Chapter -12

Thermodynamics

The foundation of thermodynamics is the Conservation of energy and the fact that heat flows spontaneously from hot to cold body and not the other way around. The study of heat and its transformation to mechanical energy is called thermodynamics. It comes from a Greek word meaning "movement of Heat".

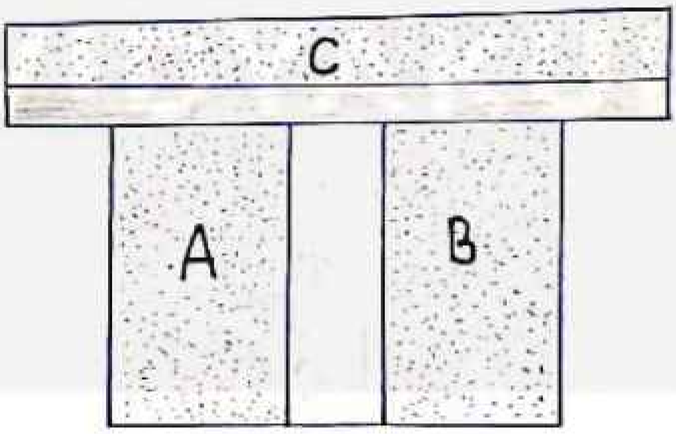
Thermal Equilibrium

When the temperature of the mixture becomes almost stable with the surrounding there is no further exchange of energy. This state in thermodynamics is called Thermal Equilibrium. So In thermal equilibrium, the temperature of the two systems are equal.

Zeroth Law of Thermodynamics

Zeroth Law of thermodynamics status that "If two systems are in thermal equilibrium with a third system separately are in thermal equilibrium with each other."

Physical quantity whose value is equal for two systems in thermal equilibrium is Called Temperature (T).



Heat, Internal Energy and work

Heat

Heat is that from of energy which gets transferred between a System and its - Surrounding because of temperature difference between them. Heat flows from the body at a higher temperature to the body at lower temperature. The flow stops when the temperature equalises. i.e., the two bodies are then in thermal equilibrium.

Internal Energy

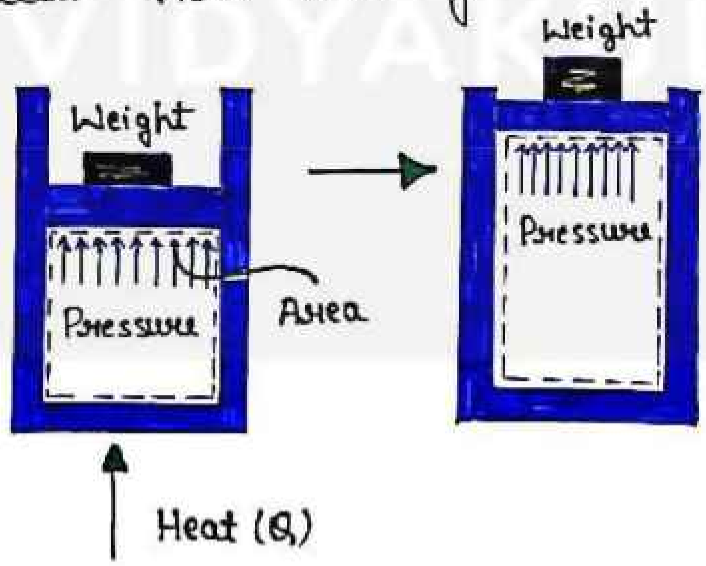
If we consider a bulk system Consisting of a large number of molecules, then internal Energy. of the system is the sum of the kinetic energies and Potential energies of these molecules.

This energy is possessed by a System due to its molecular motion and molecular Configu- -ration. The internal energy is denoted by U.

own direction. Work 'W' done on or by a system is the product of force and displacement.

First Law of thermodynamics

The first law of thermodynamics states that the total energy of an isolated system is constant. Energy can be transformed from one form to another, but can neither be created nor destroyed.



According to this law, some of the heat given to system is used to change the internal energy while the rest in doing work by the system. Mathematically,

$$\Delta Q = \Delta U + \Delta W$$

where,

ΔQ = Heat supplied to the system

ΔW = Work done by the system

ΔU = Change in the internal energy of the system.

If Q is positive, then there is a net heat transfer into the system, If W is positive, then there is work done by the system. So positive Q adds energy to the system and positive W take energy from the system.

$$\Delta U = \Delta Q - W$$

Internal energy tends to increase when heat is given to the System and Vice Versa.

Limitations of First Law of Thermodynamics

The limitation of the first Law of thermo-dynamics is that it does not say any-thing about the direction of flow of Heat. It does not say anything whether the process is a spontaneous process or not. The reverse process is not possible. In actual practice, the heat doesn't Convert Completely into work. If it would have been possible to Convert the whole heat into work, then we could drive ships across the ocean by extracting heat from the water of the Ocean.

Specific Heat Capacity

Specific heat capacity of a substance is defined as the heat required to raise the temperature of unit mass through 1°C (or 1K).

