UNIT-1

KINETIC THEORY OF GASES

Introduction: According to this theory

1. All gases are made up of molecules which are considered to be rigid, perfectly elastic and identical in all respects. There are 6.02×10^{23} molecules in one mole.
2. The molecules are in random motion with all possible speeds in all directions.
3. The inter molecular forces between the molecules are neglected.
   All collisions are perfectly elastic and there is no loss of kinetic energy.
4. The distance moved by the molecule between two successive collisions is known as "free path" of the molecule.
5. The average distance traveled by a molecule between two collisions is known as" mean free path".

Important formulae:

Pressure $P=\frac{1}{3}\frac{mn}{V}c^2$ m=mass of the molecule;n=no.of molecules

For an ideal gas PV=nRT V=volume of container

$$meanfreepath=\lambda=\frac{\square 1}{\sqrt{2}\pi d^{2}n}$$

$$=\frac{\square m}{\sqrt{2}\pi d^{2}\rho}$$

c^2=mean square speed of the molecules

MAXWELL'S LAW OF DISTRIBUTION OF MOLECULAR SPEEDS:

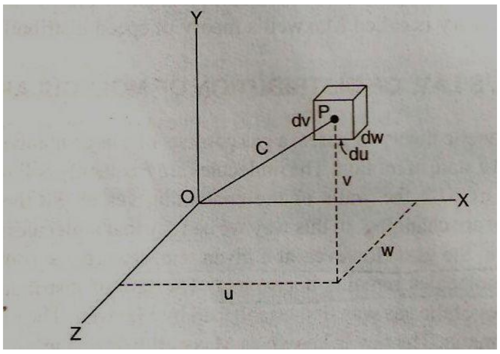
According to kinetic theory of gases, a gas consists of a large number of molecules which are frequently colliding with other molecules as well as with the walls of the containing vessels. So their speeds and directions are changing. However at a given temperature, the root mean square speed of the gas molecules remains unchanged. The rms Speed can be calculated by using Maxwell's law of distribution of molecules.

According to Maxwell's law of distribution of molecular speeds, the number of gas molecules dn_C having their speeds between C and C+dc is given by

$$dn_C = 4\pi n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mC^2/2kT}C^2\,dC`$$

Where

n = total number of gas molecules
m = mass of each gas molecule.
k = boltz Mann constant
T = absolute temperature



Proof: Let us represent the molecules in a velocity diagram with "O" as Origin and OX, OY, OZ as the co-ordinate axes as shown in the fig.Let a molecule having velocity C represented by a vector OP=C. Let the velocity components in X, Y, Z-directions be u, v, w respectively. Let all the molecules whose velocity components lie in the range u and u+du, v and v+dv, w and w+dw will be contained in the element volume du dv dw as shown in the figure.

The probability that a given molecule has its velocity lying between u and u+du=f (u) du
The probability that a given molecule has its velocity lying between v and v+dv=f (v) dv
The probability that a given molecule has its velocity lying between w and w+dw=f (w) dw

The probability that a molecule may have its velocity components lying between u and (u+du) v and (v+dv) and w and (w+dw) = f(u) f(v) f(w) du dv dw .

The resultant velocity of the molecule is a single vector C. The probability that the single velocity of value C lies in the element of volume du dv dw can be expressed as $\phi(c^2)du$ dv dw

$$\therefore f(u)\,f(v)\,f(w)\,du\,dv\,dw = \phi\left(c^2\right)du\,dv\,dw$$

$$\therefore f(u)\,f(v)\,f(w) = \phi\left(c^2\right) = \phi\left(u^2+v^2+w^2\right)\square(1)$$

Where $c^2=u^2+v^2+w^2$ --(2)

To solve eq(1) we assume that for a particular value of c, $\phi\left(c^2\right)$ is constant and hence differential of this quantity is equal to zero

$$d\left[\phi\, c^2\right]=0$$

Differentiating eq (1) we get

$$d[f(u)\,f(v)\,f(w)] = d\,\phi\left[c^2\right]=0$$

$$f^1(u)\,f(v)\,f(w)du + f(u)f^1(v)f(w)dv + f(u)f(v)f^1(w)dw = 0 \text{ ---- } (3)$$

