$$

- d. The term in the numerator of equation 4.4 is
 $52 \times 51 \times 50 \times 49 \times 48 = 311,875,200$ (4.5)
- e. Equation 4.5 is the total number of 5 card hands dealt from a 52 card deck. This number does not take into account the fact that poker hands are invariant to the order in which the cards are dealt. Therefore, equation 4.5 overcounts the number of poker hands by not taking into account the fact that two hands that differ only in the order of cards are indistinguishable.
- f. The factor of $5! = 120$ in the denominator of equation 4.4 is the number of ways in which 5 cards can be dealt. This term corrects for over-counting indistinguishable poker hands.
- g. We can apply a similar correction if the number of indistinguishable particles N is large. In the case of N indistinguishable and non-interacting particles

$$Q = \frac{q^N}{N!} \quad (4.6)$$

- h. Calculating q is pretty easy because all we have to do is know the energy of a single particle. With this in mind, let's re-write the equations for q and U :

$$Q = \frac{q^N}{N!}; U = \sum_j N_j E_j = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V = -N \left(\frac{\partial \ln q}{\partial \beta} \right) \quad (4.7)$$

where $\beta = \frac{1}{k_B T}$.

d. We have expressions for the entropy in terms of Q and q. For indistinguishable particles equation 4.6 holds so:

$$S = \frac{U}{T} + k_B \ln Q = \frac{U}{T} + k_B \left(\ln \frac{q^N}{N!} \right) \quad (4.8)$$

$$\approx \frac{U}{T} + k_B (N \ln q - N \ln N + N) = \frac{U}{T} + k_B N \ln \frac{q}{N} + k_B N$$

e. If the particles are distinguishable: $Q=qN$ and we obtain for the entropy:
(4.9)

where we used Stirling's Approximation $\ln N! = N \ln N - N$

B. Example Calculations: Two Level System (TLS)

- The two level system is a model for the energies of protons in magnetic fields, and thus describes the energetics of MRI experiments
- Suppose you have a particle with two energy levels $\varepsilon_1 = 0$ and $\varepsilon_2 = \varepsilon$. The single particle partition function is

$$q = 1 + e^{-\beta\varepsilon} \quad (4.10)$$

c. The multi-particle partition function is

$$Q = \begin{cases} q^N = (1 + e^{-\beta\varepsilon})^N & \text{distinguishable particles} \\ q^N / N! = (1 + e^{-\beta\varepsilon})^N / N! & \text{indistinguishable particles} \end{cases} \quad (4.11)$$

d. For q, if $\beta\varepsilon = \varepsilon / k_B T \gg 1$, then $q \approx 1$. If $\beta\varepsilon = \varepsilon / k_B T \ll 1$, then $q \approx 2$.

Therefore q is a sum over energy states that are fully or partly occupied. At low temperatures close to 0K only the ground state is occupied is $q=1$. As the temperature increases the second energy level becomes occupied.

e. Two methods for calculating $\langle \varepsilon \rangle$

- We could calculate the average energy using

$$U = \langle E \rangle = N \langle \varepsilon \rangle = N (P_1 \varepsilon_1 + P_2 \varepsilon_2) = \frac{N \varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$$

- We can use the expression for q directly

$$U = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad (4.12)$$

$$= -\frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V = -\frac{N}{1 + e^{-\beta\varepsilon}} \left(\frac{\partial}{\partial \beta} (1 + e^{-\beta\varepsilon}) \right)_V = \frac{N \varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$$

f. For the entropy of a TLS:

$$S \approx \frac{U}{T} + k_B (N \ln q - N \ln N + N) \quad (4.13)$$

$$= \frac{U}{T} + k_B \left(N \ln \left(\frac{q}{N} \right) + N \right) = \frac{N}{T} \frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} + N k_B \left(\ln \left(\frac{1 + e^{-\beta\varepsilon}}{N} \right) + 1 \right)$$

g. Note if the particles were distinguishable then $Q = q^N$ and while U does not change the entropy is now:

$$S \approx \frac{U}{T} + k_B \ln q^N = \frac{N}{T} \frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} + Nk_B \ln(1 + e^{-\beta\varepsilon}) \quad (4.14)$$

Example 4.1: Calculate the internal energy, entropy, and heat capacity C_V of one mole of particles distributed between two energy levels if $\Delta\varepsilon=5.00 \times 10^{-20} \text{ J}$, $T=1000 \text{ K}$, and the particles are distinguishable.

$$k_B T = (1.38 \times 10^{-23} \text{ JK}^{-1})(1000 \text{ K}) = 1.38 \times 10^{-20} \text{ J}$$

$$\therefore \frac{\varepsilon}{k_B T} = \frac{5.00 \times 10^{-20} \text{ J}}{1.38 \times 10^{-20} \text{ J}} = 3.62$$

$$\therefore e^{-\beta\varepsilon} = e^{-3.62} = 0.0268$$

$$U = N(P_1\varepsilon_1 + P_2\varepsilon_2) = \frac{N\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} = (6.02 \times 10^{23} \text{ mol}^{-1})(5.00 \times 10^{-20} \text{ J}) \frac{0.0268}{1 + 0.0268} = 786 \text{ Jmol}^{-1}$$

$$S \approx \frac{U}{T} + k_B N \ln q = \frac{N_A}{T} \frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} + N_A k_B \ln(1 + e^{-\beta\varepsilon})$$

$$= \frac{786 \text{ J}}{1000 \text{ K}} + (8.31 \text{ JK}^{-1}) \ln(1.0268) = 0.786 \text{ JK}^{-1} + 0.220 \text{ JK}^{-1} \approx 1.01 \text{ JK}^{-1}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{N\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} \right) = N\varepsilon \frac{\partial}{\partial T} (e^{\varepsilon/k_B T} + 1)^{-1}$$

$$= N \frac{\varepsilon^2}{k_B T^2} e^{\varepsilon/k_B T} (e^{\varepsilon/k_B T} + 1)^{-2} = Nk_B \left(\frac{\varepsilon}{k_B T} \right)^2 e^{-\varepsilon/k_B T} (1 + e^{-\varepsilon/k_B T})^{-2}$$

$$= (8.31 \text{ JK}^{-1})(3.62)^2 (0.0268) \left(\frac{1}{1.0268} \right)^2 = 2.77 \text{ JK}^{-1}$$