

## 2. THERMODYNAMICS

It is the study of interrelations between heat and other forms of energy

**Thermodynamic System :** A collection of large number of molecules of matter (solid, liquid or gas) which are so arranged that these possess certain values of pressure, volume and temperature forms a thermodynamic system.

- The parameters pressure, volume, temperature, internal energy etc which determine the state or condition of system are called thermodynamic state variables.

In thermodynamics we deal with the thermodynamic systems as a whole and study the interaction of heat & energy during the change of one thermodynamic state to another.

### 2.1 Thermal Equilibrium

The term 'equilibrium' in thermodynamics implies the state when all the macroscopic variables characterising the system (P, V, T, mass etc) do not change with time.

- Two systems when in contact with each other come to thermal equilibrium when their temperatures become same.
- Based on this is zeroth law of thermodynamics. According to zeroth law, when the thermodynamics systems A and B are separately in thermal equilibrium with a third thermodynamic system C, then the systems A and B are in thermal equilibrium with each other also.

### 2.2 Heat, Work and Internal Energy

Internal Energy is the energy possessed by any system due to its molecular K.E. and molecular P.E. Here K.E & P.E are with respect to centre of mass frame. This internal energy depends entirely on state and hence it is a state variable. For 1 real gases internal energy is only by virtue of its molecular motion.

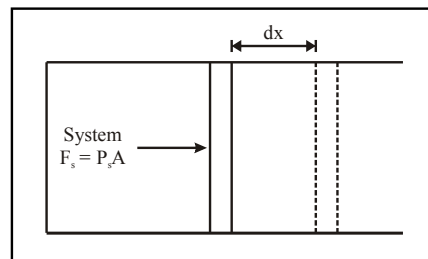
$$\text{Units } \frac{n f R T}{3} \text{ for ideal gases where}$$

- n = number of moles
- f = Degree of freedom
- R = Universal Gas Constant
- T = Temperature in Kelvin

Internal Energy can be change either by giving heat energy or by performing some work.

Heat Energy is the energy transformed to or from the system because of the difference in temperatures by conduction, convection or radiation.

The energy that is transferred from one system to another by force moving its point of application in its own direction is called work.



$$\begin{aligned} \text{Work done by the system} &= \int F \, dx \\ &= \int P_s \, A \, dx \\ &= \int P_s \, dV \end{aligned}$$

Where  $P_s$  Pressure of system on the piston. This work done by system is positive if the system expands & it is negative if the system contracts.

- Work and Heat are path functions whereas internal energy is a state function.
- Heat & work are two different terms through they might look same.

### 2.3 Important Thermodynamics Terms

**State Variables :** P, V, T, moles

They can be extensive or intensive.

**Equation of State :** The equation which connects the pressure (P), the volume (V) and absolute temperature (T) of a gas is called the equation of state.

$$PV = \text{constant} \quad (\text{Boyle's Law})$$

$$\frac{V}{T} = \text{constant} \quad (\text{Charles's Law})$$

$$\Rightarrow PV = NRT$$

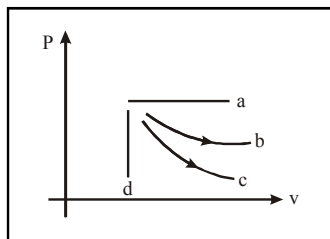
**Thermodynamic Process :** A thermodynamic process is said to take place when some changes occur in the state of a thermodynamic system, i.e., the thermodynamic parameters of the system change with some important time. Types of these thermodynamic process are Isothermal, Adiabatic, Isobaric and Isobaric

**Quasi Static Process :** A thermodynamic process which is infinitely slow is called as quasi-static process.

- In quasi static process, system undergoes change so slowly, that at every instant, system is in equilibrium, both thermal and mechanical, with the surroundings.

- Quasi-static process is an idealised process. We generally assume all the processes to be quasistatic unless stated.

**Indicator P-V, Diagram :** A graph between pressure and volume of a gas under thermodynamic operation is called P-V diagram.



- a → Isobaric
- b → Isothermal
- c → Adiabatic
- d → Isochoric

- Area under P – V diagram gives us work done by a gas.

## 2.4 1<sup>st</sup> Law of Thermodynamics

Let  $\Delta Q$  = Heat supplied to the system by the surroundings

$\Delta W$  = Work done by the system on the surroundings

$\Delta U$  = Change in internal energy of the system.

First law of thermodynamics states that energy can neither be created nor be destroyed. It can be only transformed from the form to another.

**Mathematically :**  $\Delta Q = \Delta U + \Delta Q$

**Sign Conventions :**

- When heat is supplied to the system, then  $\Delta Q$  is positive and when heat is withdrawn from the system,  $\Delta Q$  is negative.
- When a gas expands, work done by the gas is positive & when a gas contracts then  $w$  is negative
- $\Delta U$  is positive, when temperature rises and  $\Delta U$  is negative, when temperature falls.

Remember here we always take work done by the system. In chemistry, work done on the system is considered. Hence there is some different look of 1<sup>st</sup> law of Thermodynamics in chemistry.

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

where  $\Delta Q$ ,  $\Delta U$  have same meanings but  $W$  stands for work done on the system

## 2.5 Application of the First of Law of Thermodynamics

Here we see how 1<sup>st</sup> Law of Thermodynamics is applied to various thermodynamic processes.

### 2.5.1 Isothermal Process

**Description :** A thermodynamic process in which temperature remains constant

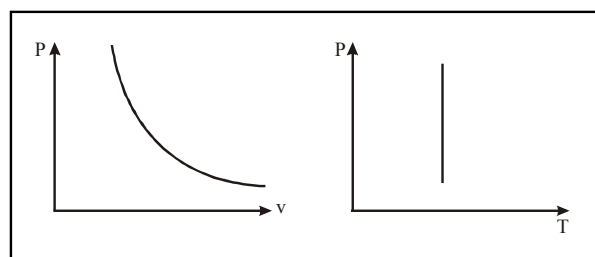
**Condition :** The walls of the container must be perfectly conducting to allow free exchange of heat between gas and its surroundings.

The process of compression or expansion should be slow so as to provide time for exchange of heat.

These both conditions are perfectly ideal.

**Equation of State :**  $T = \text{Constant}$  or  $P_v = \text{Constant}$

**Indicator Diagram :**



Slope of  $P - V^{-P}$  at any point.

$$\Delta U = 0 \quad (\text{Temperature remains constant})$$

$$W = \int_{v_1}^{v_2} P_g dv$$

$$= \int_{v_1}^{v_2} \frac{nRT}{V} \frac{dv}{V} \quad [\text{Using } PV = nRT]$$

$$= nRT \ln \frac{v_2}{v_1}$$

**First Law of Thermodynamics**

$$Q = \Delta U + W$$

$$\Rightarrow Q = nRT \ln \frac{v_2}{v_1}$$

**Remarks :** All the heat supplied is used entirely to do work against external surroundings. If heat is supplied then the gas expands & if heat is withdrawn then the gas contracts.

**Practical Examples :**

Melting of ice at 0°C

Boiling of H<sub>2</sub>O at 100°C

## 2.5.2 Adiabatic Process

**Description :** When there is not heat exchange with surroundings

**Conditions :** The walls of the container must be perfectly non-conducting in order to prevent any exchange of heat between the gas and its surroundings.

The process of compression or expansion should be rapid so there is no time for the exchange of heat.

