EPFL

ETA-Lab
Energy Transport Advances

ME-251: Thermodynamics and energetics I

2^{nd} Law of Thermodynamics

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Photo Credit: Trougnouf

Teaser Question about 2nd Law

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You've just scooped yourself a perfect bowl of **ice cream** and left it on the counter in a warm room. According to the 2nd Law of Thermodynamics, what will most likely happen over time?

- **A.** The ice cream will **stay perfectly frozen** as long as you don't touch it.
- **B.** Heat from the room will flow into the ice cream, causing it to **melt**.
- **C.** The ice cream will **get colder** because it's losing energy to the surroundings.
- **D.** The ice cream will **melt and then refreeze** itself once it's absorbed enough heat.

ILOs Today

- The need for 2nd Law
- Clausius statement and Kelvin-Planck statement of 2nd Law
- The concept of:
  - Reversible/irreversible/internally reversible processes
  - Carnot engine and Carnot theory

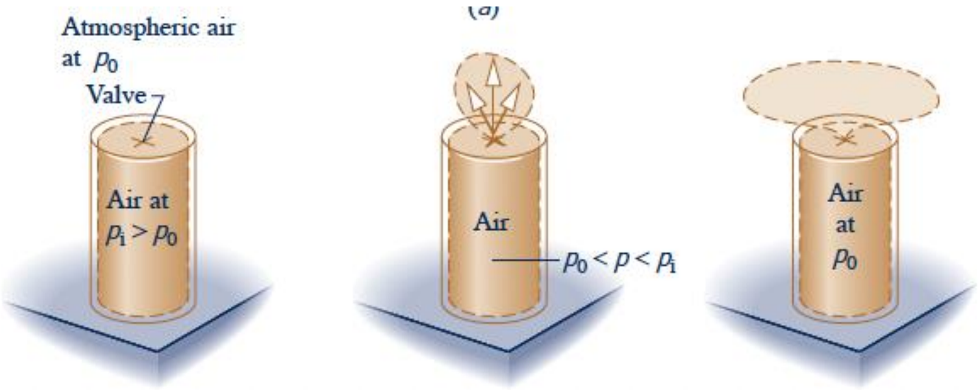
Motivating the Second Law

A cup of hot coffee can spontaneously cool down to the ambient temperature by transferring heat to the surrounding

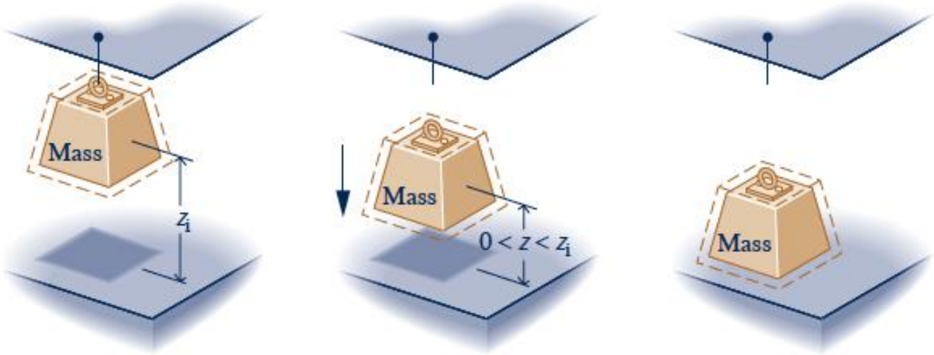
Now imagine a cup of coffee at the ambient temperature, to raise its temperature to be above the ambient, we must **do something**.

