Engineering Thermodynamics I

Lecture 9

Entropy

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Lecture learning outcomes:

At the end of this lecture, you will be able to:

i. Define entropy as a measure of disorder and explain its significance in thermodynamics.

ii. Formulate and interpret the Clausius inequality as a fundamental statement of the second law of thermodynamics.

iii. Analyze entropy changes in reversible and irreversible processes, recognizing their impact on energy efficiency.

iv. Explain why entropy increases in natural processes and how this principle governs the direction of spontaneous change.

v. Discuss practical implications of entropy analysis in heat engines, refrigeration, and other thermodynamic systems.

vi. Relate entropy to the degradation of energy quality, highlighting its role in determining the efficiency of energy conversion systems.

Content

1. Definition of Entropy

- The second law of thermodynamics establishes the foundation for a fundamental thermodynamic property known as entropy, which quantifies the dispersal of energy and the degree of disorder within a system.
- Entropy is a quantitative measure of microscopic disorder for a system [1]. (It is an abstract property and difficult to give a physical description of it)
- The more disorganized a system, the higher the entropy.
- Entropy is a function of a quantity of heat which shows the possibility

  of conversion of heat into work.

1. Definition of Entropy Cont…

Examples

- When a solid changes into a liquid, its entropy **increases**.
  - This is because the molecules in a solid are tightly packed and have very limited movement, meaning they are in a highly ordered state.
  - Since entropy is a measure of randomness or disorder in a system, the transition from solid to liquid leads to a rise in entropy.
  - This is consistent with the **second law of thermodynamics**, which states that natural processes tend to move toward higher entropy.

1. Definition of Entropy Cont…

- When a liquid transitions into a solid, its **entropy decreases**.
  - This is because the molecules in a liquid move freely and have more randomness, whereas in a solid, the molecules are more tightly arranged in a fixed structure, reducing disorder.
  - Since entropy is a measure of randomness or molecular disorder, the formation of a solid results in a lower entropy state.
- When a gas transitions into a liquid, **entropy decreases**.
  - Since entropy measures molecular disorder, the shift from

  a gas to a liquid leads to a more ordered state, reducing entropy.

1. Definition of Entropy

Cont…

- Entropy is a measure of energy that is no longer available to perform useful work within the current environment [1].

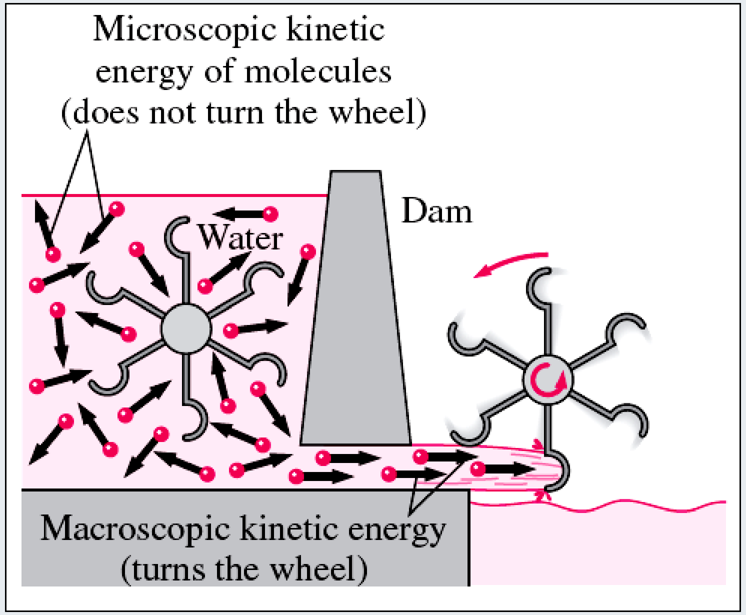

Figure 1: Useful kinetic energy of molecules of water

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1. Definition of Entropy **Cont…**

- Higher molecular disorder (entropy) reduces a system's ability to produce useful work, increasing the net power input required to sustain a process.
- Dissipative forces, such as friction, generate entropy by increasing molecular randomness.
- This demonstrates the governing influence of the Second Law of Thermodynamics, all real processes are constrained by entropy generation, which degrades energy quality and limits efficiency [2].