These conditions are again ideal condition and are hard to obtain

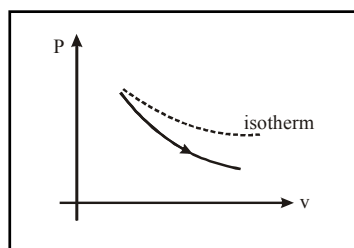
**Equation of State :**

$$Pv^r = \text{constant}$$

or  $TV^{r-1} = \text{constat}$

or  $PT^{\frac{r}{1-r}} = \text{cons tan t}$

**Indicator Diagram**



Slope of adiabatic curve  $= \frac{-rP}{V}$

- As shown in graph adiabatic curve is steeper than isothermal curve.

$$\Delta U = \frac{n\gamma R \Delta T}{2} = \frac{nR(T_2 - T_1)}{r-1} = \frac{P_2 V_2 - P_1 V_1}{r-1}$$

**Work Done by Gas :** If a gas adiabatically expands from  $V_1$  to  $V_2$

$$\begin{aligned} W &= \int_{V_1}^{V_2} P dV \\ &= \text{cons tan t} \int_{V_1}^{V_2} \frac{dV}{V^r} \\ &\left[ \because PV^r = \text{cons tan t} \right] \\ &\Rightarrow P = \frac{\text{cons tan t}}{V^r} \\ &= \text{cons tan t} \times \left[ \frac{V^{-r+1}}{1-r} \right]_{V_1}^{V_2} \end{aligned}$$

$$= \frac{\text{cons tan t}}{1-r} \left[ \frac{1}{V_2^{r-1}} - \frac{1}{V_1^{r-1}} \right]$$

Also we know

$$P_1 V_1^r = P_2 V_2^r = \text{cons tan t}$$

$$\Rightarrow \frac{1}{1-r} \left[ \frac{P_2 V_2^r}{V_2^{r-1}} - \frac{P_1 V_1^r}{V_1^{r-1}} \right]$$

$$W = \frac{P_2 V_2 - P_1 V_1}{1-r} = \frac{nR(T_1 - T_2)}{r-1}$$

**First Law of Thermodynamics**

$$Q = \Delta U + W$$

Substituting the values

$$\text{We get } Q = 0$$

$Q = 0$  is as expected

**Remarks :** It gas expands adiabatically then its temp decreases & vice versa

**Practical Example**

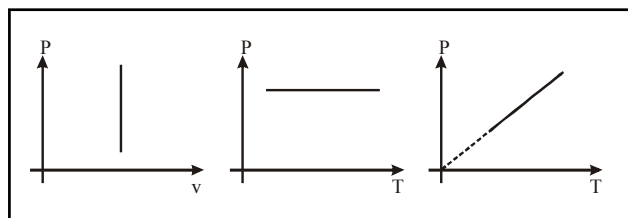
- Propagation of sound waves in the form of compression & rarefaction
- Sudden bursting of a cycle tube.

## 2.5.3 Isochoric Process

**Description :** Volume remains constant

**Condition :** A gas being heated or cooled inside a rigid container.

**Equation of State :**  $V = \text{constant}$  or  $\frac{P}{T} = \text{constant}$



$$\begin{aligned} \Delta U &= \frac{n\gamma R \Delta T}{2} \\ &= \frac{nR(T_2 - T_1)}{r-1} \end{aligned}$$

$$\Delta U = \frac{P_2 V_2 - P_1 V_1}{r-1} = \frac{nR \Delta T}{r-1}$$

Work

$W = 0$  as gas does not expand

**First Law of thermodynamics**

$$Q = \Delta U + W$$

$$\Rightarrow Q = \frac{n f R \Delta T}{2} \quad \dots(7)$$

**Remarks :** Since we have studied earlier, that when heat is supplied to any process, its temp increases according to relation

$$Q = n C \Delta T$$

$$\Rightarrow C = \frac{Q}{n \Delta T}$$

Now this  $C$  depends upon external conditions for gases.

$$\text{Here it is referred as } \left[ \frac{\Delta Q}{n \Delta T} \right]_v \quad \dots(8)$$

i.e. Molar heat capacity at constant volume

Comparing equation 7 and 8

$$\text{We get } C_v = \frac{f R}{2} \quad \dots(9)$$

#### 2.5.4 Isobaric Process

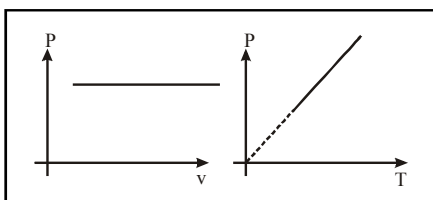
**Description :** When pressure remains constant

**Condition :** When in one container, the piston is free to move and is not connected by any agent.

**Equation of State :**  $P = \text{constant}$

$$\frac{V}{T} = \text{constant}$$

**Indicator Diagram :**



$$\Delta U = \frac{n f R \Delta T}{2} \quad \text{same as always}$$

$$\begin{aligned} W &= \int P dV = P \Delta V \\ &\quad (\text{as pressure is constant}) \\ &= P V_2 - P V_1 = n R \Delta T \end{aligned}$$

**First Law of Thermodynamics**

$$Q = \Delta U + W$$

$$\Rightarrow Q = \frac{n f R \Delta T}{2} + n R \Delta T$$

$$\Rightarrow Q = \left[ \frac{f R}{2} + R \right] \Delta T \quad \dots(10)$$

**Remarks :** Similar to  $C_v$ , we can define molar heat capacity at constant pressure

$$\Rightarrow C_p = \left[ \frac{Q}{n \Delta T} \right]_p \quad \dots(11)$$

From equation 10 & 11

$$\text{We get } C_p = \frac{f R}{2} + R \quad \dots(12)$$

From equation 9 & 12

Replacing  $\frac{f R}{2}$  by  $C_v$  we get

$$C_p = C_v + R \quad \dots(13)$$

which is also called as Mayer's Relation.

- Similar to molar specific heat at constant pressure and molar specific heat at constant volume, we can define molar specific heat for any process.

**For example :**

$C_{\text{adiabatic}} = 0$

$C_{\text{isothermal}} = \infty$

Basically gas does not possess a unique specific heat.

Mainly we have  $C_p$  &  $C_v$

**Specific Heat at Constant Volume :** It is defined as the amount of heat required to raise the temperature of 1g of a gas through  $1^\circ\text{C}$ , when its volume is kept constant. It is denoted as  $C_v$ .

**Specific Heat at Constant Pressure :** It is defined as the amount of heat required to raise the temperature of 1g of a gas through  $1^\circ\text{C}$  keeping its pressure constant. It is denoted as  $C_p$ .

