

LAW OF CONSERVATION OF ENERGY

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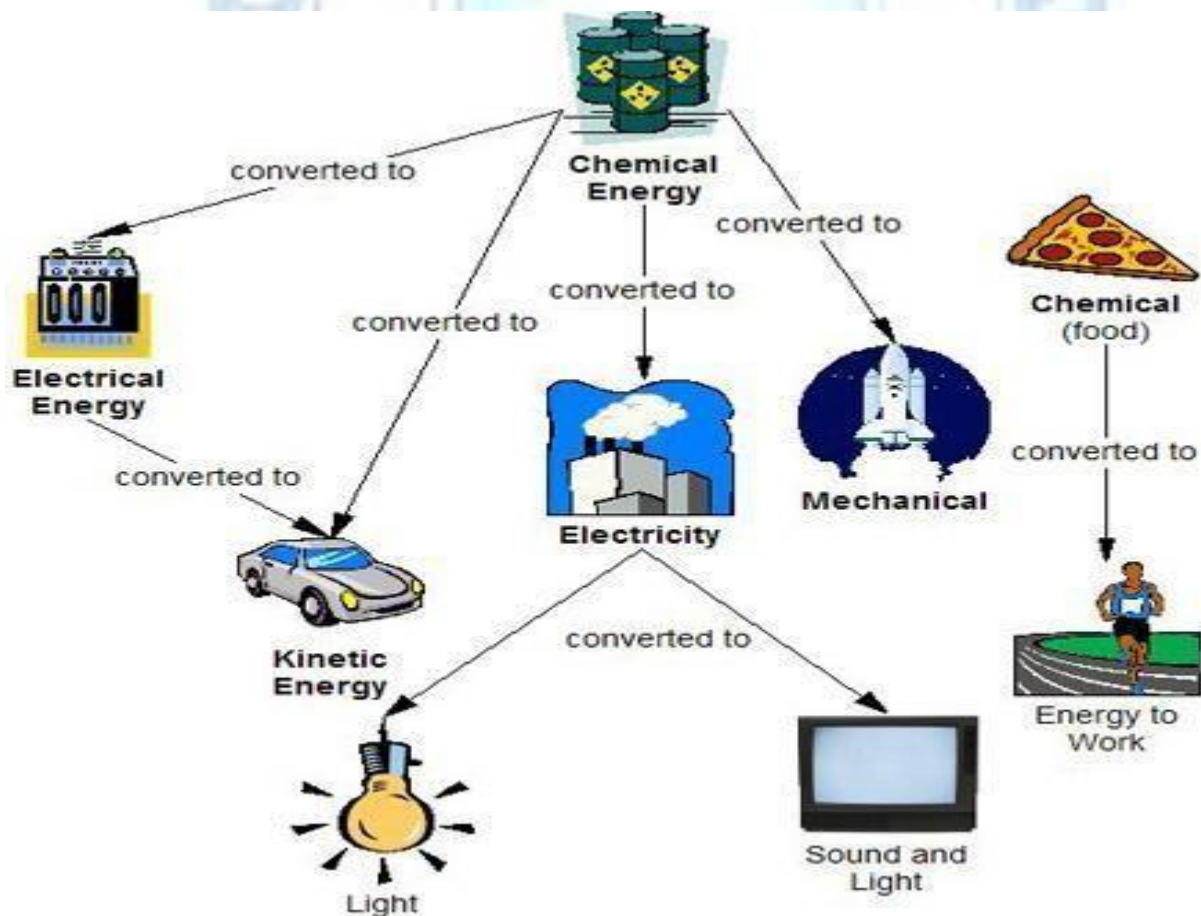
3.4.9-THIRD LAW OF THERMODYNAMICS



LAW OF CONSERVATION OF ENERGY

The law of conservation of energy states that energy can neither be created nor destroyed - only converted from one form of energy to another. This means that a system always has the same amount of energy, unless it's added from the outside. Some examples of conservation of energy are as follow:

1. Conversion of electrical energy into heat energy by flowing of current through a



resistance.

