SECOND LAW OF THERMODYNAMICS

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Thermodynamics

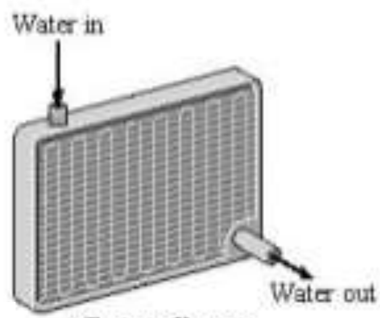
- Thermodynamics is the branch of science that deals with the relationships between heat and other forms of energy.
- Thermodynamics describes how thermal energy is converted to and from other forms of energy and how it affects matter.

Applications of Thermodynamics

The human body

Air-conditioning systems

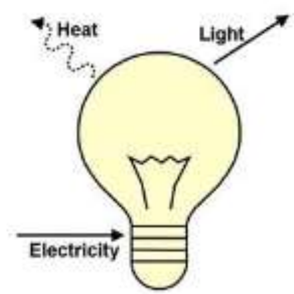
Airplanes



Car radiators

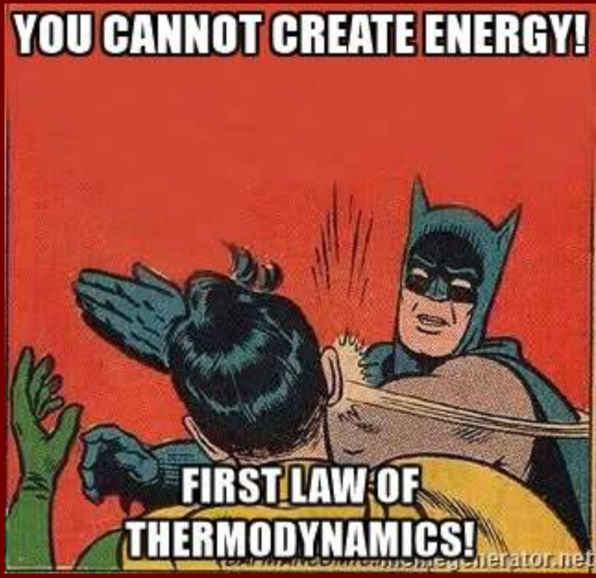
Power plants

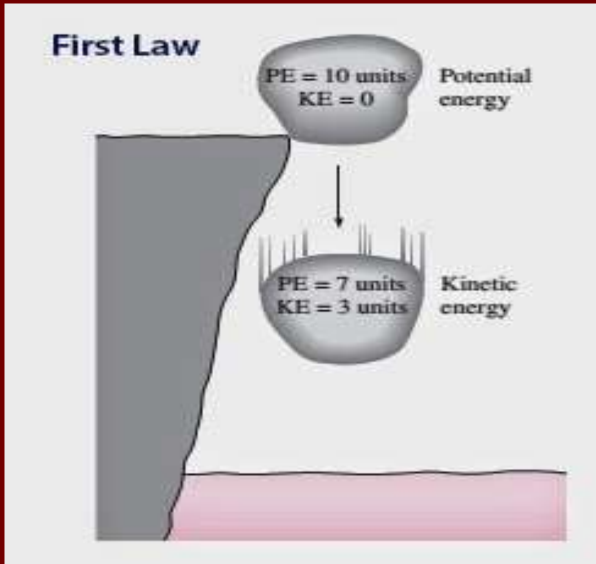
Refrigeration systems

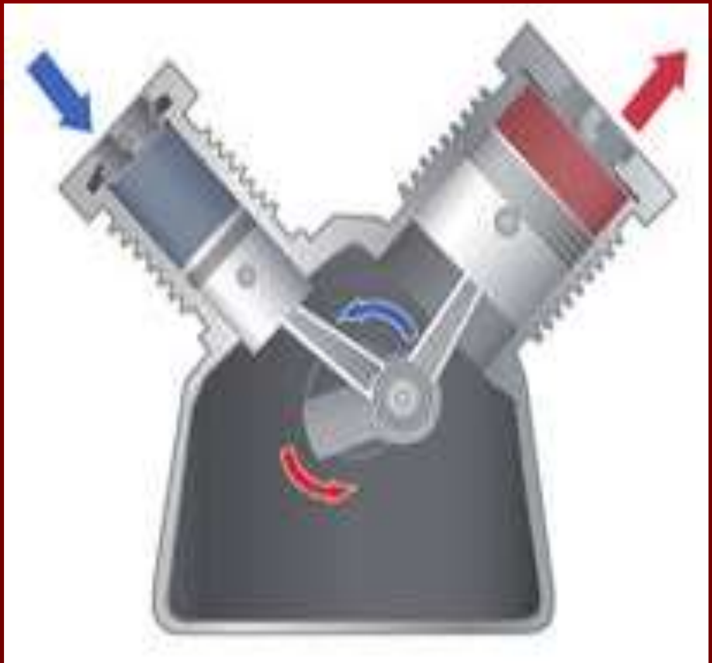


First Law of Thermodynamics

- The FLT is basically the law of conservation of energy.
- The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but cannot be created or destroyed.







A hot gas, when confined in a chamber, exerts pressure on a piston, causing it to move downward. The movement can be harnessed to do work equal to the total force applied to the top of the piston times the distance that the piston moves.

- The change in internal energy of a system is the sum of all the energy inputs and outputs to and from the system.
- More precisely, the internal energy of a system is equal to the work that is being done on the system, plus or minus the heat that flows in or out of the system and any other work that is done on the system. That is simply a restatement of energy conservation principle.