- Please Note**  $C_p, C_v$  means Molar heat Capacity &  $C_p, C_v$  means specific heat capacity
- $C_v = M_{Cv}$  &  $C_p = M_{Cp}$  where  $M$  stands for molar mass of any sample.
- $C_p - C_v = \frac{R}{M}$

## 2.5.5 Melting Process

In any case first law is always applicable

$$Q = mL_f \quad \text{as learned earlier.}$$

$$W = 0$$

(In the change of state from solid to liquid we ignore any expansion or contraction as it is very small)

According to first law of thermodynamics

$$\Delta U = Q - W$$

$$\Delta U = mL_f$$

**Remark :** The heat given during melting is used in increasing the internal energy of any substance

## 2.5.6 Boiling Process

Here

$$Q = mL_v$$

$$W = P[V_2 - V_1]$$

(Pressure is constant during boiling and it is equal to atmospheric pressure)

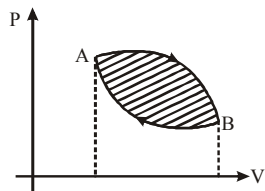
$$\Rightarrow \Delta U = Q - W$$

$$\Delta U = mL_v - P(V_2 - V_1)$$

## 2.5.7 Cyclic Process

A cyclic process is one in which the system returns to its initial stage after undergoing a series of changes

**Example Indicator Diagram**



$$\Delta U = 0$$

$W = \text{Area under the loop.}$

$Q = W$  as per First Law of thermodynamics

Here  $W$  is positive if the cycle is clockwise & it is negative if the cycle is anti clockwise.

## 2.6 Limitations of the First Law of Thermodynamics

- The first law does not indicate the direction in which the change can occur.
- The first law gives no idea about the extent of change
- The first law of thermodynamics gives no information about the source gives no information about the source of heat. i.e. whether it is a hot or a cold body.

## 2.7 Heat Engines

It is a device that converts heat energy into mechanical energy.

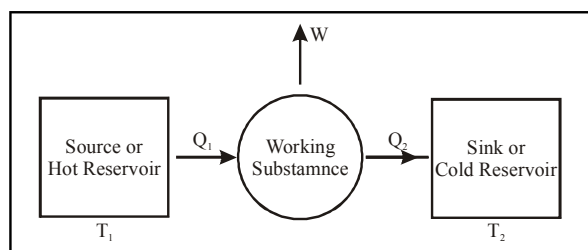
**Key Elements :**

- A source of heat at higher temperature
- A working substance
- A sink of heat at lower temperature.

**Working :**

- The working substance goes through a cycle consisting of several processes.
- In some processes it absorbs a total amount of heat  $Q_1$  from the source at temperature  $T_1$ .
- In some processes it rejects a total amount of heat  $Q_2$  to the sink at some lower temperature  $T_2$ .
- The work done by the system in a cycle is transferred to the environment via some arrangement.

**Schematic Diagram**



**First Law of Thermodynamics**

$\therefore$  Energy is always conserved

$$\Rightarrow Q_1 = W + Q_2 \quad \dots(14)$$

**Thermal Efficiency** of a heat engine is defined as the ratio of net work done per cycle by the engine to the total amount of heat absorbed per cycle by the working substance from the source. It is denoted by  $\eta$ .

$$\eta = \frac{W}{Q_1} \quad \dots(15)$$

Using equation 14 and 15 we get

$$\eta = 1 - \frac{Q_2}{Q_1} \quad \dots(16)$$

Ideally engines should have efficiency = 1

**Remarks :** The mechanism of conversion of heat into work varies for different heat engines.

- The system heated by an external furnace, as in a steam engine. Such engines are called as **external combustion engine**.

- The system in which heat is produced by burning the fuel inside the main body of the engine. Such an engine is called as **Internal Combustion Engine**.

### 2.8 Refrigerator and Heat Pumps

A refrigerator or heat pump is a device used for cooling things.

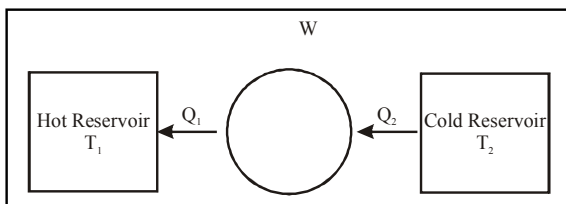
#### Key Elements :

- A cold reservoir at temperature  $T_2$ .
- A working substance.
- A hot reservoir at temperature  $T_1$

#### Working

- The working substance goes through a cycle consisting of several process.
- A sudden expansion of the gas from high to low pressure which cool it and converts it into a vapour-liquid mixture.
- Absorption by the cold fluid of heat from the region to be cooled converting it into vapour.
- Heating up of the vapour due to external work done on the working substance.
- Release of heat by the vapour to the surroundings bringing it to the initial state and completing the cycle.

#### Schematic Diagram.



#### First Law of Thermodynamics

$$Q_2 + W = Q_1 \quad \dots(17)$$

**Coefficient of Performance** of refrigerator ( $\beta$ ) is defined as the ratio of quantity of heat removed per cycle from contents of the refrigerator ( $Q_2$ ) to the energy spent per cycle ( $W$ ) to remove this heat

$$\beta = \frac{Q_2}{W} \quad \dots(18)$$

Using equation 17 and 18 we get

$$\beta = \frac{Q_2}{Q_1 - Q_2}$$

Ideally heat pumps should have  $\beta = \infty$

### 2.9 Second Law of Thermodynamics

There are number of ways in which this law can be stated.

Though all the statements are the same in their contents, the following two are significant.

**Kelvin Pnek 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.

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

**Significance :** 100% efficiency in heat engines or infinite CoP in refrigerators is not possible.

### 2.10 Reversible and Irreversible Process

**Reversible Process :** A thermodynamic process taking a system from initial state  $i$  to final state  $f$  is 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.

#### Conditions for reversibility :

- Process should proceed at an extremely slow rate, i.e., process is quasistatic so that system is in equilibrium with surroundings at every stage.
- The system should be free from dissipative forces like friction, inelasticity; viscosity etc.

**Examples :** No process exactly reversible, though a slow expansion of an ideal gas is approximately reversible.

**Irreversible Process :** A process which does not satisfy any of the conditions for reversible is called an irreversible process.

#### Causes :

- Spontaneous process
- Presence of friction, viscosity and such dissipative forces

#### Significance of Reversibility :

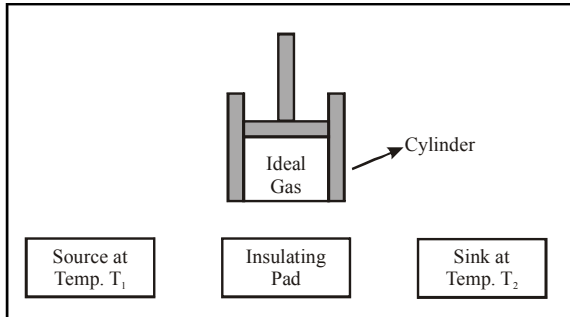
- Main concern of thermodynamics is the efficiency with which the heat is converted into Mechanical Energy.
- Second Law of Thermodynamics rules out the possibility of a perfect heat engine with 100% efficiency.
- It turns out that heat engine based on idealised reversible processes achieves the highest possible efficiency.

### 2.11 Carnot Engine

Sadi Carnot devised an ideal cycle of operation for a heat engine called as Carnot cycle.

Engine used for realising this ideal cycle is called as Carnot heat engine.