Dividing eq(3) by f(u) f(v) f(w) we have

$$\frac{f^1(u)}{f(u)}du+\frac{f^1(v)}{f(v)}dv+\frac{f^1(w)}{f(w)}dw=0 \text{ -------------- } (4)$$

Differentiating eq (2) we get

$0 = 2udu + 2vdv + 2wdw$

$\therefore udu + vdv + wdw = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$

Multiplying eq (5) by λ we have

$\lambda udu + \lambda vdv + \lambda wdw = 0$ ---------------------------- (6) λ =constant

Adding eq (4) and (6) we get

$$\left[\frac{f^1(u)}{f(u)} + \lambda u\right]du + \left[\frac{f^1(v)}{f(v)} + \lambda v\right]dv + \left[\frac{f^1(w)}{f(w)} + \lambda w\right]dw = 0 \text{ --- } (7)$$

Since u, v, w are independent of each other eq (7) can be satisfied only if each of the term is Separately equal to zero

Now we consider the first term is

$$\left[\frac{f^1(u)}{f(u)} + \lambda u\right]du = 0$$

$$\Rightarrow \frac{f^1(u)}{f(u)}du = -\lambda udu$$

Integrating we get

$$\log_e f(u) = -\lambda\frac{u^2}{2} + \log_e(a)$$

Where $\log_e a$ = integration constant

$$\log_e\left[\left(\frac{f(u)}{a}\right)\right] = -\lambda\frac{u^2}{2}$$

$$\frac{f(u)}{a} = e^{\frac{-\lambda u^2}{2}}$$

$$f(u) = ae^{\frac{-\lambda u^2}{2}}$$

$$= ae^{-bu^2} \text{ ————————————(8)} \qquad \text{where } \frac{\lambda}{2} = b$$

Similarly for two other terms

$$f(v) = ae^{-bv^2} \text{ ——————————————(9)}$$

$$f(w) = ae^{-bw^2} \text{ ————————————(10)}$$

From, eqs 8,9,10 we have

$$f(u)f(v)f(w) = a^3e^{-b\left(u^2+v^2+w^2\right)} \text{———————(11)}$$

The constants a and b can be found by integrating the above equation applying the boundary conditions.

Let n be number of molecules per c.c of the gas with all possible velocities from $-\infty$ to $+\infty$

According to the definition of probability

$$n\iint\int_{-\infty}^{+\infty} f(u)f(v)f(w)dudvdw = n$$

$$\iint\int_{-\infty}^{+\infty} f(u)f(v)f(w)dudvdw = 1$$

$$\iint\int_{-\infty}^{+\infty} a^3e^{-b\left(u^2+v^2+w^2\right)}dudvdw = 1 \text{— — — — — — — — — — — — — — — — — —(12)}$$

We know that the value of definite integral

$$\iint\int_{-\infty}^{+\infty} e^{-bu^2}du = \sqrt{\frac{\pi}{b}}$$

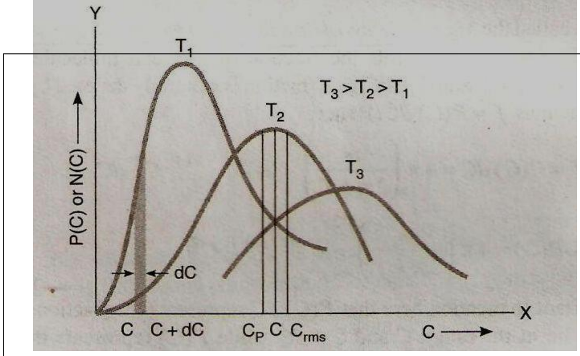
Eq (12) can be written as

$$a^3\sqrt{\frac{\pi}{b}}\sqrt{\frac{\pi}{b}}\sqrt{\frac{\pi}{b}} = 1$$

$$a^3\left(\frac{\pi}{b}\right)^{\frac{3}{2}} = 1$$

$$a = \left(\frac{b}{\pi}\right)^{\frac{1}{2}}$$

We know that



$$b=\frac{m}{2KT} \qquad \text{——}$$

Where m = mass of the molecule
K = boltz Mann constant
T = absolute temperature

The number of dn of moles having velocity components lying between u and u+du, v and v+dv, w and w+dw is given by

