Chapter V: HEAT & THERMODYNAMICS

Subtle manifestation of life is heat. But heat, is something not perceivable while temperature is. Likewise, potential and kinetic energy are not directly perceivable while height and velocity, respectively, are perceivable. Another, interesting observation that is worth experimenting is to keep Two different objects of same size and shape in the sun, together for half-an-hour and feel their temperature; one object is hotter than the other. Perception of heat is temperature while heat is not directly perceivable.

Another, interesting example is when a student is in hurry to go to school and milk gets overheated, mother mixes chilled milk to moderate the temperature so as to make milk drinkable. In another situation of making tea there are two observations, one is initially small bubbles, rising from bottom of the utensil to the top of water, used for making tea, and then bursting , while the hot utensil is held with a ebonite or wooden handle.

Another situation is encountered when same matter at same temperatures in different phases has different heat content viz. burns caused by steam and boiling water. There are many more examples encountered in day-to-day living; they are practiced without questioning, either by convention or experience. Likewise, transfer of heat in solids, liquids and gases through a medium and in absence of a medium, i.e. vacuum, involves different phenomenon. A journey into understanding these phenomenon, becomes quite interesting and involves multiple concepts to make human response intuitive.

ZEROTH LAW OF THERMODYNAMICS: Two different objects A and B when at same temperature are brought into contact, in a closed environment, they remain at the same temperature. Such a state when Two objects are at same temperature, and continue to be so, are stated to be in ***thermal equilibrium***. It is different from equilibrium encountered in mechanics; reason attributed to this difference is that forces are vectors while, temperature is scalar. Likewise, taking another object C is in *thermal equilibrium* with one of the earlier Two, say B; the latter object C is also in *thermal equilibrium* with the third object, A. Thus, *set of these objects from perspective of heat is called **Thermodynamic System***

The observation is promulgated as **Zeroth Law of Thermodynamics** and stated as ***if two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other. Thus thermal equilibrium between two systems is transitive in nature***. Essence of thermodynamic equilibrium is temperature, a perceivable attribute of a matter. Measurement of temperature involves different properties of matter, each of which in different ways. In view of this it provides an integrated perspective on measurement of temperature, which shall be elaborated at the end of the Chapter on Heat. Nevertheless, to facilitate the journey into concepts of heat Four most commonly used scales of temperature are Kelvin, Centigrade, Fahrenheit, Rankine named along with convertibility from one scale to another.

TEMPERATURE SCALE: Transition of temperature from biological experience or perception to numerical observation has a long history, An ancient Greek scientist was first to measure temperature in 170 AD in equal parts between freezing and boiling points of water, and extended to Four parts below and beyond either side of the scale. Later, Galileo around 1592 invented a Manometer type air-bulb thermometer with an open end exposed to atmosphere; changes in atmospheric pressure introduced error in measurement. These primitive efforts to measure temperature were followed by numerous scales of measurement and among them Four Scales are in prominent use.

Daniel Gabriel Fahrenheit in 1724 proposed a scale defining 0^0F for freezing temperature of brine (equal parts of ice and salt and 32ºF for melting point of ice. He extrapolated it on a linear scale to
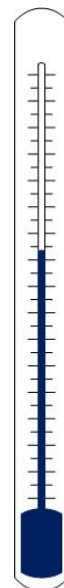
212ºF for boiling point of water at *sea level, standard atmospheric pressure*. This scale is known after the name of the inventor as *Fahrenheit*.

Later, a Swedish scientist Andres Celsius in 1742 proposed a temperature scale which identified 0ºC as freezing point of water and 100ºC as boiling point of water at 1 atmospheric pressure. These two identified temperatures are divided in 100 equal parts got a name *Centigrade* **(ºC).** In 1948, International Conference on Weights and Measures named it after the inventor as Celsius retaining the notation **(ºC).**

In 1848 Lord Kelvin of Scotland proposed a **Kelvin Scale** which had graduation of each degree equal to that in Celsius scale. It was based on a proposition that ***Absolute Zero (0ºK)*** is *a theoretical temperature of thermodynamic equilibrium corresponding to minimum energy*. This temperature is 273.15 degrees below the freezing of water. This was correlated to triple point of water, a temperature at which water can coexist in either of the three phases, solid (ice), liquid (water) and gas (vapour) states. This point is since 0.01ºC, therefore this point corresponds to 273.16K; since 1967 convention of scale as ºK has been discontinued. In normal calculations, where accuracy is not important , freezing point of water is taken as 273ºK; this approximation is similar to that in to value of acceleration due to gravity (*g*) taken as either 9.8 or 10.

Eleven years after Kelvin, in 1859 William John Macquorn Rankine, proposed a scale which had Zero corresponding to absolute Zero as postulated by Kelvin, but chose graduation with a difference equal to that of Fahrenheit scale. This is called Rankine Scale using notation (ºR). This scale is popular in United States.

In these four popular scales, the basic scales are Celsius and Fahrenheit which are related with an equation $\frac{F-32}{9} = \frac{C}{5}$, while conversion of Celsius and Fahrenheit to Kelvin and Rankine is by adding a bias 273.16 and 491.67, respectively. Accordingly, some typical temperatures on these Four scales are as under -

Reference	Kelvin (K)	Celsius (ºC)	Fahrenheit (ºF)	Rankine (ºR)
Absolute Zero	0	-273.15	-459.67	0
Freezing Point of Brine	255.37	-17.78	0	459.67
Freezing Point of Water	273.15	0	32	491.67
Triple Point of Water	273.16	0.01	32.018	491.688
Boiling Point of Water at Sea Level	373.1339	99.9839	211.97102	671.64102

Use of electrical method using property of resistance which increases monotonically with temperature has given rise to another scale called ***Platinum***. In this Wheatstone bridge is used which will be elaborated in chapter on Electromagnetism, in this Mentors' Manual. However, temperature in this scale is briefly

$t = \frac{R_t - R_0}{R_{100} - R_0} \times 100$ degrees. Grading of temperature in the Platinum

scale is equal to the grading in Celsius scale. Platinum is preferred choice due to its high melting point and chemically stability.

CALORIMETRY: It is a science used in *quantification of heat transfer* based on observation that when two substances A and B at different temperatures T_1 and T_2 such that $T_1 > T_2$ are mixed or brought in contact, with a thermal isolation from environment, transfer of heat
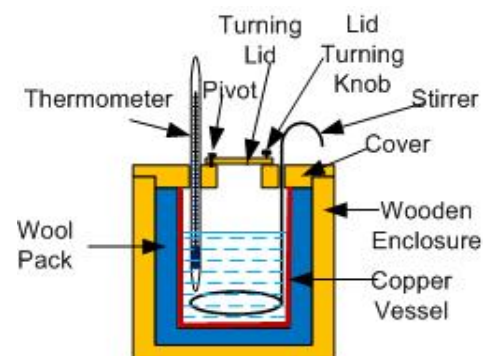
from A to B will take place till both A & B reach a common temperature T which shall be $T_1 > T > T_2$. As per *principle of conservation of energy* heat imparted by A in heat transfer is equal to heat gained by heat gained by B. Quantification of heat transfer required a **unit of heat energy** defined as **Calorie** by Nicolas Clement in 1824. Unlike other units this is not named after a scientist but, it is derived from a Latin word Calor. ***A calorie is defined as amount of heat required to increase temperature of one gram of water from 14.5 °C to 15.5 °C at One atmospheric pressure.***

Basic instrument used in Calorimetry is called Calorimeter as shown in the figure. It has copper vessel surrounded by wool pack, fitted inside a wooden enclosure to insulate walls of the vessel to check transfer of heat inside it to the environment. The box has wooden cover which has three openings – i) for thermometer, ii) for stirrer to create an equilibrium conditions and iii) turning lid to immerse an external object in liquid contained in the vessel, as per experimental requirement. Liquid in the vessel provides proper contact with the calorimeter, thermometer and any other object used in experiment.

Here, a new term ***Specific heat (s)** is introduced, which is defined as amount of heat (in Calorie abbreviated as **Cal**) required to increase temperature of One gram of substance by 1°C.* Accordingly, for a substance of mass m, heat required to raise temperature from θ_1 to θ_2°C is h Calorie, then according to the definition of *specific heat* $h = ms(\theta_2 - \theta_1)$, or $s = \frac{h}{m(\theta_2 - \theta_1)}$. This relationship is also true for loss of heat, in which case is h (–)ve, and so also $(\theta_2 - \theta_1)$ becomes (–)ve, thus s has an absolute value. Accordingly, unit of s in CGS system is $\text{Cal} \cdot \text{g}^{-1} \cdot {}^0\text{C}^{-1}$, while in SI unit is $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$. Conversion of unit of heat from CGS into SI requires to know relationship (**1 Cal = 4.186 J**), between units of energy Calorie (**Cal**) and Joule (**J**) shall be elaborated with Joule's Experiment a little later. Extending this concept of *Specific Heat*, **Heat Capacity** (**S**) of a body is the amount of heat required to raise its temperature by 1°C or 1 K and is $S = ms$. Another extension of the concept of **Molar Heat Capacity** (Ms) is equal to 1 ***gram-mol** of substance (it is equal to Molecular Weight or Molecular Mass (M gm)*, accordingly heat capacity of an object $S = nM$, where n is the Molar Mass i.e. number of Gram-Mol of substance. *Molar Heat Capacity finds extensive application in chemistry.*

Typical determination of Specific Heat of a metal ball is elaborated below: Initially, mass (m_1) of an empty dry vessel of calorimeter having specific heat s_v is determined on weighing balance. Then in the vessel enough non-volatile liquid having specific heat s_l is put which would fully immerse the metal ball. Let, m_2 be the mass of the vessel with liquid. Assume, that specific heat and mass of the metal ball to be s_b and m_b respectively. Now, mass of the ball (m_b) is determined, and it is placed in a hot air chamber till a steady temperature chamber (θ_1) is attained. Meanwhile, the calorimeter is placed in the container, packed with wool, and stirrer is stirred till temperature of water becomes steady at (θ_2). Now, by turning the lid, the ball is gently immersed in water so as to avoid splashing of water. Soonafter, the stirrer is vigorously stirred and temperature of liquid is kept under continuous observation. Maximum temperature attained by the liquid (θ_3) is noted.

Computation of these observations to arrive at specific heat and heat capacity of the metal ball is as under:

Heat Capacity of Calorimeter vessel : $S_v = m_1 s_v \; \text{Cal}^{-1} \cdot {}^0 \text{C}^{-1}$

Heat gained by the calorimeter : $h_{g1} = S_v(\theta_3 - \theta_1) \; \text{Cal}$

Mass of liquid : $m_l = m_2 - m_1$

Heat gained by liquid inside the calorimeter : $h_{g2} = m_l s_l (\theta_3 - \theta_1)$

Total Heat gained : $h_g = h_{g1} + h_{g2} = (S_v + m_l s_l)(\theta_3 - \theta_1)$

Heat Lost by metal Ball : $h_l = m_b s_b (\theta_2 - \theta_3)$

As per Law of Conservation of Energy	$: h_l = h_g \Rightarrow m_b s_b (\theta_2 - \theta_3) = (S_v + m_l s_l)(\theta_3 - \theta_1)$
Specific Heat of Metal Ball	$: s_b = \frac{(S_v + m_l s_l)(\theta_3 - \theta_1)}{m_b(\theta_2 - \theta_3)}$
Heat Capacity of metal Ball	$: S_b = m_b s_b = \frac{(S_v + m_l s_l)(\theta_3 - \theta_1)}{(\theta_2 - \theta_3)}$

LATENT HEAT: In the beginning of fluid mechanics physical states of matter solid, liquid and gas were stated to be in relation to their inter-molecular energy. As the matter changes its physical state there are two pertinent observations: **i)** change of state takes place at constant temperature, which is dependent on pressure on the prevalent ambient pressure, **ii)** it requires extra energy, much higher than Specific Heat and this extra heat is called Latent Heat of the substance.

Temperature at which a matter changes from solid to liquid state it is called Melting Point and corresponding latent heat is called *Latent Heat of Fusion*. This remains same when state of liquid changes to solid, it is called Freezing point. Likewise, temperature at which liquid changes to gaseous it is called Boiling point, corresponding to ambient pressure, and the extra heat is called *Latent Heat of Evaporation*.
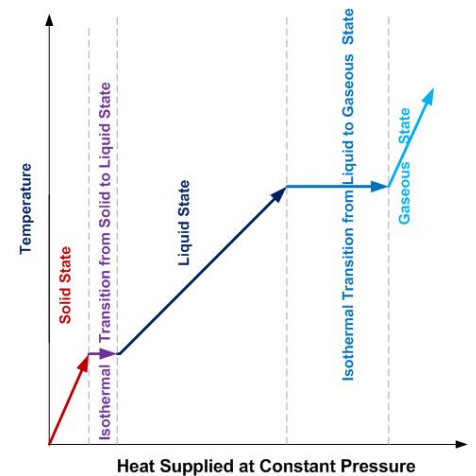
This change of state is since related to inter-molecular energy, therefore, Latent Heat is dependent upon temperature and pressure as well. Change in intermolecular distance during transition from liquid to vapour state is since much larger than that during solid to liquid state, dependence of *Latent Heat of Evaporation* on pressure is much larger than that of *Latent Heat of Fusion*. This subject matter is since outside the current domain and, therefore, discussions on this dependence of the Latent Heat is being put to a halt here.

Experimental Determination of the Latent Heat of Evaporation, taking specific heat of water to be 1, typically, is as under: In an experiment, as above, instead of metal ball, dry steam at temperature θ_2 is injected in water. It requires two precautions: a) rate of flow steam is so regulated that it does not bubble out of water , and b) stirrer is continuously and vigorously to facilitate (a). As a result there is increase in temperature of water and calorimeter. Mass of steam $m_s = m_3 - m_2$ is determined after recording maximum temperature θ_3 attained by water and steam mixture.

