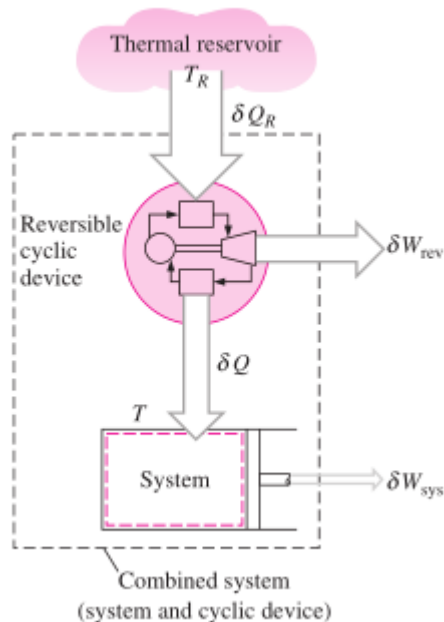


Lecture 10

Clausius Inequality

The Clausius inequality states that for any thermodynamic cycle $\oint \frac{dQ}{T} \leq 0$

where dQ represents the heat transfer at a part of the system boundary during a portion of the cycle, and T is the absolute temperature at that part of the boundary.



For proving the Clausius inequality we consider a system that is connected to a thermal energy reservoir at a constant temperature of T_R through a reversible cyclic device. The cyclic device receives heat dQ_R from the reservoir and supplies heat dQ to the system. The temperature of the system at that part of the boundary is T . The reversible cyclic device produces work dW_{rev} and the system produces work dW_{sys} . Applying the energy balance to the combined system

$$dW_C = dQ_R - dE_C$$

where dW_C is the total work of the combined system ($dW_{rev} + dW_{sys}$) and dE_C is the change in the total energy of the combined system

For the reversible cycle

$$\frac{dQ_R}{T_R} = \frac{dQ}{T}$$

Eliminating dQ_R from the two relations above gives

$$dW_C = T_R \frac{dQ}{T} - dE_C$$

We now let the system undergo a cycle while the cyclic device undergoes an integral number of cycles. The above relation then becomes

$$W_C = T_R \oint \frac{dQ}{T}$$

since the cyclic integral of energy (energy is a property) is zero. And W_C is the cyclic integral of dW_C , and it represents the net work for the combined cycle

But the combined system is exchanging heat with a single reservoir giving a net work output of W_C . According to Kelvin Planck statement this work cannot be positive, it can be zero or negative. And T_R is thermodynamic temperature which is a positive quantity. Therefore

$$\oint \frac{dQ}{T} \leq 0$$

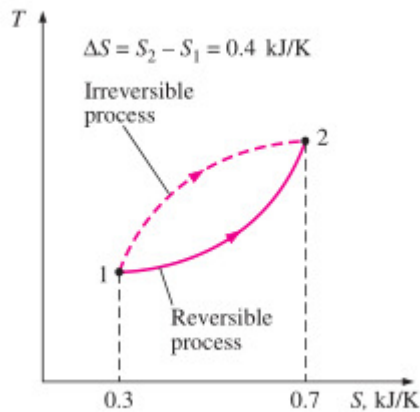
This is the Clausius inequality. This inequality is valid for all thermodynamic cycles, reversible or irreversible.

For internally reversible cycles $\oint \frac{dQ}{T} = 0$ and for irreversible cycles $\oint \frac{dQ}{T} < 0$

Since $\oint \left(\frac{dQ}{T}\right)_{int\ rev} = 0$, $\frac{dQ}{T}$ for an internally reversible process is a property in the differential form. This property was named entropy by Clausius. The symbol for entropy is S.

$$dS = \left(\frac{dQ}{T}\right)_{int\ rev}$$

The subscript int rev means that it is for an internally reversible process.



For determining the entropy change for any irreversible process 1-2, another reversible process with the same end states can be considered

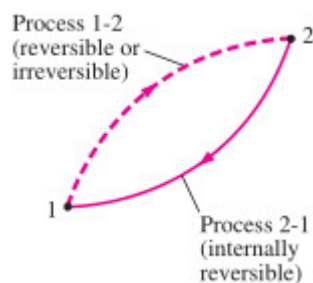
$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{dQ}{T}\right)_{int\ rev}$$

The unit for entropy is J/K

Evaluating Entropy Change for Isothermal Process

For isothermal process T is a constant, therefore $\Delta S = \frac{1}{T} \int_1^2 (dQ)_{int\ rev} = \frac{Q}{T}$

The increase of entropy principle



Consider a cycle that is made up of two processes: process 1-2, which is arbitrary (reversible or irreversible), and process 2-1, which is internally reversible, as shown in figure. From the Clausius inequality

$$\oint \frac{dQ}{T} \leq 0$$

$$\int_1^2 \frac{dQ}{T} + \int_2^1 \left(\frac{dQ}{T}\right)_{int\ rev} \leq 0 \quad , \text{But} \quad \int_2^1 \left(\frac{dQ}{T}\right)_{int\ rev} = S_1 - S_2$$

Therefore the above inequality becomes

$$\int_1^2 \frac{dQ}{T} + S_1 - S_2 \leq 0 \quad , \text{Or}$$

$$S_2 - S_1 \geq \int_1^2 \frac{dQ}{T} \quad , \text{or in the differential form}$$

$$dS \geq \frac{dQ}{T}$$

When the above inequality is applied to an isolated system (heat transfer zero)

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

That is 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**.