2. Conservation of water energy into heat energy during power generation in a hydroelectric power plant.

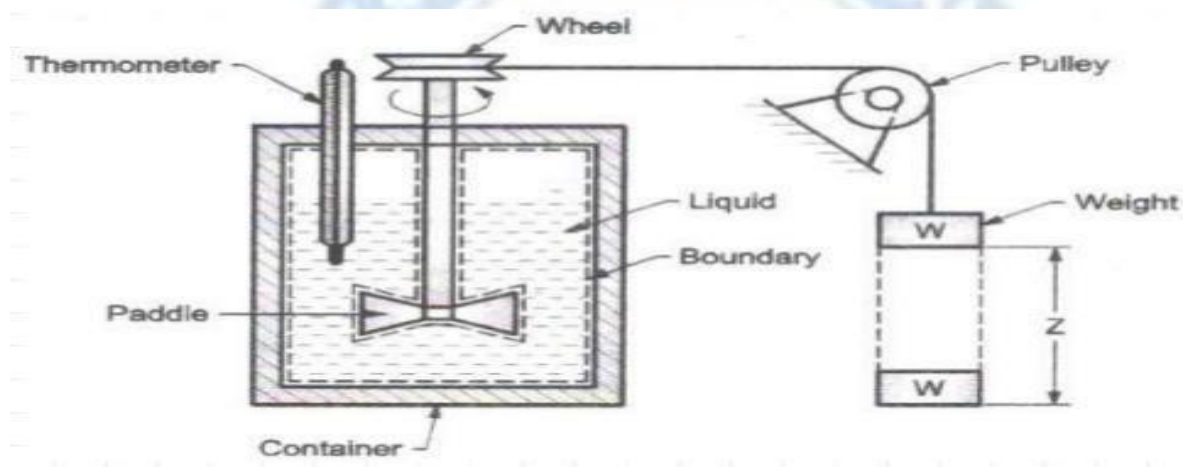
3.4.7-FIRST LAW OF THERMODYNAMICS (JOULE'S EXPERIMENT)

It is special case of law of conservation of energy and may be explained as follow for the following systems:

First law for a closed system undergoing a cycle

Let us consider a closed system which consist of a known mass of water, (m) contained in an adiabatic vessel having a thermometer and a paddle wheel as shown in fig.

Fig. 4.1 Joule experiment apparatus



Let a certain amount of work (W_{1-2}) be done upon the system by the paddle wheel. The quantity of work can be measured by the fall of weight which drives the paddle wheel through a pulley. The system initially was at temperature (T_1), the same as that of the atmosphere and after the work transfer let the temperature rise to (T_2). The process 1-2 undergone by the system is shown in the figure 8, in generalized thermodynamic coordinates X, Y.

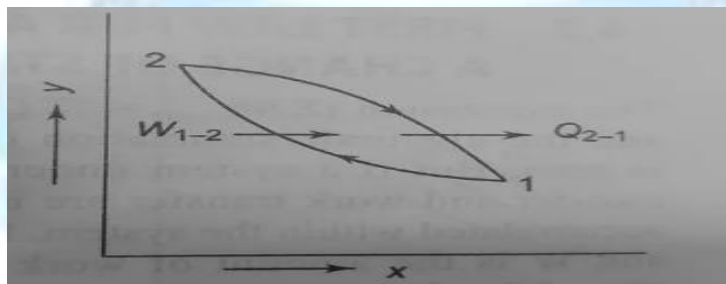


Fig. 4.2 Cyclic process

The system and the surrounding interact by heat transfer till the system returns to the original temperature (T_1), attaining the condition of thermal equilibrium with the atmosphere. The amount of heat transfer (Q_{2-1}) from the system during the process (2-1) shown in the figure

above, can be estimated from,

$$Q_{2-1} = mC_p (T_2 - T_1)$$

The systems thus execute a cycle, which consist of a definite amount of work input (W_{1-2}) to the system followed by the transfer of an amount of heat (Q_{2-1}) from the system.

The work (W_{1-2}) is always proportional to the heat (Q_{2-1}) and constant of proportionality is

$$(\sum W)_{\text{cycle}} = J (\sum Q)_{\text{cycle}}$$

called the Joule's equivalent or mechanical equivalent of heat. If the cycle involves many more heat and work quantities, the same result will be found,

$$\oint dW = J \oint dQ$$

Where,

J = Joule's equivalent.

