

Notes on the Boltzmann distribution

Chemistry 341, (01:160:341), Fall 2014

Physical Chemistry of Biochemical Systems

1 Recalling some simple thermodynamics

In many ways, the most basic thermodynamic quantity is the *equilibrium constant*, which in its simplest form, is a ratio of concentrations, or probabilities:

$$K_{AB} = \frac{[A]}{[B]} = \frac{p_A}{p_B} \quad (1)$$

We use here the fact that concentrations are proportional to the probability of being in a certain state. A fundamental conclusion from thermodynamics relates the equilibrium constant to free energy difference between A and B:

$$\Delta_{AB}G^0 = -RT \ln K_{AB} \quad (2)$$

By itself, this is not of much use, since it just substitutes one variable for another. But thermodynamics adds an additional relation:

$$G = H - TS \quad \frac{dG}{dT} = -S$$

where the *enthalpy* H is related to heat exchange and the *entropy* S always increases for spontaneous processes (if we consider the entropy of everything, both the system we are studying and its surroundings.)

2 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:

$$S = -k \sum_i p_i \ln p_i \quad (3)$$

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 $S = k \ln W$, (Eq. 5.38 in your text) 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

$$dS = -k \sum_i (1 + \ln p_i) dp_i \quad (4)$$

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

$$\sum_i dp_i = 0 \quad (5)$$

Hence the first term in Eq. 4 (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. 5 again to show that $dS = 0$, and hence that the entropy is maximized by a uniform distribution.

3 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. 5), there is a constraint that the total internal energy must be conserved: $\sum p_i E_i = U$ (see Eq. 5.28 in your text), or

$$\sum_i E_i dp_i = 0 \quad (6)$$

Now, we want to maximize the entropy (find the most random state), subject to both conservation equations 5 and 6. We already saw that we can drop the first term in Eq. 4, and we can set $dS = 0$ for a maximum:

$$dS = -k \sum_i \ln p_i dp_i = 0 \quad (7)$$

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, 5, 6 and 7, 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:

$$\boxed{\ln p_i = \alpha - \beta E_i} \quad (8)$$

(Proof: just substitute Eq. 8 into Eq. 7, and simplify using Eqs. 5 and 6).

Some notes:

1. The minus sign in Eq. 8 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*.
2. There are a variety of ways to arrive at Eq. 8. See, for example, the argument on pp. 152-153 of your text, leading to Eq. (5.4), which is the same as Eq. 8. You can decide how persuasive this argument is; it basically comes down to a consequence of the fact that energies add (top eq. on p. 153), whereas probabilities multiply (second eq. on p. 153).

3. You can also come to a similar conclusion starting from Eq. 3, by noting that entropy is additive (or “extensive”). Consider two uncorrelated systems that have a total number of states W_1 and W_2 . The total number of possibilities for the combined system is $W_1 W_2$. Then:

$$S = k \ln(W_1 W_2) = k \ln W_1 + k \ln W_2 = S_1 + S_2 \quad (9)$$

Basically, the logarithm function is the only one that combines addition and multiplication in this fashion.

4 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:

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

where Q (often also denoted by Z) is the *partition function*:

$$Q = \sum_j e^{-\beta E_j} \quad (10)$$

There are a variety of ways to determine β . On pp. 153-154 of your text, a calculation of the temperature of an ideal gas is used. Another to determine β depends on some additional results from thermodynamics. Substitute Eq. 8 into Eq. 7:

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

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. (See p. 158 in your text, especially Eq. 5.27) Since $dS = dq_{rev}/T$, we find that $\beta = 1/kT$, and hence:

$$p_i = \frac{e^{-\beta E_i}}{Q} \quad (11)$$

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 .

5 Some more connections to thermodynamics

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. 11 to compute A :

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

or

$$\boxed{A = -kT \ln Q} \tag{12}$$

(Note that $G = A + pV$, and that for (nearly) incompressible liquids there is (almost) no pressure-volume work. Hence, in liquids $G \simeq A$, just like $H \simeq U$.)

The free energy is an extremely important quantity, and hence the partition function Q is also extremely important. Other thermodynamic formulas follow:

$$\begin{aligned}
A &= U - TS = -kT \ln Q \\
S &= -(\partial A / \partial T)_V = k \ln Q + kT (\partial \ln Q / \partial T)_V \\
U &= -(\partial \ln Q / \partial \beta); C_V = T \left(\frac{\partial^2 (kT \ln Q)}{\partial T^2} \right)
\end{aligned} \tag{13}$$