❖ Entropy Changes in Reversible and Irreversible Processes

In order to understand the entropy change in reversible and irreversible processes, we need to understand the concept of entropy first. For a Carnot heat engine working at T_1 and T_2, it has been observed that the heat absorbed (q_2) and heat returned (q_1) are related as given below.

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \tag{10}$$

or

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2} \tag{11}$$

or

$$\frac{q_1}{q_2} = \frac{T_1}{T_2} \tag{12}$$

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \tag{13}$$

$$\frac{q}{T} = constant \tag{14}$$

Therefore, we can say that for any particular system, the ratio of heat absorbed or lost isothermally and reversibly to the absolute temperature at which this takes place is a constant parameter. If we consider q_1 as the heat absorbed at T_1, equation (13) becomes

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1} \tag{15}$$
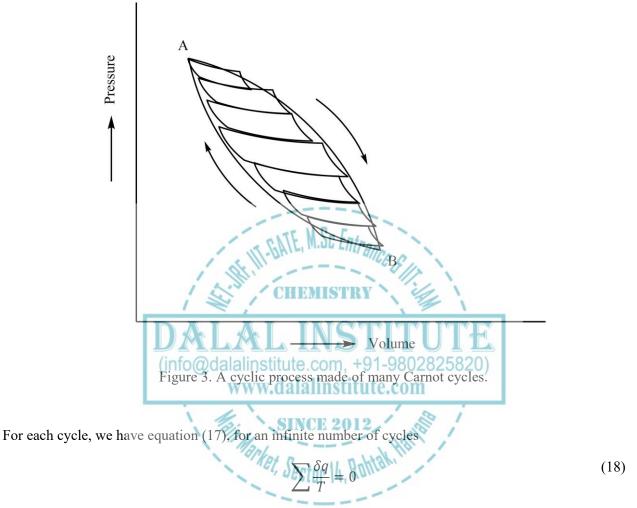
$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0 \tag{16}$$

or

$$\sum \frac{q}{T} = 0 \tag{17}$$

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Consider a reversible cyclic process, consists of many Carnot cycles. In going from point *A* to *B* and then back *A*, all the closed paths cancel each other that results in parent path *ABA*.

Figure 3. A cyclic process made of many Carnot cycles.

For each cycle, we have equation (17), for an infinite number of cycles

$$\sum \frac{\delta q}{T} = 0 \tag{18}$$

Where δq is the extremely small amount of heat absorbed at temperature T during the course of an isothermal and reversible process. Moreover, the total entropy change of the cyclic process *ABA* can be fragmented into two components as:

$$\sum \frac{\delta q}{T} = \sum_{A \to B} \frac{\delta q}{T} + \sum_{B \to A} \frac{\delta q}{T} = 0 \tag{19}$$

$$\sum_{A \to B} \frac{\delta q}{T} = -\sum_{B \to A} \frac{\delta q}{T} \tag{20}$$

or

$$\left(\frac{q}{T}\right)_{A \to B} = -\left(\frac{q}{T}\right)_{B \to A} \tag{21}$$

The physical significance of the equation (21) is that the value of q/T for the path $A{\rightarrow}B$ is the same as the path $B{\rightarrow}A$; which eventually means that the quantity q/T is actually a state function. This quantity i.e. q/T is called as entropy, and is generally labeled as S. If S_A and S_B are the entropies at point A and B, respectively; then we can say that

$$S_A - S_B = \frac{q}{T} \tag{22}$$

$$\Delta S = \frac{q}{T} \tag{23}$$

Hence, the entropy change may be defined as the amount of the heat absorbed isothermally and reversibly divided by the temperature at which the heat is absorbed. Being a state function, the change in entropy always depends upon the initial and final state and not upon the path followed. Moreover, since the heat is absorbed reversibly, it is better to use q_{rev} in equation (23) instead of simply q, therefore

$$\Delta S = \frac{q_{rev}}{T} \tag{24}$$

For an extremely minute change, the above equation becomes

$$dS = \frac{q_{rev}}{T} \tag{25}$$

The entropy is an extensive property measured in joule per Kelvin per mole ($JK^{-1}mol^{-1}$). The most important significance of entropy is that it can be used to measure the randomness in the system.

