

INDISTINGUISHABLE PARTICLES:

[Where does the N! come from? Is it correct?](#)

[How to deal with non-ideal gases?](#)

[What does this have to do with Keq?](#)

The origin of the N!

For distinguishable non-interacting particles, it is easy to see that the total partition function Q is the product of the one-particle partition functions q . However, to understand entropy of mixing (and why opening a valve between two containers of nitrogen at the same P, T does not increase the entropy) Gibbs found that for indistinguishable non-interacting particles (like nitrogen molecules) one wants instead

$$Q = \frac{q^N}{N!}$$

A very rough argument about why you might expect an $N!$ from combinatorics is given in Atkins and many other undergraduate P. Chem. textbooks. However, this argument is not rigorous, in fact it is easy to see problems with it. Here we outline a more detailed derivation (following Kittel & Kroemer's *Thermal Physics*). Fundamentally, the $N!$ comes from the Pauli condition on the wavefunction (that the wavefunction must be either symmetric or antisymmetric for permutation of identical particles) but this is pretty complicated to explain; for an attempt to derive the partition function directly from Slater determinants see Pathria's *Statistical Mechanics*. Note that the Gibbs $N!$ factor which fixes the entropy also shifts the Helmholtz free energy $F = U - TS$:

$$F = -kT \ln Q = -NkT \ln q + kT \ln(N!) \sim -NkT \ln q + NkT \ln N - NkT$$

(using Stirling's approximation for the last part - only valid for $N \gg 1$). It does not affect the energy U .

Recall that the probability that a system which can exchange particles and heat with a large reservoir will be found with N particles in the quantum state $s(N)$ is

$$P(s(N)) = \frac{e^{\left(\frac{N\mu - \epsilon_{s(N)}}{k_B T} \right)}}{Z(\mu, T)}$$

where Z is the grand canonical partition function

$$Z = \sum e^{\left(\frac{N\mu - \epsilon_{s(N)}}{k_B T} \right)}$$

the sum is over all possible quantum states of the system, with all possible numbers of particles. μ is the chemical potential, which is strictly defined as

$$\mu(T, V, N) = F(T, V, N) - F(T, V, N - 1)$$

but you may be more familiar with the continuous approximation

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V}$$

which is valid for macroscopic systems (large N). Note that by induction

$$F(T, V, N) = \sum \mu(T, V, n)$$

Where the sum is over n from 1 to N . The expected number of particles in the system

$$\langle N \rangle = \frac{\sum NP(s(N))}{Z}$$

can also be expressed $\langle N \rangle = kT (d \ln Z / d \mu)$.

A particularly simple type of system is one which can only hold one particle maximum: $N=0$ and $N=1$, and which for each occupancy there is only 1 quantum state (with energies 0 and ϵ , respectively). If

one considers a fermion ($S = N + \frac{1}{2}$) spin-orbital to be the system (all the other spin-orbitals of a real

system would be considered part of the reservoir) this is the real situation for an ideal gas of fermions. By the Pauli principle, only one fermion can occupy a spin-orbital (i.e. can have a particular set of quantum numbers).

For a fermion spin-orbital

$$Z = 1 + e^{\left(\frac{\mu - \epsilon}{kT}\right)}$$

$$\langle N \rangle = \frac{1}{e^{\left(\frac{\epsilon - \mu}{kT}\right)} + 1}$$

This result is completely general: the equilibrium probability that any ideal-gas fermion quantum state in contact with a reservoir is occupied is given by $\langle N \rangle$. This formula is called the Fermi-Dirac distribution. For a boson (Spin = integer) spin-orbital one can do a similar derivation, if one assumes that the bosons are non-interacting (i.e. ideal gas); the result is the Bose-Einstein distribution:

$$\langle N \rangle = \frac{1}{e^{\left(\frac{\epsilon - \mu}{k T}\right)} - 1}$$

At normal temperatures and densities, the plus or minus 1 is negligible compared to the exponential term, and we can make the "classical" approximation to get the expected occupancy of any state s :

$$\langle N \rangle_s = e^{\left(\frac{\mu - \epsilon_s}{k T}\right)}$$

The total number of particles in a many-quantum-state ideal gas system in contact with a reservoir is

$$N = \sum \langle N \rangle_s$$

$$N = e^{\left(\frac{\mu}{k T}\right)} \left(\sum e^{\left(-\frac{\epsilon_s}{k T}\right)} \right)$$

we recognize the second term as the one-particle partition function q :

$$N = e^{\left(\frac{\mu}{k T}\right)} q$$

We can rearrange this to

$$\mu_{ideal_gas}(T, V, N) = k T \ln\left(\frac{N}{q(T, V)}\right)$$

i.e. this is the chemical potential that a reservoir must have for it to be in equilibrium with an ideal gas system with N particles in a volume V at temperature T . Now we can add up all the μ_{ideal_gas} values as we add particles to an empty system from $n=1$ to N to get the free energy of the system:

$$F(T, V, N) = \sum \left(-k T \ln\left(\frac{q}{n}\right) \right)$$

We can evaluate the sum (a sum of ln's is a product):

$$F(T, V, N) = -k T \ln\left(\frac{q^N}{N!}\right)$$

and the term in brackets is indeed Q (since $F = -kT \ln Q$). So the $N!$ is exactly right (at least for an ideal gas).

Non-ideal gases:

To get the partition function for a non-ideal gas where you know $P(T, V, N)$ and the behavior in the dilute (ideal-gas) limit, say at volume V_0 , one can perform an integral over volume:

$$P(T, V, N) = -\left(\frac{\partial F}{\partial V}\right)_{T, N}$$

so

$$-k T \ln\left(\frac{Q_f}{Q_o}\right) = -\int_{V_o}^{V_f} P dV$$

What does the N! have to do with Keq?

At equilibrium the free energy does not change when a chemical reaction proceeds a little (if the chemical reaction proceeds a lot, the concentrations in the system will move appreciably away from equilibrium). In other words, the sum of the chemical potentials of the reactants (weighted by any stoichiometric coefficients) must equal the sum of the chemical potentials of the products (again, weighted by any stoichiometric coefficients).

Above, for an ideal gas, we found

$$\mu_{ideal_gas}(T, V, N) = k T \ln\left(\frac{N}{q(T, V)}\right)$$

so at equilibrium for a reaction $A+B = C$ at constant volume (A,B,C assumed ideal)

$$\ln(N_a N_b / q_a q_b) = \ln(N_c / q_c)$$

which can be re-arranged to

$$[C]/[A][B] = (6.02E23 \text{ molecules/mole}) (q_c/V)/(q_a/V)(q_b/V)$$

If there is some kinetic inhibition, and the reaction does not equilibrate completely (but the temperature does), one can still compute the change in free energy associated with the progress of the reaction using the expression for the chemical potential or for F given above.