

- Recap: Lecture 13: 10th Feb 2014, 1130-1230 hrs.
 - Thermodynamic temperature scale
 - Carnot heat engine
 - Quality of energy
 - Carnot refrigerator and heat pump
 - Clausius inequality
 - Property of entropy
 - T-s entropy
 - Isentropic processes

Clausius inequality

- Clausius inequality provides the criterion for the irreversibility of a process.

$\oint \frac{\delta Q}{T} = 0$, the process is reversible.

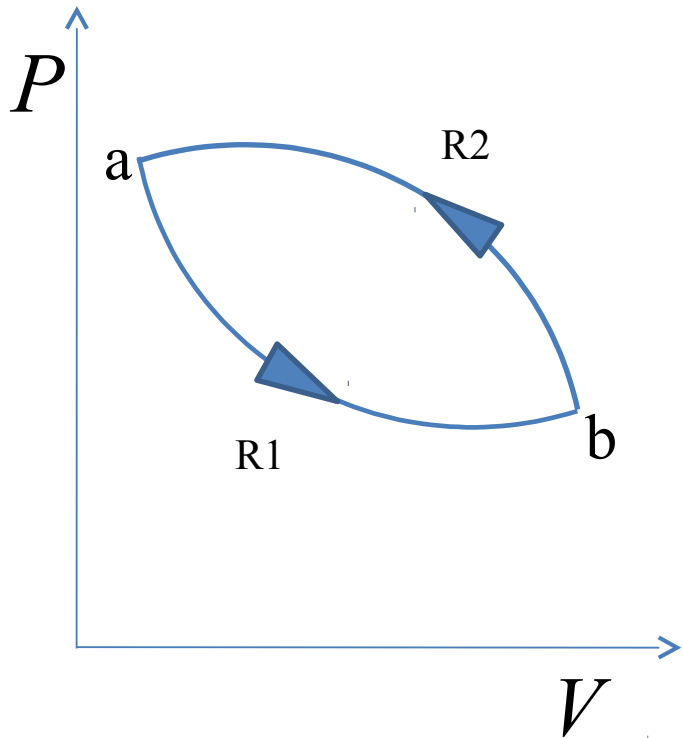
$\oint \frac{\delta Q}{T} < 0$, the process is irreversible and possible.

$\oint \frac{\delta Q}{T} > 0$, the process is impossible.

Clausius inequality and entropy

- The cyclic integral of work and heat are not zero.
- However, the cyclic integral of volume (or any other property) is zero.
- Conversely, a quantity whose cyclic integral is zero depends on the state only and not the process path, and thus it is a property
- Clausius realized in 1865 that he had discovered a new thermodynamic property, and he chose to name this property **entropy**.

The property of entropy



$$\oint_{R_1 R_2} \frac{dQ}{T} = 0$$

$$R1 \int_a^b \frac{\delta Q}{T} + \int_{R2}^a \frac{\delta Q}{T} = 0$$

$$\text{or, } \int_{R1}^b \frac{\delta Q}{T} = - \int_{R2}^a \frac{\delta Q}{T}$$

Since R_2 is a reversible path,

$$R1 \int_a^b \frac{\delta Q}{T} = \int_a^b \frac{\delta Q}{T}$$

The property of entropy

- $\int_a^b \frac{\delta Q_R}{T}$ is independent of the reversible path connecting a and b .
- This property whose value at the final state minus the initial state is equal to $\int_a^b \frac{\delta Q_R}{T}$ is called **entropy**, denoted by S .

$$\int_a^b \frac{\delta Q_R}{T} = S_b - S_a$$

- When the two equilibrium states are infinitesimally near,

$$\frac{\delta Q_R}{T} = dS$$

Entropy

- Entropy is an extensive property of a system and sometimes is referred to as **total entropy**. Entropy per unit mass, designated s , is an intensive property and has the unit kJ/kg·K
- The entropy change of a system during a process can be determined by

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

Entropy

- Entropy is a property, and like all other properties, it has fixed values at fixed states.
- Therefore, the entropy change dS between two specified states is the same no matter what path, reversible or irreversible.

