20.7: The Microstates of a Given Population Set

Thus far, we have considered only the probabilities associated with the assignments of distinguishable molecules to the allowed energy levels. In Section 20.2, we introduce the hypothesis that all of the g_i degenerate quantum states with energy ϵ_i are equally probable, so that the probability that a molecule has energy ϵ_i is $P_i = P(\epsilon_i) = g_i \rho(\epsilon_i)$. Making this substitution, the total probability sum becomes

$$\begin{aligned} 1 = & \left(P_1 + P_2 + \cdots + P_i + \ldots\right)^N \\ & = \sum_{\{N_i\}} \frac{N!}{N_1! N_2! \ldots N_i! \ldots} P_1^{N_1} P_2^{N_2} \ldots P_i^{N_i} \ldots \\ & = \sum_{\{N_i\}} \frac{N! g_1^{N_1} g_2^{N_2} \ldots g_i^{N_i} \ldots}{N_1! N_2! \ldots N_i! \ldots} \rho(\epsilon_1)^{N_1} \rho(\epsilon_2)^{N_2} \ldots \rho(\epsilon_i)^{N_i} \ldots . \\ & = \sum_{\{N_i\}} N! \prod_{i=1}^{\infty} \left(\frac{g_i^{N_i}}{N_i!}\right) \rho(\epsilon_i)^{N_i} \\ & = \sum_{\{N_i\}} W \prod_{i=1}^{\infty} \rho(\epsilon_i)^{N_i} \end{aligned}$$

where we use the notation

$$a_1 \times a_2 \times \ldots a_i \times \ldots a_\omega \times = \prod_{i=1}^{\omega} a_i$$

for extended products and introduce the function

$$\begin{aligned} W & = W(N_i, g_i) \\ & = W(N_1, g_1, N_2, g_2, \ldots, N_i, g_i, \ldots .) \\ & = N! \prod_{i=1}^{\infty} \left(\frac{g_i^{N_i}}{N_i!}\right) \\ & = C(N_1, N_2, \ldots, N_i, \ldots) \prod_{i=1}^{\infty} g_i^{N_i} \end{aligned}$$

For reasons that become clear later, W is traditionally called the ***thermodynamic probability***. This name is somewhat unfortunate, because W is distinctly different from an ordinary probability.

In Section 20.5, we note that $P_1^{N_1} P_2^{N_2} \ldots P_i^{N_i}$ is the probability that N_i molecules occupy each of the energy levels ϵ_i and that $N!/(N_1! N_2! \ldots N_i! \ldots)$ is the number of combinations of distinguishable molecules that arise from the population set $\{N_1, N_2, \ldots, N_i, \ldots\}$. Now we observe that the extended product

$$\rho(\epsilon_1)^{N_1} \rho(\epsilon_2)^{N_2} \ldots \rho(\epsilon_i)^{N_i} \ldots .$$

is the probability of any one assignment of the distinguishable molecules to quantum states such that N_i molecules are in quantum states whose energies are ϵ_i. Since a given molecule of energy ϵ_i can be in any of the g_i degenerate quantum states, the probability that it is in the energy level ϵ_i is g_i-fold greater that the probability that it is in any one of these quantum states.

Microstates

We call a particular assignment of distinguishable molecules to the available quantum states a ***microstate***. For any population set, there are many combinations. When energy levels are degenerate, each combination gives rise to many microstates. The factor $\rho(\epsilon_1)^{N_1} \rho(\epsilon_2)^{N_2} \ldots \rho(\epsilon_i)^{N_i} \ldots .$ is the probability of any one microstate of the population set $\{N_1, N_2, \ldots, N_i, \ldots\}$. Evidently, the thermodynamic probability

$$W = N! \prod_{i=1}^{\infty} \left(\frac{g_i^{N_i}}{N_i!} \right) \tag{20.7.1}$$

is the total number of microstates of that population set.

To see directly that the number of microstates is dictated by Equation 20.7.1, let us consider the number of ways we can assign N distinguishable molecules to the quantum states when the population set is $\{N_1, N_2, \ldots, N_i, \ldots\}$ and energy level ϵ_i is g_i-fold degenerate. We begin by assigning the N_1 molecules in energy level ϵ_1. We can choose the first molecule from among any of the N distinguishable molecules and can choose to place it in any of the g_1 quantum states whose energy is ϵ_1. The number of ways we can make these choices is Ng_1. We can choose the second molecule from among the $N-1$ remaining distinguishable molecules. In Boltzmann statistics, we can place any number of molecules in any quantum state, so there are again g_1 quantum states in which we can place the second molecule. The total number of ways we can place the second molecule is $(N-1)\,g_1$.

The number of ways the first and second molecules can be chosen and placed is therefore $N\,(N-1)\,g_1^2$. We find the number of ways that successive molecules can be placed in the quantum states of energy ϵ_1 by the same argument. The last molecule whose energy is ϵ_1 can be chosen from among the $(N-N_1+1)$ remaining molecules and placed in any of the g_1 quantum states. The total number of ways of placing the N_1 molecules in energy level ϵ_1 is $N\,(N-1)\,(N-2)\ldots(N-N_1+1)\,g_1^{N_1}$.

