

### Unit 2-7: Indistinguishable Particles

When the particles are indistinguishable one from another, then the state where particle 1 is at coordinates  $(q_1, p_1)$  and particle 2 is at coordinates  $(q_2, p_2)$  is indistinguishable from the state where particle 1 is at  $(q_2, p_2)$  and particle 2 is at  $(q_1, p_1)$ .

In computing the number of states  $\Omega$  as we have done in the previous sections, we have therefore over counted. The correct counting should be,

$$\Omega(E, V, N) = \frac{1}{N!} \frac{1}{h^{3N}} \int dq_i \int dp_i \mathcal{D}(\mathcal{H}[q_i, p_i] - E) \quad (2.7.1)$$

where  $\mathcal{D}(\mathcal{H}[q_i, p_i] - E)$  equals unity if  $E - \Delta E/2 \leq \mathcal{H}[q_i, p_i] \leq E + \Delta E/2$ , and zero otherwise.

The factor  $1/N!$  is now in front of the integral since there are  $N$  ways to choose which particle is at coordinates  $(q_1, p_1)$ ,  $(N-1)$  ways to choose which of the remaining particles is at coordinates  $(q_2, p_2)$ ,  $(N-2)$  ways to choose which of the remaining particles is at coordinates  $(q_3, p_3)$ , etc. So there are  $N!$  ways to choose which particle is labeled by which coordinates. The different ways to match the particles to coordinates do not represent distinguishably different states because the particles are indistinguishable. Hence, to avoid over counting when we integrate over all  $(q_i, p_i)$  we have to divide the integral by  $N!$ .

So with this correction to  $\Omega$  to account for the indistinguishability of particles, the new result for the entropy of the gas  $S = k_B \ln \Omega$  is related to our old result by,

$$S^{\text{new}} = S^{\text{old}} - k_B \ln N! = S^{\text{old}} - k_B N \ln N + k_B N \quad (2.7.2)$$

where in the last step we used Stirling's approximation,  $\ln N! \approx N \ln N - N$ . Our old result was,

$$S^{\text{old}} = \frac{3}{2} k_B N + k_B N \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] \quad (2.7.3)$$

so Eq. (2.7.2) now gives for  $S^{\text{new}}$ ,

$$\boxed{S(E, V, N) = \frac{5}{2} k_B N + k_B N \ln \left[ \frac{V}{h^3 N} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right]} \quad \text{the Sackur-Tetrode equation} \quad (2.7.4)$$

This result clearly gives an entropy  $S$  that is now *extensive*, and agrees with the result we got from integrating the Gibbs-Duhem relation.

In particular, we now find that  $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$  as required for extensivity.

We can return now to reconsider the entropy of mixing. If the two gases are of different types, then we now have,

$$S_{\text{init}} = \frac{5}{2} k_B N_1 + k_B N_1 \ln \left[ \frac{V_1}{h^3 N_1} \left( \frac{4\pi m_1 E_1}{3N_1} \right)^{3/2} \right] + \frac{5}{2} k_B N_2 + k_B N_2 \ln \left[ \frac{V_2}{h^3 N_2} \left( \frac{4\pi m_2 E_2}{3N_2} \right)^{3/2} \right] \quad (2.7.5)$$

and

$$S_{\text{final}} = \frac{5}{2} k_B N_1 + k_B N_1 \ln \left[ \frac{V}{h^3 N_1} \left( \frac{4\pi m_1 E_1}{3N_1} \right)^{3/2} \right] + \frac{5}{2} k_B N_2 + k_B N_2 \ln \left[ \frac{V}{h^3 N_2} \left( \frac{4\pi m_2 E_2}{3N_2} \right)^{3/2} \right] \quad (2.7.6)$$

and so the entropy of mixing is,

$$\Delta S = S_{\text{final}} - S_{\text{init}} = k_B N_1 \ln \left( \frac{V}{V_1} \right) + k_B N_2 \ln \left( \frac{V}{V_2} \right) = k_B N_1 \ln \left( \frac{N}{N_1} \right) + k_B N_2 \ln \left( \frac{N}{N_2} \right) \quad (2.7.7)$$

It the last step we used a result we have used before: because the two gases were initially at the same temperature and pressure, then  $V_1/N_1 = V_2/N_2 = k_B T/p$ , and so  $V = V_1 + V_2 = (N_1 + N_2)k_B T/p$  and so also  $V/N = k_B T/p$ . From this it follows that  $V/V_1 = N/N_1$  and  $V/V_2 = N/N_2$ .