Temperature-entropy plot

$$dS = \frac{\delta Q_{rev}}{T}$$

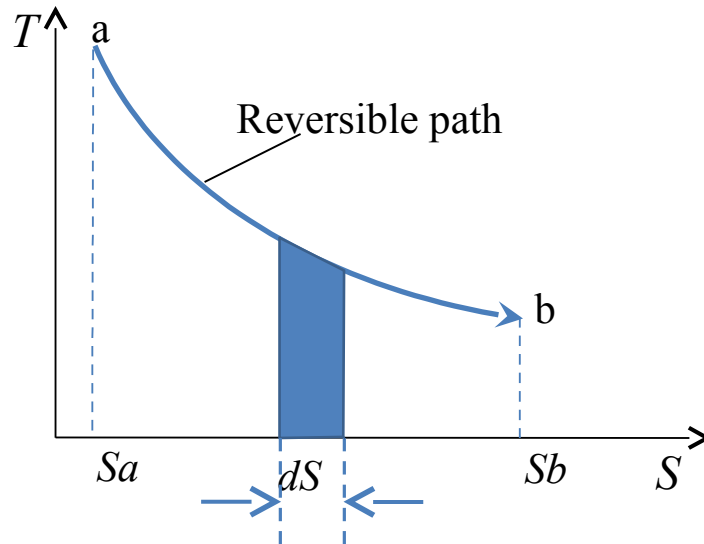
If the process is reversible and adiabatic, $\delta Q_{rev} = 0$
 $\therefore dS = 0$ or $S = \text{constant}$

- A reversible adiabatic process is, therefore, and isentropic process.

$$\delta Q_{rev} = TdS$$

or, $Q_{rev} = \int TdS$

Temperature-entropy plot



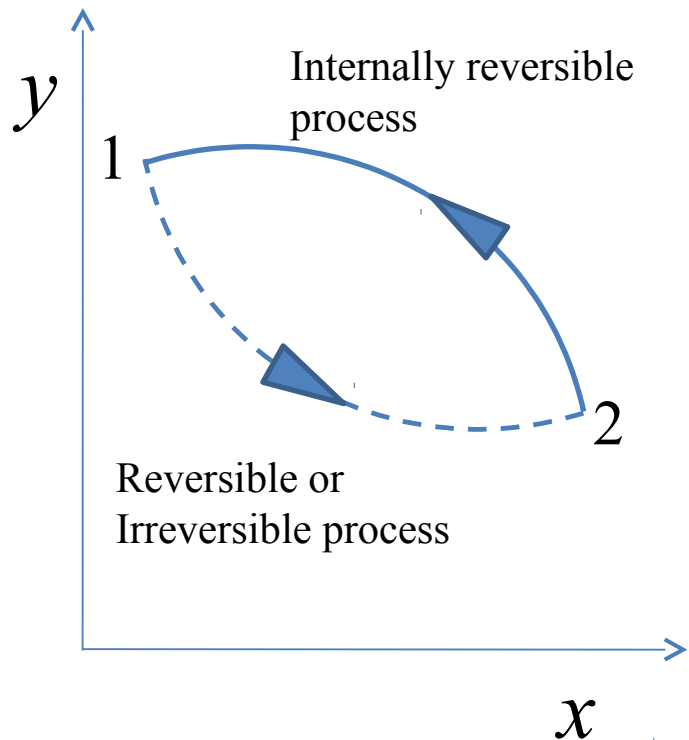
$$Q_{rev} = \int_a^b T dS = T(S_b - S_a)$$

- The area under the reversible path on the T-S plot represents heat transfer during that process.

Isentropic processes

- A process where, $\Delta s=0$
- An isentropic process can serve as an appropriate model for actual processes.
- Isentropic processes enable us to define efficiencies for processes to compare the actual performance of these devices to the performance under idealized conditions.
- A reversible adiabatic process is necessarily isentropic, but an isentropic process is not necessarily a reversible adiabatic process.

