2.30 EQUALITY OF TEMPERATURE

Consider two bodies of the same or different materials, one hot and the other cold. When these bodies are brought into contact, the hot body becomes colder, and the cold body becomes warmer. If these bodies remain in contact for some time, a state reaches when there is no further observable change in the properties of the two bodies. This is a state of thermal equilibrium, and at this stage the two bodies have the equal temperature. It thus follows that when two bodies are in thermal equilibrium with each other, their temperatures are equal. This is called equality of temperature. This forms the basis of concept of temperature.

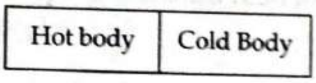


Fig. 17 Equality of temperature

2.3[illegible] ZEROTH LAW OF THERMODYNAMICS

The zeroth law of thermodynamics states that if two bodies are each in thermal equilibrium with a third body, seperately, then they are also in thermal equilibrium with each other. This is the Principle of temperature measurement.

The zeroth law is illustrated in Fig. 18. by block diagram and its utility for temperature measurement shown in Fig. 19 by block diagram.

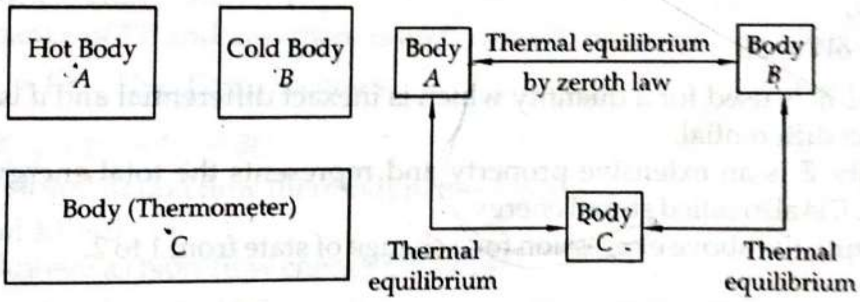


Fig. 18 Concept of Zeroth Law

Let us consider two bodies *A* (Hot) and (*B*) cold are brought in contact with each other. The heat energy will be transferred from body *A* to the body *B*. After some time when there is no further transfer of heat between them, then these bodies are said to be in thermal equilibrium with each other.

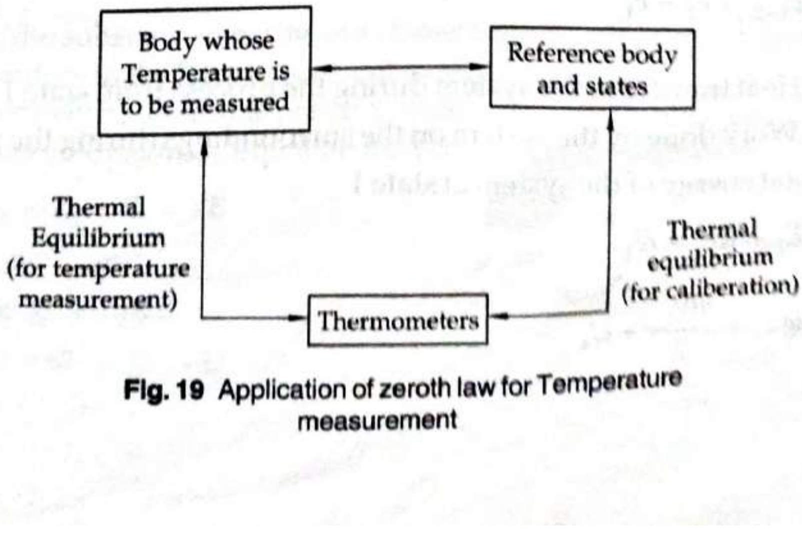


Fig. 19 Application of zeroth law for Temperature measurement

1.17. FIRST LAW OF THERMODYNAMICS

It is a special case of the law of conservation of energy and stipulates that :

- Energy can neither be created nor destroyed; it is always conserved.However, it can change from one kind into another.
- Total energy of an isolated system, in all its forms remains constant.
- All the energy that goes into a system comes out in some other form. Energy does not vanish and has the ability to be converted into any other form of energy.
- No machine can produce energy without corresponding expenditure of energy. Energy cannot appear from nothing, nor can it convert into nothing.