- Mathematically

$$\Delta U = Q - W$$

Where

ΔU = Change in the internal energy

Q = Heat added to the system

W = Work done by the system

"Now, in the *second* law of thermodynamics . . . "

Second Law of Thermodynamics

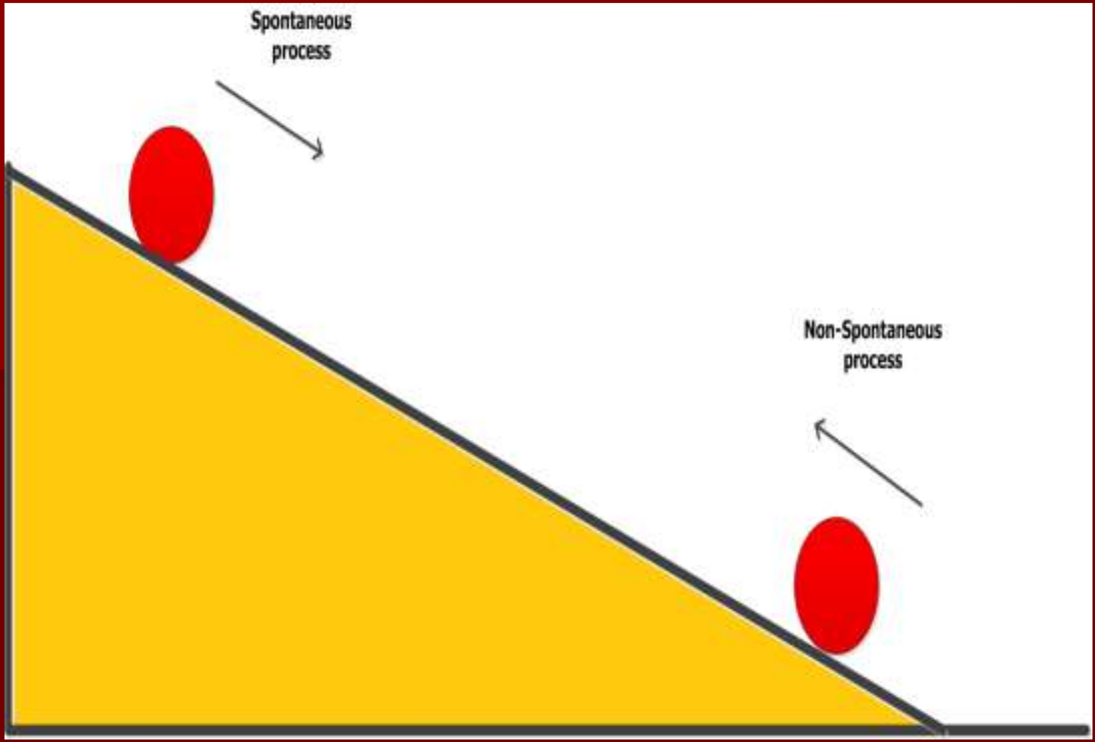
- Identifies the direction of a process (e.g. Heat can only spontaneously transfer from a hot object to a cold object, not vice versa)
- Used to determine the Quality of energy (e.g. A high-temperature energy source has a higher quality since it is easier to extract energy from it to deliver useful work)

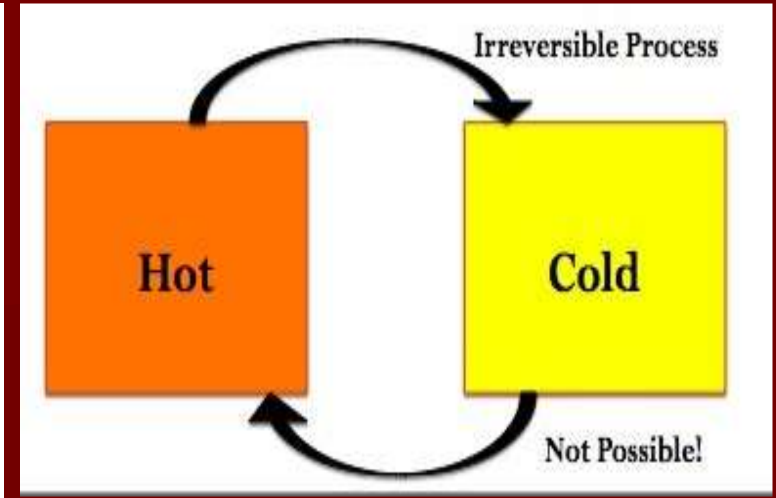
- Used to exclude the possibility of constructing 100% efficient heat engine and perpetual-motion machines (violates the Kevin-Planck and the Clausius statements of the second law)
- Determines the theoretical performance limits of engineering systems (e.g. A Carnot engine is theoretically the most efficient heat engine; its performance can be used as a standard for other practical engines)

- The FLT reflects the observation that energy is conserved, but it imposes no restriction on the process direction.
- All experience indicates that there is such a restriction; the concise statement of which constitutes the *second law.*
- The first law characterizes the balance of energy which defines the quantity of energy. The second law defines the direction in which the process can take place and its quality.

