Fundamentals of Thermodynamics
Lecture 8. The Second Law of Thermodynamics

8.1. Introduction

The first law of thermodynamics (energy cannot be created or destroyed) gives information about the quantity of energy transfer as a process, it does not tell about the direction of energy transfer and the quality of the energy.

The second law of thermodynamics puts restrictions upon the direction of heat transfer and achievable efficiencies of *heat engines*.

Heat Engine
Is a device that converts heat to work. It takes heat from a reservoir, then does some work like moving a piston,

It is the second law of thermodynamics that provides the criterion for the feasibility of any process. A process cannot occur unless it satisfies both the first and second laws of thermodynamics.

Q/ What is the main difference between the first law and the second law of thermodynamics?

Ans. The first law of thermodynamics describes how energy is conserved but does not specify the direction of the flow of energy. The direction of the flow of energy and the spontaneity of a process is described by the second law of thermodynamics.

8.2 What is the Second Law of Thermodynamics?

The second law of thermodynamics states that:

"any spontaneously occurring process will always lead to an increase in the entropy of the universe (system + surrounding). In simple words, the law explains that an isolated system's entropy will never decrease over time.

Q/ The statement that best describes the second law of thermodynamics is: heat flows spontaneously from……….

(a) hot to cold, and entropy decreases. (b) hot to cold, and entropy increases.

(c) cold to hot, and entropy increases. (d) cold to hot, and entropy decreases.

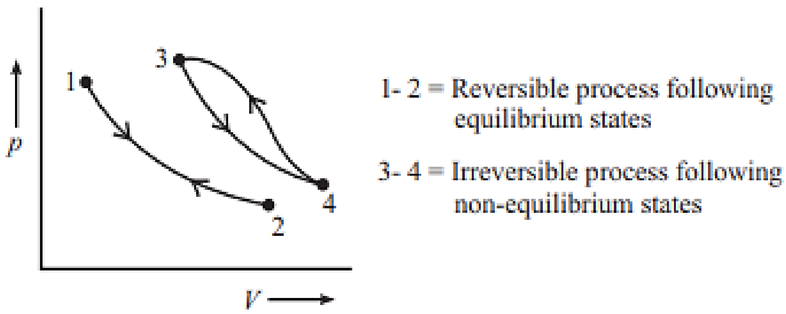
Nonetheless, in some cases, where the system is in thermodynamic equilibrium or going through a *reversible process*, the total entropy of a system and its surroundings remains constant.

Thermodynamic system that is capable of restoring its original state by reversing the factors responsible for occurrence of the process is called reversible system and the thermodynamic process involved is called **reversible process**. Thus, upon reversal of a process there shall be no trace of the process being occurred, i.e., state changes during the forward direction of occurrence of a process are exactly similar to the states passed through by the system during the reversed direction of the process.

It is quite obvious that such reversibility can be realized only if the system maintains its thermodynamic equilibrium throughout the occurrence of process.

Irreversible systems are those, which do not maintain equilibrium during the occurrence of a process. Various factors responsible for the non–attainment of equilibrium are generally the reasons responsible for irreversibility presence of friction, dissipative effects etc.

Fig.1 Reversible and irreversible process



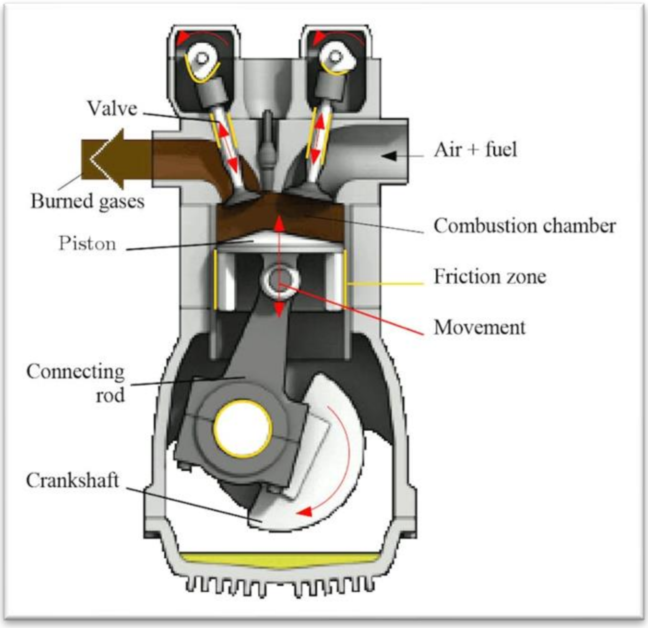
Q/ Is reversible process real?

