# TEMPERATURE SCALES

## TEMPERATURE

Temperature is a macroscopic physical quantity related to our sense of hot and cold. The natural flow of heat is from higher temperature to lower temperature, i.e. temperature determines the thermal state of a body whether it can give or receive heat.

## TEMPERATURE SCALES

**(i)** The Kelvin temperature scale is also known as thermodynamic scale. The SI unit of temperature is the kelvin and is defined as (1/273.16) of the temperature of the triple point of water. The triple point of water is that point on a P–T diagram where the three phase of water, the solid, the liquid and the gas, can coexist in equilibrium.

**(ii)** In addition to Kelvin temperature scale, there are other temperature scales also like Celsius, Fahrenheit, Reaumur, Rankine, etc. Temperature on one scale can be converted into other scale by using the following identity

$$\frac{\text{Reading on any scale} - \text{lower fixed point (LFP)}}{\text{Upper fixed point (UFP)} - \text{lower fixed point (LFP)}} = \text{constant for all scales}$$

Hence $\dfrac{C-0°}{100°-0°} = \dfrac{F-32°}{212°-32°} = \dfrac{K-273.15}{373.15-273.15}$

**(iii)** Different temperature scales :

| Name of the scale | Symbol for each degree | Lower fixed point (LFP) | Upper fixed point (UFP) | Number of divisions on the scale |
|---|---|---|---|---|
| Celsius | °C | 0°C | 100°C | 100 |
| Fahrenheit | °F | 32°F | 212°F | 180 |
| Kelvin | K | 273.15 K | 373.15 K | 100 |

**Ex.** Express a temperature of 60°F in degree celsius and in kelvin.

**Sol.** By using $\dfrac{C-0°}{100°-0°} = \dfrac{F-32°}{212°-32°} = \dfrac{K-273.15}{373.15-273.15}$

$$\Rightarrow \frac{C-0°}{100°-0°} = \frac{60°-32°}{212°-32°} = \frac{K-273.15}{373.15-273.15} \Rightarrow C = 15.15°\,C \text{ and } K = 288.7\,K$$

**Ex.** The temperature of an iron piece is heated from 30° to 90°C. What is the change in its temperature on the fahrenheit scale and on the kelvin scale?

**Sol.** $\Delta C = 90° - 30° = 60°C$

Temperature difference on Fahrenheit Scale $\Delta F = \frac{9}{5}\Delta C = \frac{9}{5}(60°C) = 108°F$

Temperature difference on Kelvin Scale $\Delta K = \Delta C = 60\,K$

# THERMAL EXPANSION

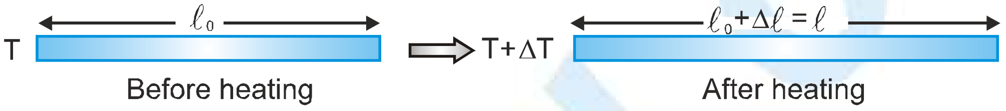
## THERMAL EXPANSION

When matter is heated without any change in it's state, it usually expands. According to atomic theory of matter, asymmetry in potential energy curve is responsible for thermal expansion. As with rise in temperature the amplitude of vibration increases and hence energy of atoms increases, hence the average distance between the atom increases. So the matter as a whole expands.

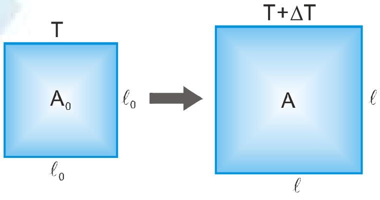
- Thermal expansion is minimum in case of solids but maximum in case of gases because intermolecular force is maximum in solids but minimum in gases.
- Solids can expand in one dimension (Linear expansion), two dimension (Superficial expansion) and three dimension (Volume expansion) while liquids and gases usually suffers change in volume only.

## Linear expansion :

$$\bullet = \bullet_0 (1 + \alpha\Delta\theta) \Rightarrow \Delta\bullet = \bullet_0\alpha\Delta\theta$$



## Superficial (areal) expansion :

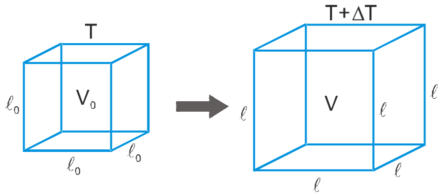


$$A = A_0 (1 + \beta\Delta\theta)$$

Also $A_0 = \bullet_0^2$ and $A = \bullet^2$

So $\bullet^2 = \bullet_0^2(1 + \beta\Delta\theta) = [\bullet_0(1 + \alpha\Delta\theta)]^2 \Rightarrow \beta = 2\alpha$

## Volume expansion :



$V = V_0 (1 + \gamma\Delta\theta)$ Also $V = \bullet^3$ and $V_0 = \bullet_0^3$ so $\gamma = 3\alpha$

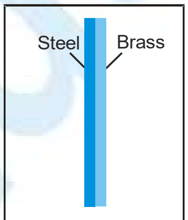
$\Rightarrow 6\alpha = 3\beta = 2\gamma$ or $\alpha : \beta : \gamma = 1 : 2 : 3$

## Contraction on heating :

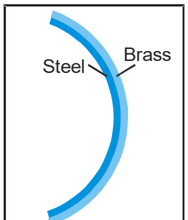
Some rubber like substances contract on heating because transverse vibration of atoms of substance dominate over longitudinal vibration which is responsible for expansion.

## Application of thermal Expansion in Solids

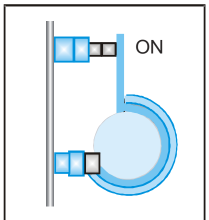
**(a) Bi–metallic strip :** Two strips of equal length but of different materials (different coefficient of linear expansion) when join together, it is called "Bi–metallic strip" and can be used in thermostat to break or make electrical contact. This strip has the characteristic property of bending on heating due to unequal linear expansion of the two metals. The strip will bend with metal of greater $\alpha$ on outer side.



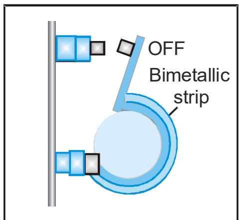
Room temperature



Higher temperature



At room temperature



At high temperature

**(b)** **Effect of temperature on the time period of a simple pendulum :** A pendulum clock keeps proper time at temperature $\theta$. If temperature is increased to $\theta'$ ( > $\theta$) then due to linear expansion, length of pendulum increases and hence its time period will increase.

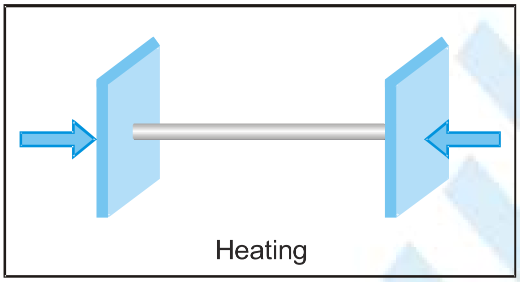
Fractional change in time period $\frac{\Delta T}{T} = \frac{1}{2}\alpha\Delta\theta$ $\left(\because T \propto \sqrt{l} \quad \therefore \frac{\Delta T}{T} = \frac{1}{2}\frac{\Delta l}{l}\right)$

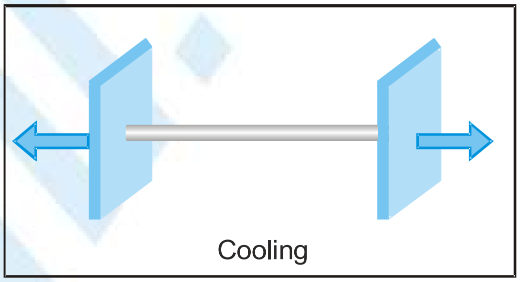
**(i)** Due to increment in its time period, a pendulum clock becomes slow in summer and will lose time. Loss of time in a time period $\Delta T = \frac{1}{2}\alpha\,\Delta\theta T$

**(ii)** The clock will lose time i.e. will become slow if $\theta' > \theta$ (in summer) and will gain time i.e will become fast if $\theta' < \theta$ (in winter).

**(iii)** Since coefficient of linear expansion ($\alpha$) is very small for invar, hence pendulums are made of invar to show the correct time in all seasons.

**(c)** When a rod whose ends are rigidly fixed such as to prevent expansion or contraction, undergoes a change in temperature due to thermal expansion or contraction, a compressive or tensile stress is developed in it. Due to this thermal stress the rod will exert a large force on the supports. If the change in temperature of a rod of length L is $\Delta\theta$ then :–

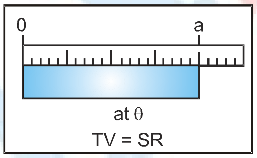


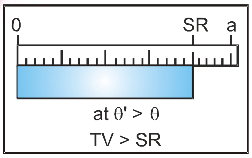


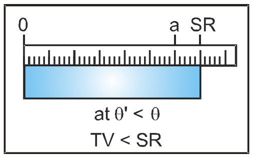
Thermal strain $= \frac{\Delta L}{L} = \alpha\Delta\theta \Rightarrow \alpha = \frac{\Delta L}{L}\times\frac{1}{\Delta\theta}$ So thermal stress $= Y\alpha\Delta\theta \Rightarrow Y = \frac{\text{stress}}{\text{strain}}$

So force on the supports $F = YA\alpha\Delta\theta$

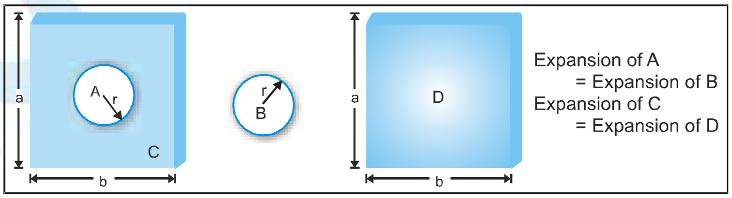
**(d)** **Error in scale reading due to expansion or contraction:** If a scale gives correct reading at temperature $\theta$. At temperature $\theta'(>\theta)$ due to linear expansion of scale, the scale will expand and scale reading will be lesser than true value so that,







**(e)** **Expansion of cavity:** Thermal expansion of an isotropic object may be imagined as a photographic enlargement.



**(f) Some other application**

- **(i)** When rails are laid down on the ground, space is left between the ends of two rails
- **(ii)** The transmission cable are not tightly fixed to the poles
- **(iii)** Test tubes, beakers and cubicles are made of pyrex–glass or silica because they have very low value of coefficient of linear expansion
- **(iv)** The iron rim to be put on a cart wheel is always of slightly smaller diameter than that of wheel
- **(v)** A glass stopper jammed in the neck of a glass bottle can be taken out by warming the neck of the bottle.

**Ex.** A steel ruler exactly 20 cm long is graduated to give correct measurements at $20^0$C. ($\alpha_{\text{steel}} = 1.2 \times 10^{-5}\ ^\circ C^{-1}$)

**(a)** Will it give readings that are too long or too short at lower temperatures?

**(b)** What will be the actual length of the ruler be when it is used in the desert at a temperature of $40^0$C?

**Sol.** **(a)** If the temperature decreases, the length of the ruler also decreases through thermal contraction. Below $20^0$C, each centimeter division is actually somewhat shorter than 1.0 cm, so the steel ruler gives readings that are too long.

**(b)** At $40^0$C, the increases in length of the ruler is

$\Delta\bullet = \bullet\alpha\Delta T = (20)(1.2 \times 10^{-5})(40^0 - 20^0) = 0.48 \times 10^{-2}$ cm

$\therefore$ The actual length of the ruler is, $\bullet' = \bullet + \Delta\bullet = 20.0048$ cm

**Ex.** A second's pendulum clock has a steel wire. The clock is calibrated at $20^0$C. How much time does the clock lose or gain in one week when the temperature is increased to $30^0$C? ($\alpha_{\text{steel}} = 1.2 \times 10^{-5}\ ^\circ C^{-1}$)

**Sol.** The time period of second's pendulum is 2 second. As the temperature increases length time period increases. Clock becomes slow and it loses the time. The change in time period is

$$\Delta T = \frac{1}{2}T\alpha\Delta\theta = \left(\frac{1}{2}\right)(2)(1.2 \times 10^{-5})(30^0 - 20^0) = 1.2 \times 10^{-4}\text{ s}$$

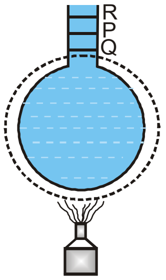
$$\therefore \text{ New Time period is } T' = T + \Delta T = (2 + 1.2 \times 10^{-4}) = 2.00012\text{ s}$$

$$\therefore \text{ Time lost in one week } \Delta t = \left(\frac{\Delta T}{T'}\right)t = \frac{(1.2 \times 10^{-4})}{(2.00012)}(7 \times 24 \times 3600) = 36.28\text{ s}$$

## Thermal Expansion in Liquids

**(i)** Liquids do not have linear and superficial expansion but these only have volume expansion.

**(ii)** Since liquids are always to be heated along with a vessel which contains them so initially on heating the system (liquid + vessel), the level of liquid in vessel falls (as vessel expands more since it absorbs heat and liquid expands less) but later on, it starts rising due to faster expansion of the liquid.



PQ → represents expansion of vessel

QR → represents the real expansion of liquid.

**(iii)** The actual increase in the volume of the liquid

= The apparent increase in the volume of liquid + the increase in the volume of the vessel.

**(iv)** Liquids have two coefficients of volume expansion.

**(A) Co–efficient of apparent expansion ($\gamma a$)**

It is due to apparent (that appears to be, but in not) increase in the volume of liquid if expansion of vessel containing the liquid is not taken into account.

$$\gamma_a = \frac{\text{Apparent expansion in volume}}{\text{Initial volume} \times \Delta\theta} = \frac{(\Delta V)}{V \times \Delta\theta}$$

**(B) Co–efficient of real expansion ($\gamma r$)**

**(a)** It is due to the actual increase in volume of liquid due to heating.

$$\gamma_r = \frac{\text{Real increase in volume}}{\text{Initial volume} \times \Delta\theta} = \frac{(\Delta V)}{V \times \Delta\theta}$$

**(b)** Also coefficient of expansion of flask $\gamma_{\text{Vessel}} = \dfrac{(\Delta V)_{\text{Vessel}}}{V \times \Delta\theta}$

**(c)** $\gamma_{\text{Real}} = \gamma_{\text{Apparent}} + \gamma_{\text{Vessel}}$

**(d)** Change (apparent change) in volume in liquid relative to vessel is

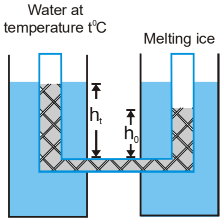
$\Delta V_{\text{app}} = V(\gamma_{\text{Real}} - \gamma_{\text{Vessel}})\,\Delta\theta = V(\gamma_r - 3\alpha)\Delta\theta$

$\alpha$ = Coefficient of linear expansion of the vessel.

## Different level of liquid in vessel

| $\gamma$ | $\Delta V$ | *Level* |
|---|---|---|
| $\gamma_{Real.} > \gamma_{Vessel}(=3\alpha) \Rightarrow \gamma_{app} > 0$ | $\Delta V_{app}$ *is positive* | *Level of liquid in Vessel will rise on heating* |
| $\gamma_{Real.} < \gamma_{Vessel}(=3\alpha) \Rightarrow \gamma_{app} < 0$ | $\Delta V_{app}$ *is negative* | *Level of liquid in vessel will fall on heating* |
| $\gamma_{Real} = \gamma_{Vessel}(=3\alpha) \Rightarrow \gamma_{app} = 0$ | $\Delta V_{app} = 0$ | *Level of liquid in vessel will remain same* |

**Ex.** In figure shown, left arm of a U–tube is immersed in a hot water bath at temperature t°C, and right arm is immersed in a bath of melting ice; the height of manometric liquid in respective columns is $h_t$ and $h_0$. Determine the coefficient of expansion of the liquid.



**Sol.** The liquid is in hydrostatic equilibrium $\Rightarrow \rho_t g h_t = \rho_0 g h_0$

Where, $\rho_t$ is density of liquid in hot bath, $\rho_0$ is density of liquid in cold bath.

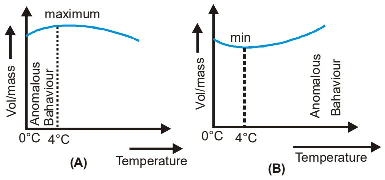
Volumes of a given mass M of liquid at temperatures t and $0^0$C

are related by $V_t = V_0(1+\gamma t)$ Since $\rho_t V_t = \rho_0 V_0 \Rightarrow \rho_t = \dfrac{\rho_0 V_0}{V_t} = \dfrac{\rho_0}{(1+\gamma t)}$

Since $h_t = \dfrac{\rho_0 h_0}{\rho_t} = h_0(1+\gamma t)$ which on solving for $\gamma$, yields $\gamma = \dfrac{(h_t - h_0)}{h_0 t}$

## Anomalous expansion of water

Generally matter expands on heating and contracts on cooling. In case of water, it expands on heating if its temperature is greater than 4°C. In the range 0°C to 4°C, water contracts on heating and expands on cooling, i.e. $\gamma$ is negative. This behaviour of water in the range from 0°C to 4°C is called anomalous expansion.



This anomalous behaviour of water causes ice to form first at the surface of a lake in cold weather. As winter approaches, the water temperature increases initially at the surface. The water there sinks because of its increased density. Consequently, the surface reaches 0°C first and the lake becomes covered with ice. Aquatic life is able to survive the cold winter as the lake bottom remains unfrozen at a temperature of about 4°C. At 4°C, density of water is maximum while its specific volume is minimum.

**Ex.** The difference between lengths of a certain brass rod and of a steel rod is claimed to be constant at all temperatures. Is this possible ?

**Sol.** If $L_B$ and $L_S$ are the lengths of brass and steel rods respectively at a given temperature, then the lengths of the rods when temperature is changed by θ °C.

$L'_B = L_B(1+\alpha_B\,\Delta\theta)$ and $L'_S = L_S(1+\alpha_B\,\Delta\theta)$ So that $L'_B = L'_S(L_B - L_S) + (L_B\,\alpha_B - L_S\alpha_S)\ \Delta\theta$

So $(L'_B - L'_S)$ will be equal to $(L_B - L_S)$ at all temperatures if, $L_B\alpha_B - L_S\alpha_S = 0$ [as $\Delta\theta \neq 0$] or $\dfrac{L_B}{L_S} = \dfrac{\alpha_S}{\alpha_B}$

i.e., the difference in the lengths of the two rods will be independent of temperature if the lengths are in the inverse ratio of their coefficients of linear expansion.

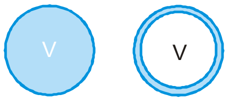
**Ex.** There are two spheres of same radius and material at same temperature but one being solid while the other hollow. Which sphere will expand more if

**(a)** they are heated to the same temperature,

**(b)** same heat is given to them ?

**Sol.** **(a)** As thermal expansion of isotropic solids is similar to true photographic enlargement, expansion of a cavity is same as if it had been a solid body of the same material i.e. $\Delta V = V\gamma\,\Delta\theta$

As here V, γ and Δθ are same for both solid and hollow spheres treated (cavity) ; so the expansion of both will be equal.



**(b)** If same heat is given to the two spheres due to lesser mass, rise in temperature of hollow sphere will be more [as $\Delta\theta = \dfrac{Q}{mc}$] and hence its expansion will be more [as $\Delta V = V\gamma\Delta\theta$].

# MODE OF HEAT TRANSFER

Heat is a form of energy which transfers from a body at higher temperature to a body at lower temperature.

The transfer of heat from one body to another may take place by any one of the following modes :

## 1. Conduction

The process in which the material takes an active part by molecular action and energy is passed from one particle to another is called conduction. It is predominant in solids.

## 2. Convection

The transfer of energy by actual motion of particle of medium from one place to another is called convection. It is predominant is fluids (liquids and gases).

## 3. Radiation

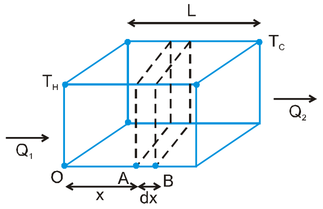
Quickest way of transmission of heat is known as radiation. In this mode of energy transmission, heat is transferred from one place to another without effecting the intervening medium.

| Conduction | Convection | Radiation |
|---|---|---|
| Heat Transfer due to Temperature difference | Heat transfer due to density difference | Heat transfer with out any medium |
| Due to free electron or vibration motion of molecules | Actual motion of particles | Electromagnetic radiation |
| Heat transfer in solid body (in mercury also) | Heat transfer in fluids (Liquid + gas) | All |
| Slow process | Slow process | Fast process ($3 \times 10^8$ m/sec) |
| Irregular path | Irregular path | Straight line (like light) |

## THERMAL CONDUCTION

The process by which heat is transferred from hot part to cold part of a body through the transfer of energy from one particle to another particle of the body without the actual movement of the particles from their equilibrium positions is called conduction. The process of conduction only in solid body (except Hg) Heat transfer by conduction from one part of body to another continues till their temperatures become equal.

The process of transmission of heat energy in which heat is transferred from one particle of the medium to the other, but each particle of the medium stays at its own position is called conduction, for example if you hold an iron rod with one of its end on a fire for some time, the handle will get hot. The heat is transferred from the fire to the handle by conduction along the length of iron rod. The vibrational amplitude of atoms and electrons of the iron rod at the hot end takes on relatively higher values due to the higher temperature of their environment. These increased vibrational amplitude are transferred along the rod, from atom to atom during collision between adjacent atoms. In this way a region of rising temperature extends itself along the rod to your hand.



Consider a slab of face area A, Lateral thickness L, whose faces have temperatures $T_H$ and $T_C(T_H > T_C)$.

Now consider two cross sections in the slab at positions A and B separated by a lateral distance of dx. Let temperature of face A be T and that of face B be T + ΔT. Then experiments show that Q, the amount of heat crossing the area A of the slab at position x in time t is given by

$$\boxed{\frac{Q}{t} = -KA\frac{dT}{dx}}$$

Here K is a constant depending on the material of the slab and is named thermal conductivity of the material, and the quantity $\left(\frac{dT}{dx}\right)$ is called temperature gradient. The (–) sign in equation (2.1) shows heat flows from high to low temperature (ΔT is a –ve quantity)

## STEADY STATE

If the temperature of a cross-section at any position x in the above slab remains constant with time (remember, it does vary with position x), the slab is said to be in steady state.

Remember steady-state is distinct from thermal equilibrium for which temperature at any position (x) in the slab must be same.

For a conductor in steady state there is no absorption or emission of heat at any cross-section. (as temperature at each point remains constant with time). The left and right face are maintained at constant temperatures $T_H$ and $T_C$ respectively, and all other faces must be covered with adiabatic walls so that no heat escapes through them and same amount of heat flows through each cross-section in a given Interval of time. Hence $Q_1 = Q = Q_2$. Consequently the temperature gradient is constant throughout the slab.

Hence, $$\frac{dT}{dx} = \frac{\Delta T}{L} = \frac{T_f - T_i}{L} = \frac{T_C - T_H}{L}$$

and $$\frac{Q}{t} = -KA\frac{\Delta T}{L} \Rightarrow \frac{Q}{t} = KA\left(\frac{T_H - T_C}{L}\right)$$

Here Q is the amount of heat flowing through a cross-section of slab at any position in a time interval of t.

**Ex.** One face of an aluminium cube of edge 2 metre is maintained at 100 °C and the other end is maintained at 0 °C. All other surfaces are covered by adiabatic walls. Find the amount of heat flowing through the cube in 5 seconds. (thermal conductivity of aluminium is 209 W/m–°C)

**Sol.** Heat will flow from the end at 100ºC to the end at 0°C.

Area of cross-section perpendicular to direction of heat flow, $A = 4m^2$ then $\frac{Q}{t} = KA\frac{(T_H - T_C)}{L}$

$$Q = \frac{(209\,W/\,m^{o}C)(4m^2)(100^{o}C - 0^{o}C)(5\,sec)}{2\,m} = 209\ kJ$$

## Thermal conductivity (K) :

(i) It's depends on nature of material.

Order of thermal conductivity Ag > Cu > Au > Al

K ⎡For Ag maximum is (410 W/mK)

K ⎣For Freon minimum is 12 (0.008 W/mK)

**(ii)** **SI Unit :** J $s^{-1}$ $m^{-1}$ $K^{-1}$ **Dimensions :** $M^1 L^1 T^{-3} \theta^{-1}$

**(iii)** For an ideal or perfect conductor of heat the value of K = ∞

**(iv)** For an ideal or perfect bad conductor or insulator the value of K = 0

**(v)** For cooking the food, low specific heat and high conductivity utensils are most suitable.

## APPLICATION OF THERMAL CONDUCTION

**(i)** In winter, the iron chairs appear to be colder than the wooden chairs.

**(ii)** Cooking utensils are made of aluminium and brass whereas their handles are made of wood.

**(iii)** Ice is covered in gunny bags to prevent melting of ice.

**(iv)** We feel warm in woollen clothes and fur coat.

**(v)** Two thin blankets are warmer than a single blanket of double the thickness.

**(vi)** Birds often swell their feathers in winter.

**(vii)** A new quilt is warmer than old one.

## THERMAL RESISTANCE TO CONDUCTION

If you are interested in insulating your house from cold weather or for that matter keeping the meal hot in your tiffin-box, you are more interested in poor heat conductors, rather than good conductors. For this reason, the concept of thermal resistance R has been introduced.

For a slab of cross-section A, Lateral thickness L and thermal conductivity K, $R = \dfrac{L}{KA}$

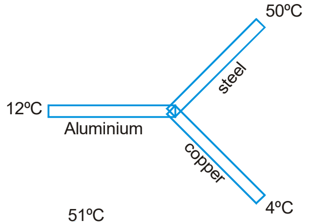
In terms of R, the amount of heat flowing though a slab in steady-state (in time t) $\dfrac{Q}{t} = \dfrac{(T_H - T_L)}{R}$

If we name $\dfrac{Q}{t}$ as thermal current $i_T$ then, $i_T = \dfrac{T_H - T_L}{R}$

This is mathematically equivalent to OHM's law, with temperature donning the role of electric potential. Hence results derived from OHM's law are also valid for thermal conduction.

More over, for a slab in steady state we have seen earlier that the thermal current $i_L$ remains same at each cross-section. This is analogous to kirchoff's current law in electricity, which can now be very conveniently applied to thermal conduction.

**Ex.** Three identical rods of length 1m each, having cross-section area of 1$cm^2$ each and made of Aluminium, copper and steel respectively are maintained at temperatures of 12ºC, 4ºC and 50ºC respectively at their separate ends. Find the temperature of their common junction. [ $K_{Cu}$=400 W/m-K , $K_{Al}$ = 200 W/m-K , $K_{steel}$ = 50 W/m-K ]

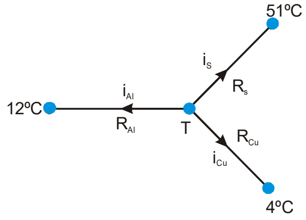


**Sol.** $R_{Al} = \dfrac{L}{KA} = \dfrac{1}{10^{-4} \times 200} = \dfrac{10^4}{200}$

Similarly $R_{steel} = \dfrac{10^4}{50}$ and $R_{copper} = \dfrac{10^4}{400}$

Let temperature of common junction = T

then from Kirchoff's current laws, $i_{Al} + i_{steel} + i_{Cu} = 0$



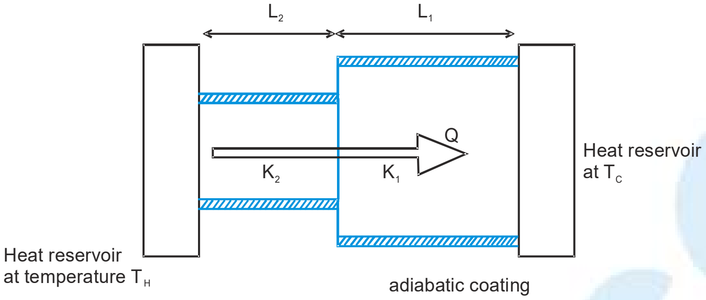
$\Rightarrow \quad \dfrac{T-12}{R_{Al}} + \dfrac{T-51}{R_{steel}} + \dfrac{T-4}{R_{Cu}} = 0 \quad \Rightarrow \quad (T-12)\,200 + (T-50)\,50 + (T-4)\,400$

$\Rightarrow \quad 4(T-12) + (T-50) + 8\,(T-4) = 0 \quad \Rightarrow 13T = 48 + 50 + 32 = 130 \Rightarrow T = 10°C$

## SLABS IN PARALLEL AND SERIES

### Slabs in series (in steady state)

Consider a composite slab consisting of two materials having different thickness $L_1$ and $L_2$ different cross-sectional areas $A_1$ and $A_2$ and different thermal conductivities $K_1$ and $K_2$. The temperature at the outer surface of the states are maintained at $T_H$ and $T_C$, and all lateral surfaces are covered by an adiabatic coating.



Let temperature at the junction be T, since steady state has been achieved thermal current through each slab will be equal. Then thermal current through the first slab.

$$I = \frac{Q}{t} = \frac{T_H - T}{R_1} \Rightarrow T_H - T = IR_1$$

and that through the second slab, $\quad i = I = \frac{Q}{t} = \frac{T - T_C}{R_2} \Rightarrow T - T_C = IR_2$

Adding equation $\qquad T_H - T_L = (R_1 + R_2)I \Rightarrow I = \dfrac{T_H - T_C}{R_1 + R_2}$

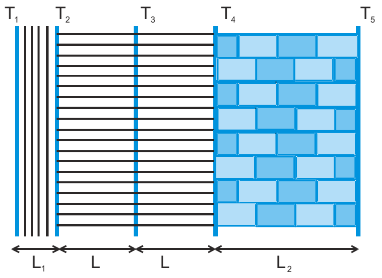
Thus these two slabs are equivalent to a single slab of thermal resistance $R_1 + R_2$.