Accordingly, computation of these observations to arrive at Latent Heat of Evaporation, taken to be L_s, shall be as under :

Heat Capacity of Calorimeter vessel	$: S_v = m_1 s_v \, \text{Cal}^{-1} \cdot^0 \text{C}^{-1}$
Heat gained by the calorimeter	$: h_{g1} = S_v(\theta_3 - \theta_1) \, \text{Cal}$
Mass of liquid	$: m_l = m_2 - m_1$
Heat gained by liquid inside the calorimeter	$: h_{g2} = m_l s_l (\theta_3 - \theta_1)$
Total Heat gained	$: h_g = h_{g1} + h_{g2} = (S_v + m_l s_l)(\theta_3 - \theta_1)$
Mass of steam	$: m_s = m_3 - m_2$
Heat Lost by Steam in Condensation	$: h_{l1} = m_s L_s$
Heat Lost by condensed steam to reach temperature of Mixture	$: h_{l2} = m_s . 1 . (\theta_2 - \theta_3)$
Total heat Lost	$: h_l = h_{l1} + h_{l2} = m_s \left(L_s + (\theta_2 - \theta_3) \right)$

As per Law of Conservation of Energy : $h_l = h_g \Rightarrow m_s\left(L_s + s_w(\theta_2 - \theta_3)\right) = (S_v + m_l s_l)(\theta_3 - \theta_1)$

Latent Heat of Evaporation of water : $L_s = \left.\dfrac{(S_v + m_l s_l)(\theta_3 - \theta_1)}{m_s} - (\theta_2 - \theta_3)\right|_{s_w=1}$

Latent Heat of Evaporation at normal atmospheric pressure , leading to 100ºC boiling point, **is 533 Calorie per gram in CGS and in SI it is 2,231.14 J/kg.** Since boiling point is pressure dependent so also the latent heat, this is precisely the reason that cooking in pressure cooker becomes fast. This would become more explicit as this journey enter into Kinetic Theory of Gases. *Effect of latent heat of evaporation is experienced during accidental exposure to steam, nevertheless, it is cautioned not to experience heat of steam by exposing to it any of the body part;* **it may cause severe burns- <u>Danger</u>.**

Experimental Verification of Latent of Fusion of Ice, taking specific heat of water to be 1, typically, is as under: In this experiment as above, instead of steam, a piece of dry ice of mass (m_i) at 0ºC, like that of metal ball, is dropped in the liquid miscible in water, since ice is condensed water. Let, Latent Heat of Fusion be L_F. After dropping the ice piece stirrer is stirred vigorously till temperature fall to minimum(θ_3), which is constantly observed. Since, calorimeter is at higher temperature; with the decrease in temperature it will lose heat, while ice would gain heat in its melting and the water to attain final temperature of water-ice mixture.

Computation of these observations to arrive at Latent Heat of Fusion L_F is as under:

Heat Capacity of Calorimeter vessel : $S_v = m_1 s_v$ Cal- ºC^{-1}
Heat lost by the calorimeter : $h_{l1} = S_v(\theta_1 - \theta_3)$ Cal
Mass of liquid : $m_l = m_3 - m_1$
Heat lost by liquid inside the calorimeter : $h_{l2} = m_l s_l(\theta_1 - \theta_3)$
Total Heat lost : $h_l = h_{l1} + h_{l2} = (S_v + m_l s_l)(\theta_1 - \theta_3)$
Heat Gained by Ice in meting to water : $h_{g1} = m_i L_F$
Heat Gained by molten ice
to attain temperature of mixture : $h_{g2} = m_i \cdot 1 \cdot (\theta_3 - 0) = m_i \theta_3$
Total Heat Gained : $h_g = h_{g1} + h_{g1} = m_i(L_F + \theta_3)$

As per Law of Conservation of Energy : $h_l = h_s \Rightarrow (S_v + m_l s_l)(\theta_1 - \theta_3) = m_i\left(L_F + \theta_3\right)$
Therefore, Latent Heat of Fusion of Ice : $L_F = \frac{(S_v + m_l s_l)(\theta_1 - \theta_3)}{m_i} - \theta_3$

Latent Heat of Fusion of water is 79.7 Cal per gram in CGS and in SI it is 333.62 kJ/kg. *Effect of latent heat of fusion of ice is experienced while holding ice which causes intense chillness as compared to dipping hand in ice-cool-water.*

MECHANICAL EQUIVALENT OF HEAT: In winter animals shake themselves to warm up, human being rub their palm and face; while sharpening knife it becomes hot and, therefore, dipping knife in water is in practices since immemorial times. This is practiced without knowledge of convertibility of work into heat. Scientific observation of friction generating heat was recorded by Count Rumford who published "An Experimental Enquiry Concerning the Source of the Heat Which is Excited by Friction" in 1798. This inspired many scientists to work in parallel and in 1845 James Prescott Joule a numerical value of 'Mechanical Equivalent of Heat' (in foot-pound force) which equates to 4.1550 J.Cal^{-1}.

A typical apparatus to determine *mechanical equivalent of heat* is shown in the figure. It has two metallic cones of brass. Inner cone, with water of mass m_1 filled in it a little below the brink to avoid spilling, is fitted with a heat insulating disk cover, circular in shape. The outer cone is fitted to a thermally insulated spindle having a mechanism to rotate it alongwith a counter to record number of rotations. Let, heat capacity of the two cones is **S**. The top cover has two holes one is to accommodate a thermometer and other a stirrer. Further, the top disk has a peripheral groove through which a rope whose one end tied in the groove and is wound around the disk in the groove. The other end of the rope has weight suspended from a pulley. The pulley is fixed such that it remains tangential to the groove at its point of exit from the groove and in the plane of the groove. Let, **m** is the mass of the pan and **M** is the weight in the pan. If the spindle is left free, the weight will turn the disk so as to lower the weight. This direction of turning of the cover, under the suspended weight, is noted.
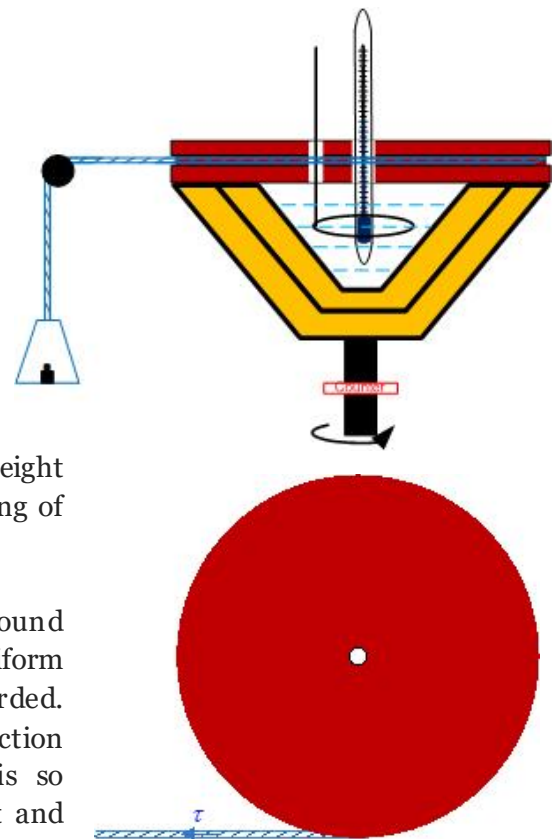
The rope is replaced, in the groove, around the disk to have rope around the pulley. Water inside the inner cone is stirred to bring a uniform temperature of water and cone, initial steady temperature θ_1 is recorded. Now, the, spindle is rotated in a direction reverse to the natural direction of turning of the disk. The speed of rotation of the spindle is so maintained that the suspended weight remains at the same height and stationary. At this state, direction of frictional torque counter balances the torque caused by the suspended weight ($\tau = 2\pi r(M + m)g$). Keeping weight suspended at the same height, the system is made to rotate **N** revolutions. During this rotation water in the inner cone is constantly stirred and θ_2 is the maximum temperature attained by the water during experimental process.

Computation of these observations to arrive at Latent Heat of Fusion L_F is as under:

Work done, during **N** rotation to overcome frictional force $: W = \tau N$ N-m $= (2\pi r(M + m)g)N$ N-m

Heat gained by water inside the inner cone and the Two metallic cones $: H = (S + m_1)(\theta_2 - \theta_1)$ Cal

As per principal of conservation of energy $: W = JH$

Therefore, Mechanical Equivalent of Heat $: J = \dfrac{(2\pi r(M+m)g)N}{(S+m_1)(\theta_2-\theta_1)}$

This Heat Equivalent was standardized to 4.1860 J.Cal⁻¹ was determined in year 1920.
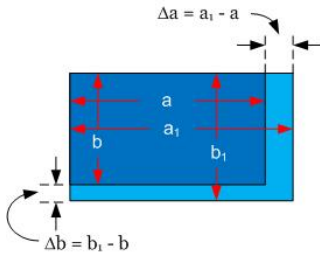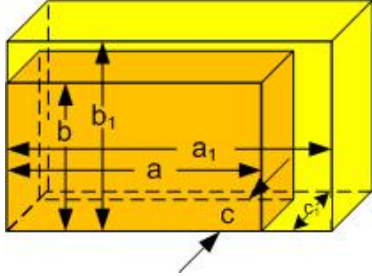
THERMAL EXPANSION: In rail tracks spacing is provided at regular spans to avoid bending of tracks. In domestic environment when two conical metal glasses tightly fit into each other, they are separated by putting outer glass into hot water. Likewise, in metal container, having ceramic lagging hot liquid when suddenly poured in, it develops cracks in the lagging. These observations are related to thermal expansion, and find many applications in practical life.

Change in volume of solid, liquid and gases, upon heating, depends upon their molecular bonding. Solids since retain their shape, during heating energy imparted to molecules sets in increased molecular vibrations which causes them to reposition for mechanical equilibrium. It results in increase in their dimensions. In ***isotropic material****, having uniform arrangement of molecules in the volume,* change in dimensions is uniform and
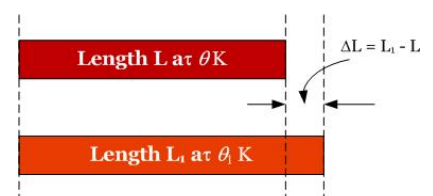
proportional to its length, width and thickness. While in **anisotropic material**, *having distribution of molecules is oriented along crystalline structure*, variation in the three dimensions is not uniform. In this elaboration, thermal expansions of isotropic materials are considered. Accordingly, $\alpha\Delta\theta = \frac{\Delta L}{L}$, here, α is **Coefficient of Linear Expansion**. At **o K**, a hypothetical Zero temperature, energy of a matter is minimum, and interpolation of the logic to thermal contraction $\alpha(\theta - 0) = \frac{(L-L_0)}{L_0}$, here, L_0 is the length at **o K**. Thus, length of a material at temperature θ_1 K is $\alpha(\theta_1 - 0) = \frac{(L_1-L_0)}{L_0}$. Taking, θ to be a reference temperature at which length is L, and combining these two equations it leads to $\alpha(\theta_1 - \theta) = \frac{(L_1-L)}{L_0} = \frac{\Delta L}{L_0}$. Since, $\Delta L << L_0 \Rightarrow L_0 \to L$, accordingly the equation used for all practical purposes is $\Delta L = \alpha L(\theta_1 - \theta)$.

Relationship between coefficient of linear, with that of coefficient area and volumetric expansions is arrived at by extrapolating linear expansion on surface and volume, as shown below -

Area Expansion	**Volume Expansion**
$\Delta A = a_1 b_1 - ab$ $\quad = a(1 + \alpha(\theta_1 - \theta)) \cdot b(1 + \alpha(\theta_1 - \theta)) - ab$ $\quad = 2\alpha ab(\theta_1 - \theta)\big|_{\alpha^2 \to 0} = 2\alpha A(\theta_1 - \theta)\big|_{ab=A}$ $= \beta A(\theta_1 - \theta)$, i.e. $\beta = 2\alpha$ Here,; i.e. **coefficient of area expansion(β) is twice the coefficient of linear expansion (α)**	$\Delta v = a_1 b_1 c_1 - abc$ $\quad = a(1 + \alpha(\theta_1 - \theta)) \cdot b(1 + \alpha(\theta_1 - \theta))$ $\qquad\qquad \cdot c(1 + \alpha(\theta_1 - \theta)) - abc$ $\quad = 3\alpha abc(\theta_1 - \theta)\big|_{\alpha^2 \to 0} = 3\alpha V(\theta_1 - \theta)\big|_{ab=A}$ $= \gamma A(\theta_1 - \theta)$, i.e. $\gamma = 3\alpha$ Here,; i.e. **coefficient of Volume expansion(γ) is thrice the coefficient of linear expansion(α)**

Liquids *since do not have their own shape, therefore, **increase of temperature causes volumetric expansion only**, and it is higher than that of solids.* Since the liquid occupies space in a container, volumetric expansion of the container is accounted to avoid **error** in determination of the Coefficient of Volumetric Expansion (γ) of liquids.

In gases, inter-molecular spacing is much larger than the liquid resulting into ineffective intermolecular force of attraction. It makes it possible for gases to expand to completely fill the space available in the container. Kinetic energy of molecules is imparted by heat content of gases which in turn creates pressure on the walls of its container. This makes **volumetric expansion of gases different from the liquid** and shall be elaborated in section **Kinetic Theory of Gases**, later in this chapter.

HEAT TRANSFER: **Change of temperature is a result of transfer of heat energy** as observed in calorimetry. Natural transfer of heat from a body at High Temperature to another body at Low Temperature is seen. Some of the r**eal life experiences of heat transfer** are holding cooking tools dipped in hot cooking stuff, heating of water from bottom of the vessel such that hot water is at the top, hot flames rising from gas burner gas, and in winter receiving heat from sunrays. It is the time to understand mechanics of heat transfer. There are basically three Types of Heat transfer: **a) Conduction, b) Convection and c) Radiation**. And fourth mode of transfer, specific to industrial applications and not in real life environment, is **Advection**. In advection fluid is transported flown from one point to the other to transfer the heat energy. Most common application of advection is in refrigerator, where gas is used to transport heat from contents of refrigerator to

the environment through compressor and radiator. Each of the three modes of heat transfer stated above is being elaborated individually.

CONDUCTION: Heat imparted to solids, as per Law of Conservation of Energy induces vibration of molecules about their mean positions retained as vibration energy. Accordingly, a molecule at higher temperature has higher vibration energy as compared to the other at lower temperature. Thus sharing of energy molecules across them tend establish a thermal equilibrium in a closed system.

In a situation a solid having uniform cross sectional area 'A' has one end or surface 'X' at higher temperature θ_1, called source, and other end 'Y' at lower temperature θ_2 called sink, heat will be continuously transferred. Experimentally, it has been observed that in a steady state rate of heat transfer 'Q' is: a) proportional to area of cross-section 'A', b) temperature difference $(\theta_1 - \theta_2)$ between two ends and c) inversely proportional to distance between the two ends points 'l'. Accordingly, $Q \propto \frac{A(\theta_1 - \theta_2)}{l}$, or $Q = k\frac{A(\theta_1 - \theta_2)}{l}$, here H is in Calorie, A in m², θ_1 **and** θ_2 in °C, l in Meter, and therefore, K- the proportionality constant is called coefficient of thermal conductivity in CGS is Cal.m⁻¹.°C⁻¹, while in SI it is Jule.m⁻¹.K⁻¹.