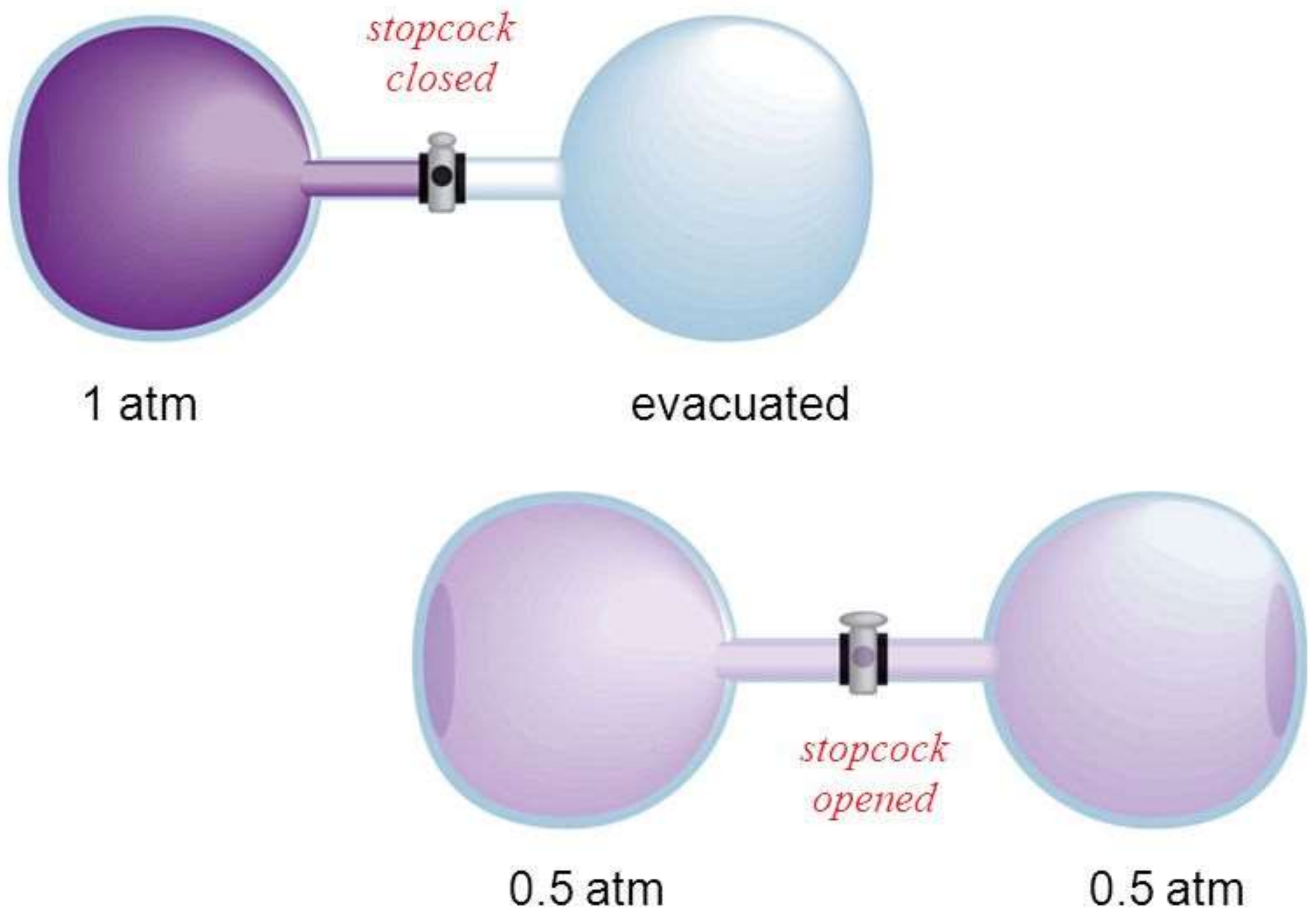
- Suppose two metal blocks of temperatures 100°C and 30°C are brought in contact.
- Analysis as per the FLT: Total energy of the system will remain conserved.
- The energy gained by one metal block would be exactly equal to that lost by the other.
- Which one is possible?
- (110°C and 20°C) or (90°C and 40°C)

- As per the FLT, both possibilities are true. But infact only second possibility is true.
- It is our knowledge of SLT which provides the criterion as to the probability of various processes.
- Spontaneous processes in nature occur only in one direction.
- Example: Transfer of heat, flow of water, movement of time, aging process, breaking of a cup, etc.

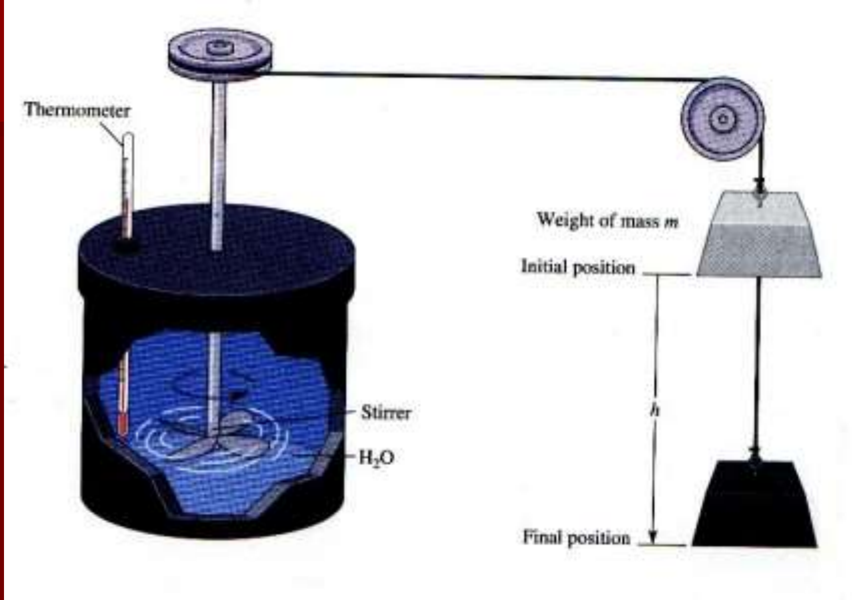

Spontaneous process
Non-Spontaneous process


Irreversible Process
Hot
Cold
Not Possible!