If more than two slabs are joined in series and are allowed to attain steady state, then equivalent thermal resistance is given by

$$R = R_1 + R_2 + R_3 + .......$$

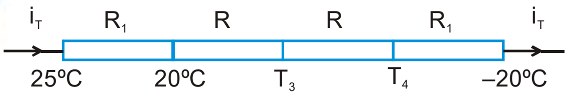
**Ex.** The figure shows the cross-section of the outer wall of a house built in a hill-resort to keep the house insulated from the freezing temperature of outside. The wall consists of teak wood of thickness $L_1$ and brick of thickness ($L_2 = 5L_1$), sand witching two layers of an unknown material with identical thermal conductivities and thickness. The thermal conductivity of teak wood is $K_1$ and that of brick is ($K_2 = 5K$). Heat conduction through the wall has reached a steady state with the temperature of three surfaces being known.

($T_1 = 25°C$, $T_2 = 20°C$ and $T_5 = -20°C$). Find the interface temperature $T_4$ and $T_3$.



**Sol.** Let interface area be A. Then thermal resistance of wood, $R_1 = \dfrac{L_1}{K_1 A}$ and that of brick wall $R_2 = \dfrac{L_2}{K_2 A} = \dfrac{5L_1}{5K_1 A} = R_1$

Let thermal resistance of the each sand witch layer = R. Then the above wall can be visualised as a circuit

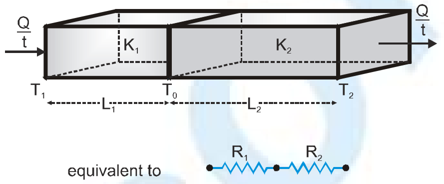


Thermal current through each wall is same.

Hence $\frac{25-20}{R_1}=\frac{20-T_3}{R}=\frac{T_3-T_4}{R}=\frac{T_4+20}{R_1}$ $\Rightarrow 25-20=T_4+20 \Rightarrow T_4=-15°C$

also, $20-T_3=T_3-T_4 \Rightarrow T_3=\frac{20+T_4}{2}=2.5°C$

- **Equivalent conductivity for Heat flow through slabs in series**



$$R_{eq}=R_1+R_2$$

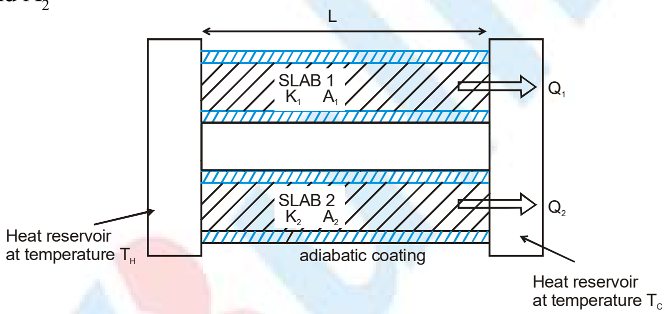
$$\frac{L_1+L_2}{K_{eq}A}=\frac{L_1}{K_1A}+\frac{L_2}{K_2A}$$

Equivalent thermal conductivity of the system is

$$K_{eq}=\frac{L_1+L_2}{\frac{L_1}{K_1}+\frac{L_2}{K_2}}=\frac{\Sigma L_i}{\Sigma\frac{L_i}{K_i}}$$

## Slabs in Parallel (in steady state):

Consider two slabs held between the same heat reservoirs, their thermal conductivities $K_1$ and $K_2$ and cross-sectional areas $A_1$ and $A_2$



then $R_1=\frac{L}{K_1A_1}$, $R_2=\frac{L}{K_2A_2}$

thermal current through slab 1 : $I_1=\frac{T_H-T_C}{R_1}$ and that through slab 2 : $I_2=\frac{T_H-T_C}{R_2}$

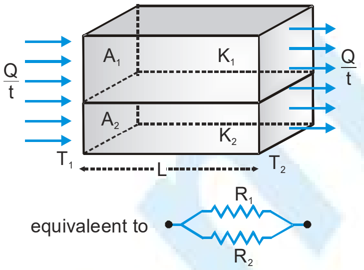
Net heat current from the hot to cold reservoir $I=I_1+I_2=(T_H-T_C)\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$

Comparing with $I=\frac{T_H-T_C}{R_{eq}}$, we get, $\frac{1}{R_{eq}}=\frac{1}{R_1}+\frac{1}{R_2}$

If more than two rods are joined in parallel, the equivalent thermal resistance is given by

$$\frac{1}{R_{eq}}=\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}+.....$$

- **Equivalent thermal conductivity for Heat flow through slabs in parallel**



$$\frac{1}{R_{eq}} = \frac{1}{R_1} + \frac{1}{R_2}, R = \frac{L}{KA}; \frac{K_{eq}}{L}(A_1 + A_2) = \frac{K_1A_1}{L} + \frac{K_2A_2}{L}$$

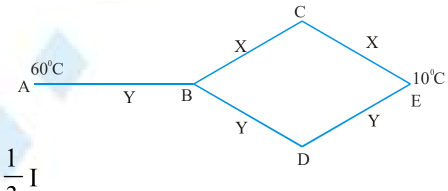
Equivalent thermal conductivity

$$K_{eq} = \frac{K_1A_1 + K_2A_2}{A_1 + A_2} = \frac{\Sigma K_iA_i}{\Sigma A_i}$$

**Ex.** Three rods of material X and three rods of material Y are connected as shown in figure. All the rods are identical in length and cross–sectional area. If the end A is maintained at $60^0$C and the junction E at at $10^0$C, calculate the temp. of the junctions B,C,D. The thermal conductivity of X is 0.92 CGS units and that of Y is 0.46 CGS units.

**Sol.** $R_X \propto \frac{1}{K_X}, R_Y \propto \frac{1}{K_Y} \Rightarrow \frac{R_X}{R_Y} = \frac{K_Y}{K_X} = \frac{0.46}{0.92} = \frac{1}{2}$ Let $R_X = R$ $\therefore R_Y = 2R$

The total resistance $\Sigma R = R_Y +$ effective resistance in the bridge



$$\Sigma R = 2R + \frac{2R \times 4R}{2R + 4R} = 2R + \frac{4}{3}R = \frac{10}{3}R$$ & ✈ $\Delta\theta = 1 \times R$

Further $I_{BCE}(2R) = I_{BDE}(4R)$ and $I_{BCE} + I_{BDE} = I \Rightarrow I_{BCE} = \frac{2}{3}I$ and $I_{BDE} = \frac{1}{3}I$

For A and B $\theta_A - \theta_B = 60^0 - \theta_B \Rightarrow 60 - \theta_B = 2R \times I$ ...(i)

For B and C $\theta_B - \theta_C = \frac{2}{3}(I \times R)$ ....(ii) $\theta_C - \theta_E = \frac{2}{3} \times R \times I$

For A and E $\theta_A - \theta_E = 60 - 10 = 50 \Rightarrow \frac{10}{3}(R \times I) = 50$ ....(iii) $\therefore R \times I = 15$

$$\therefore \theta_A - \theta_B - 2 \times 15 = 30, \theta_B = 60 - 30 = 30^0C, \theta_B - \theta_C = \left(\frac{2}{3}\right) \times 15 = 10$$

$$\therefore \theta_C = 30 - 10 = 20^0C \text{ Obviously, } \theta_C = \theta_D = 20^0C$$

## GROWTH OF ICE ON LAKES

In winter atmospheric temperature falls below 0°C and water in the lake start freezing.

Let at time t thickness of ice on the surface of the lake = x and air temperature = –θ° C

The temperature of water in contact with the lower surface of ice = 0°C

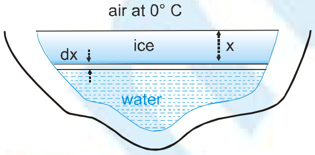
Let area of the lake = A

Due to escape of this heat increasing extra thickness of ice = dx

Mass of this extra thickness of ice is m = ρV = ρ A.dx

$$dQ = mL = (\rho A.dx)\,L$$

$$\therefore \quad KA\frac{\theta}{x}dt = (\rho A.dx)\,L \qquad \Rightarrow \quad dt = \frac{\rho L}{K\theta}x\,dx$$



So time taken by ice to grow a thickness x is $t = \frac{\rho L}{K\theta}\int_0^x x\,dx = \frac{1}{2}\frac{\rho L}{K\theta}x^2$

So time taken by ice to grow from thickness $x_1$ to thickness $x_2$ is

$$t = t_2 - t_1 = \frac{1}{2}\frac{\rho L}{KT}(x_2^2 - x_1^2) \quad \text{and} \quad t \propto (x_2^2 - x_1^2)$$

Time taken to double and triple the thickness ratio $t_1 : t_2 : t_3 :: 1^2 : 2^2 : 3^2$ So $t_1 : t_2 : t_3 :: 1 : 4 : 9$

**Ex.** One end of a brass rod 2m long and having 1 cm radius is maintained at 250°C. When a steady state is reached, the rate of heat flow across any cross–section is 0.5 cal $s^{-1}$. What is the temperature of the other end $K = 0.26$ cal $s^{-1}$ $cm^{-1}$ $°C^{-1}$.

**Sol.** $\frac{Q}{t} = 0.5$ cal $s^{-1}$; $r = 1$ cm $\quad \therefore$ Area $A = \pi r^2 = 3.142 \times 1\ cm^2 = 3.142\ cm^2$

L = Length of rod = 2m = 200 cm, $T_1 = 250°C$, $T_2 = ?$

We know $\frac{Q}{t} = \frac{KA(T_1 - T_2)}{L}$ or $(T_1 - T_2) = \frac{Q}{t} \times \frac{\Delta x}{kA} = \frac{0.5 \times 200}{0.26\,C^{-1} \times 3.142} = 122.4°C$

$\therefore$ $T_2 = 250°C - 122.4°C = 127.6°C$

**Ex.** Steam at 373 K is passed through a tube of radius 10 cm and length 2 m. The thickness of the tube is 5 mm and thermal conductivity of the material is 390 W $m^{-1}$ $K^{-1}$, calculate the heat lost per second. The outside temp. is 0°C.

**Sol.** Using the relation $Q = \frac{KA(T_1 - T_2)t}{L}$

Here, heat is lost through the cylindrical surface of the tube.

$A = 2\pi r$ (radius of the tube) (length of the tube) $= 2\pi \times 0.1 \times 2 = 0.4\ \pi m^2$

$K = 390$ W $m^{-1}$ $K^{-1}$

$T_1 = 373$ K, $\qquad T_2 = 0°C = 273$ K, $L = 5$ mm $= 0.005$ m and $t = 1$ s

$$\therefore \quad Q = \frac{390 \times 0.4\,\pi \times (373 - 273) \times 1}{0.005} = \frac{390 \times 0.4\pi \times 100}{0.005} = 98 \times 10^5\ J.$$

**Ex.** The thermal conductivity of brick is 1.7 W $m^{-1}$ $K^{-1}$, and that of cement is 2.9 W $m^{-1}$ $K^{-1}$. What thickness of cement will have same insulation as the brick of thickness 20 cm.

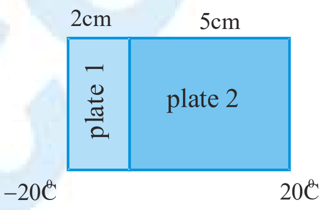
**Sol.** Since $Q = \frac{KA(T_1 - T_2)t}{L}$. For same insulation by the brick and cement Q, A $(T_1 - T_2)$ and t do not change. Hence, $\frac{K}{L}$ remain constant. If $K_1$ and $K_2$ be the thermal conductivities of brick and cement respectively and $L_1$ and $L_2$ be the required thickness then $\frac{K_1}{L_1} = \frac{K_2}{L_2}$ or $\frac{1.7}{20} = \frac{2.9}{L_2}$ $\qquad \therefore$ $L_2 = \frac{2.9}{1.7} \times 20 = 34.12$ cm

**Ex.** Two vessels of different material are identical in size and wall–thickness. They are filled with equal quantities of ice at 0°C. If the ice melts completely, in 10 and 25 minutes respectively then compare the coefficients of thermal conductivity of the materials of the vessels.

**Sol.** Let $K_1$ and $K_2$ be the coefficients of thermal conductivity of the materials, and $t_1$ and $t_2$ be the time in which ice melts in the two vessels. Since both the vessels are identical, so A and x in both the cases is same.

Now, $Q = \dfrac{K_1 A(\theta_1 - \theta_2)t_1}{L} = \dfrac{K_2 A(\theta_1 - \theta_2)t_2}{L} \Rightarrow \dfrac{K_1}{K_2} = \dfrac{t_2}{t_1} = \dfrac{25\text{ min}}{10\text{ min}} = \dfrac{5}{2}$

**Ex.** Two plates of equal areas are placed in contact with each other. Their thickness are 2.0 cm and 5.0 cm respectively. The temperature of the external surface of the first plate is –20°C and that of the external surface of the second plate is 20°C. What will be the temperature of the contact surface if the plate (i) are of the same material, (ii) have thermal conductivities in the ratio 2 : 5.



**Sol.** Rate of flow of heat in the plates is $\dfrac{Q}{t} = \dfrac{K_1 A(\theta_1 - \theta)}{L_1} = \dfrac{K_2 A(\theta - \theta_2)}{L_2}$ ...(i)

(i) Here $\theta_1 = -20°C$, $\theta_2 = 20°C$,

$L_1 = 2\text{ cm} = 0.02\text{ m}$, $L_2 = 5\text{ cm} = 0.05\text{ m}$ and $K_1 = K_2 = K$

$\therefore$ equation (i) becomes $\dfrac{KA(-20-\theta)}{0.02} = \dfrac{KA(\theta - 20)}{0.05}$

$\therefore 5(-20 - \theta) = 2(\theta - 20) \Rightarrow -100 - 5\theta = 2\theta - 40 \Rightarrow 7\theta = -60 \Rightarrow \theta = -8.6°C$

(ii) $\dfrac{K_1}{K_2} = \dfrac{2}{5}$ or $K_1 = \dfrac{2}{5}K_2$

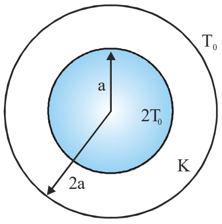
$\therefore$ from equation (i) $\dfrac{2/5\,K_2 A(-20-\theta)}{0.02} = \dfrac{K_2 A(\theta - 20)}{0.05}$ $-20 - \theta = \theta - 20$ or $-2\theta = 0$ $\quad \therefore \theta = 0°C$

**Ex.** An ice box used for keeping eatables cold has a total wall area of 1 metre$^2$ and a wall thickness of 5.0 cm. The thermal conductivity of the ice box is K = 0.01 joule/metre–°C. It is filled with ice at 0°C along with eatables on a day when the temperature is 30°C. The latent heat of fusion of ice is 334 × $10^3$ joule/kg. Calculate the amount of ice melted in one day.

**Sol.** $\dfrac{dQ}{dt} = \dfrac{KA}{L}d\theta = \dfrac{0.01 \times 1}{0.05} \times 30 = 6$ joule/sec $\qquad$ So $\dfrac{dQ}{dt} \times 86400 = 6 \times 86400$

$Q = mL$ (L – latent heat), $\quad m = \dfrac{Q}{L} = \dfrac{6 \times 86400}{334 \times 10^3} = 1.552$ kg

**Ex.** A hollow spherical ball of inner radius a and outer radius 2a is made of a uniform material of constant thermal conductivity K. The temperature within the ball is maintained at $2T_0$ and outside the ball it is $T_0$. Find, (a) the rate at which heat flows out of the ball in the steady state, (b) the temperature at r = 3a/2, where r is radial distance from the centre of shell. Assume steady state condition.

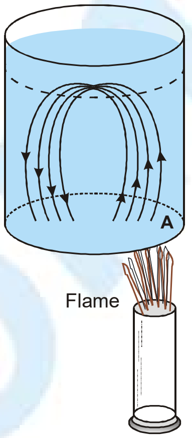


**Sol.** In the steady state, the net outward thermal current is constant, and does not depend on the radial position.

Thermal current, $C_1 = \left(\dfrac{dQ}{dt}\right) = -K.(4\pi r^2)\dfrac{dT}{dr} \Rightarrow \dfrac{dT}{dr} = -\dfrac{C_1}{4\pi K}\dfrac{1}{r^2} \qquad T = \dfrac{C_1}{4\pi kr} + C_2$

At $r = a$, $T = 2T_0$ and $r = 2a$, $T = T_0 \Rightarrow T = \dfrac{2a}{r}T_0$ (a) $\dfrac{dQ}{dt} = 8\pi a K T_0$ (b) $T(r = 3a/2) = 4T_0/3$

## CONVECTIONS



Convection requires a medium and is the process in which heat is transferred from one place to other by actual movement of heated substance (usually fluid).The type of convection which results from difference in densities is called natural convection (for example, a fluid in a container heated through its bottom). However, if a heated fluid is forced to move by a blower, fan or pump, the process is called forced convection. The rate of heat convection from an object is proportional to the temperature difference ($\Delta\theta$) between the object and convective fluid and the area of contact A, i.e.,

$$\left[\frac{dQ}{dt}\right]_{\text{convection}} = hA\ \Delta\theta$$ where, h represents a constant of proportionality called convection coefficient and depends on the properties of fluid such as density, viscosity, specific heat and thermal conductivity, etc.

## PHENOMENA BASED ON CONVECTION :

### (i) Land and sea breezes :

The heat from the Sun is absorbed more rapidly by land than by sea–water. Moreover, the specific heat of land is low as compared to that of sea–water. Consequently, the rise in temperature of land is higher as compared to that of sea–water. To sum–up, land is hotter than the sea during day time. As a result of this, the colder air over the sea blows towards the land. This is called sea–breeze.

At night, air blows from land towards sea. This is called land breeze.

### (ii) Formation of trade winds :

The surface of Earth near the equator gets heated strongly. So, the air in contact with the surface of Earth at the expands and rises upwards. As a result of this, a low pressure is created at the equator.

At the poles, the air in the upper atmosphere gets cooled and comes down. So, a high pressure is created at the poles. Due to difference of pressures at the poles and equator, the air at the poles moves towards the equator, rises up, moves the poles and so on. In this way, a wind is formed in the atmosphere.

The rotation of the Earth also affects the motion of the wind. Due to anti–clockwise rotation of Earth the warm wind blowing from equator to north drifts towards east. The steady wind blowing from north–Earth to equator, near the surface of Earth, is called trade wind.

### (iii) Monsoons :

In summer, the peninsular mass of central Asia becomes more strongly heated than the water of the Indian Ocean. This is due to the fact that the specific heat of water is much higher than that of the soil and rocks. Hot air from the heated land mass rises up and moves towards the Indian ocean. Air filled with moisture flows over the Indian ocean on the south towards heated land mass. When obstructed by mountains, the moist air rushes upwards to great height. In the process, it gets cooled. Consequently, the moisture condenses and falls as rain.

### (iv) Ventilation :

Ventilator of exhaust fan in a room help of remove impure and warm air from a room. The fresh air from outside blows into the room. This is all due to the convection current set up in the room.

### (v) To regulate temperature in the human body :

Heat transfer in the human body involves a combination of mechanisms. These together maintain a remarkably uniform temperature in the human body inspite of large changes in environmental conditions.

The chief internal mechanism is forced convection. The heart serves as the pump and the blood as the circulating fluid.

## ETOOS KEY POINTS

**(i)** Natural convection takes place from bottom to top while forced convection in any direction.

**(ii)** In case of natural convection, convection currents move warm air upwards and cool air downwards. This is why heating is done from base, while cooling from the top.

**(iii)** Natural convection is not possible in a gravity free region such as a freely falling lift or an orbiting satellite.

**(iv)** Natural convection plays an important role in ventilation, in changing climate and weather and in forming land and sea breezes and trade winds.

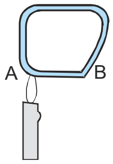
**(v)** The forced convection of blood in our body by a pump (heart) helps in keeping the temperature of body constant.

**(vi)** For heat propagation via convection, temperature gradient exists in vertical direction and not in horizontal direction.

**(vii)** Most of heat transfer that is taking place on Earth is by convection, the contribution due to conduction and radiation is very small.

**Ex.** Water in a closed tube is heated with one arm vertically placed above the lamp. In what direction water will begin the circulate along the tube ?

**Sol.** On heating the liquid at A will become lighter and will rise up. This will push the liquid in the tube upwards and so the liquid in the tube will move clockwise i.e. form B to A.



## THERMAL RADIATION

The process of the transfer of heat from one place to another place without heating the intervening medium is called radiation. When a body is heated and placed in vacuum, it loses heat even when there is no medium surrounding it. The heat can not go out from the body by the process of conduction or convection since both of these process require the presence of a material medium between source and surrounding objects. The process by which heat is lost in this case is called radiation. This does not require the presence of any material medium.

It is by radiation that the heat from the Sun reaches the Earth. Radiation has the following properties:

**(a)** Radiant energy travels in straight lines and when some object is placed in the path, it's shadow is formed at the detector.

**(b)** It is reflected and refracted or can be made to interfere. The reflection or refraction are exactly as in case of light.

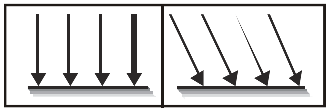
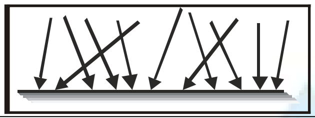
**(c)** It can travel through vacuum.

**(d)** Intensity of radiation follows the law of inverse square.

**(e)** Thermal radiation can be polarised in the same way as light by transmission through a nicol prism.

All these and many other properties establish that heat radiation has nearly all the properties possessed by light and these are also electromagnetic waves with the only difference of wavelength or frequency. The wavelength of heat radiation is larger than that of visible light.

**Types of thermal Radiation** :– Two types of thermal radiation.

| Plane Radiation | Diffuse Radiation |
|---|---|
|  |  |
| Radiations which are incident on a surface at certain angle | Incident on the surface at all angles |

- **(i)** When radiation passes through any medium then radiations slightly absorbed by medium according to its absorptive power so temperature of medium slightly increases.
- **(ii)** In order to obtain a spectrum of radiation, a special prism used like KCl prism, Rock salt prism Flourspar prism. Normal glass prism or Quartz prism can not be used (because it absorbed some radiation).
- **(iii)** Radiation intensity measured with a specific device named as Bolometer.
- **(iv)** Heat radiation are always obtained in infra–red region of electromagnetic wave spectrum so they are called Infra red rays.
- **(v)** Thermal radiations is incident on a surface, it exerts pressure on the surface, which is known as Radiation Pressure.

## BASIC FUNDAMENTAL DEFINITIONS

**1. Energy Density (u)**

The radiation energy of whole wavelength (0 to ∞) present in unit volume at any point in space is defined as energy density. **S I UNIT :** $J/m^3$

**2. Spectral energy density ($u_\lambda$) :** Energy density per unit spectral region. $u = \int_0^\infty u_\lambda d\lambda$ **SI UNIT :** $J/m^3$ Å

**3. Absorptive power or absorptive coefficient 'a' :** The ratio of amount of radiation absorbed by a surface (Qa) to the amount of radiation incident (Q) upon it is defined as the coefficient of absorption $a = \frac{Q_a}{Q}$ .It is unitless

**4. Spectral absorptive power ($a_\lambda$) :** $a_\lambda = \frac{Qa_\lambda}{Q_\lambda}$ : Also called monochromatic absorptive coefficient

At a given wavelength $a = \int_0^\infty a_\lambda d\lambda$ . For ideal black body $a_\lambda$ and $a = 1$, a and $a_\lambda$ are unitless

**5. Emissive power (e) :** The amount of heat radiation emitted by unit area of the surface in one second at a particular temperature. **SI UNIT :** $J/m^2s$

**6. Spectral Emmisive power ($e_\lambda$)** : The amount of heat radiation emitted by unit area of the body in one second in unit spectral region at a given wavelength. Emissive power or total emissive power $e = \int_0^\infty e_\lambda \, d\lambda$

**SI UNIT :** $W/m^2$ Å

## EMISSIVITY (e)

**(i) Absolute emissivity or emissivity :** Radiation energy given out by a unit surface area of a body in unit time corresponding to unit temperature difference w.r.t. the surroundings is called Emissivity.

**S I unit :** $W/m^2$ °K

**(ii)** **Relative emissivity (er) :** er $= \dfrac{Q_{GB}}{Q_{IBB}} = \dfrac{e_{GB}}{E_{IBB}} = \dfrac{\text{emitted radiation by gray body}}{\text{emitted radiation by ideal black body}}$

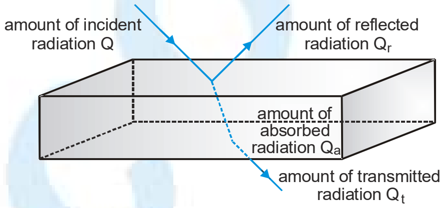
GB = gray or general body, IBB = Ideal black body

**(i)** No unit **(ii)** For ideal black body er = 1 **(iii)** range $0 < er < 1$

## Spectral, Emissive, Absorptive and Transmittive Power of a given body surface

Due to incident radiations on the surface of a body following phenomena occur by which the radiation is divided into three parts. (a) Reflection (b) Absorption (c) Transmission

- **From Energy Conservation**



$$Q = Q_r + Q_a + Q_t \Rightarrow \frac{Q_r}{Q} + \frac{Q_a}{Q} + \frac{Q_t}{Q} = 1 \Rightarrow r + a + t = 1$$

Reflective Coefficient $r = \dfrac{Q_r}{Q}$, Absorptive Coefficient $a = \dfrac{Q_a}{Q}$,

Transmittive Coefficient $t = \dfrac{Q_t}{Q}$

r = 1 and a = 0 , t = 0 ⇒ Perfect reflector

a = 1 and r = 0, t = 0 ⇒ Ideal absorber (ideal black body)

t = 1 and a = 0, r = 0 ⇒ Perfect transmitter (diathermanous)

Reflection power (r) $= \left[\dfrac{Q_r}{Q} \times 100\right]\%$, Absorption power (a) $= \left[\dfrac{Q_a}{Q} \times 100\right]\%$

Transmission power (t) $= \left[\dfrac{Q_t}{Q} \times 100\right]\%$

**Ex.** Total radiations incident on body = 400 J, 20% radiation reflected and 120 J absorbs. Then find out % of transmittive power

**Sol.** $Q = Q_t + Q_r + Q_a \Rightarrow 400 = 80 + 120 + Qt \Rightarrow Qt = 200$ . So % of transmittive power is 50%

## IDEAL BLACK BODY

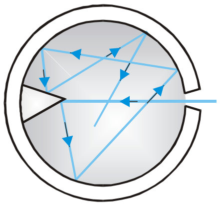
**(i)** For a body surface which absorbs all incident thermal radiations at low temperature irrespective of their wave length and emitted out all these absorbed radiations at high temperature assumed to be an ideal black body surface.

**(ii)** The identical parameters of an ideal black body is given by

$a = a_\lambda = 1$ and $r = 0 = t$, $e_r = 1$

**(iii)** The nature of emitted radiations from surface of ideal black body only depends on its temperature

**(iv)** The radiations emitted from surface of ideal black body called as either full or white radiations.



Ferry's ideal black body

**(v)** At any temperature the spectral energy distribution curve for surface of an ideal black body is always continuous and according to this concept if the spectrum of a heat source obtained to be continuous then it must be placed in group of ideal black body like kerosene lamp; oil lamp Heating filament etc.

**(vi)** There are two experimentally ideal black body

**(a)** Ferry's ideal black body **(b)** Wien's ideal black body.

**(vii)** At low temperature surface of ideal black body is a perfect absorber and at a high temperature it proves to be a good emitter.

**(viii)** An ideal black body need not be black colour (eg. Sun)

## PREVOST'S THEORY OF HEAT ENERGY EXCHANGE

According to Prevost at every possible temperature (Not absolute temperature) there is a continuous heat energy exchange between a body and its surrounding and this exchange carry on for infinite time.

The relation between temperature difference of body with its surrounding decides whether the body experience cooling effect or heating effect.

**When a cold body is placed in the hot surrounding** : The body radiates less energy and absorbs more energy from the surrounding, therefore the temperature of body increases.

**When a hot body placed in cooler surrounding** : The body radiates more energy and absorb less energy from the surroundings. Therefore temperature of body decreases.

**When the temperature of a body is equal to the temperature of the surrounding**

The energy radiated per unit time by the body is equal to the energy absorbed per unit time by the body, therefore its temperature remains constant.

### ETOOS KEY POINTS

**(i)** At absolute zero temperature (0 kelvin) all atoms of a given substance remains in ground state, so, at this temperature emission of radiation from any substance is impossible, so Prevost's heat energy exchange theory does not applied at this temperature, so it is called limited temperature of prevosts theory.

**(ii)** With the help of Prevost's theory rate of cooling of any body w.r.t. its surroundings can be worked out (applied to Stefen Boltzman law, Newton's law of cooling.)

## KIRCHHOFF'S LAW

At a given temperature for all bodies the ratio of their spectral emissive power ($e_\lambda$) to spectral absorptive power ($a_\lambda$) is constant and this constant is equal to spectral emissive power ($E_\lambda$) of the ideal black body at same temperature

$$\frac{e_\lambda}{a_\lambda} = E_\lambda = \text{constant} \qquad \left[\frac{e_\lambda}{a_\lambda}\right]_1 = \left[\frac{e_\lambda}{a_\lambda}\right]_2 = \text{constant} \quad e_\lambda \propto a_\lambda$$

Good absorbers are good emitters and bad absorbers are bad emitters

### ETOOS KEY POINTS

**(i)** For a constant temperature the spectral emmisive power of an ideal black body is a constant parameter

**(ii)** The practical confirmation of Kirchhoff's law carried out by Rishi apparatus and the main base of this apparatus is a Lessilie container.

