CHAPTER

6

Entropy

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The Clausius Inequality:

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

This inequality is valid for all cycles, reversible or irreversible

Cyclic integral

$$\left\{ \begin{array}{ll} = & \text{for reversible} \\ < & \text{for irreversible} \end{array} \right\}$$

The cyclic integral of $\delta Q/T$ can be viewed as the sum of all the differential amounts of heat transfer divided by the temperature at the boundary.

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The vaidity of the Clausius inequality:

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

Total work of the combined system:

$$\underbrace{\delta W_C}_{\delta W_{rev} + \delta W_{sys}} = \delta Q_R - \underbrace{dE_C}_{\text{Change in total energy of the combined system}}$$

$$\frac{\delta Q_R}{T_R} = \frac{\delta Q}{T} \rightarrow \delta W_C = T_R \frac{\delta Q}{T} - dE_C \rightarrow W_C = T_R \oint \frac{\delta Q}{T}$$

$$\oint \frac{\delta Q}{T} \le 0$$ Clasius inequality

Single reservoir is not possible according to Kelvin-Plank statement, $W_C = 0$

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

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \quad (\text{kJ/K})$$ Formal definition of entropy

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

The system considered in the development of the Clausius inequality.

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

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For reversible cycles:

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

$$\oint \left(\frac{\delta Q}{T}\right)_{rev} = \int \frac{\delta Q_H}{T_H} - \int \frac{\delta Q_L}{T_L}$$

$$= \frac{1}{T_H}\int \delta Q_H - \frac{1}{T_L}\int \delta Q_L$$

$$= \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

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

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For irreversible cycles:

$$Q_{L,irrev} > Q_L \quad \text{or} \quad Q_{L,irrev} = Q_L + Q_{Diff}$$

$$\oint \left(\frac{\delta Q}{T}\right)_{irrev} = \frac{Q_H}{T_H} - \frac{Q_{L,irrev}}{T_L} =$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} - \frac{Q_{Diff}}{T_L} = 0 - \frac{Q_{Diff}}{T_L}$$

$$\oint \left(\frac{\delta Q}{T}\right)_{irrev} < 0$$

For all cycles, the two results are combined:

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

Note: $\oint \frac{\delta Q}{T} > 0$ **violates the 2nd law of thermodynamics**

$\oint \frac{\delta Q}{T}$ **has to be always negative.**

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Entropy:

$$\oint dV = 0$$

Internally reversible

The net change in volume (a property) during a cycle is always zero.

→ Any property change during a cycle is zero.

Since $\oint \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = 0$, $\left(\frac{\delta Q}{T}\right)_{\text{int rev}}$ must represent a property in the differential form.

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

$$\rightarrow \int_1^2 \left(\frac{\delta Q}{T}\right)_A = \int_1^2 \left(\frac{\delta Q}{T}\right)_B$$

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→ The value of the integral depends on the end states only and not the path followed

→ This represents the change of a property

→ This property is called entropy, ***S*** .

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

Entropy is an extensive property.

The entropy change of a system:

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

Example: air temperature is raised from T_1 to T_2

$$\delta Q - \cancelto{0}{\delta W} = dU$$

$$\delta Q = dU = mC_v\,dT$$

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = \int_1^2 \frac{mC_v\,dT}{T} = mC_v \ln\frac{T_2}{T_1}$$

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A Special Case: Internally Reversible Isothermal heat transfer processes:

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

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

$$\Delta S = \frac{Q}{T_o} \qquad (\text{kJ/K})$$

Constant absolute temperature

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THE INCREASE OF ENTROPY PRINCIPLE

Consider a a cycle that is made of two processes:

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

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

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

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

This is an irrev. cycle since part of it is irreversible.

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

δQ → A different amount of actual heat transfer between a system and its surroundings

T → Absolute temp. of the boundary

The equality holds for an internally reversible process and the inequality for an irreversible process.

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

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

A different amount of actual heat transfer between a system and its surroundings

Absolute temp. of the boundary

If system is adiabatic then

$$\delta Q = 0$$

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

The entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant.

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

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

Some entropy is *generated* or *created* during an irreversible process, and this generation is due entirely to the presence of irreversibilities.

The entropy generation S_{gen} is always a *positive* quantity or zero.

Can the entropy of a system during a process decrease?

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The entropy change of an isolated system is the sum of the entropy changes of its components, and is never less than zero.

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

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

A system and its surroundings form an isolated system.

The increase of entropy principle

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Some Remarks about Entropy

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

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

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, $S_{gen} \geq 0$. A process that violates this principle is impossible.
2. Entropy is a *nonconserved 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.
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 during that process. It is also used to establish criteria for the performance of engineering devices.