1.20. HEAT ENGINE, REFRIGERATOR AND HEAT PUMP

A thermal (heat) reservoir is that part of environment which can exchange heat energy with a system. It has sufficiently large heat capacity and its temperature is not affected by the quantity of heat transferred to or from it. A thermal reservoir is thus characterised by its temperature which remains constant. The changes that do take place in the thermal reservoir as heat enters or leaves are so slow and so small that processes within it are quasi-static. The reservoir which is at high temperature and supplies heat is known as ***heat source***. Examples are a boiler furnace, a combustion chamber and a nuclear reactor etc. The reservoir which is at low temperature and to which heat is transferred is called the ***heat sink***. Atmospheric air, ocean and river etc. constitute the heat sink.

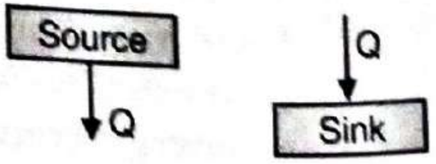


Fig. 1.24. Heat source and heat sink

A heat engine is a thermodynamic device used for continuous production of work from heat when operating in a cyclic process. Both heat and work interactions take place across the boundary of this cyclically operating device.

A heat engine is characterised by the following features:

- reception of heat Q_1 from a high temperature source at T_1
- partial conversion of heat received to mechanical work W

- rejection of remaining heat Q_2 to a low temperature sink at temperature T_2
- cyclic/continuous operation and
- working substance flowing through the engine.

The performance of any machine is expressed as the ratio of 'what we want' to 'what we have to pay for'. In the context of an engine, work is obtained at the expense of heat input. Accordingly, the performance of a heat engine is given by net work output to the entire amount of heat supplied to the working medium, and this ratio is called ***thermal efficiency***, η_{th} (Thermal efficiency is a measure of the degree of useful utilization of heat received in a heat engine).

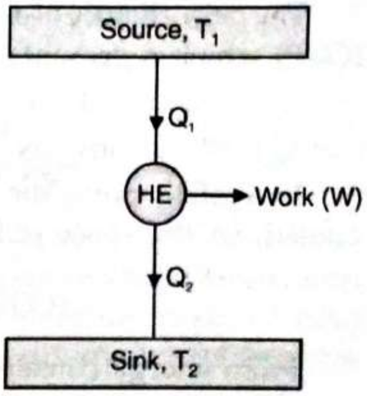


Fig. 1.25. Energy interactions in a heat engine

$$\eta_{th} = \frac{\text{net work output}}{\text{total heat supplied}}$$

Application of the principle of energy conservation (First law) to the heat engine, which undergoes a cycle gives : $W = Q_1 - Q_2$

$$\therefore \qquad \eta_{th} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \qquad \text{...(1.31)}$$

Obviously, thermal efficiency of a heat engine operating between two thermal reservoirs is always less than unity. To increase the thermal efficiency, it is necessary to reduce Q_2 (heat rejected) with Q_1 (heat supplied) remaining constant. Thermal efficiency could be equal to unity if $Q_1 \to \infty$ and $Q_2 = 0$ which, however, can not be realized in practice.

Refrigerators and heat pumps are *reversed* heat engines. The adjective 'reversed' means operating backwards. The direction of heat and work interactions are opposite to that of a heat engine, *i.e.*, work input and heat output. These machines (refrigerators and heat pumps) are used to remove heat from a body at low temperature level and then transfer this heat to another body at high potential of temperature. When the main purpose of the machine is to remove heat from the cooled space, it is called a ***refrigerator***. A refrigerator operates between the temperature of surroundings and a temperature below that of the surroundings. Refrigerators are essentially used to preserve food items and drugs at low temperature.

