Unit 17 Second Law of Thermodynamics

Teaching Periods 10 **Weightage %** 06

The neem tree, like all living systems, increases entropy in its surroundings through various processes, such as:

1. **Transpiration: Releasing water vapors into the air, increasing humidity and entropy.**
2. **Photosynthesis: Absorbing sunlight and converting it into chemical energy, releasing excess energy as heat and increasing entropy.**

These processes illustrate the second law of thermodynamics, where living systems increase entropy in their surroundings while maintaining their own organization and complexity.

In this unit student should be able to:

- State and explain second law of thermodynamics.
- State the working principle of heat engine.
- Describe the concept of reversible and irreversible processes.
- Describe the working of petrol engine and diesel engine.
- Explain the working principle of Carnot's engine
- Explain that the efficiency of a Carnot engine is independent of the nature of the working substance and depends on the temperatures of hot and cold reservoirs. Solve problems to find out the efficiency of heat engine
- Describe that refrigerator is a heat engine operating in reverse as that of an ideal heat engine and find its efficiency
- Solve problems to find out the efficiency of a refrigerator
- Describe that change in entropy is positive when heat is added and negative when heat is removed from the system.
- Explain that increase in entropy means degradation of energy.
- Show that energy is degraded during all natural processes.
- Identify that system tend to become less orderly over time
- Solve problems using the equation of entropy

Introduction:

The first law of thermodynamics is a particular form of the law of conservation of energy. However, there are some limitations regarding the transformation of heat energy into mechanical energy, which are covered by the 2^{nd} law of thermodynamics.

17.1.1 Second law of thermodynamics:

Lord Kelvin and Rudolf Clausius formulated the second law of thermodynamics. It consists of two statements.

Kelvin Statement:

According to this statement ***"It is impossible to construct an engine, operating continuously in a cycle that can take heat from a source and coverts completely into work".***

According to Kelvin statement, an engine when converting heat into mechanical work cannot convert all of it into work. A part of heat must be rejected to a cooler reservoir, the exhaust as shown in figure 17.1(a).

In other words, it is impossible to device an engine that would have an efficiency of 100%, even though the first law of thermodynamics will be satisfied.

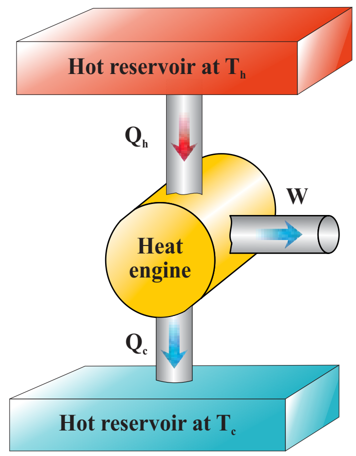


Figure 17.1 (a) the heat engine

Clausius Statement:

It is fact that no one has ever built a refrigerator which will work without a supply of energy. A refrigerator is essentially a machine for conveying heat from one body at a low temperature to another at a high temperature as shown in figure: 17.1(b). According to Clausius statement

"It is impossible to cause heat to flow from a cold body to a hot body without the expenditure of energy".

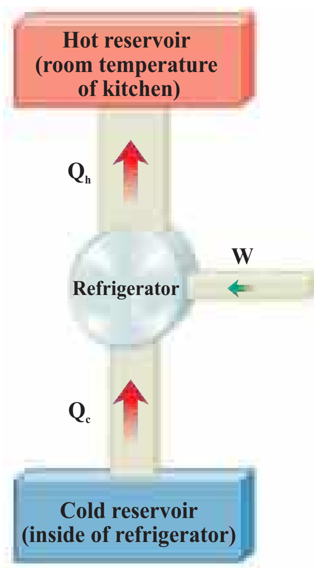


Figure 17.1 (b) the refrigerator

17.2.1 Working principle of heat engines:

Any device that transforms heat into mechanical energy (work) is called heat engine. The essentials of a heat engine are the furnace or hot body, the working substance and a condenser or cold body.

The simplest kind of engine to discuss is one in which the working substance undergoes a cyclic process, that is, a sequence of processes that eventually leaves the substance in the same state in which it started. In a steam turbine the water is recycled and used over and over. Internal combustion engines do not use the same air again but we can still analyze them in terms of cyclic processes that approximate their actual operation.

All the heat engines absorbs heat from a source at a relatively low temperature performs some mechanical work and discards some heat at a low temperature the engine treats extra heat as waste. It gets rid of this waste heat through the exhaust pipes and the cooling system in internal combustion engines.

In a heat engine, Q_1 is positive but Q_2 is negative, representing heat leaving the working substance.

We can represent the energy transformation in a heat engine by the flow diagram fig: 17.2. The engine itself is represented by the circle. The amount of heat suppliedQ_1 to the engine by the hot reservoir is proportional to the cross section of the incoming pipeline at the top of the diagram. The cross section of the outgoing of the pipeline at the bottom is proportional to the magnitude $|Q_2|$of the heat discarded in the exhaust.

The branch line to the right represents the portion of the heat supplied that the engine converts to mechanical work W.

When an engine repeats the same cycle over and over, Q_1 and Q_2 represent the quantities of heat absorbed and rejected by the engine during one cycle. The net heat absorbed per cycle is

$$\Delta Q = Q_1 - Q_2$$

Let Q_1 be the heat absorbed by an engine from a high temperature reservoir and Q_2 be the heat rejected by the engine to low temperature reservoir or sink. The rest of heat energy is converted into useful work i.e.

$$W = Q_1 - Q_2 \ldots \ldots .17.1$$

DO YOU KNOW?