**Constructions :** The essential parts of an ideal heat engine or Carnot heat engine are shown in figure.



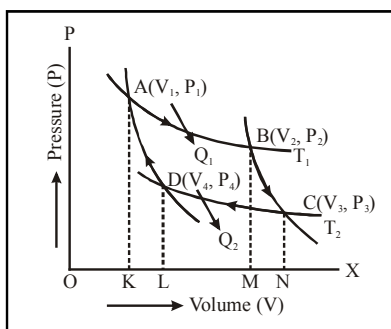
- (i) **Source of heat :** The source is maintained at a fixed higher temperature  $T_1$ , from which the working substance draws heat. The source is supposed to possess infinite thermal capacity and as such any amount of heat can be drawn from it without changing its temperature.
- (ii) **Sink of heat :** The sink is maintained at a fixed lower temperature  $T_2$ , to which any amount of heat can be rejected by the working substance. It has also infinite thermal capacity and as such its temperature remains constant at  $T_2$ , even when any amount of heat is rejected to it.
- (iii) **Working substance :** A perfect gas acts as the working substance. It is contained in a cylinder with non-conducting sides but having a perfectly conducting base. This cylinder is fitted with perfectly non-conducting and frictionless piston.

Apart from these essential parts, there is a perfectly **insulating stand or pad** on which the cylinder can be placed. It would isolate the working substance completely from the surroundings. Hence, the gas can undergo adiabatic changes.

The Carnot cycle consists of the following four stages :

1. Isothermal expansion
2. Adiabatic expansion
3. Isothermal compression
4. Adiabatic compression.

The cycle is carried out with the help of the Carnot engine as detailed below :



Consider one gram mole of an ideal gas enclosed in the cylinder. Let  $V_1, P_1, T_1$  be the initial volume, pressure and temperature of the gas. The initial state of the gas is represented by the point A on P-V diagram. We shall assume that all the four processes are quasi-static and non dissipative, the two conditions for their reversibility.

### Steps

#### 1. Isothermal Expansion :

The cylinder is placed on the source and gas is allowed to expand by slow outward motion of piston. Since base is perfectly conducting therefore the process is isothermal.

Now

$$\Delta U_1 = 0$$

$$q_1 = W_1 = RT_1/n \cdot \frac{V_2}{V_1} = \text{Area ABmKA}$$

$q_1 \rightarrow$  Heat absorbed by gas

$w_1 \rightarrow$  work done by gas

#### 2. Adiabatic Expansion :

The cylinder is now removed from source and is placed on the perfectly insulating pad. The gas is allowed to expand further from B( $P_2, V_2$ ) to C( $P_3, V_3$ ). Since the gas is thermally insulated from all sides, therefore the process is adiabatic

$$q_2 = 0$$

$$\Delta U_2 = \frac{R(T_2 - T_1)}{r - 1}$$

$$W_2 = \frac{R(T_3 - T_1)}{r - 1} = \text{Area BCNMB}$$

#### 3. Isothermal Compression :

The cylinder is now removed from the insulating pad and is placed on the sink at a temperature  $T_2$ . The piston is moved slowly so that the gas is compressed until pressure is  $P_4$  and volume is  $V_4$ .

$$\Delta U_3 = 0$$

$$W_2 = RT_2/n \cdot \frac{V_4}{V_3} = -\text{Area CDLNC}$$

$$q_3 = RT_2/n \cdot \frac{V_4}{V_3}$$

$q_3 =$  Heat absorbed in this process

$w_3 =$  Work done by Gas

#### 4. Adiabatic Compression :

The cylinder is again placed on the insulating pad, such that the process remains adiabatic. Here the gas is further compressed to its initial  $P_1$  and  $V_1$ .

$$\Delta U_4 = \frac{R(T_1 - T_2)}{r - 1}$$

$$W_4 = \frac{R(T_2 - T_1)}{r - 1} = -\text{area DAKLD}$$

$$q_4 = 0$$

$$w_4 = \text{work done by the gas}$$

#### Analysis :

Total work done by the engine per cycle.

$$= W_1 + W_2 + W_3 + W_4$$

$$= W_1 + W_3$$

$$W = RT_1/n \ln \frac{V_2}{V_1} + RT_2/n \ln \frac{V_4}{V_3}$$

$$Q_1 = \text{Total heat absorbed} = q_1$$

$$= RT_1/n \ln \frac{V_2}{V_1} \quad \dots(19)$$

$$Q_2 = \text{Total heat released} = -q_3$$

$[q_3 = \text{Heat absorbed \& not heat released}]$

$$= -RT_2/n \ln \frac{V_3}{V_4} \quad \dots(20)$$

We can see that for heat engine

$$W = Q_1 - Q_2$$

$$= \text{Area under ABCDA}$$

#### Efficiency of Carnot Engine

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

Now steps 2 is adiabatic 2 step 4 is also adiabatic

$$\Rightarrow T_1 V_2^{r-1} = T_2 V_3^{r-1}$$

$$\text{and } T_1 V_1^{r-1} = T_2 V_4^{r-1}$$

$$\Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \dots(21)$$

From equation 19, 20 and 21 we get

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

$$\therefore \eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1}$$

#### Division

- $\eta_{\text{Carnot engine}}$  - depends only upon source temperature and sink temperature.
- $\eta_{\text{Carnot engine}} = 1$  only when  $T_2 = 0 \text{ K}$  or  $T_1 = \infty$  which is impossible to attain.
- If  $T_2 = T_1 \Rightarrow \eta = 0 \Rightarrow$  Heat cannot be converted to mechanical energy unless there is same difference between the temperature of source and sink.

#### 2.12 Carnot Theorem

##### Statement :

- Working between two given temperatures,  $T_1$  of hot reservoir (the source) and  $T_2$  of cold reservoir (the sink, 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.

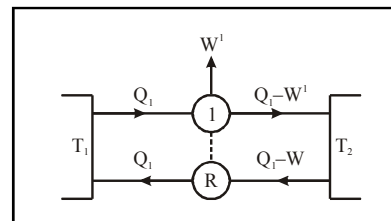
Engine used for realising this ideal cycle is called as Carnot engine.

##### Proof:

**Step - 1 :** Imagine a reversible engine R and an irreversible engine-I working between the same source (hot reservoir  $T_1$ ) and sink (cold reservoir  $T_2$ ).

**Step - 2 :** Couple two engines such that I acts like heat engine and R acts like refrigerator.

**Step - 3 :** Let engine I absorb  $Q_1$  heat from the source deliver work  $W^1$  and release the balance  $Q_1 - W^1$  to the sink in one cycle.



**Step - 4 :** Arrange R, such that it returns same heat  $Q_2$  to the source, taking  $Q_2$  from the sink and requiring work  $W = Q_1 - Q_2$  to be done on it.

**Step - 5 :** Suppose  $\eta_R < \eta_I$  (i.e.) If R were to act as an engine it would give less work output than that of I (i.e.)  $W < W^1$  for a given  $Q_1$  and  $Q_1 - W > Q_1 - W^1$



**Step - 6 :** In totality, the I-R system extracts heat  $(r_1 - W) - (Q_1 - W^1) = W^1 - W$  & delivers same amount of work in one cycle, without any change in source or anywhere else. This is against second Law of Thermodynamics. (Kelvin - Planck statement of second law of thermodynamics)

Hence the assertion  $q_1 > q_R$  is wrong.

- Similar argument can be put up for the second statement of carnot theorem, (ie) Carnot efficiency is independent of working substance.

∴ We use ideal gas to else are calculating but the relation.

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \text{ will always hold true for any working substance}$$

used in a carnot engine.

## 3. KINETIC THEORY OF GASES

In this topic, we discuss the behaviour of gases and how are the various state variable like P, V, T, moles, U are inter-related with each other

### 3.1 Molecular Nature of Matter

Same as Atomic Theory given by Delton. According to him, atoms are the smallest constituents of elements. All atoms of one element are identical, but atoms of different element are different.