Jean-Baptiste Joseph Fourier in 1822 defined conduction of heat known as Fourier's law, states that the rate of heat transfer through a material is proportional to the negative gradient in the temperature and to the area, at right angles to that gradient, through which the heat flows and is mathematically expressed as

$$\frac{dQ}{dt} \propto A\frac{\Delta\theta}{\Delta l} \Rightarrow \frac{dQ}{dt} = -kA\frac{d\theta}{dl}$$

The (-) sign in the Fourier's law is attributed to the fact that when heat conduction is in (+) direction of the length of the medium, there is fall of temperature along the length in its (+) direction and accordingly

$$\frac{d\theta}{dl} = \frac{\theta_{l+\Delta l} - \theta_l}{\Delta l}\bigg|_{\Delta l \to 0} = -\frac{|\Delta\theta|}{\Delta l}\bigg|_{\Delta l \to 0}$$. Thus difference is caused in equation of heat conduction and its

representation in the form Fourier's Law. Correlation between these two equations would become more explicit with the application of Fourier's Law.

Experimental Determination of K: Experimental setup for this is shown in the figure, and procedure of
the experiment is being elaborated. A metal rod of uniform cross-section A is fitted with one inside a steam chamber, with steam supplied from top and ejected from bottom, to maintain uniform temperature in the chamber, and in turn of the ends of the metal rod embedded inside the chamber. The rod is provided thermal insulation on its side walls to block dissipation of heat from its walls; thus it ensures flow of heat in axial direction. A spiral copper tube on the other end carries water (specific heat s) having inlet in the direction of heat flow, and two thermometers to record temperatures of water at inlet θ_3 and outlet θ_4.
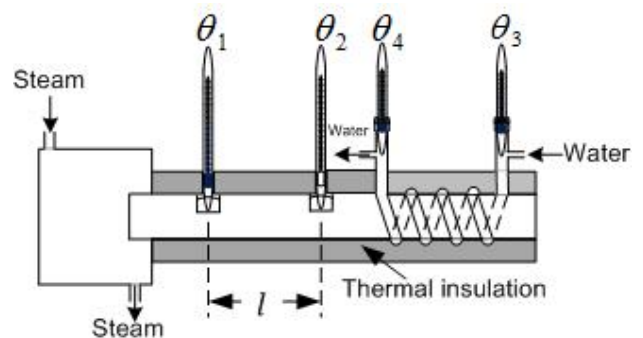
The rod has two narrow mercury pockets at a distance l, thermometers dipped in them measuring temperatures. Since, direction of flow of heat is from the end inside steam-chamber towards cooled end hence $\theta_1 > \theta_2$ the direction of flow of heat. Likewise, $\theta_4 > \theta_3$ and it is in accordance with the direction of flow of heat. Temperatures $\theta_1, \theta_2, \theta_3$ and θ_4 are noted till they get to steady values. At this steady state mass of water passed through the tube in time t, recoded through stopwatch, is measured to be m.

Computation of these observations to arrive at Latent Heat of Fusion L_F is as under:

Heat transfer in time t : $H = m.1.(\theta_4 - \theta_3)$ Cal

Rate of heat of heat Transfer as per experimental observation : $Q_1 = \frac{H}{t} = \frac{ms(\theta_4 - \theta_3)}{t}$
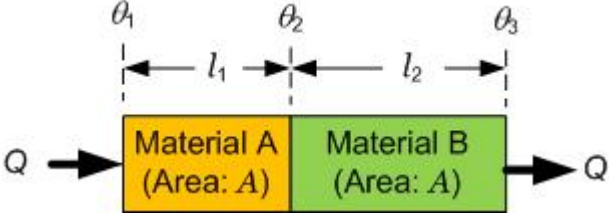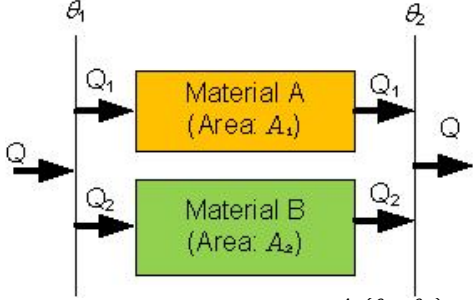
Rate of heat transfer as per definition : $Q_2 = K\frac{A(\theta_1 - \theta_2)}{l}$

As per Law of Conservation of Energy : $Q = Q_1 = Q_2 \rightarrow Q = K\frac{A(\theta_1 - \theta_2)}{l} = \frac{ms(\theta_4 - \theta_3)}{t} \rightarrow K = \frac{lms(\theta_4 - \theta_3)}{At(\theta_1 - \theta_2)}$.

Thermal Resistance(R_h): This is similar to that shall be encountered in current electricity, which shall be elaborated in separate chapter, and can be used to create a background for that. Temperature difference $(\theta_1 - \theta_2)$ is driving transfer of heat Q Cal.s^{-1}. Therefore thermal resistance to heat flow $R_h = \frac{(\theta_1 - \theta_2)}{Q} = \frac{l}{KA}$, accordingly ***thermal resistivity*** $= \frac{1}{K}$, ***it is reciprocal to thermal conductivity.***

This concept of thermal resistance is extended to determine temperature difference required to combinations of thermal insulators to transfer certain amount of heat, through Two generic arrangements: **a)** *Series Combination*, and **b)** *Parallel Combination*. In this analysis of Series Combination area of both the materials is taken to be A, while their lengths are l_1 and l_2, while Thermal Conductivities of materials A and B are K_1 and K_2. For transfer of heat Q, temperatures across Material A is θ_1 and θ_2, while that across material B is θ_2 and θ_3. Likewise for Parallel Combination, Material A and B are taken to be of length l, with temperature difference across their ends at Source Side θ_1 and Sink Side θ_3, but cross-sectional area as A_1 and A_2 respectively. Let, heat transfer shared by them be Q_1 and Q_2, respectively such that $Q_1 + Q_2 = Q$. Taking these parameter, Equivalent Thermal Resistance of the Two Combinations is elaborated below.

Series Combination of Thermal Resistance	Parallel Combination of Thermal Resistance

Series Combination:

Heat Transfer Through A: $Q = K_1\frac{A(\theta_1 - \theta_2)}{l_1} = \frac{(\theta_1 - \theta_2)}{R_{h-1}}$,

$R_{h-1} = \frac{l_1}{K_1 A}$; $(\theta_1 - \theta_2) = Q \cdot R_{h-1}$

Heat Transfer Through B: $Q = K_2\frac{A(\theta_2 - \theta_3)}{l_2} = \frac{(\theta_2 - \theta_3)}{R_{h-2}}$,

$R_{h-2} = \frac{l_2}{K_2 A}$; $(\theta_2 - \theta_3) = Q \cdot R_{h-2}$

Heat Transfer through Series Combination: $Q = \frac{(\theta_1 - \theta_2)}{R_h}$;

$(\theta_1 - \theta_2) = Q \cdot R_h = (\theta_1 - \theta_2) + (\theta_2 - \theta_3)$
$= Q \cdot R_{h-1} + Q \cdot R_{h-2}$

Or, $R_h = R_{h-1} + R_{h-2}$

Parallel Combination:

Heat Transfer Through A: $Q_1 = K_1\frac{A_1(\theta_1 - \theta_2)}{l} = \frac{(\theta_1 - \theta_2)}{R_{h-1}}$,

$R_{h-1} = \frac{l}{K_1 A_1}$; $(\theta_1 - \theta_2) = Q_1 \cdot R_{h-1}$

Heat Transfer Through B: $Q_2 = K_2\frac{A_2(\theta_1 - \theta_2)}{l} = \frac{(\theta_1 - \theta_2)}{R_{h-2}}$,

$R_{h-2} = \frac{l}{K_2 A_2}$; $(\theta_1 - \theta_2) = Q_2 \cdot R_{h-2}$

Heat Transfer through Series Combination: $Q = \frac{(\theta_1 - \theta_2)}{R_h}$;

And $Q = Q_1 + Q_2 \Rightarrow \frac{(\theta_1 - \theta_2)}{R_h} = \frac{(\theta_1 - \theta_2)}{R_{h-1}} + \frac{(\theta_1 - \theta_2)}{R_{h-2}}$

Or, $\frac{1}{R_h} = \frac{1}{R_{h-1}} + \frac{1}{R_{h-2}}$; $R_h = \frac{R_{h-1} \cdot R_{h-2}}{R_{h-1} + R_{h-2}}$

*It is seen that **thermal resistance is parametric in nature** viz. Resistivity, a characteristic parameter of the material, and its geometry derived from shape of material.*

CONVECTION: A fluid when heated, heat is transferred through conduction to the molecules of fluid in contact with the heating, it can be walls of container or a hot object immersed in it. The fluid that comes in contact with hotter substance s undergoes volumetric expansion, and as a consequence due to buoyancy it starts rising until they transfer heat to the molecules intercepted during ascend. Likewise, ascending hotter molecules, intercepted by descending cooler molecules also exchange heat. *This intermolecular transfer of heat in fluid is conduction, while the process of ascend/descend of hotter/cooler molecules, respectively, is* ***convection.*** *Thus in totality* ***convection is a hybrid process which involves conduction as stated, followed by volumetric expansion/contraction leading movement of molecules due to buoyancy effect.***

Convection is a combination of conduction and convection, in this conduction heating surface transfer heat the fluid molecules through conduction. Likewise, cooler molecules that descend after transfer of heat through convection, gain heat from hotter molecules intercepted by it through conduction. This process continues till liquid attains thermal equilibrium. After this state if heat supply continues, this additional heat is utilized in evaporation so as to retain the thermal equilibrium. This phenomenon keeps temperature in coastal region almost stable. Discussions on convections are put to a halt at this point, while readers are welcome to raise their inquisitiveness through ***Contact Us***.

RADIATION: Transfer of Heat through radiation has been of interest to human civilization, and source of light and heat were worshiped right since the predator age. Basic understanding of thermal radiation is derived from the fact that when a matter acquires, heat energy it sets molecular vibrations which are responsible for transfer of heat by conduction, convection and radiation.

A sharp metal needle held with a heat insulating material or a tool on a flame changes colour as its temperature increases and tends to be from grey to bright colour and then tending to be while, and reverse is the change in colour when cooled down. These observation in respect of radiation of rays over a wide spectrum were first documented by Pierre Prevost in 1792. He further propounded a Fluid Theory of heat transfer and that at thermal equilibrium, heat received by a body, from the surrounding objects is equal heat escaped from it.

Black Body: Two object, one with a highly reflecting surface, and the other with grey surface are kept at room temperature, it is seen in an environment having a constant temperature. It is seen that with passage of time both object attain a thermal equilibrium with the environment. The object having reflecting surface absorbs a smaller faction radiation incipient on it, as compared to the object having a grey surface. But, necessary condition of thermal equilibrium is that amount of heat radiation emitted by all bodies at all temperature is equal to the radiation absorbed by it. An ideal Black Body is that which absorbs all the radiation falling on it. An ideal black body is a hypothetical proposition, and in reality it does not exist and so also is an ideal reflecting surface. A closed chamber, with a pin hole and a diverting surface across the hole inside the chamber, as shown in the figure, is an idealized black body, since a radiation once enters it can not leave out, i.e. it is fully absorbed in it.

It is observed that matter exhibits radiation over a wide spectrum and predominant frequency is dependent

upon its temperature while intensity of other frequencies is dependent upon molecular and crystalline structure of matter. The matter is composed of charged and neutral particles. Motion of these particles creates a coupled electric and magnetic field known as Electromagnetic Radiation. Heat Radiation is as much a part of Electromagnetic Radiation Spectrum as visible light is. It was only in late nineteenth century that it was realized that transfer of heat through radiation is a part of electromagnetic radiation. This shall be discussed in detail in
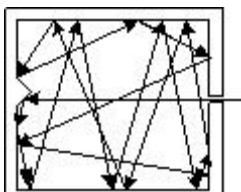
Chapters on Atomic Structure and other related topics of Modern Physics. Elaboration in this chapter is confined only to Transfer of Heat through Radiation.

Later half of 19th century was quite revealing in respect of thermal radiation. Many scientists worked independently, while their revelation complemented the earlier in furtherance of the knowledge. In this pursuit significant contributions are from Kirchhoff, Wein and Planck are discussed separately.

Newton's Law of Cooling: In 1701 Newton, stated that "***rate of cooling of an object is proportional to the difference between temperature of the body and its ambient, i.e. the surrounding***". Accordingly, $\frac{dT}{dt} \propto (T - T_a)$. Thus, the relationship comes to $\frac{dT}{dt} = -k(T - T_a)$, or $\int \frac{1}{(T-T_a)} dT = -k \int dt$; or $\ln(T - T_a) = -kt+C$; $T(t) - T_a = (T_0 - T_a)e^{-kt}$. Thus, instantaneous temperature of an object at any time t is expressed with an equation $T(t) = T_a + (T_0 - T_a)e^{-kt}$. Here, T_o- is initial temperature of an object, $T(t)$- instantaneous temperature of object at time t, T_a- is ambient temperature. Here, constant of integration takes into account other parameters viz. heat loss due to convection, surface area etc. Growth and understanding of heat, with the evolution of Stefan-Boltzmann Law, has brought limitation of Newton's Law of cooling, and is elaborated here in the following para.

Kirchhoff's Law of Thermal Radiation: In 1859 Gustav R Kirchhoff discovered universal character of radiation to solve the problem of dependence of emitted light on nature, size and shape of body. For an ordinary body transfer of heat of Thermal Radiation incident on a body (taken to be unity) is represented by equation **$a + r + e = 1$**, here a is the fraction of absorption of radiation, r is the fraction of radiation reflected and e is the fraction of emission of thermal radiation. These three fractions together constitute total heat incident on a body which is transmitted by the body. Under thermal equilibrium Kirchhoff found that: "***ratio of emissive power to absorptive power is same for all bodies at a given temperature, in thermal equilibrium, is equal to that of a black body and is defined by a function $K(\lambda, T) = \frac{e}{a}$ is independent of body.***" Here, it is pertinent to know that the Two new terms that have been introduced.

