

Unit-3

Third Law of Thermodynamics and Entropy

CLAUSIUS INEQUALITY AND ENTROPY

- second law of thermodynamics often leads to expressions that involve inequalities. For Example, An irreversible (i.e., actual) heat engine, for example, is less efficient than a reversible one operating between the same two thermal energy reservoirs.
- Another important inequality that has major consequences in thermodynamics is the **Clausius inequality** that was first stated by the German physicist R. J. E. Clausius in 1865

$$\oint \frac{\delta Q}{T} \leq 0$$

The cyclic integral of $\delta Q/T$ is always less than or equal to zero.

This inequality is valid for all cycles, reversible or irreversible. The symbol \oint is used to indicate that the integration is to be performed over the entire cycle.

To demonstrate the validity of the Clausius inequality, we consider a system as shown

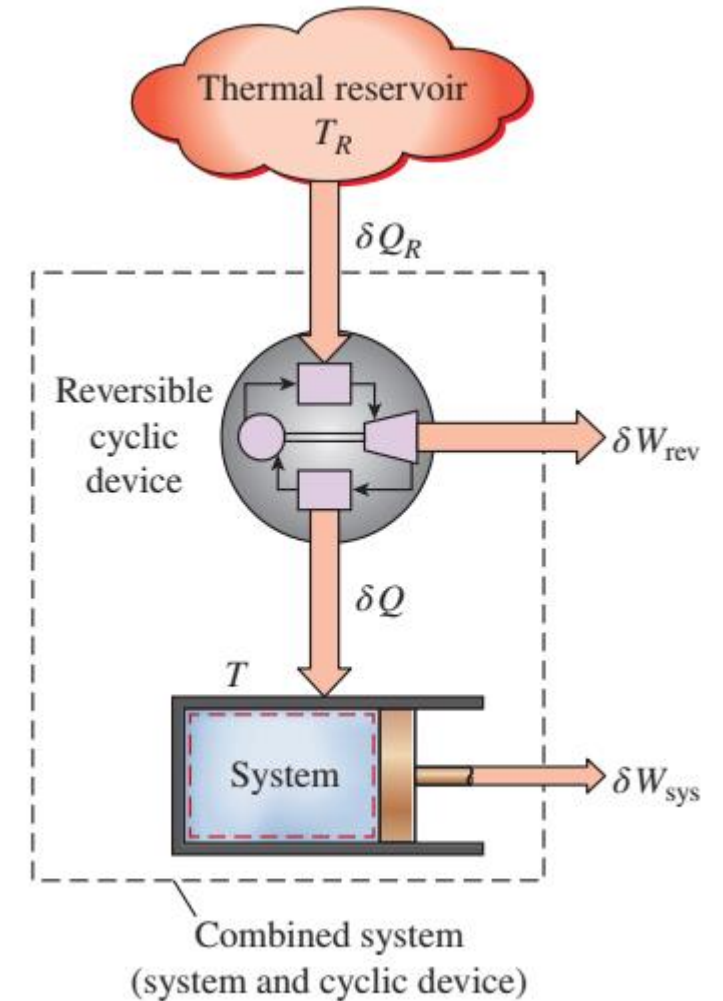
The cyclic device receives heat δQ_R from the reservoir and supplies heat δQ to the system whose temperature at that part of the boundary is T while producing work δW_{rev} . The system produces work δW_{sys} as a result of this heat transfer.

Applying the energy balance to the combined system identified by dashed lines

$$\delta W_C = \delta Q_R - dE_C$$

Considering that the cyclic device is a *reversible* one,

$$\frac{\delta Q_R}{T_R} = \frac{\delta Q}{T}$$



Combining the above two relations

$$\delta W_C = T_R \frac{\delta Q}{L} - dE_C$$

We now let the system undergo a cycle, the above relation becomes

$$W_C = T_R \oint \frac{\delta Q}{T}$$

since the cyclic integral of energy (the net change in the energy, which is a property, during a cycle) is zero. Here W_C is the cyclic integral of δW_C , and it represents the net work for the combined cycle.

It appears that the combined system is exchanging heat with a single thermal energy reservoir while involving (producing or consuming) work W_C during a cycle.