**In solids :** Atoms tightly packed, interatomic spacing about Å. Interatomic force of attraction are strong.

**In liquids :** Atoms are not as rigidly fixed as in solids. Interatomic spacing is about the same 2Å. Interatomic for a attraction are relative weaker.

**In Gases :** Atoms very free. Inter atomic spacing is about tens of Angstroms. Interatomic forces are much weaker in gases than both in solids and liquids.

In this chapter, we mainly focus on gases.

### 3.2 Molecular Nature of Matter

#### 3.2.1 Ideal Gas

That gas which strictly obeys the gas laws, (such as Boyle's Law, Charles, Gay Lussac's Law etc.)

#### Characteristics

- The size of the molecule of an ideal gas is zero.

- There is no force of attraction or repulsion amongst the molecules of an ideal gas.

#### 3.2.2 Real Gas

All gases are referred to as real Gases.

All real gas near the ideal gas behaviour at low pressures and temperatures high enough, where they cannot be liquified.

#### 3.2.3 Ideal Gas Laws

**Avogadro Hypothesis :** Equal volumes of all gas under identical conditions of pressure and temperature would contain equal number of molecule.

#### Perfect Gas Equation :

$$PV = nRT$$

$$\text{and } P = \frac{SRT}{M}$$

where  $n$  = Number of moles.

$$r = \text{Universal Gas constant} = N_A k_B$$

where  $N_D$  = Avagadro No.

$$k_B = \text{Boltzman constant}$$

$$R = 8031 \text{ J/mol K.}$$

$$R = 1.98 \text{ Cal/mol K.}$$

**Boyle's Law :** When temperature of a given mass of gas is kept constant, its pressure varies inversely as the volume of gas.

$$(i.e.) \quad PV = \text{constant}$$

**Charles Law :** When pressure of a given mass of kept constant, volume of the gas varies directly as the temperature of the gas.

$$(i.e.) \quad V \propto T$$

**Dalton's Law of Partial Pressures :** The total pressure of a mixture of ideal gases is the sum of partial pressures exerted by the individual gases in the mixture.

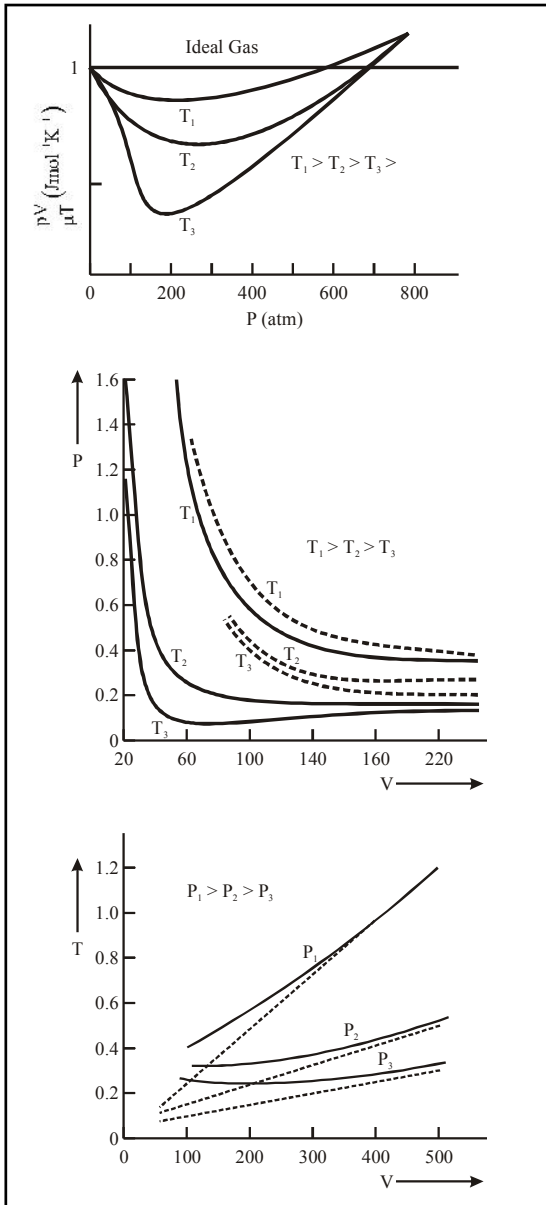
$$P-V = (n_1 + n_2 + n_3 + \dots)RT$$

$$\Rightarrow P = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V}$$

$$P = P_1 + P_2 + \dots$$

$$\text{where } P_1 = \frac{n_1 RT}{V} \text{ Pressure of gas}$$

### Deviation of Real Gas from Ideal Gas :



### 3.3 Kinetic Theory Postulates

1. A gas consists of a very large number of molecules (of the order of Avogadro's number,  $10^{23}$ ), which are perfect elastic spheres. For a given gas they are identical in all respects, but for different gases, they are different.
2. The molecules of a gas are in a state of incessant random motion. They move in all directions with different speeds, (of the order of 500 m/s) and obey Newton's laws of motion.
3. The size of the gas molecules is very small as compared to the distance between them. If typical size of molecule is  $2 \text{ \AA}$ , average distance between the molecules is  $\geq 20 \text{ \AA}$ . Hence

volume occupied by the molecules is negligible in comparison to the volume of the gas.

4. The molecules do not exert any force of attraction or repulsion on each other, except during collision.
5. The collisions of the molecules with themselves and with the walls of the vessel are perfectly elastic. As such, that momentum and the kinetic energy of the molecules are conserved during collisions, though their individual velocities change.
6. There is not concentration of the molecules at any point inside the container i.e. molecular density is uniform throughout the gas.
7. A molecule moves along a straight line between two successive collisions and the average straight distance covered between two successive collisions is called the **mean free path** of the molecules.
8. The collisions are almost instantaneous, i.e., the time of collision of two molecules is negligible as compared to time interval between two successive collisions.

### 3.4 Pressure of an Ideal Gas and its Expression

Pressure exerted by the gas is due to continuous bombardment of gas molecules against the walls of the container.

#### Expression :

Consider a gas enclosed in a cube of side 1. Take the axes to be parallel to the sides of the cube, as shown in figure. A molecule with velocity  $(v_x, v_y, v_z)$  hits the planar wall parallel to  $yz$ -plane of area  $A (= l^2)$ . Since the collision is elastic, the molecule rebounds with the same velocity; its  $y$  and  $z$  components of velocity do not change in the collision but the  $x$ -component reverses sign. That is, the velocity after collision is  $(-v_x, v_y, v_z)$ . The change in momentum of the molecule is  $:-mv_x - (mv_x) = -2mv_x$ . By the principle of conservation of momentum, the momentum imparted to the wall in the collision  $= 2mv_x$ .