2. Entropy and the Clausius Inequality

- The Clausius Inequality is a fundamental principle in thermodynamics that establishes a criterion for the direction and reversibility of processes based on entropy [3].
- It is derived from the Second Law of Thermodynamics and mathematically formalizes the concept of irreversibility in cyclic processes.
- For any thermodynamic cycle (closed-loop process), the Clausius inequality states:

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

2. Entropy and the Clausius Inequality Cont…

- Clausius realized in 1865 that he had discovered a new thermodynamic property, and he chose to name this property entropy.
- It is designated S and is defined as

$$dS = \left(\frac{\delta Q}{T}\right)_{Int,rev} \quad \left({}^{kJ}/_{K}\right)$$

- The entropy change of a system during a process can be determined by integrating:

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

2. Entropy and the Clausius Inequality **Cont…**

- 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.

$$s = \frac{S}{m} \quad \left({}^{kJ}/_{kg\ K}\right)$$

$$\bar{s} = \frac{S}{n} \quad \left({}^{kJ}/_{Kmol\ K}\right)$$

2. Entropy and the Clausius Inequality

- The Clausius inequality,

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

- This inequality is valid for all cycles, reversible and irreversible.
- Consider a reversible Carnot cycle

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

- From Carnot efficiency,

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} \qquad \eta_{th} = 1 - \frac{T_L}{T_H}$$

2. Entropy and the Clausius Inequality

Cont…

- From Carnot principle,

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

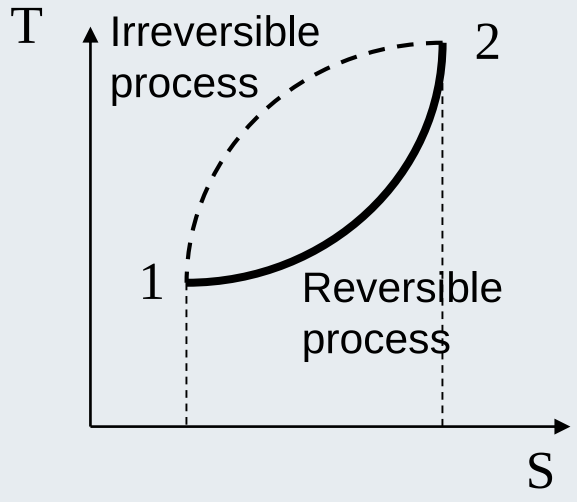
- Therefore, $\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$

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

- Define a thermodynamic property entropy (S), such that

$$\mathrm{dS} = \left.\frac{\delta Q}{T}\right|_{rev}$$

2. Entropy and the Clausius Inequality Cont…



$$W_{Irr} < W_{Rev}$$

$$Q_H - Q_{L,Irr} < Q_H - Q_{L,Rev}$$

$$Q_{L,Irr} > Q_{L,Rev}$$

$$\left(\frac{\delta Q}{T}\right)_{Irr} < \left(\frac{\delta Q}{T}\right)_{Rev}$$

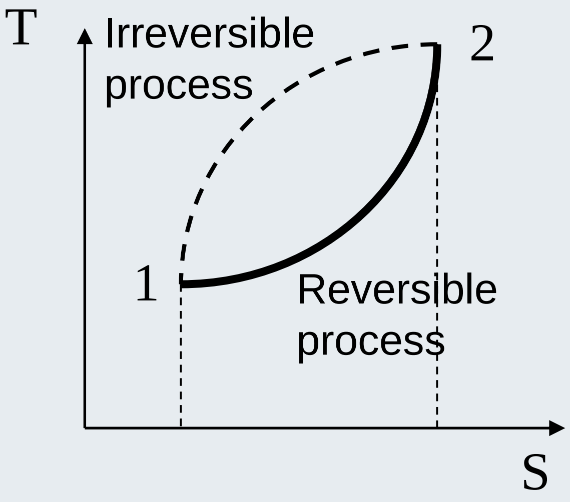
$$\left(\frac{Q_L}{T_L}\right)_{Rev} < \left(\frac{Q_L}{T_L}\right)_{Irr}$$

$$\oint \frac{\delta Q}{T} < 0, Irreversible$$

2. Entropy and the Clausius Inequality

Cont…

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T}\right)_{Irev} + \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} \leq 0$$



