Heat Engines, Entropy, and the Second Law of Thermodynamics



Part 1-2+Part 2-2



Limitations of First Law of Thermodynamics

 Heat flows from a system of higher temperature to a system of lower temperature and never from lower temperature system to higher temperature system



But never from colder to hotter side by itself by itself

- From first law of thermodynamics, "Heat lost and heat gain must be equal in both the processes"
- According to first law, it is assumed that the <u>energy transfer can take place in either</u> direction, it does not specify the direction of energy transfer

The Second Law of Thermodynamic

- Establishes which processes do occur and which do not occur.
- This directionality is governed by the second law.
- These types of processes are irreversible.
 - An irreversible process is one that occurs naturally in one direction only.
 - No irreversible process has been observed to run backwards.
 - An important engineering implication is the limited efficiency of heat engines.



William Thomson, Lord Kelvin 1824 – 1907 British physicist and mathematician

His work in thermodynamics led to the idea that energy cannot pass spontaneously from a colder object to a hotter object.

Heat Engines and the Second Law of Thermodynamics:



Heat Engines

- A heat engine is a device that takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work.
 - $W_{\rm eng}$ work done by the heat engine
- Q_h heat, entering the engine.
- Q_c energy, leaving the engine.





A heat engine carries some working substance through a cyclic process during which

- (1) the working substance absorbs energy by heat from a high-temperature energy reservoir,
- (2) work is done by the engine, and
- (3) energy is expelled by heat to a lowertemperature reservoir.

Heat Engines:





- an engine operates in a cycle
- fuel is burned to make heat
- some of the heat is converted into work
- the heat that is not converted to work is removed to bring the system back to the beginning state (cycle)
- since the system is always returned to the original state the change in internal energy is ZERO

Model Heat Engine



Q_{hot}= W+Q_{cold}
 or
 Q_{hot}-Q_{cold}=W

(what goes in must come out)

The thermal efficiency

 The *thermal efficiency e* of a heat engine is defined as the ratio of the net work done by the engine during one cycle to the energy input at the higher temperature during the cycle:

$$e = \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

This Equation shows that a heat engine has 100% efficiency (e=1) only if |Qc| = 0, that is, if no energy is expelled to the cold reservoir.

 All heat engines have e<1. (Not all heat can be converted into work.)

Example1 : The Efficiency of an Engine

An engine transfers 2×10^3 J of energy from a hot reservoir during a cycle and transfers 1.5×10^3 J as exhaust to a cold reservoir.

- 1. Find the efficiency of the engine.
- 2. How much work does this engine do in one cycle?

Example2 : The Output of a truck is 4500 J and its efficiency is 50%.

Find the input energy provided from hot reservoir to the truck

Example1 : The Efficiency of an Engine

An engine transfers 2×10^3 J of energy from a hot reservoir during a cycle and transfers 1.5×10^3 J as exhaust to a cold reservoir.

- 1. Find the efficiency of the engine.
- 2. How much work does this engine do in one cycle?

Example2 : The Output of a truck is 4500 J and its efficiency is 50%. Find the input energy provided from hot reservoir to the truck

Solution: Example 1

1.
$$e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{1.50 \times 10^3 \text{ J}}{2.00 \times 10^3 \text{ J}} = 0.250, \text{ or } 25.0\%$$

2.
$$W_{eng} = |Q_h| - |Q_c| = 2.00 \times 10^3 \text{ J} - 1.50 \times 10^3 \text{ J}$$
$$= 5.0 \times 10^2 \text{ J}$$
$$Or \quad e = \frac{W}{|Q_h|} = 7 \quad W = c |Q_h|$$
$$= 0.25 \times 200 = 50$$

Solution: Example 2

 $l = 5\sigma / = 0.5$ $Q_c = 4500 \mu$ $\hat{Q}_{h} = ($ $e = 1 - |Q_c|$ 1Qhl $\Rightarrow \left| Q_{c} \right| = \left| Q_{h} \right| \left(1 - e \right) \Rightarrow \left| Q_{h} \right| = \frac{\left| Q_{c} \right|}{\left(1 - e \right)}$ 4500 000

Heat Pumps and Refrigerators

In a heat engine: the direction of energy transfer is from the hot reservoir to the cold reservoir, which is the natural direction.



reservoir (the inside of the refrigerator) and exhausts to the kitchen. Note that $Q_{\rm h} = Q_{\rm c} + W$

The refrigerator or heat pump transfers energy from a colder body (for example, the contents of a kitchen refrigerator or the winter air outside a building) to a hotter body (the air in the kitchen or a room in the building).

