8. Kinetic Theory of Gases and Radiation

- **Atomic hypothesis**: All things are made of atoms − little particles that move around in perpetual motion, attracting each other when they are at a little distance apart and repelling when squeezed into one another.
- **Atomic theory**: Proposed by John Dalton to explain the laws of definite and multiple proportions.
- First law states that any given compound has fixed proportion by mass of its constituents.
- Second law states that when two elements form more than one compound, for a fixed mass of one element, the masses of the other elements are in the ratio of small integers.
- **Gay-Lussac's law**: When gases combine chemically to yield another gas, their volumes are in the ratio of small integers.
- **Avogadro's law**: Equal volumes of all gases at equal temperature and pressure have the same number of molecules.

- **Boyle's Law** → PV = constant, at constant temperature
- **Charles's Law** → $V \alpha T$, provided P is constant
- **Avogadro's Law**→ At the same temperature and pressure, equal volumes of all gases contain equal number of molecules.
- **Graham's Law of Diffusion**→ At same temperature and pressure, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas.

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_2}}$$

- **Dalton's Law of Partial Pressure:** The pressure exerted by a mixture of several gases equals the sum of the pressures exerted by each gas occupying the same volume as that of the mixture.

$$P=P_1+P_2+P_3+P_4+....$$

- **Equation of state of a perfect gas →**

$$\frac{PV}{T} = \text{Constant}$$

Assumptions of Kinetic Theory of Gases:

- Gases are made up of a large number of tiny molecules.
- Molecules in a gas have much space between them, such that the actual volume occupied by the gas is very small compared to the total volume of the gas .
- Molecules are perfectly rigid and perfectly elastic spheres of very small diameters.
- All the molecules have same size, shape and mass.

Random motion of gas molecules

- Gas molecules are in constant random motion. At any given time, molecules are moving in many different directions at many different speeds.
- Due to their random motion, the molecules constantly collide with each other and also with the walls of the container. Molecular collisions are perfectly elastic.
- Between two successive collisions, a molecule travels in a straight line with steady velocity. This is known as the mean free path.
- The time taken for the collision is very small compared to the time required to cover the free path between the two collisions.

- **Assumptions of kinetic theory of gases:**
    - The size of a molecule is much smaller than the average separation between the molecules. Also the volume of the gas is negligible compared to the volume of the container.
    - The molecules exert no force on each other or on the walls of the container except during collision. All collisions are perfectly elastic. And the molecules obey Newton’s laws of motion.
    - The gas comes to a steady state after a sufficient time, and at the steady state the density and the distribution of molecules with different velocities are independent of position, direction and time.
    - All gases are made of molecules moving randomly in all directions.
- **Pressure of a gas →** $P=\frac{1}{3}\frac{nm}{V}C^2$, where

n → Number of molecules

m → Mass of each molecule

V → Volume of the container

C → Root mean square speed of the molecules

- Internal energy (E) of an ideal gas is purely kinetic.

$$E = N\times\frac{1}{2}m\overline{v}^2$$

- The average kinetic energy of a molecule is directly proportional to the absolute temperature of the gas.

  $$\Rightarrow \frac{E}{N} = \frac{3}{2} K_B T$$

- Total number of co-ordinates or independent quantities required to describe the configuration of a system completely is called degree of freedom.
- **Law of Equipartition of Energy –** A dynamic system in thermal equilibrium has the energy system equally distributed amongst the various degrees of freedom and the energy associated with each degree of freedom per molecule is $\frac{1}{2} k_B T$.

- Monoatomic gas

  - It has three degrees of freedom for translational motion. Mean kinetic energy of translational motion of gas is

    $$\frac{1}{2} m v^2 = \frac{3}{2} k_B T$$

- Translational and rotational degree of freedom of molecule contributes $\frac{1}{2} k_B T$ to the energy.
- Vibrational mode has both kinetic and potential energy. Therefore, each vibrational frequency contributes $2 \times \frac{1}{2} k_B T = k_B T$

Specific heat capacity:

- Monatomic gases → $C_v = \frac{3}{2} R, C_p = \frac{5}{2} R, \gamma = \frac{5}{3}$

- Diatomic gases → $C_v = \frac{5}{2} R, C_p = \frac{7}{2} R, \gamma = \frac{7}{5}$

- Triatomic gases → $C_v = 3R, C_p = 4R, \gamma = \frac{4}{3}$

- Polyatomic Gases → Cv=3+f R, CP=3+f R+R, γ=CPCv=4+f3+f *f* is number of vibrational modes.
- Specific heat capacity can be determined using the law of equipartition of energy.
- Specific heat capacity of solids, C=ΔQΔT=3R.