Each Q is positive when heat is transferred from a reservoir into the working substance and Q is negative when the reverse happens

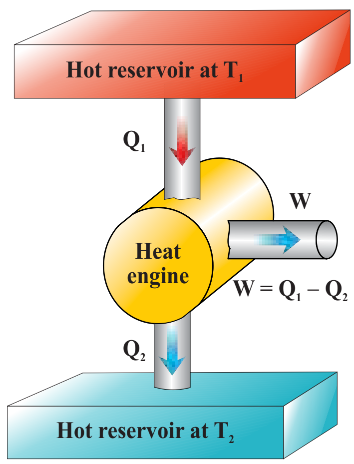


Fig: 17.2 Heat Engine

Efficiency of heat engine:

"***The thermal efficiency "η" of a cycle heat engine is defined to the ratio of the network 'W' done by the engine in each cycle to the heat absorbed Q_1 in each cycle".***

$$Efficiency\ (\eta) = \frac{output}{input} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \ldots \ldots .17.2$$

For 100% efficiency $Q_2 = 0$ i.e. no heat is rejected to low temperature reservoir (sink) and whole heat absorbed is converted into work. But experimental facts show that no cyclic engine can achieve an efficiency of 100%.

17.2.2 Reversible and Irreversible Processes:

To understand the nature of theoretical heat engine, we must first examine the concept of reversible and irreversible process. In a reversible process, the system undergoing the process can be returned to its initial condition along the same path on a PV diagram and every point along this path is an equilibrium state. A process that does not satisfy these requirements is irreversible. All natural processes are known to be irreversible.

Consider an adiabatic process where a gas in a thermally insulated container as shown in fig: 17.3. A membrane separates the gas from a vacuum. When the membrane is burst, the gas expands freely into the vacuum. The system occupies a greater volume after the expansion. No heat energy is transferred to or from the container.

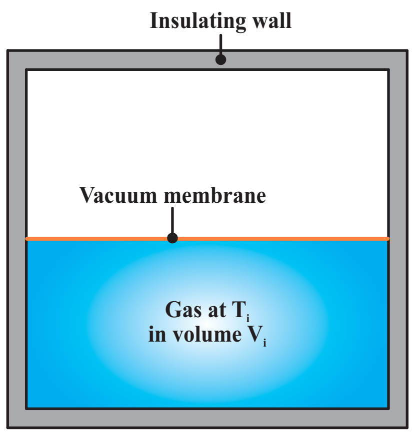


Figure 17.3 Thermally Insulated container

In this adiabatic process, the system undergoes changes without any heat exchange with its surroundings. Here is how the system changes. To make this process reversible, we must return the gas to its original volume and temperature without affecting the surroundings. If we try to reverse the process by compressing the gas back to its original volume using an engine, the surroundings change because external work is done on the system. The temperature increases during compression, which can be lowered by contact with an external energy reservoir. This returns the gas to its original state but affects the surroundings by adding energy. If this energy could drive the compression engine, the net energy transfer to the surroundings would be zero, making the process reversible. However, the Kelvin statement of the second law of thermodynamics specifies that the heat energy removed from the gas cannot be completely converted to mechanical work. Thus, the process is irreversible.

"A reversible process is one which can be retraced in exactly reverse order, without producing any change in the surroundings".

It is in equilibrium at all stages of operation. A succession of events which bring the system back to its initial condition is called a cycle. A reversible cycle is the one in which all the changes are reversible.

"The process which cannot be retraced in the backward direction by reversing the controlling factors is known as irreversible process"

It is in equilibrium only at initial and final stage. All changes which occur suddenly or which involved friction or dissipation of energy through conduction, convection or radiations are irreversible. An example of highly irreversible process is an explosion.

17.2.3 Petrol Engine:

Petrol engine is an internal combustion engine designed to run on volatile fuel such as petrol (gasoline), which has spark-ignition. In these engines air and fuel are generally mixed post-compression.

It works on the Otto cycle and the name comes from the German Engineer Nikolaus Otto (1876), who made the first working prototype. Although different engines may differ in their construction technology but they are based on the principle of Carnot cycle. A typical four stroke petrol engine Fig. (17.4) also undergoes four successive processes in each cycle.

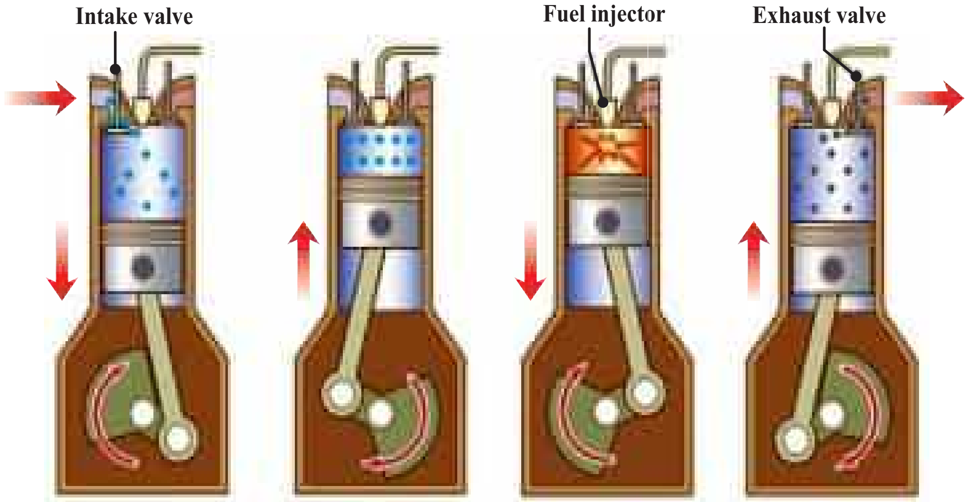


Figure17.4 Petrol Engine

1. The cycle starts on the intake stroke in which piston moves outward and petrol air mixture is drawn through an inlet valve into the cylinder from the carburetor at atmospheric pressure.
2. On the compression stroke, the inlet valve is closed and the mixture is compressed adiabatically by inward movement of the piston.
3. On the power stroke, a spark fires the mixture causing a rapid increase in pressure and temperature. The burning mixture expands adiabatically and forces the piston to move outward. This is the stroke which delivers power to crankshaft to drive the flywheels.
4. On the exhaust stroke, the outlet valves open. The residual gases are expelled and piston moves inward. The cycle then begins again. Most motorbikes have one cylinder engine but cars usually have four cylinders on the same crankshaft. The cylinders are timed to fire turn by turn in succession for a smooth running of the car. The actual efficiency of properly tuned engine is usually not more than 25% to 30% because of friction and other heat losses.