In practice, it is desirable to carry out this process with a minimum of work. The process could be accomplished without doing any work, the refrigerator or heat pump would be "perfect" (Fig. 22.5). Again, the existence of such a device would be in violation of the second law of thermodynamics, which in the form of the Clausius statement states:



Figure 22.4 Schematic representation of a heat pump.

Figure 22.5 Schematic diagram of an impossible heat pump or refrigerator, that is, one that takes in energy from a cold reservoir and expels an equivalent amount of energy to a hot reservoir without the input of energy by work.

It is impossible to construct a cyclical machine whose sole effect is to transfer energy continuously by heat from one object to another object at a higher temperature without the input of energy by work.

The effectiveness of a heat pump is described in terms of a number called the coefficient of performance (COP). The COP is similar to the thermal efficiency for a heat engine in that it is a ratio of what you gain (energy transferred to or from a reservoir) to what you give (work input)

In a refrigerator or heat pump, the engine takes in energy Qc from a cold reservoir and expels energy Q_h to a hot reservoir (Fig. 3). This can be accomplished only if work is done on the engine



Figure 3 : Schematic diagram of a heat pump, which takes in energy $Q_c > 0$ from a cold reservoir and expels energy $Q_h < 0$ to a hot reservoir. Work W is done *on* the heat pump. A refrigerator works the same way.

Reversible and Irreversible Processes



A reversible process the system undergoing the process can be returned to its initial conditions along the same path on a PV diagram, and every point along this path is an equilibrium state.

- □ An **irreversible process** does not meet these requirements.
 - □All natural processes are known to be irreversible.
 - Reversible processes are an idealization, but some real processes are good approximations.
- A real process that is a good approximation of a reversible one will occur very slowly.
 The system is always very nearly in an equilibrium state.
- □ A general characteristic of a reversible process is that there are **no dissipative** effects (friction or turbulence) that convert mechanical energy to internal energy present.

REVERSIBLE PROCESS VERSUS IRREVERSIBLE PROCESS

A reversible process is a process that can be reversed in order to obtain the initial state of a system

Can be reversed

Infinite changes occur in the system

There is an equilibrium between the initial state and the final state of the system An irreversible process is a thermodynamic process that cannot be reversed in order to obtain the initial state of a system

Cannot be reversed

Finite changes occur in the system

There is no equilibrium in the system

Visit www.pediaa.com

Second Law of Thermodynamics

- No heat engine operating in a cycle can absorb energy from a reservoir and use it entirely for the performance of an equal amount of work
 - Kelvin Planck statement
 - Means that Q_c cannot equal 0
 - Some Q_c must be expelled to the environment
 - -Means that e must be less than 100%

The Second Law The second law comes in many equivalent forms

□ It is impossible to build a cyclic machine* that converts heat into work with 100% efficiency \rightarrow Kelvin's statement of the second law.

Another way of viewing the same:

it is impossible to construct a cyclic machine** that completely (with 100% efficiency) converts heat, which is energy of *random molecular motion*, to mechanical work, which is *ordered motion*.

The unavailable work is due to the role of Entropy in the process.



* For now we are 'building' 'conceptual machines'!

** These 'engines' which use heat and try to produce work are called heat engines.

Another statement of the second law \rightarrow the Clausius statement

□Heat does not 'flow*' from a colder body to a hotter body, without an concomitant change outside of the two bodies → Clausius's statement of the second law.^(a)

This automatically implies that the spontaneous direction of the 'flow of heat*' is from a hotter body to a colder body.^(b)

The Kelvin's and Clausius's statements of the second law are equivalent. I.e. if we violate Kelvin's statement, then we will automatically violate the Clausius's statement of the second law (and vice-versa).



Entropy

- The zeroth law of thermodynamics involves the concept of temperature.
- The first law of thermodynamics involves the concept of internal energy.
- The second law of thermodynamics involves the concept of entropy.

The idea of entropy comes from a principle of thermodynamics dealing with energy. It usually refers to the idea that everything in the universe eventually moves from order to disorder, and *entropy* is the measurement of that change.





The Concept of Entropy

Consider mixing two gases: this occurs spontaneously, and the gases form a homogeneous mixture.

There is essentially no enthalpy change involved, so why is the process spontaneous?



The driving force is a thermodynamic quantity called entropy, a mathematical concept that is difficult to portray visually

Entropy is a measure of molecular disorder, or molecular randomness.

As a system becomes more disordered, the positions of the molecules becomes less predictable and the entropy increases.