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Example:

A system and its surroundings can be viewed as the two subsystems.

Total entropy change is the entropy change of all the systems:

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

Entropy generation, S_{gen}

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

The entropy generation S_{gen} is always a *positive* quantity or zero.

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The increase of entropy principle:

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

Can not be negative

$$\underbrace{\underbrace{\Delta S_{sys}}_{\text{Can be negative}} + \Delta S_{surr}}$$

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

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

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Closed Systems

The entropy change of a closed system during a process 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.

$$S_{\text{gen}} = \Delta S_{\text{total}} = \underbrace{\Delta S_{\text{sys}}}_{\substack{S_2 - S_1 \\ m(s_2 - s_1)}} + \underbrace{\Delta S_{\text{surr}}}_{\frac{Q_{surr}}{T_{surr}}} \geq 0$$

If process is adiabatic:

$$Q_{\text{surr}} = -Q_{\text{sys}} = 0$$

$$S_{gen} = \Delta S_{\text{tot}} = m(s_2 - s_1) \geq 0$$

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Example:

In a constant pressure process, vapor in the cyclinder condeses. Determine:

a) entropy change of water

b) entropy change of surrounding air

c) whether this process is possible

a) $\Delta S_{water} = \dfrac{Q_{water}}{T_{water}} = \dfrac{-600\,\text{kJ}}{373\,\text{K}} = -1.61\,\text{kJ/K}$

b) $\Delta S_{surr} = \dfrac{Q_{surr}}{T_{surr}} = \dfrac{+600\,\text{kJ}}{298\,\text{K}} = +2.01\,\text{kJ/K}$

c) $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$

$= -1.61 + 2.01 = +0.4\,\text{kJ/K}$

A frictionless piston

$Q_{surr} = -Q_{sys} = +600\,\text{kJ}$

This process is an irreversible process and is possible

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Control Volumes:

Similar to the closed systems, except that this time we consider the entropy carried by the mass from flow rates across the boundaries.

$$\Delta S_{cv} = (S_2 - S_1)_{cv}$$

$$\Delta S_{surr} = \frac{Q_{surr}}{T_{surr}} + S_e - S_i$$

$$\Delta S_{surr} = \frac{Q_{surr}}{T_{surr}} + \underbrace{m_e s_e}_{\text{Entropy flow with heat}} - \underbrace{m_i s_i}_{\text{entropy transport with mass}}$$

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

$$= \cancel{(S_2 - S_1)_{cv}} + S_e - S_i + \frac{Q_{surr}}{T_{surr}} \geq 0$$

= 0 for steady flow

The entropy of a control volume changes as a result of mass flow as well as heat transfer.

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The entropy of a substance always increases (or remains constant in the case of a reversible process) as it flows through a single-stream, adiabatic, steady-flow device.

→ **Steady flow devices in the rate form:**

$$\dot{S}_{\text{gen}} = \sum \dot{m}_e s_e - \sum \dot{m}_i s_i + \frac{\dot{Q}_{\text{surr}}}{T_{\text{surr}}} \geq 0 \quad \text{(kW/K)}$$

→ **Single stream devices:**

$$\dot{S}_{\text{gen}} = \dot{m}(s_e - s_i) + \frac{\dot{Q}_{\text{surr}}}{T_{\text{surr}}} \geq 0$$

The entropy generation of a fluid will increase as it flows through an adiabatic steady-flow device as a result of irreversibilities.

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Property Diagrams Involving Entropy:

The isentropic process appears as a *vertical* line segment on a *T-s* diagram.

During an internally reversible, adiabatic (isentropic) process, the entropy remains constant.

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T-s **diagram of a Carnot cycle**

On a *T-S* diagram, the area under the process curve represents the heat transfer for internally reversible processes.

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$$\cancelto{0}{Q} - W = \Delta H$$

For adiabatic steady-flow devices, the vertical distance Δ*h* on an *h*-*s* diagram is a measure of work, and the horizontal distance Δ*s* is a measure of irreversibilities.

Mollier diagram: The *h*-*s* diagram (see Fig. A-10 for the Mollier diagram of water)

ISENTROPIC EFFICIENCIES OF STEADY-FLOW DEVICES

The isentropic process involves no irreversibilities and serves as the ideal process for **adiabatic devices**.

Isentropic Efficiency of Turbines

$$\eta_T = \frac{\text{Actual turbine work}}{\text{Isentropic turbine work}} = \frac{w_a}{w_s}$$

$$\eta_T \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$

The *h-s* diagram for the actual and isentropic processes of an adiabatic turbine.

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Entropy is a property, and thus the value of entropy of a system is fixed once the state of the system is fixed.

The entropy of a pure substance is determined from the tables (like other properties).

Schematic of the *T-s* diagram for water.