From entropy definition

$$\mathrm{d}S = \left(\frac{\delta Q}{T}\right)_{rev}$$

$$\oint dS = 0 = \oint \left(\frac{\delta Q}{T}\right)_{rev} = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{rev}$$

Therefore,

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

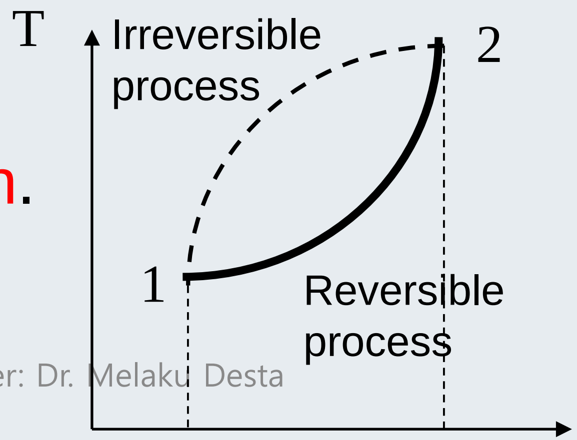
2. Entropy and the Clausius Inequality

- For any reversible process,

$$\int_1^2 dS = \int_1^2 \frac{\delta Q}{T}\bigg|_{rev} = S_2 - S_1$$

- The change of entropy can be defined based on a reversible process.
- Since entropy is a thermodynamic property, it has fixed values at a fixed thermodynamic states.
- The entropy change between two specified states is the same no matter what path, reversible or irreversible.

It's because entropy is a state function.



2. Entropy and the Clausius Inequality **Cont…**

- The change in entropy can be:

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

- This is valid for all processes.

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

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

$$dS > \left(\frac{\delta Q}{T}\right)_{irrev}$$

2. Entropy and the Clausius Inequality Cont…

- To summarize:
  - During an **irreversible process**, the entropy change exceeds the integral of $\frac{\delta Q}{T}$ over the process, reflecting additional entropy generation due to inefficiencies.
  - In contrast, for a **reversible process**, the entropy change precisely equals the integral of $\frac{\delta Q}{T}$, as no entropy is generated internally.
  - Additionally, for the same entropy change, the heat transfer required in a **reversible process** is always lower than that in an **irreversible** process, emphasizing the efficiency advantage of reversibility in thermodynamic systems.

2. Entropy and the Clausius Inequality Cont…

Example 1:

A heat engine operates between a hot reservoir at $T_H = 600K$ and a cold reservoir at $T_L = 300K$. It receives $Q_H = 1000J$ of heat from the hot reservoir and rejects $Q_L = 600J$ of heat to the cold reservoir.

Determine:

- The entropy change for the hot and cold reservoirs.
- Whether this process satisfies the Clausius inequality, confirming if it is reversible or irreversible.

2. Entropy and the Clausius Inequality

Solution:

The entropy change for each reservoir:

$$\Delta S = \frac{Q}{T}$$

For the hot reservoir: $\Delta S_{hot} = \frac{-Q_H}{T_H} = \frac{-1000J}{600K} = -1.67\ J/K$

For the cold reservoir: $\Delta S_{cold} = \frac{Q_L}{T_L} = \frac{600J}{300K} = 2.00\ J/K$

2. Entropy and the Clausius Inequality

Cont…

- The total entropy change can be:

$$\Delta S_{total} = \Delta S_H + \Delta S_C$$

$$\Delta S_{total} = (-1.67) + (2.00)$$

$$\Delta S_{total} = 0.33\ J/K$$

- Since $\Delta S_{total} > 0$, the process increases entropy, meaning it is irreversible.
- To check the Clausius inequality,
- The Clausius inequality states:

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

2. Entropy and the Clausius Inequality

Cont…

- For a reversible cycle,

$$\Delta S_{total} = 0$$

- Since our calculation resulted in a positive entropy change, it confirms that this process is irreversible and obeys the Clausius inequality.
- Therefore, this heat engine increases entropy and operates irreversibly.
- The Clausius inequality holds, reinforcing that real-world heat engines always produce entropy due to irreversibilities.

3. The Increase of Entropy Principle

- In real-world systems, most processes involve irreversibilities (such as friction, heat loss, and mixing), leading to entropy generation and an overall increase in entropy.
- Only ideal, perfectly reversible processes maintain constant entropy without increasing it.
- Natural processes, like heat transfer from hot to cold or the mixing of gases, result in greater disorder and higher entropy [3].
- As entropy increases, the ability to convert energy into useful work decreases, affecting efficiency in thermodynamic systems.