**(iii)** The main conclusion predicted from Kirchhof's law can be expressed as

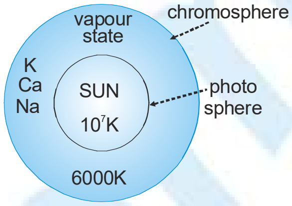
Good absorber *f* Good emitter

Bad absorber *f* Bad emitter

(at Low temperature) (at high temperature)

## APPLICATIONS OF KIRCHOFF LAW

### (i) Fraunhoffer's lines



Fraunhoffer lines are dark lines in the spectrum of the Sun. When white light emitted from the central core of the Sun (Photosphere) passes. Through its atmosphere (Chromosphere) radiations of those wavelengths will be absorbed by the gases present, resulting in dark lines in the spectrum of Sun. At the time of total solar eclipse direct light rays emitted from photosphere cannot reach on the Earth and only rays from chromosphere are able to reach on the Earth surface. At that time we observe bright fraunhoffer lines.

### (ii) In deserts days are hot and nights cold

Sand is rough and black, so it is a good absorber and hence in deserts, days (When radiation from Sun is incident on sand) will be very hot. Now in accordance with Kirchhoff's Law, good absorber is a good emitter.

So nights (when send emits radiation) will be cold.

## STEFAN'S LAW

The amount of radiation emitted per second per unit area by a black body is directly proportional to the fourth power of its absolute temperature.

Amount of radiation emitted $E \propto T^4$ where T = temperature of ideal black body (in K)

$E = \sigma T^4$ This law is true for only ideal black body

**SI Unit :** $E = \text{watt/m}^2$ $\sigma$ = Stefen's constant = $5.67 \times 10^{-8}$ watt /m$^2$ K$^4$

**Dimensions of $\sigma$ :** $M^1 L^0 T^{-3} \theta^{-4}$

Total radiation energy emitted out by surface of area A in time t :

Ideal black body $Q_{IBB} = \sigma A T^4 t$ and for any other body $Q_{GB} = e_r \sigma A T^4 t$

**Rate of emission of radiation**

When Temperature of surrounding $T_0$ (Let $T_0 < T$)

Rate of emission of radiation from ideal black body surface $E_1 = \sigma T^4$

Rate of emission of radiation from surrounding $E_2 = \sigma T_0^4$

Net rate of loss of radiation from ideal black body surface is $E = E_1 - E_2 = \sigma T^4 - \sigma T_0^4 = \sigma(T^4 - T_0^4)$

Net loss of radiation energy from entire surface area in time t is $Q_{IBB} = \sigma A(T^4 - T_0^4)t$

For any other body $Q_{GB} = e_r A\sigma(T^4 - T_0^4)t$

If in time dt the net heat energy loss for ideal black body is dQ and because of this its temperature falls by $d\theta$

Rate of loss of heat $$R_H = \frac{dQ}{dt} = \sigma A(T^4 - T_0^4)$$

It is also equal to emitted power or radiation emitted per second

Rate of fall in temperature (Rate of cooling) $$R_F = \frac{d\theta}{dt} = \frac{\sigma A}{msJ}(T^4 - T_0^4)\left[Q\ \frac{dQ}{dt} = msJ\frac{d\theta}{dt}\right]$$

**Note :**

**(i)** If all of T, $T_0$, m, s, V, $\rho$, are same for different shape body then $R_F$ and $R_H$ will be maximum in the flat surface.

**(ii)** If a solid and hollow sphere are taken with all the parameters same then hollow will cool down at fast rate.

**(iii)** Rate of temperature fall , $R_F \propto \frac{1}{s} \propto \frac{d\theta}{dt}$ so dt $\propto$ s. If condition in specific heat is $\Rightarrow$ $s_1 > s_2 > s_3$

If all cooled same temperature i.e. temperature fall is also identical for all then required time

$t \propto s \quad \therefore t_1 > t_2 > t_3$

## When a body cools by radiation the cooling depends on :

**(i)** Nature of radiating surface : greater the emissivity ($e_r$), faster will be the cooling.

**(ii)** Area of radiating surface : greater the area of radiating surface, faster will be the cooling.

**(iii)** Mass of radiating body : greater the mass of radiating body slower will be the cooling.

**(iv)** Specific heat of radiating body : greater the specific heat of radiating body slower will be the cooling.

**(v)** Temperature of radiating body : greater the temperature of radiating body faster will be the cooling.

**Ex.** The operating temperature of a tungsten filament in an incandescent lamp is 2000 K and its emissivity is 0.3. Find the surface area of the filament of a 25 watt lamp. Stefan's constant $\sigma = 5.67 \times 10^{-8}\ \mathrm{Wm^{-2}K^{-4}}$

**Sol.**

✈ Rate of emission = wattage of the lamp

$$\therefore\ W = Ae\sigma T^4 \Rightarrow A = \frac{W}{e\sigma T^4} = \frac{25}{0.3 \times 5.67 \times 10^{-8} \times (200)^4} = 0.918\ \mathrm{m^2}$$

## NEWTON'S LAW OF COOLING

Rate of loss of heat $\left(\frac{dQ}{dt}\right)$ is directly proportional to excess of temperature of the body over that of surrounding.

$$[(\text{when } (\theta - \theta_0) \not> 35°\text{C}] \quad \frac{dQ}{dt} \propto (\theta - \theta_0) \Rightarrow \frac{dQ}{dt} = ms\frac{d\theta}{dt}$$

$\theta$ = temperature of body [ in °C], $\theta_o$ = temperature of surrounding, $\theta - \theta_0$ = excess of temperature ( $\theta > \theta_0$ )

If the temperature of body decrease $d\theta$ in time dt then rate of fall of temperature $-\frac{d\theta}{dt} \propto (\theta - \theta_0)$

Where negative sign indictates that the rate of cooling is decreasing with time.

## Excess of temperature

If the temperature of body decreases from $\theta_1$ to $\theta_2$ and temperature of surroundings is $\theta_0$ then average excess of temperature $= \left[\frac{\theta_1 + \theta_2}{2} - \theta_0\right] \Rightarrow \left[\frac{\theta_1 - \theta_2}{t}\right] = -K\left[\frac{\theta_1 + \theta_2}{2} - \theta_0\right]$

**Ex.** If a liquid takes 30 seconds in cooling of 80°C to 70°C and 70 seconds in cooling 60°C to 50°C, then find the room temperature.

**Sol.** $\frac{\theta_1 - \theta_2}{t} = K\left[\frac{\theta_1 + \theta_2}{2} - \theta_0\right]$

In first case, $\frac{80 - 70}{30} = K\left(\frac{80 + 70}{2} - \theta_0\right) \qquad \frac{1}{3} = K(75 - \theta_0) \qquad$ ...(i)

In second case , $\frac{60-50}{70} = K\left(\frac{60+50}{2} - \theta_0\right)\frac{1}{7} = K(55-\theta_0)$ ... **(ii)**

Equation **(i)** divide by equation **(ii)** $\frac{7}{3} = \frac{(75-\theta_0)}{(55-\theta_0)} \Rightarrow 385 - 7\theta_0 = 225 - 3\theta_0 \Rightarrow \theta_0 = \frac{160}{4} = 40°C$

## Limitations of Newton's Law

**(i)** Temperature difference should not exceed 35° C, $(\theta - \theta_0) \not> 35°$ C

**(ii)** Loss of heat should only be by radiation.

**(iii)** This law is an extended form of Stefan–Boltzman's law.

**For Heating, Newton's law of heating** $\frac{\theta_1 - \theta_2}{t} = +H\left[\theta_0 - \frac{\theta_1 + \theta_2}{2}\right]$ where H heating constant.

**Derivation of Newton's law from Steafen's Boltzman law**

$$\frac{d\theta}{dt} = \frac{\sigma A}{m\,s\,J}(T^4 - T_0^{\ 4}) \qquad \left\{\begin{matrix} T - T_0 = \Delta T \\ T = T_0 + \Delta T \end{matrix}\right\}$$

$$\frac{d\theta}{dt} = \frac{\sigma A}{m\,s\,J}\left[(T_0 + \Delta T)^4 - T_0^4\right] \qquad \text{If } x <<< 1 \text{ then } (1+x)^n = 1 + nx$$

$$\frac{d\theta}{dt} = \frac{\sigma A}{m\,s\,J}\left[T_0^4\left(1 + \frac{\Delta T}{T_0}\right)^4 - T_0^4\right] = \frac{\sigma A}{m\,s\,J}T_0^4\left[\left(1 + \frac{\Delta T}{T_0}\right)^4 - 1\right] = \frac{\sigma A}{m\,s\,J}T_0^4\left[1 + 4\frac{\Delta T}{T_0} - 1\right]$$

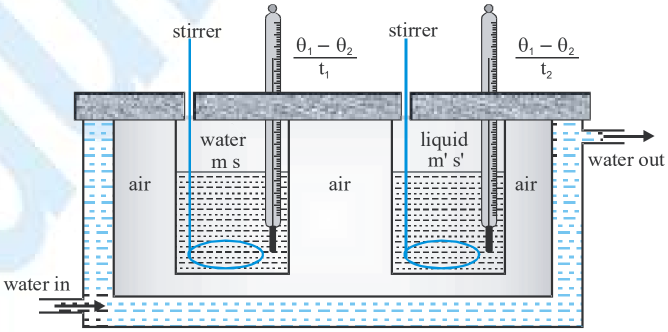
$$\frac{d\theta}{dt} = \left[4\frac{\sigma A}{m\,s\,J}T_0^3\right]\Delta T \Rightarrow \frac{d\theta}{dt} = K\,\Delta T \qquad \text{constant } K = \frac{4\sigma A\,T_0^3}{m\,s\,J}$$

**Newton's law of cooling** $\frac{d\theta}{dt} \propto \Delta T$ (for small temperature difference)

## APPLICATION OF NEWTON'S LAW OF COOLING

- ### To find out specific heat of a given liquid

If for the two given liquids their volume, radiating surface area, nature of surface, initial temperature are allowed to cool down in a common environments then rate of loss of heat of these liquids are equal .

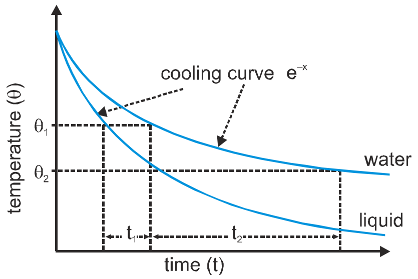


fall of temperature from $\theta_1 \to \theta_2$ in time $t_1$ for water and $t_2$ for liquid

✈ $\left[\frac{dQ}{dt}\right]_{\text{Water}} = \left[\frac{dQ}{dt}\right]_{\text{Liquid}}$ $\quad\therefore\quad (m\,s+w)\left[\frac{\theta_1-\theta_2}{t_1}\right] = (m's'+w)\left[\frac{\theta_1-\theta_2}{t_2}\right] \quad\Rightarrow\quad \frac{m\,s+w}{t_1} = \frac{m's'+w}{t_2}$

where $w$ = water equivalent of calorimeter.

**Cooling curve :**



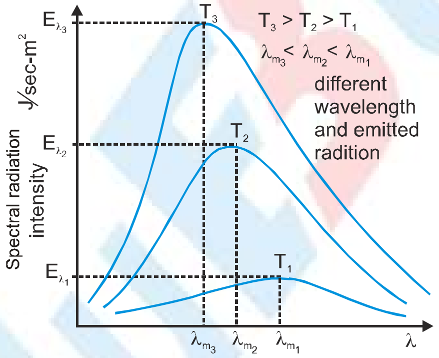
**Ex.** When a calorimeter contains 40g of water at 50°C, then the temperature falls to 45°C in 10 minutes. The same calorimeter contains 100g of water at 50°C, it takes 20 minutes for the temperature to become 45°C. Find the water equivalent of the calorimeter.

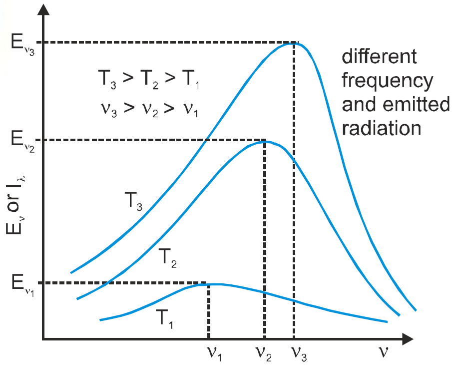
**Sol.** $\frac{m_1s_1+W}{t_1} = \frac{m_2s_2+W}{t_2}$ where W is the water equivalent

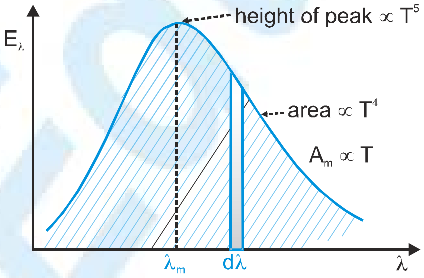
$$\Rightarrow \frac{40\times1+W}{10} = \frac{100\times1+W}{20} \Rightarrow 80+2W = 100+W \Rightarrow W = 20\text{ g}$$

## SPECTRAL ENERGY DISTRIBUTION CURVE OF BLACK BODY RADIATIONS

Practically given by : Lumers and Pringshem Mathematically given by : Plank







spectral energy distribution curve ($E_\lambda$–$\lambda$)

**(i)** $\lambda_m \propto \frac{1}{T}$

**(ii)** $E_{\lambda_m} \propto T^5$

**(iii)** Area $\int_0^\infty E_\lambda\, d\lambda = E = \sigma T^4$ $\quad \frac{A_1}{A_2} = \left[\frac{T_1}{T_2}\right]^4$

## ETOOS KEY POINTS

**(i)** Spectral energy distribution curves are continuous. At any temperature in between possible wavelength $(0 - \infty)$ radiation emitted but for different wavelength quantity of radiations are different.

**(ii)** As the wave length increases, the amount of radiation emitted first increase, becomes maximum and then decreases.

**(iii)** At a particular temperature the area enclosed between the spectral energy curve shows the spectral emissive power of the body. Area $= \int_0^\infty E_\lambda d\lambda = E = \sigma T^4$

## WEIN'S DISPLACEMENT LAW

The wavelength corresponding to maximum emission of radiation decrease with increasing temperature $\left[\lambda_m \propto \frac{1}{T}\right]$.

This is known as Wein's displacement law. $\lambda_m T = b$ where b Wein's constant = = 2.89 x $10^{-3}$ mK.

**Dimensions of b :** $= M^0 L^1 T^0 \theta^1$

**Relation between frequency and temperature** $\nu_m = \frac{c}{b} T$

**Ex.** The temperature of furnace is 2000°C, in its spectrum the maximum intensity is obtained at about 4000Å, If the maximum intensity is at 2000Å calculate the temperature of the furnace in °C.

**Sol.** By using $\lambda_m T = b$, $4000\,(2000+273) = 2000(T) \Rightarrow T = 4546K$

The temperature of furnace = 4546 – 273 = 4273 °C

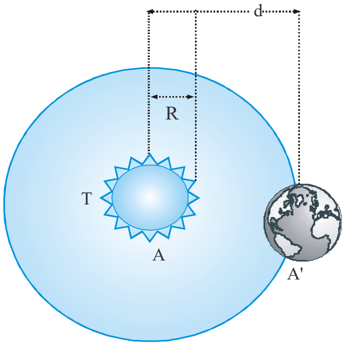
## SOLAR CONSTANT 'S'

The Sun emits radiant energy continuously in space of which an in significant part reaches the Earth. The solar radiant energy received per unit area per unit time by a black surface held at right angles to the Sun's rays and placed at the mean distance of the Earth (in the absence of atmosphere) is called solar constant.

The solar constant S is taken to be 1340 watts/m$^2$ or 1.937 Cal/cm$^2$–minute

- ### Temperature of the Sun

Let R be the radius of the Sun and 'd' be the radius of Earth's orbit around the Sun. Let E be the energy emitted by the Sun per second per unit area. The total energy emitted by the Sun in one second = E.A = E × $4\pi R^2$. (This energy is falling on a sphere of radius equal to the radius of the Earth's orbit around the Sun i.e., on a sphere of surface area $4\pi d^2$)



So, The energy falling per unit area of Earth $= \frac{4\pi R^2 \times E}{4\pi d^2} = \frac{E R^2}{d^2}$

$R = 7 \times 10^8 m$, $d = 1.5 \times 10^{11} m$, $s = 5.7 \times 10^{-8}\ W\ m^{-2}\ K^{-4}$

Solar constant $S = \frac{E R^2}{d^2}$

By Stefan's Law $E = \sigma T^4$

$$S = \frac{\sigma T^4 R^2}{d^2} \Rightarrow T = \left[\frac{S \times d^2}{\sigma \times R^2}\right]^{\frac{1}{4}} = \left[\frac{1340 \times (1.5 \times 10^{11})^2}{5.7 \times 10^{-8} \times (7 \times 10^8)^2}\right]^{\frac{1}{4}} = 5732\ K$$

# CALORIMETERY

## HEAT

When a hot body is put in contact with a cold one, the former gets colder and the latter warmer. From this observation it is natural to conclude that a certain quantity of heat has passed from the hot body to the cold one. Heat is a form of energy.

Heat is felt by its effects. Some of the effects of heat are :

**(a)** Change in the degree of hotness

**(b)** Expansion in length, surface area and volume

**(c)** Change in state of a substance

**(d)** Change in the resistance of a conductor

**(e)** Thermo e.m.f. effect

**SI Unit :** J (joule) Also measured in the unit calorie.

### (i) Calorie

It is defined as the amount of heat required to raise the temperature of 1 g water by 1°C.

### (ii) International calorie

International calorie is the amount of heat required to raise the temperature of 1g water from 14.5 °C to 15.5 °C rise of temperature.

### (iii) Kilo Calorie

Kilo calorie is defined as the amount of heat required to raise the temperature of 1 kg water from 14.5 °C to 15.5 °C. (1 kcal = 1000 calorie).

### (iv) British thermal unit (B. T. U.)

It is the amount of heat required to raise the temperature of one pound water by 1°F. (1 B.T.U. = 252 calorie).

## MECHANICAL EQUIVALENT OF HEAT

According to Joule, work may be converted into heat and vice–versa. The ratio of work done to heat produced is always constant. $\frac{W}{H} = \text{constant (J)} \Rightarrow W = J\,H$

W must be in joule, irrespective of nature of energy or work and H must be in calorie.

J is called mechanical equivalent of heat. It is not a physical quantity but simply a conversion factor.

It converts unit of work into that of heat and vice–versa.

$J = 4.18$ joule/cal or $4.18 \times 10^3$ joule per kilo–cal. For rough calculations we take $J = 4.2$ joule/cal

## SPECIFIC HEAT (s or c )

It is the amount of energy required to raise the temperature of unit mass of that substance by 1°C (or 1K) is called specific heat. It is represented by s or c.

If the temperature of a substance of mass m changes from T to T + dT when it exchanges an amount of heat dQ with its surroundings then its specific heat is $c = \frac{1}{m}\frac{dQ}{dT}$

The specific heat depends on the pressure, volume and temperature of the substance.

For liquids and solids, specific heat measurements are most often made at a constant pressure as functions of temperature, because constant pressure is quite easy to produce experimentally.

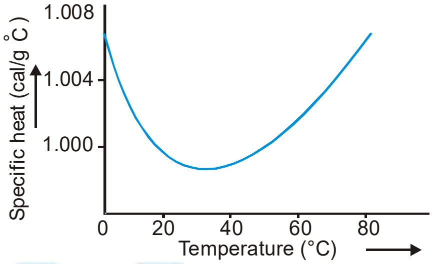
**SI unit :** joule/kg–K **CGS unit :** cal/g –°C

Specific heat of water : $c_{water} = 1$ cal/g–°C = 1 cal/g–K = 1 kcal/kg–K = 4200 joule/kg–K

When a substance does not undergo a change of state (i.e., liquid remains liquid or solid remains solid), then the amount of heat required to raise the temperature of mass m of thesubstance by an amount $\Delta\theta$ is $Q = ms\Delta\theta$.

The temperature dependence of the specific heat of water at 1 atmospheric pressure is shown in figure. Its variation is less than 1% over the interval from 0 to 100°C. Such a small variation is typical for most solids and liquids, so their specific heats can generally be taken to be constant over fairly large temperature ranges.

The temperature dependence of the specific heat of water at 1 atm



**(i)** There are many processes possible to give heat to a gas.

A specific heat can be associated to each such process which depends on the nature of process.

**(ii)** Value of specific heats can vary from zero (0) to infinity.

**(iii)** Generally two types of specific heat are mentioned for a gas –

**(a)** Specific heat at constant volume ($C_V$) **(b)** Specific heat at constant pressure ($C_P$)

**(iv)** These specific heats can be molar or gram.

## MOLAR HEAT CAPACITY

The amount of energy needed to raise the temperature of one mole of a substance by 1°C (or 1K) is called molar heat capacity. The molar heat capacity is the product of molecular weight and specific heat i.e.,

Molar heat capacity C = Molecular weight (M) × Specific heat( c) $\Rightarrow C = \frac{1}{\mu}\left(\frac{dQ}{dT}\right)$

If the molecular mass of the substance is M and the mass of the substance is m then number of moles of the substance $\mu = \frac{m}{M} \Rightarrow C = \frac{M}{m}\left(\frac{dQ}{dT}\right)$ **SI Unit :** J/mol–K

## THERMAL CAPACITY

The quantity of heat required to raise the temperature of the whole of that substance through 1°C is called thermal capacity. The thermal capacity of mass m of the whole of substance of specific heat s is = ms

Thermal capacity = mass × specific heat

Thermal capacity depends on property of material of the body and mass of the body.

**SI Unit** : cal/°C or cal/K, **Dimensions :** $ML^2T^{-2}K^{-1}$

## WATER EQUIVALENT OF A BODY

As the specific heat of water is unity so the thermal capacity of a body (ms) represents its water equivalent also.

**(i)** Mass of water having the same thermal capacity as the body is called the water equivalent of the body

**(ii)** The water equivalent of a body is the amount of water that absorbs or gives out the same amount of heat as is done by the body when heated or cooled through 1°C.

Water equivalent= mass of body × specific heat of the material $\Rightarrow$ (w = ms).

## LATENT HEAT OR HIDDEN HEAT

When state of a body changes, change of state takes place at constant temperature [melting point or boiling point] and heat released or absorbed is $Q = mL$ where L is latent heat. Heat is absorbed if solid converts into liquid (at melting point) or liquid converts into vapours (at boiling point) and heat is released if liquid converts into solid or vapours converts into liquid.

### (i) Latent heat of fusion

It is the quantity of heat (in kilocalories) required to change its 1 kg mass from solid to liquid state at its melting point. Latent heat of fusion for ice : 80 kcal/kg = 80 cal /g.

### (ii) Latent heat of vaporization

The quantity of heat required to change its 1 kg mass from liquid to vapour state at its boiling point.

Latent heat of vaporisation for water : 536 kcal/kg = 536 cal/g

## CHANGE OF STATE

### (i) Melting

Conversion of solid into liquid state at constant temperature is known as melting.

### (ii) Boiling

Evaporation within the whole mass of the liquid is called boiling. Boiling takes place at a constant temperature known as boiling point. A liquid boils when the saturated vapour pressure on its surface is equal to atmospheric pressure. Boiling point reduces on decreasing pressure.

### (iii) Evaporation

Conversion of liquid into vapours at all temperatures is called evaporation. It is a surface phenomenon. Greater the temperature, faster is the evaporation. Smaller the boiling point of liquid, more rapid is the evaporation. Smaller the humidity, more is the evaporation. Evaporation increases on decreasing pressure that is why evaporation is faster in vacuum.

**Heat of evaporation**

Heat required to change unit mass of liquid into vapour at a given temperature is called heat of evaporation at that temperature.

### (iv) Sublimation

Direct conversion of solid in to vapour state is called sublimation.

**Heat of sublimation**

Heat required to change unit mass of solid directly into vapours at a given temperature is called heat of sublimation at that temperature.

- Camphor and ammonium chloride sublimates on heating in normal conditions.
- A block of ice sublimates into vapours on the surface of moon because of very–very low pressure on its surface

### (v) Condensation

The process of conversion from gaseous or vapour state to liquid state is known as condensation .

These materials again get converted to vapour or gaseous state on heating.

### (vi) Hoar frost

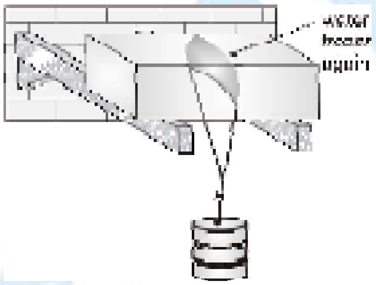
Direct conversion of vapours into solid is called hoar frost. This process is just reverse of the process of sublimation. **Ex. :** Formation of snow by freezing of clouds.

### (vii) Regelation

Regelation is the melting of ice caused by pressure and its resolidification when the pressure is removed. Ice shrinks when it melts, and if pressure is applied, deliberately promoting shrinkage, it is found that melting is thereby assisted. In other words, melting of cold ice is ordinarily effected by raising the temperature, but if pressure is present to help with the shrinkage the temperature need not be raised so much.

Ice heals up after being cut through by the wire. Melting takes place under the wire because pressure lowers the melting temperature. Refreezing (regelation) occurs above the wire when the water escapes to normal pressure again.

Increase of pressure lowers the melting (or freezing) point of water. Conversely, if a substance expands on melting, the melting point is raised by pressure.



## PHASE OF A SUBSTANCE

The phase of a substance is defined as its form which is homogeneous, physically distinct and mechanically separable from the other forms of that substance.

### Phase diagram

A phase diagram is a graph in which pressure (P) is represented along the y–axis and temperature (T) is represented along the x–axis.

### Characteristics of Phase diagram

**(i)** Different phases of a substances can be shown on a phase diagram.

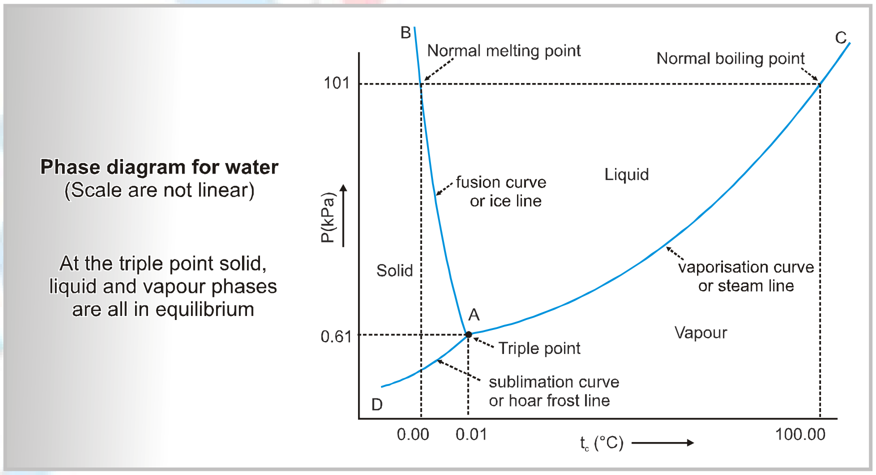
**(ii)** A region on the phase diagram represents a single phase of the substance, a curve represents equilibrium between two phases and a common point represents equilibrium between three phases.

**(iii)** A phase diagram helps to determine the condition under which the different phases are in equilibrium.

**(iv)** A phase diagram is useful for finding a convenient way in which a desired change of phase can be produced.

## PHASE DIAGRAM FOR WATER

The phase diagram for water consists of three curves AB, AC and AD meeting each other at the point A, these curves divide the phase diagram into three regions.


**Phase diagram for water**
(Scale are not linear)

At the triple point solid, liquid and vapour phases are all in equilibrium

Region to the left of the curve AB and above the curve AD represents the solid phase of water ( ice). The region to the right of the curve AB and above the curve AC represents the liquid phase of water. The region below the curves AC and AD represents the gaseous phase of water (i.e. water vapour). A curve on the phase diagram represents the boundary between two phases of the substance.

## Along any curve the two phases can coexist in equilibrium

**(i)** Along curve AB, ice and water can remain in equilibrium.This curve is called fusion curve or ice line. This curve shows that the melting point of ice decreases with increase in pressure.

**(ii)** Along the curve AC, water and water vapour can remain in equilibrium. The curve is called vaporisation curve or steam line. *The curve shows that the boiling point of water increases with increase in pressure.*

**(iii)** Along the curve AD, ice and water vapour can remain in equilibrium.

This curve is called sublimation curve or hoar frost line.

## TRIPLE POINT OF WATER

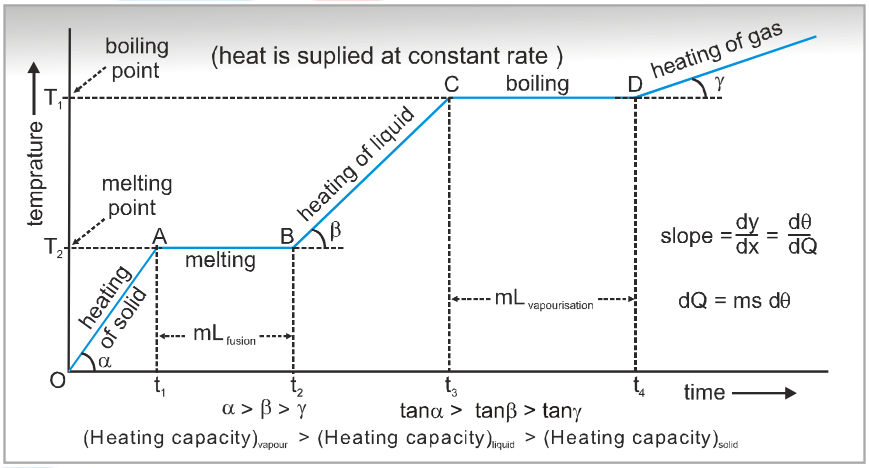
The three curves in the phase diagram of water meet at a single point A, which is called the triple point of water. The triple point of water represents the co–existance of all the three phases of water ice water and water vapour in equilibrium. The pressure corresponding to triple point of water is $6.03 \times 10^{-3}$ atmosphere or 4.58 mm of Hg and temperature corresponding to it is 273.16K.