DO YOU KNOW?

No real engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs in accordance with Carnot theorem.

17.2.4 Diesel Engine:

The diesel engine named after Rudolf Diesel (German inventor and Mechanical Engineer), is an internal combustion engine. He patented his original design in 1892. When the fuel comes into contact with high temperature, it ignites, creating energy that drives the piston down transferring energy to the crankshaft. There are two classes of diesel engine: two strokes and four strokes. Most diesel engines generally use the four-stroke cycle.

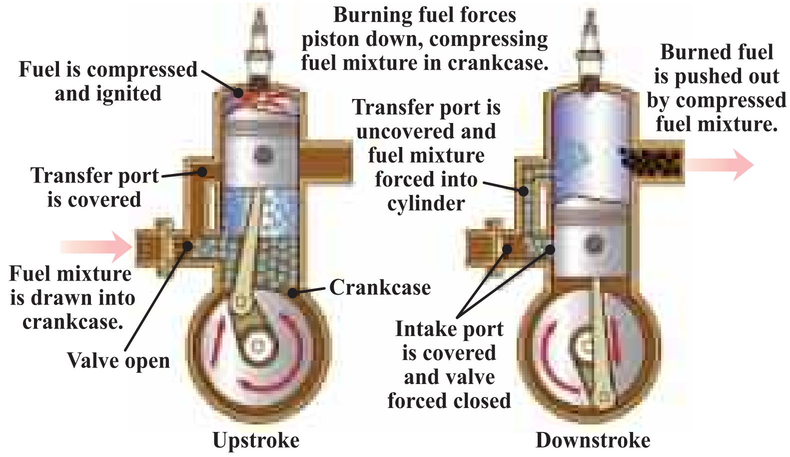


Fig: 17.5 Diesel Engine

No spark plug is needed in the diesel engine (fig: 17.5). Diesel is sprayed into the cylinder at maximum compression. Because air is at very high temperature immediately after compression, the fuel mixture ignites on contact with air in the cylinder and pushes the piston outward. The efficiency of diesel engine is about 35% to 40%.

17.3.1 The Carnot Engine:

A French Engineer named Sadi Carnot in 1824 described an ideal engine, now called a Carnot Engine, which is free from all sort of heat losses and friction. It consists of a hot body of infinite thermal capacity, a similar cold body, a perfect heat insulator and cylinder fitted with a piston enclosing any working substance. The cylinder has a heat conducting base and non-conducting walls and piston. The working substance is taken through the following cycle of operations known as the Carnot cycle. All real engines are less efficient than the Carnot engine because they do not operate through a reversible cycle. A cycle of a heat engine is completed when the properties of a system have returned to the original state. The operating cycle of the Carnot engine is called Carnot cycle. It consists of four processes, two isothermal and two adiabatic.

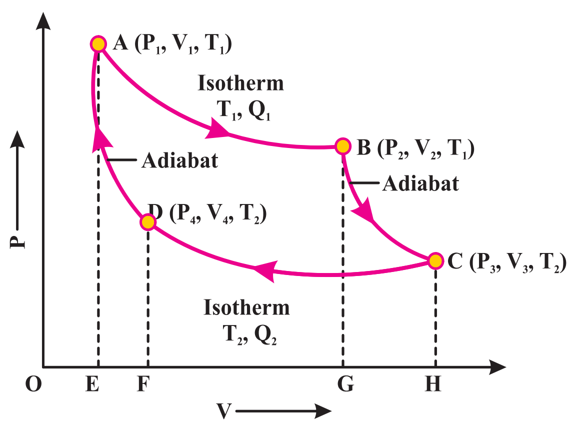


Figure 16.6 Carnot Cycle

1. In process A→B (fig.17.7 a) is isothermal expansion at temperature T_1. The cylinder is placed in thermal contact with an energy reservoir at temperature T_1.During the expansion, we decrease load on piston, the gas absorbs energy Q_1 from the reservoir through the base of the cylinder, volume of gas increases from V_1 to V_2 and does work W_{AB} in raising the piston.
2. In Process B→C (fig: 17.7 b), the base of the cylinder is replaced by a thermally non conducting wall and the gas expands adiabatically due to decrease in load on the piston; that is, no heat energy enters or leaves the system during the expansion, the temperature of the gas decreases from T_1 to T_2, volume increases from V_2 to V_3 and gas does work W_{BC} in raising the piston.
3. In process C→D (fig.17.7 c), the cylinder is placed in thermal contact with an energy reservoir at temperature T_2 is compressed isothermally at temperature T_2 by increasing the load on the piston. The volume decreases from V_3 to V_4. During this time, the gas expels energy Q_2 to the reservoir and the work done by the piston on the gas is $W_{CD.}$
4. In the final process D → A (fig. 17.7 d), the base of the cylinder is replaced by a non-conducting wall and the gas is compressed adiabatically by increasing the load on the piston. The temperature of the gas increases from T_2 to T_1 and volume decreases from V_4 to V_1 and work done by the piston on the gas is W_{DA}.