3. The Increase of Entropy Principle Cont…

- The increase of entropy principle helps explain why some processes occur spontaneously while others do not and is crucial in understanding energy efficiency and resource utilization [4].
- From the Clausius inequality,

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

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{Irr} + \int_1^2 \left(\frac{\delta Q}{T}\right)_{Int.rev} \leq 0$$

3. The Increase of Entropy Principle

Cont…

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{Irr} + \int_1^2 \left(\frac{\delta Q}{T}\right)_{Int.rev} \leq 0$$

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

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

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

Where:- the equality holds for an internally reversible process

and the inequality for an irreversible process.

3. The Increase of Entropy Principle Cont…

- The quantity $S = S_2 - S_1$ represents the entropy change of the system.
- For a reversible process, it becomes equal to $\int_1^2 \left(\frac{\delta Q}{T}\right)$ which represents the entropy transfer with heat.
- From preceding relations, 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.

3. The Increase of Entropy Principle **Cont…**

- The entropy generated during a process is called entropy generation and is denoted by S_{gen}.
- The difference between the entropy change of a closed system and the entropy transfer is equal to entropy generation, the above equation can be rewritten as an equality as:

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

- In the absence of any entropy transfer, the entropy change of a system is equal to the entropy generation.

3. The Increase of Entropy Principle

Cont…

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

$$\Delta S_{sys} = S_2 - S_1$$

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

Where $S_{gen} \geq 0$.

- The entropy will still increase or stay the same but never decrease.

$$\Delta S_{sys} = S_{gen} \geq 0$$

Entropy increase principle

- A process can occur only in the direction that aligns with the increase of entropy principle, ensuring that the overall disorder of an isolated system never decreases [5].

3. The Increase of Entropy Principle

Cont…

- For an isolated system (or simply an adiabatic closed system), the heat transfer is zero, and the above equation reduces to:

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

- This equation can be expressed as 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.

3. The Increase of Entropy Principle Cont…

- The increase of entropy principle can be summarized:

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

It can be concluded as:

- Entropy is non-conservative since it is always increasing.
- The entropy of the universe is continuously increasing, in other words, it is more disorganized and is approaching chaotic.
- The entropy generation is due to the existence of irreversibilities.

3. The Increase of Entropy Principle **Cont…**

- Therefore, the higher the entropy generation the higher the irreversibilities and, accordingly, the lower the efficiency of a device since a reversible system is the most efficient system.
- To summarize the implications of the increase of entropy generation and the Clausius inequality,
  - For Reversible Processes:

    No entropy is generated.

    Example: Carnot cycle.
  - For Irreversible Processes:

    Entropy is generated ($S_{gen} > 0$).

    Example: Real engines with friction.

3. The Increase of Entropy Principle **Cont…**

Example 1:

A heat engine operates between a source at 800 K and a sink at 300 K. During one cycle, it absorbs 1000 kJ of heat from the source and rejects 600 kJ of heat to the sink.

Determine:

- The entropy change of the source, sink, and total.
- The entropy generated during the cycle.
- The efficiency of the engine and compare it to the Carnot efficiency.

3. The Increase of Entropy Principle

Cont…

Solution:

Entropy Change of Source: (Loses 1000 kJ of heat, entropy decreases)

$$T_H = 800K$$

$$\Delta S_H = \frac{-Q_H}{T_H} = \frac{-1000\ kJ}{800\ K} = -1.25\ kJ/K$$

Entropy Change of Sink: (Gains 600 kJ of heat, entropy increases)

$$T_L = 300K$$

$$\Delta S_L = \frac{+Q_L}{T_L} = \frac{600\ kJ}{300\ K} = +2.0\ kJ/K$$

3. The Increase of Entropy Principle **Cont…**

- The total entropy change is the sum of the entropy changes of the reservoirs:

$$\Delta S_{total} = \Delta S_H + \Delta S_L$$

$$\Delta S_{total} = -1.25 + 2.0 = +0.75\ kJ/K$$

Since $\Delta S_{total} > 0$, the process is irreversible (As expected for real engines)