To calculate the force (and pressure) on the wall, we need to calculate momentum imparted to the wall per unit time, if it is within the distance  $v_x \Delta t$  from the wall. that is, all molecules within the volume,  $Av_x \Delta t$  only can hit the wall in time  $\Delta t$  is  $1/2 Av_x \Delta t n$  where  $n$  is the number of molecules per unit volume. The total momentum transferred to the wall by these molecules in time  $\Delta t$  is :

$$Q = (2mv_x) (1/2 n Av_x \Delta t)$$

The force on the wall is the rate of momentum transfer  $Q/\Delta t$  and pressure is force per unit area :

$$P = Q/(A \Delta t) = nm v_x^2$$

Actually, all molecules in a gas do not have the same velocity; there is a distribution in velocities. The above equation therefore, stands for pressure due to the group of molecules with speed  $v_x$  in the x-direction and  $n$  stands for the number density of that group of molecules. The total pressure is obtained by summing over the contribution due to all groups:

$$P = nm\overline{v_x^2}$$

where  $\overline{v_x^2}$  is the average of  $v_x^2$ . Now the gas is isotropic, i.e. there is no preferred direction of velocity of the molecules in the vessel. Therefore by symmetry,

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

$$= \left(\frac{1}{3}\right) [\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}] = \left(\frac{1}{3}\right) \overline{v^2}$$

where  $v$  is the speed and  $\overline{v^2}$  denotes the mean of the squared speed. Thus

$$P = \left(\frac{1}{3}\right) nm\overline{v^2}$$

$$P = \frac{1}{2} mn\overline{v^2} = \frac{1}{2} \frac{M}{V} \overline{v^2} \quad \dots(22)$$

$M$  = Total mass of gas molecules

$V$  = Total volume of gas molecules

## 3.4.1 Relation between Pressure and KE of Gas Molecules

From equation 22

$$P = \frac{1}{3} S\overline{v^2}$$

$$\Rightarrow P = \frac{2}{3} E$$

$\Rightarrow$  Pressure exerted by an ideal gas is numerically equal to two third of mean kinetic

## 3.4.2 Average KE per molecule of the Gas

From equation 22

We know

$$P = \frac{1}{3} \frac{M}{V} \overline{v^2}$$

$$\Rightarrow PV = \frac{1}{3} M\overline{v^2} \quad \dots(23)$$

with equation 23 and Ideal gas equation

$$nRT = \frac{1}{3} M\overline{v^2}$$

$$\Rightarrow nRT = \frac{1}{3} Nm\overline{v^2}$$

$$\Rightarrow \frac{n}{N} \frac{3RT}{2} = \frac{1}{2} m\overline{v^2}$$

$$\text{Also } N = nN_A$$

$$\Rightarrow \frac{3}{2} \frac{R}{N_A} = \frac{1}{2} m\overline{v^2}$$

$$\text{Average KE of translation per molecule of the gas } = \frac{3}{2} k_B T$$

## 3.5 Kinetic Interpretation of Temperature

From above equations, we can easily see that KE of one molecule is only dependent upon its Temperature.

$\Rightarrow$  KE of molecule will cease if, the temperature of the gas molecules become absolute zero.

$\therefore$  Absolute zero of a temperature may be defined as that temperature at which the root mean square velocity of the gas molecule reduces to zero.

All the ideal gas laws can be derived from Kinetic Theory of gases.

## 3.6 Derivation of Gas Laws from Kinetic Theory

### 3.6.1 Boyle's Law

$$\text{We know that } PV = \frac{2}{3} N\overline{K}$$

where  $\overline{K}$  is the average kinetic energy of translation per gas molecule. At constant temperature,  $\overline{K}$  is constant and for a given mass of the gas,  $N$  is constant.

Thus,  $PV = \text{constant}$  for given mass of gas at constant temperature, which is the Boyle's Law.

### 3.6.2 Charle's Law

$$\text{We know that } PV = \frac{2}{3} N\overline{K}$$

For a given mass of gas,  $N$  is constant.

Since  $\bar{K} = \frac{3}{2} k_B T$ ,  $\bar{K} \propto T$  and as such  $PV \propto T$ .

If  $P$  is constant,  $V \propto T$ , which is the Charles' Law.

### 3.6.3 Constant Volume Law

We know that  $PV = \frac{2}{3} N\bar{K}$

For a given mass of gas,  $N$  is constant. Since

$$\bar{K} = \frac{3}{2} k_B T, \bar{K} \propto T$$

Thus,  $PV \propto T$

If  $V$  is constant,  $P \propto T$ , which is the constant volume law.

### 3.6.4 Ideal Gas Equation

$$\text{As } PV = \frac{2}{3} N\bar{K} \text{ and } \bar{K} = \frac{3}{2} k_B T$$

$$PV = \frac{2}{3} N \left( \frac{3}{2} k_B T \right) \text{ or } PV = Nk_B T$$

which is the ideal gas equation.

### 3.6.5 Avogadro's Law

Consider two gases 1 and 2. We can write

$$P_1 V_1 = \frac{2}{3} N_1 \bar{K}_1, P_2 V_2 = \frac{2}{3} N_2 \bar{K}_2$$

If their pressures, volumes and temperatures are the same, then

$$P_1 = P_2, V_1 = V_2, \bar{K}_1 = \bar{K}_2.$$

Clearly,  $N_1 = N_2$ . Thus:

**Equal volumes of all ideal gases existing under the same conditions of temperature and pressure contain equal number of molecules which is Avogadro's Law or hypothesis.**

This law is named after the Italian physicist and chemist, Amedeo Avogadro (1776–1856).

**Alliter :** As  $PV = Nk_B T$ ,  $N = \frac{PV}{k_B T}$

If  $P$ ,  $V$  and  $T$  are constants,  $N$  is also constant.

### 3.6.6 Graham's Law of Diffusion

The rate ( $r$ ) of diffusion of a gas through a porous pot or into another gas is determined by the rms speed of its molecules, i.e.,

$$r \propto v_{rms}$$

$$\text{But as } v_{rms} = \sqrt{\frac{3P}{\rho}}, r \propto \sqrt{\frac{3P}{\rho}} \text{ or } r \propto \frac{1}{\sqrt{\rho}}$$

Therefore, if  $r_1$  and  $r_2$  are the rates of diffusion of two gases of densities  $\rho_1$  and  $\rho_2$  respectively,

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

**The rates of diffusion of two gases are thus inversely proportional to the square roots of their densities which is Graham's Law of diffusion.**

### 3.6.7 Dalton's Law of Partial Pressures

The kinetic theory of gases attributes the gas pressure to the bombardment of the walls of the containing vessel by molecules. In a mixture of ideal gases, we might therefore expect the total pressure ( $P$ ) to be the sum of the partial pressures ( $p_1, p_2, \dots$ ) due to each gas, i.e.,

$$P = p_1 + p_2 + \dots = \frac{2}{3} \frac{N_1}{V_1} \bar{K}_1 + \frac{2}{3} \frac{N_2}{V_2} \bar{K}_2 + \dots$$

$$\text{or } P = \frac{2}{3} \left( \frac{N_1}{V_1} \bar{K}_1 + \frac{N_2}{V_2} \bar{K}_2 + \dots \right)$$