Spontaneous expansion of a gas



- The spontaneity of the process is due to a finite driving potential, like temperature gradient, concentration gradient, pressure difference, electric potential gradient, etc.
- These transfer processes can never spontaneously occur from a lower to a higher potential.
- SLT puts a directional limitation on transformation of energy in addition to that imposed by the FLT.



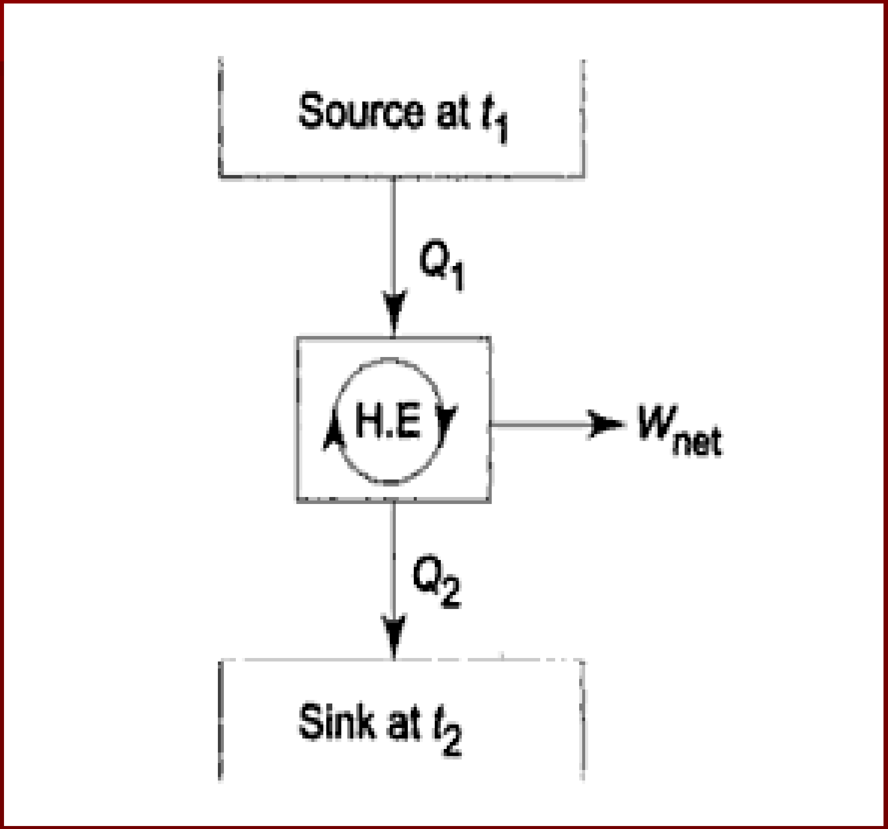
Joule's energy conservation experiment

- Work can be completely converted into heat.
- But the complete conversion of heat into work in a cycle is not possible.
- Heat and work are not completely interchangeable forms of energy.

- Work is said to be a *high grade energy* and heat a *low grade energy*.
- *The complete conversion of low grade energy into high grade energy in a cycle is not possible.*
- SLT is best expressed with the help of a heat engine cycle.
- A heat engine is a thermodynamic system operating in a cycle in which there is a net heat transfer to the system and a net work transfer from the system.

- The function of a heat engine cycle is to produce work continuously at the expense of heat input to the system.
- The net work W_{net} and heat input Q_1 referred to the cycle are of primary interest.
- A heat engine is very often required to extract as much work as possible for a given heat input to maximize the cycle efficiency.

Efficiency of heat engine



$$\eta = \frac{Net\ work\ output\ of\ the\ cycle}{Total\ heat\ input\ to\ the\ cycle}$$

$$= \frac{W_{net}}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Thermal Energy Reservoir (TER)

- TER is a large body of infinite heat capacity, capable of absorbing or rejecting unlimited quantity of heat without any noticeable change in its thermodynamic coordinates.
- Source - a TER from which heat is transferred to a heat engine cycle without any decrease in its temperature (like a furnace)
- Sink - a TER to which heat is rejected from a heat engine cycle without any increase in its temperature (like a lake, river, ocean)

Kelvin-Planck Statement

- *It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single fixed temperature.*
- A heat engine can never be 100% efficient.
- There has always to be a heat rejection.

Clausius Statement

- *It is impossible to construct a device which, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body.*
- Heat can not flow of itself from a body at a lower temperature to a body at a higher temperature.
- Such reverse process never occurs spontaneously. Some external work must be expended to achieve this.

