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 first law cannot indicate whether a metallic bar of uniform temperature can spontaneously become warmer at one end and cooler at others.

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

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/ Which best describes the first law of thermodynamics as compared to the second law?

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.

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

Q/ Which of the following statements best describes the second law of thermodynamics?

a. Heat flows spontaneously from hot to cold, and entropy decreases.

b. Heat flows spontaneously from hot to cold, and entropy increases.

c. Heat flows spontaneously from cold to hot, and entropy increases.

d. Heat flows spontaneously from 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.

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.

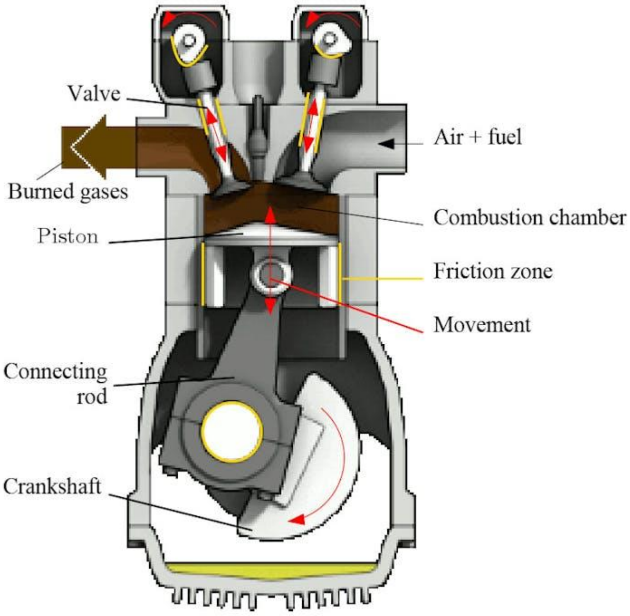


Fig.1 A Schematic of car engine piston (ref. https://theconversation.com/how-cars-waste-two-thirds-of-their-fuel-197752)

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, or it is the measure of energy or chaos within an isolated system. It can be considered a quantitative index that describes the quality of energy.

Meanwhile, 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, and they are:

1. Kelvin- lank Statement
2. Clausius Statement

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 sole purpose is to convert the heat from a high-temperature source/reservoir into an equal amount of work.

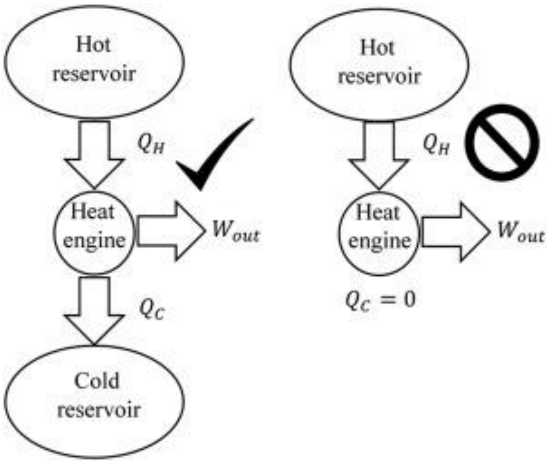


Fig.2 Explain the Kelvin-Planck Statement

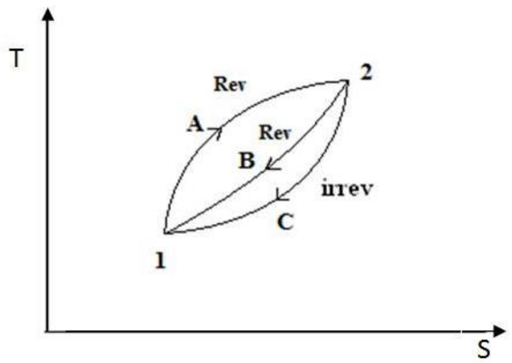


Fig.3 Reversible and irreversible process

Exceptions:

If $Q_c = 0$ $(i.e., Wnet = Q_H, or\ efficiency = 100\ \%)$, the heat engine produces work in a complete cycle by exchanging heat with only one reservoir, thus violating 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.

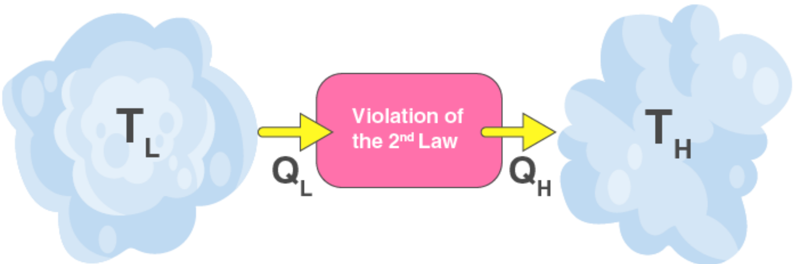
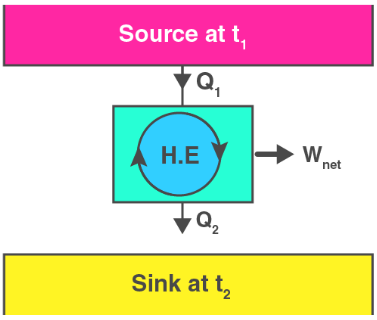


Fig.4 This scenario is impossible

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.

Both Clausius's and Kelvin's statements are equivalent, i.e., a device violating Clausius's statement will also violate Kelvin's statement and vice versa.

Thus, a heat engine has to interact with at least two thermal reservoirs at different temperatures to produce work in a cycle. So long as there is a difference in temperature, motive power (i.e., work) can be produced. If the bodies with which the heat engine exchanges are of finite heat capacities, work will be produced by the heat engine until the temperature of the two bodies is equalised.



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

   $Q_H = W + Q_C$
   $Q_H = 300\,J + 400\,J \,, Q_H = 700\,J$
   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. $Q_1 = 4000\,KJ \quad , T_1 = 600K \quad , T_0 = 300\,K$

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

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

   $Change\ in\ entropy = 4.44\,KJ/K$
   $The\ availability\ of\ heat\ energy,$
   $A = Q_1 - T_0(\Delta S)$
   $A = 4000 - 300(4.44) = 2668\,KJ$
   $Unavailable\ heat\ (U.A) = T0\ (\Delta S)$
   $(U.A) = 300\ (4.44) = 1332\,KJ$

Frequently Asked Questions on Second Law of Thermodynamics

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

According to the 2nd law of thermodynamics by Kelvin, it is impossible to get a continuous supply of work by cooling a body to a temperature lower than that of the coolest of surroundings.

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

It is impossible for a self-acting machine unaided by an external agency to heat from one body at a lower temperature to another body at a higher temperature.

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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