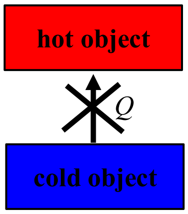
Introduction to the Second Law
Irreversibilities

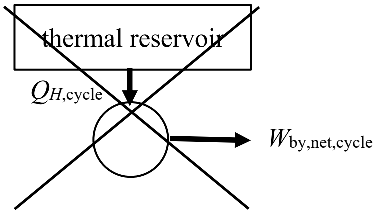
Clausius Statement of the Second Law of Thermodynamics

It is impossible for any system to operate in such a way that the sole result is the transfer of energy via heat transfer from a cooler object to a hotter object.



Kelvin-Planck Statement of the Second Law of Thermodynamics

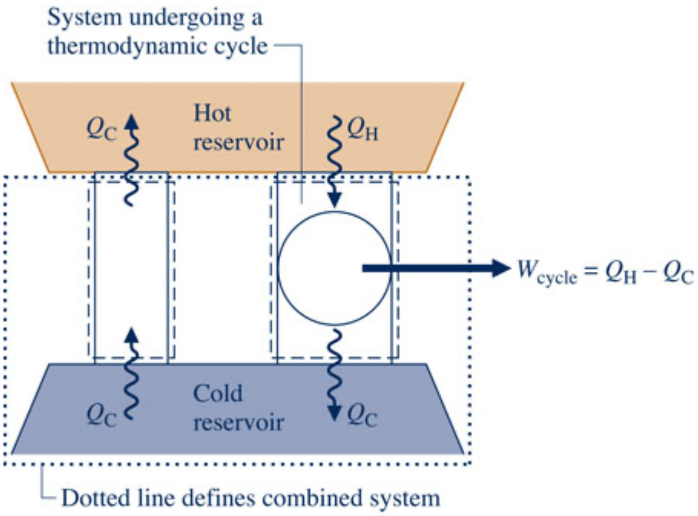
It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.



From the First Law applied to the system shown above, $W_{\text{by,net,cycle}} = Q_{H,\text{ cycle}}$. From the Kelvin-Planck Statement, we cannot have $W_{\text{by,net,cycle}} > 0$ for these conditions. Hence, a more quantitative form of the Kelvin-Plank Statement of the Second Law is,

$$W_{by,net,cycle} \leq 0 \begin{cases} < 0\text{: Internal irreversibilities are present} \\ = 0\text{: No internal irreversibilites} \end{cases} \quad \text{(single reservoir)}$$

Equivalence of the Two Statements



A **reversible process** is one in which the system is in a state of equilibrium at all points in its path. In a reversible process, the system and the surroundings can be restored exactly to their initial states.

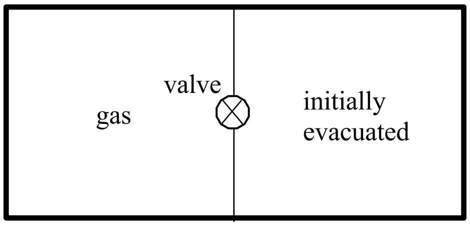
An **irreversible process** is one where the system is not in a state of equilibrium at all points in its path. The system and surroundings cannot be returned to their exact initial states in an irreversible process. Note that all natural processes are irreversible.

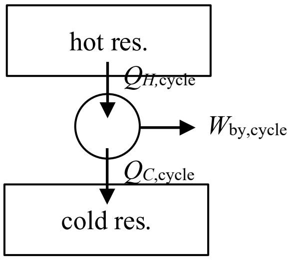
Examples of irreversibilities

- Heat transfer due to a finite temperature difference
- Unrestrained expansion of a gas or liquid to a lower pressure
- Spontaneous mixing
- Friction
- Electric current flow through a resistance

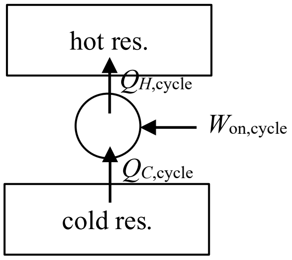
Internal Irreversibilities are those that occur within the system.
External Irreversibilities are those that occur within the surroundings.

Example:
A rigid insulated tank is divided into halves by a partition. On one side of the partition is a gas. The other side is initially evacuated. A valve in the partition is opened and the gas expands to fill the entire volume. Using the Kelvin-Planck statement of the Second Law, demonstrate that this process is irreversible.





power cycle



refrigeration or heat pump cycle

From the First Law for the cycle,

$$\Delta E_{sys,cycle} = 0 = Q_{into,cycle} - W_{by,cycle} = Q_{into,cycle} + W_{on,cycle}$$

power cycle: $0 = \left(Q_{H,cycle} - Q_{C,cycle}\right) - W_{by,cycle}$ => $W_{by,cycle} = Q_{H,cycle} - Q_{C,cycle}$

refrigeration or heat pump cycle: $0 = \left(Q_{C,\text{cycle}} - Q_{H,\text{cycle}}\right) + W_{\text{on,cycle}} \Rightarrow W_{\text{on,cycle}} = Q_{H,\text{cycle}} - Q_{C,\text{cycle}}$

Power cycle thermal efficiency

$$\eta = \frac{W_{\text{by,cycle}}}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Since $Q_C \neq 0$ (from the Kelvin-Planck Statement of the Second Law) => $\boldsymbol{\eta < 1}$.

Refrigeration cycle coefficient of performance

$$COP_{\text{ref}} = \frac{Q_C}{W_{\text{on,cycle}}} = \frac{Q_C}{Q_H - Q_C} = \frac{1}{Q_H / Q_C - 1}$$

Heat pump cycle coefficient of performance

$$COP_{\text{hp}} = \frac{Q_H}{W_{\text{on,cycle}}} = \frac{Q_H}{Q_H - Q_C} = \frac{1}{1 - Q_C / Q_H}$$

Since $W_{\text{on}} \neq 0$ (from the Clausius Statement of the Second Law, otherwise $Q_C = Q_H$ and heat is transferred from the cold reservoir to the hot reservoir) => **COP_{ref} and COP_{hp} must be finite**.

Second Law Corollaries

1. $\eta_{\text{irreversible}} < \eta_{\text{reversible}}$ (same thermal reservoirs)
2. $\eta_{\text{peversible},1} = \eta_{\text{reversible},2}$ (same thermal reservoirs)
3. $COP_{\text{irreversible}} < COP_{\text{reversible}}$ (same thermal reservoirs)
4. $COP_{\text{reversible},1} = COP_{\text{reversible},2}$ (same thermal reservoirs)