Entropy change and entropy generation



- Consider a cycle made up of two processes (1-2 and 2-1)

$$\oint \frac{\delta Q}{T} \leq 0 \quad (\text{Clausius inequality})$$

$$\text{or, } \int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T} \right)_{\text{int.rev}} \leq 0$$

Entropy change and entropy generation

- The second integral is equal to entropy change during that process.

$$\int_1^2 \frac{\delta Q}{T} + (S_1 - S_2) \leq 0$$



$$\text{or, } S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \quad \text{which can be written as } dS \geq \frac{\delta Q}{T}$$

- Here, the equality holds for an internally reversible process and the inequality for an irreversible process.

Entropy change and entropy generation

- 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.
- Note: T in these relations is the temperature at the boundary where the differential heat δQ is transferred between the system and the surroundings.

Entropy change and entropy generation

- Inequality sign: entropy change of a closed system during an irreversible process is always greater than the entropy transfer.
- Some entropy is generated or created during an irreversible process, and this generation is entirely due to the irreversibilities.
- This entropy generated during a process is called **entropy generation** and is denoted by *S_{gen}* .

Entropy change and entropy generation

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

- The entropy generation S_{gen} is always a positive quantity or zero.
- Its value depends on the process, and thus it is not a property of the system.
- For an isolated system (or simply an adiabatic closed system), the heat transfer is zero.

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

Increase of entropy principle

- The entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant.
- This is known as the **increase of entropy principle**.
- In the absence of any heat transfer, entropy change is due to irreversibilities only, and their effect is always to increase entropy.

Increase of entropy principle

- The entropy of the universe is continuously increasing.
- No entropy is generated during reversible processes.
- The increase of entropy principle does not imply that the entropy of a system cannot decrease.
- The entropy change of a system can be negative during a process, but entropy generation cannot.

Increase of entropy principle

$$\begin{aligned} S_{gen} &> 0 \text{ Irreversible process} \\ S_{gen} &= 0 \text{ Reversible process} \\ S_{gen} &< 0 \text{ Impossible process} \end{aligned}$$

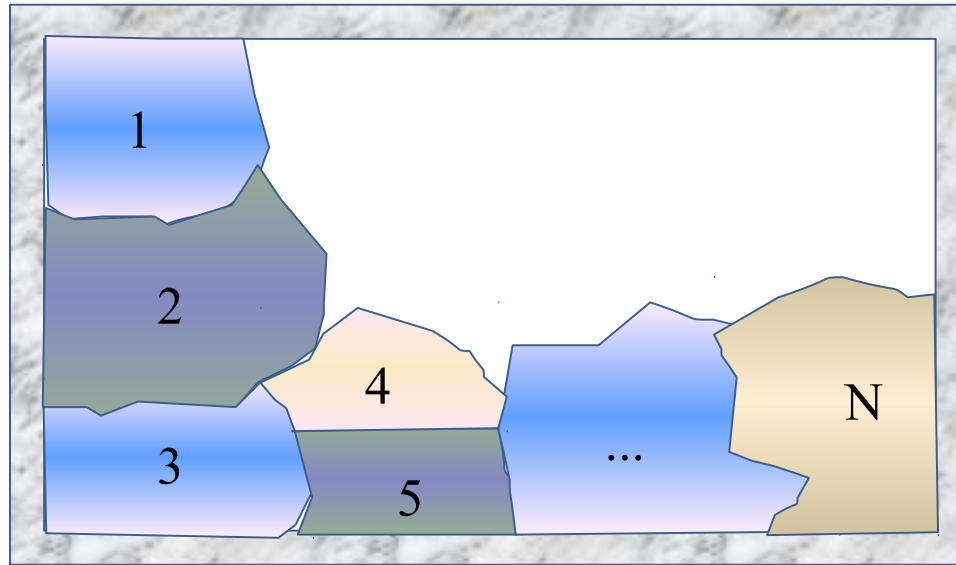
- A system and its surroundings form an isolated system.