This inverse process is not spontaneous although it's not prohibited by the 1st law

Motivating the Second Law



A high-pressure gas tank **spontaneously** reduces to the atmospheric pressure once opened



A mass suspended at an elevation **spontaneously** falls to the ground when released

This inverse processes are not spontaneous although it’s not prohibited by the 1st law

Motivating the Second Law

Spontaneous processes take place

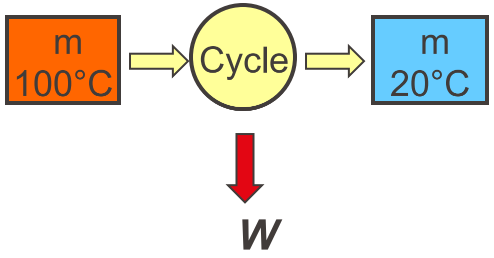
- in a preferred direction
- only if there is non-equilibrium (difference in T, p, z,…)
- until an equilibrium is achieved

In all three previous cases (coffee, gas tank, suspended mass), initial conditions cannot be restored without providing external energy input

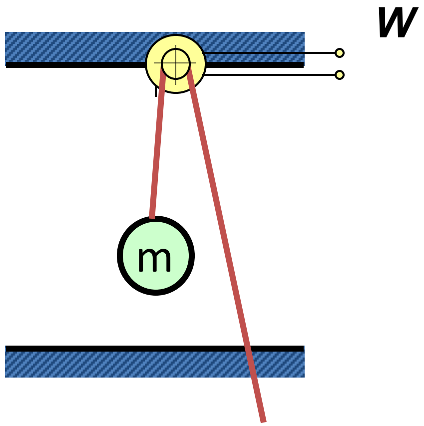
Not every process consistent with the 1st law will actually occur

Opportunity for Developing Work

Spontaneous processes can be exploited: it is possible that work can be developed as equilibrium is reached



The energy transferred to the surrounding by the coffee could be used to drive a power cycle and to extract work



The falling mass can be coupled to a wheel which would allow you to do work, for example, to lift another mass

Motivating the Second Law

The opportunity for work would be irreversibly lost if the systems achieves the equilibrium in a spontaneous, uncontrolled way

Energy is not destructed; it’s devaluated or dissipated: high quality energy becomes low quality energy

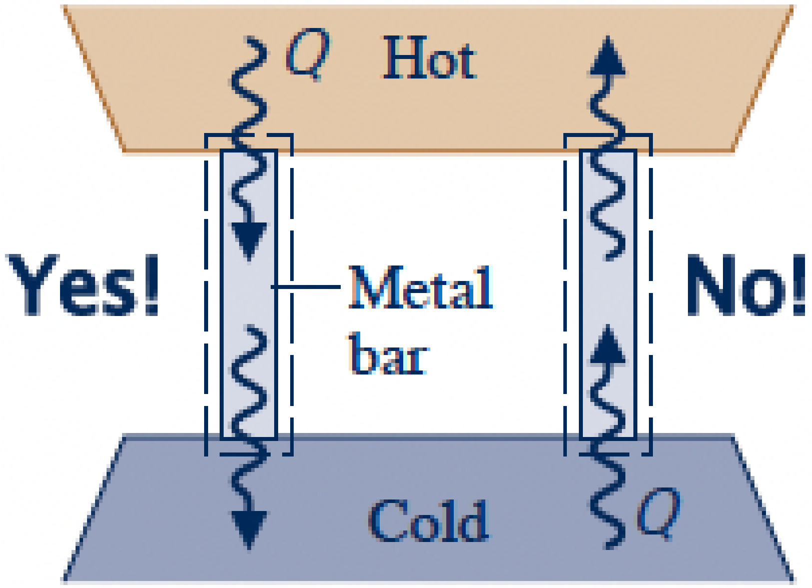
We need the 2nd law to quantify this “quality” and determine the maximum obtainable work and how to approach the maximum

Motivating the Second Law

With the 2nd law of thermodynamics, we will:

- Predict the direction of processes
- Establish conditions for equilibrium
- Determine the best theoretical performance for processes, cycles, …
- Quantitatively evaluate the factors that hinder the achievement of best theoretical performance
- Define the absolute temperature scale independent of the thermal properties of a substance
- Evaluate enthalpy and internal energy in alternative ways