In equilibrium, the average kinetic energy of the molecules of different gases will be equal, i.e.,

$$\bar{K}_1 = \bar{K}_2 = \dots = \bar{K} = \frac{3}{2} k_B T$$

Thus,

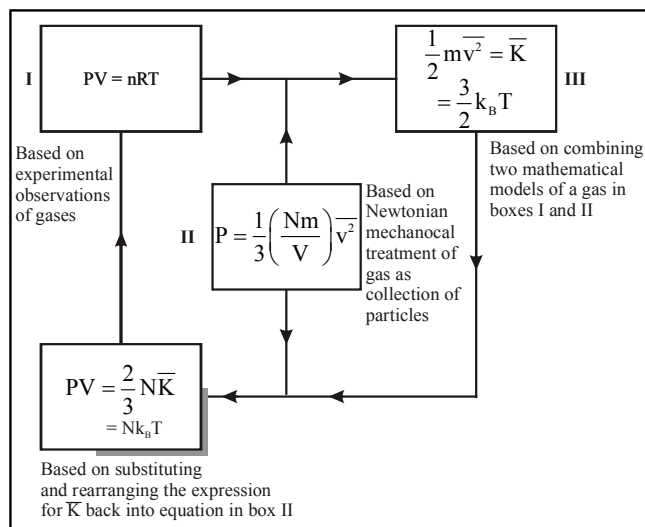
$$P = \frac{2}{3} (n_1 + n_2 + \dots) \left( \frac{3}{2} k_B T \right) = (n_1 + n_2 + \dots) k_B T \quad \dots(24)$$

$$\text{where } n_1 = \frac{N_1}{V_1}, n_2 = \frac{N_2}{V_2} \dots$$

Equation (24) represents Dalton's Law of partial pressures which states that :

**The resultant pressure exerted by a mixture of gases or vapours which do not interact in any way is equal to the sum of their individual (i.e., partial) pressures.**

Figures shows a model explaining kinetic theory of gases. It has been constructed in accordance with theory on one hand and real experimental observations on the other hand.



The above piece of logic is tempting but false. This is due to the reason that though the equation in box IV is useful, it does not tell us anything new, since it results from combining equations in boxes II and III.

## 3.7 Internal Energy

As studied in thermodynamics, Internal Energy of any substance is the combination of Potential Energies & Kinetic Energies of all molecules inside a given gas.

- In real gas

Internal Energy = P.E of molecules + K.E of Molecules

- In real gas

Internal Energy = K.E of Molecules

Here PE of molecules is zero as assumed in Kinetic theory postulates; There is no interaction between the molecules hence its interactional energy is zero.

## 3.8 Degree of Freedom

The number of degrees of freedom of a dynamical system is defined as the total number of co-ordinates or independent quantities required to describe completely the position & configuration of the system.

**Example :**

- A particle moving in straight line, say along X-axis need only x coordinate to define itself. It has only degree of freedom.
- A particle in a plane, needs 2 co-ordinates, hence has 2 degree of freedom.

In general if

A = number of particles in the system

R = number of independent relations among the particles

N = Number of degrees of freedom of the system

$$N = 3A - R$$

### 3.8.1 Monoatomic Gases

The molecules of a monoatomic gas (like neon, argon, helium etc) consists only of one atom.

$$\therefore A = 1$$

$$R = 0$$

$$\therefore N = 3$$

Here 3 degrees of freedom are for translational motion

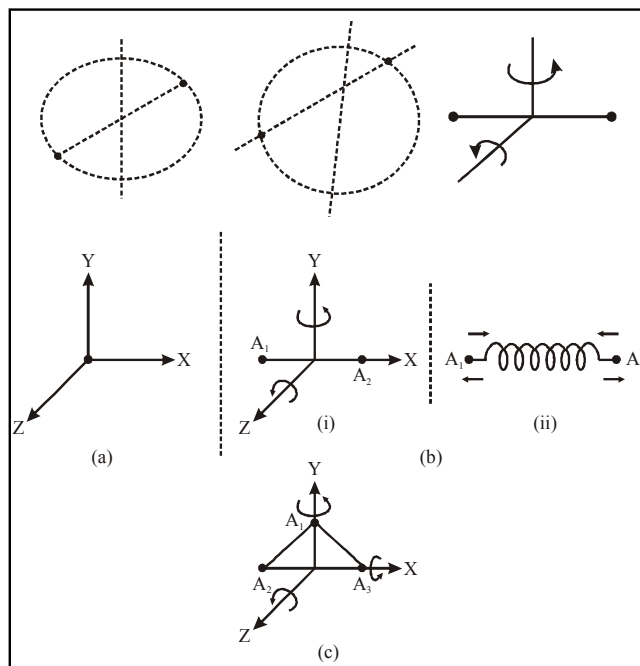
### 3.8.2 Diatomic Gases

$$A = 2$$

Assuming the distance between the two molecules is fixed then R = 1

$$\Rightarrow N = 3 \times 2 - 1 = 5$$

Here 5 degrees of freedom implies combination of 3 translational energies and 2 rotational energies.



If vibrational motion is also considered then [only at very high temperatures

$$N = 7$$

where 3 for translational

2 for rotational

2 for vibrational

### 3.8.3 Triatomic Gas

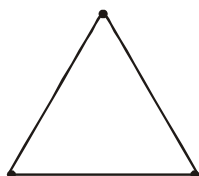


**Linear**

$$A=3$$

$$R=2$$

$$\Rightarrow N=3 \times 3 - 2 = 7$$

**Non-Linear**


$$A=3$$

$$R=2$$

$$\Rightarrow N=3 \times 3 - 3 = 6$$

- Here again vibrational energy is ignored.

**3.8.4 Polyatomic Gas**

A polyatomic gas has 3 translational, 3 rotational degrees of freedom. Apart from them if there are  $v$  vibrational modes then there will be additional  $2v$  vibrational degrees of freedom.

$\therefore$  Total degree of freedom

$$n = 3 + 3 + 2V = 6 + 2V$$

**3.9 Law of Equipartition of Energy**

**Statement :** According to this law, for any dynamical system in thermal equilibrium, the total energy is distributed equally amongst all the degrees of freedom, and the energy associated with each molecule per degree of freedom is

$\frac{1}{2} k_B T$ , where  $k_B$  is Boltzmann constant and  $T$  is temperature of the system.

**Application :**  $U = f \frac{k_B T}{2}$  where  $f$  = Total degree of freedom.

This law is very helpful in determining the total internal energy of any system be it monoatomic, diatomic or any polyatomic. Once the internal energy is known we can very easily predict  $C_v$  &  $C_p$  for such systems.

**Remark :** In case vibrational motion is also there in any system, say for diatomic molecule, then there should be energy due to vibrational as well given by

$$E_v = \frac{1}{2} m \left( \frac{dy}{dt} \right)^2 + \frac{1}{2} ky^2$$

where  $\frac{dy}{dt}$  = vibrational velocity

and  $\frac{ky^2}{2}$  = Energy due to configuration

According to Law of Equipartition

Energy per degree of freedom =  $\frac{1}{2} k_B T$

$$\Rightarrow = \frac{1}{2} k_B T + \frac{1}{2} K_B T = K_B T \text{ is energy for}$$

complete one vibrational mode.

**3.10 Specific Heat Capacity**

With the knowledge of law of equipartition, we can predict the heat capacity of various gases.

**3.10.1 Monoatomic Gas**

Degree of freedom = 3.

$\therefore$  Average Energy of a molecule at temperature  $T$

$$\Rightarrow E = 3 \left( \frac{1}{2} k_B T \right)$$

Energy for one mole  $\Rightarrow E \times N_A$

$$\Rightarrow U = \frac{3}{2} (k_B N_A) T$$

$$\Rightarrow U = \frac{3}{2} RT$$

In thermodynamics, we studied

$$C_v = \left[ \frac{\Delta Q}{\Delta T} \right]_v = \frac{\Delta U}{\Delta T} \quad [\because W = 0 \text{ for constant } v]$$

$$\Rightarrow C_v = \frac{3R}{2}$$

$$\therefore C_p = \frac{5R}{2} \quad \& \quad \gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

**3.10.2 Diatomic Gases**

When no vibration

Degree of freedom = 5

Average energy for one mole =  $\frac{5}{2} RT$

$$\therefore C_v = \frac{\Delta U}{\Delta T} = \frac{5}{2} R$$

$$C_p = \frac{7R}{2}$$

$$r = \frac{C_p}{C_v} = \frac{7}{5}$$

When vibration is present.