Ans. Reversible processes are hypothetical but central to the second law of thermodynamics. Melting or freezing of ice in water is an example of a realistic process that is nearly reversible.

The second law is also known as the *Law of Increased Entropy*. The second law clearly explains that it is impossible to convert heat energy to mechanical energy (i.e. work) with 100 % efficiency.

Example, if we look at the piston in an engine, the gas is heated to increase its pressure and drive the piston. However, even as the piston moves, there is always some leftover heat in the gas that cannot be used for carrying out any other work. Heat is wasted, and it has to be discarded. In this case, it is done by transferring it to a heat sink or in the case of a car engine, waste heat is discarded by exhausting the used fuel and air mixture to the atmosphere. Additionally, heat generated from friction that is generally unusable should also be removed from the system.

Fig.2 A Schematic of car engine piston (ref. https://theconversation.com/how-cars-waste-two-thirds-of-their-fuel-197752)



Q/ How much fuel energy in cars is consumed?

Ans. Only 20% to 30% of the energy in the fuel is converted into useful work (i.e., moving the car). A large portion of the energy (around 70% to 80%) is lost as heat through: (1) The exhaust gases. (2) The engine block and coolant system. (3) Friction between moving parts.

8.3 The Second Law of Thermodynamics Equation

Mathematically, the second law of thermodynamics is represented as:

$$\Delta S_{univ} > 0$$

Where ΔS_{univ} is the change in the entropy of the universe.

Entropy is a measure of the randomness of the system. It can be considered a quantitative index that describes the quality of energy.

There are a few factors that cause an increase in the entropy of the closed system:

- Firstly, in a closed system, while the mass remains constant, there is an exchange of heat with the surroundings. This change in the heat content creates a disturbance in the system, thereby increasing the entropy of the system.
- Secondly, internal changes may occur in the movements of the molecules of the system. This leads to disturbances which further cause irreversibilities inside the system resulting in the increment of its entropy.

8.4 Different Statements of the Law

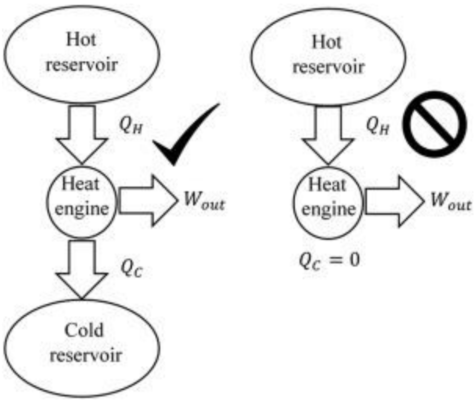
There are two statements on the second law of thermodynamics, Kelvin- Plank statement and Clausius statement:

1. **Kelvin-Planck Statement**

Kelvin Planck statement states that "it is impossible to construct a device or engine which operates on a cycle and produces no other effect than the transfer of heat from a single body to produce work."

This means that it is impossible to construct an engine whose only purpose is to convert the heat from a high-temperature source into an equal amount of work.

Fig.3 Explain the Kelvin-Planck Statement

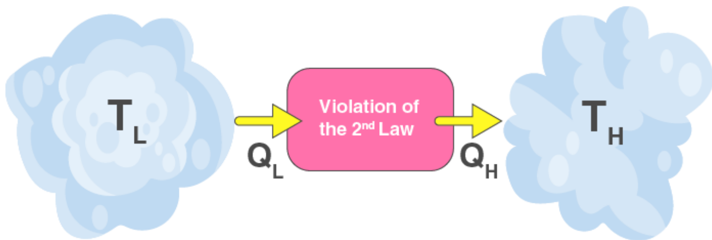


Clausius's Statement

Clausius's Statement states that "It is impossible to construct a device operating in a cycle that can transfer heat from a colder body to a warmer one without consuming any work. Also, energy will not flow spontaneously from a low-temperature object to a higher-temperature object."

The situation in Figure 4 is impossible.

