7.1: Changes in a State Function are Independent of Path

We can specify an equilibrium state of a physical system by giving the values of a sufficient number of the system's measurable properties. We call any measurable property that can be used in this way a state function or a state variable. If a system undergoes a series of changes that return it to its original state, any state function must have the same value at the end as it had at the beginning. The relationship between our definition of a physical state and our definition of a state function is tautological. A system can return to its initial state only if every state variable returns to its original value.

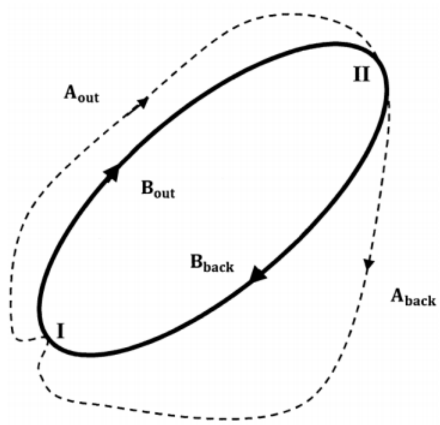

Figure 1. Paths between states I and II.

It is evident that the change in a state function when the system goes from an initial state, I, to some other state, II, must always be the same. Consider the state functions X, Y, Z, and W. Suppose that functions Y, Z, and W are sufficient to specify the state of a particular system. Let their values in state I be X_I, Y_I, Z_I, and W_I. We can express their interdependence by saying that X_I is a function of the other state functions Y_I, Z_I, and W_I: $X_I = f\left(Y_I,\ Z_I, W_I\right)$. In state II, this relationship becomes $X_{II} = f\left(Y_{II},\ Z_{II}, W_{II}\right)$. The difference

$$X_{II} - X_I = f\left(Y_{II},\ Z_{II}, W_{II}\right) - f\left(Y_I,\ Z_I, W_I\right)$$

depends only on the states I and II. In particular, $X_{II} - X_I$ is independent of the values of Y, Z, and W in any intermediate states that the system passes through as it undergoes the change from state I to state II. We say that the change in the value of a state function depends only on the initial and final states of the system; the change in the value of a state function does not depend on the path along which the change is effected.

We can also develop this conclusion by a more explicit argument about the path. Suppose that the system goes from state I to state II by path A_{out} and then returns to state I by path A_{back}, as sketched in Figure 1. Let X be some state function. If the change in X as the system traverses path A_{out} is $X_{II} - X_I = \Delta X\left(A_{out}\right)$, and the change in X as the system traverses A_{back} is $X_I - X_{II} = \Delta X\left(A_{back}\right)$, we must have $\Delta X\left(A_{out}\right) + \Delta X\left(A_{back}\right) = 0$, so that

$$\Delta X\left(A_{out}\right) = -\Delta X\left(A_{back}\right)$$

For some second path comprising B_{out} followed by B_{back}, the same must be true:

$$\Delta X\left(B_{out}\right) + \Delta X\left(B_{back}\right) = 0$$

and

$$\Delta X\left(B_{out}\right) = -\Delta X\left(B_{back}\right)$$

The same is true for any other path. In particular, in must be true for the path A_{out} followed by B_{back}, so that $\Delta X\left(A_{out}\right) + \Delta X\left(B_{back}\right) = 0$, and hence

$$\Delta X\left(A_{out}\right) = -\Delta X\left(B_{back}\right)$$

But this means that

$$\Delta X\left(A_{out}\right) = \Delta X\left(B_{out}\right)$$

Since the paths A and B are arbitrary, the change in X in going from state I to state II must have the same value for any path.

Notes

[1] Since the temperature of the water increases and the process is to be reversible, we must keep the temperature of the thermal reservoir just dT greater than that of the water throughout the process. We can accomplish this by using a quantity of ideal gas as the heat reservoir. By reversibly compressing the ideal gas, we can reversibly deliver the required heat while maintaining the required temperature. We consider this operation further in §12-5.