5.62 Physical Chemistry II
Spring 2008

# 5.62 Lecture #6: Q Corrected for Molecular Indistinguishability

Transformed Q from *sum over states of an entire N-molecule assembly* to *sum over states of an individual molecule*

$$Q = \sum_j e^{-E_j/kT} = \left(\sum_i e^{-\varepsilon_j/kT}\right)^N = q^N$$

sum over states of assembly — sum over states of a molecule

$$\underbrace{\sum_{\{n_j\}}}_{\text{sum over all sets of occupation numbers}} \Omega(\{n_j\}) e^{-E(\{n_j\})/kT} = \sum_{\{n_j\}} \frac{N!}{\prod_j n_j!} e^{-\sum_i n_i \varepsilon_i/kT}$$

FOR INDEPENDENT, <u>DISTINGUISHABLE</u> PARTICLES

| <u>BIG PROBLEM</u>: Identical molecules are INDISTINGUISHABLE!! |
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We have implicitly been assuming that we can distinguish particle 1 from particle 2, but quantum mechanics tells us that two identical particles are not distinguishable. [Even if we could label individual atoms by their position at $t_1$, then follow each of the atoms until $t_2$, these positional labels will be corrupted each time there is a collision.] Exceptions? Molecules in a crystal or in spatially confined traps on the surface of a solid.

Thus we will need to modify the above result for molecules, since molecules of the same type are indistinguishable. We had shown that

$$\Omega(\{n_i\}) = \frac{N!}{\prod_{i=1}^{t} n_i!}$$

is the number of ways of putting N distinguishable particles into t states with occupation numbers $\{n_i\}$. But if all the particles are identical, the number of ways is just 1. How do we know this to be true? Do example of 3 molecules in 2 states.

$$\boxed{\text{That is, for INDISTINGUISHABLE PARTICLES, } \Omega(\{n_i\}) = 1}$$

However $\Omega = N!/\Pi n_i!$ is a multinomial coefficient that was needed to produce this "tidy" result relating Q to q:

$$Q = \sum_j e^{-E_j/kT} = \sum_{\{n_j\}} \Omega\left(\{n_j\}\right) e^{-E\left(\{n_j\}\right)/kT} = \left(\sum_i e^{-\varepsilon_i/kT}\right)^N = q^N$$

No way to exploit this simplification if $\Omega\{n_i\} = 1$. That is the reason why we did the distinguishable particle case first. Now we have to take this "tidy" result and fix it for indistinguishability. Problem is that each term in this sum is too large by a factor $N!/\Pi n_i!$ Will solve this problem by dividing Q by $N!/\Pi n_i!$ for a special limiting case (which turns out to be *almost* universally applicable).

## CORRECTED BOLTZMANN STATISTICS – AN APPROXIMATE CORRECTION FOR INDISTINGUISHABILITY

Define $\bar{n}_i \equiv$ average occupation number of $i^{th}$ molecular state in ensemble
<u>or</u> ensemble average # of molecules in $i^{th}$ state

probability of finding $n_i$ molecules in state i of $j^{th}$ assembly

number of molecules in $i^{th}$ state of $j^{th}$ assembly

$$\bar{n}_i = \sum_j P_j(n_i)\, n_i(j)$$

sum over assemblies

If the number of molecular states i is much greater than N, then

$$\bar{n}_i << 1$$

The average occupation number will be much less than 1. So, most of the occupation numbers will be

$n_i = 0$ or $n_i = 1$ with $n_i > 1$ occurring **very** rarely.

Under these conditions

because $1! = 0! = 1$

$$\Omega = \frac{N!}{\prod_i n_i!} = \frac{N!}{1} = N! \qquad \text{when } \bar{n}_i << 1$$

For $\bar{n}_i \ll 1$, $\Omega$ is too large by a factor of N! in *each* term of

$$Q = \sum \Omega e^{-E/kT}$$

owing to our neglect of indistinguishability.

Remember, we want $\Omega = 1$. So, take the distinguishable molecule result $Q = q^N$ and divide by N!. This division will make $\Omega = 1$ and is a valid correction as long as *all* $\bar{n}_i \ll 1$. Therefore by dividing by N!, we have "corrected" for indistinguishability

$$\boxed{Q(N,V,T) = q^N / N!}$$

corrected for indistinguishability

**Boltzmann statistics**

In other words, we used $\Omega = \frac{N!}{\prod_i n_i!}$ earlier to get a "tidy" result and now we are dividing it out. But the value we're dividing by is N! Not $\frac{N!}{\prod n_i!}$ because all $\bar{n}_i \ll 1$. So, we have fixed the "canonical" partition function to account for indistinguishability. How generally can we depend on this to be true?