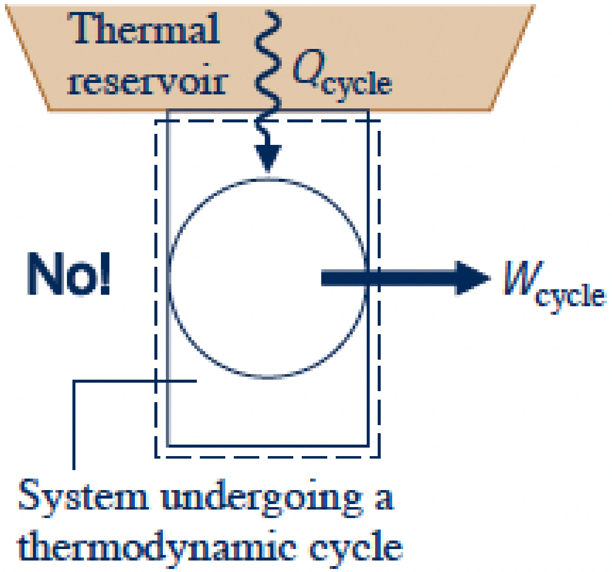
2nd Law of Thermodynamics



Clausius statement. It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.

It is possible for a system to transfer energy by heat from a cooler body to a hotter body (refrigerators, heat pumps, …) but there must be some other effects accompanying this

2nd Law of Thermodynamics

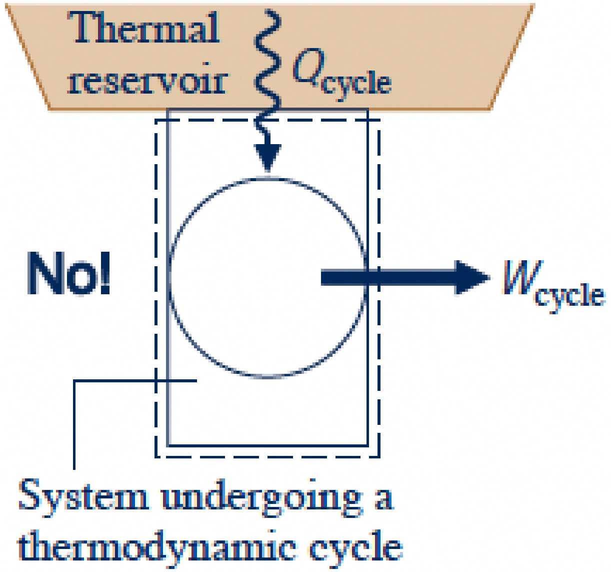


Kelvin-Planck statement. It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.

A **thermal reservoir** is a special kind of system that always remains at constant temperature even though energy is added or removed by heat transfer.