$$S_{gen} = \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

Increase of entropy principle

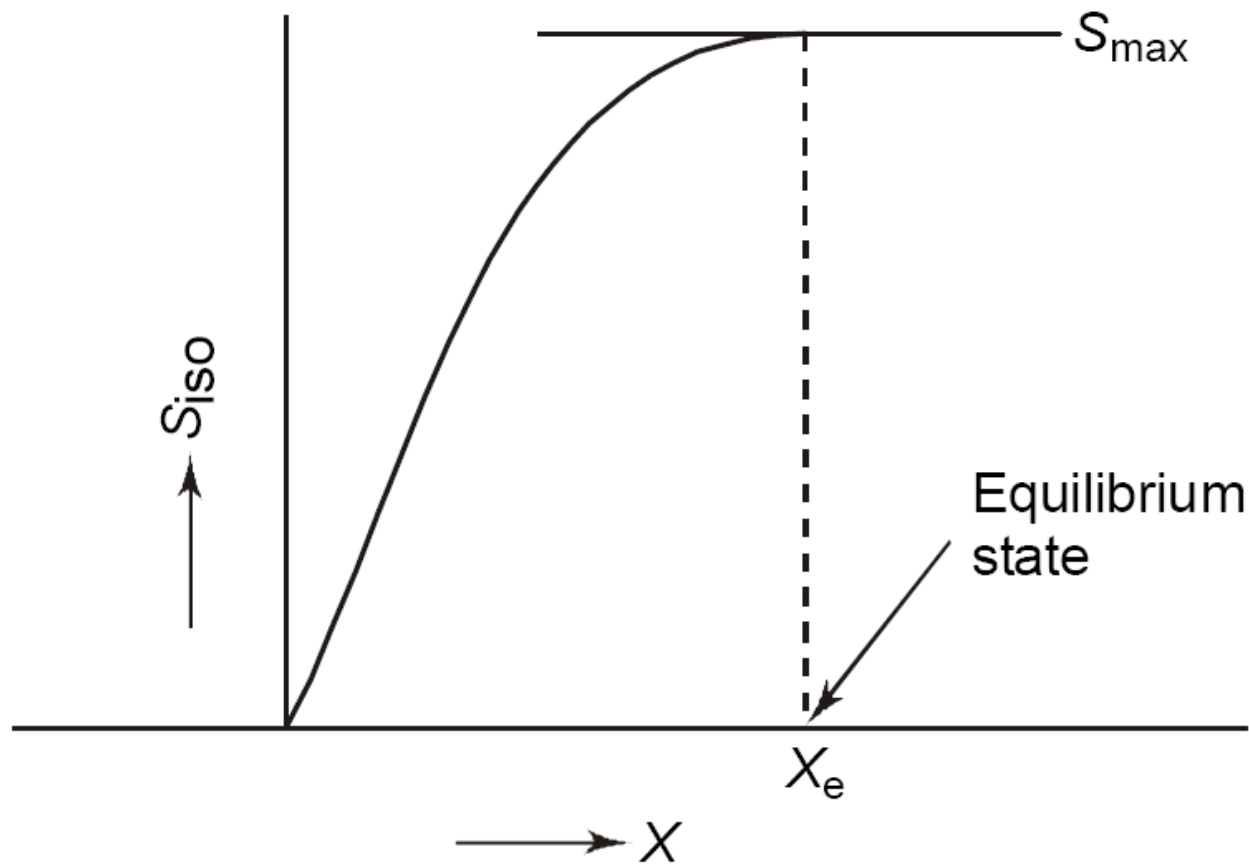
- Processes can occur in a certain direction only, not in any direction.
- A process must proceed in the direction that complies with the increase of entropy principle, that is, $S_{gen} \geq 0$.
- Entropy is a non-conserved property, and there is no such thing as the conservation of entropy principle.
- Entropy is conserved during the idealized reversible processes only and increases during all actual processes.

Increase of entropy principle



The entropy change of an isolated system is the sum of the entropy changes of its components, and is always greater than zero.

$$\Delta S_{total} = \sum_{i=1}^N \Delta S_i > 0$$



TdS equations

- From the first law for an internally reversible process, we know that

$$\delta Q_{\text{intrev}} - \delta W_{\text{intrev,out}} = dU$$

Since, $\delta Q_{\text{intrev}} = TdS$ and $\delta W_{\text{intrev,out}} = PdV$

$$TdS = dU + PdV \text{ or, } Tds = du + Pdv$$

- This is known as the **First TdS equation**.