When is $\bar{n}_i \ll 1$? Need to obtain an expression for $\bar{n}_i$. Express the ensemble average in terms of *sets* of state occupation numbers rather than *single state* occupation numbers.

$$\bar{n}_i = \sum_j P_j(n_i)\, n_i(j) = \sum_{\{n_j\}} P(\{n_j\})\, n_i(\{n_j\})$$

number of molecules in $i^{th}$ state in $j^{th}$ assembly

averaged over all sets of occupation numbers in ensemble

number of molecules in $i^{th}$ molecular state for the specified set of occupation numbers $\{n_j\}$

Need $P(\{n_j\})$

$$P(E) = \frac{\Omega(E)e^{-E/kT}}{Q} \Rightarrow P(\{n_j\}) = \frac{\Omega(\{n_j\})e^{-E(\{n_j\})/kT}}{Q}$$

$$P(\{n_i\}) = \frac{N!}{\prod_j n_j!} \exp\left\{\sum_i -n_i\varepsilon_i / kT\right\} \Big/ Q$$

Plug $P(\{n_j\})$ into the above equation for $\bar{n}_i$ ; $\beta = 1/kT$

calculating average value of $n_i$

$$\bar{n}_i = \sum_{\{n_j\}} \left(\frac{N!}{n_1!n_2!\ldots n_i!\ldots}\right) e^{-\beta n_1\varepsilon_1} e^{-\beta n_2\varepsilon_2} \ldots n_i\, e^{-\beta n_i\varepsilon_i} \ldots / Q$$

partition out factor N from N! and factor $e^{-\beta\varepsilon_i}$ from product

$$= \sum_{\{n_j\}} \left(\frac{N(N-1)!}{n_1!n_2!\ldots(n_i-1)!\ldots}\right) e^{-\beta n_1\varepsilon_1} e^{-\beta n_2\varepsilon_2} \ldots \left(e^{-\beta(n_i-1)\varepsilon_i} \underbrace{e^{-\beta\varepsilon_i}}_{\text{removed term}}\right) \ldots / Q$$

cancelled factor of $n_i$ in numerator

$$\bar{n}_i = \frac{Ne^{-\varepsilon_i/kT}}{Q} \sum_{\{n_j\}} \left(\frac{(N-1)!}{n_1!n_2!\ldots(n_i-1)!\ldots}\right) e^{-n_1\varepsilon_1/kT} e^{-n_2\varepsilon_2/kT} \ldots e^{-(n_i-1)\varepsilon_i/kT} \ldots$$

The sum over $\{n_j\}$ looks like Q(N–1, V, T), but we will need to check this.

$$\bar{n}_i = \frac{Ne^{-\varepsilon_i/kT}}{Q(N,V,T)} Q(N-1,V,T)$$

check to be sure $\bar{n}_i$ is correctly normalized

$$\sum_i \bar{n}_i = N$$

$$\sum_i \bar{n}_i = \frac{NQ(N-1,V,T)}{Q(N,V,T)} \sum_i e^{-\varepsilon_i/kT} = \frac{N\left(q^{N-1}/(N-1)!\right)}{\left(q^N/N!\right)} q$$

$$= \frac{Nq^{N-1}N!}{q^N (N-1)!} q = N^2$$

too large by a factor of N.

So original equation for $\bar{n}_i$ must be divided by N. So we get

$$\bar{n}_i = e^{-\varepsilon_i/kT} \left[ \frac{Q(N-1,V,T)}{Q(N,V,T)} \right]$$

$$\bar{n}_i = \frac{Ne^{-\varepsilon_i/kT} q^{N-1}}{q^N} = \frac{Ne^{-\varepsilon_i/kT}}{q}$$

Since $e^{-\varepsilon_j/kT} < 1$ always (because $\varepsilon_j \geq 0$)

$$\bar{n}_i \ll 1 \text{ if } q \gg N$$

$$\boxed{\frac{N}{q} \ll 1}$$ condition for validity of corrected Boltzmann statistics

Thus whenever the value of the single particle partition function is larger than the number of molecules in the system, it is OK to correct for particle indistinguishability merely by dividing $q^N$ by N! But is this ever true? Typically $N \sim 10^{23}$. How can q be so much larger than this?