$$dn = nf(u)f(v)f(w)dudvdw$$

$$dn = na^3e^{-b\left(u^2+v^2+w^2\right)}dudvdw$$

$$dn = n\left(\frac{m}{2\pi KT}\right)^{\frac{3}{2}} e^{\frac{-mc^2}{2KT}} dudvdw - - - - - - - - - - - - (13)$$

The total number of molecules that lie in a speed range C and C+dC is given by

$$\frac{4}{3}\pi\left[(C+dC)^3 - C^3\right] = 4\pi C^2 dC \qquad \text{(Neglecting smaller terms)}$$

The above value is equal to du dv dw

Eq (13) can be written as

$$dn_C = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mC^2}{2kT}} 4\pi C^2 dC$$

$$dn_C = 4\pi n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mc^2}{2kT}} C^2 dC - - - - - - - - - - (14)$$

The above eq is known as Maxwell's law of distribution of molecular speeds in a gas

Eq (14) can be written as

$$\frac{dn_c}{n} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mc^2}{2kT}} C^2 dC$$

The fraction $\frac{dn_c}{n}$ is generally denoted by f and this can be written as

f = P(C) dC

$$P(c)dC = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mC^2}{2kT}} C^2 dC$$

$$P(C) = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mc^2}{2kT}} C^2$$

Hence P(C) is known as Maxwell's speed distribution function.

SPEED DISTRIBUTION CURVES:

(1) Speed distribution curve with constant temperature:

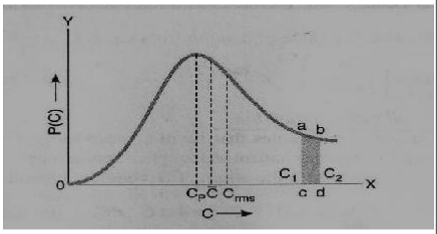
Fig

The above fig represents the speed distribution function P(C) as a function of C at a particular temperature.

The following points are observed:

1. The distribution curve at any temperature is asymmetrical about its peak.
2. It is observed from the curve that the mean speed of molecules $\bar{c}$ is slightly higher than C_p is that speed for which the curve has its maximum value.

(2) Speed distribution curves at different temperatures:



The above figure represents the speed distribution function P(C) as a function of C at different temperatures. The following important points are noted

(1) The number of molecules in a given speed interval increases upto a maximum and then decreases asymmetrically towards zero at any temperature.

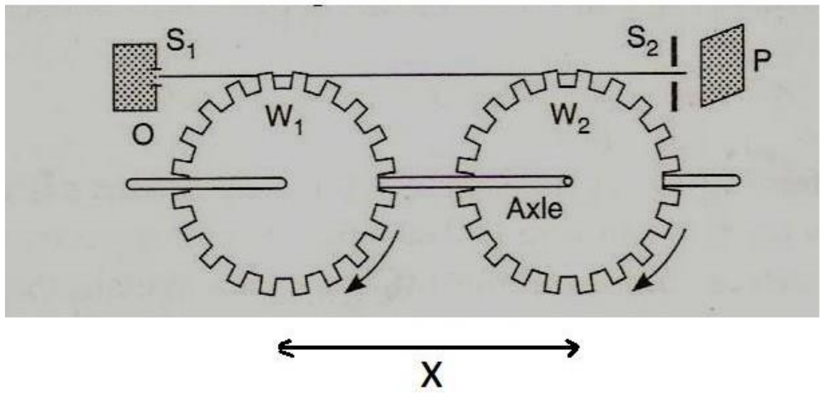
(2) At any temperature the number of molecules in a given speed interval is obtained by the area under the curve shown by shaded area.

