

# Entropy as a state function

In the last article, we have seen the following equation.

$$dQ = nC_v dT + PdV \quad (1)$$

Also, in our earlier article “What is entropy? From a macroscopic point of view,” we have seen the following equation.

$$dS = \frac{dQ}{T} \quad (2)$$

Combining these two, and using Boyle-Charles law, we obtain:

$$dS = nC_v \frac{dT}{T} + \frac{PdV}{T} = nC_v \frac{dT}{T} + nR \frac{dV}{V} \quad (3)$$

Now, suppose  $n$  moles of gas molecules begin from initial state  $(P_i, V_i, T_i)$  to the final state  $(P_f, V_f, T_f)$ . (Of course, these variables are redundant since we know  $P_i V_i / T_i = P_f V_f / T_f = nR$ ) Then, what would be the entropy change during process? Let's calculate:

$$\Delta S = \int dS = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i} \quad (4)$$

Notice that the entropy change only depends on the initial state and the final state and not on the path it was taken from the initial state and the final state. Not sure what I mean?  $\Delta Q = \int dQ$  is actually path dependent while the combination  $\int dQ/T$  is not. Let me give you an example that shows that  $\Delta Q$  is path dependent. Let's consider two paths, whose initial states are same, and whose the final states are same. Let's say that the initial state is given by  $(P_0, V_0, T_0)$  and the final state by  $(2P_0, 2V_0, 4T_0)$ . Let's say the first path is given as follows:

$$(P_0, V_0, T_0) \rightarrow (P_0, 2V_0, 2T_0) \rightarrow (2P_0, 2V_0, 4T_0) \quad (5)$$

where, in the first process, pressure is held constant and in the second process the volume is held constant. In the first process, we have:

$$\Delta Q(\text{first process of path 1}) = nC_v(2T_0 - T_0) + P_0(2V_0 - V_0) = nC_v T_0 + P_0 V_0 \quad (6)$$

In the second process, we have:

$$\Delta Q(\text{second process of path 1}) = nC_v(4T_0 - 2T_0) + 0 = 2nC_v T_0 \quad (7)$$

where we have used the fact that the work done is zero, as volume was held constant. Adding these two  $\Delta Q$ s, the total  $\Delta Q$  of path 1 is given as follows:

$$\Delta Q(\text{path 1}) = 3nC_v T_0 + P_0 V_0 \quad (8)$$

Now, consider the second path:

$$(P_0, V_0, T_0) \rightarrow (2P_0, V_0, 2T_0) \rightarrow (2P_0, 2V_0, 4T_0) \quad (9)$$

where, in the first process, volume is held constant and in the second process the pressure is held constant. In the first process, we have:

$$\Delta Q(\text{first process of path 2}) = nC_v(2T_0 - T_0) + 0 = nC_vT_0 \quad (10)$$

where we have used the fact that the work done is zero, as volume was held constant. In the second process, we have:

$$\Delta Q(\text{second process of path 2}) = nC_v(4T_0 - 2T_0) + 2P_0(2V_0 - V_0) = 2nC_vT_0 + 2P_0V_0 \quad (11)$$

Adding these two  $\Delta Q$ s during the two processes, the total  $\Delta Q$  of path 2 is given as follows:

$$\Delta Q(\text{path 2}) = 3nC_vT_0 + 2P_0V_0 \quad (12)$$

We notice that  $\Delta Q(\text{path 1}) \neq \Delta Q(\text{path 2})$ .  $\Delta Q$  is not path independent.

Now, let us explain the necessity of the path independence in the change of the entropy. Recall that we had Boltzmann's equation  $S = k \ln W$  in our earlier article "What is combination? What is entropy?" Remember what  $W$  was. It was "the number of microstates consistent with a given macrostate." More precisely speaking, it is the number of "current" microstates consistent with a "current" given macrostate. It never depends on the number of "past" microstates. A function that satisfies such a property is called "state function." Therefore, entropy is a state function. Notice that this property forces the path independence of entropy difference. To calculate entropy, all you need is the current state. Your history doesn't matter.

## Summary

- Entropy is a state function; to calculate entropy, all you need is the current state. Your history doesn't matter.