Heat Capacity of a Substance is given by

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

If we divide S by mass of the substance m in kg, we get

$$C = \frac{S}{m} = \frac{1}{m} \frac{\Delta Q}{\Delta T}$$

here s is known as the specific heat Capa-city of the substance. It depends on the nature of the substance and its temperature. The unit of s is $J\ kg^{-1}\ K^{-1}$.

The specific heat at Constant Volume C_V

It is defined as the amount of heat required to raise the temperature of a 1 mole of a gas through 1°C. when its volume is kept constant. It is denoted by (C_V) and given by

$$C_V = \left(\frac{\Delta Q}{\Delta T}\right)_V$$

The Specific heat at Constant pressure C_P -

It is defined as the amount of Heat required to raise the temperature of 1 mole of the gas through 1°C. when its pressure is kept Constant. It is denoted by (C_P) and given by

$$C_P = \left(\frac{\Delta Q}{\Delta T}\right)_P$$

Derivation of Mayer's Formula

From Ist Law

$$\Delta Q = \Delta U + \Delta W = \Delta U + P\Delta V$$

At Constant volume $\Delta V = 0$ so $\Delta Q = \Delta U$

$$C_v = \left(\frac{\Delta Q}{\Delta T}\right)_v = \left(\frac{\Delta U}{\Delta T}\right)_v$$

$$C_v = \frac{\Delta U}{\Delta T}$$

On the other hand, at constant pressure,

$$\Delta Q = \Delta U + P\Delta U$$

$$C_p = \left(\frac{\Delta Q}{\Delta T}\right)_p = \left(\frac{\Delta U}{\Delta T}\right)_p + P\left(\frac{\Delta V}{\Delta T}\right)_p$$

Now, for a mole of an ideal gas

$$PV = RT$$

$$\frac{\Delta V}{\Delta T} = \frac{R}{P}$$

$$C_p = \left(\frac{\Delta U}{\Delta T}\right)_P + \frac{P \times R}{P}$$

$$C_p = C_v + R$$

$$\boxed{C_p - C_v = R}$$

This formula is known as Mayer's formula. All the three quantities (C_p), (C_v) and R in this equation should be expressed in the same units either in joule/mole°C or in cal/mole°C.

Thermodynamic State Variables and equation of State –

Thermodynamic State Variables

Thermodynamic state variables of a System are the parameters which describe equilibrium states of the system.

Example - Equilibrium state of gas is completely specified by the values of pressure, volume, temperature, mass and composition.

Equation of State

The equation of states represents the connection between the state variables of a system.

Example - the those equation of state of an ideal / perfect gas in represented as

$$PV = \mu RT$$

where μ is number of moles of the gas and R is gas constant for one mole of the gas.

Thermodynamics state variables are of two kinds, extensive and intensive.

Extensive variables indicates the size of the system but intensive variables do not indicate the size. Volume, mass, internal energy of a system are extensive variables but pressure, temperature and density are intensive variables.

Thermodynamic Process

Any change in the thermodynamic coordinates of a system is called a process. The following are familiar process in the Thermodynamics.

Quasi-Static Process

A quasi-Static process is defined as the process in which the deviation from thermodynamics equilibrium is infinitesimal and all the States through which the System passes during quasi-Static process may be treated as equilibrium States. Thus it may be defined as a succession of equilibrium States.

Isothermal Process

When a thermodynamic system undergoes a process under the Condition that its temperature remains Constant, then the process is said to be isothermal process. The essential Condition for an isothermal process is that the System must be Contained in a perfectly Conducting Chamber.

For isothermal process,

$$\Delta U = 0$$

From the first law of thermodynamics,

$$\Delta U = Q - W$$

$$0 = Q - W$$

$$\boxed{Q = W}$$

Hence, for an ideal gas all heat is converted into work in isothermal process.

Adiabatic Process

When a thermodynamic system undergoes a process under the condition that no heat comes into or goes out of the system, then the process is said to be adiabatic process. Such a process can occur when a system is perfectly insulated from the surroundings.

For adiabatic Process,

$$Q = 0$$

From the first Law of thermodynamics,

$$\Delta U = Q - W$$

$$\Delta U = 0 - W$$

$$\boxed{\Delta U = -W}$$

Isochoric Process

If a substance undergoes a process in which the volume remains unchanged, the process is called an isochoric process. The increase of pressure and temperature produced by the heat supplied to a working substance contained in a non-expanding chamber is an example of isochoric process.

For isochoric process,

$$\Delta V = 0 \ , \ W = P\Delta V \ , \ W = 0$$

From the first Law of thermodynamics,

$$\Delta U = Q - W$$

$$\Delta U = Q - 0$$

$$\boxed{\Delta U = Q}$$

Isobaric Process

If the working substance is taken in expanding Chamber in which the pressure is kept Constant, the process is called isobaric Process. In this process the gas either expands or shrinks to maintain a Constant pressure and hence a net amount of work is done by the System or on the System.

Cyclic Process

When a thermodynamic system returns to initial State after passing through several States, then it is Called Cyclic Process.