There is only one mode of vibration between 2 molecules.

$$\therefore \text{Degree of freedom} = 7$$

$$\therefore U = \frac{7}{2} RT$$

$$\Rightarrow C_v = \frac{7}{2} R$$

$$\text{and } C_p = \frac{9}{2} R$$

$$\text{and } r = \frac{9}{7}$$

### 3.10.3 Polyatomic Gases

Degree of freedom

= 3 for translational

+ 3 for rotational

+ 2v for vibrational

= 6 + 2v

if v = Number of vibrational modes

$$\therefore U = (6 + 2v) K \frac{RT}{2}$$

$$\Rightarrow C_v = (3 + V)R$$

$$C_p = (4 + V)R$$

$$\text{and } r = \frac{4 + V}{3 + V}$$

### 3.10.4 Specific heat capacity of solids

- In solids, there is very less difference between heat capacity at constant pressure or at constant volume. Therefore we do not differentiate between  $C_p$  &  $C_v$  for solids.

$$\therefore C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T}$$

{As solids hardly expand or expansion is negligible}

Now in solid the atoms are arranged in an array structure and they are not free to move independently like in gases.

Therefore the atoms do not possess any translational or rotational degree of freedom.

On the other hand, the molecules do possess vibrational motion along 3 mutually perpendicular directions.

Hence for 1 mole of a solid, there are  $N_A$  number of atoms.

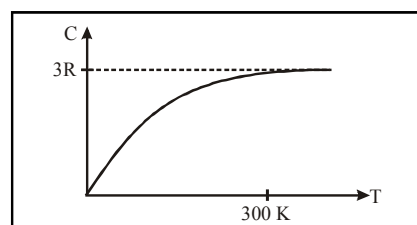
The energy associated with every molecule

$$= 3 \left[ 2 \times \frac{1}{2} k_B T \right] = 3K_B T$$

$$\therefore U = 3 R t \text{ for one mole}$$

$$\therefore C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3R$$

- The above equation is called as Dulong & Petit's Law.
- At low temperatures the vibrational mode may not be that active hence, heat capacity is low at low temperatures for solids.



### 3.10.5 Specific heat capacity of Water

Water is treated like solid.

Water has three atoms, 2 of hydrogen and one of oxygen

$$\therefore \text{Total degree of freedom for every atom} = 3 \times 2 = 6$$

$$\therefore \text{Total degree of freedom for every molecule of water} = 3 \times 2 = 18$$

$$\therefore C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = \frac{\left( 18 \times \frac{1}{2} R \Delta T \right)}{\Delta T}$$

$$C = 9R$$

### 3.11 Maxwell Law of Distribution of Molecular

#### Assumptions of Maxwell Distribution

- Molecules of all velocities between 0 to  $\infty$  are present.
- Velocity of one molecule, continuously changes, though fraction of molecules in one range of velocities is constant.

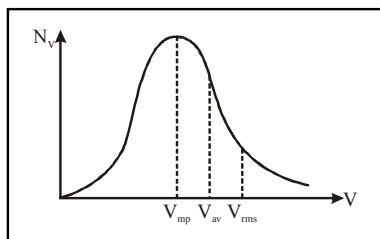
#### Result

$$N_v = 4\pi N \left( \frac{M}{2\pi k_B T} \right)^{3/2} V^2 e^{-\frac{mv^2}{2k_B T}}$$

Where  $N_v = \frac{dN_v}{d_v}$

Where  $N_v$  = Total number of molecules with speeds between  $V$  &  $V + dV$

$N$  = Total number of molecules.



Based on this we define three types of speed of molecules of gas

$$V_{rms} = (\overline{V^2})^{1/2} = \left[ \frac{1}{N} \int V^2 dN(V) \right]^{1/2}$$

$$V_{rms} = \sqrt{\frac{3RT}{M}}$$

Where  $M$  = Molecular Mass of Gas

Similarly  $V_{av} = \bar{V} = \frac{1}{N} \int V dN_v$

$$= \sqrt{\frac{8RT}{\pi M}}$$

But  $V_{MP}$  is velocity at which  $\frac{dN_v}{dv} = 0$

$$\Rightarrow V_{MP} = \sqrt{\frac{3RT}{M}}$$

Physically  $V_{MP}$  is velocity possessed by Maximum number of molecules.

**Remarks :**

$$V_{rms} > V_{av} > V_{MP}$$

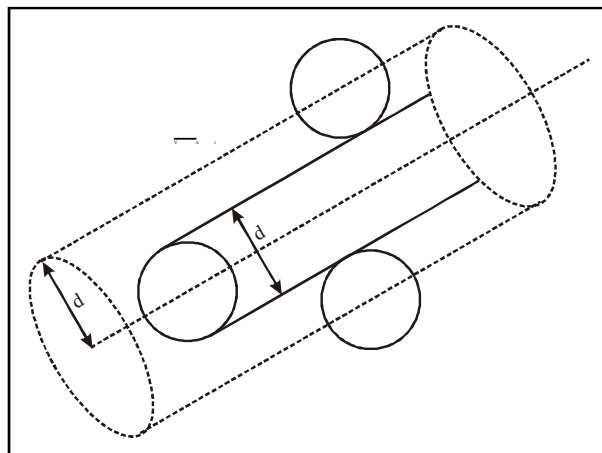
### 3.12 Mean Free Path

The path traversed by a molecule between two successive collisions with other molecule is called the free path

$$\bar{l} = \frac{\text{Total distance travelled by a molecule}}{\text{No. of collisions it makes with other molecules.}}$$

**Expression :**

**Mean Free Path**



Suppose the molecules of a gas are spheres of diameter  $d$ . Focus on a single molecule with the average speed  $\langle v \rangle$ . It will suffer collision with any molecule that comes within a distance  $d$  between the centres. In time  $\Delta t$ , it sweeps a volume  $\pi d^2 \langle v \rangle \Delta t$  wherein any other molecule will collide with it (as shown in figure). If  $n$  is the number of molecules per unit volume, the molecule suffers  $n\pi d^2 \langle v \rangle \Delta t$  collisions in time  $\Delta t$ . thus the rate of collisions is  $n\pi d^2 \langle v \rangle$  or the time between two successive collisions is on the average.

$$\tau = 1/(n\pi \langle v \rangle d^2)$$

The average distance between two successive collisions, called the mean free path  $l$ , is :

$$l = \langle v \rangle \tau = 1/(n\pi d^2)$$

In this derivation, we imagined the other molecules to be at rest. But actually all molecules are moving and the collision rate is determined by the average relative velocity of the molecules. Thus we need to replace  $\langle v \rangle$  by  $\langle vr \rangle$  in equation. A more exact treatment.

$$l = \frac{1}{(\sqrt{2}n\pi d^2)}$$

**Result**

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

**Remark :** Mean free path depends inversely on the number density and size of the molecule.

### 3.13 Brownian Motion

The irregular movement of suspended particles like tiny dust particles or pollen grains in a liquid is called Brownian Motion.