- The entropy generation (S_{gen})

$$S_{gen} = \Delta S_{total} = 0.75\ kJ/K$$

- Entropy generation quantifies irreversibilities

  (friction or heat leakage)

3. The Increase of Entropy Principle

Cont…

- The efficiency of the engine:

Actual efficiency: $\eta = 1 - \frac{Q_L}{Q_H} = 1 - \frac{600}{1000} = 0.4\ (40\%)$

Carnot efficiency: $\eta_{rev} = 1 - \frac{T_L}{T_H} = 1 - \frac{300}{800} = 0.625\ (62.5\%)$

- Therefore, the actual efficiency is lower than the Carnot limit

  due to entropy generation ($S_{gen} = 0.75\ kJ/K$)

3. The Increase of Entropy Principle Cont…

Example 2:

Show that the heat can not transfer from the low-temperature sink at 500K to the high-temperature source at 1000K based on the increase of entropy principle. Assume 2000 kJ of heat is to be transferred from the sink to the source.

Solution:

$$\Delta S_{source} = \frac{2000}{800} = 2.5\ kJ/K$$

$$\Delta S_{sink} = \frac{-2000}{500} = -4\ kJ/K$$

$$S_{gen} = \Delta S_{source} + \Delta S_{sink} = -1.5\ kJ/K$$

3. The Increase of Entropy Principle **Cont…**

- Therefore, since the $S_{gen} < 0$, it is impossible based on the entropy increase principle, i.e. $S_{gen} \geq 0$, therefore, the heat can not transfer from low temperature to high temperature without external work input.
- However, if the process is reversed, 2000kJ of heat is transferred from the source to the sink, $S_{gen} = 1.5\ kJ/K > 0$, and the process can occur according to the second law of thermodynamics.

3. The Increase of Entropy Principle

Cont…

- If the sink temperature is increased to 700 K, how about the entropy generation?

$$\Delta S_{source} = \frac{2000}{800} = 2.5\ kJ/K$$

$$\Delta S_{sink} = \frac{-2000}{700} = -2.86\ kJ/K$$

$$S_{gen} = \Delta S_{source} + \Delta S_{sink} = -0.36\ kJ/K$$

$$0.36\ kJ/K < 1.5\ kJ/K$$

- Entropy generation is less than when the sink temperature is 500 K, less irreversibility.
- Heat transfer between objects having large temperature difference generates higher degree of irreversibilities.

4. The T-S Diagram of the Carnot Cycle

- T-S diagrams visualize heat transfer and entropy changes.
- Recall that a Carnot Cycle is based on an idealized heat engine with maximum possible efficiency.

Four Reversible Processes:

Process 1-2: **Reversible Isothermal Expansion** (Heat addition at T_H).

Process 2-3: **Reversible Adiabatic Expansion** (No heat transfer, temperature drops).

Process 3-4: **Reversible Isothermal Compression** (Heat rejection at T_L).

Process 4-1: **Reversible Adiabatic Compression** (Temperature rises back to T_H).