### • Significance of triple point of water

Triple point of water represents a unique condition and it is used to define the absolute temperature. While making Kelvin's absolute scale, upper fixed point is 273.16 K and lower fixed point is 0 K. One kelvin of temperature is fraction $\frac{1}{273.16}$ of the temperature of triple point of water.

## HEATING CURVE

If to a given mass (m) of a solid, heat is supplied at constant rate and a graph is plotted between temperature and time as shown in figure is called heating curve.



**(i) In the region OA**

Rate of heat supply P is constant and temperature of solid is changing with time

So, $Q = mc_S \Delta T \Rightarrow P\,\Delta t = mc_S\,\Delta T$ [Q $Q = P\,\Delta t$] ✈ $\frac{\Delta T}{\Delta t} =$ The slope of temperature–time curve so specific heat of solid $c_S \propto \frac{1}{\text{slope of line OA}}$ specific heat (or thermal capacity) is inversely proportional to the slope of temperature–time curve.

**(ii) In the region AB**

Temperature is constant, so it represents change of state, i.e., melting of solid with melting point $T_1$. At point A melting starts and at point B all solid is converted into liquid. So between A and B substance is partly solid and partly liquid. If $L_F$ is the latent heat of fusion then

$Q = mL_F \Rightarrow L_F = \frac{P(t_2 - t_1)}{m}$ [as $Q = P(t_2 - t_1)$] $\Rightarrow L_F \propto$ length of line AB

i.e., Latent heat of fusion is proportional to the length of line of zero slope.

[In this region specific heat $\propto \frac{1}{\tan 0°} = \infty$]

**(iii) In the region BC**

Temperature of liquid increases so specific heat (or thermal capacity) of liquid will be inversely proportional to the slope of line BC, $c_L \propto \frac{1}{\text{slope of line BC}}$

**(iv) In the region CD**

Temperature in constant, so it represents change of state, i.e., liquid is boiling with boiling point $T_2$. At C all substance is in liquid state while at D is vapour state and between C and D partly liquid and partly gas. The length of line CD is proportional to latent heat of vaporisation, i.e., $L_V \propto$ Length of line CD.

[In this region specific heat $\propto \frac{1}{\tan 0°} = \infty$]

The line DE represents gaseous state of substance with its temperature increasing linearly with time. The reciprocal of slope of line will be proportional to specific heat or thermal capacity of substance in vapour state.

## LAW OF MIXTURES

**(a)** When two bodies (one being solid and other liquid or both being liquid) at different temperatures are mixed, heat will be transferred from body at higher temperature to a body at lower temperature till both acquire same temperature. The body at higher temperature released heat while body at lower temperature absorbs it, so that Heat lost = Heat gained. Principle of calorimetry represents the law of conservation of heat energy.

**(b)** Temperature of mixture (T) is always ≥ lower temperature ($T_L$) and ≤ higher temperature ($T_H$), $T_L \le T \le T_H$

The temperature of mixture can never be lesser than lower temperature (as a body cannot be cooled below the temperature of cooling body) and greater than higher temperature (as a body cannot be heated above the temperature of heating body). Further more usually rise in temperature of one body is not equal to the fall in temperature of the other body though heat gained by one body is equal to the heat lost by the other.

**Ex.** 5g ice at 0°C is mixed with 5g of steam at 100°C . What is the final temperature?

**Sol.** Heat required by ice to raise its temperature to 100°C,

$Q_1 = m_1L_1 + m_1c_1\Delta\theta_1 = 5 \times 80 + 5 \times 1 \times 100 = 400 + 500 + 900 = 1800$ cal

Heat given by steam when condensed $Q_2 = m_2L_2 = 5 \times 536 = 2680$ cal

As $Q_2 > Q_1$. This means that whole steam is not even condensed.

Hence temperature of mixture will remain at 100°C.

**Ex.** A calorimeter of heat capacity 100 J/K is at room temperature of 30°C. 100 g of water at 40°C of specific heat 4200 J/kg–K is poured into the calorimeter. What is the temperature of water in calorimeter?

**Sol.** Let the temperature of water in calorimeter is t. Then heat lost by water = heat gained by calorimeter

$(0.1) \times 4200 \times (40 - t) = 100\,(t - 30) \Rightarrow 42 \times 40 - 42t = 10t - 300 \Rightarrow t = 38.07°C$

**Ex.** Find the quantity of heat required to convert 40 g of ice at –20°C into water at 20°C.

Given $L_{ice} = 0.336 \times 10^6$ J/kg. Specific heat of ice = 2100 J/kg–K, specific heat of water = 4200 J/kg–K

**Sol.** Heat required to raise the temperature of ice from –20°C to 0°C $= 0.04 \times 2100 \times 20 = 1680$ J

Heat required to convert the ice into water at 0°C $= mL = 0.04 \times 0.336 \times 10^6 = 13440$ J

Heat required to heat water from 0°C to 20°C $= 0.04 \times 4200 \times 20 = 3360$ J

Total heat required $= 1680 + 13440 + 3360 = 18480$ J

**Ex.** Steam at 100°C is passed into 1.1 kg of water contained in a calorimeter of water equivalent 0.02 kg at 15°C till the temperature of the calorimeter and its contents rises to 80°C. What is the mass of steam condensed? Latent heat of steam = 536 cal/g.

**Sol.** Heat required by (calorimeter + water)

$$Q = (m_1c_1 + m_2c_2)\,\Delta\theta = (0.02 + 1.1 \times 1)\,(80 - 15) = 72.8 \text{ kcal}$$

If m is mass of steam condensed, then heat given by steam

$$Q = mL + mc\,\Delta\theta = m \times 536 + m \times 1 \times (100 - 80) = 556\,m \quad \therefore 556\,m = 72.8$$

$\therefore$ Mass of steam condensed $m = \dfrac{72.8}{556} = 0.130$ kg

# KINETIC THEORY OF GASES

The properties of the gases are entirely different from those of solid and liquid. In case of gases, thermal expansion is very large as compared to solids and liquids .To state the conditions of a gas, its volume, pressure and temperature must be specified.

**Intermolecular force** Solid > liquid > real gas > ideal gas (zero)

**Potential energy** Solid < liquid < real gas < ideal gas (zero)

## Internal energy, internal kinetic energy, internal potential energy

**At a given temperature for solid, liquid and gas:**

**(i)** Internal kinetic energy : Same for all

(ii) Internal potential Energy : Maximum for ideal gas (PE = 0) and Minimum for solids (PE = –ve)

(iii) Internal Energy : Maximum for Ideal gas and Minimum for solid

## At a given temperature for rared and compressed gas :

(i) Internal kinetic energy → Same

(ii) Internal potential energy → $(PE)_{Rared} > (PE)_{compressed}$

(iii) Internal Energy → $(U)_{Rared} > (U)_{compressed}$

| | **N.T.P.** **(Normal temperature)** | **S.T.P.** **(Standard Temperature and Pressure)** |
|---|---|---|
| Temperature | $0° C = 273.15\ K$ | $0.01° C = 273.16 K$ |
| Pressure | $1\ atm = 1.01325 \times 10^5\ N/m^2$<br>$= 1.01325 \times 10^5$ pascal | 1 atm |
| Volume | 22.4 litre | 22.4 litre |

## IDEAL GAS CONCEPT

**(i)** A gas which follows all gas laws and gas equation at every possible temperature and pressure is known as ideal or perfect gas.

**(ii)** Volume of gas molecules is negligible as compared to volume of container so volume of gas = volume of container (Except 0K)

**(iii)** No intermolecular force act between gas molecules.

**(iv)** Potential energy of ideal gas is zero so internal energy of ideal gas is perfectly translational K.E. of gas. It is directly proportional to absolute temperature.

So, internal energy depends only and only on its temperature.

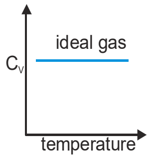
$E_{trans} \propto T$

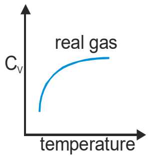
For a substance $U = U_{KE} + U_{PE}$

$U_{KE}$ : depends only on T, $U_{PE}$ : depends upon intermolecular forces (Always negative)

**(v)** Specific heat of ideal gas is constant quantity and it does not change with temperature

**(vi)** All real gases behaves as ideal gas at high temperature and low pressure.





**(vii)** Volume expansion coefficient ($\alpha$) and pressure expansion coefficient ($\beta$) is same for a ideal gas and value of each is

$$\frac{1}{273}\text{ per °C} \qquad \alpha = \beta = \frac{1}{273}\text{ per °C}$$

**(viii)** Gas molecule have point mass and negligible volume and velocity is very high ($10^7$ cm/s). That's why there is no effect of gravity on them.

## EQUATION OF STATE FOR IDEAL GAS

$$PV = \mu RT \quad \text{where } \mu = \text{number of moles of gas} \Rightarrow PV = \frac{M}{M_w}RT = \left[\frac{mN}{mN_0}\right]RT = \left[\frac{R}{N_0}\right]NT = NkT$$

**Ex.** By increasing temperature of gas by 5° C its pressure increases by 0.5% from its initial value at constant volume then what is initial temperature of gas ?

**Sol.** ✈ At constant volume $T \propto P$ $\therefore \frac{\Delta T}{T} \times 100 = \frac{\Delta P}{P} \times 100 = 0.5 \Rightarrow T = \frac{5 \times 100}{0.5} = 1000K$

**Ex.** Calculate the value of universal gas constant at STP.

**Sol.** Universal gas constant is given by $R = \frac{PV}{T}$

One mole of all gases at S.T.P. occupy volume $V = 22{\cdot}4$ litre $= 22{\cdot}4 \times 10^{-3}$ m$^3$

$P = 760$ mm of Hg $= 760 \times 10^{-3} \times 13{\cdot}6 \times 10^3 \times 9.80$ N m$^{-2}$ $\qquad T = 273$ K

$$\therefore R = \frac{760 \times 10^{-3} \times 13.6 \times 10^3 \times 9.80 \times 22.4 \times 10^{-3}}{273} = 8{\cdot}31 \text{ J mol}^{-1}\text{ K}^{-1}$$

**Ex.** A closed container of volume 0.02 m$^3$ contains a mixture of neon and argon gases at a temperature of 27°C and pressure of $1 \times 10^5$ Nm$^2$. The total mass of the mixture is 28 g. If the gram molecular weights of neon and argon are 20 and 40 respectively, find the masses of the individual gases in the container, assuming them to be ideal. Given : R = 8.314 J/mol/K.

**Sol.** Let m gram be the mass of neon. Then, the mass of argon is (28 – m)g.

Total number of moles of the mixture, $\mu = \frac{m}{20} + \frac{28 - m}{40} = \frac{28 + m}{40}$ ...(i)

Now, $\mu = \frac{PV}{RT} = \frac{1 \times 10^5 \times 0.02}{8.314 \times 300} = 0.8$ ...(ii)

By (i) and (ii), $\frac{28 + m}{40} = 0.8 \Rightarrow 28 + m = 32 \Rightarrow m = 4$ gram or mass of argon $= (28 - 4)$g $= 24$ g

**Ex.** Calculate the temperature of the Sun if density is 1.4 g cm$^{-3}$, pressure is $1.4 \times 10^9$ atmosphere and average molecular weight of gases in the Sun in 2 g/mole. [Given R = 8.4 J mol$^{-1}$K$^{-1}$]

**Sol.** $PV = \mu RT \Rightarrow T = \frac{PV}{\mu R}$ ...(i) But $\mu = \frac{M}{M_w}$ and $\rho = \frac{M}{V}$ $\therefore \mu = \frac{\rho V}{M_w}$

From equation (i) $T = \frac{PVM_w}{\rho VR} = \frac{PM_w}{\rho R} = \frac{1.4 \times 10^9 \times 1.01 \times 10^5 \times 2 \times 10^{-3}}{1.4 \times 1000 \times 8.4} = 2.4 \times 10^7$ K

**Ex.** At the top of a mountain a thermometer reads 7°C and barometer reads 70 cm of Hg. At the bottom of the mountain they read 27°C and 76 cm of Hg respectively. Compare the density of the air at the top with that at the bottom.

**Sol.** By gas equation $PV = \frac{M}{M_w}RT \Rightarrow \frac{P}{\rho T} = \frac{R}{M_w}$ $\left[\because \mu = \frac{M}{M_w} \text{ and } \frac{M}{V} = \rho\right]$

Now as $M_W$ and R are same for top and bottom $\left[\frac{P}{\rho T}\right]_T = \left[\frac{P}{\rho T}\right]_B$ So $\frac{\rho_T}{\rho_B} = \frac{P_T}{P_B} \times \frac{T_B}{T_T} = \frac{70}{76} \times \frac{300}{280} = \frac{75}{76} = 0.9868$

**Ex.** During an experiment an ideal gas is found to obey an additional law $VP^2$ = constant. The gas is initially at temperature T and volume V. What will be the temperature of the gas when it expands to a volume 2V.

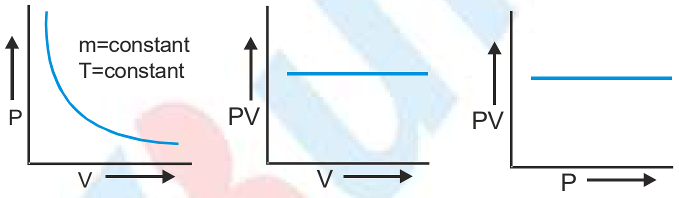
**Sol.** By gas equation $PV = \mu RT$ and $VP^2$ = constant on eliminating P

$$\left[\frac{A}{\sqrt{V}}\right]V = \mu RT \Rightarrow \sqrt{V} = \frac{\mu R}{A}T \quad \therefore \frac{\sqrt{V_1}}{\sqrt{V_2}} = \left[\frac{T_1}{T_2}\right] \Rightarrow \frac{\sqrt{V}}{\sqrt{2V}} = \frac{T}{T'} \Rightarrow T' = \left(\sqrt{2}\right)T$$

## GAS LAWS

### 1. Boyle's Law

According to it for a given mass of an ideal gas at constant temperature, the volume of a gas is inversely proportional to its pressure, i.e., $V \propto \frac{1}{P}$ if m and T = Constant



**Ex.** A sample of oxygen with volume of 500 cc at a pressure of 2 atm is compressed to a volume of 400 cc. What pressure is needed to do this if the temperature is kept constant ?

**Sol.** Temperature is constant, so $P_1V_1 = P_2V_2$ $\quad \therefore P_2 = P_1\frac{V_1}{V_2} = 2\left[\frac{500}{400}\right] = 2.5$ atm

**Ex.** An air bubble doubles in radius on rising from bottom of a lake to its surface. If the atmosphere pressuer is equal to that due to a column of 10 m of water, then what will be the depth of the lake.

(Assuming that surface tension is negligible) ?

**Sol.** Given that constant temperature, we use $P_1V_1 = P_2V_2$

$P_2 = (10)$ dg (for water column) $\qquad P_1 = (10+h)$ dg (where h=depth of lake)

$V_1 = \frac{4\pi}{3}r^3$, $V_2 = \frac{4\pi}{3}(2r)^3 = 8\left(\frac{4\pi}{3}r^3\right) = 8V_1$ Thus for $P_2V_2 = P_1V_1$,

We have $10\,dg\,(8V_1) = (10 + h)\,dg\,V_1 \Rightarrow 80 = 10 + h \Rightarrow h = 70$ m

**Ex.** A vessel of volume $8.0 \times 10^{-3}$ m$^3$ contains an ideal gas at 300 K and 200 k Pa. The gas is allowed to leak till the Pressure falls to 125 kPa. Calculate the amount of the gas leaked assuming that the temperature remains constant.

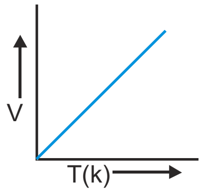
**Sol.** As the gas leaks out, the volume and the temperature of the remaining gas do not change. The number of moles of the gas in the vessel in given by $n = \frac{PV}{RT}$.

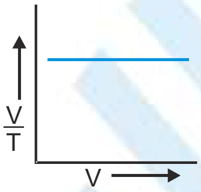
The number of moles in the vessel before the leakage is $n_1 = \frac{P_1 V}{RT}$ and that after the leakage is $n_2 = \frac{P_2 V}{RT}$.

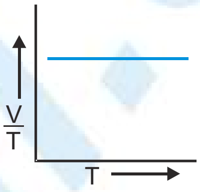
The amount leaked is $n_1 - n_2 = \frac{(P_1 - P_2)V}{RT} = \frac{(200-125)\times 10^3 \times 8.0 \times 10^{-3}}{8.3 \times 300} = 0.24$ mole

## 2. Charle's Law

According to it for a given mass of an ideal gas at constant pressure, volume of a gas is directly proportional to its absolute temperature, i.e. $V \propto T$ if m and $P =$ Constant







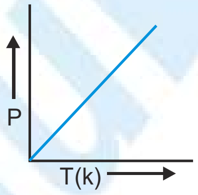
**Ex.** 1500 ml of a gas at a room temperature of 23°C is inhaled by a person whose body temperature is 37°C, if the pressure and mass stay constant, what will be the volume of the gas in the lungs of the person ?

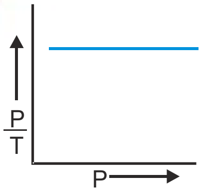
**Sol.** $T_1 = 273 + 37 = 310$ K; $T_2 = 273 + 23 = 296$ K. Pressure and amount of the gas are kept constant,

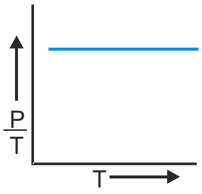
So $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ $\quad \therefore V_2 = V_1 \times \frac{T_2}{T_1} = 1500 \times \frac{293}{310} = 1417.74$ ml

## 3. Gay–Lussac's Law

According to it, for a given mass of an ideal gas at constant volume, pressure of a gas is directly proportional to its absolute temperature, i.e., $P \propto T$ if m and $V =$ constant







**Ex.** A sample of $O_2$ is at a pressure of 1 atm when the volume is 100 ml and its temperature is 27°C. What will be the temperature of the gas if the pressure becomes 2 atm and volume remains 100 ml.

**Sol.** $T_1 = 273 + 27 = 300$ K

For constant volume $\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow T_2 = T_1 \times \frac{P_2}{P_1} = 300 \times \frac{2}{1} = 600\text{ K} = 600 - 273 = 327°\text{C}$

### 4. Avogadro's Law

According to it, at same temperature and pressure of equal volumes of all gases contain equal number of molecules, i.e., $N_1 = N_2$ if P,V and T are same.

### Dalton's Partial Pressure Mixture Law :

According to it, the pressure exerted by a gasesous mixture is equal to the sum of partial pressure of each component gases present in the mixture, ie., $P = P_1 + P_2 + ....$

**Ex.** The mass percentage in composition of dry air at sea level contains approximately 75.5% of $N_2$. If the total atmospheric pressure is 1 atm then what will be the partial pressure of nitrogen ?

**Sol.** The mole fraction of nitrogen $\mu_1 = \left(\frac{M_{\text{nitrogen}}}{\text{Molecular} \quad \text{weight}}\right) = 0.755 \times \frac{29}{28} = 0.78$

The partial pressure of nitrogen $P_1 = \mu_1 \frac{RT}{V} = \frac{\mu_1}{\mu}\frac{\mu RT}{V} = \left(\frac{\mu_1}{\mu}\right)P = (0.78) \times 1 = 0.78$ atm

### The Kinetic Theory of Gases

Rudolph Claussius (1822–88) and James Clark Maxwell (1831–75) developed the kinetic theory of gases in order to explain gas laws in terms of the motion of the gas molecules. The theory is based on following assumptions as regards to the motion of molecules and the nature of the gases.

### Basic Postulates of Kinetic Theory of Gases

**(a)** Every gas consists of extremely small particles known as molecules. The molecules of a given gas are all identical but are different than those another gas.

**(b)** The molecules of a gas are identical, spherical, rigid and perfectly elastic point masses.

**(c)** The size is negligible in comparision to inter molecular distance ($10^{-9}$ m)

### Assumptions regarding motion :

**(a)** Molecules of a gas keep on moving randomly in all possible direction with all possible velocities.

**(b)** The speed of gas molecules lie between zero and infinity (very high speed).

**(c)** The number of molecules moving with most probable speed is maximum.

### Assumptions regarding collision:

The gas molecules keep colliding among themselves as well as with the walls of containing vessel. These collision are perfectly elastic. (ie., the total energy before collision = total energy after the collisions.)

### Assumptions regarding force:

**(a)** No attractive or repulsive force acts between gas molecules.

**(b)** Gravitational attraction among the molecules is ineffective due to extremely small masses and very high speed of molecules.

### Assumptions regarding pressure:

Molecules constantly collide with the walls of container due to which their momentum changes. This change in momentum is transferred to the walls of the container. Consequently pressure is exerted by gas molecules on the walls of container.

### Assumptions regarding density:

The density of gas is constant at all points of the container.

## PROPERTIES/ASSUMPTIONS OF IDEAL GAS

**(i)** The molecules of a gas are in a state of continuous random motion. They move with all possible velocities in all possible directions. They obey Newton's law of motion.

**(ii)** Mean momentum = 0; Mean velocity = 0. $< \vec{v} > = 0$;  $< v^2 > \neq 0$ (Non zero); $< v^3 > = < v^5 > = 0$

**(iii)** The average distance travelled by a molecule between two successive collisions is called as mean free path ($\lambda_m$) of the molecule.

**(iv)** The time during which a collision takes place is negligible as compared to time taken by the molecule to cover the mean free path so NTP ratio of time of collision to free time of motion $10^{-8} : 1$.

**(v)** When a gas taken into a vessel it is uniformly distributed in entire volume of vessel such that its density, moleculer density, motion of molecules etc. all are identical for all direction, therefore root mean velocity

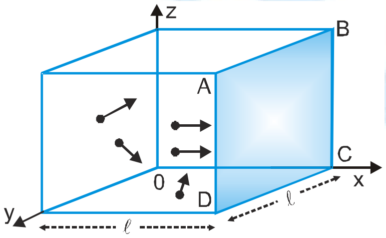
$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \rightarrow$ equal  Pressure exerted by the gas in all direction $P_x = P_y = P_z = P \rightarrow$ equal

**(vi)** All those assumptions can be justified, if number of gas molecules are taken very large

i.e., $10^{23}$ molecules/cm$^3$.

## EXPRESSION FOR PRESSURE OF AN IDEAL GAS

Consider an ideal gas enclosed in a cubical vessel of length ●. Suppose there are 'N' molecules in a gas which are moving with velocities $\vec{v}_1, \vec{v}_2 \ldots\ldots\ldots \vec{v}_N$ .



If we consider any single molecule than its instantaneous velocity $\vec{v}$ can be expressed as $\vec{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}$

Due to random motion of the molecule  $v_x = v_y = v_z$  $|v| = v_x\sqrt{3} = v_y\sqrt{3} = v_z\sqrt{3} = \sqrt{v_x^2 + v_y^2 + v_z^2}$

Suppose a molecule of mass m is moving with a velocity $v_x$ towards the face ABCD. It strikes the face of the cubical vessel and returns back to strike the opposite face.

Change in momentum of the molecule per collision $\Delta p = -mv_x - mv_x = -2\,mv_x$

Momentum transferred to the wall of the vessel per molecule per collision $\Delta p = 2\,mv_x$

The distance travelled by the molecule in going to face ABCD and coming back is 2●.

So, the time between two successive collision is $\Delta t = \dfrac{21}{v_x}$

Number of collision per sec per molecule is $f_c = \dfrac{v_x}{21} = \dfrac{\text{molecule velocity}}{\text{mean free path}}$, $f_c = \dfrac{v_{rms}}{\lambda_m}$ or $f_c = \dfrac{v_m}{\lambda_m}$

Hence momentum transferred in the wall per second by the molecule is = force on the wall

$$\text{force } F = (2\,mv_x)\frac{v_x}{21} = \frac{mv_x^2}{1} = \frac{mv^2}{31}$$

Pressure exerted by gas molecule $P = \frac{F}{A} = \frac{1}{3}\frac{mv^2}{1 \times A} \Rightarrow P = \frac{1}{3}\frac{mv^2}{V}$ $[\because A \times l = V]$

Pressure exerted by gas $P = \sum \frac{1}{3}\frac{mv^2}{V} = \sum \frac{1}{3}\frac{mv^2}{V} \times \frac{N}{N} = \frac{1}{3}\frac{mN}{V}\frac{\sum v^2}{N} = \frac{1}{3}\frac{mN}{V}v_{rms}^2$

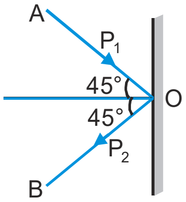
$$v_{rms}^2 = \frac{3PV}{M} = \frac{3\mu RT}{\mu M_w} \Rightarrow v_{rms} = \sqrt{\frac{3RT}{M_w}}, P = \frac{1}{3}\frac{M}{V}v_{rms}^2 = \frac{1}{3}\rho v_{rms}^2$$

**(i)** Average number of molecules for each wall $= \frac{N}{6}$. No. of molecules along each axis $= \frac{N}{3}$ $(N_x = N_y = N_z)$

**(ii)** $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = \frac{\bar{v}_{rms}^2}{3}$ Root mean square velocity along any axis for gas molecule is $(v_{rms})_\chi = (v_{rms})_y = (v_{rms})_z = \frac{v_{rms}}{\sqrt{3}}$

All gas laws and gas equation can be obtained by expression of pressure of gas (except Joule's law)

**Ex.** The mass of a hydrogen molecule is $3.32 \times 10^{-27}$ kg. If $10^{23}$ molecules are colliding per second on a stationary wall of area 2 cm$^2$ at an angle of 45° to the normal to the wall and reflected elastically with a speed $10^3$ m/s. Find the pressure exerted on the wall will be (in N/m$^2$)



**Sol.** As the impact is elastic $\therefore |\vec{p}_1| = |\vec{p}_2| = p = mv = 3.32 \times 10^{-24}$ kg m/s

The change in momentum along the normal $\Delta p = |\vec{p}_2 - \vec{p}_1| = 2p\cos 45° = \sqrt{2}p$

If f is the collision frequency then force applied on the wall $F = \frac{\Delta p}{\Delta t} = \Delta p \times f = \sqrt{2}pf$

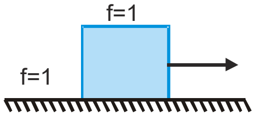
$$\therefore \quad \text{Pressure } P = \frac{F}{A} = \frac{\sqrt{2}pf}{A} = \frac{\sqrt{2} \times 3.32 \times 10^{-24} \times 10^{23}}{2 \times 10^{-4}} = 2.347 \times 10^3 \text{ N/ m}^2$$

## DEGREE OF FREEDOM (f)

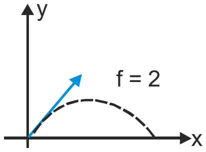
**(i)** The number of independent ways in which a molecule or an atom can exhibit motion or have energy is called it's degrees of freedom.

**(ii)** The number of independent coordinates required to specify the dynamical state of a system is called it's degrees of freedom.

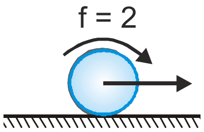
### For example



**(a)** Block has one degree of freedom, because it is confined to move in a straight line and has only one transistional degree of freedom.



**(b)** The projectile has two degrees of freedom becomes it is confined to move in a plane and so it has two translational degrees of freedom.



**(c)** The sphere has two degrees of freedom one rotational and another translational. Similarly a particle free to move in space will have three translational degrees of freedom.

**Note** : In pure rolling sphere has one degree of freedom as $KE = \frac{1}{2}mv^2(1+\frac{K^2}{R^2}) = \frac{7}{10}mv^2$

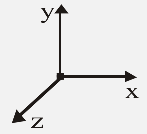
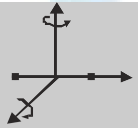
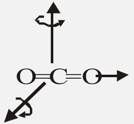
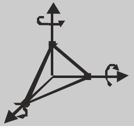
## THE DEGREES OF FREEDOM ARE OF THREE TYPES :

(a) **Translational Degree of freedom :** Maximum three degree of freedom are there corresponding to translational motion.

(b) **Rotational Degree of freedom** : The number of degrees of freedom in this case depends on the structure of the molecule.

(c) **Vibrational Degree of freedom :** It is exhibited at high temperatures.

### Degree of freedom for different gases according to atomicity of gas at low temperature

| Atomicity of gas | Translational | Rotational | Total | |
|---|---|---|---|---|
| Monoatomic<br>**Ex.** Ar, Ne, Ideal gas etc | 3 | 0 | 3 |  |
| Diatomic<br>**Ex.** $O_2$, $Cl_2$, $N_2$ etc. | 3 | 2 | 5 |  |
| Triatomic (linear)<br>**Ex.** $CO_2$, $C_2H_2$ | 3 | 2 | 5 |  |
| Triatomic (Non–linear)<br>or Polyatomic<br>**Ex.** $H_2O$, $NH_3$, $CH_4$ | 3 | 3 | 6 |  |

At high temperatures a diatomic molecule has 7 degrees of freedom. (3 translational, 2 rotational and 2 vibrational)

**Ex.** Calculate the total number of degrees of freedom possessed by the molecules in one $cm^3$ of $H_2$ gas at NTP.

**Sol.** 22400 $cm^3$ of every gas constains $6.02 \times 10^{23}$ molecules.

$\therefore$ Number of molecules in 1 $cm^3$ of $H_2$ gas $= \dfrac{6.02 \times 10^{23}}{22400} = 0.26875 \times 10^{20}$

Number of degrees of freedom of a $H_2$ gas molecule = 5

$\therefore$ Total number of degrees of freedom of $0.26875 \times 10^{20} \times 5 = 1.34375 \times 10^{20}$.