Emissive Power: Taking Ω a small surface area ΔA of a body, subtending a solid angle $\Delta\Omega$, emits thermal energy Δu in time Δt, then

Emissive Power $E = \dfrac{\Delta u}{\Delta A \Delta \Omega \Delta t}$.
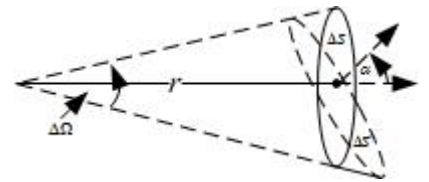
Absorptive Power: It is a fraction α of the incident radiation U_I that is absorbed by the body U_a. Then,

$\alpha = \frac{U_a}{U_I}$. Combining the Two laws, $\dfrac{E}{\alpha} = \dfrac{\dfrac{\Delta u}{\Delta A \Delta \Omega \Delta t}}{\dfrac{U_a}{U_I}} = \dfrac{\Delta u}{\Delta A \Delta \Omega \Delta t} \times \dfrac{U_I}{U_a} = \left(\dfrac{U_I}{\Delta A \Delta \Omega \Delta t}\right) \times \left(\dfrac{\Delta u}{U_a}\right) = K \dfrac{\Delta u}{U_a}$. Here, K is a constant term which involves rate of incident energy and geometrical property of the surface, without involving property of surface. In case of thermal equilibrium $\frac{\Delta u}{U_a} = 1$. ***This proves that the ratio emissive power to absorptive power is same for all bodies.***

Stephan and Boltzmann Law: Stefan through rough experiments revealed that total amount of power radiated at any temperature increases in fourth power of the absolute temperature and in 1879, he propounded that $\int_9^\infty u(\nu, T)d\nu = \sigma T^4$, here ν is the frequency of radiation. In 1884, L. Boltzmann deduced this equation

theoretically, accordingly, it is known as Stefan and Boltzmann Law of Thermal radiation stating that – "**total thermal energy radiated by a body per unit time is proportional to fourth power of temperature in the form** $u = \sigma A T^4$", here σ – Stefan-Boltzmann Constant $=5.67 \times 10^{-8}$ W.m^{-2}.K^{-4}, A - surface area and T – Absolute Temperature.

Extending this law into the domain of Newton's Law of cooling into a state of thermal equilibrium with the environment,

$\Delta u = e\sigma A(T^4 - T_a^4);$ $\qquad T = T_a + \Delta T;$ $\quad \Delta u = e\sigma A((T_a + \Delta T)^4 - T_a^4) = e\sigma A T_a^4\left(\left(1 + \frac{\Delta T}{T_a}\right)^4 - 1\right).$ It leads to simplification using binomial theorem, where in terms containing higher power ΔT of are neglected, $\Delta u = e\sigma A T_a^4 \frac{\Delta T}{T_a} = e\sigma A T_a^3 (T - T_a)|_{\Delta T \text{ is small}}$.

Recalling the concept of heat capacity $\frac{\Delta u}{\Delta t} = ms\frac{\Delta\theta}{\Delta t}$, together with this when temperature of object is comparable the ambient temperature, the factor $\frac{e\sigma A T_a^3}{ms}$ is a close approximation of proportionality constant of Newton's Law of Cooling.

Wien's Displacement Law : W. Wien had studied intensity of radiation from a body at different temperatures and propounded in 1893 that wavelength of the maximum radiation of maximum intensity is inversely proportional to the temperature of the body and expressed as $\lambda_{max} \cdot T = b$. Here, b is a Wien's Displacement Constant $=2.8977685 \times 10^{-3}$mK, and this equation is known as Wien's Displacement Law.
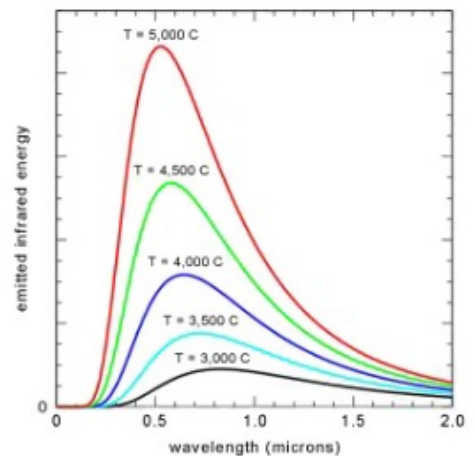

Planck's Law: In 1900, Max Planck while analyzing radiation of black body empirically derived a formula for observed spectrum. He assumed that there is a minimal increment in change in energy of radiation and accordingly arrived at a proportionality constant based on experiment h known as Planck's constant equal to 6.6260693 x10^{-24}J.s. Later in 1905, Albert Einstein associated the minimal energy with the electromagnetic wave with Planck-Einstein equation $E = h\upsilon$, here E is the energy of the quanta and υ is the frequency of radiation. This was the beginning of exploration of Quantum Mechanics, which is briefly touched upon in chapter on **Modern Physics** in this manual.

Planck through his series of papers in later part of 19th century postulated radiating power of black body and he propounded it in a form known as Plank's Law in infinitesimal form as a equation, as function of frequency (υ) and temperature (T) : $u(\upsilon, T)d\upsilon = \frac{2h\upsilon^3}{c^2} \cdot \frac{1}{\left(e^{\frac{h\upsilon}{K_B T}}\right)-1} \cdot d\upsilon$; here, υ - Frequency of radiation, c - velocity of

light$=2.00392458$ ms^{-1}, K$_B$– Boltzmann Constant$=1.380650 \times 10^{-23}$ JK^{-1}, and T -Temperature in Kelvin. Expressing this equation in terms of wave length $\lambda = \frac{c}{\upsilon}$, , i.e. $d\lambda = -\frac{c}{\upsilon^2}d\upsilon$. Introduction of –ve sign represents reflection of graph into second quadrant, and hence it is neglected. Accordingly, substituting this in the above equation leads to, $u(\lambda, T) \cdot d\lambda = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\left(e^{\frac{hc}{\lambda K_B T}}\right)-1} \cdot d\lambda$. Occurrence of $d\upsilon$ and $d\lambda$ on both the sides of the both
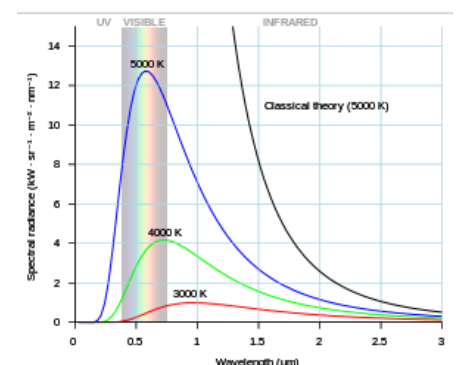
the Plank's equation, lead to $u(v, T) = \frac{2hv^3}{c^2} \cdot \frac{1}{\left(e^{\frac{hv}{K_B T}}\right) - 1}$ and $u(\lambda, T) = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\left(e^{\frac{hc}{\lambda K_B T}}\right) - 1}$, and is shown in the figure.

Summary of Heat Transfer: It is an important phenomena in understanding of Heat Energy and takes place in Three modes, advection being a special application is being skipped in the comparison. Salient differences in the three modes of heat transfer are summarized, for comparison, below:

Comparison in Three Modes Heat Transfer			
Particulars	**Conduction**	**Convection**	**Radiation**
Medium	*Solid:* required	*Fluid:* required	*Vacuum:* Medium not required
Mechanism of heat transfer	Molecules vibrate about their mean position	It is a process induced due to buoyancy effect and is sandwiched between transfer of heat by conduction at the initiation and termination, till establish thermal equilibrium in fluid	Transfer of energy is through electromagnetic wave energy. Any object which obstruct these waves experiences absorption, reflection and emission.
Algebraic Expression for rate of heat transfer	$= \frac{ms(\theta_4 - \theta_3)}{t}$	Not quantified, since it depends upon ambient conditions also.	$u = \sigma A T^4$; Stepfan and Boltzmann Law
Loss of Energy	To the extent heat is transferred through the surface of the medium, perpendicular to the direction of heat transfer	To the extent heat is transferred into and through surface of the container of the fluid.	In medium either by reflection or emission.

KINETIC THEORY OF GASES: In childhood one must have blown balloons. In this fun it must have been experienced that more force is required with increase in balloon size, so also a careful observation would reveal that as balloon is blown its temperature also increases. This observation can be best explained with the understanding of Kinetic Theory of Gases. Its beginning in scientific observations of motion of particles in fluid was made **Robert Brown** in 1827. He postulated an ***Ideal Gas*** having following properties :
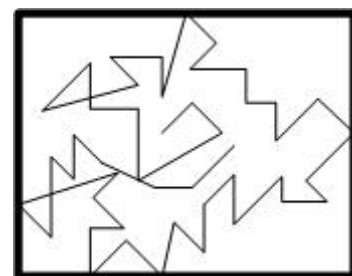
1) Number of molecules is large.
2) Molecules of gas keep undergoing random chaotic motion, which is called Brownian Motion. The adjoining figure conceptualizes changes in path of a molecule, on occurrence of every collision.
3) Size of molecules is insignificant to the volume of gas, and hence neglected.
4) Intermolecular space in gases is large enough to be able to ignore intermolecular force.
5) During motion, collision of molecules caused by interception each other is perfectly elastic and obey Newton's Laws of Motion,
6) A volume of gas over a period of time reaches a steady state in respect of density, molecular distribution and velocities of molecules are independent of position, direction and time.

Extending the theory, consider a cubical container placed such that its walls parallel *to i-j, j-k,* and *k*-i planes. This container is filled with an idea gas, whose molecules are performing Brownian Motion. Let, velocity of a typical molecule and its components along three axes are as shown in the figure, such that $v = \sqrt{v_i^2 + v_j^2 + v_k^2}$. Since, all collisions are perfectly elastic therefore change of momentum of a molecule after rebounds from

hatched face parallel to plane (L-j-k) shall be $p = 2mv_i$. Let, time between Two consecutive collisions any of the hatched surface be $t = \frac{2L}{v_i}$, here use of $2L$ corresponds to distance travelled in completing one cycle of collision. Therefore, frequency (number) of rebounds between surfaces (o-j-k) and (L-j-k) shall be $f = \frac{1}{t} = \frac{v_i}{2L}$. Since, force exerted by the molecules is equal to rate of change of momentum, i.e. $F_i = f \cdot p = \left(\frac{v_i}{2L}\right) \cdot (2mv_i)$. Accordingly, total force exerted on the surface shall be summation of forces exerted by all molecules, thus $F_i = \sum \frac{mv_i^2}{L} = \frac{m}{L}\sum v_i^2$, here $\boldsymbol{m}$ is characteristic to gas molecules. Considering property (6) of the ideal gas, velocity component of force $\sum v_i^2 = \sum v_j^2 = \sum v_k^2$. This can be normalized as $\sum v_i^2 = \sum v_j^2 = \sum v_k^2 = \frac{1}{3}\left(\sum v_i^2 + \sum v_j^2 + \sum v_k^2\right) = \frac{1}{3}\sum v^2$. It leads to concept of

equi-partitioning of energy to be discussed a little later. Let, N be the number of molecules of the gas under consideration then $F = \frac{1}{3}\frac{mN}{L}\cdot\frac{\sum v^2}{N} = \frac{1}{3}\frac{mN}{L}v_{rms}^2$. Here, a new term v_{rms} is introduced which is called **root mean square (rms)** value of the velocity; it implies that *root of the mean of squares of velocities of individual molecule* and mathematically expressed as $v_{rms} = \sqrt{\frac{\sum v^2}{N}}$. It leads to pressure $P = \frac{F}{L^2} = \frac{1}{3}\frac{mN}{L^3}v_{rms}^2$ and it can be further improvised as $P = \frac{2}{3}\cdot\frac{1}{2}\cdot\frac{M}{V}\cdot v_{rms}^2 \rightarrow PV = \frac{2}{3}\cdot\left(\frac{1}{2}Mv_{rms}^2\right) \rightarrow PV = \frac{2}{3}E \rightarrow E = \frac{3}{2}PV$; here M is the total mass and E total kinetic energy of the gas under consideration, respectively.

As per *Law of Conservation of Energy* with supply of heat energy kinetic energy of the molecules/atoms of the gas increase and at 0 K the gas atoms/molecules cease to have kinetic energy, Accordingly, it can be expressed as $E = f_1(T) \rightarrow T = f_2(v_{rms}) \Rightarrow E = f_3(v_{rms})$. Therefore, comparing pressure of gas, keeping volume to be

constant, at any thermodynamic temperature T and at T_{tr}, the triple point, $\frac{PV}{P_{tr}V} = \frac{\frac{2}{3}E}{\frac{2}{3}E_{tr}} \Rightarrow \frac{P}{P_{tr}} = \frac{E}{E_{tr}} \Rightarrow \frac{P}{P_{tr}} = \frac{v^2}{v_{tr}^2}$

.

Further, heat energy (H) of gas at constant volume is $H \propto M; H \propto s; H \propto T \Rightarrow H = kT$ and therefore as per Law of Conservation of Energy at any thermodynamic temperature $\frac{E}{E_{tr}} = \frac{H}{H_{tr}} \Rightarrow \frac{P}{P_{tr}} = \frac{T}{T_{tr}}$, here $T_{tr} = 273.16\,\text{K}$.

Ideal Gas Equation: Initial elaborations of Kinetic Theory of Gas (KTG), for an ideal gas, it has been proved that $pV = \frac{1}{3}mNv^2$, here v is used for v_{rms} at TK. Since kinetic energy of molecules is proportional to temperature, as discussed earlier, therefore, at triple point of water where velocity of molecules represented by v_{tr}, $\frac{E}{E_{T_{tr}}} = \frac{\frac{1}{2}mNv^2}{\frac{1}{2}mNv_{tr}^2} = \frac{T}{T_{tr}}$, it leads to $v^2 = \frac{v_{tr}^2}{273.16}T$. Accordingly, Ideal Gas Equation can be written as $pV =$

$N\left(\frac{1}{3}\cdot\frac{mv_{tr}^2}{273.16}\right)T = NkT = nRT$. Here, three new constants are being introduced; firstly : $k = 1.38 \times 10^{-23}\,\text{JK}^{-1}$, is called **Boltzmann Constant**, Secondly, constant is **Avogadro's Number** $N_A = 6.02 \times 10^{28}$, *which represents **number of molecules in One Gram Mol of gas*** (Gas of mass in grams equal to molecular weight of gas), and third is derived from the earlier Two constants and is known as **Universal Gas Constant** $R = N_A k = 8.314\,\text{JK}^{-1}$. This definition of N_A leads to $N = nN_A$, here $n -$ represents number of moles of gas, as defined above.

The above two equivalents of pV lead to $\frac{1}{3}mNv^2 = NkT$, or $v = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3kN_AT}{mN_A}} = \sqrt{\frac{3RT}{M_A}}$; here, $M_A = mN_A$ is called molecular weight of the gas.

These variants of basic equation of KTG find application in different situations while handling concepts associated with ***properties of gases*** propounded through experimental verification by different scientist and is as under:

Boyle's Law: Since kinetic energy of the gas at constant temperature is constant, and so also would be v_{rms}, therefore, $pV = Constant$ **at a constant temperature known as Boyle's Law.** It was published by Robert Boyle's in 1662 from experimental observation.

Charles's Law: Taking a sample of gas, if its pressure is kept constant, and its temperature is raised gradually, then through law of conservation of energy, as discussed above $\frac{1}{2}\rho V v_{rms}^2 = mNsT \rightarrow \left(\frac{1}{2}\rho v_{rms}^2\right)V = mNsT \rightarrow pV = mNsT$. Accordingly, $V \propto T$; it is known as **Charles's Law**. In 1780, Jacques Charles formulated this law, but he could not publish it. Later in 1802, Joseph Lious Gay-Lussac confirmed the unpublished discovery naming it after Charles. This can be realized with a balloon filled air, when placed under the sun its volume increases.