TdS equations

- From the definition of enthalpy, we know that,

$$h = u + Pv$$

$$\text{or, } dh = du + Pdv + vdP$$

$$\text{since, } Tds = du + Pdv,$$

$$Tds = dh - vdP$$

- This is known as the **second TdS equation**.

TdS equations

- Since the TdS equations are property relations, they are therefore independent of the type of the processes.
- The Tds relations are hence, valid for both reversible and irreversible processes and for both closed and open systems.

Entropy change of liquids and solids

- Liquids and solids can be approximated as incompressible substances since their specific volumes remain nearly constant during a process.
- Thus, $dv = 0$ for liquids and solids.

$$ds = \frac{du}{T} = \frac{c dT}{T} \quad (\square \quad c_p = c_v = c \text{ and } du = cdT)$$
$$s_2 - s_1 = \int_1^2 c(T) \frac{dT}{T} \cong c_{avg} \ln \frac{T_2}{T_1} \quad (\text{kJ/kg} \cdot \text{K})$$

Entropy change of ideal gases

- For ideal gases we know that,

$$du = c_v dT, P = RT / v$$

From the Tds relations,

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

- The entropy change for a process,

$$s_2 - s_1 = \int_1^2 c_v \left(\frac{dT}{T} + R \ln \frac{v_2}{v_1} \right)$$

Entropy change of ideal gases

If we use these relations,

$$dh = c_p dT, \quad v = RT / P$$

Then, from the TdS relations,

$$s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

- Usually, we assume average values of c_p and c_v in the above equations and thus can replace $c_p(T)$ with $c_{p,av}$ and $c_v(T)$ with $c_{v,av}$.

Third law of thermodynamics

- Entropy can be viewed as a measure of molecular disorder, or molecular randomness.
- As a system becomes more disordered, the positions of the molecules become less predictable and the entropy increases.
- The entropy of a system is related to the total number of possible microscopic states of that system, called thermodynamic probability p , by the [Boltzmann relation](#).

Third law of thermodynamics

- Boltzmann relation is expressed as

- $S = k \ln p$

Where, $k = 1.3806 \times 10^{-23}$ J/K is the Boltzmann constant.

- From a microscopic point of view, the entropy of a system increases whenever the molecular randomness or uncertainty (i.e., molecular probability) of a system increases.

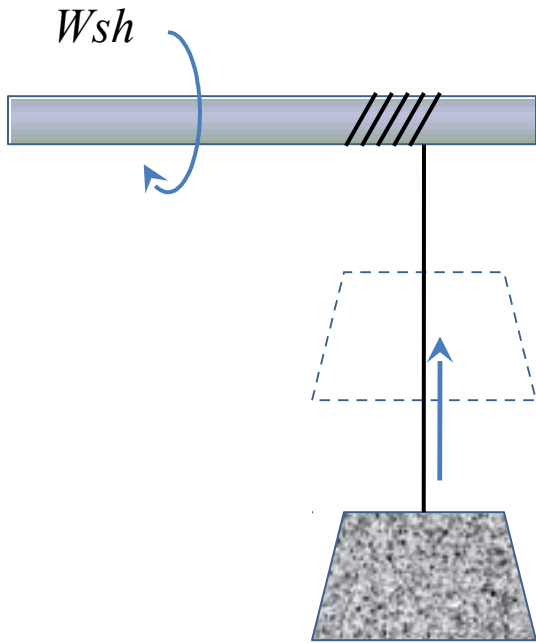
Third law of thermodynamics

- The entropy of a pure crystalline at absolute zero temperature is zero since there is no uncertainty about the state of the molecules at that instant: [the third law of thermodynamics](#).
- The entropy determined relative to this point is called [absolute entropy](#).
- A pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero.