Equivalence of Kelvin-Planck and Clausius Statement

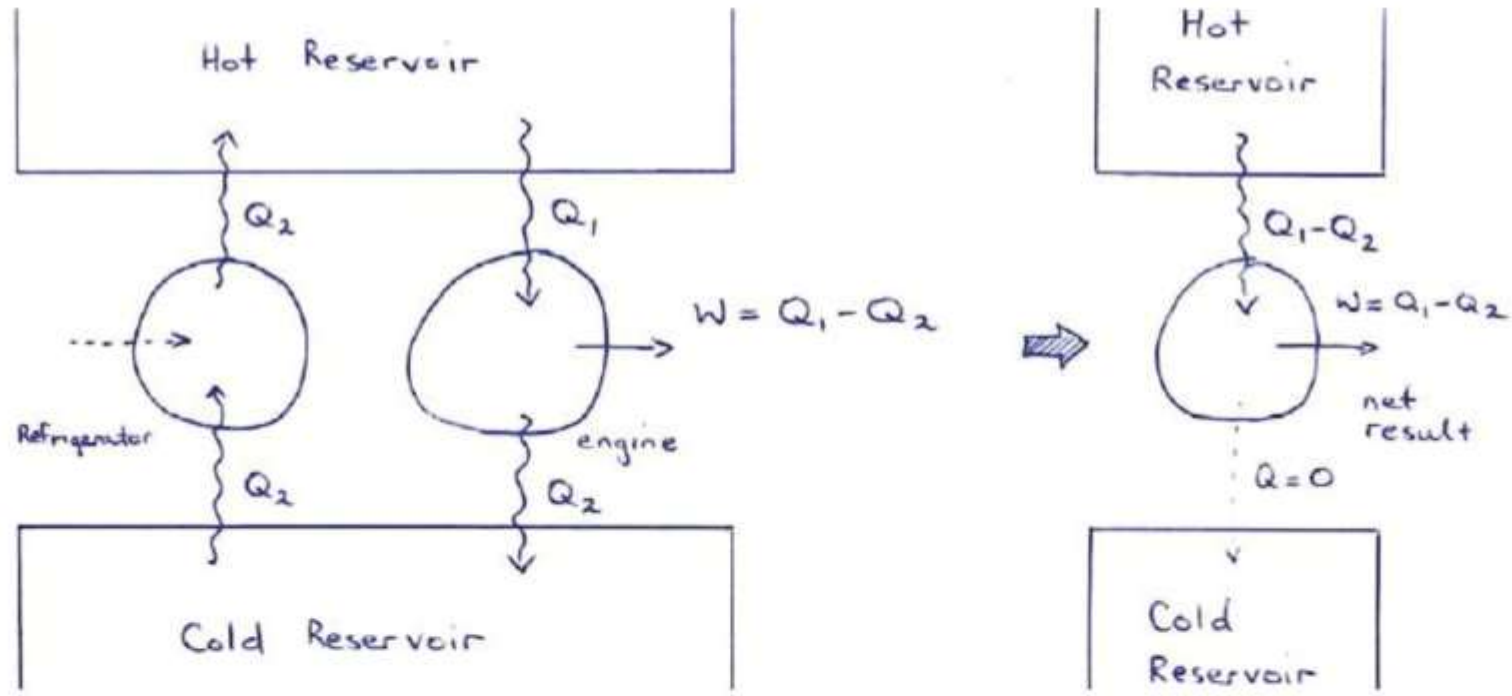


Figure (a): Violation of Clausius' statement leading to violation of Kelvin-Planck statement