The above result of Eq. (2.7.7) is exactly the same as we found before using  $S^{\text{old}}$ . So the fact that the particles are indistinguishable does not change the entropy of mixing *if* the two gases are of *different* types.

Now we reconsider the case where the two gases are of the *same* type. In this case,  $S_{\text{init}}$  is the same as in Eq. (2.7.5) above, except with  $m_1 = m_2 = m$ ,

$$S_{\text{init}} = \frac{5}{2}k_B N_1 + k_B N_1 \ln \left[ \frac{V_1}{h^3 N_1} \left( \frac{4\pi m E_1}{3N_1} \right)^{3/2} \right] + \frac{5}{2}k_B N_2 + k_B N_2 \ln \left[ \frac{V_2}{h^3 N_2} \left( \frac{4\pi m E_2}{3N_2} \right)^{3/2} \right] \quad (2.7.8)$$

When the partition is removed, the system is a single gas of  $N = N_1 + N_2$  particles, with total energy  $E_1 + E_2$ , confined to a volume  $V$ . The entropy is then,

$$S_{\text{final}} = S(E, V, N) = \frac{5}{2}k_B N + k_B N \ln \left[ \frac{V}{h^3 N} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] \quad (2.7.9)$$

Since initially the two gases were at the same temperature, and after mixing they remain at the same temperature, we can write  $E_1/N_1 = E_2/N_2 = E/N = \frac{3}{2}k_B T$ . The entropy of mixing is then,

$$\Delta S = S_{\text{final}} - S_{\text{init}} = k_B N \ln \left( \frac{V}{N} \right) - k_B N_1 \ln \left( \frac{V_1}{N_1} \right) - k_B N_2 \ln \left( \frac{V_2}{N_2} \right) \quad (2.7.10)$$

$$= k_B (N_1 + N_2) \ln \left( \frac{V}{N} \right) - k_B N_1 \ln \left( \frac{V_1}{N_1} \right) - k_B N_2 \ln \left( \frac{V_2}{N_2} \right) \quad (2.7.11)$$

$$= k_B N_1 \ln \left( \frac{V N_1}{N V_1} \right) + k_B N_2 \ln \left( \frac{V N_2}{N V_2} \right) \quad (2.7.12)$$

But since the gases were both at the same initial pressure we have  $V_1 = N_1 k_B T/p$  and  $V_2 = N_2 k_B T/p$ , and so also  $V = V_1 + V_2 = (N_1 + N_2)k_B T/p = N k_B T/p$ . So we therefore have

$$\frac{V}{V_1} = \frac{N}{N_1} \quad \text{and} \quad \frac{V}{V_2} = \frac{N}{N_2} \quad (2.7.13)$$

and so

$$\Delta S = k_B N_1 \ln \left( \frac{V N_1}{N V_1} \right) + k_B N_2 \ln \left( \frac{V N_2}{N V_2} \right) = k_B N_1 \ln \left( \frac{N N_1}{N_1 N} \right) + k_B N_2 \ln \left( \frac{N N_2}{N_2 N} \right) \quad (2.7.14)$$

$$= k_B N_1 \ln(1) + k_B N_2 \ln(1) = 0 \quad (2.7.15)$$

so now the entropy of mixing vanishes, as we expect that it should!

Note: If one has  $N_1$  particles of one type of gas, and  $N_2$  particles of a *different* type of gas, both in the same box of volume  $V$ , then the entropy of the mixture is,

$$S(E, V, N_1, N_2) = S_1(E_1, V, N_1) + S_2(E_2, V, N_2) \quad (2.7.16)$$

where  $E_1/N_1 = E_2/N_2 = \frac{3}{2}k_B T$ , since the two gases must be at equal temperature if they are in equilibrium.