Gay-Lussac's Law: In 1809, *Joseph Louis Gay-Lussac* extended the experimentations on Charle's Law to conclude that for a given mass and constant volume of an ideal gas, the pressure exerted on the sides of its container is directly proportional to its absolute temperature $\boldsymbol{p \propto T}|_{V=Constant}$. In fact, it is another variant of Charles's Law taking volume to be constant, while pressure is proportional to the temperature, extending the logic applied substantiate the Law. In view of this in some references ***it is also called Charles's Pressure Law***. A sealed container filled with gas when heated, it bursts, and this happens due to pressure built up with increase of temperature.

Dalton's Law of Partial Pressure: John Dalton in 1801, propounded an empirical of partial pressure exerted by non-reacting gases. Pressure on the walls of containers of a gas, as per KTG is due change of momentum during collision of gas molecules with the walls. Therefore, *total pressure on the walls is equal to pressure exerted by the molecules of the constituent gases*, which mathematically comes to $p = p_1 + p_2 + p_3 + \cdots p_i + \cdots$, here p_i is called partial pressure of ith gas. Let, F_i is the force exerted by ith gas having N_i molecules of the gas. Accordingly, pressure on the wall of area A, which is common to all the constituent molecules is $p_i = \frac{F_i}{A}$. Total force on a wall of container of gas $F = F_1 + F_2 + F_3 + \cdots F_i + \cdots$, accordingly, $p = \frac{F}{A} = \frac{F_1}{A} + \frac{F_2}{A} + \frac{F_3}{A} + \cdots \frac{F_i}{A} + \cdots$, this is equivalent to statement of Dalton's Law.

Avogadro's Law: In 1811, Amedeo Avogadro proposed an hypothesis that two samples of different gases of same volume, temperature and pressure contain same number of molecules. According to KTG, $pV = \frac{1}{3}mNv_{rms}^2$, it leads to $pV = \frac{2}{3}N\left(\frac{1}{2}mv_{rms}^2\right)$. Accordingly, for same volume, pressure and temperature for two different samples o gases, $m_1 N_1 v_{rems-1}^2 = m_2 N_2 v_{rms-2}^2$. Since, KE of molecules at same temperature is same i.e. $\frac{1}{2}m_1 v_{rms-1}^2 = \frac{1}{2}m_2 v_{rms-2}^2$; it implies $N_1 = N_2$.

Graham's Law of Diffusion: A Scottish scientist ***Thomas Graham*** in 1848 had experimentally established that *rate of diffusion of gas is inversely proportional to square root of the mass of the particle; it is known as Graham's Law. This is mathematically expressed as* $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$, here r_1 and r_2 are the rate of diffusion of two different gases while M_1 and M_2, respectively are molar masses. It is *logical to believe that rate of diffusion is proportional to velocities of molecules* and therefore, $\frac{r_1}{r_2} = \frac{v_{rms-1}}{v_{rms-2}}$. As per KTE, at constant pressure and temperature it would lead to $m_1 v_{rms-1}^2 = m_2 v_{rms-2}^2$, accordingly, combining KTE with logic of diffusion, it leads to $\frac{v_{rms-1}^2}{v_{rms-2}^2} = \frac{m_2}{m_1} => \frac{v_{rms-1}}{v_{rms-2}} = \sqrt{\frac{m_2}{m_1}} => \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$, ***Graham's Law*** *in its the final form.*

Intermolecular Force: One of the premises of KTG is that collisions of molecules are elastic in accordance with Newton's Laws of Motion, and was appropriate in the beginning. But developments into understanding of atomic structure of atom, according to which there is a nucleus containing positive charges is enveloped by vacuum filled with electrons revolving around it, these molecules retain their structure so long they are away. Collision of molecules is neither like that of Billiard Balls impinging on each other nor like an arrow piercing a vacuum space. As the molecules with kinetic energy approach closer to each other their potential energy reduces and energy of electrons increases as they undergo rearrangement due to electrostatic forces. First

graph above in the figure here, indicates Potential Energy (PE) of a molecule at a distance from another molecule, represented on X-axis, while the second graph represents forces between the molecules. As distance decreases, due to force of attraction, PE reduces and there is gain of KE. But, at r_0, the distance between their center of mass, which is less that the Twice molecular radii, there is a force of repulsion across the Two Nucleus, as also redistribution of electrons, resulting into minimum PE. Any further reduction in distance causes increase in force of repulsion. As a consequence, there is gain of potential energy till velocity of the molecule reduces to zero. At this point, repulsion of molecules results in rebounding like that of an elastic collision. Typically, radius of Helium atom at a separation of 4×10^{-10} m net force is 6×10^{-13} N. This net force comprises of 7×10^{-42} N gravitational force. Thus, it is seen that as intermolecular distance decreases net force increases by a factor 10^{29}, making gravitational force negligible. With this quantitative comparison deeper understanding of the phenomenon requires knowledge of electrostatics and structure of atoms, which at this age is not covered. Nevertheless, readers are welcome to raise their inquisitiveness through *Contact Us* or wait until they reach the corresponding chapter of this Mentors' Manual.
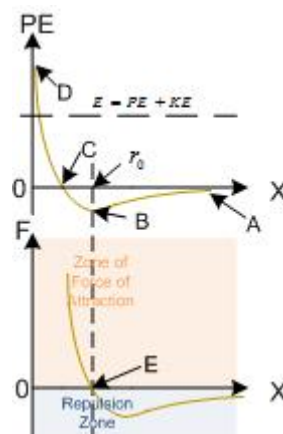
Van der Wall's Equation and Correction in Gas Equation: Two of the premises of the KTG, that – **a)** *volume of gas molecules is negligible* and **b)** *there are no intermolecular forces,* were questioned by van der Wall. Regarding first premise, it is nearly true under very low pressure. Whereas, the second premise is invalid since intermolecular repulsion dominates the gravitational attraction as in the range of molecular diameter, as illustrated above. In 1873, Johannes Diderik van der Wall proposed a modified equation: $\left(p + \frac{an^2}{v^2}\right)(V - nb) - nRT$, known as ***Van der Wall's Equation***. This earned him Nobel Prize in 1910. Here, a and *b* are constants, known as *(known as Van der Wall's volume correction and pressure correction constants, respectively)*. Values of *these constants need to be determined experimentally. These constants a and b when equated to ZERO, the Van der Wall's equation reduces to ideal* gas equation.

Maxwell's Speed Distribution Law: The equation of an ideal gas recognizes rms velocity of molecules and not velocity of an individual molecule. In reality velocity of all molecules are different. Boltzmann had come forward with a statistical concept to suggest probability of occurrence different velocities as function of temperature and is known as Maxwell-Boltzmann Distribution of velocities of gas. $p(v) = \frac{N(v)}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$. A plot of speed distribution of O₂ molecules is shown in the figure. It is seen that as temperature increases real velocity reduces, but the number of molecules having higher velocities increase and thus kinetic energy $\left(= \frac{1}{2}mv^2\right)$ of the molecules in the volume increases. This is an advanced concept in Statistics and it leads to mean velocity of a molecule $v_{avg} = \sqrt{\frac{8RT}{\pi M}}$, and is derived in Appendix-II to this chapter. This concept is extremely useful in explaining evaporation and boiling of liquid.
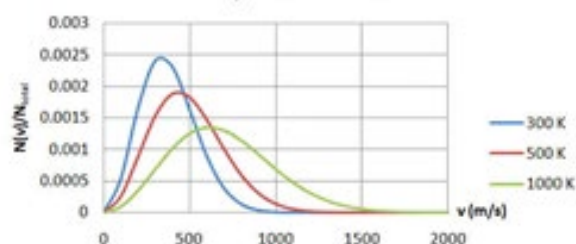
Vaporization: This is process during which those molecules of liquid reaching, its surface open to environment, with a kinetic energy greater than the escape potential of the liquid surface get mixed in environment and do not return back to the liquid. Probability of liquid molecules having that kinetic energy is explained by **Maxwell's Speed Distribution**, while the escape energy is explained by ***Intermolecular Forces*** discussed above. Molecules of liquid mixed in air/gas above the liquid surface are called vapour. Vaporization has three manifestations: **a)** Unsaturated Vapour, **b)** Saturated Vapour, and **c)** boiling. Drying of clothes in rainy season is extremely slow vaporization process and is attributed to high relative humidity.

Take an example of equal volumes volatile liquid in a pan and a bottle. The pan containing liquid, kept open to the environment, dries up after some time; lower the volatility greater is the drying time and vice-versa. In addition to this rate of evaporation is dependent upon temperature, pressure and wind flow which replaces

vapour so generated. Nevertheless, the liquid in an air tight bottle maintains its level. This must have been observed with scared water like गंगा जल, maintaining it same level if the bottle remains unopened and air-tight. The reason of the liquid level in bottle remaining unaltered is the saturated vapour inside the bottle at which rate of molecules escaping the surface of liquid is equal to rate of molecules from the ambient air inside bottle returning to the liquid surface. Return of these molecules is explained by **Law Partial Pressure** exerted by vapour on the liquid surface. But, in case of an open pan the vapor is replaced by a fresh air and thus does not allow it to become saturated. Saturated steam pressure at different temperatures finds application in ventilation and air-conditioning applications. Accordingly, **Relative Humidity** (**RH**) is defined as :

$$RH = \frac{(Amount\ of\ water\ vapour\ present\ in\ a\ given\ volume\ of\ air\ at\ a\ given\ temperature)}{(Amount\ of\ water\ vapour\ required\ to\ saturate\ the\ same\ volume\ of\ air\ at\ the\ same\ temperature)}$$

$$= \frac{(Vapour\ Pressure\ of\ air)}{(Saturated\ Vapour\ Pressure\ (SVP)\ at\ the\ same\ temperature\ )} = \frac{(SVP\ at\ dew\ point)}{(SVP\ at\ the\ same\ temperature\ )}.$$

This adds **Dew Point** to the vocabulary of Physics; *it is that temperature at which vapour starts condensing, i.e. formation of water droplets (dew) out of vapour starts.*

Boiling is the thermodynamic process where conversion of liquid into steam is in thermal equilibrium and temperature of liquid. Temperature at which boiling starts depends upon ambient pressure; and during this process, saturated vapour pressure is equal to ambient pressure, During change of phase from liquid to vapour or vice-versa system either absorbs or dissipates heat equivalent to Latent Heat for per gram of liquid.

Phase Diagram: Illustration on vaporization brought out above leads to conclusion that saturated vapour pressure depends upon temperature at which water and vapour co-exist. This happen with every liquid which upon further cooling at higher pressure changes into solid, the Third Phase. There are some substances which directly transform from solid to vapour phase viz. camphor (कपूर). This temperature dependent coexistence of liquid-vapour, solid-liquid and liquid-vapour is shown with a curve. At this point a question that occurs is – can there be coexistence of three phases solid, liquid and vapour for any material. Answer is assertive and water, which is most

accessible, has it at 4.58 mm Hg pressure and 273.16 K and is called *Triple Point* of Water as shown in the P-T graph; this graph is different for different substance. Triple Point for CO2 it is 216.55 K at 5.11 atmospheric pressure (760 mm Hg). At atmospheric temperature solid CO2 directly converts into vapour and has extensive application in industry, and is known as dry ice.
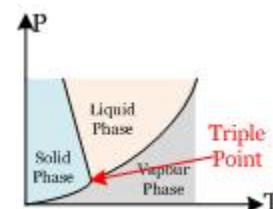
Thermodynamics: Basic understanding of heat started with Zeroth Law of Thermodynamics, which defines thermal equilibrium in respect of temperature, elaborated iat the beginning of this chapter. This is akin to Newton's First law of Motion. But, the whole world would have gone static if only the state of equilibrium was to prevail. In mechanics concern of energy conservation was confined to potential and kinetic energy. Nature is dynamic and every object keep interacting with the environment during which its internal energy changes. Introduction to heat adds a third dimension of energy and convertibility of work into heat has been discussed. Understanding of this dynamics is in the domain of Thermodynamics and is defined in Three *Laws as First, Second and Third Law of Thermodynamics* related to the *Conservation of energy, efficiency of heat engines* and *Entropy of a system*, respectively. **Entropy** another property of matter shall be introduced in elaborations on Second Law of Thermodynamics. In essence, every work that you see from cooking at home to rocket propulsion is a thermodynamic process and its understanding is developed with the Laws of Thermodynamics.

First Law of Thermodynamics (FLT): It is since related to law of conservation of energy, convertibility of energy is translated into an equation $\Delta Q = \Delta U + \Delta W$, or alternatively $\Delta Q - \Delta U - \Delta W = 0$, here, ΔQ - is amount of heat exchanged by the system with its environment, ΔU – is change in internal energy of the system which depends upon temperature, and ΔW – is the difference in amount of work done by the system and on the system. This equation, as usual is sign sensitive and therefore, the sign convention that is adopted is as under:

Sign Convention	Heat	Internal Energy	Work Done
+ve	Heat given to the system	Increase in Internal Energy	Work done by the system on environment
-Ve	Heat taken away or extracted from the system	Decrease in internal energy	Work done on the system by environment

Forward journey into thermodynamics require first to determine work done on or by gas and amount of heat required to change thermodynamic state of gas. p-v curve of gas. The **ideal gas equation (IGE)** $pv = nRT$ can be written as $y = f(p, v)$. Accordingly, $\Delta y = v \cdot \Delta p + p \cdot \Delta v = p \cdot \Delta v$; here, $v \cdot \Delta p$ represents change of pressure at constant volume. Accordingly, as per definition of work, since despite change of pressure there is no displacement, $v \cdot \Delta p = 0$. In view of this in moving from state A to B, work done $w = \int_{v_1}^{v_2} p dv$, i.e. area under the p-v curve.
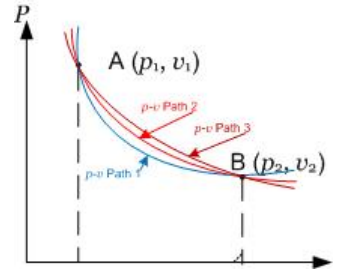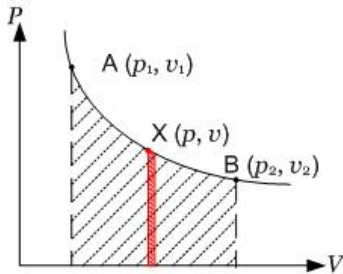
It is to be noted this area would depend upon shape of the path traversed by the system to change state on p-v diagram, and accordingly the work done is different for each path as shown in the figure.