\oint = Denotes the cyclic integral for the closed path.

This is the first law for a closed system undergoing a cycle. It is accepted as a general law of nature, since no violation of it has ever been demonstrated. In this, the algebraic summation of all energy transfer i.e. heat energy transfer and work energy transfer across the system boundaries will be zero.

3.4.8-STATEMENT OF SECOND LAW OF THERMODYNAMICS

The Second Law of Thermodynamics states that the state of entropy of the entire universe, as an isolated system, will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative. However, 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. The second law is also known as the law of degradation of energy.

There are two statements on the second law of thermodynamics which are;

1. Kelvin- Planck statement
2. Clausius statement

(A) Kelvin – Planck statement

It is impossible for any device that operates on a cycle, to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine converts or can convert whole of the heat energy into mechanical work and there will always be a heat rejection.

Let us assume that heat energy (Q_1) at temperature T_1 is supplied to heat engine from source and heat energy (Q_2) at temperature T_2 is rejected to the sink. Then remaining or net energy ($Q_1 - Q_2$) will be converted into mechanical work (W_{net}). The ratio of maximum mechanical work obtained to the total heat supplied to the engine is known as thermal efficiency of heat engine.

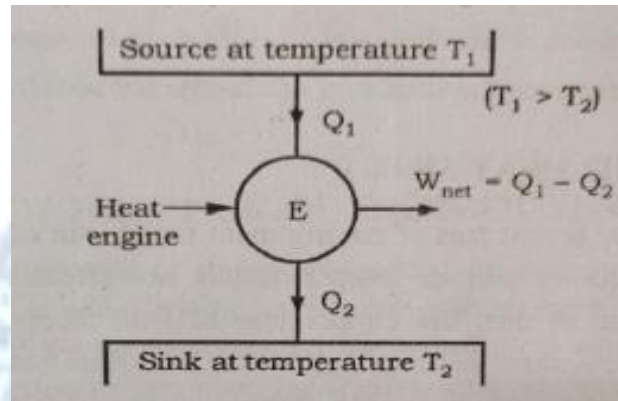


Fig. 4.10 Heat engine

$$\eta_{\text{th}} = \frac{W_{\text{net}}}{\text{Total heat supplied}} = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta_{\text{th}} = 1 - \frac{Q_2}{Q_1}$$

If $Q_2 = 0$ (i.e., $W_{\text{net}} = Q_1$, or efficiency = 1), the heat engine produces work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement of second law is known as perpetual motion machine of second kind (PMM-II).

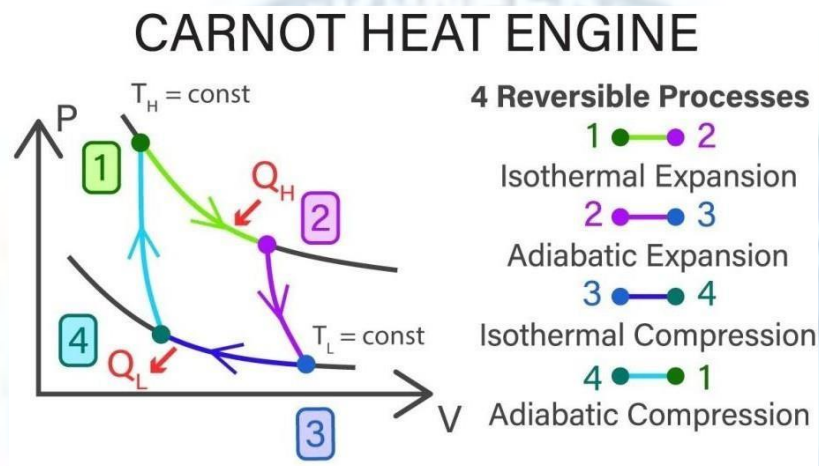
(B) Clausius statement

It is impossible to construct a device operating in a cycle that can transfer heat from a colder body to warmer without consuming any work. Therefore, heat cannot flow is itself from a body at a higher temperature. The applications of this law are found in a heat pump and refrigerator.

