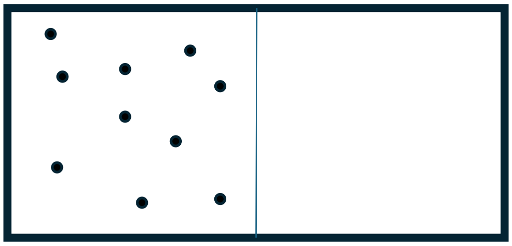
Teacher notes
Topic B

Entropy in the free expansion of an ideal gas

An insulated container is divided by a partition into two sub-containers each of volume V. N molecules are placed in the left sub-container and the partition is removed. The gas expands freely so that $\frac{N}{2}$ molecules are in each sub-container.



What is the change in the entropy of the gas?

A first thought would be that $\Delta S_{\text{gas}} = 0$ because the container is insulated and so no heat can enter or leave the gas. So, we might conclude that $\Delta S_{\text{gas}} = \frac{Q}{T} = 0$. From $Q = \Delta U + W = 0$ and $W = 0$ (the gas is expanding into an empty container) we deduce that $\Delta U = 0$ and so the temperature stays the same in a free expansion. But the expansion of the gas is irreversible; the molecules will not leave the right sub-container and assemble themselves back into the left sub-container. Entropy must increase in an irreversible process. An additional reason for expecting entropy to increase is that with a larger volume the gas has more microstates available and so larger entropy. So, how do we resolve this?

The resolution of this puzzle is that the formula $\Delta S = \frac{Q}{T}$ must be used very carefully. We must consider the transfer of an infinitesimal amount of heat dQ at temperature T and write $dS = \frac{dQ}{T}$. Then the total change in entropy from state 1 to state 2 is given by

$\Delta S = \int_1^2 \frac{dQ}{T}$. The path that takes the system from state 1 to state 2 must be **reversible**. But the free expansion of the gas that we are considering is not reversible so we cannot conclude that $\Delta S_{\text{gas}} = 0$. However, entropy is a state function, it depends on the state and not on how the system was brought into that state. So, to calculate the entropy change for the free expansion we may calculate the entropy change for a reversible, isothermal expansion between states 1 and 2.

In an isothermal expansion from volume V to volume $2V$ at constant temperature T an ideal gas would suffer a change in entropy of

$$\begin{aligned}
\Delta S_{\text{gas}} &= \int_V^{2V} \frac{dQ}{T} \\
&= \int_V^{2V} \frac{dU}{T} + \int_V^{2V} P\frac{dV}{T} \\
&= 0 + \int_V^{2V} \frac{NkT}{V}\frac{dV}{T} \quad . \\
&= kN\int_V^{2V} \frac{dV}{V} \\
&= kN\ln\frac{2V}{V} \\
\Delta S_{\text{gas}} &= kN\ln 2
\end{aligned}$$

An isothermal expansion is reversible so the change in the entropy of the Universe must be zero. This means that the surroundings suffered an entropy decrease of the same amount (heat entered the gas from the surrounding) and so $\Delta S_{\text{Universe}} = 0$.

We conclude that in the free expansion of an ideal gas from volume V to volume $2V$ at constant temperature T the gas increases its entropy by $\Delta S_{\text{gas}} = kN\ln 2$. The surroundings have no entropy change (no heat exchanged) and so the entropy of the Universe increases by $\Delta S_{\text{Universe}} = kN\ln 2$.

We can reach the same conclusion in terms of microstates. Initially all N molecules are in the left sub-container. There is only one way in which we can arrange N identical molecules in the left sub-container.

The number of ways of putting $\frac{N}{2}$ molecules in the left sub-container and $\frac{N}{2}$ in the other is $\frac{N!}{(\frac{N}{2})!(\frac{N}{2})!}$ (see later). The change in entropy is then

$\Delta S = k\ln\dfrac{N!}{(\frac{N}{2})!(\frac{N}{2})!} - k\ln 1 = k\ln(N!) - 2k\ln((\frac{N}{2})!)$. We use Stirling's approximation $\ln(n!) \approx n\ln n - n$ so that:

$$\begin{aligned}\Delta S_{\text{gas}} &= kN\ln(N) - kN - 2k\frac{N}{2}\ln(\frac{N}{2}) + 2k\frac{N}{2}\\ &= kN\ln N - kN\ln\frac{N}{2}\\ &= kN\ln 2\end{aligned}$$

Why is the number of ways of putting $\frac{N}{2}$ molecules in the left sub-container and $\frac{N}{2}$ in the other $\dfrac{N!}{(\frac{N}{2})!(\frac{N}{2})!}$?

Remember, the particles are identical i.e. indistinguishable. Let's start with a simple example. Suppose $N = 4$.

In how many ways can we put all 4 particles in one half of the container and zero in the other? Clearly, there is only one way this can be done.

How about 3 in one and 1 in the other? We need to select the 3 particles out of the 4 that will go in one container. This is the number of combinations of 3 things out of 4 i.e. it is the binomial coefficient ${}^4C_3 = \dfrac{4!}{3!\times 1!} = 4$. We use combinations rather than permutations because the particles are identical.

Now we put 2 in the left container and 2 in the right. We need the number of combinations of 2 things out of 4 i.e. ${}^4C_2 = \dfrac{4!}{2!\times 2!} = 6$.

In general, we want to put n_1 particles in the left container and n_2 in the right with $n_1 + n_2 = N$. Then, the required number is the binomial coefficient ${}^NC_{n_1} = \dfrac{N!}{n_1!(N-n_1)!} = \dfrac{N!}{n_1!n_2!}$

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The total number of microstates for $N = 4$ is:

${}^4C_0 + {}^4C_1 + {}^4C_2 + {}^4C_3 + {}^4C_4 = 1 + 4 + 6 + 4 + 1 = 16 = 2^4$.

The total number for N particles is:

$^{N}C_0 + {}^{N}C_1 + {}^{N}C_2 + {}^{N}C_3 + \ldots + {}^{N}C_N = 2^N$

With just 10 particles (N = 10) the microstate with 5 particles in one box and 5 in the other can be achieved in $^{10}C_5 = \frac{10!}{5!5!} = 252$ ways. This means that finding 5 particles in one box and 5 in the other is 252 times more likely than finding all 10 particles in one box.

The situation is made extreme when we have 100 particles. Finding half in one box and half in the other is $^{100}C_{50} \approx 10^{29}$ more likely than finding all 100 in one box. With $N = 10^{23}$ particles the likelihood of half and half in each box is astronomically greater than all 10^{23} particles in one box.