

Notes on the Boltzmann distribution

Chemistry 341, (01:160:341), Fall 2013

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:

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

By itself, this is not of much use, since it just substitutes one variable for another. But thermodynamics (gone over in detail in the second semester of this course) 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 $S = k \ln W$, 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: $\sum p_i E_i = U$, 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 their equation (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 (or exponential) 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. 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

This an aside, to help you understand other texts and papers; material in this little section with *not* be covered on any exam or homework, and will only really make sense after you have studied thermodynamics more fully. But the basic point, that the partition function is a key quantity, will come up many times.

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

$$\boxed{A = -kT \ln Q} \quad (12)$$

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

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