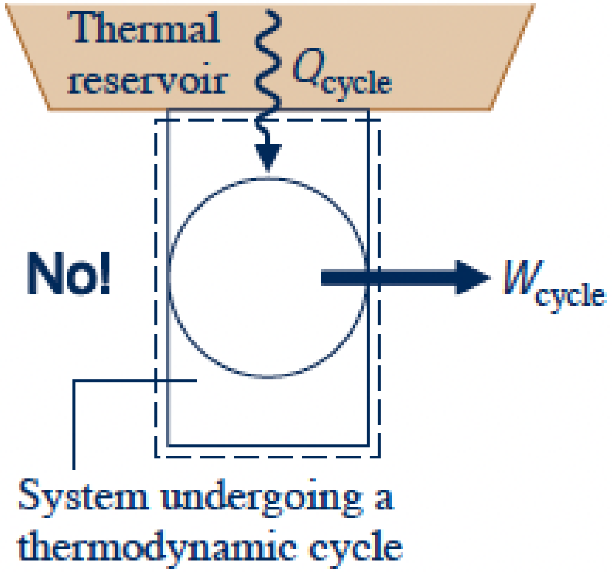
2nd Law of Thermodynamics

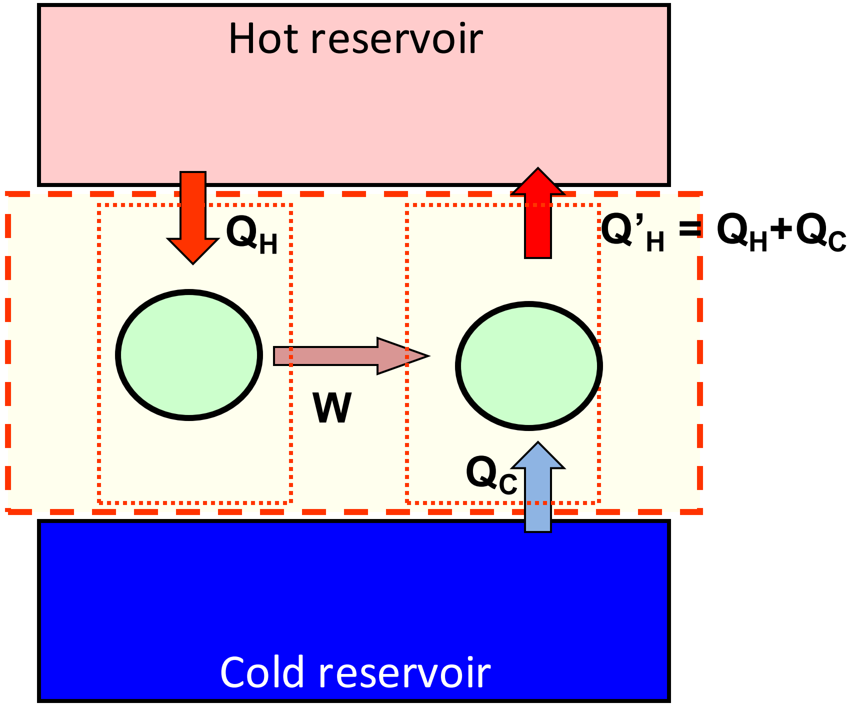
- The Kelvin-Planck statement does not rule out the possibility of a system developing a net amount of work from a heat transfer drawn from a single reservoir. **It only denies this possibility if the system undergoes a thermodynamic cycle.**



Equivalence Between Two Statements

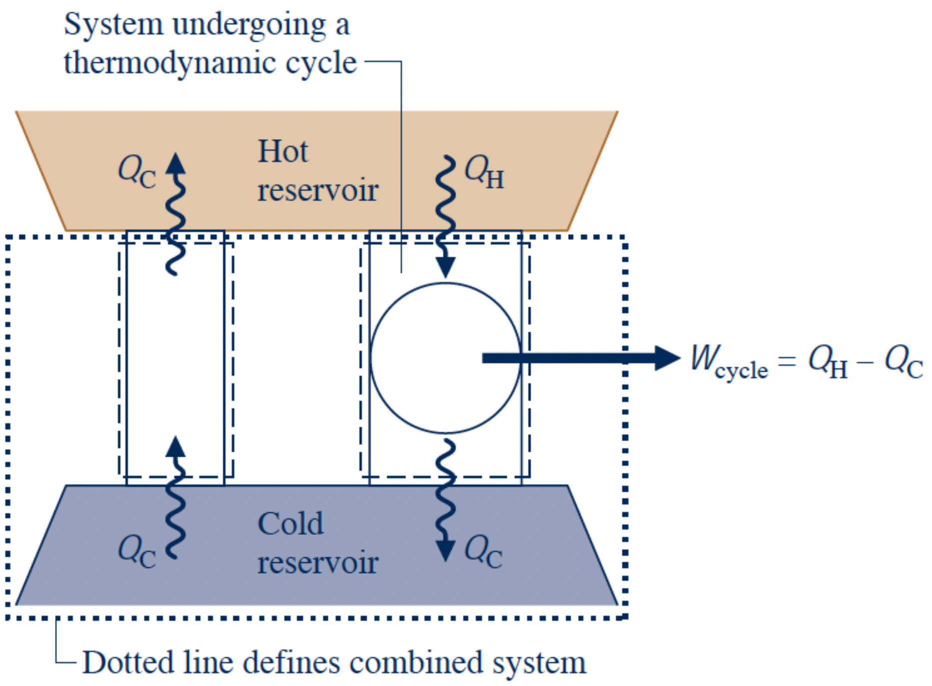
If we have a machine that violates Kelvin-Planck statement, $W_{cycle} > 0$, we can use this work output to drive a refrigerator, with the net outcome of transferring heat from a cold reservoir to a hot reservoir, violating Clausius statement