The FLT can be viewed to define different thermodynamic processes as under –
a) **Reversible Process** – it is that process in which sequence of states are repeated, but in reverse sequence, viz freezing of water, evaporation.
b) **Irreversible Process** – in this process sequence can not be traced in reverse order, example age.
c) **Cyclic Process** - where system return to same thermodynamic state (P, V and T), in this process $\Delta U = 0$, and hence $\Delta Q = \Delta W$. Carnot's cycles, that shall be elaborated a little later, is a reversible cycle and explains Carnot's Engine.
d) **Isothermal Process** - in which temperature remains unchanged i.e. $\Delta T = 0$. In elaborations of KTG is seen that internal energy of gas depends upon its temperature and if $\Delta Q = 0$ and hence $\Delta U = 0$; therefore, $\Delta Q = \Delta W$. Further, using IGE in this process $p\Delta v + \Delta p \cdot v = 0$, thus gradient of p-v curve at any point is $\frac{dp}{dv}\Big|_{Isothermal} = \frac{\Delta p}{\Delta v}\Big|_{\Delta v \to 0} = -\frac{p}{v}$. Thus work done in this process, using IGE $W = \int_{v_1}^{v_2} p dv = \int_{v_1}^{v_2} \frac{nRT}{v} dv = nRT \int_{v_1}^{v_2} \frac{1}{v} dv = nRT \log_e \left(\frac{v_2}{v_1}\right) = nRT \log_e \left(\frac{p_1}{p_2}\right)$., Using Boyle's Law this relationship can be written as $W = nRT \log_e \left(\frac{v_2}{v_1}\right) = nRT \log_e \left(\frac{p_1}{p_2}\right)$, or $\log_e \left(\frac{v_2}{v_1}\right) = \log_e \left(\frac{p_1}{p_2}\right)$.
e) **Adiabatic Process** - in which system does not exchange heat with the environment and hence $\Delta Q = 0$. Accordingly, $\Delta U + \Delta W = 0$, or $\Delta U = -\Delta W$. This process is more complex and its understanding requires to appreciate relationship between specific heat of gas separately at constant pressure and volume, and shall be discussed after elaboration of this relationship.
f) **Isobaric Process** – in this process pressure remains unchanged and it is not necessary that change in volume during process is isothermal. In such a process all finds its full manifestation i.e. $\Delta U = \Delta U + \Delta W$.

Specific Heat Capacity of Gases: Exchange of heat in thermodynamic process involves three variables, mass of substance (m), specific heat capacity of substance (S) and change of temperature (ΔT). Among these three variables (S) is constant as long its state remains either liquid or solid due to their practically negligible thermal expansion with change of temperature. In respect of gases the concept changes due its highly compressible nature. It can be understood with taking a sample of gas of mass m kept at constant volume V pressure is supplied heat ΔQ undergoes a temperature rise ΔT. As per First Law of

Thermodynamics $\Delta Q = \Delta U + \Delta W \Rightarrow \Delta Q = \Delta U + p \cdot \Delta V$. Since it is a constant volume process and hence $\Delta V = 0 \Rightarrow \Delta Q = \Delta U$, and $\Delta Q_V = m \cdot S_V \cdot \Delta T_V$, here subscript $_p$ designates value of the variables at constant pressure.

Taking another constant pressure process when heat is supplied as per ideal gas equation $pV = nRT \Rightarrow p\Delta V = nR\Delta T_p$, here n is number of moles of the gas in a sample under consideration and R is universal gas constant. Accordingly, $\Delta Q = \Delta U + \Delta W \Rightarrow \Delta Q_p = \Delta U + p \cdot \Delta V$. And $\Delta Q_p = m \cdot S_p \cdot \Delta T_p$. Using these two equations molar heat capacities of gas under constant volume and constant pressure can be compared here under, for which change in temperatures are taken to be equal i.e. $\Delta T_V = \Delta T_p = \Delta T$. Accordingly –

| Particulars	Constant Volume process	Constant Volume Process
Heat supplied	• $\Delta Q_V = \Delta U_V + \Delta W_V$ • $\Delta W_V = 0$, since $\Delta V = 0$ in the process • $\Delta Q_V = \Delta U_V = m \cdot S_V \cdot \Delta T$	• $\Delta Q_p = \Delta U_p + \Delta W_p \Rightarrow \Delta Q_p = \Delta U_p + p \cdot \Delta V$ • $\Delta Q_p = m \cdot S_p \cdot \Delta T$
Internal energy of gas	Since internal energy of gas is $U = k \cdot n \cdot R \cdot T$. Here k is a constant characteristic to gas based on its molecular composition. Therefore, for a given sample of gas $\Delta U_V = \Delta U_p = \Delta U$	
Quantity of gas in Moles	$m = nM \Rightarrow n = \dfrac{m}{M}$. Here, M is molar mass of gas and n is number of moles gas in the given sample	
Molar Heat Capacity of Gas		
Heat Equation in number of moles	$\Delta Q_V = \Delta U = n \cdot M \cdot S_V \cdot \Delta T$	• $\Delta Q_p = n \cdot M \cdot S_p \cdot \Delta T = \Delta U + p \cdot \Delta V$
Molar Heat Capacities of Gas C_V and C_p	$\dfrac{\Delta Q_V}{n \cdot \Delta T} = M \cdot S_V = C_V$. Here, M and S_V are characteristic to the gas. Accordingly, C_V is called molar specific heat capacity of gas is constant at constant volume.	$\dfrac{\Delta Q_p}{n \cdot \Delta T} = M \cdot S_p = C_p$. Here, M and S_P are characteristic to the gas. Accordingly, C_p is called molar specific heat capacity of gas is constant at constant volume.
Relation between C_p and C_V	$\Delta Q_p = \Delta Q_V + p \cdot \Delta V$ As per ideal gas equation $pV = nRT \Rightarrow p\Delta V = nR\Delta T$ Accordingly, $n \cdot M \cdot S_P \cdot \Delta T = n \cdot M \cdot S_V \cdot \Delta T + n \cdot R \cdot \Delta T \Rightarrow n \cdot C_p \cdot \Delta T = n \cdot C_v \cdot \Delta T + n \cdot R \cdot \Delta T$ Dividing the equation by $n \cdot \Delta T$ we get $C_p = C_v + R$	

This can be better illustrated with an example where a system, in initial condition, is placed on heat source with piston unlocked, heat absorbed by the system increases temperature of the gas, and in-turn increase in internal energy shall cause increase in internal pressure Δp. Since piston is free to move, this increased internal pressure would effect into expansion of the gas until equilibrium in pressure w.r.t. environment is achieved. This is the case of work done by the system on environment, hence Δw is +ve. This is since a case of

transfer of heat under constant pressure heat transferred $\Delta Q = C_p \Delta T$, is utilized first in change of internal energy $\Delta U = C_v \Delta T$, and doing work as a consequence of change in internal energy such that $\Delta W = p\Delta v$. Using values of these constituents of FLT, the equation emerges as : $\Delta Q = \Delta U + \Delta w = C_v \Delta T + p \Delta v$.

From IGE $pv = nRT$, and in constant pressure case $p \cdot (V + \Delta v) = nR \cdot (T + \Delta T)$, thus for an incremental change in volume in this case $p\Delta v = nR\Delta T$. Thus $\Delta v = \frac{nR\Delta T}{p}$ and using this value in the above equation arrived at from FLT it leads to $C_p \Delta T = C_v \Delta T + p \cdot \frac{R\Delta T}{p}$, or, $C_p = C_v + R$, here all the constituents are in $\text{Cal} \cdot \text{Mol}^{-1} \cdot \text{K}^{-1}$. In case constituents are taken in Joule-equivalent (i.e. $\text{Joule} \cdot \text{Mol}^{-1} \cdot \text{K}^{-1}$), then $C_p = C_v + \frac{R}{J}$, since **R** is a ***universal gas constant.***
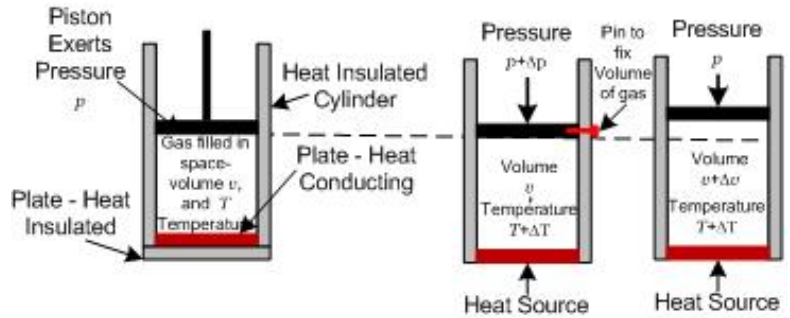
Equi-partitioning of Energy in Monatomic, Diatomic and Polyatomic Gases: Kinetic behaviour of gases, in a state of thermal equilibrium, is seen to be uniform across each degree of freedom. It is attributed to aggregate energy of the gas across degrees of freedom uniformly distributed. Accordingly, gases in KTG are classified into three categories (i) Monatomic gases, (ii) Diatomic Gases and (iii) Polyatomic Gases. Each of the case is being analyzed separately.

(i) **Monatomic gases** : In this motion of atoms is translational motion is along three axes and accordingly its kinetic energy of a molecule is represented as $E_m = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$, and based on principle of equi-partitioning of energy aggregate kinetic energy of the gas is $E = \frac{3}{2}m\sum v^2$. Accordingly, applying IGE $U = nN_A\left(\frac{3}{2}kT\right) = n\frac{3}{2}RT$ is the internal energy of the gas.

(ii) **Diatomic Gases**: In monatomic gases size of atom being small is taken as a point mass, while it has been enlarged only for pictorial purposes in diatomic gases with inter-atomic space shown as electron cloud. This formation is like a dumbbell typically aligned to Z-axis. This formation will have two additional degree of freedom of rotation along X-axis and Y-axis, while along Z-axis it would be insignificant due size of atoms. Kinetic energy of rotation along these axes would add on to translational energy and thus total kinetic energy would be $E = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2\right) + \left(\frac{1}{2}I_x\omega_x^2 + + \frac{1}{2}I_y\omega_y^2\right)$. Extending the logic of equi-partitioning of energy monatomic gas aggregate energy would be $U = nN_A(5kT) = n\frac{5}{2}RT$

(iii) **Polyatomic Gases:** All atoms in addition to Two atoms of diatomic configuration are aggregated in third atom as shown in the figure as tri-atomic molecules. This configuration will set in vibration in two directions (a) third equivalent atom vibrating in a direction transverse to the diatomic alignment and (b) diatomic configuration along the line of diatom. These two vibrations are electro-mechanical in nature. Due to centrifugal action when diatoms tend to depart the third equivalent atoms tries to fill the gap due to electrostatic forces. As a result of this centripetal force increases to pull together diatoms to come closer and setting up vibration in them along the line joining them. Likewise, when diatoms come closer, it creates a repelling force in third equivalent atom to move way along the line transverse to line of diatoms. Thus two additional degree of freedom add on and accordingly energy of atom in polyatomic

gases would be $E = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \right) + \left(\frac{1}{2}I_x\omega_x^2 + + \frac{1}{2}I_y\omega_y^2 \right) + \left(\frac{1}{2}\mu v^2 + + \frac{1}{2}kx^2 \right)$. This is best possible simplistic explanation of partitioning of energy of a molecule of polyatomic gas, and accordingly aggregate energy of the gas would be $U = nN_A(7kT) = n\frac{7}{2}RT$.

Adiabatic Process (Contd.): A man walking fast to reach bus-stop, a student running to reach school in time, pumping air in cycle, all these activities are close to adiabatic process. In this speed of work is so fast that heat generated in the process of work is nearly not having sufficient time to dissipate into the environment and thus ideally Isothermal process is not achievable. Likewise, it is not possible to fully prevent dissipation of heat into environment, and therefore ideal adiabatic process is also not achievable. Nevertheless, a typical adiabatic process is visualized in the figure below.
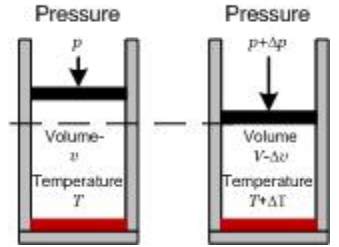
The FLT states, $\Delta Q = \Delta U + \Delta W$, since $\Delta Q = 0$, and hence $\Delta U = -\Delta W = -p\Delta v$. In discrete form this equation takes a form $\Delta U = nC_v \cdot \Delta T$ and in infinitesimal form it is written as $dU = nC_v \cdot dT$. But, from IGE $pdv + vdp = nRdT$. This leads to

$dT = \dfrac{pdv + vdp}{nR}$, and using this in equation of FLT $nC_v\left(\dfrac{pdv + vdp}{nR} \right) + pdv = 0 => C_v\left(\dfrac{pdv + vdp}{R} \right) + pdv = 0$.

Using relation of specific heat of gases, it leads to $C_v\left(\dfrac{pdv + vdp}{C_p - C_v} \right) + pdv = 0 \Rightarrow \dfrac{C_p}{C_p - C_v} \cdot pdv + \dfrac{C_v}{C_p - C_v} \cdot vdp = 0$

. On separating the variables it leads to $\dfrac{C_p}{C_v} \cdot \dfrac{dv}{v} + \dfrac{dp}{p} = 0 => \gamma \cdot \dfrac{dv}{v} + \dfrac{dp}{p} = 0$. Here, a new constant γ i.e. ratio of

specific heats is introduced such that $\gamma = \dfrac{C_p}{C_v}$ whose value of **is always greater than One and is evident**

from basic definition of specific heats C_p and C_v . Integrating the differential equation yields to $\gamma \log_e v + \log_e p = C$, here C is constant of integration. Combining the two logarithmic terms it is $pv^\gamma = C$. This equation is known as **Poisson's Law of Adiabatic Process**. This law together with IGE can be written

v-T form as $\left(\dfrac{nRT}{v} \right)v^\gamma = nRTv^{\gamma-1} = C$, and in **p-T** form it is $p\left(\dfrac{nRT}{p} \right)^\gamma = (nR)^\gamma \dfrac{T^\gamma}{p^{\gamma-1}} = C$.

Next inference is the gradient of p-v curve in this process, derived Poison's Law, goes : $p\gamma v^{\gamma-1}dv + v^\gamma dp = 0$, it leads to $\dfrac{dp}{dv}\Big|_{Adiabatic} = -\gamma \cdot \dfrac{p}{v}$. It leads to an interesting finding that ratio of gradient of p-v curve in adiabatic

and isothermal process leads to: $\dfrac{\dfrac{dp}{dv}\Big|_{Adiabatic}}{\dfrac{dp}{dv}\Big|_{Isothermal}} = \dfrac{-\gamma \dfrac{p}{v}}{-\dfrac{p}{v}} = \gamma$. Thus, γ is characterizes correlations between

isothermal and adiabatic processes.