Entropy Generation

Consider the inequality

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

Since the LHS is a greater quantity, to balance both sides we add another quantity to the RHS, S_{gen} to convert it into an equation

$$dS = \frac{\delta Q}{T} + S_{gen}$$

The above equation shows us that entropy change can be the contribution of two quantities

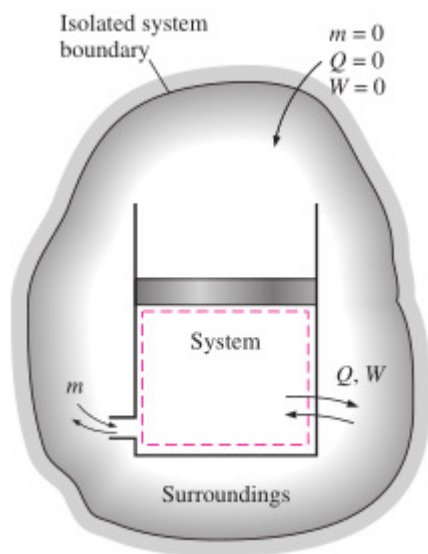
1. $\frac{\delta Q}{T}$ is the change in entropy due to heat transfer and it is called **entropy transfer by heat**.
2. S_{gen} is the entropy increase due to the irreversibilities and it is called **entropy generated** or **entropy produced**.

For a reversible process entropy generated is zero and for an irreversible process entropy generated is positive.

Therefore for an isolated system (or an adiabatic closed system, $Q = 0$) entropy change of a system is equal to entropy generation. i.e.

$$\Delta S_{isolated} = S_{gen}$$

Evaluating S_{gen}



If we take a system and its surroundings together, the combined system is an isolated system.

Entropy is an extensive property. So the total entropy change of the system and surroundings can be found out as

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

But system + surroundings = isolated system

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

And according to increase of entropy principle $\Delta S_{isolated} \geq 0$

Therefore

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

$$S_{gen} \geq 0$$

$S_{gen} = 0$: Reversible process

$S_{gen} > 0$: Irreversible process

$S_{gen} < 0$: Impossible process

Uses of S_{gen}

To find the direction of processes: All process must proceed in a direction that obeys the increase of entropy principle, or $S_{gen} \geq 0$ Therefore we can specify whether a process is impossible or possible by evaluating S_{gen} .

Measure of irreversibilities: Entropy generation is a measure of the irreversibilities present during a process. The greater the extent of irreversibilities, the greater the entropy generation

Performance of engineering devices: The performance of engineering systems is degraded by the presence of irreversibilities and S_{gen} is a measure of irreversibilities.

Isentropic processes

The entropy of a closed system can be changed by (1) heat transfer and (2) irreversibilities

For a **reversible adiabatic** process heat transfer = 0 and $S_{gen} = 0$ because of no irreversibilities.

Therefore all reversible adiabatic process are **isentropic processes**, i.e. a process with constant entropy.

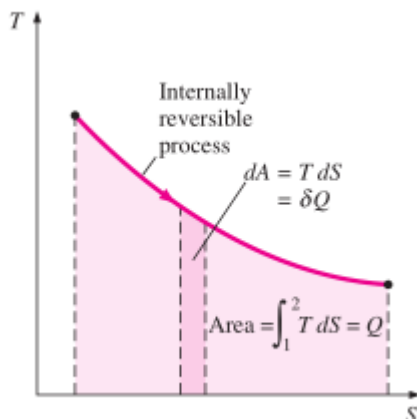
But all isentropic processes need not be reversible adiabatic. Entropy change can be zero with a negative heat transfer and positive S_{gen} in an irreversible process

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

If $-\int_1^2 \frac{\delta Q}{T} = S_{gen}$ ΔS can be zero.

But the term isentropic process is used generally in thermodynamics to imply a reversible adiabatic process.

T-S Diagram



A temperature entropy diagram can be used to represent processes.

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

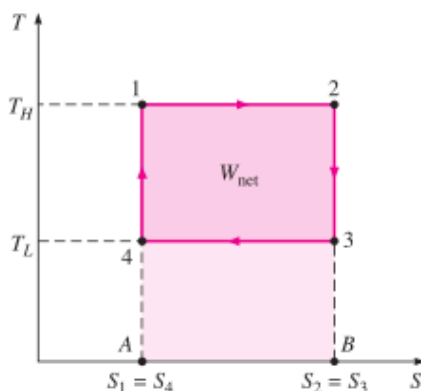
$$(\delta Q)_{int, rev} = T dS$$

For the process 1-2

$$Q = \int_1^2 T dS$$

For an internally reversible process the area under the curve in the T-S diagram is the heat transfer during the process

T-S Diagram of the Carnot Cycle



The Carnot cycle is made up of two reversible isothermal ($T = \text{constant}$) processes and two isentropic ($s = \text{constant}$) processes.

These four processes form a rectangle on a T-S diagram

The enclosed area is the net heat transfer (area under the curve in a T-S diagram is heat transfer)

For a cycle net heat transfer = net work transfer. Therefore the enclosed area also represents net work.