On the basis of the Kelvin–Planck statement of the second law, which states that *no system can produce a net amount of work while operating in a cycle and exchanging heat with a single thermal energy reservoir*, we reason that W_C cannot be a work output, and thus it cannot be a positive quantity thereby getting the relation

$$\oint \frac{\delta Q}{T} \leq 0 \quad \text{which is the Clausius inequality.}$$

For a reversible cycle,

$$\oint \left(\frac{\delta Q}{T} \right)_{\text{int rev}} = 0$$

the equality in the Clausius inequality holds for totally or just internally reversible cycles and the inequality for the irreversible ones

Here we have a quantity whose cyclic integral is zero. A quantity whose cyclic integral is zero depends on the *state* only and not the process path, and thus it is a property.

Therefore, the quantity $(\delta Q/T)_{\text{int rev}}$ must represent a property in the differential form. This property is named as Entropy and is designated as S .

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{int rev}}$$

The entropy change of a system during a process can be determined by integrating the above equation between the initial and the final states:

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{int rev}}$$

A Special Case: Internally Reversible Isothermal Heat Transfer Processes

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{int rev}} = \int_1^2 \left(\frac{\delta Q}{T_0} \right)_{\text{int rev}} = \frac{1}{T_0} \int_1^2 (\delta Q)_{\text{int rev}}$$

which reduces to $\Delta S = \frac{Q}{T_0}$

useful for determining the entropy changes of thermal energy reservoirs that can absorb or supply heat indefinitely at a constant temperature

ENTROPY GENERATION AND THE INCREASE OF ENTROPY PRINCIPLE

From the Clausius inequality,

$$\oint \frac{\delta Q}{T} \leq 0$$
$$\Rightarrow \int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T} \right)_{\text{int rev}} \leq 0$$
$$\Rightarrow \int_1^2 \frac{\delta Q}{T} + S_1 - S_2 \leq 0$$
$$\Rightarrow S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

It can also be expressed in differential form as

$$dS \geq \frac{\delta Q}{T}$$

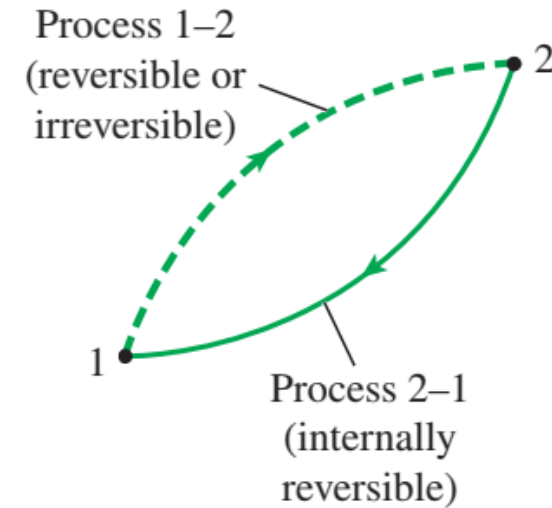


FIGURE 7-5

A cycle composed of a reversible and an irreversible process.

The entropy change of a closed system during an irreversible process is greater than the integral of $\delta Q/T$ evaluated for that process. In the limiting case of a reversible process, these two quantities become equal.

The inequality sign in the preceding relations is a constant reminder that the entropy change of a closed system during an irreversible process is always greater than the entropy transfer. That is, some entropy is *generated* or *created* during an irreversible process, and this generation is due entirely to the presence of irreversibilities.

$$\Delta S_{\text{sys}} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}}$$

The entropy generated during a process is called **entropy generation** and is denoted by S_{gen} .