The term ***heat pump*** is applied to a machine whose objective is to heat a medium which may already be warmer than its surroundings. A heat pump thus operates between the temperature of the surroundings and a temperature above that of the surroundings. Heat pumps are generally used to keep the rooms warm in winter. The transfer of heat against a reverse temperature gradient in a refrigerator and heat pump is accomplished by supplying energy to the machine. A schematic representation of heat pump and a refrigerator has been shown in Fig. 1.26.

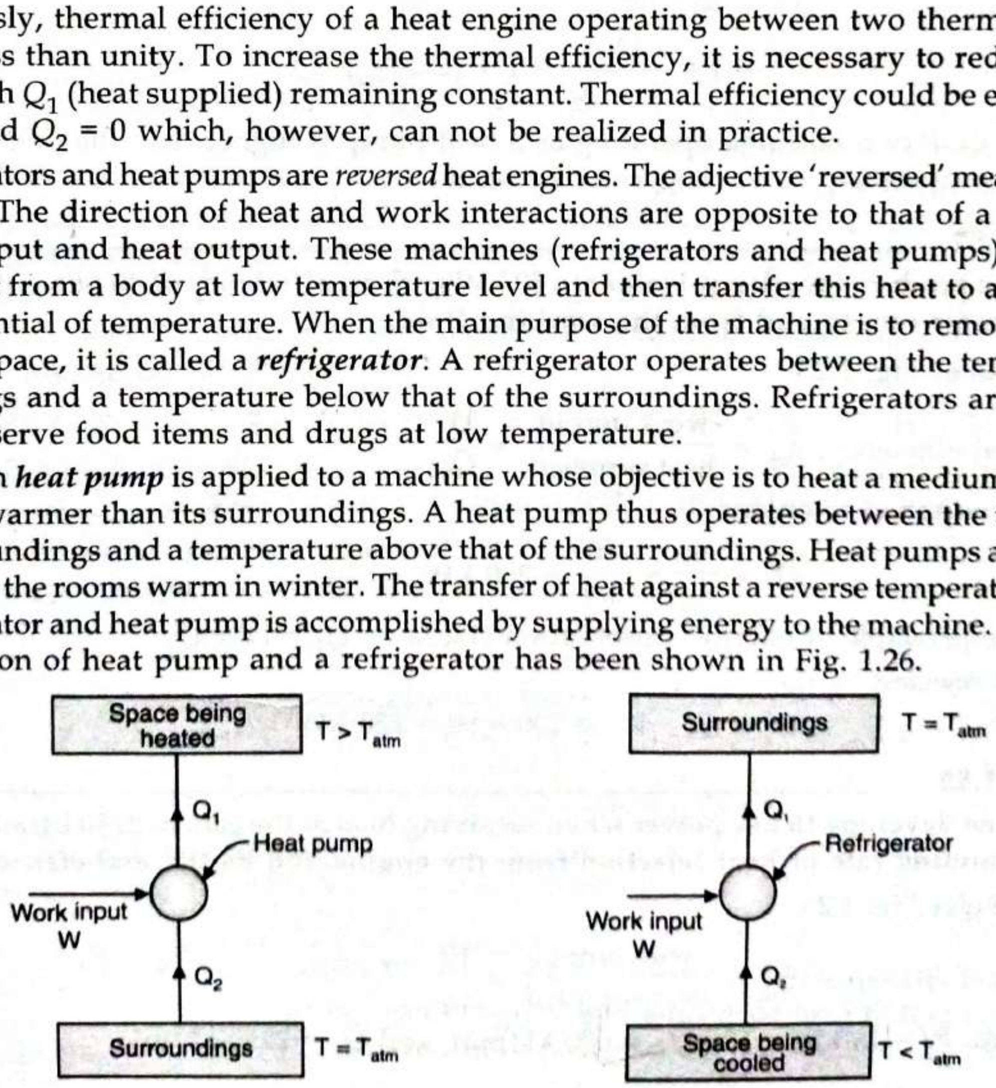


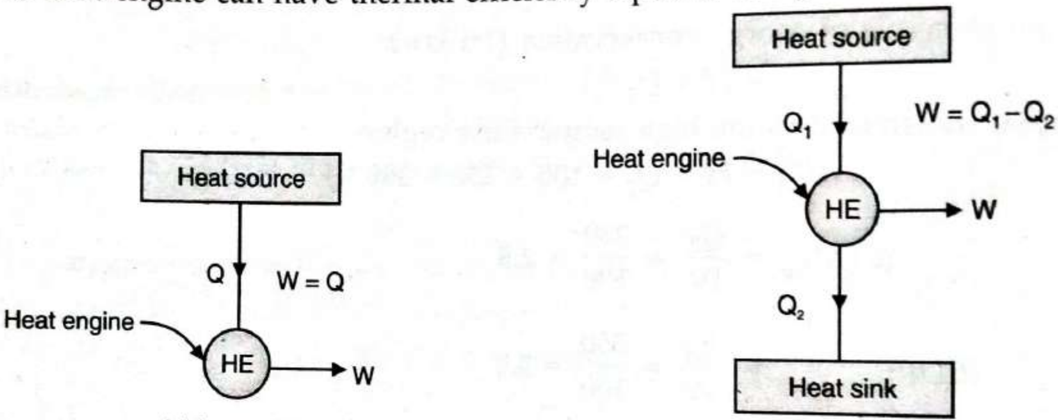
Fig. 1.26. Functional difference between a heat pump and a regrigerator

1.21. SECOND LAW OF THERMODYNAMICS

1.21.1. Kelvin-Planck Statement

"It is impossible to construct an engine that operates in a cycle and produces no effect other than work output and exchange of heat with a single heat reservoir"

The statement implies that no heat engine can be developed that receives a certain amount of heat from a high temperature source and converts that into an equivalent amount of work. *i.e,* $W = Q$. The thermal efficiency of such a engine $\eta = W/Q = 1$ or 100 percent. Fig. 1.27(*a*) represents the schematic arrangement of a heat engine that exchanges heat with a single heat source and is 100 percent efficient. Such a system satisfies the principle of energy conservation (1st law) but violates the Kelvin statement of second law. Obviously Kelvin-Planck statement tells that no heat engine can have thermal efficiency equal to 100 percent.



(a) Impossible

(b) Possible

Fig. 1.27. Schematic representation of a heat engine

The only alternative for continuous power output from a heat engine is that a portion of the heat received must be rejected to a heat reservoir at low temperature (heat sink). This engine receives Q_1 units of heat, rejects Q_2 units of heat and converts $(Q_1 - Q_2)$ units of heat into work per cycle. All possible heat engines conform to this representation (Fig. 1.27(*b*)).

1.21.2. Clausius Statement

"It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a system at low temperature to another system at high temperature".