4. The T-S Diagram of the Carnot Cycle Cont...

Process 4-1 (Reversible Adiabatic

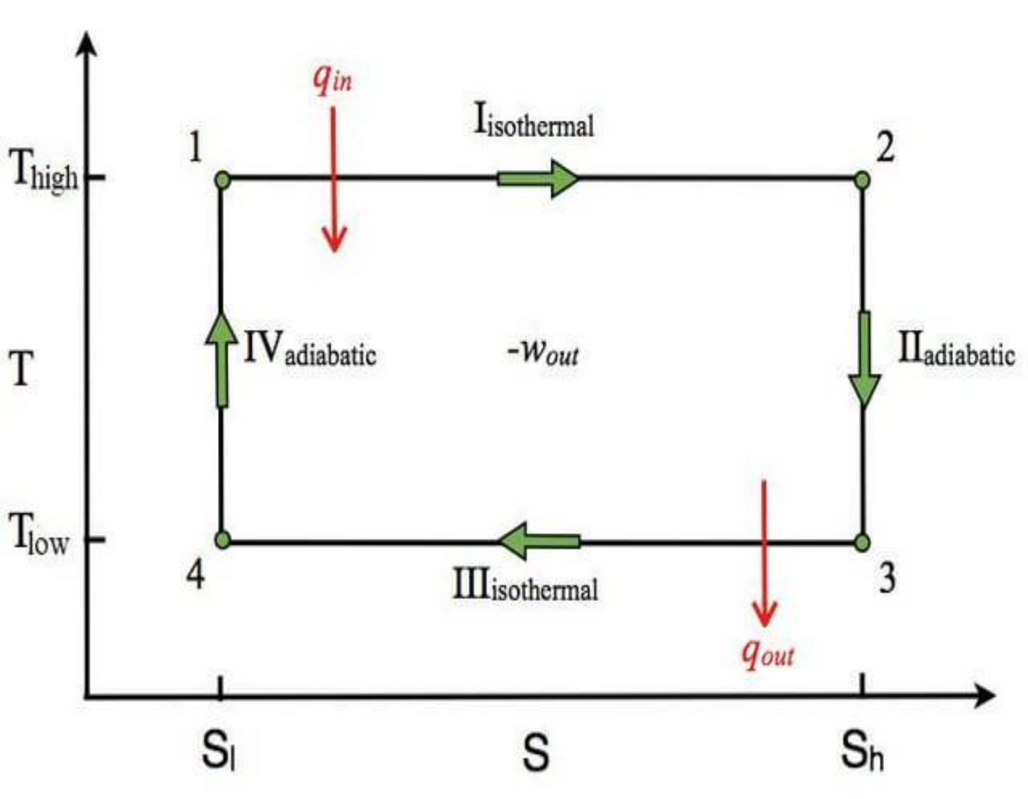


Figure 2: T-S Diagram of a Carnot Cycle

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4. The T-S Diagram of the Carnot Cycle **Cont…**

The T-s diagram of internally reversible process

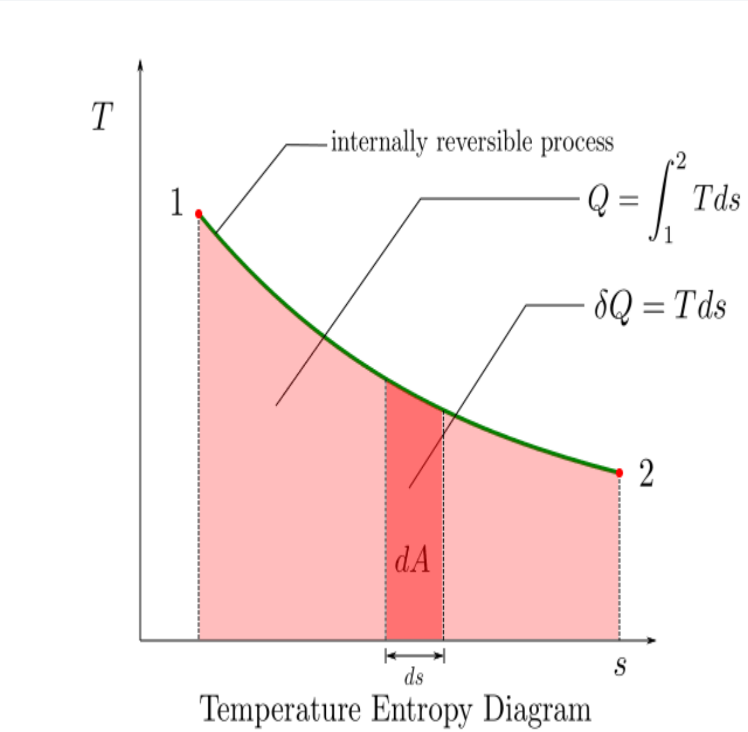

Figure 3: T-S Diagram of a Carnot Cycle

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Summary

- Entropy is a measure of the disorder or randomness in a system, closely linked to the second law of thermodynamics. It quantifies the amount of energy unavailable for useful work.
- The Clausius inequality states that for a cyclic process, the sum of heat transfer divided by the temperature at which it is absorbed is always less than or equal to zero, reinforcing the irreversibility of natural processes.
- Entropy always increases in an isolated system, meaning that natural processes tend to move towards greater disorder, making perfect efficiency impossible in real-world applications.
- The Carnot cycle, when plotted on a Temperature-Entropy (T-S) diagram, visually represents the reversible heat exchange process, with isothermal

  and adiabatic segments showing ideal energy

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Thank you !