(3)As the temperature increases, the distribution curve becomes flatten.

(4) The distribution at any temperature is non-symmetrical about its peak.

(5) The speed at which the number of molecules is a maximum corresponds to the peak value as shown by curve is called the most probable speed C_P.

EXPERIMENTAL VERIFICATION OF MAXWELL'S SPEED DISTRIBUTION LAW:



Fig

LAMMERT'S TOOTHED WHEEL METHOD:

As shown in the fig two equal toothed wheels W_1 and $W_2$are mounted at a distance x on the same axle. The slits in W_2 are not parallel to those in W_1 but are displaced at an angle of 2° behind them. An oven O contains mercury vapour which comes out of a slit S_1.The wheels are set in rapid motion .The mercury beam passing through slit S_1 falls on the slot in W_1.The molecules passing through the slot of W_1 now fall on the wheel W_2. If the molecules having particular speed can be separated from the rest. These molecules are deposited on the plate P. By rotating the wheels with various speeds, the molecules of different speeds are collected at different places on the plate P. The relative intensities of these collections are measured by micro photometer. From these we can calculate the relative numbers of molecules lying in different ranges are calculated.

A graph is plotted by taking $\frac{C}{C_p}$values on X- axis and intensity of spot formed on P on Y –axis. The graph is shown below.

It is observed that the graph is exactly coincides with the theoretical curve for Maxwell's distribution law of molecular speeds.

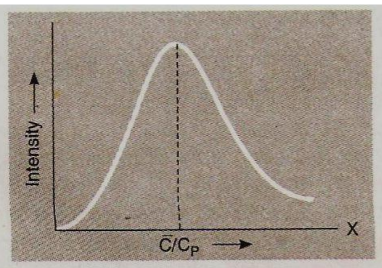


Fig. (5)

TRANSPORT PHENOMENA:

We have applied the kinetic theory of gases when the gas is in equilibrium state. But the gas is not in equilibrium state in the following three cases.

(1) The component of velocity may not have same value in all parts of the gas. This will result in relative motion of the gas layers with respect to one another. Now the layers moving faster transport momentum to the slower moving layers. This gives rise to the phenomenon of viscosity.

(2) The different parts of the gas may be at different temperatures. Now to bring the equilibrium state, the molecules of the gas will transport kinetic energy from regions of higher temperature to lower temperature. This gives rise to the phenomenon of conduction.

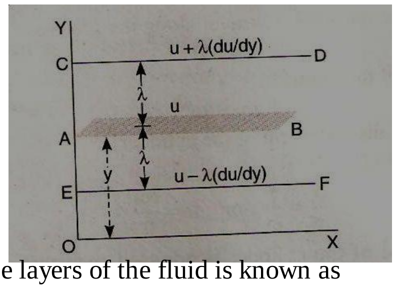
(3) The different parts of the gas may have different densities. Now to bring the equilibrium state, the molecules of the gas transport mass from regions of higher density to regions of lower density. this gives rise to the phenomenon of diffusion .

Hence the transport of momentum, energy and mass represent viscosity, conduction and diffusion respectively. These are called transport phenomenon.

VISCOSITY OF GASES :

As shown in the fig. the velocity of the layer in contact with the surface OX is zero and it gradually increases as we move up from "O" in Y direction at a uniform rate (du/dy). Let u be the velocity of the layer AB. There are two layers CD and EF on either side of AB at a distance λ [mean free path] whose velocities are

— — respectively.



CO-EFFICIENT OF VISCOSITY:

The tangential force per unit area per unit velocity gradient between the layers of the fluid is known as coefficient of viscosity. i.e.,

$$F = \eta \frac{du}{dy}$$

$$= F / \frac{du}{dy}$$

EXPRESSION FOR VISCOSITY :

Let n be the number of molecules per unit volume of the gas and $\bar{C}$ be their average velocity due to thermal agitation. According to joule’s law the number crossing unit area per second either way will be $\frac{n\bar{C}}{6}$