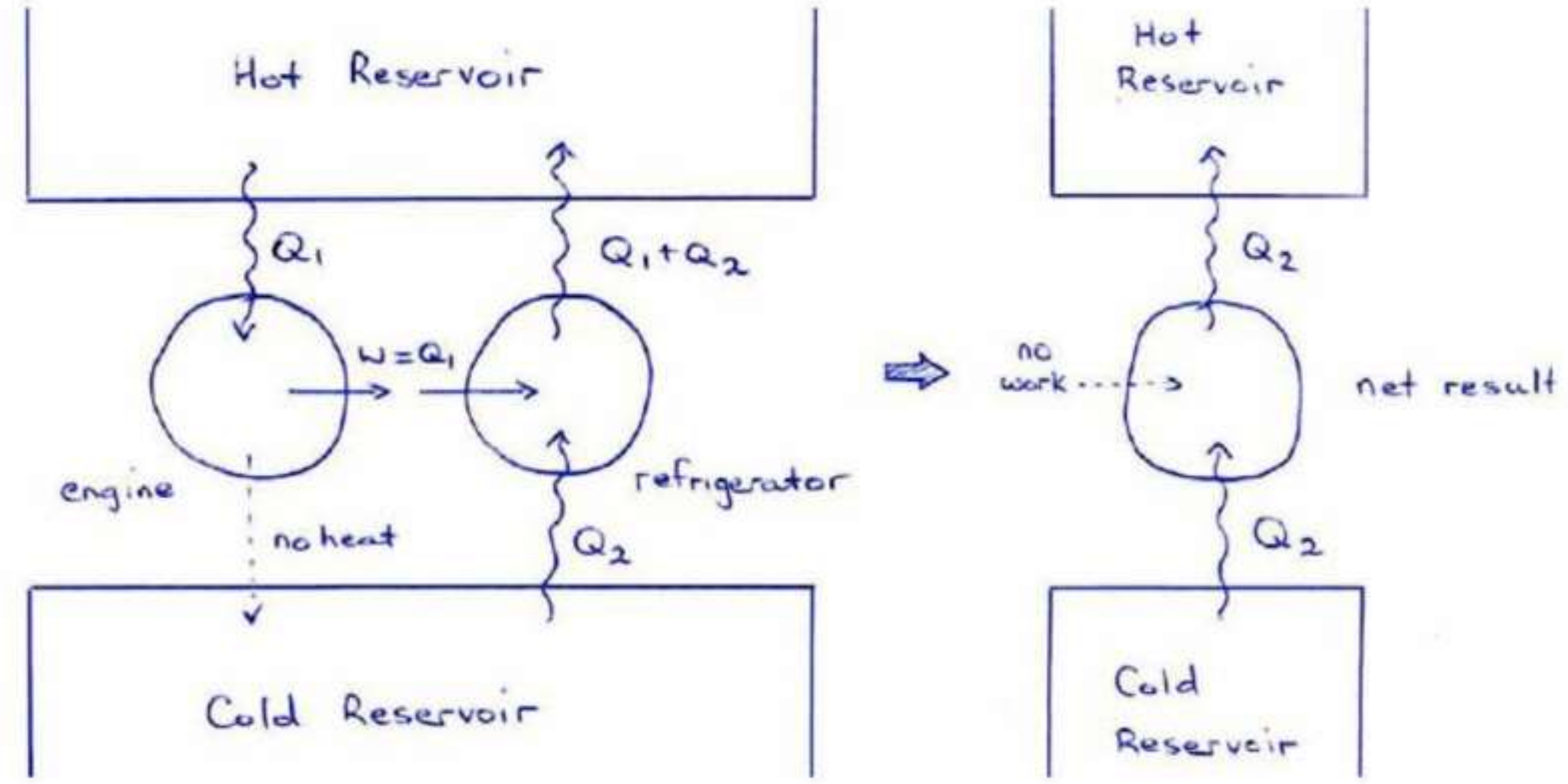
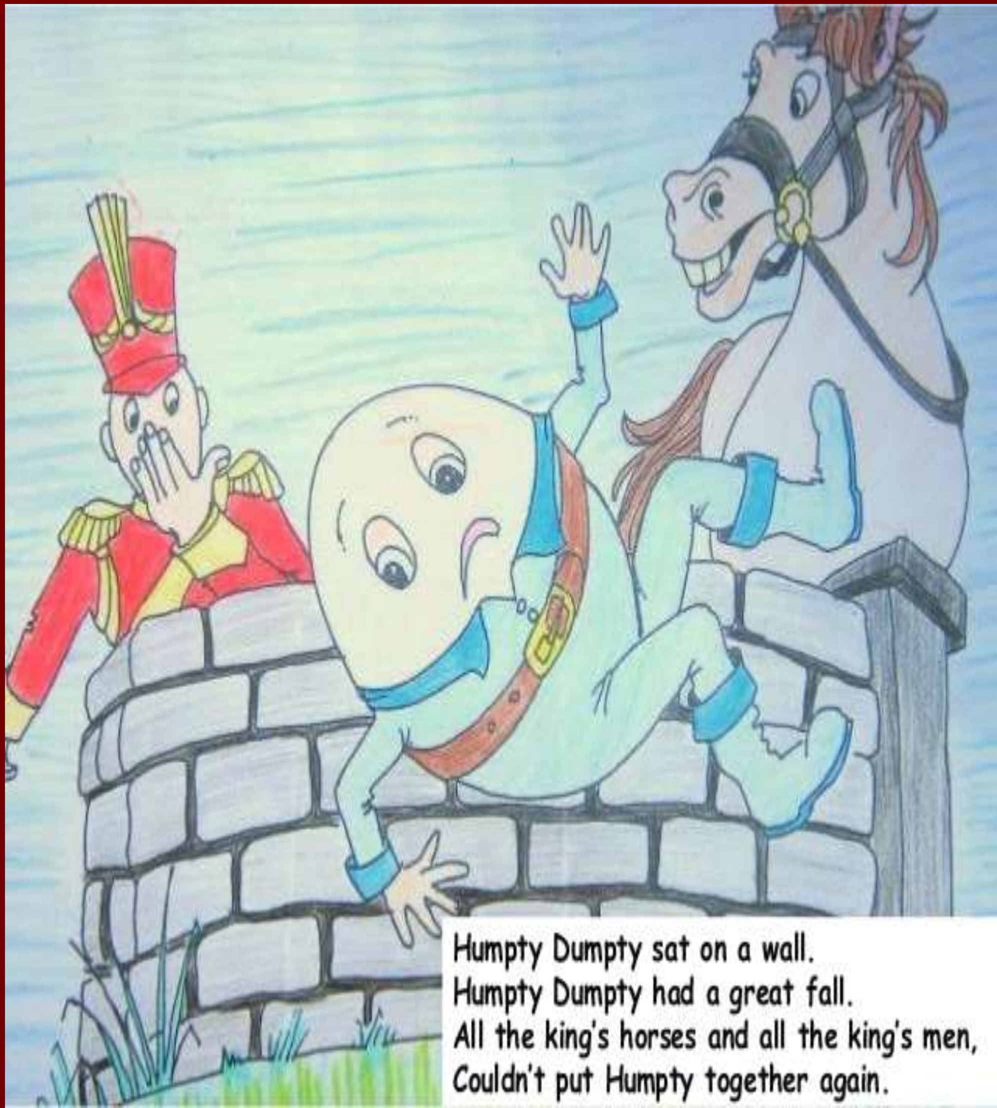


Figure (b): Violation of Kelvin-Planck statement leading to violation of Clausius' statement

- The second law of thermodynamics has two unique characteristics.
- First is the generalisation that any spontaneous process occurs in the direction of high potential to low potential.
- Second, it is the only law of nature that restricts a journey back in time. All the other laws of mechanics and thermodynamics are valid regardless of movement with or against the time. Only the second law of thermodynamics is violated when time is reversed.

Time's arrow is a catch phrase introduced by Arthur Eddington in his *The Nature of the Physical World*.

Eddington made an interesting analogy between the SLT and fall of Humpty Dumpty in classic nursery rhyme to demonstrate the irrevocable nature of SLT (p. 64).



Pertetual Motion Machine (PMM)

- Any device that violates either the first law or second law of thermodynamics is called the perpetual motion machine.
- Two types
  - Perpetual motion machine of first kind (PMM1)
  - Perpetual motion machine of second kind (PMM2)

PMM1

- There can be no machine which would continuously supply mechanical work without some other form of energy disappearing simultaneously.
- A PMM1 violates FLT and is thus impossible.

