5.62 Physical Chemistry II
Spring 2008

5.62 Lecture #5: Molecular Partition Function: Replace E(assembly) by ε(molecule)

Readings: Hill, pp. 59-70; Maczek, pp. 16-19; Metiu pp. 49-55

Overview: We've learned to calculate thermodynamic (macroscopic) properties of a system from the partition function. However, the partition function, as it is presently written, depends on the energy levels available to the *entire many-particle system*. We still need to input an understanding of the energy levels of a single molecule (microscopic) into a description of the energy levels of the entire many-particle system (= assembly). Today we will do this, using statistics (combinatorics).

Goal: Reformulate Q as a function of the energies, ε_i, of states of **individual** molecules rather than the energies E_j of an assembly of molecules.

Procedure: Change labeling of states from "α-type" (assembly centered) description to an occupation number, n_i, (molecule centered) n-type description.

α-type assembly description (list of the state of each molecule in assembly)

$m_{1x}m_{1y}m_{1z}$	$m_{2x}m_{2y}m_{2z}$	$m_{3x}m_{3y}m_{3z}$	$m_{4x}m_{4y}m_{4z}$	$m_{5x}m_{5y}m_{5z}$
1 1 1	2 1 1	1 1 1	1 2 2	2 1 1
molecule 1 state #1 energy ε_1	molecule 2 state #2 energy ε_2	molecule 3 state #1 energy ε_1	molecule 4 state #3 energy ε_3	molecule 5 state #2 energy ε_2

To construct an n-type description (list of number of systems in each allowed molecule state: less information) of the same assembly state:

Define $n_i \equiv$ occupation number = number of molecules in i^{th} molecular state. For example (2, 2, 1) means:

$n_1 = 2$ molecules in state #1 with energy ε_1

$n_2 = 2$ molecules in state #2 with energy ε_2

$n_3 = 1$ molecule in state #3 with energy ε_3

Thus, an α–type state could be re-expressed in terms of a set of individual particle energy level occupation numbers (called a "configuration"):

$\{n_i\} = \{n_1, n_2, n_3, \cdots\}$ where $N = \sum_{i \text{ levels}} n_i$ and $E = \sum_{i \text{ levels}} n_i \varepsilon_i$

shorthand; total # of molecules; sum over molecular states; energy of assembly; energy of ith molecular state

This is a change of focus from labels that identify $\approx 10^{23}$ individual molecules to labels that identify molecular states and the number of molecules in each of those states.

Note that different (α-type) assembly states can have the same (n-type) occupation numbers. For example, switch the occupied energy states between molecules 1 and 2.

Expand definition of <u>degeneracy</u> to include occupation numbers:

$\Omega(\{n_i\})$ ≡ degeneracy = number of (α-type) assembly states with the same set $\{n_i\}$ of occupation numbers (or total E)

Rewrite Q ...

$$Q(N,V,T) = \sum_j e^{-E_j/kT}$$

sum over possible (α-type) states of assembly

$$= \sum_{\{n_i\}} \Omega(\{n_i\})\, e^{-E(\{n_i\})/kT}$$

sum over all sets of occupation numbers $\{n_i\}$ such that $\sum_i n_i = N$

COMBINATORICS

Determining Ω for a given set of $\{n_i\}$:

How many ways are there to arrange molecules such that occupation numbers are given by $\{n_i\}$? This is Ω. Another way to ask the question ... How many ways are there to put N molecules into a set of molecular states with n_1 in state #1, n_2 in state #2, etc.

state #	energy	# molecules
1	ε_1	n_1
2	ε_2	n_2
3	ε_3	n_3
⋮	⋮	⋮
i	ε_i	n_i
⋮	⋮	⋮

This is a simple combinatorial problem. We put all N molecules in sequence and put the first n_1 in state #1, the next n_2 in state #2, etc. Then the number of ways of arranging molecules into states is just the number of sequences, which is just $N! = N(N–1)(N–2)(N–3)\cdots(2)(1)$, because there are N places in the sequence to put the first molecule, (N–1) places to put the second, etc.

However, this overcounts because the order of molecules chosen for molecular state #1 is not important. That is, all ways of renumbering molecules in state #1 are equivalent. There are $(n_1!)$ of them. A similar factor of $(n_i!)$ needs to be used to correct for overcounting in each state.

For distinguishable molecules, the # of ways of putting N molecules in a set of states such that the first state gets n_1 molecules, the second state gets n_2 molecules, etc. is ...

$$\Omega(\{n_i\}) = \frac{N!}{n_1!n_2!n_3!\cdots n_i!\cdots} = \frac{N!}{\prod_i n_i!}$$

a multinomial coefficient

What is a multinomial coefficient?

In the expansion of $(a + b + c)^N$

the term $a^{n_1}b^{n_2}c^{n_3}$ is multiplied by the coefficient $\frac{N!}{n_1!n_2!n_3!}$

where $\sum_i n_i = N$

$$(a + b + c + d)^3 = a^3 + 3a^2b + 6abc + \cdots$$

$$\frac{N!}{n_1!n_2!n_3!n_4!} \qquad \frac{3!}{3!0!0!0!} \qquad \frac{3!}{2!1!0!0!} \qquad \frac{3!}{1!1!1!0!}$$

Note: $0! = 1$

Rewrite Q in Terms of the New Expression for **Ω**

$$Q(N,V,T) = \sum_{\{n_i\}} \Omega\left(\{n_i\}\right) e^{-E(\{n_i\})/kT}$$

$$= \sum_{\{n_i\}} \frac{N!}{\prod_j n_j!} e^{-\sum_j n_j \varepsilon_j / kT}$$

This is a sum over all sets of occupation numbers, and $E\left(\{n_i\}\right) = \sum_j n_j \varepsilon_j$.

Reformulate the expression for Q

$$Q(N,V,T) = \sum_{\{n_i\}} \frac{N!}{\prod_j n_j!} e^{-\Sigma_i n_i \varepsilon_i / kT}$$

energy of i-th molecular state

where $E(\{n_i\}) = \sum_i n_i \varepsilon_i$

# of molecules in state i

Reduce this to a function of the sum over states of a single molecule:

$$= \sum_{\{n_i\}} \left(\frac{N!}{\prod_j n_j!} \right) \left[\prod_i \left(e^{-\varepsilon_i / kT} \right)^{n_i} \right]$$

note that $e^{-\varepsilon_i/kT}$ is raised to the n_i-th power

Now impose multinomial trick

$$= \left(e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT} + e^{-\varepsilon_3/kT} \ldots \right)^N$$

$$= \left(\sum_i e^{-\varepsilon_i/kT} \right)^N$$

sum over states of a single molecule

Define:

$$q = \sum_i e^{-\varepsilon_i/kT}$$

sum over states of a single molecule

MOLECULAR PARTITION FUNCTION

ε_i = molecular energy of state i

$$Q(N,V,T) = [q(V,T)]^N$$

N-molecule Canonical Partition Function

Single Molecule Canonical Partition Function

FOR **INDEPENDENT**, **DISTINGUISHABLE** PARTICLES!