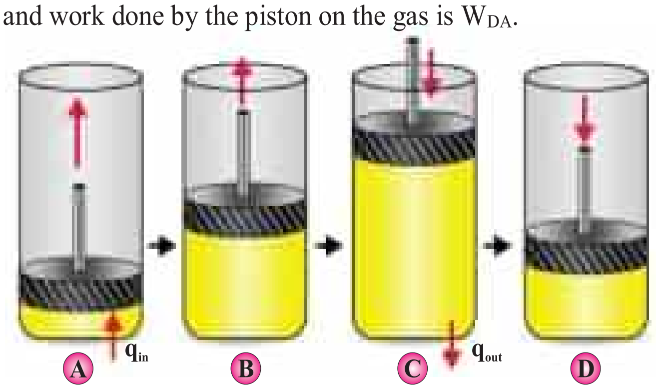


Fig: 17.7 (a,b,c,d) Carnot Engine cycle

If Q_1 is the heat absorbed by the working substance from the body in the isothermal expansion AB and Q_2 is the heat rejected to the cold body during the isothermal compression CD. In this cycle, the system comes back to its initial state and hence, there is no change in its internal energy. W is the external work done by the engine in one cycle; then from the 1st law of thermodynamics.

$$W = Q_1 - Q_2 \ldots\ldots\ldots\ldots\ldots 17.3$$

17.3.2 Efficiency of Carnot Engine:

Thermal efficiency (η) of a heat engine is the ratio of output to input.

$$Efficiency\ (\eta) = \frac{output}{input} = \frac{W}{Q_1} \ldots\ldots\ldots\ldots\ldots 17.4$$

From eq: 17.3, $W = Q_1 - Q_2$ then

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \ldots\ldots\ldots\ldots\ldots 17.5$$

Eq: 17.5 show that the efficiency of the engine increases as the ratio $\frac{Q2}{Q1}$ decreases. It can also be proved that the heat transferred to or from a Carnot engine is directly proportional to the temperature of the hot or cold body.

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \ldots\ldots\ldots\ldots\ldots 17.6$$

Thus, the efficiency of Carnot engine can be written as

$$\eta = 1 - \frac{T_2}{T_1} \ldots\ldots\ldots\ldots\ldots 17.7$$

The efficiency is usually taken in percentage, in that case.

$$\text{Percentage efficiency } (\eta) = \left(1 - \frac{T_2}{T_1}\right) \times 100\%$$

Thus, the efficiency of Carnot engine depends on the temperature of hot and cold reservoirs. The larger the temperature difference of two reservoirs the greater is the efficiency but it can never be one or 100% unless cold reservoir is at absolute zero temperature ($T_2 = 0^0K$)

Such reservoirs are not available and hence the maximum efficiency is always less than one. Nevertheless, the Carnot cycle establishes are upper limits on the efficiency of all heat engines.

No Practical heat engine can be perfectly reversible and also energy dissipation is inevitable. This fact is stated Carnot's theorem.

"No heat engine can be more efficient than a Carnot engine operating between the same two temperatures".

The Carnot's theorem can be extended to state that "all Carnot's engines operating between the same two temperatures have the same efficiency, irrespective of the nature of working substance". All real engines are less efficient than Carnot engine due to friction and other heat losses.

Worked Example 17.1

A Carnot's engine operates between two temperature reservoirs' of 227°C and 27°C, what is maximum efficiency of Carnot's engine?

Solution:

Step 1: Write down the known quantities and quantities to be found.

$T_1 = 227$ °C $\quad T_1 = 227 + 273 = 500K \quad T_2 = 27$ °C $\quad T_2 = 27 + 273 = 300K$

Maximum efficiency = η =?

Step 2: Write down the formula and rearrange if necessary.

$$\eta = 1 - \frac{T_2}{T_1}$$

Step 3: Put the values and calculate

$$\eta = 1 - \frac{300}{500} = 1 - 0.6 = 0.4$$

$$\eta = 0.4 \times 100\%$$

$$\eta = 40\ \%$$

Result: 40 %

17.4.1 Refrigerator:

According to the 2nd law of the thermodynamics heat will always flow spontaneously from hot to cold body, and never the other way around.

A refrigerator causes heat to flow from cold to hot by doing work, which cools the space inside the refrigerator.

In a heat engine, the direction of energy transfer is from the hot reservoir to the cold reservoir, which is the natural direction. The role of heat engine is to process the energy from the hot reservoir so as to do useful work. What we wanted to transfer energy from the cold reservoir to the hot reservoir, because that is not the natural direction of energy transfer. We must put some energy into a device to be successful. Devices that perform this task are called refrigerator.

For example, houses in summer are cooled using refrigerators called air conditioners. The air conditioner transfers energy from the cool room in the home to the warm air outside.

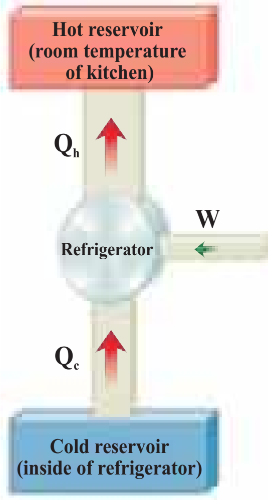


Fig: 17.8
Refrigerator or heat pump

In a refrigerator or heat pump, the engine takes in energy $|Q_C|$ from cold reservoir and expels energy $|Q_h|$ to a hot reservoir as shown in fig: 17.8, which can be accomplished only if work is done on the engine. From the first law of thermodynamics, we know that the energy given up to the hot reservoir must equal to sum of the work done and the energy taken in the form of the work done and the energy taken in the form of the cold reservoir.

$$Q_h = W + Q_c \dots\dots\dots\dots\dots 17.8$$

Therefore, the refrigerator transfers energy from a colder body to a hotter body.

In Practice, a refrigerator includes a circulating fluid that gases through two sets of metal coils that can exchange energy with the surroundings. The fluid is cold and at low pressure when it is in the coils located in a cool environment, where it absorbs energy by heat. The resulting warm fluid is then compressed and enters the other coils as a hot, high-pressure fluid. There it releases its stored energy to the warm surroundings. In an air conditioner, energy is absorbed into the fluid in coils located in a building's interior; after the fluid is compressed, energy leaves the fluid through coil. In a refrigerator, the external coils are behind or underneath the unit Fig: 17.9 the internal coils are in the walls of the refrigerator and absorb energy from the food.