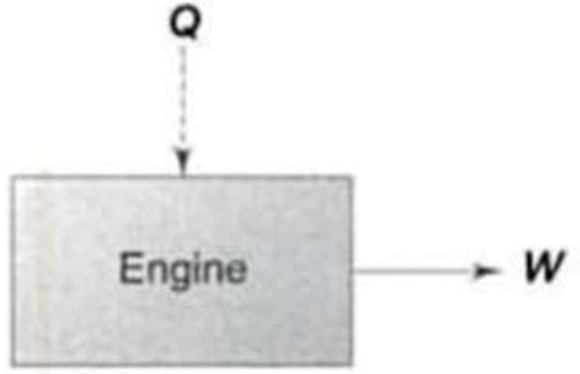


Figure: A PMM1

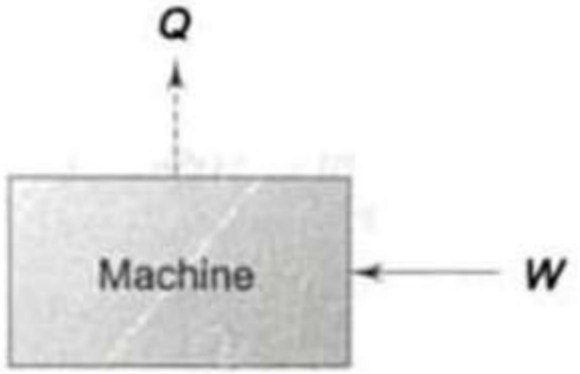


Figure: The converse of PMM1

PMM2

- If $Q_2 = 0$ ($W_{net} = Q_1$, or $\eta = 100\%$), the heat engine will produce net work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement.
- Such a heat engine is called a perpetual motion machine of the second kind (PMM2), which is impossible.

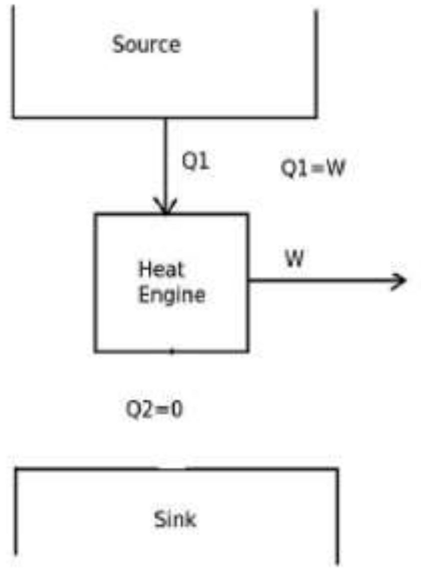


Figure: A PMM2

Reversible Processes and Irreversibilities

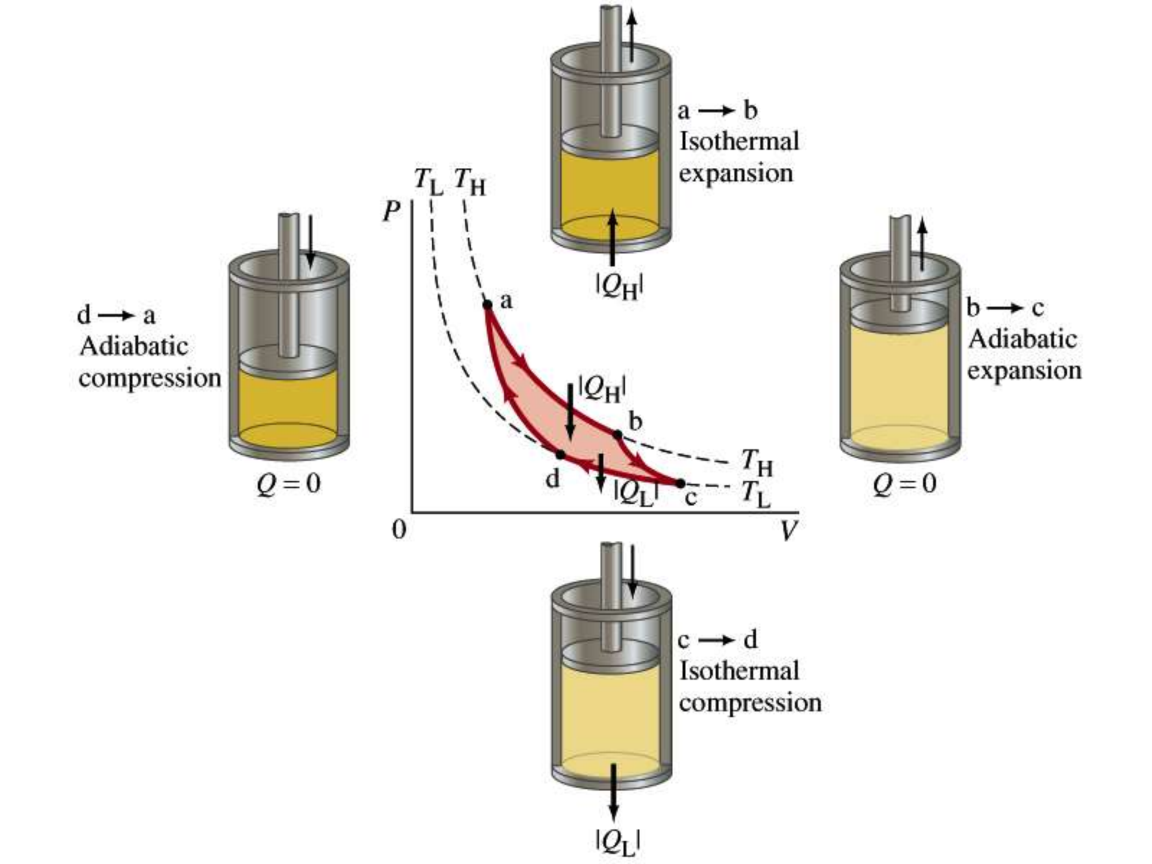
- A reversible process is one that can be executed in the reverse direction with no net change in the system or the surroundings.
- At the end of a forward and backward reversible process, both system and the surroundings are returned to their initial states.
- No real processes are reversible.