## MAXWELL'S LAW OF EQUIPARTITION OF ENERGY

The total kinetic energy of a gas molecules is equally distributed among its all degree of freedom and the energy associated with each degree of freedom at absolute temperature T is $\frac{1}{2}kT$

### For one molecule of gas

Energy related with each degree of freedom $= \frac{1}{2}kT$

Energy related with all degree of freedom $= \frac{f}{2}kT$ ✈ $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = \frac{\bar{v}_{rms}^2}{3} \Rightarrow \frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT$

So energy related with one degree of freedom $= \frac{1}{2}m\frac{v_{rms}^2}{3} = \frac{3}{2}\frac{kT}{3} = \frac{1}{2}kT$

**Ex.** A cubical box of side 1 meter contains helium gas (atomic weight 4) at a pressure of 100 N/m$^2$. During an observation time of 1 second, an atom travelling with the root–mean–square speed parallel to one of the edges of the cube, was found to make 500 hits with a particular wall, without any collision with other atoms. Take R = $\frac{25}{3}$ J/mol–K and k = 1.38 × 10$^{-23}$ J/K.

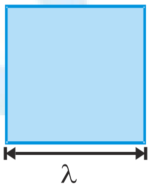
**(a)** Evaluate the temperature of the gas.

**(b)** Evaluate the average kinetic energy per atom.

**(c)** Evaluate the total mass of helium gas in the box.

**Sol.** Volume of the box = 1m$^3$, Pressure of the gas = 100 N/m$^2$. Let T be the temperature of the gas

**(a)** Time between two consecutive collisions with one wall $= \frac{1}{500}$ sec



This time should be equal to $\frac{2l}{v_{rms}}$, where $l$ is the side of the cube.

$$\frac{2l}{v_{rms}} = \frac{1}{500} \Rightarrow v_{rms} = 1000 \text{ m/s} \quad \therefore \sqrt{\frac{3RT}{M}} = 1000 \Rightarrow T = \frac{(1000)^2 M}{3R} = \frac{(10)^6 (3 \times 10^{-3})}{3\left(\frac{25}{3}\right)} = 160\text{K}$$

**(b)** Average kinetic energy per atom $= \frac{3}{2}kT = \frac{3}{2}$ [(1.38 × 10$^{-23}$) = 160] J = 3.312 ×$^{-21}$ J

**(c)** From $PV = nRT = \frac{m}{M}RT$, Mass of helium gas in the box $m = \frac{PVM}{RT}$

Substituting the values, $m = \frac{(100)(1)(4 \times 10^{-3})}{\left(\frac{25}{3}\right)(160)} = 3.0 \times 10^{-4}$ kg

## DIFFERENT K.E. OF GAS (INTERNAL ENERGY)

**(i)** **Translatory kinetic energy (ET)** $E_T = \frac{1}{2}Mv_{rms}^2 = \frac{3}{2}PV$

Kinetic energy of volume V is $= \frac{1}{2}Mv_{rms}^2$ Note : Total internal energy of ideal gas is kinetic

**(ii)** **Energy per unit volume or energy density (EV)**

$$E_V = \frac{\text{Total energy}}{\text{Volume}} = \frac{E}{V}\ ; \quad E_V = \frac{1}{2}\left[\frac{M}{V}\right]v_{rms}^2 = \frac{1}{2}\rho v_{rms}^2 \quad ✈ \quad P = \frac{2}{3}\left[\frac{1}{2}\rho v_{rms}^2\right] \quad \therefore E_V = \frac{3}{2}P$$

**(iii)** **Molar K.E. or Mean Molar K.E. (E)**

$$E = \frac{1}{2}M_w v_{rms}^2 \text{ for } N_0 \text{ molecules or } M_w \text{ (gram) } E = \frac{3}{2}RT = \frac{3}{2}N_0 kT$$

**(iv)** **Molecular kinetic energy or mean molecular K.E. ($\bar{E}$)**

$$E = \frac{1}{2}M_w v_{rms}^2\ , \ \bar{E} = \frac{E}{N_0} = \frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}kT$$

## ETOOS KEY POINTS

**(i)** Except 0 K, at any temperature T, $E > E_m > \overline{E}$

**(ii)** At a common temperature, for all ideal gas E and $\overline{E}$ are same while $E_m$ is different and depends upon nature of gas ($M_w$ or m)

**(iii)** For thermal equilibrium of gases, temperature of each gas is same and this temperature called as temperature of mixture ($T_m$) which can be find out on basis of conservation of energy (All gases are of same atomicity). $T_m = \frac{\sum NT}{\sum N} = \frac{N_1T_1 + N_2T_2 + ......... + N_nT_n}{N_1 + N_2......N_n}$

**(iv)** **1 mole gas :** Mean kinetic energy $= \frac{3}{2}RT$ ; Total kinetic energy $= \frac{f}{2}RT$

**(v)** **1 molecule of gases :** Mean kinetic energy $= \frac{3}{2}kT$ ; Total kinetic energy $= \frac{f}{2}kT$

$f \rightarrow$ Degree of freedom

**Ex.** Two ideal gases at temperature $T_1$ and $T_2$ are mixed. There is no loss of energy. If the masses of molecules of the two gases are $m_1$ and $m_2$ and number of their molecules are $n_1$ and $n_2$ respectively. Find the temperature of the mixture.

**Sol.** Total energy of molecules of first gas $= \frac{3}{2}n_1kT_1$ , Total energy of molecules of second gas $= \frac{3}{2}n_2kT_2$

Let temperature of mixture be T then total energy of molecules of mixture $= \frac{3}{2}k(n_1 + n_2)T$

$$\therefore \frac{3}{2}(n_1 + n_2)kT = \frac{3}{2}k(n_1T_1 + n_2T_2) \Rightarrow T = \frac{n_1T_1 + n_2T_2}{(n_1 + n_2)}$$

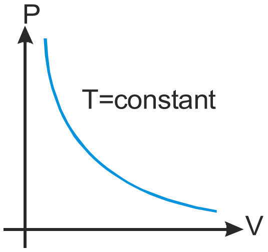
**Ex.** The first excited state of hydrogen atom is 10.2 eV above its ground state. What temperature is needed to excite hydrogen atoms to first excited level.

**Sol.** K.E. of the hydrogen atom $\frac{3}{2}kT = 10.2\text{ eV} = 10.2 \times \left(1.6 \times 10^{-19}\right)\text{J}$

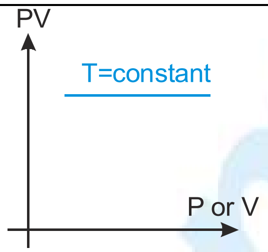
$$\Rightarrow T = \frac{2}{3} \times \frac{10.2 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} = 7.88 \times 10^4\text{ K}$$

## EXPLANATION OF GAS LAWS FROM KINETIC THEORY

### 1. Boyle's Law



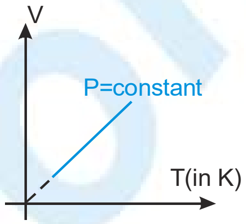
According to this law, the product of the pressure and the volume of a given mass of gas at constant temperature is constant. From the kinetic theory of gases, the pressure of a given mass of an ideal gas is given by $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$. mN is the mass of the gas



which is constant. If the temperature remains constant, the mean–square–velocity of the molecules. $(v_{rms}^2)$ also remains constant. Thus, from the above equation, we have PV = constant.

This is Boyle's law. $V \propto \frac{1}{P}$ (T = constant) or $P_iV_i = P_fV_f$

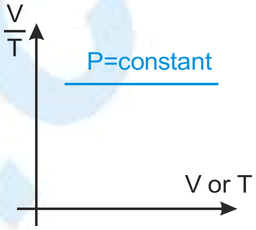
## 2. Charle's Law



According to this law, the volume of a given mass of gas at constant pressure is directly proportional to the absolute temperature of the gas.

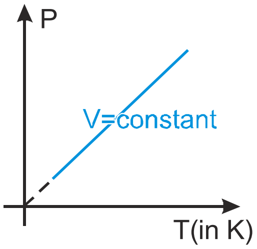
From kinetic theory, we have $V = \frac{2}{3}\frac{N}{P}\left(\frac{1}{2}mv_{rms}^2\right)$

$$V = \frac{2}{3}\frac{N}{P}\left(\frac{3}{2}kT\right) = \frac{N}{P}kT \quad \left[Q \quad \frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT\right]$$



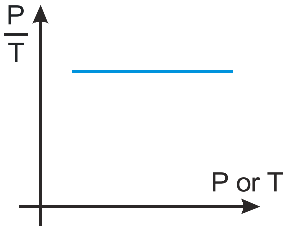
If the pressure P is constant, then for a given mass of the gas, we have $V \propto T$ This is Charle's Law.

## 3. Gay Lussac's law of Pressure law



For a given mass of a gas the pressure of a gas at constant volume (called Isochoric process) is directly proportional to its absolute temperature, $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$ ✈ $v_{rms}^2 \propto T$ ∴ $P \propto T$ (V = constant)

or $\frac{P}{T}$ = constant or $\frac{P_i}{T_i} = \frac{P_f}{V_f}$



P–T graph in an isochoric process is a straight line passing through origin or $\frac{P}{T}$ v/s P or T graph is a straight line parallel to P or T axis.

## 4. Avogadro's Law

Equal volumes of 'all gases' under the same conditions of temperature and pressure contain equal number of molecules.

At same pressure equal volumes V of different gases contain respectively $N_1$ and $N_2$ molecules of masses $m_1$ and $m_2$. $PV = \frac{1}{3}m_1N_1v_{rms_1}^2$ and $PV = \frac{1}{3}m_2N_2v_{rms_2}^2$ $\Rightarrow m_1N_1v_{rms_1}^2 = m_2N_2v_{rms_2}^2$

Now, if the gases are at the same temperature, their average kinetic energies of translation per molecule are equal. That is $\frac{1}{2}m_1v_{rms_1}^2 = \frac{1}{2}m_2v_{rms_2}^2 \Rightarrow N_1 = N_2$.

## 5. Dalton's Law of Partial Pressures

The total pressure exerted by a mixture of non–reacting gases occupying a vessel is equal to the sum of the individual pressures which each gas would exert if it alone occupied the whole vessel.

Let as consider a mixture of gases occupying a volume V. Suppose the first gas contains $N_1$ molecules, each of mass $m_1$ having mean–square–speed $v^2_{rms_1}$, the second gas contains $N_2$ molecules each of mass $m_2$ and mean–square–speed $v^2_{rms_2}$, and so on. Let $P_1$, $P_2$,........ respectively the partial pressures of the gases. Each gas fills the whole volume V. According to kinetic theory, we have

$$P_1V = \frac{1}{3}m_1N_1v^2_{rms_1}, \qquad P_2V = \frac{1}{3}m_2N_2v^2_{rms_2}, \text{ and so on.}$$

Additing, we get $$(P_1 + P_2 + \ldots\ldots)V = \frac{1}{3}(m_1N_1v^2_{rms_1} + m_2N_2v^2_{rms_2} + \ldots\ldots) \qquad \ldots\ldots\text{(i)}$$

Now, the whole mixture is at the same temperature. $\therefore \frac{1}{2}m_1v^2_{rms_1} = \frac{1}{2}m_2v^2_{rms_2}\ldots\ldots = \frac{1}{2}mv^2_{rms}$

Substituting this result in eq$^n$. (i) we have $(P_1 + P_2 + \ldots\ldots)V = \frac{1}{3}(N_1 + N_2 + \ldots\ldots)mv^2_{rms}$

The mixture has a total number of molecules ($N_1 + N_2$ + .......). Hence the pressure P exerted by the mixture is given by $PV = \frac{1}{3}(N_1 + N_2 + \ldots\ldots)\ mv^2_{rms}$

That $P = P_1 + P_2 + \ldots\ldots$ This is Dalton's law of partial pressures.

## DIFFERENT SPEEDS OF GAS MOLECULES

### Average Velocity

Because molecules are in random motion in all possible direction in all possible velocity. Therefore, the average velocity of the gas in molecules in container is zero. $<\vec{v}> = \dfrac{\vec{v}_1 + \vec{v}_2 + \ldots\ldots\ldots\ldots \vec{v}_N}{N} = 0$

### RMS Speed of Molecules

$$v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3kT}{m}} = 1.73\sqrt{\frac{kT}{m}}$$

### Mean Speed of Molecules

By maxwell's velocity distribution law $v_M$ or $<|\vec{v}|> = v_{mean}$

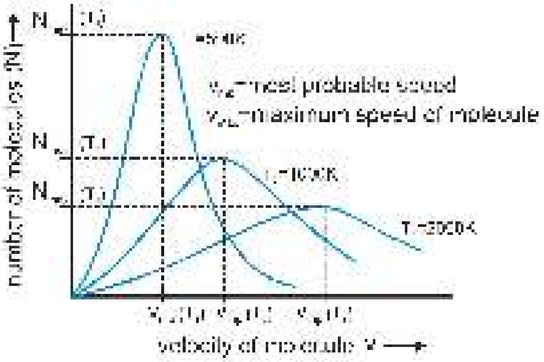
$$<\vec{v}> = v_{mean} = \frac{|\vec{v}_1| + |\vec{v}_2| + \ldots\ldots\ldots|\vec{v}_n|}{N} = \sqrt{\frac{8}{\pi}\frac{P}{\rho}} = \sqrt{\frac{8RT}{\pi M_w}} = \sqrt{\frac{8kT}{\pi m}} = 1.59\sqrt{\frac{kT}{m}}$$

### Most Probable Speed of Molecules ($v_{mp}$)

At a given temperature, the speed to which maximum number of molecules belongs is called as most probable speed

$$(v_{mp}) \qquad v_{mp} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2RT}{M_w}} = \sqrt{\frac{2kT}{m}} = 1.41\sqrt{\frac{kT}{m}}$$

## MAXWELL'S LAW OF DISTRIBUTION OF VELOCITIES



### ETOOS KEY POINTS

(i) At any given temperature graph drawn in between molecular velocity and number of molecules is known as velocity distribution curve.

(ii) The velocities of molecules of a gas are in between zero and infinity (0 – ∞)

(iii) With the increase in the temperature, the most probable velocity and maximum molecule velocity both increases.

(iv) The number of molecules within certain velocity range is constant although the velocity of molecule changes continuously at particular temperature.

(v) The area enclosed between the (N – v) curve and the velocity axis presents the total number of molecules.

On the basis of velocity distribution Maxwell established gives the law of equipartition of energy for gases of any temperature.

**Velocity of Sound in Gas Medium ($V_s$)** $\quad v_{sound} = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma RT}{M_w}} = \sqrt{\frac{\gamma kT}{m}}$

(i) At any temperature $\quad v_{rms} > v_{avg} > v_{mp} > v_{sound}$ (always)

(ii) For a gas at any temperature (T) $\quad \frac{v_{rms}}{v_{sound}} = \sqrt{\frac{3}{\gamma}}, \quad \frac{v_{rms}}{v_{mp}} = \sqrt{\frac{3}{2}}$

(iii) A temperature is not possible at which above order can be changed.

$$v_{rms} \neq v_{avg} \neq v_{mp} \neq v_{sound} \qquad \text{(always)}$$

**Ex.** The velocities of ten particles in ms$^{-1}$ are 0, 2, 3, 4, 4, 4, 5, 5, 6, 9. Calculate

(i) average speed and (ii) rms speed (iii) most probable speed.

**Sol.** (i) average speed, $v_{av} = \frac{0+2+3+4+4+4+5+5+6+9}{10} = \frac{42}{10} = 4.2 \text{ ms}^{-1}$

(ii) rms speed, $v_{rms} = \left[\frac{(0)^2+(2)^2+(3)^2+(4)^2+(4)^2+(4)^2+(5)^2+(5)^2+(6)^2+(9)^2}{10}\right]^{1/2} = \left[\frac{228}{10}\right]^{1/2} = 4.77 \text{ ms}^{-1}$

(iii) most probable speed $v_{mp} = 4$ m/s

**Ex.** At what temperature, will the root mean square velocity of hydrogen be double of its value at S.T.P., pressure remaining constant ?

**Sol.** Let $v_1$ be the r.m.s. velocity at S.T.P. and $v_2$ be the r.m.s. velocity at unknown temperature $T_2$.

$$\therefore \quad \frac{v_1^2}{v_2^2} = \frac{T_1}{T_2} \quad \text{or} \quad T_2 = T_1\left[\frac{v_2}{v_1}\right]^2 = 273 \times (2)^2 = 273 \times 4 = 1092\text{ K} = (1092 - 273) = 819°\text{C}$$

**Ex.** Calculate rms velocity of oxygen molecule at 27°C

**Sol.** Temperature, $T = 27°\text{ C} \Rightarrow 273 + 27 = 300\text{ K}$,

Molecular weight of oxygen $= 32 \times 10^{-3}$ kg and $R = 8{\cdot}31\text{ J mol}^{-1}\text{ K}^{-1}$

rms velocity is $v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8{\cdot}31 \times 300}{32 \times 10^{-3}}} = 483{\cdot}5\text{ ms}^{-1}$

**Ex.** Calculate the kinetic energy of a gram molecule of argon at 127°C.

**Sol.** Temperature, $T = 127°\text{C} = 273 + 127 = 400\text{ K}$, $R = 8.31$ J/mol K

K.E. per gram molecule of argon $= \frac{3}{2}RT = \frac{3}{2} \times 8.31 \times 400 = 4986$ J

# THERMODYNAMICS

## Thermal equilibrium

Branch of physics which deals with the inter–conversion between heat energy and any other form of energy is known as thermodynamics. In this branch of physics we deals with the processes involving heat, work and internal energy. In this branch of science the conversion of heat into mechanical work and vice versa is studied.

### Thermodynamical System

The system which can be represented in of pressure (P), volume (V) and temperature (T), is known thermodynamic system. A specified portion of matter consisting of one or more substances on which the effects of variables such as temperature, volume and pressure are to be studied, is called a system. e.g. A gas enclosed in a cylinder fitted with a piston is a system.

### (i) Surroundings

Anything outside the system, which exchanges energy with the system and which tends to change the properties of the system is called its surroundings.

### (ii) Heterogeneous System

A system which is not uniform throughout is said to be heterogeneous. e.g. A system consisting of two or more immiscible liquids.

### (iii) Homogeneous System

A system is said to be homogeneous if it is completely uniform throughout. e.g. Pure solid or liquid.

### (iv) Isolated System

A system in which there can be no exchange of matter and energy with the surroundings is said to be an isolated system.

### (v) Universe

The system and its surroundings are together known as the universe.

## Thermodynamic variables of the system

**(i)** Composition ($\mu$) **(ii)** Temperature (T) **(iii)** Volume (V) **(iv)** Pressure (P)

## Thermodynamic state

The state of a system can be described completely by composition, temperature, volume and pressure.

If a system is homogeneous and has definite mass and composition, then the state of the system can be described by the remaining three variables namely temperature, pressure and volume. These variables are interrelated by equation $PV = \mu RT$ The thermodynamic state of the system is its condition as identified by two independent thermodynamic variables (P, V or P, T or V, T).

## 1. ZEROTH LAW OF THERMODYNAMICS

If objects A and B are separately in thermal equilibrium with a third object C (say thermometer), then objects A and B are in thermal equilibrium with each other. Zeroth law of thermodynamics introduce the concept of temperature. Two objects (or systems) are said to be in thermal equilibrium if their temperatures are the same.

In measuring the temperature of a body, it is important that the thermometer be in the thermal equilibrium with the body whose temperature is to be measured.

Thermal equilibrium is a situation in which two objects in thermal contact cease to exchange energy by the process of heat. Heat is the transfer of energy from one object to another object as a result of a difference in temperature between them.

## Internal Energy

Internal energy of a system is the energy possessed by the system due to molecular motion and molecular configuration. The energy due to molecular motion is called internal kinetic energy ($U_k$) and that due to molecular configuration is called internal potential energy ($U_p$). $dU = dU_k + dU_p$

If there no intermolecular forces, then $dU_p = 0$ and $dU = dU_k = m c_v dT$

$c_v$ = Specific heat at constant volume and $dT$ = Infinitesimal change in temperature

m = Mass of system M = Molecular weight

Molar heat capacity $C_v = Mc_v$ For μ–moles of ideal gas $dU = \mu C_v dT = \frac{m}{M} C_v dT$

Internal energy in the absence of intermolecular forces is simply the function of temperature and state only, it is independent of path followed. $\Delta U = U_f - U_i$

$U_i$ = Internal energies in initial state and $U_f$ = Internal energies in final state

## Thermodynamic Processes

In the thermodynamic process pressure, volume, temperature and entropy of the system change with time.

Thermodynamic process is said to take place if change occurs in the state of a thermodynamic system.

## Sign convention used for the study of thermodynamic processes

| | |
|---|---|
| Heat gained by a system | Positive |
| Heat lost by a system | Negative |
| The work done by a system | Positive |
| Work done on the system | Negative |
| Increase in the internal energy of system | Positive |
| Decrease in the internal energy of system | Negative |

## Indicator Diagram or P–V Diagram

In the equation of state of a gas $PV = \mu RT$

Two thermodynamic variables are sufficient to describe the behavior of a thermodynamic system.

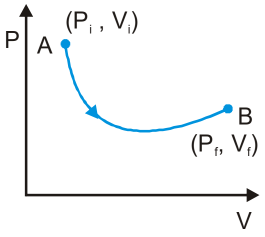
If any two of the three variables P, V and T are known then the third can be calculated.

P–V diagram is a graph between the volume V and the pressure P of the system.

The volume is plotted against X–axis while the pressure is plotted against Y–axis.

The point A represents the initial stage of the system. Initial pressure of the system is $P_i$ and initial volume of the system $V_i$ .

The point B represents the final state of the system. $P_f$ and $V_f$ are the final pressure and final volume respectively of the system. The points between A and B represent the intermediate states of the system. With the help of the indicator diagram we calculate the amount of work done by the gas or on the gas during expansion or compression.



### (i) Cyclic process

Cyclic process is that thermodynamic process in which the system returns to its initial stage after undergoing a series of changes.

### (ii) Non–cyclic process

Non–cyclic process is that process in which the system does not return to its initial stage.

### (iii) Quasi–static or equilibrium process

Quasi–static is a thermodynamic process which proceeds extremely slowly such that at every instant of time, the temperature and pressure are the same in all parts of the system.

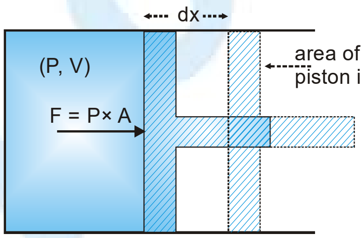
### (iv) Reversible and Irreversible processes

A reversible process is one in which the changes in heat and work of direct process from initial to a final state are exactly retraced in opposite sense in the reverse process and the system and surroundings are left in their initial states. The reversibility is an ideal concept and can not be realized in practice.

The process which is not reversible is the irreversible process. In nature the processes are irreversible.

## WORK DONE BY THERMODYNAMIC SYSTEM

One of the simple example of a thermodynamic system is a gas in a cylinder with a movable piston.



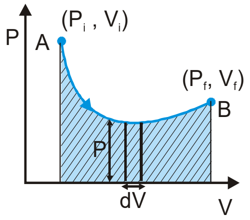
**(i) If the gas expands against the piston**

Gas exerts a force on the piston and displace it through a distance and does work on the piston.

**(ii) If the piston compresses the gas**

When piston moved inward, work is done on the gas.

**(iii) The work associated with volume changes**



If pressure of gas on the piston = P.

Then the force on the piston due to gas is F = PA

When the piston is pushed outward an infinitesimal distance dx, the work done by the gas is dW = F × dx = PA dx

The change in volume of the gas is dV = Adx, ∴ dW = PdV

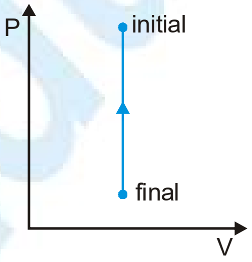
For a finite change in volume from $V_i$ to $V_f$, this equation is then integrated between $V_i$ to $V_f$ to find the

$$\text{net work done } W = \int_{V_i}^{V_f} dW = \int_{V_i}^{V_f} PdV$$

Hence the work done by a gas is equal to the area under P–V graph.

Following different cases are possible.

**(i) Volume is constant**



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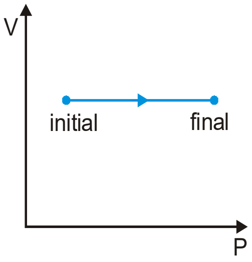
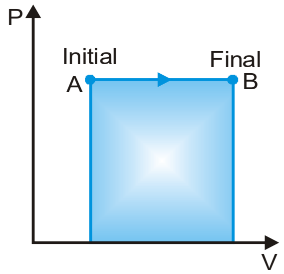


V = constant and $W_{AB} = 0$

**(ii) Volume is increasing**



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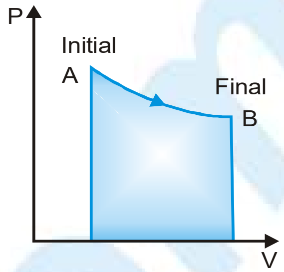
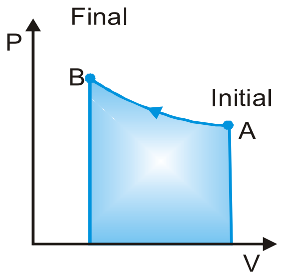


V is increasing $W_{AB} > 0$ $W_{AB}$ = Shaded area

**(iii) Volume is decreasing**



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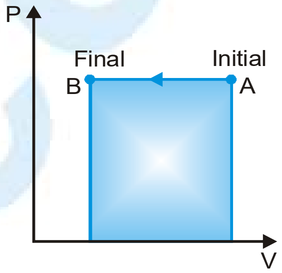
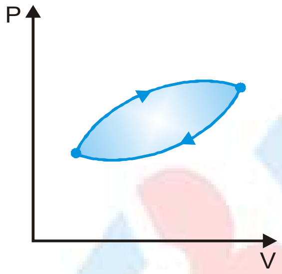
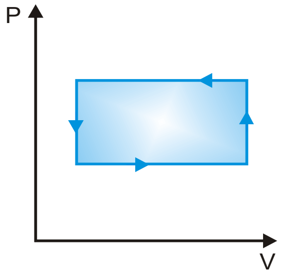


V is decreasing $W_{AB} < 0$ $W_{AB}$ = – Shaded area

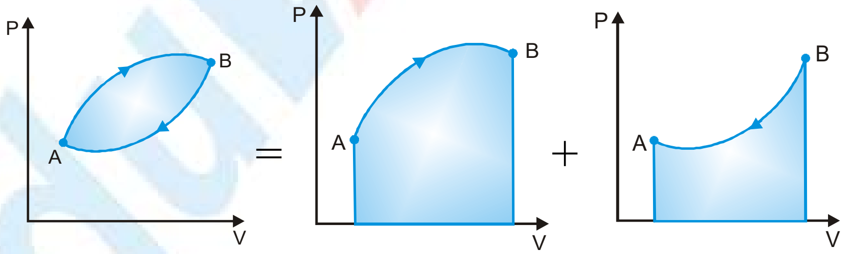
**(iv) Cyclic process**





$W_{\text{clockwise cycle}}$ = + Shaded area $W_{\text{anticlockwise cycle}}$ = – Shaded area

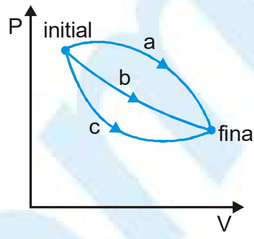
## WORK DONE IN CLOCKWISE CYCLE



$W_{AB\ I}$ Positive $W_{AB\ II}$ Negative

$W_{cyclic} = W_{AB\ I}$ (positive) + $W_{AB\ II}$ (negative) =

## 2. FIRST LAW OF THERMODYNAMICS



Let a gas in a cylinder with a moveable piston changes from an initial equilibrium state to a final equilibrium state.

System change its state through path 'a' :

The heat absorbed by the system in this process = $\delta Q_a$

The work done by the system = $\delta W_a$

### Again for path 'b' :

Heat absorbed by the system = $\delta Q_b$ , Work done by the system = $\delta W_b$.

It is experimental fact that the $\delta Q_a - \delta W_a = \delta Q_b - \delta W_b$

Both $\delta Q$ and $\delta W$ depend on the thermodynamic path taken between two equilibrium states, but difference $(\delta Q - \delta W)$ does not depends on path in between two definite states of the system.

So, there is a function (internal energy) of the thermodynamic coordinates (P, V and T) whose final value ($U_f$) minus its initial value ($U_i$) equals the change $\delta Q - \delta W$ in the process.

**$dU = \delta Q - \delta W$.** This is the first law of thermodynamics.

Heat supplied to the system and work done by the system are path dependent so they are denoted by $\delta Q$ and $\delta W$ respectively. Change in internal energy $\Delta U = U_f - U_i$ does not depends on path it depends only on initial and final positions of the system. So, it is denoted by dU (or $\Delta U$)

### First Law of Thermodynamics

If some quantity of heat is supplied to a system capable of doing external work, then the quantity of heat absorbed by the system is equal to the sum of the increase in the internal energy of the system and the external work done by the system. $\delta Q = dU + \delta W$ or $Q = W + \Delta U$

**(i)** This law is applicable to every process in nature

**(ii)** The first law of thermodynamics introduces the concept of internal energy.

**(iii)** The first law of thermodynamics is based on the law of conservation of energy.

**(iv)** $\delta Q$, dU and $\delta W$ must be expressed in the same units (either in units of work or in units of heat).

**(v)** This law is applicable to all the three phases of matter, i.e., solid, liquid and gas.

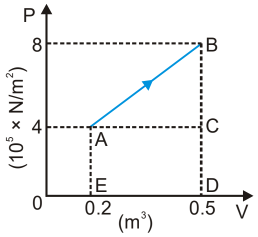
**(vi)** dU is a characteristic of the state of a system, it may be any type of internal energy–translational kinetic energy, rotational kinetic energy, binding energy etc.

**Ex.** The pressure in monoatomic gas increases linearly from $4 \times 10^5$ Nm$^{-2}$ to $8 \times 10^{+5}$ Nm$^{-2}$ when its volume increases from 0.2m$^3$ to 0.5 m$^3$. Calculate.