Fig.4 This scenario is impossible



The net transfer will occur from the hot object to the cold object in any *spontaneous* process. We have to do some form of work to transfer the energy to the hot object. In other words, unless the compressor is driven by an external source, the refrigerator will not be able to operate. The heat pump and refrigerator work on Clausius's statement.

Exercises

1. **A heat pump uses 300 J of work to remove 400 J of heat from the low-temperature reservoir. How much heat is delivered to a higher-temperature reservoir?**

   Sol. $W = 300\,J$, $Q_C = 400\,J$

   $Q_H = W + Q_C$

   $Q_H = 300\,J + 400\,J = 700\,J$

   Heat delivered to the higher temperature reservoir is 700 J.

2. **A reversible heat engine receives 4000 KJ of heat from a constant temperature source at 600 K. If the surrounding is at 300K, then determine (a) the availability of heat energy (b) unavailable heat.**

   [Note: Available energy, also known as exergy, represents the maximum theoretical work that can be extracted from a system or combination of system and surrounding under specific conditions. The unavailable energy is that incapable of doing work under existing conditions].

   Sol. $Q_1 = 4000\,KJ$, $T_1 = 600K$, $T_0 = 300\,K$

   $$Change\ in\ entropy\ (\Delta S) = \int \frac{dQ}{T}$$

   $$\Delta S = \frac{Q_1}{(T_1 + T_o)}$$

   $Change\ in\ entropy = 4.44\,KJ/K$

   $The\ availability\ of\ heat\ energy,$

   $A = Q_1 - T_0(\Delta S)$

   $A = 4000 - 300(4.44) = 2668\,KJ$

   $Unavailable\ heat\ (U.A) = T_0\,(\Delta S)$

   $(U.A) = 300\,(4.44) = 1332\,KJ$

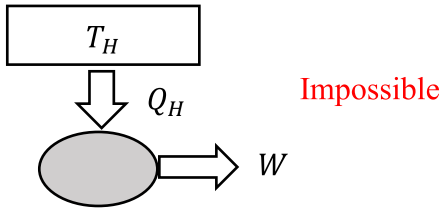
3. **Make a simple comparison between the first law and the second law of thermodynamics**

Aspect	First Law	Second Law
Core principle	Conservation of energy	Increase of entropy (irreversibility)
What it answers	*Can energy be accounted for?*	*Can the process actually happen? In which direction?*
Concerned with	Quantity of energy	Quality of energy
Allows for	Any process that conserves energy	Only processes that increase total entropy
Example	You can convert heat to work	But you can't convert *all* heat to work

Frequently Asked Questions on Second Law of Thermodynamics

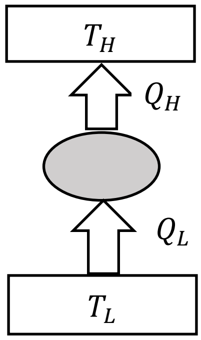
Q1. What is Kelvin's statement of the second law of thermodynamics?

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce only a net amount of work.



Q2. What is Clausius' statement of the second law of thermodynamics?

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower temperature body to a higher temperature body.



Impossible

Q3. When is there a violation of Kelvin's statement of the second law?

Suppose we have an engine which gives a continuous supply of work when it is cooled below the temperature of the surroundings. This is a violation of the Kelvin statement.

Q4. Give one application of the second law of thermodynamics.

The second law of thermodynamics is applied in refrigerators.

Q5. How is entropy related to the second law of thermodynamics?

According to the second law of thermodynamics, the total entropy of the system will either increase or remain constant, it will never decrease.

Q6. Will entropy decrease?

Entropy will not decrease. Entropy will increase for an irreversible process and will be zero for a reversible process.

Q7. What factors influence entropy?

A substance's entropy rises with its molecular weight and complexity, as well as with temperature. As the pressure or concentration decreases, the entropy increases.

Q8. List a few properties of entropy.

(1) It only depends on the mass of the system since it is an extensive quantity.
(2) There is an increase in the entropy of the universe.
(3) Entropy is never zero.
(4) For an adiabatic thermodynamic system, the entropy will remain constant.
(5) Entropy and temperature are inversely proportional.
(6) In a cyclic process, there is no change in state. Therefore, the entropy remains constant.
(7) For an irreversible process, entropy increases.
(8) For reversible processes, entropy decreases.

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