Definition:

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.



The 2nd Law of Thermodynamics

In any spontaneous process there is always an increase in the entropy of the universe.

Order to Disorder

Entropy is a measure of the disorder of a system.

This gives us yet another statement of the second law:

Natural processes tend to move toward a state of greater disorder.

Example: If you put milk and sugar in your coffee and stir it, you wind up with coffee that is uniformly milky and sweet. No amount of stirring will get the milk and sugar to come back out of solution. Entropy increases, energy becomes less available, and the universe becomes more random or more "run down".



"SPONTANEOUS" REACTION

ORGANIZED EFFORT REQUIRING ENERGY INPUT

Microscopic Interpretation of Entropy

• A measure that determines the amount of irregularity in molecular systems.

• When the gas absorbs the amount of heat the gas molecules will It acquires an amount of kinetic energy that makes it move randomly More quickly than before and will collide harder than ever Before

Changes in Entropy for Thermodynamic Systems

Consider any infinitesimal process in which a system changes from one equilibrium state to another. If dQ_r is the amount of energy transferred by heat when the system follows a reversible path between the states, the change in entropy dS is equal to this amount of energy divided by the absolute temperature of the system:

$$dS = \frac{dQ_r}{T} \tag{1}$$

The subscript r on the quantity dQ_r is a reminder that the transferred energy is to be measured along a reversible path even though the system may actually have followed some irreversible path. Notice that Equation does not define entropy but rather the change in entropy. To calculate the change in entropy for a finite process, first recognize that T is generally not constant during the process. Therefore, we must integrate eq(1):

$$\Delta S = \int_{i}^{f} dS = \int_{i}^{f} \frac{dQ_{r}}{T}$$

Entropy and the Second Law

If we consider a system and its surroundings to include the entire Universe, the Universe is always moving toward a higher-probability macrostate, corresponding to the continuous spreading of energy. An alternative way of stating this behavior is as follows:

The entropy of the Universe increases in all real processes.

This statement is yet another wording of the second law of thermodynamics that can be shown to be equivalent to the Kelvin-Planck and Clausius statements.

Changes in Entropy for Thermodynamic Systems

Consider any infinitesimal process in which a system changes from one equilibrium state to another. If dQ_r is the amount of energy transferred by heat when the system follows a reversible path between the states, the change in entropy dS is equal to this amount of energy divided by the absolute temperature of the system:

$$dS = \frac{dQ_r}{T} \tag{1}$$

The subscript r on the quantity dQ_r is a reminder that the transferred energy is to be measured along a reversible path even though the system may actually have followed some irreversible path. Notice that Equation does not define entropy but rather the change in entropy. To calculate the change in entropy for a finite process, first recognize that T is generally not constant during the process. Therefore, we must integrate eq(1):

$$\Delta S = \int_{i}^{f} dS = \int_{i}^{f} \frac{dQ_{r}}{T}$$

Entropy and the Second Law

If we consider a system and its surroundings to include the entire Universe, the Universe is always moving toward a higher-probability macrostate, corresponding to the continuous spreading of energy. An alternative way of stating this behavior is as follows:

The entropy of the Universe increases in all real processes.

This statement is yet another wording of the second law of thermodynamics that can be shown to be equivalent to the Kelvin-Planck and Clausius statements.

Changes in Entropy for reversible and irreversible process



The entropy change in a reversible transformation is equal to zero.

$$\Delta S = \oint \frac{dQ_r}{dT} = 0 \ (reversible \ cycle)$$

The entropy change in an irreversible transformation is not equal to zero.

$$\Delta S = \frac{1}{T} \int_{i}^{f} dQ > 0$$

- If the process is irreversible, then the total entropy of an isolated system always increases
 - In a reversible process, the total entropy of an isolated system remains constant
- The change in entropy of the Universe must be greater than zero for an irreversible process and equal to zero for a reversible process

 If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes.

 $\Delta S \ge 0$

Example 1

A Styrofoam cup holding 125 g of hot water at 100°C cools to room temperature, 20.0°C. What is the change in entropy of the room? Neglect the specific heat of the cup and any change in temperature of the room.

Solution



Summary of 2nd law of Thermodynamics

- Second law of thermodynamics:
 - heat flows spontaneously from a hot object to a cold one, but not the reverse
 - a given amount of heat cannot be changed entirely to work
 - natural processes tend to increase entropy.
- Change in entropy:
- Entropy is a measure of disorder.
- As time goes on, less and less energy is available to do useful work.