**(i)** Work done by the gas, **(ii)** Increase in the internal energy,

**(iii)** Amount of heat supplied, **(iv)** Molar heat capacity of the gas $R = 8.31$ J mol$^{-1}$ K$^{-1}$

**Sol.** $P_1 = 4 \times 10^5$ Nm$^{-2}$ $P_2 = 8 \times 10^{+5}$ Nm$^{-2}$, $V_1 = 0.2$ m$^3$, $V_2 = 0.5$ m$^3$



**(i)** Work done by the gas = Area under P–V graph (Area ABCDEA)

$$= \frac{1}{2}(AE + BD) \times AC = \frac{1}{2}(4 \times 10^5 + 8 \times 10^5) \times (0.5–0.2)$$

$$= \frac{1}{2} \times 12 \times 10^5 \times 0.3 = 1.8 \times 10^5 \text{ J}$$

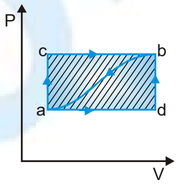
**(ii)** Increase in internal energy $\Delta U = C_V(T_2 - T_1) = \frac{C_V}{R} R(T_2 - T_1) = \frac{C_V}{R}(P_2V_2 - P_1V_1)$

For monoatomic gas

$$C_V = \frac{3}{2}R \quad \therefore \Delta U = \frac{3}{2}[(8\times10^5\times0.5)-(4\times10^5\times0.2)] = \frac{3}{2}[4\times10^5 - 0.8\times10^5] = 4.8\times10^5\text{ J}$$

**(iii)** $Q = \Delta U + W = 4.8\times10^5 + 1.8\times10^5 = 6.6\times10^5$ J

**(iv)** $C = \frac{Q}{\eta\Delta T} = \frac{QR}{\eta R\Delta T} = \frac{QR}{\eta(P_2V_2 - P_1V_1)} = \frac{6.6\times10^5\times8.31}{1\times3.2\times10^5} = 17.14$ J/mole K



**Ex.** When a system is taken from state a to state b, in figure along the path a → c → b, 60 J of heat flow into the system, and 30 J of work is done :

**(i)** How much heat flows into the system along the path a → d → b if the work is 10 J.

**(ii)** When the system is returned from b to a along the curved path, the work done by the system is –20 J. Does the system absorb or liberate heat, and how much?

**(iii)** If, $U_a = 0$ and $U_d = 22$ J, find the heat absorbed in the process a → d and d → b.

**Sol.** For the path a, c, b, $\Delta U = Q - W = 60 - 30 = 30$ J or $U_b - U_a = 30$ J

**(i)** Along the path a, d, b, $Q = \Delta U + W = 30 + 10 = 40$ J

**(ii)** Along the curved path b, a, $Q = (U_a - U_b) + W = (-30) + (-20) = -50$ J, heat flows out the system

**(iii)** $Q_{ad} = 32$ J; $Q_{db} = 8$ J

## APPLICATION OF FIRST LAW OF THERMODYNAMICS

### (i) Melting Process :

When a substance melts, the change in volume (dV) is very small and can, therefore, be neglected. The temperature of a substance remains unchanged during melting process.

Let us consider the melting of a mass m of the solid. Let L be the latent heat of fusion i.e., the heat required L to change a unit mass of a solid to liquid phase at constant temperature.

Heat absorbed during melting process, $\delta Q = mL$

By the first law of thermodynamics , $\delta Q = \Delta U + \delta W \Rightarrow mL = \Delta U$ [$\because$ $\delta W = P\delta V = P\times0 = 0$]

So, the internal energy increases by mL during the melting process.

### (ii) Boiling Process :

When a liquid is heated, it changes into vapour at constant temperature (called boiling point) and pressure. When water is heated at normal atmospheric pressure, it boils at 100°C. The temperature remains unchanged during the boiling process.

Let us consider the vaporisation of liquid of mass m. Let $V_\ell$ and $V_v$ be the volumes of the liquid and vapours respectively.

The work done in expanding at constant temperature and pressure P, $\delta W = P\Delta V = P(V_v - V_\ell)$

Let the latent heat of vaporisation = L $\therefore$ Heat absorbed during boiling process, $\delta Q = mL$

Let $U_\ell$ and $U_v$ be the internal energies of the liquid and vapours respectively then $\Delta U = U_v - U_\ell$

According to the first law of thermodynamics, $\delta Q = \Delta U + \delta W$ $\therefore$ $mL = (U_v - U_\ell) + P(V_v - V_\ell)$

**Ex.** 1 kg of water at 373 K is converted into steam at same temperature. Volume of 1 cm$^3$ of water becomes 1671 cm$^3$ on boiling. What is the change in the internal energy of the system if the latent heat of vaporisation of water is $5.4 \times 10^5$ cal kg$^{-1}$?

**Sol.**

Volume of 1 kg of water = 1000 cm$^3$ = $10^{-3}$ m$^3$ , Volume of 1 kg of steam = $10^3 \times 1671$ cm$^3$ = 1.671 m$^3$

Change in volume, $\Delta V = (1.671 - 10^{-3})$ m$^3$ = 1.670 m$^3$ , Pressure, P = 1 atm. = $1.01 \times 10^5$ N m$^{-2}$

In expansion work done, $W = P\Delta V = 1.01 \times 10^5 \times 1.67\text{ J} = \dfrac{1.691 \times 10^5}{4.2}\text{ cal} = 4.026 \times 10^4\text{ cal}$

But $\Delta U = Q - W$ (first law of thermodynamics) or $\Delta U = (5.4 \times 10^5 - 0.4026 \times 10^5)\text{ cal} = 4.9974 \times 10^5\text{ cal}$

## ISOMETRIC OR ISOCHORIC PROCESS

Isochoric process is a thermodynamic process that takes place at constant volume of the system, but pressure and temperature varies for change in state of the system.

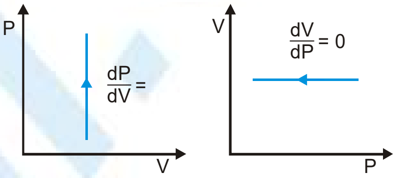
**Equation of state** P = constant × T (P and T are variable, V is constant)

**Work done** In this process volume remains constant $\Delta V = 0$ or $dV = 0 \Rightarrow W = \int_{V_i}^{V_f} PdV = 0$

**Form of first Law** $Q = \Delta U$

It means whole of the heat supplied is utilized for change in internal energy of the system. $Q = \Delta U = \mu C_v \Delta T$

**Slope of the P–V curve** $\dfrac{dP}{dV} = \infty$



## Specific heat at constant volume ($C_V$)

The quantity of heat required to raise the temperature of 1 gram mole gas through 1 °C at constant volume is equal to the specific heat at constant volume.

**(a)** A gas enclosed in a cylinder having rigid walls and a fixed piston. When heat is added to the gas, there would be no change in the volume of the gas.

**(b)** When a substance melts, the change in volume is negligibly small. So, this may be regarded as a nearly isochoric process.

**(c)** Heating process in pressure cooker is an example of isometric process.

**Ex.** An ideal gas has a specific heat at constant pressure $C_P = \dfrac{5R}{2}$. The gas is kept in a closed vessel of volume 0.0083 m$^3$ at a temperature of 300K and a pressure of $1.6 \times 10^6$ Nm$^{-2}$. An amount of $2.49 \times 10^4$ J of heat energy is supplied to the gas. Calculate the final temperature and pressure of the gas.

**Sol.** $C_V = C_P - R = \dfrac{5R}{2} - R = \dfrac{3R}{2}$, $\Delta V = 0$, $T_1 = 300$ K, $V = 0.0083$ m$^3$, $P_1 = 1.6 \times 10^6$ Nm$^{-2}$

From first law of thermodynamics $Q = \Delta U + P\Delta V \Rightarrow \Delta U = Q = 2.49 \times 10^4$ J

From gas equation $n = \dfrac{PV}{RT} = \dfrac{1.6 \times 10^6 \times 0.0083}{8.3 \times 300} = \dfrac{16}{3}$

$\therefore \Delta U = nC_V\Delta T \Rightarrow \Delta T = \dfrac{\Delta U}{nC_v} = \dfrac{2.49 \times 10^4 \times 6}{3 \times 8.3 \times 16} = 375$ K

Final temperature = 300 + 375 = 675K

According to pressure law $P \propto T \Rightarrow \dfrac{P_2}{P_1} = \dfrac{T_2}{T_1} \Rightarrow P_2 = \dfrac{T_2}{T_1} \times P_1 = \dfrac{1.6 \times 10^6 \times 675}{300} = 3.6 \times 10^6$ Nm$^{-2}$

**Ex.** 5 moles of oxygen is heated at constant volume from 10°C to 20°C. What will be change in the internal energy of the gas? The gram molecular specific heat of oxygen at constant pressure.

$C_P = 8$ cal/mole and $R = 8.36$ joule/mole °C.

**Sol.** Q $C_V = C_P - R = 8 - 2 = 6$ cal/mole °C

$\therefore$ Heat absorbed by 5 moles of oxygen at constant volume

$$Q = nC_V \Delta T = 5 \times 6\,(20 - 10) = 30 \times 10 = 300 \text{ cal}$$

At constant volume $\Delta V = 0$. $\therefore \Delta W = 0$

$\therefore$ From first law of thermodynamics $Q = \Delta U + W \Rightarrow 300 = \Delta U + 0 \Rightarrow \Delta U = 300$ cal

## ISOBARIC PROCESS

Isobaric process is a thermodynamic process that takes place at constant pressure, but volume and temperature varies for change in state of the system.

**Equation of state** : $V = \text{constant} \times T$ or $V \propto T$

**Work done** In this process pressure remains constant $\Delta P = 0$

$$\text{Work done} \quad W = \int_{V_i}^{V_f} P\,dV = P(V_f - V_i)$$

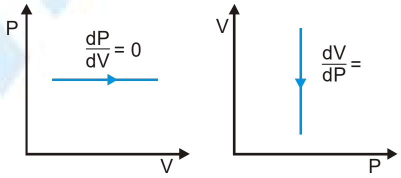
**Form of first Law** $Q = \Delta U + P\,(V_f - V_i)$

$$\mu\, C_p\, dT = \mu\, C_v\, dT + P(V_f - V_i)$$

It is clear that heat supplied to the system is utilized for :

**(i)** Increasing internal energy and

**(ii)** Work done against the surrounding atmosphere.



**Slope of the PV curve :** $\left(\dfrac{dP}{dV}\right)_{\text{isobaric}} = 0$

**Specific heat at constant pressure ($C_P$)**

The quantity of heat required to raise the temperature of 1 gram mole gas through 1°C at constant pressure is equal to the specific heat. Heating of water at atmospheric pressure. • Melting of solids and boiling of liquids at atmospheric pressure.

**Ex.** At normal pressure and 0°C temperature the volume of 1 kg of ice is reduced by 91 $cm^3$ on melting. Latent heat of melting of ice is $3.4 \times 10^5$ J/kg. Calculate the change in the internal energy when 2kg of ice melts at normal pressure and 0°C. ($P = 1.01 \times 10^5\ Nm^{-2}$)

**Sol.** Heat energy absorbed by 2 kg of ice for melting $Q = mL = 2 \times 3.4 \times 10^5 = 6.8 \times 10^5$J

Change in volume of 2 kg of ice $= 2 \times 91 = 182\ cm^3 = 182 \times 10^{-6}\ m^3$

$\therefore W = P\Delta V = 1.01 \times 10^5 \times (-182 \times 10^{-6}) = -18.4$ J

Since, work is done on ice so work W is taken –ve. Now from first law of thermodynamics

$$Q = \Delta U + W \Rightarrow \Delta U = Q - W = 6.8 \times 10^5 - (-18.4) = (6.8 \times 10^5 + 18.4)\text{J}$$

**Ex.** What amount of heat must be supplied to $2.0 \times 10^{-2}$ kg of nitrogen (at room temperature) to raise the temperature by 45°C at constant pressure. Molecular mass of $N_2 = 28$, $R = 8.3\ J\ mol^{-1}\ K^{-1}$.

**Sol.** Here $m = 2 \times 10^{-2}$ kg, $\Rightarrow n = \dfrac{m}{M} = \dfrac{2 \times 10^{-2}}{28 \times 10^{-3}} = \dfrac{5}{7}$ & $C_P = \dfrac{7}{2}R$ $\therefore Q = nC_P\Delta T = \dfrac{5}{7} \times \dfrac{7}{2} \times 8.3 \times 45 = 933.75$ J

## ISOTHERMAL PROCESS

In this process pressure and volume of system change but temperature remains constant.

In an isothermal process, the exchange of heat between the system and the surroundings is allowed.

Isothermal process is carried out by either supplying heat to the substance or by extracting heat from it.

A process has to be extremely slow to be isothermal.

### Equation of state

P V = constant (μRT) (T is constant)

### Work Done

Consider μ moles of an ideal gas, enclosed in a cylinder, at absolute temperature T, fitted with a frictionless piston. Suppose that gas undergoes an isothermal expansion from the initial state $(P_1, V_1)$ to the final state $(P_2, V_2)$.

$$\therefore \text{ Work done : } W = \int_{V_1}^{V_2} \frac{\mu RT}{V} dV = \mu RT \int_{V_1}^{V_2} \frac{dV}{V} = \mu RT \left[\log_e V\right]_{V_1}^{V_2} = \mu RT\,[\log_e V_2 - \log_e V_1] = \mu RT \log_e \left[\frac{V_2}{V_1}\right]$$

$$\Rightarrow W = 2.303 \mu RT \log_{10} \left[\frac{P_1}{P_2}\right] \quad [\because \; P_1V_1 = P_2V_2]$$

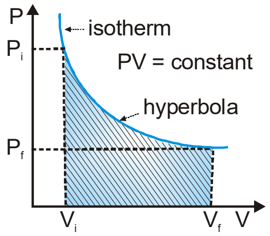
### Form of First Law

There is no change in temperature and internal energy of the system depends on temperature only

So $\quad \Delta U = 0, Q = 2.303\ \mu RT \log_{10} \left[\frac{V_2}{V_1}\right]$

It is clear that Whole of the heat energy supplied to the system is utilized by the system in doing external work. There is no change in the internal energy of the system.

### Slope of the isothermal curve



For an isothermal process, PV = constant

Differentiating, $\quad PdV + VdP = 0 \quad \Rightarrow VdP = -PdV \Rightarrow \frac{dP}{dV} = -\frac{P}{V}$

Slope of isothermal curve, $\left[\frac{dP}{dV}\right]_{\text{isothermal}} = -\frac{P}{V}$

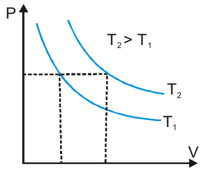
### For a given system :

**(i)** The product of the pressure and volume of a given mass of a perfect gas remains constant in an isothermal process.

**(ii)** Boyle's law is obeyed in an isothermal process.

**(iii)** A graph between pressure and volume of a given mass of a gas at constant temperature is known as isotherm or isothermal of the gas.

**(iv)** Two isotherms for a given gas at two different temperatures $T_1$ and $T_2$ are shown in figure.



at const P V T so $T_2 > T_1$

**(v)** The curves drawn for the same gas at different temperatures are mutually parallel and do not cut each other.

**(vi)** If two isotherms intersect each other at a single point we get same value of P and V at intersection point. PV = μ $RT_1$ for temperature $T_1$ and PV = μ $RT_2$ for temperature $T_2$.

It means $T_1 = T_2$ which is not possible.

**(vii)** An ideal gas enclosed in a conducting cylinder fitted with a conducting piston. Let the gas be allowed to expand very–very slowly.

**(viii)** This shall cause a very slow cooling of the gas, but heat will be conducted into the cylinder from the surrounding. Hence the temperature of the gas remains constant. If the gas is compressed very–very slowly, heat will be produced, but this heat will be conducted to the surroundings and the temperature of the gas shall remain constant.

**(ix)** The temperature of a substance remains constant during melting. So, the melting process is an isothermal process.

**(x)** Boiling is an isothermal process, when a liquid boils, its temperature remains constant.

**(xi)** If sudden changes are executed in a vessel of infinite conductivity then they will be isothermal.

**Ex.** Two moles of a gas at 127°C expand isothermally until its volume is doubled. Calculate the amount of work done.

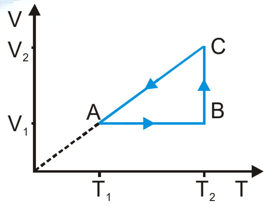
**Sol.** $n = 2, \quad T = 127 + 273 = 400\text{K}, \ \frac{V_2}{V_1} = 2$

From formula $W = 2.3026\, nRT \log_{10}\frac{V_2}{V_1} = 2.3026 \times 2 \times 8.3 \times 400 \times \log_{10} 2$

$$= 2.3026 \times 2 \times 8.3 \times 400 \times 0.3010 \approx 4.6 \times 10^3 \text{J}$$

**Ex.** Figure shows a process ABCA performed on an ideal gas.

Find the net heat given to the system during the process.



**Sol.** Since the process is cyclic, hence the change in internal energy is zero.

The heat given to the system is then equal to the work done by it.

The work done in part AB is $W_1 = 0$ (the volume remains constant). The part BC represents an isothermal process so that the work done by the gas during this part is $W_2 = nRT_2 \ln \frac{V_2}{V_1}$

During the part CA $\quad V \propto T \quad$ So, V/T is constant and hence, $P = \frac{nRT}{V}$ is constant

The work done by the gas during the part CA is $W_3 = P(V_1 - V_2) = nRT_1 - nRT_2 = -nR(T_2 - T_1)$.

The net work done by the gas in the process ABCA is $W = W_1 + W_2 + W_3 = nR\left[T_2 \ln\frac{V_2}{V_1} - (T_2 - T_1)\right]$

The same amount of heat is given to the gas.

## ADIABATIC PROCESS

It is that thermodynamic process in which pressure, volume and temperature of the system do change but there is no exchange of heat between the system and the surroundings.

A sudden and quick process will be adiabatic since there is no sufficient time available for exchange of heat so process adiabatic.

**Equation of state :** $PV = \mu RT$

Equation for adiabatic process $PV^\gamma$ = constant

## Work done

Let initial state of system is ($P_1$, $V_1$, $T_1$) and after adiabatic change final state of system is ($P_2$, $V_2$, $T_2$) then we can write $P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = K$ (here K is const.)

So $$W = \int_{V_1}^{V_2} P\,dV = K\int_{V_1}^{V_2} V^{-\gamma} dV = K\left(\frac{V^{-\gamma+1}}{-\gamma+1}\right)_{V_1}^{V_2} = \frac{K}{(-\gamma+1)}\left[V_2^{-\gamma+1} - V_1^{-\gamma+1}\right] \quad \left(\because \;K = P_1 V_1^{\gamma} = P_2 V_2^{\gamma}\right)$$

$$\Rightarrow W = \frac{1}{(\gamma-1)}\left[P_1 V_1^{\gamma} V_1^{-\gamma}.V_1 - P_2 V_2^{\gamma} V_2^{-\gamma}.V_2\right] = \frac{1}{(\gamma-1)}[P_1V_1 - P_2V_2]$$

$$\Rightarrow W = \frac{\mu R}{(\gamma-1)}(T_1 - T_2) \qquad (\because PV = \mu RT)$$

**Form of first law** : $dU = -\delta W$

It means the work done by an ideal gas during adiabatic expansion (or compression) is on the cost of change in internal energy proportional to the fall (or rise) in the temperature of the gas.

If the gas expands adiabatically, work is done by the gas. So, $W_{adia}$ is positive.

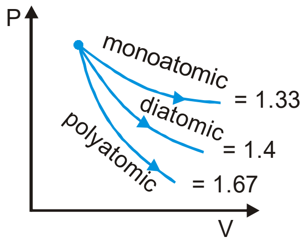
The gas cools during adiabatic expansion and $T_1 > T_2$.

If the gas is compressed adiabatically, work is done on the gas. So, $W_{adia}$ is negative.

The gas heats up during adiabatic compression and $T_1 < T_2$.

## Slope of the adiabatic curve

(Adiabatic expansion of gas)



For an adiabatic process, $PV^{\gamma}$ = constant

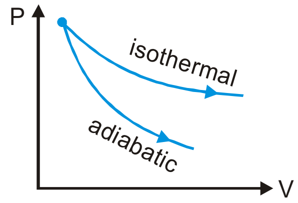
Differentiating, $P^{\gamma} V^{\gamma-1} dV + V^{\gamma} dP = 0$

$$\Rightarrow V^{\gamma} dP = -\gamma PV^{\gamma-1} dV \Rightarrow \frac{dP}{dV} = -\frac{\gamma PV^{\gamma-1}}{V^{\gamma}} = -\gamma\frac{P}{V} = \gamma\left(-\frac{P}{V}\right)$$

Slope of adiabatic curve, $$\left[\frac{dP}{dV}\right]_{adiabatic} = -\frac{\gamma P}{V}$$

## Slope of adiabatic is greater than the slope of isotherm

(expansion of gas)



$$\left[\frac{dP}{dV}\right]_{adia} = \gamma\left[-\frac{P}{V}\right] = \gamma\left[\frac{dP}{dV}\right]_{iso} \Rightarrow \frac{\text{slope of adiabatic changes}}{\text{slope of isothermal changes}} = \gamma$$

Since $\gamma$ is always greater than one so an adiabatic is steeper than an isotherm

## Examples of adiabatic process

**(i)** A gas enclosed in a thermally insulated cylinder fitted with a non–conducting piston. If the gas is compressed suddenly by moving the piston downwards, some heat is produced. This heat cannot escape the cylinder. Consequently, there will be an increase in the temperature of the gas.

**(ii)** If a gas is suddenly expanded by moving the piston outwards, there will be a decrease in the temperature of the gas.

**(iii)** Bursting of a cycle tube.

**(iv)** Propagation of sound waves in a gas.

**(v)** In diesel engines burning of diesel without spark plug is done due to adiabatic compression of diesel vapour and air mixture

**Ex.** Why it is cooler at the top of a mountain than at sea level?

**Sol.** Pressure decreases with height. Therefore if hot air rises, it suffers adiabatic expansion.

From first law of thermodynamics $\Delta Q = \Delta U + \Delta W \Rightarrow \Delta U = -\Delta W$ [$\because \Delta Q = 0$]

This causes a decrease in internal energy and hence a fall of temperature.

**Ex.** $2m^3$ volume of a gas at a pressure of $4 \times 10^5\ Nm^{-2}$ is compressed adiabatically so that its volume becomes $0.5m^3$. Find the new pressure. Compare this with the pressure that would result if the compression was isothermal. Calculate work done in each process. $\gamma = 1.4$

**Sol.** $V_1 = 2m^3, P_1 = 4 \times 10^5\ Nm^{-2},\ V_2 = 0.5m^3$

In adiabatic process $$P_1V_1^\gamma = P_2V_2^\gamma \Rightarrow P_2 = 4 \times 10^5\left[\frac{2}{0.5}\right]^{1.4} = 4 \times 10^5 (4)^{1.4} = 2.8 \times 10^6\ Nm^{-2}$$

In isothermal process $$P_1V_1 = P_2V_2 \Rightarrow P_2 = \frac{P_1V_1}{V_2} = \frac{4 \times 10^5 \times 2}{0.5} = 1.6 \times 10^6 Nm^{-2}.$$

Now work done in adiabatic process $$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{(2.8 \times 10^6 \times 0.5) - (4 \times 10^5 \times 2)}{1.4 - 1} = 1.48 \times 10^6\ J.$$

Work done in isothermal process $$W = 2.3026RT \log\frac{V_2}{V_1} = 2.3026P_1V_1 \log\frac{V_2}{V_1}$$

$$= 2.3026 \times 4 \times 10^5 \times 2 \times \log\left[\frac{0.5}{2.0}\right] = 2.3026 \times 4 \times 10^5 \times 2\log\left(\frac{1}{4}\right) = -1.1 \times 10^6\ J$$

**Ex.** Two samples of a gas initially at same temperature and pressure are compressed from a volume V to $\frac{V}{2}$. One sample is compressed isothermally and the other adiabatically. In which sample is the pressure greater?

**Sol.** Let initial volume, $V_1 = V$ and pressure, $P_1 = P$, final volume, $V_2 = \frac{V}{2}$ and final pressure, $P_2 = ?$

For isothermal compression $P_2V_2 = P_1V_1$ or $P_2 = \frac{P_1V_1}{V_2} = \frac{PV}{\frac{V}{2}} = 2P$

For adiabatic compression $P_2' = P_1\left[\frac{V_1}{V_2}\right]^\gamma \Rightarrow P_2' = P\left[\frac{V}{V/2}\right]^\gamma = 2^\gamma P \Rightarrow P_2' = 2^\gamma P \quad \gamma > 1 \therefore 2^\gamma > 2$ and $P_2' > P_2$

Pressure during adiabatic compression is greater than the pressure during isothermal compression.

**Ex.** Calculate the work done when 1 mole of a perfect gas is compressed adiabatically. The initial pressure and volume of the gas are $10^5\ N/m^2$ and 6 litre respectively. The final volume of the gas is 2 liters. Molar specific heat of the gas at constant volume is $\frac{3R}{2}$ [$(3)^{5/3} = 6.19$]

**Sol.** For an adiabatic change $PV^{\gamma} = \text{constant}\ P_1V_1^{\gamma} = P_2V_2^{\gamma}$

As molar specific heat of gas at constant volume $C_v = \frac{3}{2}R$

$$C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R \Rightarrow \gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

$$\therefore\ P_2 = \left[\frac{V_1}{V_2}\right]^{\gamma} P_1 = \left[\frac{6}{2}\right]^{5/3} \times 10^5 = (3)^{5/3} \times 10^5 = 6.19 \times 10^5\ \text{N/m}^2$$

Work done $W = \frac{1}{1-\gamma}[P_2V_2 - P_1V_1] = \frac{1}{1-(5/3)}[6.19 \times 10^5 \times 2 \times 10^{-3} - 10^{-5} \times 6 \times 10^{-3}]$

$$= -\left[\frac{2 \times 10^2 \times 3}{2}(6.19 - 3)\right] = -3 \times 10^2 \times 3.19 = -957\ \text{joules}$$

– ive sign shows external work done on the gas

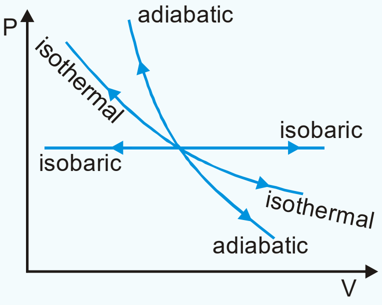
**Ex.** A motor tyre pumped to a pressure of 3 atm. It suddenly bursts. Calculate the fall in temperature due to adiabatic expansion. The temperature of air before expansion is 27°C. Given $\gamma$=1.4.

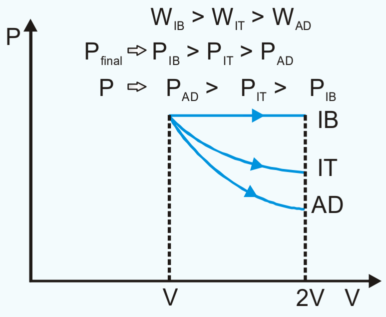
**Sol.** We know that $T_2^{\gamma}P_2^{1-\gamma} = T_1^{\gamma}P_1^{1-\gamma} \Rightarrow \left[\frac{T_2}{T_1}\right]^{\gamma} = \left[\frac{P_1}{P_2}\right]^{1-\gamma} \Rightarrow \left[\frac{T_2}{300}\right]^{1.4} = \left[\frac{3}{1}\right]^{1-1.4}$

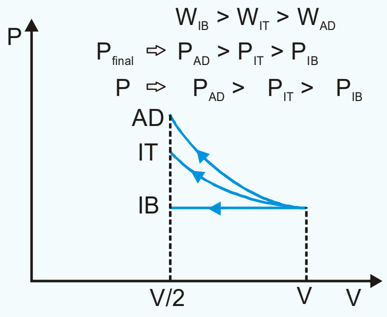
$$\Rightarrow \left[\frac{T_2}{300}\right]^{1.4} = \left[\frac{1}{3}\right]^{0.4} \Rightarrow T_2 = 219.2\ \text{K} \Rightarrow T_1 - T_2 = (300 - 219.2)\ \text{K} = 80.8\ \text{K}$$

## ETOOS KEY POINTS

**(i)** When a gas expands its volume increases, then final pressure is less for adiabatic expansion. But, when a gas compresses its volume decreases, then the final pressure is more in case of adiabatic compression.



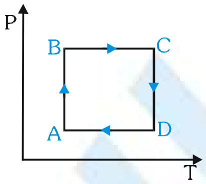




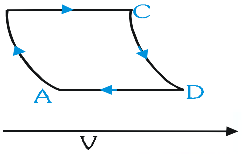
## First Law of Thermodynamics Applied to Different Processes

| Process | Q | $\Delta U$ | W |
|---|---|---|---|
| Cyclic | W | 0 | Area of the closed curve |
| Isochoric | $\Delta U$ | $\mu C_V \Delta T$ ($\mu$ mole of gas) | 0 |
| Isothermal | W | 0 | $\mu RT \log_e \left[\frac{V_f}{V_i}\right] = \mu RT \log_e \left[\frac{P_i}{P_f}\right]$ |
| Adiabatic | 0 | –W | $\frac{\mu R(T_f - T_i)}{1-\gamma}$ |
| Isobaric | $\mu C_P \Delta T$ | $\mu C_V \Delta T$ | $P(V_f - V_i) = \mu R(T_f - T_i)$ |

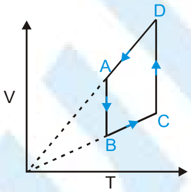
**Ex.** Plot P – V , V – T graph corresponding to the P–T graph for an ideal gas shown in figure. Explain your answers.