Equivalence Between Two Statements

If a machine violates Clausius statement, we can construct a combined system including this machine, a cold reservoir, and a power engine. We can adjust the work output of the power engine, such that the cold reservoir receives net-zero heat



Reversible Process

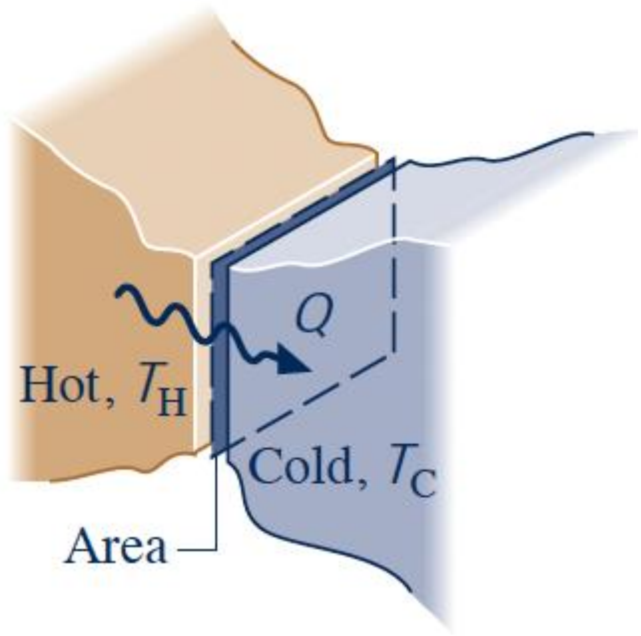
A process is reversible if the **system** and all parts of its **surrounding** can be exactly restored to their respective initial states.

A reversible process is one that can be run backward in time by simply reversing its inputs and outputs; it’s the thermodynamic equivalent of frictionless motion in mechanics

Common Irreversible Processes

- Heat transfer through a finite temperature difference
- Unrestrained expansion of a gas or liquid to a lower pressure
- Spontaneous chemical reaction
- Spontaneous mixing of matter at different composition or states
- All kinds of friction
- Electric current flowing through a resistance
- Magnetization and polarization with hysteresis
- Inelastic deformation
- **All actual processes**

Heat Transfer Example



Spontaneous heat transfer occurs between two bodies with finite temperature difference

The importance of this source of irreversibility diminishes for temperature difference diminishes

When the two temperatures are almost the same, the process is almost reversible.

However, the heat transfer rate will almost be zero

Almost zero-rate heat transfer is clearly impractical, but is how we think of heat transfer approaching reversibility