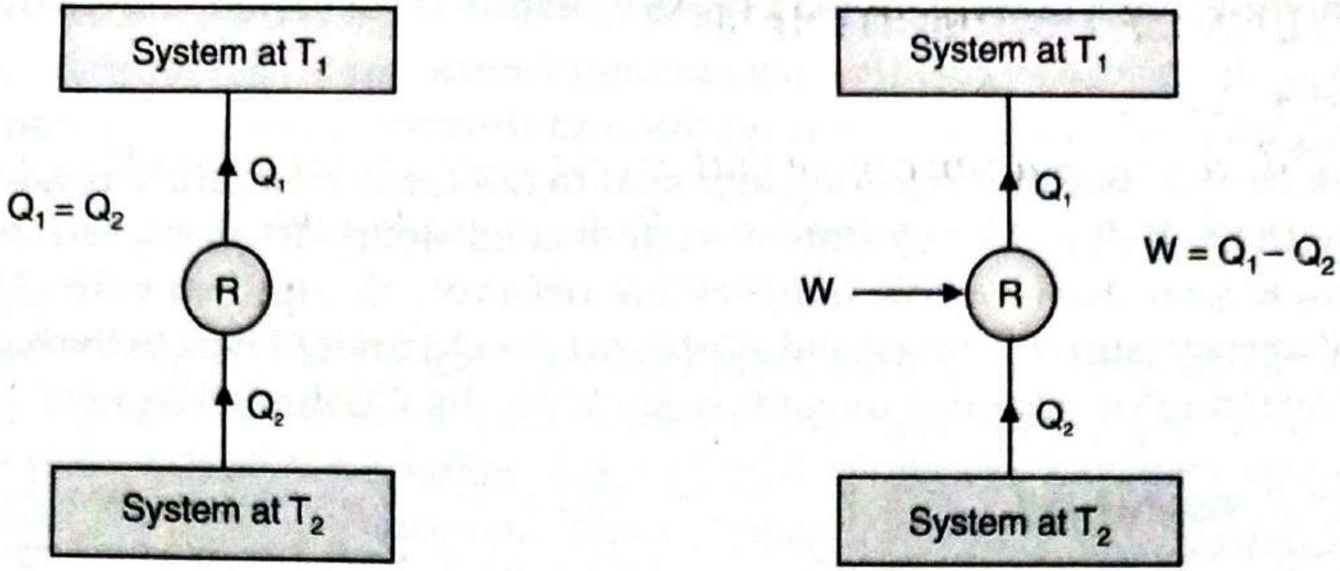
The statement implies that heat cannot flow of itself from a system at low temperature to a system at high temperature. The schematic arrangement that is prohibited by Clausius statement is shown in Fig. 1.28(*a*). The coefficient of performance of such an arrangement equals :

$$COP = Q/W = Q/0 = \infty$$

Obviously the Clausius statement tells that COP of a heat pump/refrigerator cannot be equal to infinity.

The only alternative for the transfer of heat from low temperature to high temperature level is that some external work must be supplied to the machine as shown in Fig. 1.28(*b*).

Whereas the Kelvin-Planck statement is applied to heat engines, the Clausius statement concerns heat pumps and refrigerators. Both the Kelvin-Planck and Clausius statements are negative statements, they have no mathematical proof. The law is based on experimental observations and to-date no observation has been made that contradicts the law and this aspect is taken as sufficient evidence of its validity.



(a) Impossible (b) [redacted]possible

Fig. 1.28. Schematic representation of a heat pump/refrigerator

The Kelvin-Planck and Clausius statements, though worded differently, are interlinked and are complementary to each other. It is impossible to have a device satisfying one statement and violating the other. Any device that violates Clausius statement leads to violation of Kelvin-Planck statement and vice-versa.

1.33. THIRD LAW OF THERMODYNAMICS (NERNST LAW)

The degree of atomic or molecular activity of a substance depends upon its temperature. As absolute zero temperature is approached, the randomness of molecules ceases and the entropy becomes equal to zero. This is the essence of third law of thermodynamics which states that :

"At absolute zero temperature, the entropy of all homogeneous crystalline (condensed) substances in a state of equilibrium becomes zero."

When expressed mathematically : $\underset{T\to 0}{dt}\ S = 0$. This implies that at absolute zero temperature, the entropy ceases to be a function of state and approaches a constant value independent of the parameters of the state. However, for many substances like alloys, all amorphous bodies, chemical compounds CO, NO etc., the entropy does not tend to zero as $T \to 0$, but takes a finite positive value. This is because these substances are not found in equilibrium state.

The third law provides an absolute base from which the entropy of each substance can be measured. The entropy relative to this base is referred to as the absolute entropy. Further, this law is helpful in

- measurement of chemical affinity, *i.e.*, the action of chemical forces of the reacting substances.
- explaining the behaviour of solids at very low temperatures.
- analysing the chemical and phase equilibrium.