**Sol.**



(P - V curve)



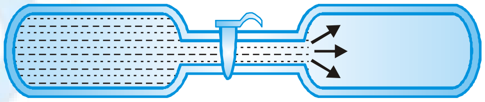
(V - T curve)

For process AB T = constant so $P \propto \frac{1}{V}$ For process BC P = constant so $V \propto T$

For process CD T = constant so $V \propto \frac{1}{P}$ For process DA P = constant so $V \propto T$

## FREE EXPANSION

Take a thermally insulated bottle with ideal gas at some temperature $T_1$ and, by means of a pipe with a stopcock, connect this to another insulated bottle which is evacuated. If we suddenly open the stopcock, the gas will rush from the first bottle into the second until the pressures are equalized.


free expansion of a gas

Experimentally, we find that this process of free expansion does not change the temperature of the gas – when the gas attains equilibrium and stops flowing, the final temperature of both botles are equal to the initial temperature $T_1$. This process is called a free expansion.

The change in the internal energy of the gas can be calculated by applying the first law of thermodynamics to the free–expansion process.

The process is adiabatic because of the insulation, So Q = 0.

No part of the surroundings moves so the system does no work on its surroundings.

**(i) For ideal gas** $(\delta W)_{\text{ext.}}$ = Work done against external atmosphere

$= P\,dV = 0$ (because $P = 0$)

$(\delta W)_{\text{int.}}$ = Work done against internal molecular forces $= 0$

$\delta Q = dU + \delta W \quad \Rightarrow \quad 0 = dU + 0$

The internal energy does not change $dU = 0$ So U and T are constant.

The initial and final states of this gas have the same internal energy.

Which implies that the internal energy of an ideal gas does not depend on the volume at all.

The free–expansion process has led us to the following conclusion :

The internal energy U(T) of an ideal gas depends only on the temperature.

**(ii) For real gas**

In free expansion of real gases, measurements show that the temperature changes slightly in a free expansion. Which implies that the internal energy of a real gas depends on the volume also.

$\delta Q = 0 \qquad (\delta W)_{\text{ext.}} = 0$ (✈ $P = 0$)

$(\delta W)_{\text{int.}} \neq 0$ (Intermolecular forces are present in real gases)

$\delta Q = dU + \delta W \quad \Rightarrow 0 = dU + (\delta W)_{\text{int.}} \Rightarrow dU = -(\delta W)_{\text{int.}}$

$\Rightarrow$ U decreases. So T decreases.

## RELATION BETWEEN DEGREE OF FREEDOM AND SPECIFIC HEAT OF GAS

Energy related with each degree of freedom $= \frac{1}{2}kT$ , Energy related with all degree of freedom $= \frac{f}{2}kT$

Internal energy of one mole of ideal gas (total K.E.) $U = \frac{f}{2}RT$ for Isometric process (volume constant) $\delta W = 0$

By first law of thermodynamics $\quad \delta Q = \delta W + dU \quad \Rightarrow \quad C_V\,dT = dU \quad \Rightarrow \quad C_V = \frac{dU}{dT}$

$$C_V = \frac{dU}{dT} = \frac{f}{2}R = \frac{R}{\gamma - 1} \quad . \; C_P = C_V + R = \left[\frac{f}{2} + 1\right]R = \frac{\gamma R}{\gamma - 1} \quad \text{and} \quad \gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}$$

$$C_V = \frac{R}{\gamma - 1} \quad , \quad C_P = \frac{\gamma R}{\gamma - 1} \quad \text{and} \quad \gamma = 1 + \frac{2}{f}$$

**General expression for C ($C_P$ or $C_V$) in the process PVx = constant** $C = \frac{R}{\gamma - 1} + \frac{R}{1 - x}$

For isobaric process P = constant so $x = 0$ $\therefore$ $C = C_P = \frac{R}{\gamma - 1} + R = C_V + R$

For isothermal process, PV = constant so $x = 1$ $\therefore$ $C = \infty$

For adiabatic process $PV^{\gamma}$ = constant so $x = \gamma$ $\therefore$ $C = 0$

**Values of f, U, $C_V$, $C_P$ and $\gamma$ for different gases are shown in table below.**

| Atomicity of gas | f | $C_V$ | $C_P$ | $\gamma$ |
|---|---|---|---|---|
| Monoatomic | 3 | $\frac{3}{2}R$ | $\frac{5}{2}R$ | $\frac{5}{3}=1.67$ |
| Diatomic | 5 | $\frac{5}{2}R$ | $\frac{7}{2}R$ | $\frac{7}{5}=1.4$ |
| Triatomic and Triatomic linear (at high temperature) | 7 | $\frac{7}{2}R$ | $\frac{9}{2}R$ | $\frac{9}{7}=1.28$ |
| Poly atomic Triangular Non-linear | 6 | $\frac{6}{2}R=3R$ | $\frac{8}{2}R=4R$ | $\frac{4}{3}=1.33$ |

**(i)** $1<\gamma<2$

**(ii)** If atomicity of gases is same U, $C_P$, $C_V$ and $\gamma$ is same for gas mixture.

**(iii)** If in a gas mixture gases are of different atomicity, then for gas mixture $\gamma$ changes according to following condition. Diatomic $\gamma_1 \le \text{mixture} \le \gamma_2$ mono atomic where $\gamma_1<\gamma_2$

**(iv)** If 'f' is the degree of freedom per molecule for a gas, then

Total energy of each molecule $=\frac{fkT}{2}$

Total energy per mole of gas $= N_0\frac{f}{2}kT=\frac{f}{2}RT$

**(v)** According to kinetic theory of gases, the molecule are not interacting with each other. So potential energy is zero and internal energy of gas molecules is only their kinetic energy.

**(vi)** For 'μ' mole of a gas : Internal energy at temperature T is $U=\frac{\mu fRT}{2}=\mu C_V T$

**(vii)** Change in internal energy is given by $dU=\frac{\mu fR}{2}(dT)=\mu C_V dT$

This change is process independent.

## $C_P$ is greater than $C_V$

If a gas is heated at constant volume, the gas does no work against external pressure. In this case, the whole of the heat energy supplied to the gas is spend in raising the temperature of the gas.

If a gas is heated at constant pressure, its volume increases. In this case, heat energy is required for the following two purpose :

**(i)** To increase the volume of the gas against external pressure.

**(ii)** To increase the temperature of 1 mole of gas through 1 K.

Thus, more heat energy is required to raise the temperature of 1 mole of gas through 1 K when it is heated at constant pressure than when it is heated at constant volume. $\therefore\ C_P>C_V$

The difference between $C_P$ and $C_V$ is equal to thermal equivalent of the work done by the gas in expanding against external pressure.

**Mayor's formula :** $C_P-C_V=R$

✈ At constant pressure $dQ=\mu C_P dT$, $dU=\mu C_V dT$ & $dW=PdV=\mu RdT$

Now from first law of thermodynamics $dQ=dW+dU$

$\Rightarrow \mu C_P dT=\mu RdT+\mu C_V dT \ \Rightarrow\ C_P=R+C_V \ \Rightarrow\ C_P-C_V=R$

**Ex.** Calculate the difference between two specific heats of 1 g of helium gas at NTP. Molecular weight of helium = 4 and J = 4.186 × $10^7$ erg $\text{cal}^{-1}$.

**Sol.** Gas constant for 1 g of helium, $r = \frac{R}{M_w} = \frac{PV}{T \times M_w} = \frac{76 \times 13.6 \times 981 \times 22400}{273 \times 4} = 2.08 \times 10^7 \text{ erg g}^{-1} \text{K}^{-1}$

$$C_P - C_V = \frac{r}{J} = \frac{2.08 \times 10^7}{4.186 \times 10^7} = 0.5 \text{ cal g}^{-1} \text{K}^{-1}$$

**Ex.** Calculate the molar specific heat at constant volume. Given : specific heat of hydrogen at constant pressure is 6.85 cal $\text{mol}^{-1}$ $\text{K}^{-1}$ and density of hydrogen = 0.0899 g $\text{cm}^{-3}$. One mole of gas = 2.016 g, J = 4.2 × $10^7$ erg $\text{cal}^{-1}$ and 1 atmosphere = $10^6$ dyne $\text{cm}^{-2}$.

**Sol.** Since the density of hydrogen is 0.0899 g $\text{cm}^{-3}$ therefore volume occupied by 0.0899 g of hydrogen at NTP is 1000 $\text{cm}^3$. So, volume of 1 mole (2.016 g) of gas, $V = \frac{1000}{0.0899} \times 2.016 \text{ cm}^3$

$$C_P - C_V = \frac{R}{J} = \frac{PV}{T \times J} = \frac{10^6 \times 1000 \times 2.016}{0.0899 \times 273 \times 4.2 \times 10^7} = 1.96 \text{ cal mol}^{-1} \text{K}^{-1}$$

$\therefore C_V = C_P - 1.96 = (6.85 - 1.96) = 4.89 \text{ cal mol}^{-1} \text{K}^{-1}$

**Ex.** The specific heat of argon at constant volume is 0.075 kcal/kg K. Calculate its atomic weight, [R = 2cal/mol K]

**Sol.** As argon is monoatomic, its molar specific heat at constant volume will be

$$C_V = \frac{3}{2}R = \frac{3}{2} \times 2 = 3 \text{ cal/mol K}, \quad C_V = M_w c_V \text{ and } \quad c_V = 0.075 \text{ cal/g K}$$

So $\quad 3 = M_w \times 0.075 \Rightarrow M_w = \frac{3}{0.075} = 40$ gram/mole

## Effeciency of a cycle ($\eta$) :

$$\eta = \frac{\text{total Mechanical work done by the gas in the whole process}}{\text{Heat absorbed by the gas (only + ve)}}$$

$$= \frac{\text{area under the cycle in P-V curve}}{\text{Heat injected into the system}}$$

**Ex.** n moles of a diatomic gas has undergone a cyclic process ABC as shown in figure. Temperature at a is $T_0$. Find

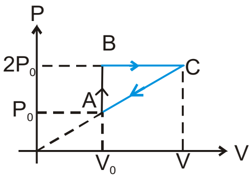
**(i)** Volume at C.

**(ii)** Maximum temperature.

**(iii)** Total heat given to gas.

**(iv)** Is heat rejected by the gas, if yes how much heat is rejected.

**(v)** Find out the efficiency.



**Sol.** **(i)** Since triangle $OAV_0$ and OCV are similar therefore $\frac{2P_0}{V} = \frac{P_0}{V_0} \Rightarrow V = 2V_0$

**(ii)** Since process AB is isochoric hence $\frac{P_A}{T_A} = \frac{P_B}{T_B} \Rightarrow T_B = 2T_0$

Since process BC is isobaric therefore $\frac{T_B}{V_B} = \frac{T_C}{V_C} \Rightarrow T_C = 2T_B = 4\,T_0$

**(iii)** Since process is cyclic therefore Q = W = area under the cycle = $\frac{1}{2}P_0V_0$.

**(iv)** Since U and W both are negative in process CA

$\therefore$ Q is negative in process CA and heat is rejected in process CA

$$Q_{CA} = W_{CA} + U_{CA}$$

$$= -\frac{1}{2}[P_0 + 2P_0]V_0 - \frac{5}{2}nR(T_c - T_a)$$

$$= -\frac{1}{2}[P_0 + 2P_0]V_0 - \frac{5}{2}nR\left(\frac{4P_0V_0}{nR} - \frac{P_0V_0}{nR}\right)$$

$= -9P_0V_0 =$ Heat injected.

**(v)** $\eta$ = efficiency of the cycle $= \frac{\text{work done by the gas}}{\text{heat injected}} = \frac{P_0V_0/2}{Q_{\text{injected}}} \times 100$

where $Q_{inj} = Q_{AB} + Q_{BC} = \left[\frac{5}{2}nR(2T_0 - T_0)\right] + \left[\frac{5}{2}nR(2T_0) + 2P_0(2V_0 - V_0)\right] = \frac{19}{2}P_0V_0.$

Therefore $\eta = \frac{100}{19}\%$

## Carnot cycle

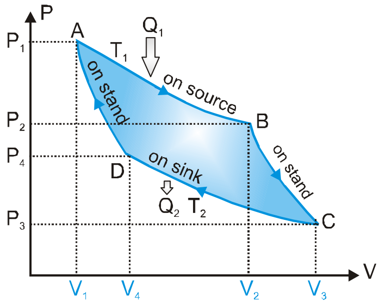
Cannot devised an ideal engine which is based on a reversible cycle of four operations in succession :

**(i)** Isothermal expansion, $A \to B$

**(ii)** Adiabatic expansion, $B \to C$

**(iii)** Isothermal compression $C \to D$

**(iv)** Adiabatic compression. $D \to A$



## MAIN PARTS OF CARNOT'S ENGINE ARE

**(i) Source of heat :**

It is a hot body of very large heat capacity kept at a constant high temperature $T_1$. Its upper surface is perfectly conducting so that working substance can take heat from it.

### (ii) Mechanical arrangements and working substance :

It is a hollow cylinder whose walls are perfectly non–conducting and its base is perfectly conducting fitted with non–conducting piston. This piston move without any friction. Ideal gas enclosed in cylinder as a working substance.

### (iii) Heat sink :

It is a cold body at low temperature $T_2$. It is a body of large heat capacity and its upper surface is highly conducting so that working substance can reject heat to it.

### (iv) Stand :

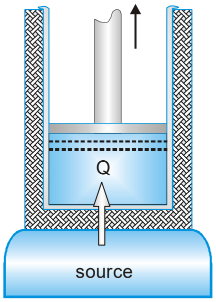
It is made by perfectly insulating material. When cylinder placed on it working substance can expended or compressed adiabatic.

### (v) Working :

A set of reversible processes through them working substance is taken back to initial condition to get maximum work from this type of ideal engine.

## PROCESSES OF CARNOT'S CYCLE CAN BE DENOTED BY AN INDICATOR DIAGRAM.

### (a) Isothermal expansion A → B

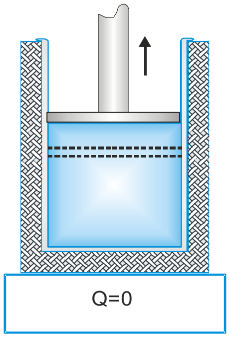


Initially the cylinder is taken to be in thermal equilibrium with the high temperature $T_1$, this is initial state of working substance denoted by point A $(P_1, V_1, T_1)$. After that the piston is allowed to move outward slowly. With the movement of the piston. The process is very slow so that it is isothermal. Heat from reservoir flows through the base of cylinder into the gas so temperature of the gas remains $T_1$. Gas expand and receive heat $Q_1$ from source and gets state $B(P_2, V_2, T_1)$

This heat input $Q_1$ to the gas from path A to B is utilized for doing work $W_1$.

By path A to B the heat input to the gas = the work done against the external pressure. $W_1 = Q_1 = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{\mu RT_1}{V} dV = \mu RT_1 \ln \frac{V_2}{V_1}$

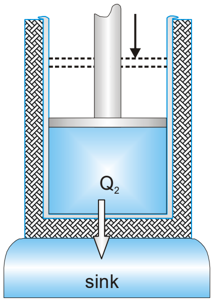
### (b) Adiabatic expansion B → C



Now cylinder is put in contact with a non–conducting stand and piston is allowed to move outward, because no heat can enter in or leave out so the expansion of gas is adiabatic. The temperature falls to $T_2$K and gas describes the adiabatic from B to point C $(P_3, V_3, T_2)$. During this expansion more work is done $(W_2)$ at the expense of the internal energy.

Work done in adiabatic path BC is $W_2 = \frac{\mu R}{\gamma - 1}(T_1 - T_2)$

### (c) Isothermal compression C → D

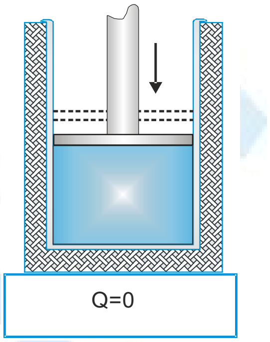


Now the gas cylinder is placed in contact with sink at temperature $T_2$.

The piston is moved slowly inward so that heat produced during compression passes to the sink. The gas is isothermally compressed from C to point D $(P_4, V_4, T_2)$. The heat rejected $Q_2$ to the cold reservoir (sink) at $T_2$ occurs over this path. Amount of work done on gas $W_3$ = amount of heat rejected to the sink

$$Q_2 = W_3 = \mu RT_2 \ln\left(\frac{V_4}{V_3}\right) \Rightarrow Q_2 = \mu RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

### (d) Adiabatic compression D → A



The cylinder is removed from the sink and is put in contact with insulating stand now piston moves inward. Heat is not allowed to go out and it increases the internal energy of the system. Now work is done on the gas during adiabatic compression from state D to initial point A $(P_1, V_1, T_1)$. No heat exchanges occur over the adiabatic path. Work done on the system $W_4 = \frac{\mu R}{\gamma - 1}(T_2 - T_1)$

This cycle of operations is called a Carnot cycle.

In first two steps work is done by engine $W_1$ and $W_2$ are positive

In last two steps work is done on gas $W_3$ and $W_4$ are negative

The work done in complete cycle W = the area of the closed part of the P–V cycle.

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

$$\therefore \quad W = \mu RT_1 \ln\frac{V_2}{V_1} + \frac{\mu R}{\gamma - 1}(T_1 - T_2) + \mu RT_2 \ln\frac{V_4}{V_3} + \frac{\mu R}{\gamma - 1}(T_2 - T_1) = \mu RT_1 \ln\frac{V_2}{V_1} + \mu RT_2 \ln\frac{V_4}{V_3}$$

Efficiency of Carnot Engine, $\eta = \frac{W}{Q_1} \Rightarrow \eta = \frac{\mu RT_1 \ln\frac{V_2}{V_1} + \mu RT_2 \ln\frac{V_4}{V_3}}{\mu RT_1 \ln\frac{V_2}{V_1}}$

B to C and D to A are adiabatic paths

$$\text{so } T_1V_2^{(\gamma-1)} = T_2V_3^{(\gamma-1)} \text{ and } T_1V_1^{(\gamma-1)} = T_2V_4^{(\gamma-1)} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\Rightarrow \eta = \frac{T_1 - T_2}{T_1} = \frac{Q_1 - Q_2}{Q_1} \Rightarrow \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

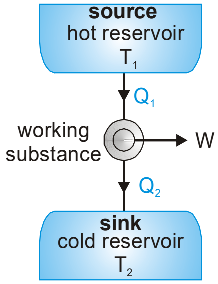
$$\eta = \frac{T_1 - T_2}{T_1} \times 100\% \quad \Rightarrow \eta = \frac{Q_1 - Q_2}{Q_1} \times 100\%$$

The efficiency for the Carnot engine is the best that can be obtained for any heat engine. The efficiency of a Carnot engine is never 100% because it is 100% only if temperature of sink $T_2 = 0$ which is impossible.

## CARNOT THEOREM

No irreversible engine **(I)** can have efficiency greater than Carnot reversible engine (R) working between same hot and cold reservoirs. $\eta_R > \eta_I \Rightarrow \boxed{1 - \frac{T_2}{T_1} > 1 - \frac{Q_2}{Q_1}}$

## HEAT ENGINE



Heat engine is a device which converts heat into work.

Three parts of a heat engine:

**(i)** Source of high temperature reservoir at temperature $T_1$

**(ii)** Sink of low temperature reservoir at temperature $T_2$

**(iii)** Working substance.

In a cycle of heat engine the working substance extracts heat $Q_1$ from source, does some work W and rejects remaining heat $Q_2$ to the sink.

Efficiency of heat engine $\eta = \frac{\text{work done (W)}}{\text{heat taken from source }(Q_1)} \Rightarrow \frac{T_1 - T_2}{T_1} = \frac{Q_1 - Q_2}{Q_1}$

## TYPES OF HEAT ENGINE

**(i) External combustion engine**

Steam engine is the example of external combustion engine. Its efficiency is 10 to 20% (small).

**(ii) Internal combustion engine**

The examples are petrol engine and diesel engine.

There are four strokes in internal combustion engine.

**(i)** Intake stroke or Charging stroke

**(ii)** Compression stroke

**(iii)** Working (or power) stroke of Expansion stroke

**(iv)** Exhaust stroke

The useful work is done in third stroke called work stroke or power stroke.

The efficiency of internal combustion engine is 40 to 60%.

**Ex.** A carnot engine working between 400 K and 800 K has a work output of 1200 J per cycle. What is the amount of heat energy supplied to the engine from source per cycle?

**Sol.** $W = 1200$ J, $T_1 = 800$ K, $T_2 = 400$ K $\therefore \eta = 1 - \frac{T_2}{T_1} = \frac{W}{Q_1} \Rightarrow 1 - \frac{400}{800} = \frac{1200}{Q_1} \Rightarrow 0.5 = \frac{1200}{Q_1}$

Heat energy supplied by source $Q_1 = \frac{1200}{0.5} = 2400$ joule per cycle

**Ex.** The temperatures $T_1$ and $T_2$ of the two heat reservoirs in an ideal carnot engine are 1500°C and 500°C respectively. Which of the following : increasing $T_1$ by 100°C or decreasing $T_2$ by 100°C would result in a greater improvement in the efficiency of the engine?

**Sol.** $T_1 = 1500°C = 1500 + 273 = 1773$ K and $T_2 = 500°C = 500 + 273 = 773$ K.

The efficiency of a carnot's engine $\eta = 1 - \frac{T_2}{T_1}$

When the temperature of the source is increased by 100°C, keeping $T_2$ unchanged, the new temperature of the source is $T'_1 = 1500 + 100 = 1600°C = 1873$ K.

The efficiency becomes $\eta' = 1 - \frac{T_2}{T_1'} = 1 - \frac{773}{1873} = 0.59$

On the other hand, if the temperature of the sink is decreased by 100°C, keeping $T_1$ unchanged, the new temperature of the sink is $T'_2 = 500 - 100 = 400°C = 673$ K. The efficiency now becomes

$$\eta'' = 1 - \frac{T'_2}{T_1} = 1 - \frac{673}{1773} = 0.62$$

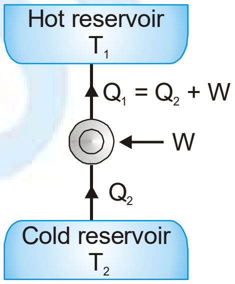
Since $\eta''$ is greater than $\eta'$, decreasing the temperature of the sink by 100°C results in a greater efficiency than increasing the temperature of the source by 100°C.

**Ex.** A heat engine operates between a cold reservoir at temperature $T_2 = 300$ K and a hot reservoir at temperature $T_1$. It takes 200 J of heat from the hot reservoir and delivers 120 J of heat to the cold reservoir in a cycle. What could be the minimum temperature of hot reservoir?

**Sol.** Work done by the engine in a cycle is $W = 200 - 120 = 80$ J. $\eta = \dfrac{W}{Q} = \dfrac{80}{200} = 0.4$

From carnot's Theorem $0.4 \le 1 - \dfrac{T_2}{T_1} = 1 - \dfrac{300}{T_1} \Rightarrow \dfrac{300}{T_1} \le 0.6 \Rightarrow T_1 \ge \dfrac{300}{0.6} \Rightarrow T_1 \ge 500$

## REFRIGERATOR



It is inverse of heat engine. It extracts heat ($Q_2$) from a cold reservoir, same external work W is done on it and rejects heat ($Q_1$) to hot reservoir. The coefficient of performance of a refrigerator.

$$\beta = \frac{\text{Heat extracted from cold reservoir}}{\text{Work done on refrigerator}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\dfrac{Q_1}{Q_2} - 1}$$

For Carnot reversible refrigerator $\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$ $\therefore \beta = \dfrac{Q_2}{W} \dfrac{1}{\left[\dfrac{Q_1}{Q_2} - 1\right]} = \dfrac{1}{\left[\dfrac{T_1}{T_2} - 1\right]} \Rightarrow \beta = \dfrac{T_2}{T_1 - T_2}$

**Ex.** A carnot engine works as a refrigrator between 250 K and 300 K. If it receives 750 cal of heat from the reservoir at the lower temperature. Calculate the amount of heat rejected at the higher temperature.

**Sol.** $T_1 = 300$ K $\quad T_2 = 250$ K $\quad Q_2 = 750$ $Q_1 = ?$

$\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$ $\qquad Q_1 = \dfrac{300}{250} \times 750 = 900$ cal

**Ex.** The temperature inside and outside of refrigerator are 260 K and 315 K respectively. Assuming that the refrigerator cycle is reversible, calculate the heat delivered to surroundings for every joule of work done.

**Sol.** $T_2 = 260$ K, $T_1 = 315$ K ; $W = 1$ joule

Coefficient of performance of Carnot refrigerator $\beta = \dfrac{Q_2}{W} = \dfrac{T_2}{T_1 - T_2}$

$$\therefore \frac{Q_2}{1} = \frac{260}{315 - 260} = \frac{260}{42} \Rightarrow Q_2 = \frac{260}{42} = 6.19 \text{ J}$$

**Ex.** A refrigerator takes heat from water at 0°C and transfer it to room at 27°C. If 100 kg of water is converted in ice at 0°C then calculate the work done. (Latent heat of ice is $3.4 \times 10^5$ J/kg)

**Sol.** Coefficient of performance (COP) $= \dfrac{T_2}{T_1 - T_2} = \dfrac{273}{300 - 273} = \dfrac{273}{27}$

$$W = \frac{Q_2}{COP} = \frac{mL}{COP} = \frac{100 \times 3.4 \times 10^5}{273/27} = \frac{100 \times 3.4 \times 10^5 \times 27}{273} = 3.36 \times 10^7 \text{ J}$$

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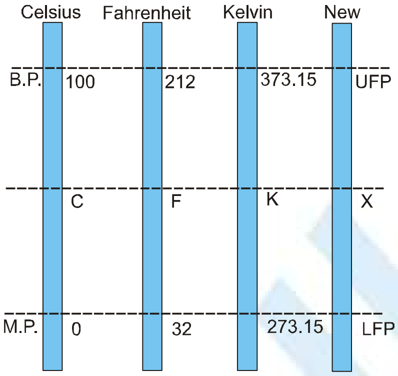
### THERMAL SCALE & THERMAL EXPENSION

### 1. TEMPERATURE SCALES

| Name of the scale | Symbol for each degree | Lower fixed point (LFP) | Upper fixed point (UFP) | Number of divisions on the scale |
|---|---|---|---|---|
| Celsius | °C | 0°C | 100°C | 100 |
| Fahrenheit | °F | 32°F | 212°F | 180 |
| Kelvin | K | 273.15 K | 373.15 K | 100 |



$$\frac{C-0°}{100°-0°}=\frac{F-32°}{212°-32°}=\frac{K-273.15}{373.15-273.15}=\frac{X\text{–}LFP}{UFP\text{–}LFP}$$

$$\Rightarrow \frac{\Delta C}{100}=\frac{\Delta F}{180}=\frac{\Delta K}{100}=\frac{\Delta X}{UFP-LFP}$$

**(i) Old thermometry**

$$\frac{\theta-0}{100-0}=\frac{X-X_0}{X_{100}-X_0}$$ [two fixed points – ice & steam points]

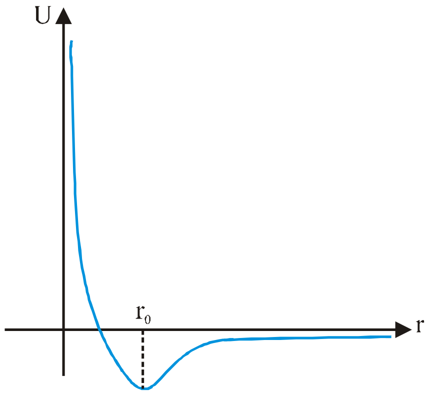
where X is the thermometric property i.e. length, resistance etc.

**(ii) Modern thermometry** $\frac{T-0}{273.16-0}=\frac{X}{X_{tr}}$

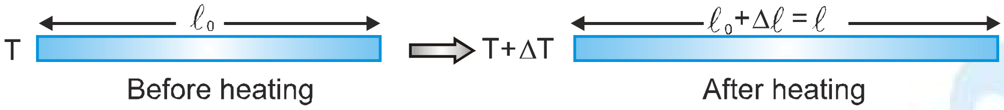
[Only one reflection point – triple point of water is chosen]

### 2. THERMAL EXPANSION

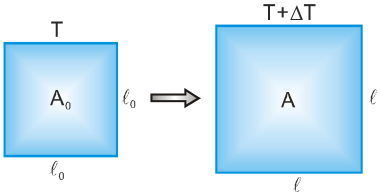
It is due to asymmetry in potential energy curve



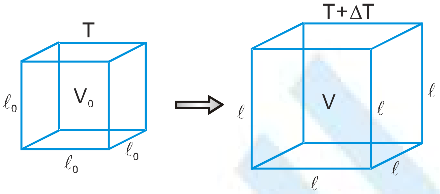
**In solids** → Linear expansion $\ell = \ell_0(1+\alpha\Delta T)$



**In solids** → Areal Expansion $A = A_0\,(1 + \beta\Delta T)$



**In solids, liquids and gases** → volume expansion $V = V_0\,(1 + \gamma\Delta T)$



[For isotropic solids : $\alpha : \beta : \gamma = 1 : 2 : 3$]

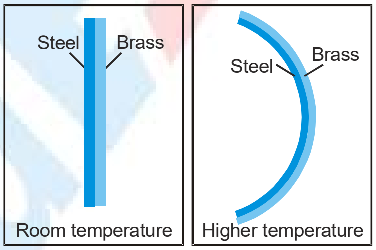
Thermal expansion of an isotropic object may be imagined as a photographic enlargement.

