Thermodynamics

1. Thermodynamic System, Surroundings and Boundary

Thermodynamic system is an assembly of an extremely large number of particles (atoms or molecules), so that the assembly has a certain value of pressure, volume and temperature.

Everything outside the system which has a direct effect on the system is called its surroundings. All space in universe outside the system is surroundings, e.g. Environment.

A system is separated from its surroundings by a boundary.

2. Thermodynamic Equilibrium

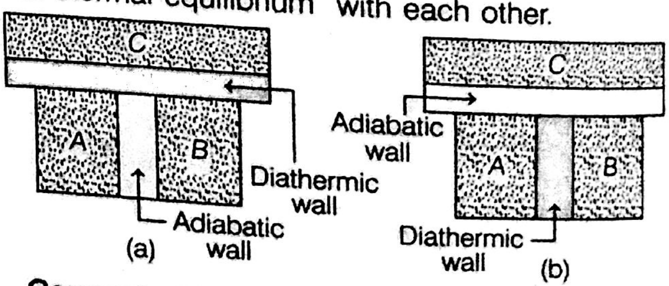
A thermodynamic system is said to be in thermodynamical equilibrium when macroscopic variables (like pressure, volume, temperature, mass, composition, etc.) that characterise the system do not change with time.

3. Thermal Equilibrium

Two systems are said to be in thermal equilibrium with each other if they are at the same temperature.

4. Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that, if two systems A and B are separately in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other.



Concept of Temperature Zeroth law of thermodynamics implies that temperature is a physical quantity which has the same value for all systems which are in thermal equilibrium with each other.

Hence, zeroth law says that, if systems A and B are separately in thermal equilibrium with C, i.e.

$$T_A = T_C \quad \text{and} \quad T_B = T_C$$

$$\Rightarrow \quad T_A = T_B$$

So, systems A and B will also be in thermal equilibrium with each other.

5. **Internal Energy**

Internal energy of a system is defined as the total energy possessed by the system due to molecular motion and molecular configuration. It is represented by U. The energy due to molecular motion is called internal kinetic energy U_K.

The energy due to molecular configuration is called internal potential energy U_P.

Then, internal energy, $U = U_K + U_P$

Thus, the sum of molecular kinetic and potential energies in the frame of reference relative to which the centre of mass of the system is at rest.

6. **Heat and Work**

- **Heat** It is the energy that is transferred between a system and its environment because of the temperature difference between them. SI unit of heat is joule.

i.e. $\Delta Q \propto m\Delta T$ or $\Delta Q \propto m(T_f - T_i)$

or $\boxed{\text{Change in heat, } \Delta Q = ms(T_f - T_i)}$

where, m = mass of body, T_i = initial temperature, T_f = final temperature

and s = specific heat of material

- **Work** By work, we mean work done by the system or on the system.

$dW = Fdx = pAdx = pdV$

and for a finite volume change from V_i to V_f,

$$\text{Work done, } W = \int_{V_i}^{V_f} dW$$

$$\boxed{\text{Work done, } W = \int_{V_i}^{V_f} pdV}$$

Here, p could be variable or constant.

7. **First Law of Thermodynamics as Energy Balance**

First law of thermodynamics is a statement of conservation of energy applied to any system in which energy transfer from or to the surroundings is taken into account.

It states that heat given to a system is either used in doing external work or it increases the internal energy of the system or both.

i.e. Heat supplied, $\Delta Q = \Delta U + \Delta W$

where, ΔQ = Heat supplied to the system by the surroundings,

ΔW = Work done by the system on the surrounding.

and ΔU = Change in internal energy of the system.

ΔU depends only on the initial and final states.

8. **Thermodynamic State Variables and Equation of State**

Every equilibrium state of a thermodynamic system is completely described by specific values of some macroscopic variables and these are called state variables. e.g. Pressure, volume, temperature and mass.

- **Equilibrium State** A system is not always in a thermodynamic state but with time it comes in mechanical and thermal equilibrium state.
- **Equation of State** The equation which represents the relationship between the state variables of a system is called its equation of state.

e.g. For an ideal gas, the equation of state is the ideal gas equation $pV = \mu RT$

For a fixed amount of gas given, there are thus only two independent variables, say p and V or T and V. The pressure-volume curve for a fixed temperature is called an **isotherm**.

9. **Thermodynamic Processes**

When state of a system changes or the state variables changes with time, then this process is known as thermodynamic process.

- **Quasi-Static Process** Quasi-static process is a hypothetical concept. Practically, processes that are sufficiently slow are considered as quasi-static.

  The processes that do not involve accelerated motion of piston, large temperature gradient and pressure gradient are quasi-static.