- However, reversible processes are theoretically the most efficient processes.
- All real processes are irreversible due to irreversibilities. Hence, real processes are less efficient than reversible processes.
- Common causes of irreversibility
  - Friction
  - Sudden expansion and compression
  - Heat transfer between bodies with a finite temperature difference

- A quasi-equilibrium process, e.g. very slow, frictionless expansion or compression is a reversible process.
- A work-producing device which employs quasi-equlibrium or reversible processes produces the maximum amount of work theoretically possible.
- A work-consuming device which employs quasi-equilibrium or reversible processes requires the minimum amount of work theoretically possible.

Carnot Cycle

- One of the most common idealized cycles that employs all reversible processes is called the Carnot Cycle proposed in 1824 by Sadi Carnot.
- Though Carnot reversible heat engine is an idealization and no real engine can be perfectly reversible.
- Carnot was the first to show that even under ideal conditions an engine can not convert all of the heat supplied to it in to work.

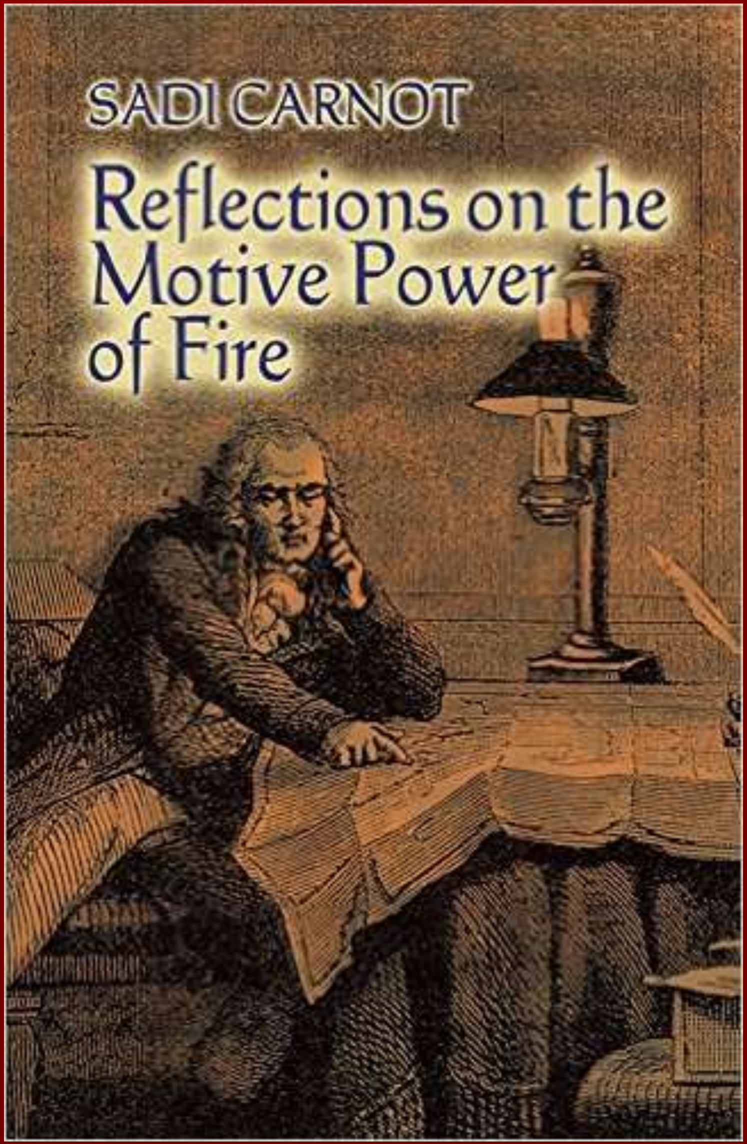


A Carnot heat engine is a perfect engine which is used to determine the limits on efficiency.

Carnot's Theorem

The maximum-efficiency heat engine is described in Carnot's theorem:

"If an engine operating between two constant-temperature reservoirs is to have maximum efficiency, it must be an engine in which all processes are reversible. In addition, all reversible engines operating between the same two temperatures, T_H and T_L, have the same efficiency."



Sadi Carnot at age of 34

BRIEF BIOGRAPHY OF SADI CARNOT

- 1 June, 1796 - 24 August, 1832
- Eldest son of French mathematician, military engineer and leader of the revolution army Lazare Carnot
- Sent to École Polytechnique in Paris at the age of 16 in 1812
- Eminent faculty at École Polytechnique during that time - Ampère, Arago, Gay-Lussac, Thénard and Poisson
- In 1814, Carnot joined French army as an officer and studied military engineering for 2 years at the École du Génie in Metz
- Transferred to the General Staff in Paris in 1819
- From this time forward, Carnot became interested in improving the efficiency of steam engines that led to the investigations the results of which were published in his book "Reflections on the Motive Power of Fire".

- Reflections on the Motive Power of Fire was a slim book of 118 pages and published in 200 copies on June 12, 1824 by Bachelier.
- The book received very little attention and quickly went out of print and for some time was very difficult to obtain.
- The book became successful in securing a place in history and academic world, when it was modernized by Émile Clapeyron in 1834 and then further elaborated upon by Rudolf Clausius and Lord Kelvin.
- Carnot retired from the army in 1828 without a pension.
- Carnot was restrained in a private asylum in 1832 as suffering from "mania" and "general delirum".

- Shortly thereafter, he died during a cholera epidemic at a young age of 36 at the hospital in Ivry-sur-Seine.
- Because of the contagious nature of cholera and custom of that time, most of his belongings and writings were burned after his death.
- Only a handful of his manuscripts survived, which were posthumously published by his brother Hippolyte Carnot in 1878.

Resting place of Sadi Carnot in Ivry-sur-Seine (France)


Thank You