The third and most important inference is work done in adiabatic process, which again evolves from Poisson' Law using basic definition of work, $W = \int\limits_{v_1}^{v_2} pdv = \int\limits_{v_1}^{v_2} \dfrac{C}{v^\gamma}dv = C\int\limits_{v_1}^{v_2} \dfrac{C}{v^\gamma}dv = \dfrac{1}{1-\gamma}\left[\dfrac{p_2 v_2^\gamma}{v_2^{\gamma-1}} - \dfrac{p_1 v_1^\gamma}{v_1^{\gamma-1}} \right] = \dfrac{1}{1-\gamma}[p_2 v_2 - p_1 v_1]$.

This equation together with IGE leads to $W = \dfrac{1}{1-\gamma}\left[nRT_2 - nRT_1\right] = \dfrac{nR}{1-\gamma}\left[T_2 - T_1\right] \Rightarrow W = \dfrac{nR}{\gamma-1}\left[T_1 - T_2\right]$ in its
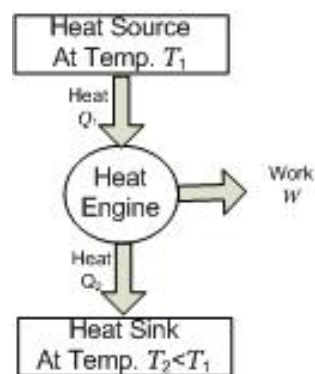
final form is most convenient since $\gamma > 1$.

Poisson Ratio For Different Gases: Thermodynamically classification of gases based on number of atoms in its molecule was made during elaboration of equi-partitioning of energy and accordingly internal energy U for monatomic, diatomic and polyatomic gases were determined earlier. Using those inferences Poisson's Ration for each of them are tabulated below.

Particulars	Monatomic Gas	Diatomic Gas	Polyatomic Gas
Internal Energy	$U = n\dfrac{3}{2}RT$	$U = n\dfrac{5}{2}RT$	$U = n\dfrac{7}{2}RT$
Specific Heat at Constant Volume $\left(C_v\right)$	$C_v = \dfrac{1}{n}\dfrac{dU}{dT} = \dfrac{3}{2}R$	$C_v = \dfrac{1}{n}\dfrac{dU}{dT} = \dfrac{5}{2}R$	$C_v = \dfrac{1}{n}\dfrac{dU}{dT} = \dfrac{7}{2}R$
Specific Heat at Constant Pressure $\left(C_p\right)$	$C_p = C_v + R = \dfrac{5}{2}R$	$C_p = C_v + R = \dfrac{7}{2}R$	$C_p = C_v + R = \dfrac{9}{2}R$
Poisson's Ratio $\left(\gamma\right)$	$\gamma = \dfrac{C_p}{C_v} = \dfrac{\frac{5}{2}R}{\frac{3}{2}R} = \dfrac{5}{3} \approx 1.67$	$\gamma = \dfrac{C_p}{C_v} = \dfrac{\frac{7}{2}R}{\frac{5}{2}R} = \dfrac{7}{5} = 1.40$	$\gamma = \dfrac{C_p}{C_v} = \dfrac{\frac{9}{2}R}{\frac{7}{2}R} = \dfrac{9}{7} \approx 1.29$

**Heat Engine:** These discussions have laid basic premise for elaboration of Ideal Heat Engine (IHE) which is a combination of isothermal and adiabatic processes. It is conceptualized as shown in the figure. It takes heat from a source at high temperature and utilizes it doing work and part of unutilized heat is ejected into a sink at temperature lower than that of the source. Accordingly, efficiency of the Heat Engine $\eta = \dfrac{W}{Q_1} = \dfrac{Q_1 - Q_2}{Q_1}$. Here Q_1 is the amount of heat taken from source at high temperature T_1, and Q_2 is the amount of heat returned to the sink at low temperature T_2. Car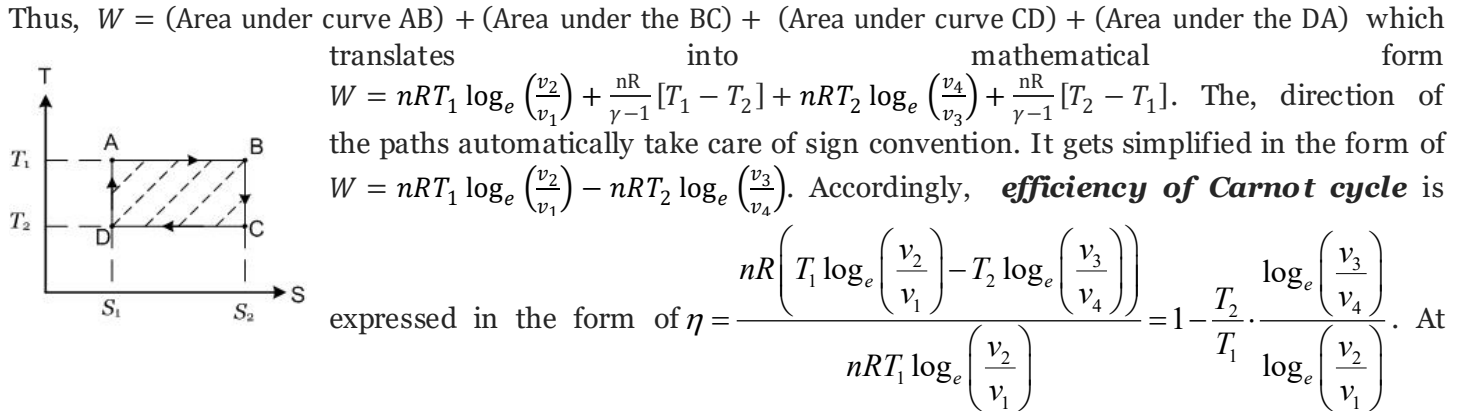not proposed an Ideal Heat Engine (IHE) which work in a cycle ABCD as shown on a p-v diagram. The cycle works within Two isothermals at temperature T_1 and T_2 such that $T_1 > T_2$. These two isothermals are coupled by Adiabatic processed represented by BC during expansion and DA during contraction to return to the initial state at A.
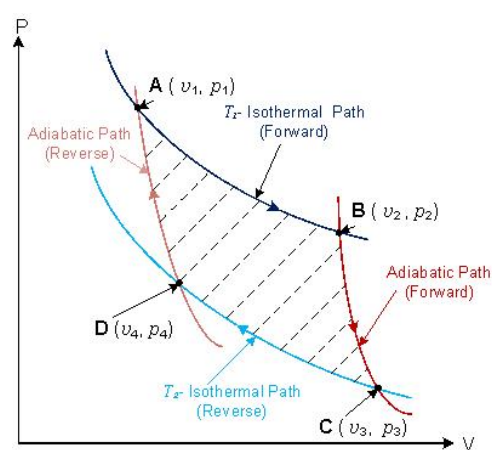
Accomplishing this cycle through a system of gas filled
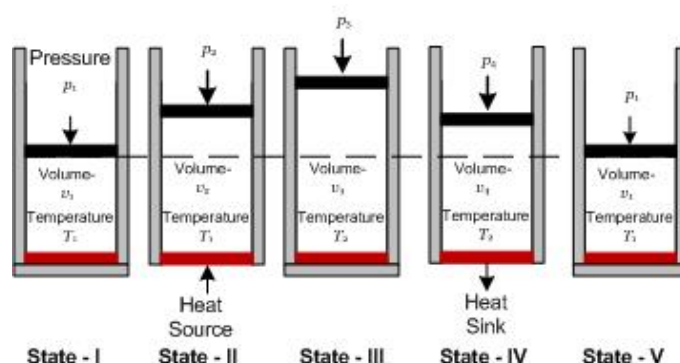
in an insulated cylinder, in stages, is shown in the figure. Stage-I represents point A on the graph, while after traversing along isothermal path AB the system absorbs heat from a source at a temperature T_1 so as to reach a point B represented by Stage-II. Next, the adiabatic path BC is brings system to a lower temperature T_2 corresponding to the point C, represented by Stage-III. Again an isothermal at temperature T_2 ejects heat to heat sink to reach point D, represented by Stage-IV. The last part of the cycle is path DA, which is an adiabatic process to bring back the system to initial state represented by point A. Thus, stage-V is identical to stage-I. Accordingly, work done is equal to area within the curve ABCD comprising of isothermal and adiabatic processes.

Thus, W = (Area under curve AB) + (Area under the BC) + (Area under curve CD) + (Area under the DA) which

translates into mathematical form $W = nRT_1 \log_e \left(\frac{v_2}{v_1}\right) + \frac{nR}{\gamma-1}[T_1 - T_2] + nRT_2 \log_e \left(\frac{v_4}{v_3}\right) + \frac{nR}{\gamma-1}[T_2 - T_1]$. The, direction of the paths automatically take care of sign convention. It gets simplified in the form of $W = nRT_1 \log_e \left(\frac{v_2}{v_1}\right) - nRT_2 \log_e \left(\frac{v_3}{v_4}\right)$. Accordingly, **efficiency of Carnot cycle** is

expressed in the form of $\eta = \dfrac{nR\left(T_1 \log_e\left(\frac{v_2}{v_1}\right) - T_2 \log_e\left(\frac{v_3}{v_4}\right)\right)}{nRT_1 \log_e\left(\frac{v_2}{v_1}\right)} = 1 - \dfrac{T_2}{T_1} \cdot \dfrac{\log_e\left(\frac{v_3}{v_4}\right)}{\log_e\left(\frac{v_2}{v_1}\right)}$. At

this point a like *pressure (P), volume (V), temperature (T)* and *internal energy (U)* another parameter **Entropy (S)** is introduced. It simplifies representation of the thermodynamic processes. A system in thermodynamic equilibrium has a definite entropy and if small amount of heat (ΔQ) is given to the system at temperature T then change in entropy $\Delta S = \frac{\Delta Q}{T}$. As per LCE, ΔQ has to occur between two discrete systems and, therefore, it is inferred that **entropy of an isolated system remains constant**. The Carnot cycle shown above in p-v diagram is represented in T-S diagram. As per definition of Entropy, path AB of the cycle during involves extraction of heat from source and thus entropy at temperature T_1 changes from S_1 to S_2. And during isothermal path CD heat is ejected to sink at temperature T_2. During adiabatic processes represented by BC and DA since there is no exchange of heat by the system with the environment, therefore, entropy of the system remains unaltered. Since, path AD returns the system to initial state A, therefore, entropy of the system must be restored to S_1, and this in accordance with the above inference and is in conformance with the definition of *Entropy*. Accordingly, during AB, $S_2 - S_1 = \frac{Q_1}{T_1}$, or $Q_1 = (S_2 - S_1)T_1$, and during BA, $S_1 - S_2 = -\frac{Q_2}{T_2}$, or $Q_2 = (S_1 - S_2)T_2$. Thus efficiency of Carnot cycle shall be

$\eta = \dfrac{(S_2 - S_1)T_1 - (S_2 - S_1)T_2}{(S_2 - S_1)T_1} = 1 - \dfrac{(S_1 - S_2)T_2}{(S_2 - S_1)T_1} = 1 - \dfrac{T_2}{T_1}$. Here, temperatures are represented in Kelvin. Further,
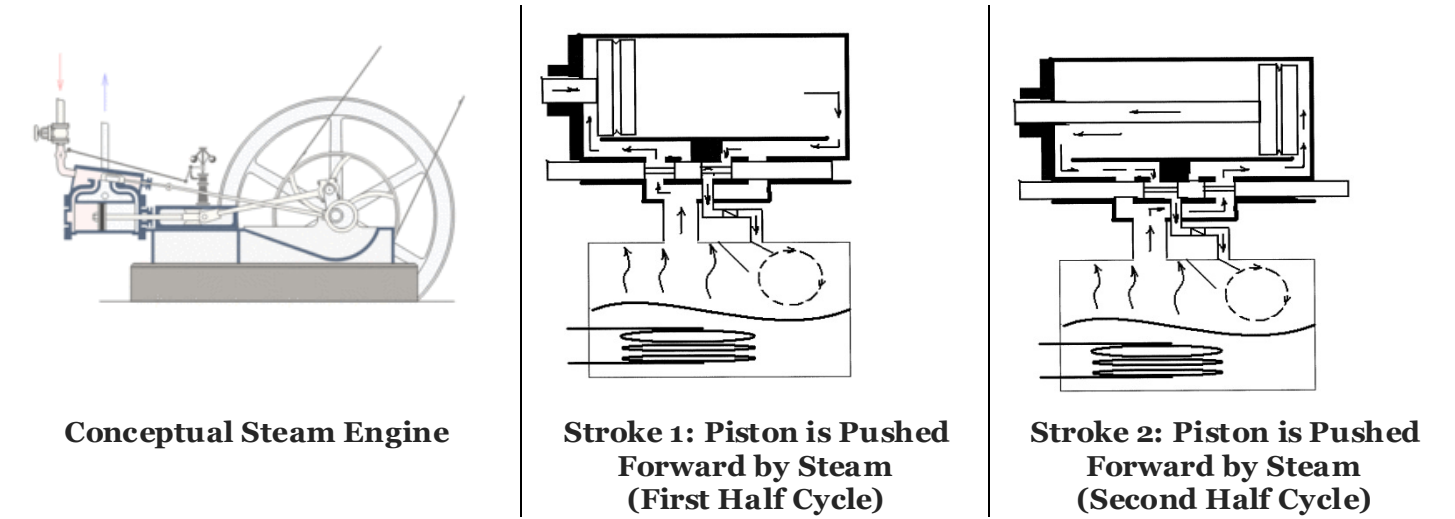
0K i.e. absolute Zero t cannot be achieved and $T_2 < T_1 \Rightarrow \dfrac{T_2}{T_1} < 1$ hence unity efficiency (100%) cannot be

achieved. Accordingly, **Carnot's Theorem** propounds that – **All reversible engines operating between two same temperatures have equal efficiency or alternatively no engine operating between the same two temperatures can have an efficiency greater than this**.

Second Law of Thermodynamics: It is an evolution of understanding of heat engines which states that – **It is not possible to design a heat engine which works on cyclic process and whose only result is to take heat from a body at a single temperature and convert it completely into mechanical work**. This is also known as **Kelvin-Planck statement**.