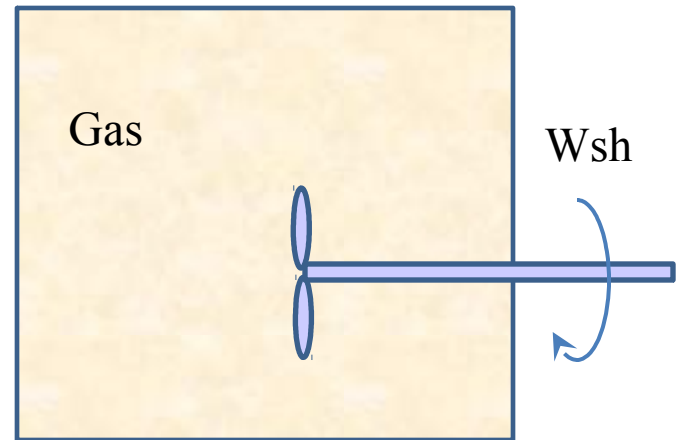
Entropy and energy transfer

- An organized form of energy like work is free of disorder or randomness and thus free of entropy.
- There is no entropy transfer associated with energy transfer as work.
- The quantity of energy is always preserved during an actual process (the 1st law), but the quality is bound to decrease (the 2nd law).

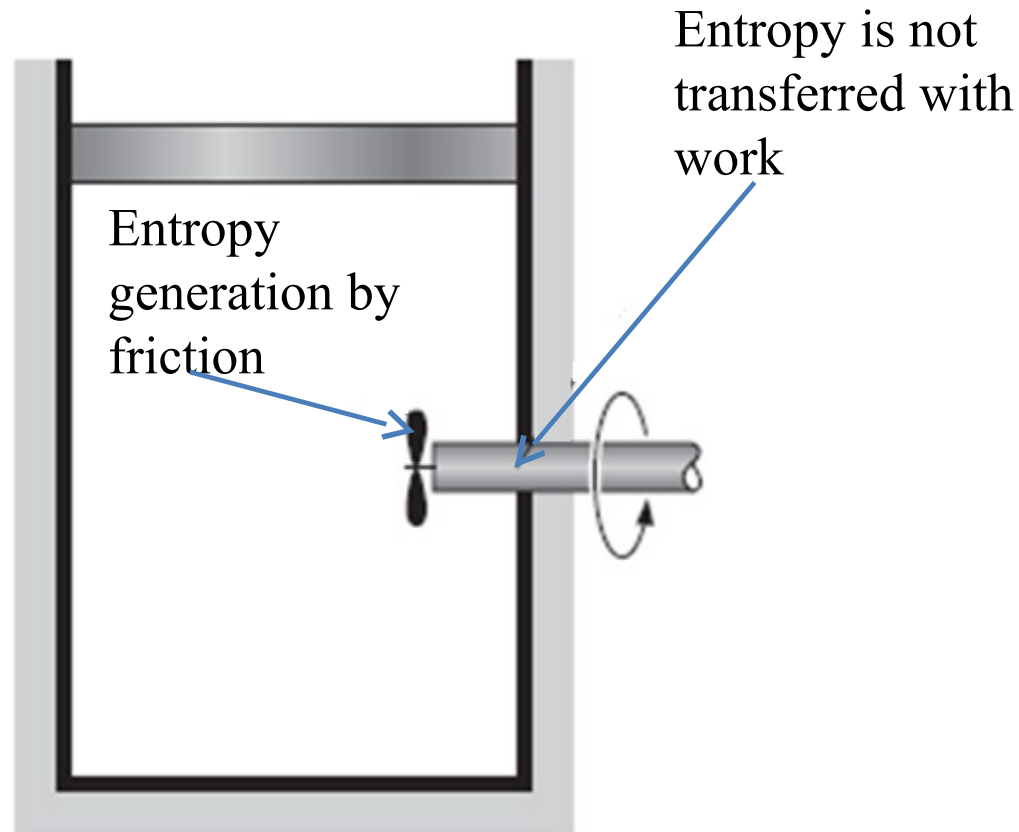
Entropy and energy transfer



Raising of a weight by a rotating shaft does not generate entropy, and so energy is not degraded during this process (if we assume frictional effects can be neglected).



The work done on a gas increases the entropy of the gas, and thus energy is degraded during this process.