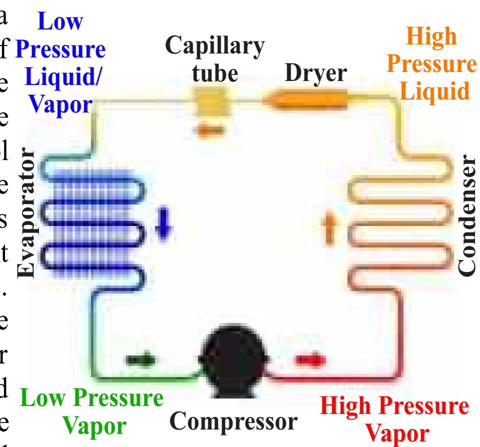


Figure 17.9 Refrigeration cycle

Efficiency of a Refrigerator:

The effectiveness of a refrigerator 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). For a refrigerator operating in the cooling mode, "what you gain" energy is removed from the cold reservoir the most effective refrigeration or air conditioner is one that removes the greatest amount of energy from the cooler reservoir in exchanges for the least amount of work. Therefore, for these devices operating in the cooling mode, we define the COP in terms of $|Q_C|$. The Coefficient of performance of a refrigerator is defined as

"The heat removed from the cold reservoir Q_C (i.e. inside refrigerator) divided by the work done to remove the heat (i.e. the work done by the compressor)".

$$\text{COP of refrigerator} = \frac{heat\ extracted}{work}$$

$$\text{COP} = K = \frac{Q_c}{w}$$

$$\therefore Q_h = Q_c + w$$

$$w = Q_h - Q_c$$

$$COP = K = \frac{Q_c}{Q_h - Q_c} \quad \ldots\ldots\ldots\ldots\ldots 17.9$$

We know that for Carnot cycle $Q_1 \propto T_1$ and $Q_2 \propto T_2$

$$\therefore COP = K = \frac{T_c}{T_h - T_c} \quad \ldots\ldots\ldots\ldots 17.10$$

T_c is the cryogenic temperature at which the heat is removed

T_h is the temperature at which the heat is rejected

It can also be seen from above relations that the coefficient of performance of refrigerator can be larger than 100% unlike the efficiency of heat engine which is always less than 100%. A good refrigerator should have a high COP, typically 5 or 6.

Worked Example 17.2

A certain refrigerator has a COP of 5.00. When the refrigerator is running, its power input is 500 watts. A sample of water of mass 500g and temperature 20.0°C is placed in the freezer component. How long does it take to freeze the water to ice at 0°C? Assume all other parts of refrigerator stay at the same temperature and there is no leakage of energy from the exterior, so the operation of the refrigerator result only is energy being extracted from the water.

Solution:

Step 1: Write down the known quantities and quantities to be found.

COP = K = 5.00,

P = 500 watt

Mass of water = m = 500g = 0.50 kg,

T_1 = 20°C

T_2 = 0°C,

$\Delta T = T_2 - T_1$ = -20°C

Specific heat of water = c = 4186 J/kg.°C

Latent heat of fusion = L_f = 3.36×10^5 J/kg
Time = t =?

Step 2: Write down the formula and rearrange if necessary.

$$|Qc| = mc\Delta T - mL_f = m\,(c\Delta T - L_f)$$

$$= 0.50\ kg\ [(4186 J/kg.°C)(-20°C) - 3.36 \times 10^5\ J/kg]$$

$$= 2.08 \times 10^5 J$$

$$COP = \frac{|Q_c|}{w} \rightarrow w = \frac{|Q_c|}{COP} = \frac{2.08 \times 10^5}{5.00}$$

$$W = 4.17 \times 10^4 J$$

$$P = \frac{w}{t} \rightarrow t = \frac{w}{P} = \frac{4.17 \times 10^4 J}{500w} = 83.4\ sec$$

Result: In reality the time interval for the water to freeze in a refrigerator is much longer than 83.4 s, which suggests that the assumptions of our model not valid. Only a small part of the energy extracted from the refrigerator interior in a given time interval comes from the water. Energy must also be extracted from the container in which the water is placed, and energy that continuously leak into the interior from the exterior must be extracted.

Worked Example 17.3

What is the coefficient of performance (COP) of a refrigerator that operates with Carnot efficiency between temperatures -3.00°C and +27.0°C?

Solution:

Step 1: Write down the known quantities and quantities to be found.

Tc = -3.00°C = 270K
Th = 27.0°C = 300K
COP = K =?

Step 2: Write down the formula and rearrange if necessary.

$$COP = K = \frac{Tc}{Th - Tc}$$

$$COP = K = \frac{270}{300-270} = \frac{270}{30} = 9$$

Result: The coefficient of performance of a refrigerator is 9.

Self-Assessment Questions:

1. An inventor claims that he has construct an engine which give efficiency of 56%. When working between -10 and 900, check whether his claim is true or false.
2. Why is the coefficient of performance (COP) used instead of efficiency in refrigerators?

17.5.1 Entropy:

Entropy was first expressed by German physicist and mathematician, Rudolf Clausius in 1865 into the study of thermodynamics to give a quantitative basis for the 2nd law of thermodynamics. The disorderness of the system is known as entropy. Entropy is also defined as

"The measure of a system's thermal energy per unit temperature that is unavailable for doing useful work".

We have discussed several processes that proceed naturally in the direction of increasing disorder. Irreversible heat flow increases disorder because the molecules are initially sorted into hotter and cooler regions; this sorting is lost when the system comes to thermal equilibrium. Adding heat to a body increases its disorder because it increases average molecular speed and therefore the randomness of molecular motion. Free expansion of a gas increases its disorder because the molecules have more randomness of position after the expansion than before.