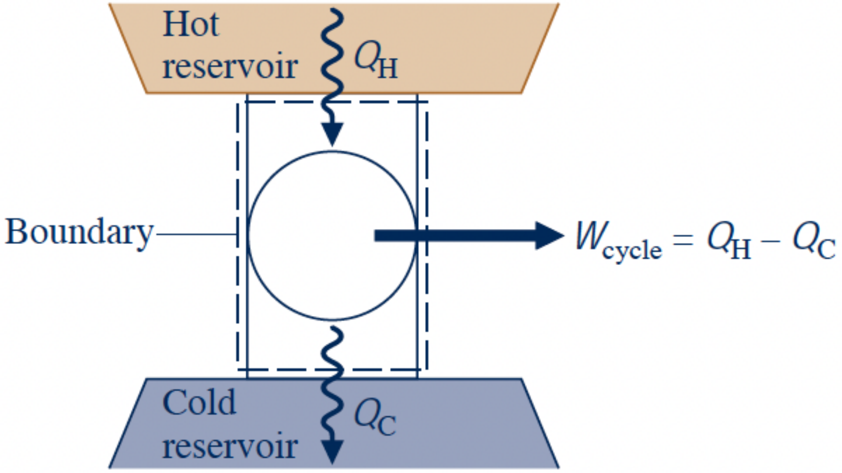
Internally Reversible Process

There is no irreversibility within the system throughout the process
(external irreversibility in the surrounding still possible)

At every intermediate state of an internally reversible process of a closed system, all intensive properties (T, p, v, …) are uniform throughout each phase present. Otherwise, spontaneous processes associated with internal irreversibility will occur.

An internally reversible process consists of a series of quasi-equilibrium states; it is a quasi-equilibrium process

Carnot Engine

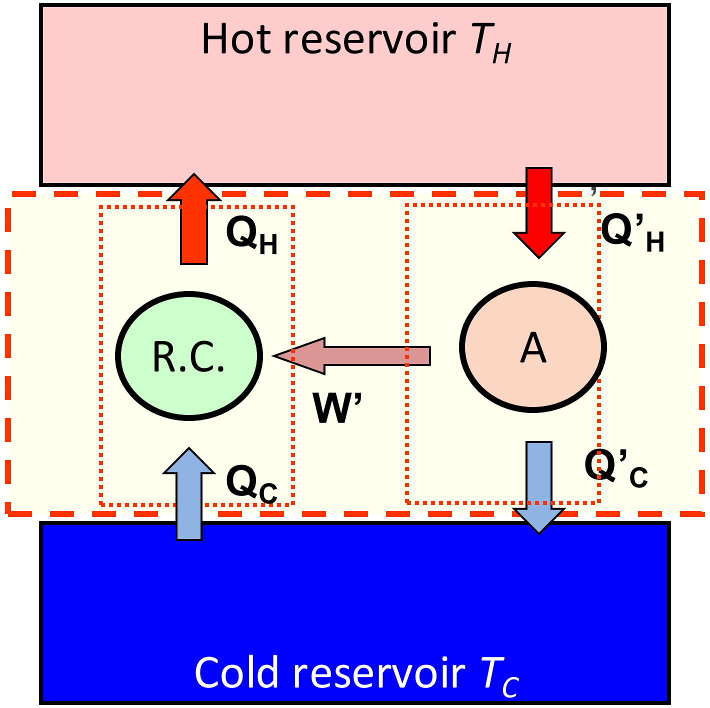


$$\eta = W_{cycle}/Q_H$$

A Carnot engine is any engine that is reversible, runs in a cycle, exchanging heat only with a hot reservoir (source) at temperature T_H and a cold reservoir (sink) at temperature T_C

Carnot's Theorem: No engine operating between two reservoirs (at temperatures T_H and T_C) is more efficient than a Carnot engine operating between them.

Proof of Carnot's Theorem



Since a Carnot engine is reversible, it can be run backward as a refrigerator.

Consider an arbitrary power engine A between T_H and T_C. It generates work W' which can be used run reversed Carnot engine (R.C.)

Consider the combined cycle (A + R.C.) between T_H and T_C, which has no net work input/output.

Corollary

All reversible (Carnot) engines have the same universal efficiency $\eta(T_H, T_C)$

Consider any two Carnot engines with η_1 and η_2 :
each can be used to run the other backward