But if both gases are the same (i.e. we have only mentally divided them up into one group of  $N_1$  particles and another group of  $N_2$  particles), then Eq. (2.7.16) will no longer be correct, i.e.

$$S(E, V, N) \neq S(E_1, V, N_1) + S(E_2, V, N_2) \quad (2.7.17)$$

because the particles in the one gas are indistinguishable from the particles in the other gas, and so  $S$  must be extensive, which Eq. (2.7.17) is not. To see this, imagine that initially the gases were equal with  $E_1 = E_2 = E/2$  and  $N_1 = N_2 = N/2$ . Then Eq. (2.7.17) would be,

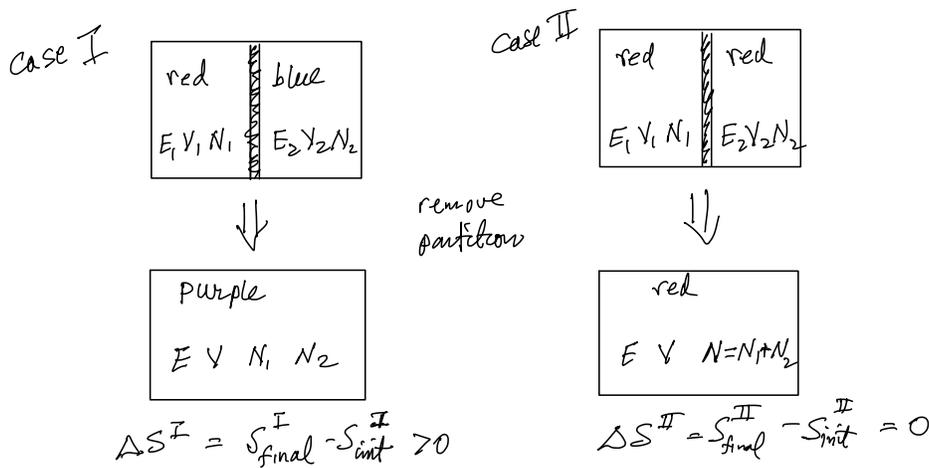
$$S(E, V, N) = S(E/2, V, N/2) + S(E/2, V, N/2) \Rightarrow S(E, V, N) = 2S(E/2, V, N/2) \quad (2.7.18)$$

But extensivity would require instead,

$$S(E, V, N) = 2S(E/2, V/2, N/2) \quad (2.7.19)$$

### Another, more general way, to think about the entropy of mixing and the indistinguishability of particles:

Again imagine we have two gases on two sides of a box, separated by a partition. Initially both gases are at the same  $T$  and  $p$ . When the partition is removed, the mixtures will remain at the same  $T$  and  $p$ . We then have,



If the red gas and the blue gas are exactly the same except for different colors (i.e.  $m_1 = m_2 = m$ ), then we expect the initial entropies of the two cases will be the same,  $S_{\text{init}}^{\text{I}} = S_{\text{init}}^{\text{II}}$ .

Now since in case II we must have  $\Delta S^{\text{II}} = 0$ , since case II is a reversible process, so we must have  $S_{\text{final}}^{\text{II}} = S_{\text{init}}^{\text{II}} = S_{\text{init}}^{\text{I}}$ .

We therefore can write the entropy of mixing for case I as,

$$\Delta S^{\text{I}} = S_{\text{final}}^{\text{I}} - S_{\text{init}}^{\text{I}} = S_{\text{final}}^{\text{I}} - S_{\text{final}}^{\text{II}} \quad (2.7.20)$$

Now let us compute  $S_{\text{final}}^{\text{I}}$  and  $S_{\text{final}}^{\text{II}}$ .

#### Case I

Consider the total number of states available to a system composed of the mixture of two gases with  $N_1$  and  $N_2$  particles respectively, both in volume  $V$ .

If the two gases are of *different* types, i.e. red and blue, so that the particles of gas 1 can be distinguished from the particles of gas 2, then the total number of states is,

$$\Omega_T(E, V, N_1, N_2) = \int_0^E \frac{dE_1}{\Delta E} \Omega_1(E_1, V, N_1) \Omega_2(E - E_1, V, N_2) \quad (2.7.21)$$

Here  $\Omega_T$  is the total number of states available to the combined system,  $\Omega_1$  is the number of states available to the particles of gas 1 with energy  $E_1$ , and  $\Omega_2$  is the number of states available to the particles of gas 2 with energy  $E_2 = E - E_1$ .

We already noted that, for large  $N_1$  and  $N_2$ , the integrand will be strongly peaked about some particular  $\bar{E}_1$ , so that we can write,

$$\Omega_T(E, V, N_1, N_2) \approx \Omega_1(\bar{E}_1, V, N_1) \Omega_2(E - \bar{E}_1, V, N_2) \quad (2.7.22)$$

We then get for the entropy  $S = k_B \ln \Omega$ ,

$$S_T(E, V, N_1, N_2) = S_1(\bar{E}_1, V, N_1) + S_2(E - \bar{E}_1, V, N_2) \quad (2.7.23)$$

where  $\left(\frac{\partial S_1}{\partial E_1}\right)\bigg|_{E_1=\bar{E}_1} = \left(\frac{\partial S_2}{\partial E_2}\right)\bigg|_{E_2=E-\bar{E}_1}$  so that the two gases are at the same temperature.