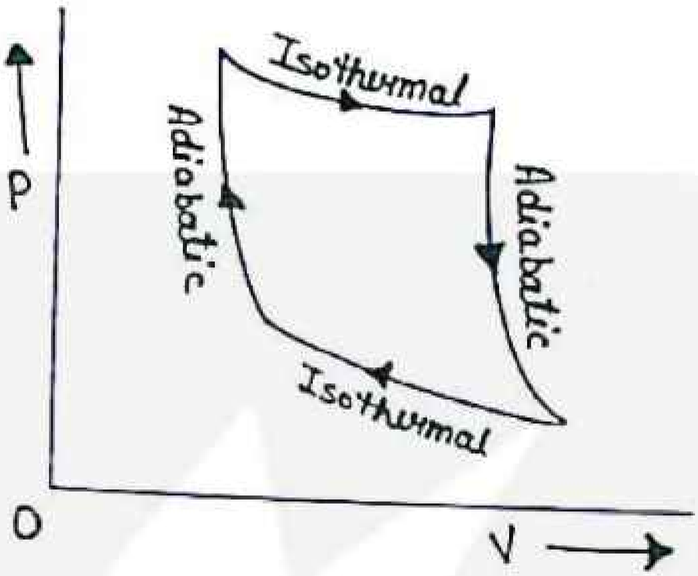
Efficiency of the cycle is given by

$$\eta = \frac{\text{Work done}}{\text{Heat Supplied}}$$

Work done by the Cycle Can be computed from area enclosed Cycle on P-V Curve.

P-V Diagram

A graph representing the variation of pressure with the variation of Volume is Called P-V diagram. The work done by the thermodynamic System is equal to the area under P-V diagram. It is given as



Second Law of thermodynamics

This has two statements. First is kelvin-Planck statement which is based upon the performance of heat engine and second is Clausis statement which is based upon the performance of refrigerator.

Kelvin - Planck Statement

This may be stated as, " It is impossible to Construct a device which operating in a cycle, has a sole effect of extracting heat from a reservoir at performing an equivalent amount of work". Thus, a single reservoir at a single temperature can not continuously transfer heat into work.

Clausius Statement

This may be stated as, "It is impossible for a self-acting machines working in a cycle process, unaided by any external agency to transfer heat from a body at a lower temperature to a body at a higher temp-erature." In other words it may be stated as " Heat cannot flow itself from a colder to a hotter body.

Heat Engines

Any "Cyclic" device by which heat is converted into mechanical work is called a heat Engine. For a heat engine there are three essential requirements:

Source

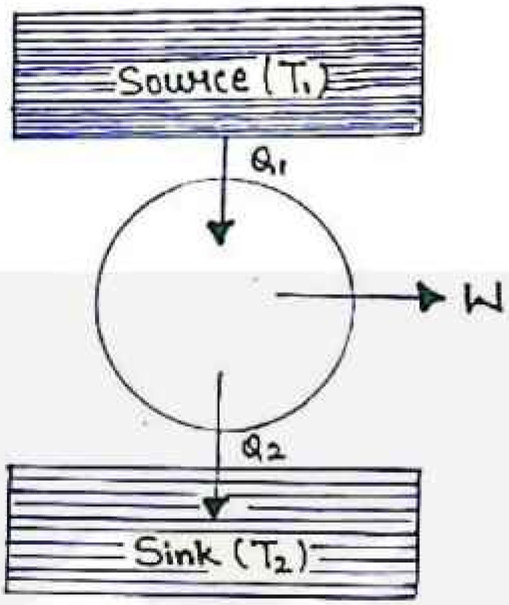
A hot body, at a fixed high temperature T_1 from which the heat can be drawn heat, is called Source or hot reservoir.

Sink

A Cold body at a fixed lower temperature T_2 to which any amount of heat can be rejected is called Sink or cold reservoir.

Working substance

The material, which on being supplied with heat, performs mechanical work is called the working substance.



In a heat engine, the working substance takes in Heat from the Source, Converts a part of it into external work, gives out the rest to the Sink and returns to its initial status. The series of Operations Constitute a Cycle. The work Can be continuously obtained by performing the same cycle over the over again.

Suppose the working Substance takes in an amount of heat Q_1 from the Source and gives out an amount Q_2 To the Sink. Let W be the amount of work obtained. The net amount of heat absorbed by the

Substance is $Q_1 - Q_2$, which has been actually converted into work. Applying the first law of thermodynamics to one complete cycle. we get

$$Q_1 - Q_2 = W$$

Reversible and Irreversible Processes

Reversible Process

A thermodynamics process is said to be reversible if the process can be turned back such that both the system and the surroundings return to their original states with no other change anywhere else in the universe. Ex- extension of springs, slow adiabatic compression or expansion of gases.

Irreversible Process

An irreversible process can be defined as a process in which the system and the surroundings do not return to their original condition once the process is initiated. Ex - Relative motion with friction, heat transfer.

Carnot Engine

A reversible heat engine operating between two temperatures is called a Carnot Engine. The sequences of steps constituting one cycle is called the Carnot Cycle.

Carnot Theorem

Carnot gave the most important results which are :

⇒ No engine can have efficiency more than that of the Carnot engine.

The efficiency of the Carnot engine is independent of the nature of the working substance.