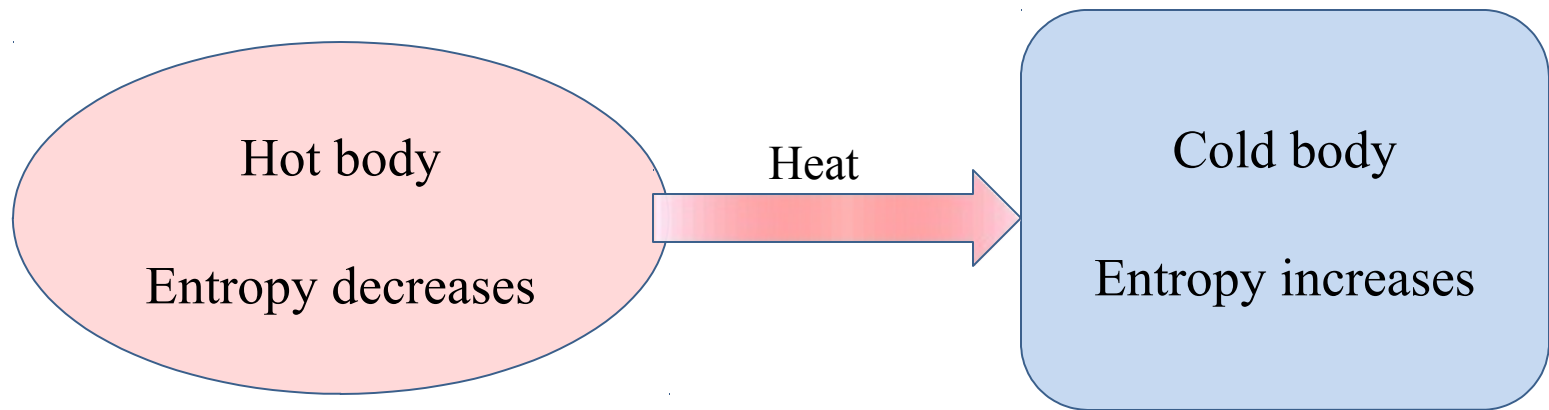


No entropy accompanies work as it crosses the system boundary. But entropy may be generated within the system as work is dissipated into a less useful form of energy.

Entropy and energy transfer

- This decrease in quality is always accompanied by an increase in entropy.
- Heat is a form of disorganized energy, and hence, there is increase in entropy with heat.
- Processes can occur only in the direction of increased overall entropy or molecular disorder.
- That is, the entire universe is getting more and more chaotic every day.

Entropy and energy transfer



- During a heat transfer process, the net entropy increases.
- This is because, the increase in the entropy of the cold body is more than the decrease in the entropy of the hot body.

Entropy and energy transfer

- Work is entropy-free, and no entropy is transferred by work.
- Closed systems
 - Energy is transferred by both heat and work, whereas entropy is transferred only by heat (closed systems).
 - Only energy is exchanged during work interaction whereas both energy and entropy are exchanged during heat transfer.
- Open systems
 - Entropy transfer in open systems: heat and mass flow.

Entropy balance

- Entropy balance for any system undergoing any process is:

$$\dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen} = \Delta \dot{S}_{system}$$

Net entropy transfer by heat and mass Entropy generation Change in entropy

This can also be expressed in the rate form as,

$$\dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen} = \Delta \dot{S}_{system}$$

Rate of net entropy transfer by heat and mass Rate of entropy generation Rate of change in entropy

Entropy balance

For a closed system :

$$\sum \frac{Q}{T} + S_{gen} = \Delta S_{system} = S_2 - S_1$$

The entropy change of a closed system is equal to the sum of the net entropy transferred through the system boundary by heat transfer and the entropy generated within the system boundaries.

Entropy balance

For an open system :

$$\sum \frac{Q}{T} + \sum m_i s_i - \sum m_e s_e + S_{gen} = \Delta S_{system} = (S_2 - S_1)_{CV}$$

The entropy change of a closed system is equal to the sum of the net entropy transferred through the control volume by heat transfer, the net entropy transfer into the control volume through mass flow and the entropy generated within the system boundaries.