

# A few additional notes about the statistical entropy

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## 1 Another equation for the entropy

The authors of your textbook missed an opportunity (by just a couple of easy steps) to derive an important equation for the entropy. Equation (15.58) gives the following expression for the entropy:

$$S = -k \sum_i a_i \ln p_i.$$

In this equation,  $a_i$  is the number of molecules in state  $i$  out of  $N$  total molecules. If we want the molar entropy, we divide equation (15.58) by the number of moles of molecules, i.e. by  $N/N_A$ :

$$S_m = \frac{S}{N/N_A} = -kN_A \sum_i \frac{a_i}{N} \ln p_i.$$

If we have a sufficiently large number of molecules, then  $a_i/N$  should equal  $p_i$ . We get

$$S_m = -R \sum_i p_i \ln p_i. \quad (1)$$

This turns out to be a really central equation which we will use later when we talk about the statistical mechanics of ensembles other than the canonical ensemble. It also shows up in communication theory, among other unexpected places.

Note that equation 1 implies the usual Boltzmann formula: Recall the central postulate of statistical mechanics (textbook, p. 313):

Every possible microstate of an isolated system occurs with equal probability.

If  $p_i$  is the probability that the system is in a particular microstate, then the central postulate says that  $p_i = 1/W$ , where  $W$  is the number of microstates. Then we have

$$\begin{aligned} S_m &= -R \sum_{i=1}^W \frac{1}{W} \ln \frac{1}{W} \\ &= -RW \frac{1}{W} \ln \frac{1}{W}, \end{aligned}$$

because all the terms in the sum are equal, and there are  $W$  of these.

$$\therefore S_m = -R \ln \frac{1}{W} = -R \ln W.$$

## 2 An alternative derivation of equation (15.60)

Once we have a statistical definition of  $U$ , we can get all of the other state functions using purely thermodynamic arguments. Recall that

$$\begin{aligned} \left. \frac{\partial S}{\partial T} \right|_V &= \frac{C_V}{T}. \\ \therefore \int_{S(0)}^{S(T)} &= \int_0^T \frac{C_V}{T} dT, \\ \text{or } S(T) - S(0) &= \int_0^T \frac{C_V}{T} dT. \end{aligned}$$

We also know that can get  $C_V$  from  $U$ :

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V.$$

Finally, we know how to calculate  $U$  from the partition function:

$$U = kT^2 \left. \frac{\partial(\ln Q)}{\partial T} \right|_V.$$

We can now back-substitute:

$$\begin{aligned} C_V &= 2kT \left. \frac{\partial(\ln Q)}{\partial T} \right|_V + kT^2 \left. \frac{\partial^2(\ln Q)}{\partial T^2} \right|_V. \\ \therefore S(T) &= S(0) + \int_0^T \left( 2k \left. \frac{\partial(\ln Q)}{\partial T} \right|_V + kT \left. \frac{\partial^2(\ln Q)}{\partial T^2} \right|_V \right) dT \\ &= S(0) + 2k (\ln Q(T) - \ln Q(0)) + k \int_0^T T \left. \frac{\partial^2(\ln Q)}{\partial T^2} \right|_V dT. \end{aligned}$$

This last integral can be evaluated using integration by parts. Let  $u = T$  and  $dv = (\partial^2(\ln Q)/\partial T^2)_V dT$ . Then  $du = dT$  and  $v = (\partial(\ln Q)/\partial T)_V$ . Thus,

$$\begin{aligned} \int_0^T T \left. \frac{\partial^2(\ln Q)}{\partial T^2} \right|_V dT &= \left[ T \left. \frac{\partial(\ln Q)}{\partial T} \right|_V \right]_0^T - \int_0^T \left. \frac{\partial(\ln Q)}{\partial T} \right|_V dT \\ &= T \left. \frac{\partial(\ln Q)}{\partial T} \right|_V - [\ln Q(T) - \ln Q(0)]. \\ \therefore S(T) &= S(0) + 2k (\ln Q(T) - \ln Q(0)) + kT \left. \frac{\partial(\ln Q)}{\partial T} \right|_V - k [\ln Q(T) - \ln Q(0)] \\ &= S(0) + k (\ln Q(T) - \ln Q(0)) + kT \left. \frac{\partial(\ln Q)}{\partial T} \right|_V. \end{aligned}$$

The value of the entropy at 0 K is somewhat arbitrary. (The third law only guarantees that  $S$  tends to a constant at 0 K, without saying what that constant should be. Setting  $S(0) = 0$  is a convention.) We can choose  $S(0) = k \ln Q(0)$ , and then we get

$$S = k \ln Q + kT \left. \frac{\partial(\ln Q)}{\partial T} \right|_V.$$

If we then just recognize that the last term in this equation is  $U/T$ , we get equation (15.60).

These two very different derivations of the entropy (the one in the book and the one presented here) are yet another demonstration of the extent to which classical thermodynamics and statistical mechanics agree.

### 3 Entropy and the canonical ensemble

Suppose that we have a gas of  $N$  indistinguishable molecules. The canonical partition function is

$$\begin{aligned} Q &= \frac{q^N}{N!}. \\ \text{or } \ln Q &= N \ln q - \ln N! \\ &\approx N \ln q - (N \ln N - N). \end{aligned}$$

The molecular partition function can be written

$$\begin{aligned} q &= q_T q_R q_V q_E. \\ \therefore \ln Q &\approx N (\ln q_T + \ln q_R + \ln q_V + \ln q_E - \ln N + 1). \end{aligned}$$

Now recall that

$$S = \left. \frac{\partial}{\partial T} (kT \ln Q) \right|_V.$$

If we substitute  $\ln Q$  into this equation, we see that we can clearly break up the calculation into several pieces, one for each type of energy. There are however extra terms arising from the expansion of  $\ln N!$ . What do we do with those? We could just tack these terms on separately at the end of the calculation. However, since they arise from the indistinguishability of the particles, which is due to the motion of the particles in the gas, by convention we add those terms to the translational part of the entropy *only*. For any other entropy contribution, we leave these terms out or, equivalently, we treat the particles as if they are

distinguishable. Thus, we get

$$\begin{aligned}S_T &= \left. \frac{\partial}{\partial T} \left\{ NkT \left[ \ln \left( \frac{q_T}{N} \right) + 1 \right] \right\} \right|_V . \\S_R &= \left. \frac{\partial}{\partial T} (NkT \ln q_R) \right|_V . \\S_V &= \left. \frac{\partial}{\partial T} (NkT \ln q_V) \right|_V . \\S_E &= \left. \frac{\partial}{\partial T} (NkT \ln q_E) \right|_V .\end{aligned}$$

Because  $q_T$  is always large at reasonable temperatures,  $\ln(q_T/N)$  is always positive, which makes the translational entropy positive. The other entropy terms will also be positive because the partition functions tend to increase with  $T$ . We could not guarantee that the entropy contributions would all be positive if we added the terms arising from the  $\ln N!$  expansion to any of the entropy contributions other than the translational entropy.