> ➤ *Entropy Changes in Reversible Processes*

Suppose that the heat absorbed by the system and heat lost by the surrounding are under completely reversible conditions. In other words, q_{rev} is the heat absorbed and lost by the surrounding at temperature T, then we can say that the entropy change in the system will be given by the following relation.

$$\Delta S_{system} = \frac{q_{rev}}{T} \tag{26}$$

Similarly, the entropy change in the surrounding will be

$$\Delta S_{sorrounding} = -\frac{q_{rev}}{T} \tag{27}$$

Therefore, the total entropy change will be

$$\Delta S_{system} + \Delta S_{sorrounding} = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \tag{28}$$

Hence, we can conclude that the entropy change in an isolated system is always zero i.e. the sum of entropy change in system and entropy change in the surrounding is zero under reversible conditions.

➢ *Entropy Changes in Irreversible Processes*

Every reversible process becomes irreversible even if only one part of it becomes irreversible. To understand this, let us suppose that q_{irrev} heat lost by the surrounding. Although this heat would be absorbed by the system, the entropy of the system depends upon the heat absorbed reversibly. Therefore, entropy change of the system at an absolute temperature T will be

$$\Delta S_{system} = \frac{q_{rev}}{T} \tag{29}$$

Similarly, the entropy change of the surrounding will be

$$\Delta S_{sorrounding} = -\frac{q_{irrev}}{T} \tag{30}$$

The total entropy of the isolated system (system + surrounding) will be

$$\Delta S_{system} + \Delta S_{sorrounding} = \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} \tag{31}$$

Furthermore, as we know that the $w_{rev} > w_{irrev}$, and internal energy is a state function that is independent of whether the process is reversible or irreversible. Mathematically, it is

$$\Delta E = q_{rev} - w_{rev} = q_{irrev} - w_{irrev} \tag{32}$$

we can conclude that,

$$q_{rev} > q_{irrev} \tag{33}$$

$$\frac{q_{rev}}{T} > \frac{q_{irrev}}{T} \tag{34}$$

or

$$\frac{q_{rev}}{T} + \frac{q_{irrev}}{T} > 0 \tag{35}$$

After comparing equation (35) with equation (31), we get

$$\Delta S_{system} + \Delta S_{sorrounding} > 0 \tag{36}$$

The physical interpretation of the above equation lies in the fact that all irreversible processes occur via a net increase in entropy. In other words, the total entropy change of an isolated system in any irreversible process is always greater than zero. The results of equation (28) and equation (36) can be combined to give a more generalized form as:

$$\Delta S_{system} + \Delta S_{sorrounding} \geq 0 \tag{37}$$

Where the sign of '=' stands from reversible and '>' stands for irreversible phenomena, respectively.

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The entropy change in the irreversible process like the flow of heat from the hot end (T_2) to cold end (T_1) can be calculated using the following relation.

$$\Delta S_{total} = -\frac{q_{rev}}{T_2} + \frac{q_{rev}}{T_1} = q_{rev}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{38}$$

Where q_{rev} is the amount of heat transferred from T_2 to T_1.

Furthermore, the Clausius inequality can also be proved from equation (36) which governs that all the irreversible processes are accompanied by a net increase in the entropy.

$$\Delta S_{system} > \Delta S_{sorrounding} \tag{39}$$

This can be illustrated with the help of the following examples.

i) Irreversible isothermal expansion of an ideal gas: Suppose an ideal gas expanding isothermally and irreversibly against vacuum. The condition isothermal means $\Delta T = 0$, which in turn implies that $\Delta U = 0$. Hence from the first law of thermodynamics, we have $dq = 0$ i.e. no heat is transferred from, or to the surrounding giving $dS_{surrounding} = 0$.

However, since the $dS_{system} = R\ ln\ (V_2/V_1)$. Since V_2 is definitely greater than V_1, therefore

$$dS_{total} = dS_{system} + dS_{sorrounding} = dS_{system} + 0 \geq 0 \tag{40}$$

ii) Heat flow from hot to the cold end: Suppose dq is the amount of heat transferred from temperature T_2 to T_1. The entropy change at the source will be

$$dS_{source} = -\frac{dq}{T_2} \tag{41}$$

Similarly, the entropy change at the sink will be

$$dS_{sink} = \frac{dq}{T_1} \tag{42}$$

The total entropy change of the system can be calculated as

$$dS_{total} = dS_{source} + dS_{sink} = \frac{dq}{T_1} - \frac{dq}{T_2} \tag{43}$$

or

$$dS_{total} = dq\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{44}$$

Now because the source is always at a higher temperature than sink ($T_2 > T_1$), dS_{total} will be positive for sure, proving that transfer of heat from a hot body to the cold body occurs via a net entropy increment.

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Volume I

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