- **Some Important Processes**

(*i*) An **isothermal process** occurs at constant temperature.

e.g. Freezing of water at 0°C to form ice at 0°C.

(*ii*) An **isobaric process** occurs at constant pressure.

e.g. Boiling of water in an open container.

(*iii*) An **isochoric process** is one in which volume is kept constant, meaning that the work done by the system will be zero.

e.g. Heat given to a system with fixed walls.

(*iv*) An **adiabatic process** does not allow transfer of heat by or to the system.

e.g. Rapid compression, like filling of a cycle tube by a hand pump.

(*v*) **Cyclic and non-cyclic process** In cyclic process, initial and final states are same while in non-cyclic processes they are different.

10. **Work Done in an Isothermal Process**

For an isothermal process temperature remains constant.

For an ideal gas, the equation of state is given by

$$pV = \text{constant}$$

So, gas follows Boyle's law

$$p_iV_i = p_fV_f, \text{ for isothermal process}$$

$$\text{Work done, } W_{iso} = 2.303\,\mu RT \log\left(\frac{V_f}{V_i}\right)$$

As temperature of ideal gas remains constant.

$\therefore \quad \Delta U = 0$

So, by first law of thermodynamics,

$$\Delta Q = \Delta W = \mu RT \log\left(\frac{V_f}{V_i}\right)$$

where, V_f and V_i are the final and initial volumes of the gas, respectively.

1. Work Done in an Adiabatic Process

In an adiabatic process, there is no exchange of heat between system and the surroundings.

$$p_iV_i^{\gamma} = p_fV_f^{\gamma} = \text{constant}$$

Work done, $W = \dfrac{\mu R(T_i - T_f)}{\gamma - 1}$

$$\Delta Q = 0$$

Now, by first law of thermodynamics,

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

So, if work is done by the system, the internal energy and so the temperature of system falls i.e. $W > 0$ $T_f < T_i$. Conversely, if work is done on the system, the internal energy and so the temperature of system increases.

i.e. $W < 0, T_f > T_i$

All nearly practical adiabatic processes occur so rapidly that no transfer of energy as heat occurs between the system and surroundings.

e.g. Sudden bursting of bicycle tube and propagation of sound waves in air.

12. Work Done in an Isochoric Process

In case of an isochoric process, volume of the system remains constant. So, if heat is added to system, its pressure increases and if heat is extracted from the system, pressure will be reduced.

Equation of State

In this process, p and T change but V = constant, Gay-Lussac's law is obeyed.

$$\Rightarrow \quad p \propto T$$

$$\Rightarrow \quad \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

where, V = constant

So, work done, $\Delta W = 0$

$$\Delta W = p\,\Delta V = 0 \qquad [\because \Delta V = 0]$$

From first law of thermodynamics, $\Delta Q = \Delta U$

Hence, in an isochoric process, the entire heat given to or taken from the system goes to change its internal energy and temperature of the system.

The change in temperature can be determined by the equation

$$\Delta U = \Delta Q = \mu C_V \Delta T$$

13. Work Done in an Isobaric Process

When a thermodynamic system undergoes a physical change at constant pressure, then this thermodynamic process is known as isobaric process. Suppose the pressure p of a gas remains constant and its volume changes from V_i to V_f, then the work done by the gas is

$$W = \int_{V_i}^{V_f} p\,dV = p\int_{V_i}^{V_f} dV = p(V_f - V_i)$$

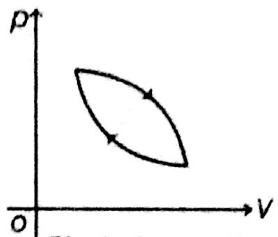
Work done, $W = \mu R(T_f - T_i)$

As the temperature of the gas changes, so its internal energy also changes. Hence, in an isobaric process, the absorbed heat goes partly to increase internal energy and partly to do work.

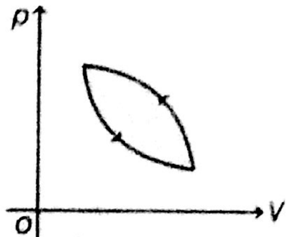
14. Work Done in a Cyclic Process

A single process or a series of processes in which, after certain interchanges of heat and work, the system is restored to its initial state known as a cyclic process. As both initial and final states are same in a cyclic process,

$$\Delta U = U_f - U_i = 0$$



Clockwise cyclic process



Anti-clockwise cyclic process

For a cyclic process, p-V graph is a closed curve and area enclosed by the curve is equal to the work done. From first law of thermodynamics,

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

[$\because$ for a cyclic process, $\Delta U = 0$]

Therefore, heat supplied to the system is utilised in work done by the system.