Entropy provides a quantitative measure of disorder. T_0 introduce the concept, let's consider an isothermal expansion of an ideal gas; we add heat Q and let the gas expand just enough that the temperature remains constant. Because the internal energy of an ideal gas depends only on its temperature, the internal energy is also constant, so from the first law of thermodynamics the work w done by the gas during this expansion is equal to the heat Q added to it. That is

$$\Delta Q = \Delta W = P.\Delta V$$

The gas is in a more disordered state after the expansion than before, because the molecules are moving in a large volume and have more randomness of position. Thus ΔV is a measure of the increase in disorder of the molecules, and we see that it is proportional to the quantity$\frac{\Delta Q}{T}$. We introduce the symbol S, called the entropy of the system, and we define the entropychange ΔS during a reversible isothermal process as

$$\Delta S = \frac{\Delta Q}{T} \ldots\ldots\ldots\ldots\ldots 17.11$$

Change in entropy is positive when heat is added and negative when heat is removed from the system. Suppose an amount of heat Q flows from a reservoir at temperature T_1through a conducting rod to a reservoir at temperature when $T_1 > T_2$. The change in entropy of the reservoir at temperature T_1, which loses heat, decreases by $\frac{Q}{T_1}$, and of the reservoir at temperature T_2 which gains heat increases by$\frac{Q}{T_2}$. As $T_1 > T_2$ so $\frac{Q}{T_2}$ will be greater than$\frac{Q}{T_1}$. i.e.$\frac{Q}{T_2} > \frac{Q}{T_1}$. Hence, net change in entropy = $\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1}$ is positive. It follows that in all natural processes where heat flows from one system to another; there is always a net increase in entropy. This is another statement of 2^{nd} law of thermodynamics.

"The entropy of the universe during any process either remains constant or increases"

Similarly, we can prove that in every natural process the entropy always increases provided we considered the whole system. It seems to be a law of nature that a natural process always takes place in such a direction as to cause an increase in the entropy of the system and its surroundings. It is known as the law of increase of entropy.

The S.I unit of entropy is JK^{-1}. If heat is removed from a system, the change in entropy is written as negative.

17.5.2 Increase in Entropy Means Degradation of Energy:

Suppose a quantity of heat Q in a reservoir at temperature T_1. Let the temperature of the coldest available reservoir be T_o. A Carnot engine working between the temperatures T_1 and T_o can absorb heat Q at temperature T_1 and do useful work W_1 given by:

$$W_1 = Q - Q_o$$

The efficiency of Carnot engine is

$$\eta = \frac{W_1}{Q} = 1 - \frac{T_o}{T_1}$$

$$W_1 = Q\,(1 - \frac{T_o}{T_1}) \ldots\ldots\ldots 17.12$$

Equation (17.12) gives maximum available energy which can be converted into useful work, when heat Q is stored in the reservoir at temperature T_1.

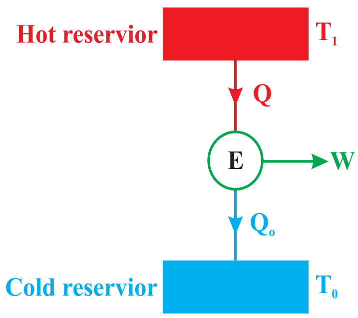


Figure:17.10 (a) Entropy

Consider an irreversible process, in which heat Q flows from the reservoir at temperature T_1. to another reservoir at a lower temperature T_2. A Carnot engine working between the temperatures T_2. and To can now take heat Q from the reservoir at temperature T_2. and do useful work W_2given by:

$$Efficiency = \eta = \frac{W_2}{Q} = 1 - \frac{T_o}{T_2}$$

$$W_2 = Q\,(1 - \frac{T_o}{T_2}) \ldots\ldots 17.13$$

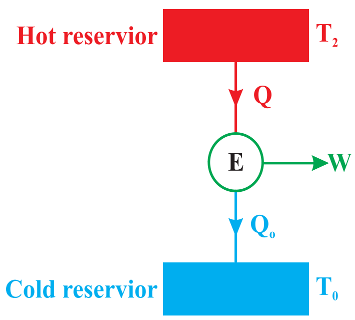


Figure:17.10 (b) Entropy

Equation (17.13) gives the maximum available energy which can be converted into useful work. When heat Q is stored in the reservoir at lower temperature T_2. As $T_2 < T_1$, we see from equation (17.12) and (17.13) that W_2 is less than W_1, i.e. available energy decreases with the increase of entropy during an irreversible process. Since all natural processes are irreversible, we conclude that the energy of the universe is continuously becoming unavailable for useful work. This is called the degradation of energy. From the equation (17.12) and (17.13), we get

$$W_1 - W_2 = Q\,(\frac{T_o}{T_2} - \frac{T_o}{T_1})$$

$$W_1 - W_2 = \left(\frac{Q}{T_2} - \frac{Q}{T_1}\right) T_o \quad \ldots\ldots 17.14$$

Now $\frac{Q}{T_1}$ = decrease in entropy of the reservoir at temperature T_1 and $\frac{Q}{T_2}$ = increase in entropy of the reservoir at temperature T_2.

Thus $(\frac{Q}{T_2} - \frac{Q}{T_1})$ is increase in entropy of the universe. Also $(W_1 - W_2)$ is the amount of energy which has been degraded or made available for useful work. Hence equation (17.14) shows that the increase of unavailable energy is equal to the increase in entropy of the universe multiplied by the temperature of the coldest available reservoir. Using eq: (17.14) an entropy increases, so unavailable energy also increases, so the useful energy decreases. It is called degradation of energy.

17.5.3 Energy is Degraded During All-Natural Processes:

It is believed that the temperature of the universe is increasing gradually and its entropy is also increasing. The mode of increase of entropy indicates that after a very long time, the entropy of the universe will be maximum and all the objects will be at the same temperature. At that time, no useful energy will be available and life will cease to exist, which is known as the "Heat Death" of the universe, which may not occur in near future.

It seems to be a law of nature that all natural processes always take place in such a direction so as to cause an increase in the entropy of a system and its surroundings.

Thus the 2nd law of thermodynamics is also expressed as the "Law of increase of entropy".

It states that, ***"when all the systems taking part in a process are included, the entropy either remains constant or increases".***

Symbolically, $\Delta S \geq 0$

The 2nd law of thermodynamics reveals that all the natural processes proceed towards a state of greater entropy, i.e. greater disorder or greater unavailability.