So we have,

$$S_{\text{final}}^I = S_1(\bar{E}_1, V, N_1) + S_2(E - \bar{E}_1, V, N_2) \quad (2.7.24)$$

## Case II

Now suppose the two gases are of the *same* type, i.e. red and red, so that the particles of gas 1 cannot be distinguished from the particles of gas 2. Then the total number of states available to the combined system will be,

$$\Omega_T(E, V, N_1, N_2) = \int_0^E \frac{dE_1}{\Delta E} \frac{N_1! \Omega_1(E_1, V, N_1) N_2! \Omega_2(E - E_1, V, N_2)}{N!} \quad (2.7.25)$$

Here the factor  $\frac{N_1! N_2!}{N!}$  appears in the integrand because of the indistinguishability of the two gases.

This is because  $N_1! \Omega_1$  is the number of states available to the  $N_1$  particles *if* they were *distinguishable*, and  $N_2! \Omega_2$  is the number of states available to the  $N_2$  particles *if* they were also *distinguishable*. So  $N_1! \Omega_1 N_2! \Omega_2$  would be the number of states available to the combined system if all particles were distinguishable. But since the particles are in fact all *indistinguishable* (particles in gas 1 are indistinguishable from each other, *and* particles in gas 2 are indistinguishable from each other, *and* particles in gas 1 are indistinguishable from particles in gas 2) then we know that the correct number of states available to the combined system of  $N = N_1 + N_2$  indistinguishable particles is  $[N_1! \Omega_1 N_2! \Omega_2]/N!$

Now the integrand in Eq. (2.7.25) will be strongly peaked about some  $\bar{E}_1$ , so we then have,

$$\Omega_T(E, V, N_1, N_2) \approx \frac{N_1! N_2!}{N!} \Omega_1(\bar{E}_1, V, N_1) \Omega_2(E - \bar{E}_1, V, N_2) \quad (2.7.26)$$

and so the entropy  $S = k_B \ln \Omega$  is,

$$S_T(E, V, N_1, N_2) = S_1(\bar{E}_1, V, N_1) + S_2(E - \bar{E}_1, V, N_2) - k_B \ln \left( \frac{N!}{N_1! N_2!} \right) \quad (2.7.27)$$

So we conclude that

$$S_{\text{final}}^{\text{II}} = S_1(\bar{E}_1, V, N_1) + S_2(E - \bar{E}_1, V, N_2) - k_B \ln \left( \frac{N!}{N_1! N_2!} \right) \quad (2.7.28)$$

So now, using Eq. (2.7.20), we can compute the entropy of mixing for case I by subtracting Eq. (2.7.28) from Eq. (2.7.24),

$$\Delta S^I = S_{\text{final}}^I - S_{\text{final}}^{\text{II}} = k_B \ln \left( \frac{N!}{N_1! N_2!} \right) \quad (2.7.29)$$

Using Stirling's formula,  $\ln N! \approx N \ln N - N$ , we then get,

$$\Delta S^I = k_B \left[ N \ln N - N - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2 \right] \quad (2.7.30)$$

$$= k_B \left[ (N_1 + N_2) \ln N - N_1 \ln N_1 - N_2 \ln N_2 \right] \quad \text{since } N = N_1 + N_2 \quad (2.7.31)$$

$$= k_B N_1 \ln \left( \frac{N}{N_1} \right) + k_B N_2 \ln \left( \frac{N}{N_2} \right) \quad (2.7.32)$$

But the above result is exactly the same as we found in Eq. (2.7.7). So what have we gained by this new presentation?

In the earlier calculation leading to Eq. (2.7.7) we used the explicit formula for the entropy  $S$  of the ideal gas, and also the ideal gas law and the relation between energy and temperature for an ideal gas. In the current derivation we did not make any assumption that we were dealing with an ideal gas; the number of states  $\Omega_1$  and  $\Omega_2$  are general. So the entropy of mixing of two different types of gas, given by Eq. (2.7.32), holds even if the gas is not ideal, but has interactions among the particles.