The concept of IHE has found application in actual heat engines used in advanced applications of conversion of heat energy into mechanical energy. These Heat Engines are classified in two broad categories: **a)** *External Combustion Engine* and **b)** *Internal Combustion Engine*.
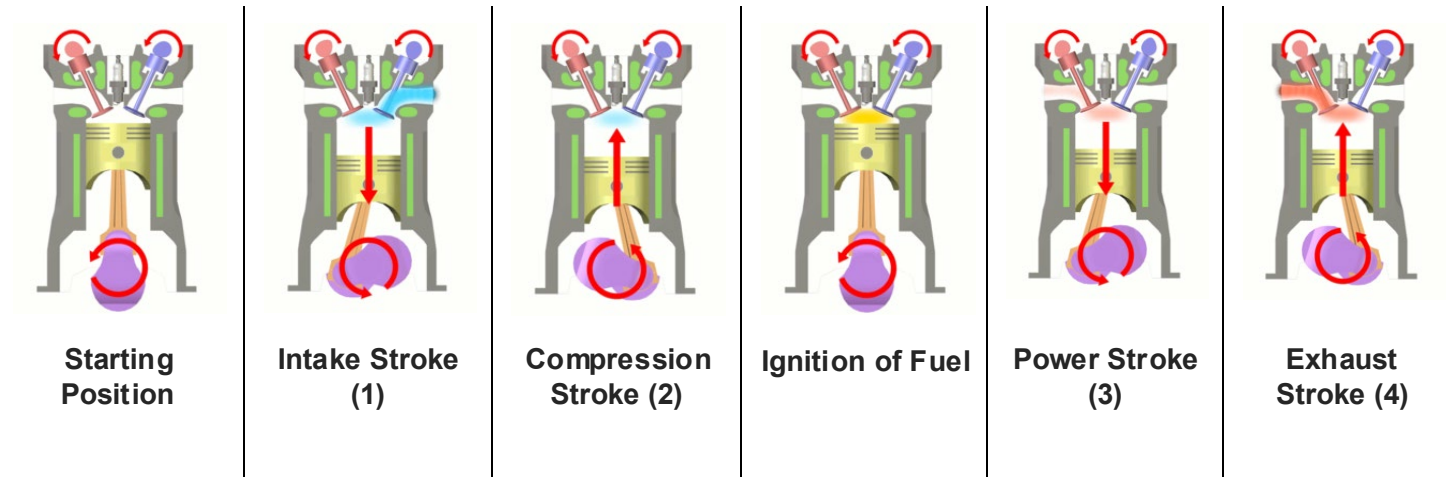
External Combustion Engine: These type of engines carryout combustion outside the engine to produce heat and best example is steam engine. In this externally produced heat is used to evaporate water at high pressure, and thus utilizing latent heat of steam, as shown in the figure below. This pressurized steam is

injected into the steam engine cylinder. It is a two stroke engine; in first stroke steam pushes piston forward, and during this, steam behind the piston is exhausted. This forward motion causes half-revolution of the wheel. In second stroke, through movement of valves, steam is injected into the evacuated part of the cylinder. Thus piston is pushed back to evacuate the steam utilized in first-half of the cycle; this complete the cycle and in turn remaining half of revolution of the wheel. Thus *these two strokes make a complete revolution, called cycle of the steam engine and it is called* **Double Stroke Engine.** *The exhaust steam, despite having given away its latent heat for conversion into mechanical energy, its heat content is considerable. Therefore, in all steam engines exhaust steam is reused in a closed cycle to improve upon thermal efficiency of the heat engine.* Regulation of fresh steam and exhaust is done with the help of valves whose movements are coupled through a separate mechanism to the movement of piston.

| **Conceptual Steam Engine** | **Stroke 1: Piston is Pushed Forward by Steam (First Half Cycle)** | **Stroke 2: Piston is Pushed Forward by Steam (Second Half Cycle)** |

Typical Steam Engine (Source: https://en.wikipedia.org/wiki/Steam_engine)

Internal Combustion Engine: These engines use inflammable gas or liquid like petrol or diesel and missed with air in an atomizer to produce inflammable liquid/gas. This mixture is injected inside the engine and ignited there. Broadly, there are two types of external combustion engines- a) Petrol Engine, where ignition is caused by an electrical spark and b) Diesel Engine, in this gas is compressed at a pressure enough to cause self-combustion. Likewise in gas engines mixture is produced by supplementing it with oxygen to facilitate combustion. Atomizer is suitably designed and tuned to ensure that exhaust air does not have either unused oxygen or un-burnt fuel. Typical operation of petrol engine, in six stages, comprising of Four Strokes is shown in the figure below.

| **Starting Position** | **Intake Stroke (1)** | **Compression Stroke (2)** | **Ignition of Fuel** | **Power Stroke (3)** | **Exhaust Stroke (4)** |

A Typical Four Stroke Internal Combustion Engine *(Source: https://en.wikipedia.org/wiki/Four-stroke_engine)*

Summary: *This part brings basic concepts of Heat Energy, its transmission, thermodynamics including heat engines. Details of thermometry, the science of measurement of temperature involves concepts other than that of heat, which have not been touched upon until now. In view of this Thermometry shall be taken together instrumentation after covering electricity. This is a strategic decision and is in line with the philosophy of this manual to make it intrinsic.. Examples drawn from real life are to help to build visualization and an insight into the phenomenon occurring around. A deeper journey into the problem solving would make integration and application of concepts intuitive. This is absolutely true for any real life situations, which requires multi-disciplinary knowledge, a skill necessary for evolving solutions. Thus, problem solving process is more a conditioning of the thought process, rather than just learning the subject. Practice with wide range of problems is the only pre-requisite to develop proficiency and speed of problem solving, and making formulations more intuitive rather than a burden on memory, as much as overall personality of a person. References cited below provide an excellent repository of problems. Readers are welcome to pose their difficulties to solve any-problem from anywhere, but only after two attempts to solve. It is our endeavour to stand by upcoming student in their journey to become a scientist, engineer and professional, whatever they choose to be.*

This manual is being supplemented with representative problems from contemporary text books and Question papers from various competitive examinations. These questions will be supported with illustrations to the solutions which covers thought process behind every solution from first principle to the extent possible. It is a dynamic exercise to catalyse the conceptual thought process.

References:
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Appendix I: Application of Fourier's Law of Heat Conduction

Application of Fourier's Law $\dfrac{dQ}{dt} = -KA\dfrac{d\theta}{dl}$ is made in two cases to determine rate of heat transfer through conduction for different geometry..

Case 1-Axial Conduction: Taking element of pipe of thickness Δx at a distance x from the end whose cross-section is at temperature T_1. Let cross-section of pipe having area $A = \pi\left(r_2^2 - r_1^2\right)$. Thus heat flow through the cross-sectional element of tube of thickness Δx as per Fourier's Law is , $\dfrac{dQ}{dt} = -k\pi\left(r_2^2 - r_1^2\right)\dfrac{d\theta}{dl} = K$ this is constant since in steady state as there is no absorption of heat and therefore
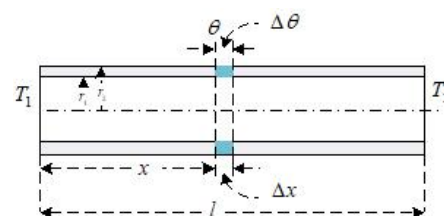
temperature remains at each cross-section. Accordingly, $K\Delta x = -k\pi\left(r_2^2 - r_1^2\right)\Delta\theta \Rightarrow \int_0^l K dx = -\int_{T_1}^{T_2} k\pi\left(r_2^2 - r_1^2\right)d\theta$. This

resolves into $Kl = -k\pi\left(r_2^2 - r_1^2\right)\left(T_2 - T_1\right) \Rightarrow K = \dfrac{dQ}{dt} = -\dfrac{k\pi\left(r_2^2 - r_1^2\right)\left(T_2 - T_1\right)}{l}$. Since, $T_1 > T_2$ i.e. sending temperature

at sending end of heat is greater than that at the receiving end and hence $\dfrac{dQ}{dt} = \dfrac{kA\left(T_1 - T_2\right)}{l} = \dfrac{kA\Delta T}{l}$.

Case 2-Radial conduction: In this case outward radial heat transfer by conduction in a washer of thickness d though an

element of inner radius r and outer radius $r + \Delta r$ is $\dfrac{dQ}{dt} = -\dfrac{k\left(2\pi rd\right)\Delta\theta}{dr} = K$. In this case of

heat transfer, temperatures at inner radius and outer radius of the washers are T_1 and T_2 respectively. The rate of heat transfer in steady state remains constant all through every infinitesimal element, without any build-up of temperature in the washer. It leads to

$\displaystyle\int_{T_1}^{T_2} d\theta = -\dfrac{K}{2k\pi d}\cdot\int_{r_1}^{r_2}\dfrac{dr}{r} \Rightarrow T_2 - T_1 = -\dfrac{K}{2k\pi d}\left[\ln r\right]_{r_1}^{r_2}$. Since $T_1 > T_2$ and hence $K = \dfrac{dQ}{dt} = \left(T_1 - T_2\right)\cdot\dfrac{2k\pi d}{\ln\dfrac{r_2}{r_1}}$
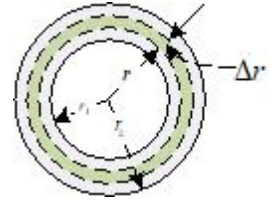
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Appendix II: Derivation of Mean Velocity of a Molecule in a Gas

Mean speed of a gaseous molecule is determined based on Maxwell Distribution as depicted in the figure which is empirically expressed as Maxwell-Boltzmann relation where probability of a certain velocity of a molecule is:

$P(v) = \left(\dfrac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 e^{\frac{mv^2}{2KT}}$. This $P(v)$ is

called Probability Density Function (PDF) and mean speed, which is always positive,

of a molecule is $v_{avg} = \displaystyle\int_0^\infty vP(v)\,dv$. This
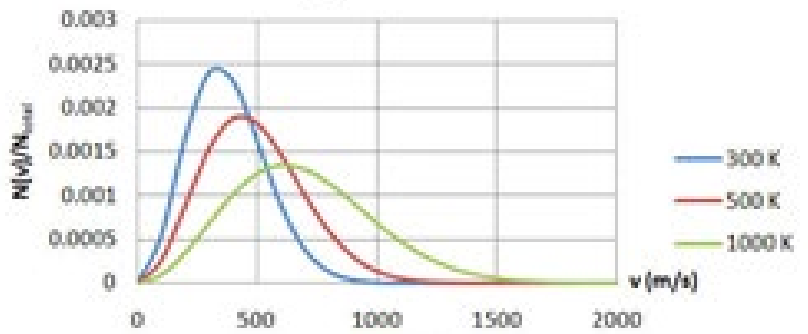
takes a form : $v_{avg} = \displaystyle\int_0^\infty vP(v)dv = \int_0^\infty v\left(\left(\dfrac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 e^{\frac{mv^2}{2KT}}\right)dv = 4\pi\left(\dfrac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_0^\infty v^3 e^{\frac{mv^2}{2KT}}dv$. This integration can be

simplified by comparing it with a standard integral $v = \displaystyle\int x^3 e^{-ax^2}dx = \dfrac{1}{2a^2}$ where for instant case $a = \dfrac{m}{2kT}$.

Thus, it simplifies into $v_{avg} = 4\pi\left(\dfrac{m}{2\pi kT}\right)^{\frac{3}{2}}\displaystyle\int_0^\infty v^3 e^{\frac{mv^2}{2KT}}dv = 4\pi\left(\dfrac{m}{2\pi kT}\right)^{\frac{3}{2}}\times\dfrac{2k^2 T^2}{m^2} = \sqrt{\dfrac{8kT}{m}} = \sqrt{\dfrac{8N_A kT}{N_A m}} = \sqrt{\dfrac{8RT}{M}}$.

Here, Avogadro's number N_A is Avogadro's number and Universal Gas Constant $R = N_A k$, where k is Boltzmann Constant and Molar Mass $M = N_A m$, where m is the mass of each molecule.

$$\langle v \rangle = \int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2} \Rightarrow \langle v \rangle = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \left. \frac{4k^2 T^2}{2m^2} \right|_{a=\frac{m}{2kT}} = \sqrt{\frac{8kT}{\pi m}}$$

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Appendix II-a: Derivation of Standard Integral Used in Mean Velocity

Integral $\int_0^\infty x^3 e^{-ax^2} dx$ in Appendix A is reduced to a problem of Integration by parts as under:

$$I = \int_0^\infty x^3 e^{-ax^2} dx = \int_0^\infty x^2 e^{-ax^2} \left(xdx\right)$$

Substituting $u = ax^2 \Rightarrow du = 2axdx \Rightarrow xdx = \frac{du}{2a}$ and $x^2 = \frac{u}{a}$. Accordingly, $I = \int_0^\infty \frac{u}{a} e^{-u} \left(\frac{du}{2a}\right) = \frac{1}{2a^2} \int_0^\infty u e^{-u} du$.

Now by method of Integration by parts $\int (p \cdot q) dx = p \int q dx - \int \left(\left(\frac{d}{dx} p\right)\left(\int q dx\right)\right) dx$. Applying this formula to solve the instant integral $\int u e^{-u} du = u \int e^{-u} du - \int \left(\left(\frac{d}{du} u\right)\left(\int e^{-u} du\right)\right) du = u\left(-e^{-u}\right) - \int \left(\int -e^{-u} du\right) du = -u e^{-u} + \int e^{-u} du = -u e^{-u} - e^{-u}$. Thus it leads to: $I = \frac{1}{2a^2} \int_0^\infty u e^{-u} du = \frac{1}{2a^2} \left[-u e^{-u} - e^{-u} \right]_0^\infty$. Taking the values, elaborated in Appendix I-b, it converges to

: $I = \frac{1}{2a^2}\left(-(0-0)-(0-1)\right) = \frac{1}{2a^2}$. Since average speed is always positive and hence $I = \int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$.

Appendix II-b: Limiting Values (in Appendix I-a)

(i) $\quad e^{-u} = \frac{1}{e^u} \Rightarrow e^{-u} = \left.\frac{1}{e^\infty}\right|_{u\to\infty} = \frac{1}{\infty} = 0$

(ii) $\quad e^{-u} = \frac{1}{e^u} \Rightarrow e^{-u} = \left.\frac{1}{e^0}\right|_{u\to 0} = \frac{1}{1} = 1$

(iii) $\quad u e^{-u} = \frac{1}{\dfrac{e^u}{u}} = \frac{1}{\dfrac{1+u+\dfrac{u^2}{2}+\dfrac{u^3}{3}...}{u}} = \frac{1}{\dfrac{1}{u}+1+\dfrac{u}{2}+\dfrac{u^2}{3}...} = \frac{1}{0+1+\infty+\infty...} = \frac{1}{\infty} = 0$

(iv) $\quad u e^{-u} = \frac{1}{\dfrac{e^u}{u}} = \frac{1}{\dfrac{1+u+\dfrac{u^2}{2}+\dfrac{u^3}{3}...}{u}} = \frac{1}{\dfrac{1}{u}+1+\dfrac{u}{2}+\dfrac{u^2}{3}...} = \left.\frac{1}{\infty+1+0+0...}\right|_{u\to 0} = \frac{1}{\infty} = 0$

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