This total includes all possible orders for placing every set of N_1 distinguishable molecules into every possible set of quantum states. However, the order doesn't matter; the only thing that affects the state of the system is which molecules go into which quantum state. (When we consider all of the ways our procedure puts all of the molecules into any of the quantum states, we find that any assignment of molecules A, B, and C to any particular set of quantum states occurs six times. Selections in the orders A, B,C; A,C,B; B,A,C; B,C,A; C,A,B; and C,B,A all put the same molecules in the same quantum states.) There are $N_1!$ orders in which our procedure chooses the N_1 molecules; to correct for this, we must divide by $N_1!$, so that the total number of assignments we want to include in our count is

$$N\,(N-1)\,(N-2)\ldots(N-N_1+1)\,g_1^{N_1}/N_1!$$

The first molecule that we assign to the second energy level can be chosen from among the $N-N_1$ remaining molecules and placed into any of the g_2 quantum states whose energy is ϵ_2. The last one can be chosen from among the remaining $(N-N_1-N_2+1)$ molecules. The number of assignments of the N_2 molecules to g_2-fold degenerate quantum states whose energy is ϵ_2 is

$$(N-N_1)\,(N-N_1-1)\ldots(N-N_1-N_2+1)\,g_2^{N_2}/N_2!$$

When we consider the number of assignments of molecules to quantum states with energies ϵ_1 and ϵ_2 we have

$$N\,(N-1)\ldots(N-N_1+1)\,(N-N_1)\,(N-N_1-1)\ldots$$
$$\times\,(N-N_1-N_2+1)\left(\frac{g_1^{N_1}}{N_1!}\right)\left(\frac{g_2^{N_2}}{N_2!}\right)$$

Let the last energy level to contain any molecules be ϵ_ω. The number of ways that the N_ω molecules can be assigned to the quantum states with energy ϵ_ω is $N_\omega\,(N_\omega-1)\ldots(1)\,g_\omega^{N_\omega}/N_\omega!$ The total number of microstates for the population set $\{N_1, N_2, \ldots, N_i, \ldots\}$ becomes

$$N\,(N-1)\ldots(N-N_1)\,(N-N_1-1)\ldots$$
$$\times\,(N_\omega)\,(N_\omega-1)\ldots(1)\prod_{i=1}^{\infty}\left(\frac{g_i^{N_i}}{N_i!}\right) = N!\prod_{i=1}^{\infty}\left(\frac{g_i^{N_i}}{N_i!}\right)$$

When we consider Fermi-Dirac and Bose-Einstein statistics, it is no longer true that the molecules are distinguishable. For Fermi-Dirac statistics, no more than one molecule can be assigned to a particular quantum state. For a given population set, Boltzmann, Fermi-Dirac, and Bose-Einstein statistics produce different numbers of microstates.

It is helpful to have notation that enables us to specify different combinations and different microstates. If ϵ_i is the energy associated with the wave equation that describes a particular molecule, it is convenient to say that the molecule is in energy level ϵ_i; that is, its quantum state is one of those that has energy ϵ_i. Using capital letters to represent molecules, we indicate that

molecule A is in energy level ϵ_i by writing $\epsilon_i\,(A)$. To indicate that A, B, and C are in ϵ_i, we write $\epsilon_i\,(A, B, C)$. Similarly, to indicate that molecules D and E are in ϵ_k, we write $\epsilon_k\,(D, E)$. For this system of five molecules, the assignment $\epsilon_i\,(A, B, C)\,\epsilon_k\,(D, E)$ represents one of the possible combinations. The order in which we present the molecules that have a given energy is immaterial: $\epsilon_i\,(A, B, C)\,\epsilon_k\,(D, E)$ and $\epsilon_i\,(C, B, A)\,\epsilon_k\,(E, D)$ represent the same combination. When any one molecule is distinguishable from others of the same substance, assignments in which a given molecule has different energies are physically different and represent different combinations. The assignments $\epsilon_i\,(A, B, C)\,\epsilon_k\,(D, E)$ and $\epsilon_i\,(D, B, C)\,\epsilon_k\,(A, E)$ represent different combinations. In Figure 2, we represent these assignments more schematically.

Any two assignments in which a particular molecule occupies different quantum states give rise to different microstates. If the i^{th} energy level is three-fold degenerate, a molecule in any of the quantum states $\psi_{i,1}$, $\psi_{i,2}$, or $\psi_{i,3}$ has energy ϵ_i. Let us write

$$\psi_{i,1}\,(A, B)\,\psi_{i,2}\,(C)\,\psi_{k,1}\,(DE)$$

to indicate the microstate arising from the combination $\epsilon_i\,(A, B, C)\,\epsilon_k\,(D, E)$ in which molecules A and B occupy $\psi_{i,1}$, molecule C occupies $\psi_{i,2}$, and molecules D and E occupy $\psi_{k,1}$. Then,

$$\psi_{i,1}\,(A, B)\,\psi_{i,2}\,(C)\,\psi_{k,1}\,(DE)$$

$$\psi_{i,1}\,(B, C)\,\psi_{i,2}\,(A)\,\psi_{k,1}\,(DE)$$

$$\psi_{i,1}\,(A)\,\psi_{i,2}\,(B, C)\,\psi_{k,1}\,(DE)$$

are three of the many microstates arising from the combination $\epsilon_i\,(A, B, C)\,\epsilon_k\,(D, E)$. Figure 3 shows all of the microstates possible for the population set $\{2, 1\}$ when the quantum states of a molecule are $\psi_{1,1}$, $\psi_{1,2}$, and $\psi_{2,1}$.

Microstates		$\psi_{1,1}$	$\psi_{1,2}$	$\psi_{2,1}$
	1	AB		C
	2	A	B	C
	3	B	A	C
	4		AB	C
	5	AC		B
	6	A	C	B
	7	C	A	B
	8		AC	B
	9	BC		A
	10	B	C	A
	11	C	B	A
	12		BC	A

Figure 3. Microstates for {2,1} with quantum states $\Psi_{1,1}$, $\Psi_{1,2}$, and $\Psi_{2,1}$.

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