The velocity of gas in layer CD = $u + \lambda \frac{du}{dy}$

The velocity of gas in layer EF = $u - \lambda \frac{du}{dy}$

The momentum carried downward by the molecules crossing unit area of AB per second from the plane CD is given by

P$_1$= mass x velocity

$$p_1 = \frac{1}{6} mn\bar{C}\left(u + \lambda \frac{du}{dy} \right)$$

Similarly, the momentum carried upwards

$$p_1 = \frac{1}{6} mn\bar{C}\left(u - \lambda \frac{du}{dy} \right)$$

Net momentum transferred per second downwards

$$p_1 - p_2 = \frac{1}{6} mn\bar{C}\left(u + \lambda \frac{du}{dy} - u + \lambda \frac{du}{dy} \right)$$

$$= \frac{1}{6} mn\bar{C}\left(2\lambda \frac{du}{dy} \right)$$

$$= \frac{1}{3} mn\bar{C}\lambda \frac{du}{dy} ----------- (1)$$

The co efficient of viscosity is defined as the ratio of the tangential force to the velocity gradient.

$$\therefore \eta = \frac{\frac{1}{3} mn\bar{C}\lambda \frac{du}{dy}}{\frac{du}{dy}}$$

where mn = ρ = density

$$= \frac{1}{3} mn\bar{C}\lambda = \frac{1}{3} \rho\bar{C}\lambda$$

Substituting the value of $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$ we get

$$= \frac{m\bar{C}}{3\sqrt{2}\pi d^2}$$

From he above expression it is observed that

(1) is independent of pressure or density.

(2) is directly proportional to the $\bar{C}$.

(3) is directly proportional to $\sqrt{T}$ .since $\bar{c} \propto \sqrt{T}$

(4) is inversely proportional to square of the diameter of the molecule.

(5) is directly proportional to the mass of the molecule of the gas .

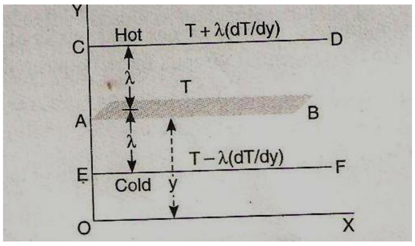
THERMAL CONDUCTIVITY:

The transport of heat energy from one region of the gas which is at higher temperature to the region of lower temperature gives rise to the transport phenomenon of thermal conduction.

EXPRESSION FOR THERMAL CONDUCTION:

Imagine the gas to be at rest and divided into several layers. Let the layer represented by OX be the coldest and the temperature gradually increases in OY direction as shown in the fig. Consider a layer AB at a distance y from OX which is at a temperature T. There are two layers CD and EF on either side of AB at a distance λ whose temperatures are

$T + \lambda \frac{dT}{du}$ And $T - \lambda \frac{dT}{dy}$ respectively.



Fig

The number of molecules crossing the layer AB in one direction per unit area per second can be written as $\frac{n\bar{C}}{6}$.

Where n is the number of molecules. Let m be the mass of the molecules. The total mass crossing unit area of AB per second is given by $\frac{mn\bar{C}}{6}$

The total heat energy Q_1 carried by all the molecules in crossing layer AB downwards per unit area of AB per second is given by

Q_1 = mass x specific heat x temperature

$$\left(\frac{mn\bar{C}}{6}\right)C_v\left[T+\lambda\frac{dT}{dy}\right]$$

Similarly, the total heat energy Q_2 carried by all the molecules in crossing layer AB upwards per unit area per second is given by

$$Q_2=\left(\frac{mn\bar{C}}{6}\right)C_v\left[T-\lambda\frac{dT}{dy}\right]$$

Transfer of energy $Q = Q_1 - Q_2$

$$Q=\frac{mn\bar{C}}{6}C_v\left[T+\lambda\frac{dT}{dy}-T+\lambda\frac{dT}{dy}\right]$$

$$Q=\frac{mn\bar{C}}{6}C_v\left(2\lambda\frac{dT}{dy}\right)$$

$$Q=\frac{1}{3}mn\bar{C}C_v\lambda\frac{dT}{dy}-----------(1)$$

The coefficient of thermal conductivity of a gas is defined as the quantity of heat that flows per unit area per second per unit temperature gradient.

