Thermodynamics

- **Thermal equilibrium:**
    - State of a system is an equilibrium state if the macroscopic variables that characterise the system do not change.
    - Two systems at the same temperature are said to be in thermal equilibrium with each other.

- **Adiabatic wall:** Insulating wall that does not allow the flow of energy through it

- **Diathermic wall:** Conducting wall that allows the flow of energy through it

- **Zeroth law of thermodynamics :** If two bodies A and B are in thermal equilibrium and A and C are also in thermal equilibrium then B and C are also in thermal equilibrium.

Heat

- It is a form of energy.
- The flow of heat between two bodies stops when their temperatures equalise.
- Heat is transfer of energy due to the temperature difference between a system and its surroundings.

Internal energy

- The internal energy of a system is the sum of kinetic and potential energies of the molecules of the system.

$U = K_e + P_e$

- It includes the energy associated with the random motion of molecules of the system.
- Internal energy (as a state variable) depends on the given state of the system, and not on the path taken to reach the state.

Sign conventions

- Heat gained by a system - Positive
- Heat lost by a system - Negative
- Work done by a system - Positive
- Work done on a system - Negative

First law of thermodynamics

- The first law of thermodynamics is based on the law of conservation of energy .
- The equation for the first law of thermodynamics is
  increment Q equals increment U plus W.

  - **First law of thermodynamics:** According to first law of thermodynamics, when an amount of heat ΔQ is added to a system, a part of it increases its internal energy by ΔU and the remaining part is used up as the external ΔW done by the system.

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

    $\Delta \Delta Q$ →→ Heat supplied to the system

    $\Delta \Delta W$ →→Work done by the system

    $\Delta \Delta U$ →→ Change in internal energy of the system

  - **Specific heat capacity :**

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

Δ ΔQ $\rightarrow\rightarrow$ Heat required to change the temperature

Δ ΔT $\rightarrow\rightarrow$ Change in temperature

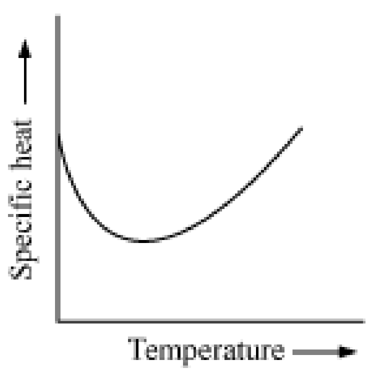
m $\rightarrow\rightarrow$ Mass of the substance

- **Molar specific heat capacity :**

$$C = \frac{1}{\mu}\frac{\Delta Q}{\Delta T}$$

μ μ $\rightarrow\rightarrow$Number of moles of the substance

- **Variation of specific heat of water**



Thermodynamic state variables

- The thermodynamic state variables are of two kinds.
  - Extensive: Indicate the ‘size’ of the system

- Intensive: They do not indicate the 'size' of the system. Example: pressure, temperature, etc.

Equation of State

- The relation between the pressure, temperature and volume of a system is called the equation of state

  For an ideal gas, the relation of the equation of state is $PV = \mu RT$

Thermodynamic processes:

- **Isothermal process:** Process in which the pressure and volume of system change, but temperature remains constant
  - **Work done in an Isothermal process:**

$$W_{iso} = 2.3026RT\log_{10}\frac{V_2}{V_1}$$

- **Adiabatic process:** Process in which there is no exchange of heat between the system and the surroundings
  - **Work done in an adiabatic process :**

$$W_{adia} = C_v(T_1 - T_2) = \frac{R}{\gamma - 1}(T_1 - T_2)$$

- **Isochoric process:** Thermodynamic process that takes place at constant volume of the system. Now work done.

- **Isobaric process:** Thermodynamic process that takes place at constant pressure. Work done = $P\Delta V$

- **Cyclic process:** Thermodynamic process in which the system returns to its initial stage after undergoing a series of changes

- **Quasi-static process:** Thermodynamic process which proceeds extremely slowly such that at every instant of time, the temperature and pressure are the same in all parts of the system

- **Heat engine** is a device in which a system undergoes a cyclic process resulting in conversion of heat into work. The efficiency $\eta\eta$ of the engine is:

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Q_1 →→Heat absorbed from the source

Q_2 →→ Heat released to the sink

W →→ Work output

- **Refrigerator –** The system extracts heat Q_2 from the cold reservoir and releases Q_1 amount of heat to the hot reservoir with work W done on the system. The co-efficient of performance of refrigerator is given by,

$$\alpha = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

  - Heat is never fully converted to work and refrigerator cannot work without some external work done on the system. Therefore, co-efficient of performance cannot be infinite.

Second law of Thermodynamics

- **Kelvin−Planck Statement:** It is not possible to design a heat engine which works in cyclic process and whose only result is to take heat from a body at a single temperature and convert it completely into mechanical work.
- **Clausius Statement:** It is impossible for a self-acting machine, unaided by any external agency, to transfer heat from a body at lower temperature to another at higher temperature.

Reversible and Irreversible Processes

- **Reversible process**:Any process which can be made to proceed in reverse direction with equal ease, by variations in its conditions, so that all changes occurring in the direct process are exactly reversed in the reverse process.

- **Irreversible process**:Any process which cannot be made to proceed in reverse direction.

- For a reversible process, the following conditions must be obeyed:

    - The process must take place very slowly.

    - The system must be free from dissipative forces like friction, viscosity, etc.

Carnot engine

- It is a reversible engine operating between two temperatures T_1 (Source) and T_2 (sink). The Carnot cycle consists of two isothermal processes connected by two adiabatic processes. The efficiency of a Carnot engine is given by,

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

Carnot's Theorem

- Working between the two given temperatures of the hot (T_1) and cold (T_2) reservoirs, efficiency of no engine can be more than that of a Carnot engine.
- Efficiency of the Carnot engine is independent of the nature of the working substance
- For a Carnot cycle

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

  - It is independent of the nature of the system.