2.51 ENTHALPY

The sum of internal energy and product of pressure (p) and volume V. (Flow work) or work done is defined as Enthalpy,

$$H = U + pV$$

H = U + PV

Specific Enthalpy h is given by

Enthalpy, $h = u + pv$ J/Kg

where h = Enthalpy
u = Internal energy, and
pv = Flow work or work done

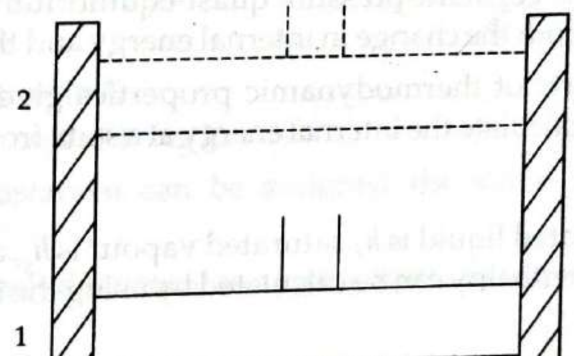


Fig. 53 Constant Pressure Heating Process

Consider a control mass of gas as shown in Fig. 53 undergoing a quasi-equilibrium constant-pressure heating process without changes in kinetic or potential energy. Assume that the only work done during the process is that which is associated with the boundary movement. Applying the first law of thermodynamics.

$$Q_{1-2} = U_2 - U_1 + W_{1-2}$$

where U_2 and U_1 are internal energies of the mass at state 2 and 1 respectively.

The work can be calculated as:

$$W_{1-2} = \int_1^2 p\,dV$$

As the pressure is constant

$$W_{1-2} = \int_1^2 p\,dV$$

$$= p(V_2 - V_1)$$

Hence,

$$Q_{1-2} = (U_2 - U_1) + (p_2V_2 - p_1V_1)$$

$$= (U_2 + p_2V_2) - (U_1 + p_1V_1)$$

The heat transfer during the process is represented in terms of the change in the quantity $(U + pV)$ between the initial and final states. A new extensive property, enthalpy is defined as:

$$H = U + pV$$

and for unit mass

$$h = u + pv$$

where h is an intensive property.

The heat transfer in the constant-pressure quasi-equilibrium process is equal to the change in enthalpy, which includes both the change in internal energy and the work for this particular process.

Many tables and charts of thermodynamic properties give values for enthalpy and not for internal energy, Hence to calculate the internal energy at a state from the table values.

$$u = h - pv$$

The enthalpy of saturated liquid is h_f saturated vapour is h_g, and the latent heat of vaporization is h_{fg}. The saturation state enthalpy can be calculated by using the following equation:

$$h = h_f + xh_{fg}$$

where x = dryness fraction of steam.

2.52 INTERNAL ENERGY

Internal energy is defined as the sum of all the microscopic forms of energy of a system. It is the energy associated with the molecular structure and the molecular activity of the constituent particles of the system.

It may be viewed as the sum of the kinetic and potential energies of the molecules.

In general, the individual molecules of a system will move around with some velocity, vibrate about each other and rotate about an axis during their random motion. Associated with these motions are the translational, vibrational and rotational kinetic energies, the sum of which constitutes the kinetic energy of a molecules.

The average velocity and activity of the molecules are proportional to the temperature of the system. Thus, at higher temperatures the molecules will possess higher kinetic energies, and as a result the system will have a higher internal energy.

In other words, internal energy is the energy possessed by a body or a system due to its molecular arrangement and motion of the molecules.

It is usually represented by U and for unit mass u.

2.58 ENTROPY

Entropy is a function of the quantity of heat which shows the possibility of conversion of that heat into useful work.

It is an important thermodynamic property of a working substance, which increases with the addition of heat and decreases with its removal. Entropy is usually defined with respect to a reversible process. The physical significance of entropy is important to understand and evaluate thermal changes.

In a reversible process, over a small 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,

Heat absorbed by the working substance $\delta Q = TdS$

where

T = Absolute temperature, and
dS = Increase in entropy

But as a fact, it is tedious to define the term entropy and it is comparatively easy to define change of entropy of a working substance.

The change in entropy of a system can be defined as $ds = \delta Q / T$

where

δQ = Heat transfer
T = Absolute temperature in K

Entropy is expressed as S and unit as J/Kg K.

The entropy of all pure substances can be assigned the value of zero at absolute zero temperature.