CARNOT ENGINE

Carnot engine is a theoretical thermodynamic cycle proposed by Leonard Carnot. It gives the

estimate of the maximum possible efficiency that a heat engine during the conversion process of heat into work and conversely, working between two reservoirs, can possess. It is an idealized engine whose working is perfectly reversible. This engine uses an ideal gas as the working substance and performs a 4-stroke process to complete one cycle. The reversible cycles cannot be achieved in practice because of irreversibility's associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles.



Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:

- 1. Reversible isothermal expansion (1-2):** The cylinder containing ideal gas is working substance allowed to expands slowly at this constant temperature (T_H).
- 2. Reversible adiabatic expansion (2-3):** The cylinder-piston is now insulated (adiabatic) and gas continues to expand reversibly (slowly). So, the gas is doing work on the surroundings, and as a result of expansion the gas temperature reduces from T_H to T_L .
- 3. Reversible isothermal compression (3-4):** The gas is allowed to exchange heat with a sink at temperature T_L as the gas is being slowly compressed. So, the surroundings are doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at T_L .
- 4. Reversible adiabatic compression (4-1):** The gas temperature is increasing from T_L to T_H as a result of compression.

$$\eta_{\max} = \eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$$

3.4.9-THIRD LAW OF THERMODYNAMICS

This law states, 'At absolute zero temperature, the entropy of system is zero'. Zero entropy means the absence of all molecular, atomic, nuclear and electronic disorders. It has two important consequences, it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.

CONCEPT OF IRREVERSIBILITY

A process is said to be reversible if both the system and the surroundings can be restored to their respective initial states, by reversing the direction of the process. A reversible process is a process that can be reversed without leaving a trace on the surroundings. Processes that are not reversible are called Irreversible processes.

Irreversibilities

The factors that cause a process to be irreversible are called irreversibilities.

1. Friction
2. Unrestrained expansion
3. Mixing of two gases
4. Heat transfer across a finite temperature difference
5. Spontaneous chemical reactions
6. Expansion or Compression with finite pressure difference
7. Mixing of matter at different states

CONCEPT OF ENTROPY

The term entropy means transformation. It is a function of quantity of heat which shows the possibility of conversion of that heat into work. As a matter of fact, it is difficult to define entropy. But change of entropy of a substance can be easily defined. In a reversible process,

over a range of temperature, the increase or decrease of entropy when multiplied by the absolute temperature gives the heat absorbed or rejected by the working substance. Mathematically,

$$\delta Q = T dS$$

Where, T = Absolute temperature, dS = Change in entropy

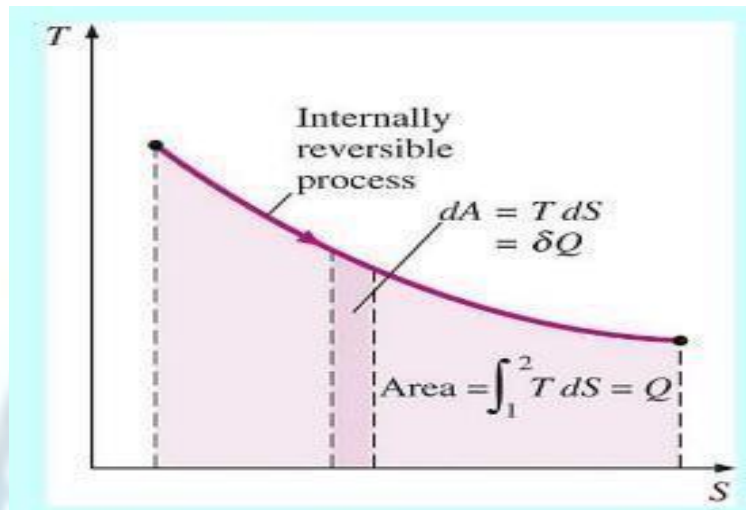


Fig. 4.13 T-S diagram

The relation between heat and entropy is given by Clausius. To prove this, let us consider the heating of a working substance by reversible process. Entropy is represented on the abscissa and absolute temperature on the ordinate. This diagram is known as temperature – entropy diagram.

$$dS = \frac{\delta Q}{T}$$

Importance of entropy: The change in entropy represents the maximum amount of work done per degree drop in temperature. In other words, change in entropy may be regarded as the rate of availability or unavailability of heat for transformation into work.