

Notes on the Boltzmann distribution

January 29, 2012

Chemistry 342, (01:160:342), Spring 2012

Physical Chemistry of Biochemical Systems

1 Molecular interpretation of entropy

Suppose we have a system with a set of possible states $\{i\}$, such that the probability of finding a particular state is p_i . Now we *postulate* that the entropy of such a system is:

$$S = -k \sum_i p_i \ln p_i \quad (1)$$

We can show that S is a measure of randomness. For example, if only one state is populated, and all the rest have zero probability, then $S = 0$ for this very non-random state. Similarly, if there are a total of W possible states, and each has equal probability $p_i = 1/W$, then $S = k \ln W$, and this is the largest entropy one can get. We can show this by considering the change in entropy upon changing the populations:

$$\frac{dS}{dp_i} = -k \sum_i \left(p_i \frac{d \ln p_i}{dp_i} + \ln p_i \right)$$

or

$$dS = -k \sum_i (1 + \ln p_i) dp_i \quad (2)$$

Now we know that probability must be conserved, so that $\sum p_i = 1$, or

$$\sum_i dp_i = 0 \quad (3)$$

Hence the first term in Eq. 2 (with the "1") vanishes; furthermore, if you set $\ln p_i$ to be independent of i , it can be taken outside of the sum, and you can use Eq. 3 again to show that $dS = 0$, and hence that the entropy is maximized by a uniform distribution.

2 The canonical distribution

Now, instead of having a single, isolated system (where the maximum entropy comes from uniform distribution), we want to consider a large collection (“ensemble”) of identical subsystems, which can transfer energy amongst themselves. Now, in addition to the constraint on conservation of probability (Eq. 3), there is a constraint that the total internal energy must be conserved: $\sum p_i E_i = U$, or

$$\sum_i E_i dp_i = 0 \quad (4)$$

Now, we want to maximize the entropy (find the most random state), subject to both conservation equations 3 and 4. We already saw that we can drop the first term in Eq. 2, and we can set $dS = 0$ for a maximum:

$$dS = -k \sum_i \ln p_i dp_i = 0 \quad (5)$$

Here, think of $\ln p_i$ as the coefficient of the dp_i terms which are to be varied, and note that all three Equations, 3, 4 and 5, have a similar form, with a sum where the dp_i terms are multiplied by different coefficients. The only way to satisfy all three equations for arbitrary values of the dp_i variables is if $\ln p_i$ is a linear combination of the coefficients in the constraint equations:

$$\boxed{\ln p_i = \alpha - \beta E_i} \quad (6)$$

(*Proof*: just substitute Eq. 6 into Eq. 5, and simplify using Eqs. 3 and 4). [Note the minus sign in Eq. 6 is for convenience: β can be any constant, and using a minus sign here rather than a plus sign will make β be positive later on. Also note that α and β are (initially) unknown constants, often called *Lagrange multipliers*.]

3 The connection to classical thermodynamics

All that remains is to figure out what α and β must be. Getting α is easy by the conservation of total probability:

$$e^\alpha = \frac{1}{Z} \text{ or } \alpha = -\ln Z$$

where Z is the partition function:

$$Z = \sum_j e^{-\beta E_j} \quad (7)$$

To determine β , substitute Eq. 6 into Eq. 5:

$$dS = -k \sum_i dp_i (\alpha - \beta E_i) = k\beta \sum_i dp_i E_i = k\beta dq_{rev}$$

Here we have removed the term involving α by our usual arguments involving conservation of probability; next we note that $dp_i E_i$ is the amount of heat energy exchanged when the probabilities are changed by dp_i ; since these are infinitesimal changes in probability, the heat exchanged is also infinitesimal, and hence must be reversible. Since $dS = dq_{rev}/T$, we find that $\beta = 1/kT$, and hence:

$$\boxed{p_i = \frac{e^{-\beta E_i}}{Z}} \quad (8)$$

What we have shown is that this *Boltzmann distribution* maximizes the entropy of a system in thermal equilibrium with other systems kept at a temperature T .

4 Free energies at constant volume

As an aside, to help you understand other texts and papers: We have introduced the Gibbs free energy, $G = H - TS$, which is useful for the most common task of interpreting experiments at constant pressure. There is an analogous “constant volume” free energy A (usually called the *Helmholtz free energy*) which is defined as $A = U - TS$. It is instructive to use Eq. 8 to compute A :

$$\begin{aligned} A &= U - TS \\ &= \sum_i p_i E_i + kT \sum_i p_i \ln p_i \\ &= \sum_i \frac{e^{-\beta E_i}}{Z} E_i + kT \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i - \ln Z) \\ &= \sum_i \frac{e^{-\beta E_i}}{Z} (E_i - E_i - kT \ln Z) \end{aligned}$$

or

$$\boxed{A = -kT \ln Z} \quad (9)$$

The free energy is an extremely important quantity, and hence the partition function Z is also extremely important. We will make good use of Eq. 9 later on in the class.