In all natural processes, energy always tends to pass from a more available (useful) form to a less available (degradation) form unavailability is a measure of entropy. A reversible process does not change total entropy of the universe. Thus $\Delta S = 0$; any irreversible process increases the total entropy of the universe $\Delta S > 0$, Total entropy change in one cycle of any Carnot engine is zero. All natural processes are irreversible and therefore, during all-natural process's energy is degraded.

17.5.3 Systems Tends to Become Less Orderly Over Time:

The disorder of the system increases during any natural process, a stage will reach when universe will approach a stage of maximum disorder. At this stage, matter will become a uniform mixture i.e. whole universe will be at uniform temperature. No work can then be done and heat flow will cease.

Time arrow concept of entropy tells us in which direction the time is going. It is the change in entropy that ultimately provides us with the answer to why systems will naturally evolve in one direction with time and not the other. Systems always evolve in time in such a way that the total entropy of system plus environment increases. If you observe a system in which the entropy appears to decrease, you can be sure that somewhere there is change in the entropy of the environment large enough to make the total entropy change positive. Entropy has been called a time arrow: i.e. events occur in the direction of increasing disorder with time.

In all the processes going on in practical life, the entropy always increases with time and disorder is produced more and more. Hence this increase of entropy is identification for the time passage.

Worked Example 17.4

What is the change in entropy of 30gm of water at 0°C as it is changed into ice at 0°C? Take latent heat of fusion of ice 336000 J kg^{-1}.

Solution:

Step 1: Write down the known quantities and quantities to be found.

Change in entropy = ΔS =?

Mass of water = m =30gm = 0.03kg

T = 0°C = 0 + 273 = 273K

Specific latent heat of fusion of ice = H_f = 336000J kg^{-1}

Step 2: Write down the formula and rearrange if necessary.

$\Delta S = \frac{\Delta Q}{T}$

∴ Heat required freezing 30gm of water at 0°C to ice at 0°C.

$\Delta Q = mH_f = 0.03 \times 336000 = 10800J$

Put the values and calculate

$\Delta S = \frac{10080\ J}{273\ K} = 36.92\ Jk^{-1}$

Result: The change in entropy comes out 36.92 Jk^{-1}.

Worked Example 17.5

Calculate change in entropy when 10kg of water is heated from 90°C to 100°C. Specific heat of water = 4180J.$kg^{-1}K^{-1}$.

Solution:

Step 1: Write down the known quantities and quantities to be found.

Change in entropy = ΔS =?

Mass of water = m =10kg

T_1 = 90°C

T_2 = 100°C

ΔT = 100 – 90 = 10°C

Average temperature = $T = \frac{T_1+T_2}{2} = \frac{90+100}{2}$ =95°C

T = 95°C + 273 = 368K

Step 2: Write down the formula and rearrange if necessary.

$\Delta S = \frac{\Delta Q}{T} = \frac{mc\Delta T}{T}$

Put the values and calculate

$\Delta S = \frac{10 \times 4180 \times 10}{368} = 1135.87\ Jk^{-1}$

Result: The change in entropy comes out 1135.87 Jk^{-1}

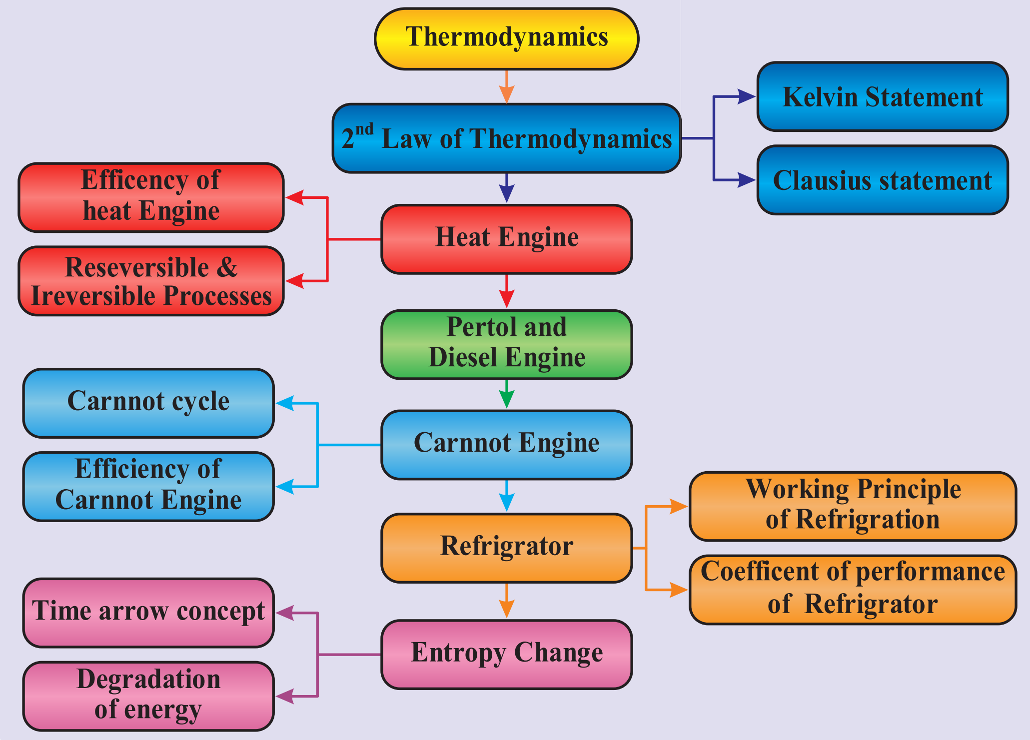
SUMMARY

- ✓ Second law of thermodynamics can be states as:
  - ➢ There is no perpetual motion machine that can convert the given amount of heat completely into work.
  - ➢ The total entropy of any system plus that of its environment increases as a result of any natural process.
- ✓ A heat engine is a device which converts a part of thermal energy into useful work.
- ✓ Reversible Process: A process in which system and its surroundings can be returned to their initial conditions.
- ✓ Irreversible Process: A process which cannot be retraced in the backward direction by reversing the controlling factors.
- ✓ Efficiency of Carnot Engine is the ratio of output to input temperature and is $1 - \frac{T_2}{T_1}$
- ✓ Refrigerator is a heat engine operating in reverse as that of an ideal engine.
- ✓ Coefficient of performance of refrigerator (COP) is equal to the ratio of the heat taken from the cold reservoir to the work done by the refrigerator.

