4.4 THE SECOND LAW IN TERMS OF ENTROPY

Recall that, based on the second law of thermodynamics, Clausius proved that for any cyclic process, whether it be reversible or irreversible, the following inequality must hold true.

$$\oint \frac{dQ}{T} \leq 0 \quad \text{(All cyclic processes)} \tag{4.13}$$

Here the equality holds only when the process is reversible. Now, let us consider a cyclic process that is made up of an unknown process from state A to state B and a reversible process from B to A as shown in the Fig. 4.4. When Clausius's result is applied to this cyclic process it yields the following result.

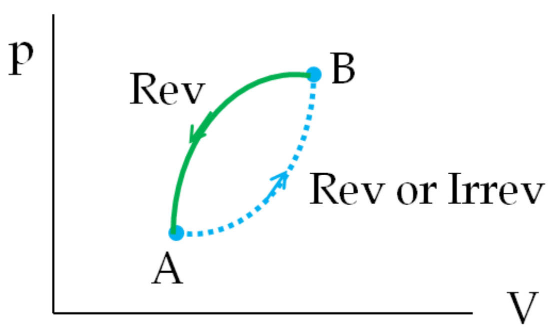

Figure 4.4: Reversible path from B to A and unknown path from A to B.

$$\left(\int_A^B \frac{dQ}{T}\right)_{\text{unknown}} + \left(\int_B^A \frac{dQ}{T}\right)_{rev} \leq 0, \tag{4.14}$$

where the equality will be the case if the A to B process was also reversible.

Now, from the definition of entropy, the integral over the reversible process is equal to the difference in entropy of states A and B.

$$\left(\int_A^B \frac{dQ}{T}\right)_{\text{unknown}} + S(A) - S(B) \leq 0. \tag{4.15}$$

Moving the entropy change on the other side of the inequality, we obtain the following for change of entropy for the A to B process.

$$S(B) - S(A) \geq \left(\int_A^B \frac{dQ}{T}\right)_{\text{unknown}}. \tag{4.16}$$

Now, we apply this result to a combined system consisting of two systems, X and Y, as shown in Fig. 4.5. Let the combined system be thermally insulated, so that, when the state of the combined isolated system changes from some state A to another state B, there will be no heat exchanged between the combined system and the outside world.

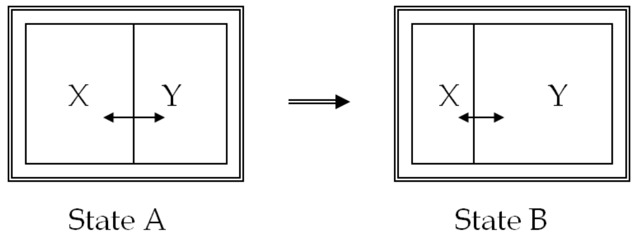

Figure 4.5: An isolated combined system undergoing change from a state A to another state B.

Since there is no heat exchange with the outside world, the right side of Eq. 4.16 is zero. The final entropy of the isolated combined system $S(B)$ will then be greater than the entropy of the initial state $S(A)$.

$$S(B) - S(A) \geq 0 \quad \text{(Isolated system, state A to B transformation)}, \tag{4.17}$$

where the equality sign holds when A to B transformation in the isolated system is conducted reversibly. This means that if the subsystem X is our finite system and Y the rest of the universe, then the net entropy of the universe does not decrease in any process.

$$\boxed{\Delta S_{\text{system}} + \Delta S_{\text{environment}} \geq 0.} \tag{4.18}$$

If the process is reversible, then the reduction in entropy of the system will be balanced by increase in entropy of the environment and vice-versa. If the process is irreversible, however, then the increase in entropy of the environment will be more than any reduction in the entropy of the system, or vice-versa. This leads to the following statement of second law of thermodynamics in terms of entropy.

The entropy of the universe cannot decrease.