- The mean free path, *l*, is the average distance covered by a molecule between two successive collisions.

$$\bar{l} = \frac{1}{\sqrt{2}n\ d^2}$$

Here, *n* is the number density and *d* is the diameter of the molecule.

- We assumed that other molecules are at rest.

- For an ideal gas containing N molecules with velocities C_1, C_2 ....C_N .

  C=C1+C2+....CNN
    - Mean Velocity (Average velocity) C of an ideal gas,

- Mean Square Velocity C2 of an ideal gas,

  C2=C12+C22+.....CN2N

- Root Mean Square Velocity C2 of an ideal gas,
- CRMS=C2=C12+C22+.....CN2N
- **Maxwell's Distribution :**
    - In a given mass of gas, the velocities of all the molecules are different, even if the bulk parameters like pressure, volume and temperature are fixed.

- **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.

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

ΔQ → Heat supplied to the system

ΔW →Work done by the system

ΔU → Change in internal energy of the system

- **Specific heat capacity :**

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

ΔQ → Heat required to change the temperature

ΔT → Change in temperature

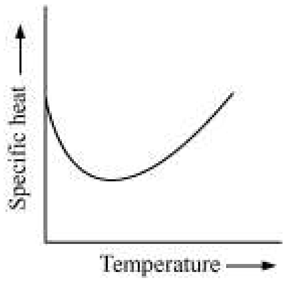
m → Mass of the substance

- **Molar specific heat capacity :**

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

μ →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:**

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

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

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

- **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 = PΔV

- **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

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.

- **Heat engine** is a device in which a system undergoes a cyclic process resulting in conversion of heat into work. The efficiency η 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.

Coefficient of absorption(a): It is the ratio of the quantity of radiant energy absorbed by a body(Q_a) to the quantity of radiant energy incident on the body (Q) in a given time.
$a =$ QaQ

Coefficient of reflection(r): It is the ratio of the quantity of radiant energy reflected by a body(Q_r) to the quantity of radiant energy incident on the body (Q) in a given time.
$r =$ QrQ

Coefficient of transmission(t): It is the ratio of the quantity of radiant energy transmitted through a body (Q_t) to the quantity of radiant energy incident on the body (Q) in a given time.
$t =$QtQ

Athermanous substances: They do not allow any heat radiation to pass through them. Wood, water, iron etc. are athermanous substances.

Diathermanous substances: They allow heat radiation to pass through them. Glass, quartz and oxygen are diathermanous substances.**Black and grey bodies:** A body that absorbs the entire radiation incident on it is called a perfect black body. A body that is not a black body is called a grey body.

Ferry's black body: Ferry's black body is an artificial black body consisting of a double-walled hollow metal sphere blackened inside, with a small fine hole on the surface.

Wein's Displacement Law: According to this law, the wavelength for which emissive power of a black body is maximum is inversely proportional to the temperature of the black body.

$$\lambda_{max}.T = b$$

Absorptive Power: It is the ratio of the radiant energy absorbed in a given time to the total radiant energy incident on a body at the same time.

$$a = \frac{\text{energy absorbed}}{\text{energy incident}}$$

It is dimensionless.

Emissive Power: It is the radiant energy emitted per second, per unit area of the surface of a body.
E=QAt
S.I. unit of emissive power is J/m^{2}s or W/m^2. Its dimensions are [M^{1}L^{0}T^{-3}].

Coefficient of emission (emissivity): It is the ratio of emissive power of a body to the emissive power of a black body at a given temperature .
e=EEb

Kirchhoff's Law of Radiation: According to this law, the coefficient of absorption of a body is equal to its coefficient of emission at any given temperature.
$a = e$ or Ea=Eb

Prevost's Law of Exchange: According to this law, the rate of energy lost by a body at temperature T through radiation is
$P_1 = eA\sigma T^4$.
and the rate of energy received by the body through absorption of radiation is
$P_2 = eA\sigma T_0^4$.
Net rate of loss of energy by the body through radiation, $P = P_1 - P_2 = eA\sigma(T^4 - T_0^4)$.

Stefan's Law: According to this law, the radiant energy emitted by a perfect black body per unit area per second is directly proportional to the fourth power of its absolute temperature, i.e.
$E \propto T^4$ or $E = \sigma T^4$

Newton’s Law Of Cooling: According to this law, the rate of cooling of a body is directly proportional to the temperature difference of the body and the surroundings, if temperature difference is small.
dTdt=-bA(T-T0)

Greenhouse Effect: It is a natural phenomenon that keeps the earth’s atmosphere warm due to absorption of heat of the sun and the earth by greenhouse gases. The heat absorbed by the gases is reflected back to the earth's surface.