$$COP = \frac{T_c}{T_h - T_c}$$

- ✓ T_c is the cryogenic temperature at which the heat is removed and T_h is the temperature at which the heat is rejected.
- ✓ Entropy:
  - ➢ It is a measure of disorder (microscopic randomness) of a system.
  - ➢ It is a measure of unavailable energy of a system.
  - ➢ In terms of 2nd law of thermodynamics, "Every process in nature takes place such that the entropy of an isolated system either remains unchanged or it increases". $\Delta S \geq 0$.
- ✓ Entropy change ΔS due to heat transfer at absolute temperature T is given by $\Delta S = \pm \frac{\Delta Q}{T}$
- ✓ The S.I units of entropy are $J.K^{-1}$

CONCEPT MAP



EXERCISE

Section (A): **Multiple Choice Questions (MCQs)**
Choose the correct answer:

1. A frictionless heat engine can be 100% efficient only if its exhaust temperature is:
   (a) 0°C (b) Equal to its input temperature
   (c) 0 K (d) half of its input temperature
2. A refrigerator, with its door open. The temperature of the room will
   (a) Rise (b) Fall
   (c) Remains the same (d) Rise or fall depending on the area of the room
3. Which device is not used in a diesel engine
   (a) Outlet Valve (b) Piston
   (c) Sparking Plug (d) Injector

4. Which one of the following processes is irreversible?
   (a) Slow compression of an elastic spring
   (b) Slow evaporation of a substance in an isolated vessel
   (c) Slow compression of a gas
   (d) A chemical explosion
5. According to 2nd law of thermodynamics, 100% conversion of heat into mechanical work is:
   (a) Possible (b) Possible, if the conditions are ideal
   (c) Not possible (d) Possible, if the process is adiabatic
6. The change in entropy is given by
   (a) $\Delta S = \frac{\Delta Q}{T}$ (b) $\Delta S = \Delta Q.\,T$ (c) $\Delta S = \frac{\Delta U}{T}$ (d) $\Delta S = \frac{\Delta W}{T}$
7. The net change in entropy as a system in a natural process is
   (a) Positive (b) Negative (c) Zero (d) Infinite
8. The efficiency of diesel engine is
   (a) Greater than petrol engine (b) Less than petrol engine
   (c) Equal to petrol engine (d) both have efficiency 1
9. Second law of thermodynamics states that:
   (a) Energy can't be converted. (b) Entropy decreases over time.
   (c) Heat flows from cold to hot. (d) Entropy increases over time
10. The process violates the 2nd law of thermodynamics is:
   (a) Refrigerator cooling. (b) Heat engine working.
   (c) Gases mixing. (d) Heat flowing from cold to hot.

Section (B): CRQs (Short Answered Questions):

1. What are some factors that affect the efficiency of automobile engines?
2. What happens to the temperature of a room in which an air conditioner is left running on table in the middle of the room?
3. Under what conditions can heat be added to a system without changing its temperature?
4. Is it possible to cool a room by keeping the refrigerator door open?
5. When does the entropy of a system decrease?
6. Is it possible, according to the 2nd law of thermodynamics to construct an engine that is free from thermal pollution?
7. Can heat be completely converted to work?
8. Define that why entropy has often been called as "time arrow".

Section (C): ERQs (Long Answered Questions):

1. Give the two statements of the second law of the thermodynamics. Elaborate the concept of entropy and state the second law of thermodynamics in terms of this concept.
2. Explain the working principle of heat engine and also derive the formula for its efficiency.
3. Describe the concept of reversible and irreversible process.
4. What is Carnot engine? Give the operation of Carnot cycle and show that the efficiency of even this engine is less than 100%.

5. Describe that refrigerator is a heat engine operating in reverse as that of an ideal heat engine and find its efficiency.
6. Explain that change in entropy is positive when heat is added and negative when heat is removed from the system.
7. Explain that increase in entropy means degradation of energy.

Section (D): **Numerical:**

1. A Carnot engine takes 2000J of heat from a reservoir at 500K does some work, and discards some heat to a reservoir at 350K. How much heat is discarded, how much work does the engine do, and what is the efficiency? **(Ans: 1400J, 600J, 30%)**
2. One kilogram of ice at 0°C is melted and converted to water at 0°C. Compute its change in entropy. **(Ans: 1220 J.K^{-1})**
3. In a high-pressure steam turbine engine, the steam is heated to 600°C and exhausted at about 90°C. What is the highest possible efficiency of any engine that operates between these two temperatures? **(Ans: 58.4 %)**
4. Temperature difference between the surface water and bottom water in Manchester Lake might be 5°C.Assuming the surface water to be at 20°C. What highest efficiency a steam engine could have if it operates between these two temperatures? **(Ans: 1.71%)**
5. A heat engine works at the rate of 500kW. The efficiency of the engine is 30%. Calculate the loss of heat per hour. **(Ans: 4.2 x 10^9J)**
6. A heat engine performs work of 0.4166 watts in one hour and rejects 4500J of heat to the sink. What is the efficiency of engine? **(Ans: 24.9%)**
7. A Carnot engine operates between the temperatures 850K and 300K. the engine performs 1200J of work in each cycle, which takes 0.25 sec
   (a) What is the efficiency of this engine?
   (b) What is the average power of this engine?
   (c) How much energy is extracted as heat from the high temperature reservoir?
   (d) How much energy is delivered as heat to the low temperature reservoir?
   [Ans (a) 65% (b) 4.8KW (c) 1855J (d) 655J]
8. A Carnot engine absorbs 52kJ as heat and exhaust 36kJ as heat in each cycle. Calculate:
   (a) The engine efficiency
   (b) The work done per cycle in kilojoules. **[Ans (a) 30.76% (b) 16KJ]**