15. Heat Engine

Heat engine is a device by which a system is made to undergo a cyclic process, that results in conversion of heat to work.

16. Thermal Efficiency

The ratio of the work done by the heat engine and the heat absorbed by the working substance is called the efficiency of the heat engine $\eta_{th} = \dfrac{W}{Q_1}$

where, $W = Q_1 - Q_2$

Thermal efficiency, $\eta_{th} = 1 - \dfrac{Q_2}{Q_1}$

For ideal heat engine $Q_2 = 0$

So, $\eta_{th} = 1$, i.e. 100% (practically not possible)

where, Q_1 = heat absorbed by the working substance,

Q_2 = heat released by the working substance to the sink,

η_{th} = thermal efficiency of heat engine

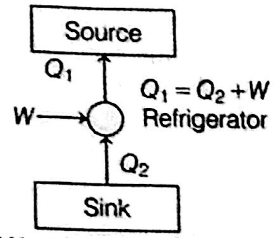
and W = work done

17. Refrigerator or Heat Pump

A refrigerator or heat pump is basically a heat engine which runs in reverse direction. It essentially consists of three parts

Source at higher temperature T_1.

Working Substance It is called refrigerant containing liquid ammonia and freon



Working of refrigerator

Sink at lower temperature T_2.

The performance of a refrigerator is expressed by means of coefficient of performance β which is defined as the ratio of the heat extracted from the cold body to the work needed to transfer it to the hot body. i.e. $\beta = \frac{\text{Heat extracted}}{\text{Work done}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$

Relation between Coefficient of Performance and Efficiency of Heat Engine

We know, $$\beta = \frac{Q_2}{Q_1 - Q_2} = \frac{Q_2/Q_1}{1 - Q_2/Q_1} \quad \ldots(\text{i})$$

But $$\eta = 1 - \frac{Q_2}{Q_1} \text{ or } \frac{Q_2}{Q_1} = 1 - \eta \quad \ldots(\text{ii})$$

Form Eqs. (i) and (ii), we get

$$\beta = \frac{1-\eta}{\eta}$$

18. Second Law of Thermodynamics

The principle that put a restriction on the first law of thermodynamics is known as the second law of thermodynamics. The second law of thermodynamics gives a fundamental limitation to the efficiency of a heat engine and the coefficient of performance of a refrigerator. Two statements of Kelvin-Planck and Clausius put restrictions on the possibility of perfect heat engine and perfect refrigerator, respectively.

Kelvin-Planck's Statement No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

Clausius Statement No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

19. Reversible Process

A process which could be reversed in such a way that the system and its surrounding returns exactly to their initial states with no other changes in the universe is known as reversible process.

20. Irreversible Process

Any process which is not reversible exactly is an irreversible process. All natural processes such as conduction, radiation, radioactive decay, etc. are irreversible processes. All practical processes such as free expansion, Joule-Thomson expansion, electrical heating of a wire are also irreversible.

21. Carnot Engine

The reversible engine which operates between two temperatures of source and sink is known as Carnot heat engine.

- **Carnot Cycle** As the engine works, the working substance of the engine undergoes a cycle known as Carnot cycle. *The Carnot cycle consists of the following four strokes*
  - (*i*) First Stroke (Isothermal Expansion)
  - (*ii*) Second Stroke (Adiabatic Expansion)
  - (*iii*) Third Stroke (Isothermal Compression)
  - (*iv*) Fourth Stroke (Adiabatic Compression)
- **Efficiency of Carnot Cycle** The efficiency of engine is defined as the ratio of work done to the heat supplied, i.e. $\eta = \frac{\text{Work done}}{\text{Heat input}} = \frac{W_{net}}{Q_1}$

  So, efficiency of Carnot engine, $\eta = 1 - \frac{T_2}{T_1}$
- **Carnot Theorems** According to Carnot theorem,
  - (*i*) A heat engine working between the two given temperatures T_1 of hot reservoir, i.e. source and T_2 of cold reservoir, i.e. sink cannot have efficiency more than that of the Carnot engine.
  - (*ii*) The efficiency of the Carnot engine is independent of the nature of working substance.
- **Coefficient of Performance of Carnot Engine**

  For Carnot refrigerator, $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

  $$\Rightarrow \frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2} \text{ or } \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

  So, coefficient of performance, $\beta = \frac{T_2}{T_1 - T_2}$

  where, T_1 = temperature of surrounding

  and T_2 = temperature of cold body.

  It is clear that $\beta = 0$ when $T_2 = 0$, i.e. the coefficient of performance will be zero, if the cold body is at the temperature equal to absolute zero.