Note that the entropy generation S_{gen} is always a *positive* quantity or zero

For an isolated system, the heat transfer is zero, and the equation reduces to

$$\Delta S_{\text{isolated}} \geq 0$$

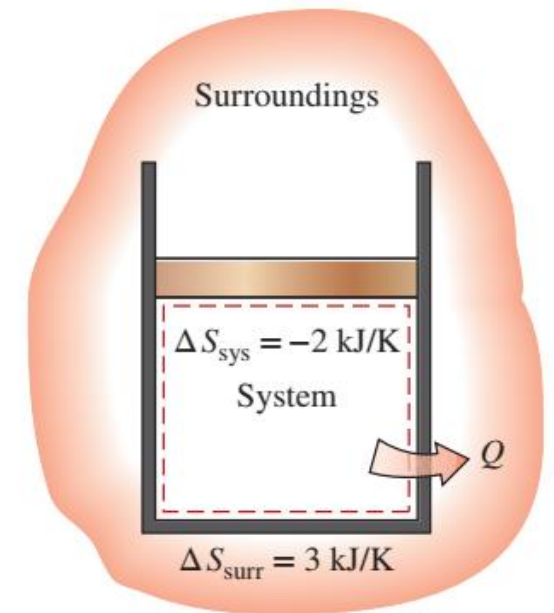
the entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant. In other words, it *never* decreases. This is known as the **increase of entropy principle**.

Note that in the absence of any heat transfer, entropy change is due to irreversibilities only, and their effect is always to increase entropy.

A system and its surroundings together form an isolated system. Therefore,

$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$S_{\text{gen}} \begin{cases} > 0 & \text{irreversible process} \\ = 0 & \text{reversible process} \\ < 0 & \text{impossible process} \end{cases}$$



$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 1 \text{ kJ/K}$$

FIGURE 7-8

The entropy change of a system can be negative, but the entropy generation cannot.

Some Remarks About Entropy

1. Processes can occur in a *certain* direction only, not in *any* direction. A process must proceed in the direction that complies with the increase of entropy principle, that is, $S_{\text{gen}} \geq 0$.
2. Entropy is a *nonconserved property*, and there is *no* such thing as the *conservation of entropy principle*.
3. The performance of engineering systems is degraded by the presence of irreversibilities, and *entropy generation* is a measure of the magnitudes of the irreversibilities present during that process. The greater the extent of irreversibilities, the greater the entropy generation. Therefore, entropy is also used to establish criteria for the performance of engineering devices.

Third law of thermodynamics

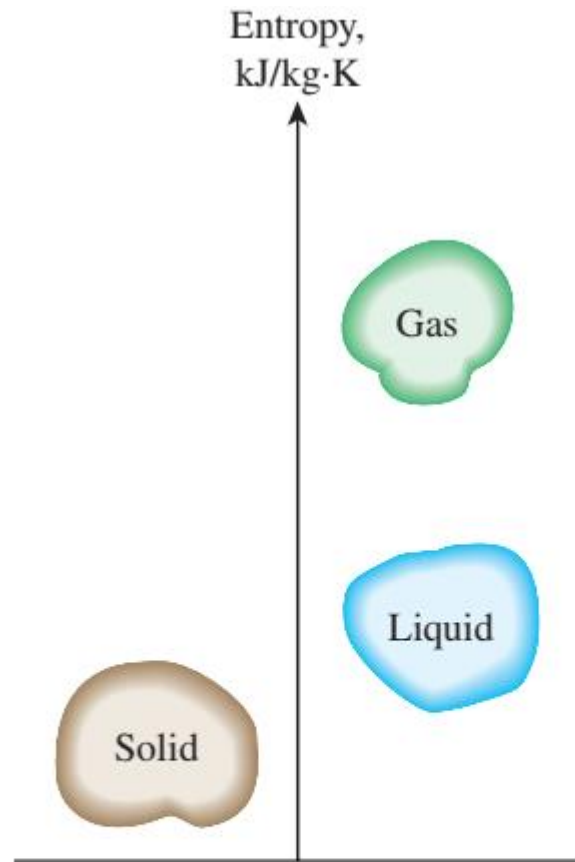


FIGURE 7–20

The level of molecular disorder (entropy) of a substance increases as it melts or evaporates.

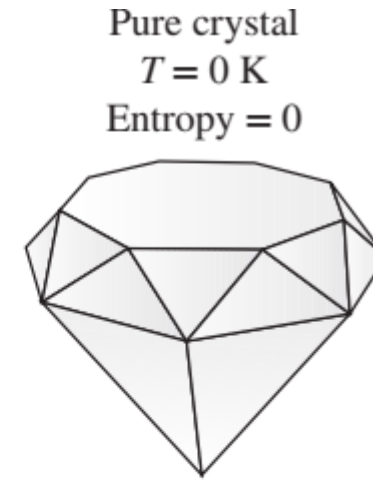


FIGURE 7–22

A pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero (the third law of thermodynamics).