For anisotropic materials $\beta_{xy} = \alpha_x + \alpha_y$ and $\gamma = \alpha_x + \alpha_y + \alpha_z$

If α is variable : $\Delta l = \int_{T_1}^{T_2} l_0 \alpha\, dT$

## 3. Application of thermal Expansion in Soli

(a) **Bi–metallic strip :** Used as thermostat or auto-cutin electring heating circuits)

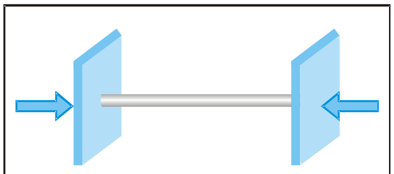


(b) **Simple Pendulum :** $T = 2\pi\sqrt{\dfrac{l}{g}}$ $\left(\because T \propto \sqrt{l} \quad \therefore \dfrac{\Delta T}{T} = \dfrac{1}{2}\dfrac{\Delta l}{l}\right)$

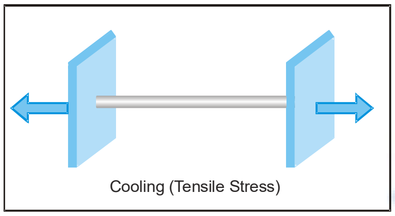
Fractional change in time period $\dfrac{\Delta T}{T} = \dfrac{1}{2}\alpha\Delta\theta$

(c) **Scale reading :** Due to linear expansion / contraction, scale reading will be lesser / more than actual value. If temperature ↑ then actual value = scale reading $(1 + \alpha\Delta\theta)$

**(d) Thermal Stress**



Heating (Compressive Stress)

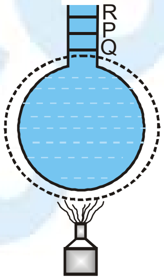


Cooling (Tensile Stress)

Thermal strain $= \frac{\Delta l}{l} = \alpha\Delta\theta$

As Young's modulus $Y = \frac{F/A}{\Delta l / l}$ ; So thermal stress = $F = YA\alpha\Delta\theta$

## 4. Thermal expansion in liquids (Only volume expansion)

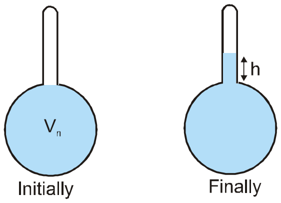


$$\gamma_a = \frac{\text{Apparent expansion in volume}}{\text{Initial volume} \times \text{Temperature rise}} \Rightarrow$$

$$\gamma_r = \frac{\text{Real increase in volume}}{\text{Initial volume} \times \text{temperature rise}} \Rightarrow \quad \gamma_r = \gamma_a + \gamma_{\text{Vessel}}$$

Change in volume of liquid w.r.t. vessel $\Delta V = V_0(\gamma_r - 3\alpha)\Delta T$

## 5. Expansion in enclosed volume



Initially Finally

$[\alpha \rightarrow \text{vessel} \ ; \ \gamma_L \rightarrow \text{liquid}]$

Increase in height of liquid level in tube when bulb was initially completely filled.

$$h = \frac{\text{apparent change in volume of liquid}}{\text{area of tube}} = \frac{V_0(\gamma_L - 3\alpha)\Delta T}{A_0\ (1+2\alpha)\Delta T}$$

## 6. Anomalous expansion of water :

In the range 0°C to 4°C warter contract on heating and expands on cooling.

At 4°C → density is maximum

Aquatic life is able to survive in very cold countries as the lake bottom remains unfrpzen at the temperature around 4°C.

## 7. Thermal expansion of gases :

**(a)** Coefficient of volume expansion $\gamma_V = \frac{\Delta V}{V_0\Delta T} = \frac{1}{T}$

[PV = nRT at constant pressure $V \propto T \Rightarrow \frac{\Delta V}{V} = \frac{\Delta T}{T}$]

**(b)** Coefficient of pressure expansion $\gamma_P = \frac{\Delta P}{P_0\Delta T} = \frac{1}{T}$

**8.** Liquids usually expand more than solids because the intermolecular forces in liquids are weaker than in solids.

**9.** Rubber contract on heating because in rubber as temperature increases, the amplitude of transverse vibrations increases more than the amplitude of longitudinal vibrations.

**10.** Water expands both when heated or cooled from 4°C because volume of water at 4°C is minimum.

**11.** In cold countries, water pipes sometimes burst, because water expands on freezing.

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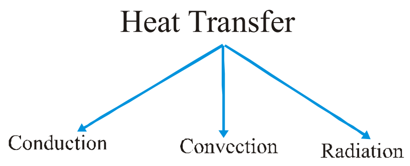
## MODE OF HEAT TRANSFER

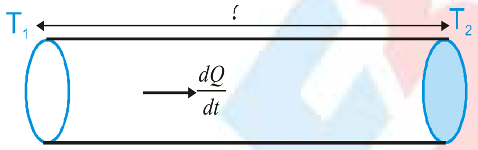
**1.**



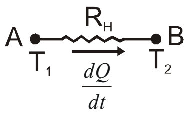
In conduction, heat is transferred from one point to another without the actual motion of heated particles.
In the process of convection, the heated particles of matter actually move.
In radiation, intervening medium is not affected and heat is transferred without any material medium.

| Conduction | Convection | Radiation |
|---|---|---|
| Heat Transfer due to Temperature difference | Heat transfer due to density difference | Heat transfer with out any medium |
| Due to free electron or vibration motion of molecules | Actual motion of particles | Electromagnetic radiation |
| Heat transfer in solid body (in mercury also) | Heat transfer in fluids (Liquid + gas) | All |
| Slow process | Slow process | Fast process (3 × $10^8$ m/sec) |
| Irregular path | Irregular path | Straight line (like light) |

## 2. THERMAL CONDUCTION



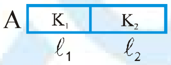
**Electrical equivalent**



Rate of heat flow $\frac{dQ}{dt} = -KA\frac{dT}{dx}$ or $\frac{Q}{t} = \frac{KA(T_1 - T_2)}{l}$

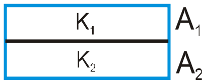
Thermal resistance $R_H = \frac{l}{KA}$

**Rods in series**



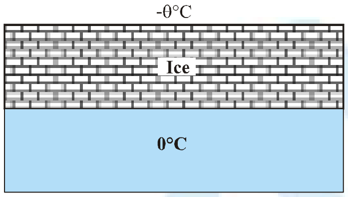
$$K_{eq} = \frac{\Sigma l}{\Sigma l / K}$$

**Rods in parallel**



$$K_{eq} = \frac{\Sigma KA}{\Sigma A}$$

## 3. Growth of Ice on Ponds



Time taken by ice to grow a thickness from $x_1$ to $x_2$ : $t = \frac{\rho L}{2K\theta}\left(x_2^2 - x_1^2\right)$

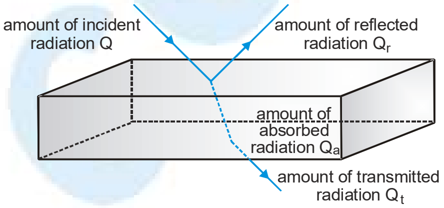
[K = thermal conductivity of ice, ρ = density of ice]

## 4. Radiation

### (a) Spectral, emissive, absorptive and transmittive power of a given body surface

Due to incident radiations on the surface of a body following phenomena occur by which the radiation is divided into three parts. (a) Reflection (b) Absorption (c) Transmission

### (b) From energy conservation



$$Q = Q_r + Q_a + Q_t \Rightarrow \frac{Q_r}{Q} + \frac{Q_a}{Q} + \frac{Q_t}{Q} = 1 \Rightarrow r + a + t = 1$$

Reflective Coefficient $r = \frac{Q_r}{Q}$ , Absorptive Coefficient $a = \frac{Q_a}{Q}$ ,

Transmittive Coefficient $t = \frac{Q_t}{Q}$

$r = 1$ and $a = 0$, $t = 0$ ⇒ Perfect reflector
$a = 1$ and $r = 0$, $t = 0$ ⇒ Ideal absorber (ideal black body)
$t = 1$ and $a = 0$, $r = 0$ ⇒ Perfect transmitter (daithermanons)

Reflection power (r) $= \left[\frac{Q_r}{Q} \times 100\right]\%$,

Absorption power (a) $= \left[\frac{Q_a}{Q} \times 100\right]\%$

Transmission power (t) $= \left[\frac{Q_t}{Q} \times 100\right]\%$

## 4. Stefan's Boltzmann law :

Radiated energy emitted by a perfect block body per unit area/sec $E = \sigma T^4$

For a general body $E = \sigma e_r T^4$ [where $0 \le e_r \le 1$]

## 5. Prevost's theory of heat exchange

A body is simultaneously emitting radiations to its surrounding and absorbing radiations from the surroundings.

If surrounding has temperature $T_0$ then $E_{net} = e_r \sigma (T^4 - T_0^4)$

## 6. Kirchhoff's law

The ratio of emissive power to absorptive power is same for all surfaces at the same temperature and is equal to the emissive power of a perfectly black body at that temperature.

$$\frac{e}{a} = \frac{E}{A} = \frac{E}{1} \Rightarrow \frac{e}{a} = E \Rightarrow e \propto a$$

Therefore a good absorber is a good emitter.

## 7. Perfectly Black Body

A body which absorbs all the radiations incident on it is called a perfectly black body.

## 8. Absorptive Power (a)

Absorptive power of a surface is defined as the ratio of the radiant energy absorbed by it in a given time to the total radiant energy incident on it in the same time.

For ideal black body, absorptive power = 1

## 9. Emissive power (e)

For a given surface it is defined as the radiant energy emitted per second per unit area of the surface.

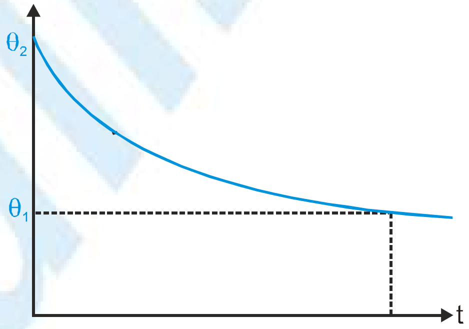
## 10. Newton's law of cooling:

If temperature difference is small

Rate of cooling $\frac{d\theta}{dt} \propto (\theta - \theta_0)$

$\Rightarrow \theta = \theta_0 + (\theta_1 - \theta_0)\, e^{-kt}$

[where k = constant]

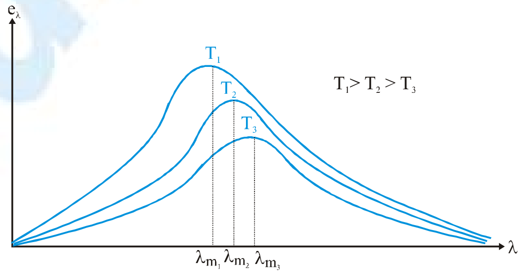


when a body cools from $\theta_1$ to $\theta_2$ in time 't' in a surrounding of temperature $\theta_0$ then

$$\frac{\theta_1 - \theta_2}{1} = k\left[\frac{\theta_1 + \theta_2}{2} - \theta_0\right] \quad \text{[where k = constant]}$$

## 11. Wien's Displacement Law :

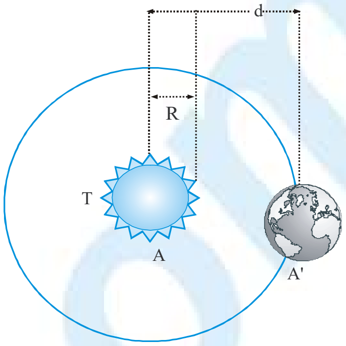
Product of the wavelength $\lambda_m$ of most intense radiation emitted by a black body and absolute temperature of the black body is a constant $\lambda_m T = b = 2.89 \times 10^{-3}$ mK = Wein's constant



Area under $e_\lambda - \lambda$ graph $= \int_0^\infty e_\lambda \, d\lambda = e = \sigma T^4$

## 12. Solar constant

The Sum emits radiant energy continuously in space of which an insignificant part reaches the Earth. the solar radiant energy received per unit area per unit time by a black surface held at right angles to the Sun's rays and placed at the mean distance of the Earth (in the absence of atmosphere) is called solar constant.



$$S = \frac{P}{4\pi r^2} = \frac{4\pi R_s^2 \sigma T^4}{4\pi r^2} = \left(\frac{R_s}{r}\right)^2 T^4$$

where $R_s$ = radius of sun

r = average distance between sun and earth

**Note :** $S = 2\ \text{cal cm}^{-2}\ \text{min} = 1.4\ \text{kWm}^{-2}$

T = temperature of sun = 5800 K

**13.** Stainless steel cooking pans are preferred with extra copper bottom because thermal conductivity of copper is more than steel.

**14.** Two layers of cloth of same thickness because air (which is better insulator of heat) is trapped between them.

**15.** Animals curl into a bell when they feel very cold to reduce the surface area of the body.

**16.** Water cannot be boiled inside a satellite by convection because in weightlessness conditions, natural movement of heated fluid is not possible.

**17.** Metals have high thermal conductivity because metals have free electrons.

## • Etoos Tips & Formulas •

# CALORIMETRY

**1 cal = 4.186 J ; 4.2 J**

1. **Thermal capacity of a body** $= \dfrac{Q}{\Delta T}$

   Amount of heat required to raise the temp. of a given body by 1°C (or 1K)

2. **Specific heat capacity** $= \dfrac{Q}{m\Delta T}$ (m = mass)

   Amount of heat required to raise the temperature of unit mass of a body through 1°C (or 1K)

3. **Molar heat capacity** $= \dfrac{Q}{n\Delta T}$ (n = number of moles)

4. **Water equivalent**

   If thermal capacity of a body is expressed in terms of mass of water, it is called water equivalent. Water equivalent of a body is the mass of water which when given same amount of heat as to the body, changes the temperature of water through same range as that of the body.

   Therefore water equivalent of a body is the quantity of water, whose heat capacity is the same as the heat capacity of the body. Water equivalent of the body,

$$W = \text{mass of body} \times \left(\frac{\text{specific heat of body}}{\text{specific heat of water}}\right)$$

   Unit of water equivalent is g or kg.

5. **Latent Heat (Hidden heat) :** The amount of heat that has to supplied to (or removed from) a body for its complete change of state (from solid to liquid, liquid to gas etc) is called latent heat of the body. Remember that phase transformation is an isothermal (i.e. temperature = constant) change.

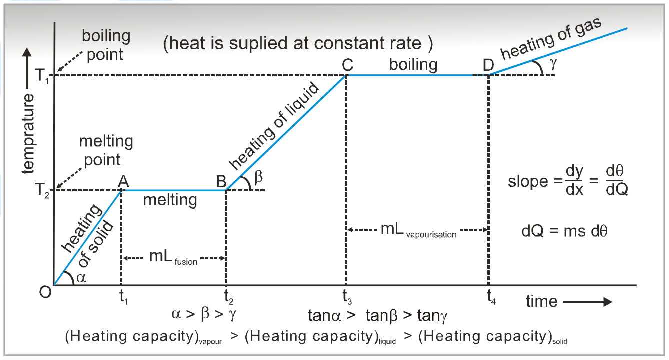
6. **Principle of calorimetry**

   Heat lost = heat gained

   For temperature change $Q = ms\Delta T$, For phase change $Q = mL$

7. **Heating curve**

   If to a given mass(m) of a solid, heat is supplied at constant rate (Q) and a graph is plotted between temperature and time, the graph is called heating curve.



Specific heat (or thermal capacity) $\propto \dfrac{1}{\text{slope of curve}}$

Latent heat $\propto$ length of horizontal line

**8.** Specific heat of a body may be greater than its thermal capacity as mass of the body may be less than unity.

**9.** The steam at 100°C causes more severe burn to human body than the water at 100°C because steam has greater internal energy than water due to latent heat of vaporization.

**10.** Heat is energy in transit which is transferred from hot body to cold body.

**11.** One calorie is the amount of heat required to raise the temperature of one gram of water through 1°C (more precisely from 14.5°C to 15.5°C).

**12.** Clausins & clapeyron equation (effect of pressure on boiling point of liquids & melting point of solids related with latent heat) $\dfrac{dP}{dT} = \dfrac{L}{T(V_2 - V_1)}$

## KINETIC THEORY OF GASES

It related the macroscopic properties of gases to the microscopic properties of gas molecules.

### 1. Basic postulates of Kinetic theory of gases

**(a)** Every gas consists of extremely small particles known as molecules. The molecules of a given gas are all identical but are different than those another gas.

**(b)** The molecules of a gas are identical, spherical, rigid and perfectly elastic point masses.

**(c)** The size is negligible in comparision to inter molecular distance ($10^{-9}$ m)

### 2. Assumptions regarding motion :

**(a)** Molecules of a gas keep on moving randomly in all possible direction with all possible velocities.

**(b)** The speed of gas molecules lie between zero and infinity (very high speed).

**(c)** The number of molecules moving with most probable speed is maximum.

### 3. Assumptions regarding collision:

The gas molecules keep colliding among themselves as well as with the walls of containing vessel. These collision are perfectly elastic. (ie., the total energy before collision = total energy after the collisions.)

### 4. Assumptions regarding force:

**(a)** No attractive or repulsive force acts between gas molecules.

**(b)** Gravitational attraction among the molecules is ineffective due to extremely small masses and very high speed of molecules.

### 5. Assumptions regarding pressure:

Molecules constantly collide with the walls of container due to which their momentum changes. This change in momentum is transferred to the walls of the container. Consequently pressure is exerted by gas molecules on the walls of container.

### 6. Assumptions regarding density:

The density of gas is constant at all points of the container.

### 7. Kinetic interpretation of pressure : $PV = \frac{1}{3}mNv_{rms}^2$

[ m = mass of a molecule, N = no. of molecules]

### 8. Ideal gas equation $PV = \mu RT \Rightarrow P = \frac{\mu RT}{V} = \frac{\mu N_A kT}{V} = \left(\frac{N}{V}\right)kT = nkt$

### 9. GAS LAWS

**(a) Boyle's Law :** For a given mass of an ideal gas at constant temperature. $V \propto \frac{1}{P}$

**(b) Charle's Law :** For a given mass of an ideal gas at constant pressure. $V \propto T$

**(c) Gay–Lussac's Law :** For a given mass of an ideal gas at constant volume. $P \propto T$

**(d) Avogadro's Law :** P,V and T are same then number of molecules. $N_1 = N_2$

**(e)** **Graham's Law :** At constant P and T, Rate of diffusion $\propto \dfrac{1}{\sqrt{p}}$

**(f)** **Dalton's law :** $P = P_1 + P_2 + .......$

Total pressure = Sum of partial pressure

## 10. Real gas equation (Vander Waal's equation) $\left(P+\frac{\mu^2 a}{v^2}\right)(V-\mu b) = \mu RT$

where a & b are under waal's constant and depend on the nature of gas.

## 11. Critical temperature $T_c = \frac{8a}{27Rb}$

The maximum temperature below which a gas can be liquefied by pressure above.

## 12. Critical volume $V_c = 3b$

## 13. Critical pressure $P_c = \frac{a}{27b^2}$

**Note :** For a real gas $\dfrac{P_c V_c}{RT_c} = \dfrac{3}{8}$

## 14. Different speeds of molecules

$$v_{rms} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3kT}{m}} \qquad v_{mp} = \sqrt{\frac{2RT}{M_w}} = \sqrt{\frac{2kT}{m}} \qquad v_{av} = \sqrt{\frac{8RT}{\pi M_w}} = \sqrt{\frac{8kT}{\pi m}}$$

## 15. Kinetic Interpretation of Temperature

Temperature of an ideal gas is proportional to the average KE of molecules,

$$PV = \frac{1}{3} mNV_{rms}^2 \quad \& \quad PV = \mu RT = \frac{1}{2} mv_{rms}^2 = \frac{3}{2} kT$$

## 16. Degree of Freedom (F)

**(a)** Number of minimum coordinates required to specify the dynamical state of system.

**(b)** For monoatomic gas (He, Ar etc.) f = 3 (Only tarnslational)

**(c)** For diatomic gas ($H_2$, $O_2$ etc.) f = 5 (3 translational + 2 rotational)

**(d)** At higher temperature, diatomic molecules have two degree of freedom due to vibrational motion (one for KE + one for PE)

**(e)** At higher temperature diatomic gas has f = 7

## 17. Maxwell's Law of equipartition of energy

Kinetic energy associated with each degree of freedom of particles of an ideal gas is equal to $\frac{1}{2}kT$

**(a)** Average KE of a particle having f degree of freedom = $\frac{f}{2}kT$

**(b)** Translational KE of a molecule = $\frac{3}{2}kT$

(c) Translational KE of a mole $= \frac{3}{2}RT$

(d) Internal energy of an ideal gas : $U = \frac{f}{2}\mu RT$

## 18. Specific heats (Cp and Cv)

(a) Molar specific heat of a gas $C = \frac{dQ}{\mu RT}$

(b) $C_V = \left(\frac{dQ}{\mu dT}\right)_{V=\text{constant}} = \frac{dU}{\mu dT}$

(c) $C_P = \left(\frac{dQ}{\mu dT}\right)_{P=\text{constant}} = C_V + R \leftarrow$ Mayer's equation

| Atomicity | Translational | Rotational | Total (f) | $\gamma = \frac{C_P}{C_V}$ | $C_V = \frac{f}{2}R$ | $C_P = C_V + R$ |
|---|---|---|---|---|---|---|
| Monoatomic [He, Ar, Ne] | 3 | 0 | 3 | $\frac{5}{3} = 1.67$ | $\frac{3}{2}R$ | $\frac{5}{2}R$ |
| Diatomic [H$_2$, N$_2$] | 3 | 2 | 5 | $\frac{7}{5} = 1.4$ | $\frac{5}{2}R$ | $\frac{7}{2}R$ |
| Triatomic (Linear CO$_2$) | 3 | 2 | 5 | $\frac{7}{5} = 1.4$ | $\frac{5}{2}R$ | $\frac{7}{2}R$ |
| Triatomic (Non-Linear NH$_3$) & Polyatomic | 3 | 3 | 6 | $\frac{4}{3} = 1.33$ | 3R | 4R |

## 19. Mean free path

Average distance between two consecutive collisions $\lambda_n = \frac{1}{\sqrt{2}\pi d^2 n}$

where d = diameter of molecule, n = molecular density $= \frac{N}{V}$

## 20. For mixture of non-reacting gases

(a) Molecular weight $M_{w_{mix}} = \frac{\mu_1 M_{w_1} + \mu_2 M_{w_2} + \ldots\ldots}{\mu_1 + \mu_2 + \ldots\ldots}$

(b) Specific heat at constant V $C_{V_{mix}} = \frac{\mu_1 C_{V_1} + \mu_2 C_{V_2} + \ldots\ldots}{\mu_1 + \mu_2 + \ldots\ldots}$

(c) Specific heat at constant P $C_{P_{mix}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2} + \ldots\ldots}{\mu_1 + \mu_2 + \ldots\ldots}$

$$\gamma_{mix} = \frac{C_{P_{mix}}}{C_{V_{mix}}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2} + \ldots\ldots}{\mu_1 C_{V_1} + \mu_2 C_{V_2} + \ldots\ldots}$$

**21.** Kinetic energy per unit volume $E_v = \frac{1}{2}\left(\frac{mN}{V}\right)v_{mix}^2 = \frac{3}{2}P$

**22.** At absolute zero, the motion of all molecules of the gas stops.

**23.** At higher temperature and low pressure or at higher temperature and low density, a real gas behaves as an ideal gas.

## 24. For any general process

**(a)** Internal energy change $\Delta U = nC_v dT$

**(b)** Heat supplied to a gas $\Delta Q = nCdT$

where C for any polytropic process $PV^x$ = constant is $C = C_v + \frac{R}{1-x}$

**(c)** Work done for any process $\Delta W = P\Delta V$

It can be calculated as area under P-V curve

**(d)** Work done $\Delta Q - \Delta U = \frac{nR}{1-x}dT$

For any polytropic process $PV^x$ = constant

# THERMODYNAMICS

## 1. Zero$^{th}$ law of thermodynamics

If two system are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

## 2. First law of thermodynamics

Heat supplied (Q) to a system is equal to algebraic sum of change in internal ($\Delta U$) of the system and mechanical work (W) done by the system.

$$Q = W + \Delta U \text{ [ Here } W = \int PdV : \Delta U = nC_v\Delta T \text{ ]}$$

For differential change

$$\boxed{\underbrace{\delta Q = \delta W}_{\text{path dependent}} + \underset{\text{path independent}}{dU}}$$

## 3. Sign convention

| | | |
|---|---|---|
| Heat absorbed by the system | → | Positive |
| Heat rejected by the system | → | Negative |
| Increase in the internal energy (i.e. rise in temperature) | → | Positive |
| Decrease in the internal energy (i.e. fall in temperature) | → | Negative |
| Work done by the system | → | Positive |
| Work done on the system | → | Negative |

## 4. For cyclic process

$\Delta U = 0 \Rightarrow Q = W$

## 5. For isochoric process

$V = \text{constant} \Rightarrow P \propto T \;\&\; W = 0$

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

## 6. For isobaric process

$P = \text{constant} \Rightarrow V \propto T \;\&\; W = 0$

$Q = \mu C_p \Delta T, \Delta U = \mu C_v \Delta T$

$W = P(V_2 - V_1) = \mu R \Delta T$

## 7. For adiabatic process

$PV^{\gamma} = \text{constant}$

or $T^{\gamma}P^{1-\gamma} = \text{constant}$

or $TV^{\gamma-1} = \text{constant}$

In this process Q = 0 and

$$W = -\Delta U = \mu C_v(T_1 - T_2) = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

**8.** **For Isothermal Process**

T = constant

or $\Delta T = 0 \Rightarrow PV = \text{constant}$

In this process $\Delta U = \mu C_v \Delta T = 0$

So, $Q = W = \mu RT\ \ln\left(\frac{V_2}{V_1}\right) = \mu RT\ \ln\left(\frac{P_1}{P_2}\right)$

**9.** **For any general polytropic process** $PV^x = \text{constant}$

**(a)** Molar heat capacity $C = C_v + \frac{R}{1-x}$

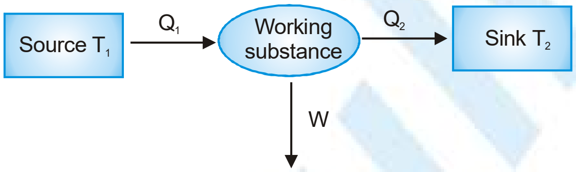
**(b)** Work done by gas $W = \frac{nR(T_1 - T_2)}{x-1} = \frac{(P_1V_1 - P_2V_2)}{x-1}$

**(c)** Slope of P-V diagram

(also known as indicator diagram at any point $\frac{dP}{dV} = -x\frac{P}{V}$)

**10.** **Efficiency of a cycle**

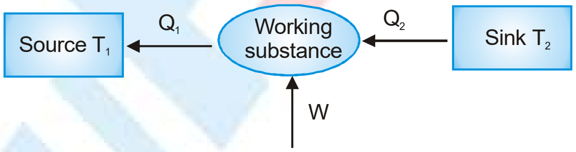
$$\eta = \frac{\text{Work done by working substance}}{\text{Heat supplied}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$



**11.** **For carnot cycle** $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$ so $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

**12.** **For refrigerator**

Certificate pf performance $\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$

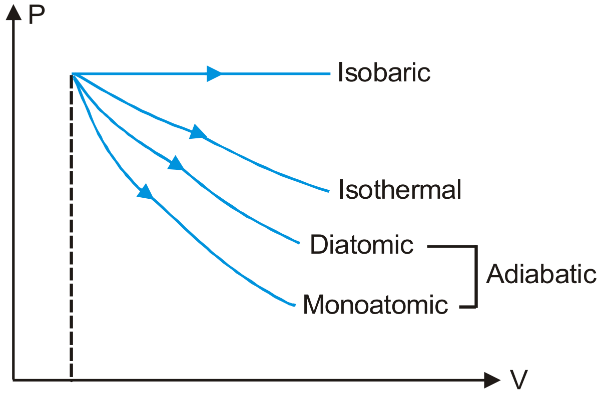


**13.** **Bulk modulus of gases** $B = \frac{\Delta P}{-\frac{\Delta V}{V}}$

Isothermal bulk modulus of elasticity, $B_{IT} = -V\left(\frac{\partial P}{\partial V}\right)_{T = \text{constant}}$

Adiabatic bulk modulus of elasticity, $B_{AD} = -\gamma V\left(\frac{\partial P}{\partial V}\right) \Rightarrow B_{AD} = \gamma B_{IT}$

**14.** Work done is least for monoatomic gas (adiabatic process) in shown expansion.

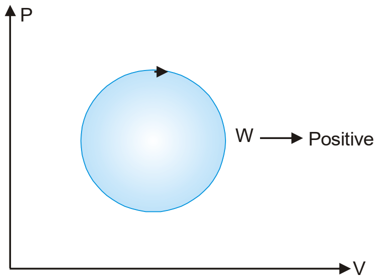


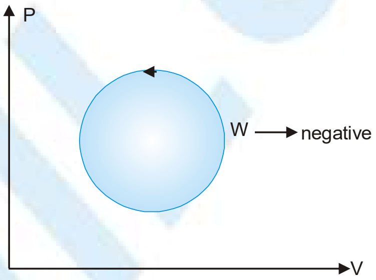
**15.** Air quickly leading out of a balloon becomes cooler as the leaking air undergoes adiabatic expansion.

**16.** First law of thermodynamics does not forbid flow of heat from lower temperature to higher temperature.

**17.** First law of thermodynamics allows many processes which actually don't happen.

**18.**



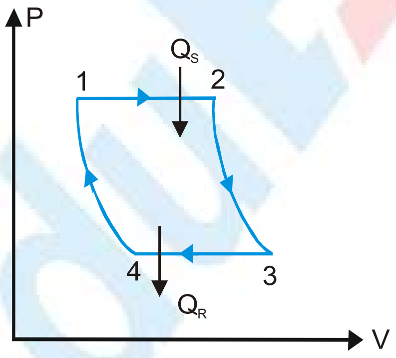


**19.** **Carnot Engine**

It is a hypothetical engine with maximum possible efficiency

Process 1 $\rightarrow$ 2 & 3 $\rightarrow$ 4 are isothermal

Process 2 $\rightarrow$ 3 & 4 $\rightarrow$ 1 are adiabatic



$$\eta = 1 - \frac{T_{3-4}}{T_{1-2}}$$