$$\therefore Q=K\frac{dT}{dy}$$

$$K=\frac{Q}{\frac{dT}{dy}}-----------------(2)$$

From eq (1) and (2)we have

$$K=\frac{\frac{1}{3}mn\bar{C}C_v\lambda\frac{dT}{dy}}{\frac{dT}{dy}}$$

$$K=\frac{1}{3}mn\bar{C}C_v\lambda$$

$$but\,\lambda=\frac{1}{\sqrt{2}\pi d^2n}$$

$$K=\frac{1}{3}mn\bar{C}C_v\frac{1}{\sqrt{2}\pi d^2n}$$

$$K=\frac{1}{3\sqrt{2}}\frac{m\bar{C}C_v}{\pi d^2}$$

$$\therefore K=\frac{1}{3\sqrt{2}}\frac{m\bar{C}C_v}{\pi d^2}$$

From the above eq it is clear that

(1)K is independent of pressure.

(2)K is proportional to $\bar{C}$ i.e., proportional to $\sqrt{T}$

(3)K is inversely proportional to d^2

(4) $\frac{K}{\eta}=C_v$

DIFFUSION OF GASES:

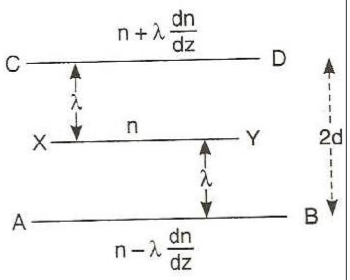
Diffusion:

It is the process by which the mass gets transferred inside a gas from a region of high concentration to a region of lower concentration.

COEFFICIENT OF DIFFUSION:

The number of molecules of the gas crossing per unit surface area per second per unit concentration gradient.

EXPRESSION FOR DIFFUSION COEFFICIENT:



As shown in the fig let the concentration at plane XY = n

The concentration at a plane CD which is at a distance λ above XY

$$= n + \lambda \frac{dn}{dz}$$

The concentration at a plane AB which is at a distance λ below XY

$$= n - \lambda \frac{dn}{dz}$$

The number of molecules crossing plane XY downwards per unit area per second will be

$$= \frac{1}{6}\bar{C}\left(n + \lambda \frac{dn}{dz}\right)$$

And then upward will be

$$= \frac{1}{6}\bar{C}\left(n - \lambda \frac{dn}{dz}\right)$$

The net number crossing unit area per second of plane AB in downward direction is given by

$$= \frac{1}{6}\bar{C}\left(n + \lambda \frac{dn}{dz} - n + \lambda \frac{dn}{dz}\right)$$

$$= \frac{1}{6}\bar{C}\left(2\lambda \frac{dn}{dz}\right)$$

$$= \frac{1}{3}\bar{C}\lambda \frac{dn}{dz}$$

$$D = \frac{\frac{1}{3} C\lambda \frac{dn}{dz}}{\frac{dn}{dz}}$$

$$D = \frac{1}{3}\bar{C}\lambda$$

$$D = \frac{1}{3}\bar{C}\lambda \frac{\rho}{\rho} = \frac{\eta}{\rho} \qquad \because \eta = \frac{1}{3}\bar{C}\lambda\rho$$

$$D = \frac{\eta}{\rho}$$

From the above expression it is clear that

(1) D is directly proportional to $T^{\frac{3}{2}}$

$$\because \lambda \alpha \frac{T}{P}$$

$$\therefore \bar{c} \alpha \sqrt{T}$$

$$D \alpha T^{\frac{3}{2}} P^{-1}$$

(2) D is inversely proportional to pressure P.

THERMODYNAMICS

Introduction:

It is a branch of thermal physics which deals with the transformation of heat energy into mechanical work or vice –versa. It also deals with the transformation of heat energy to electrical, chemical and light energy.

System:

A definite quantity of the matter bounded by some closed surface is known as a System.

Ex: A gas contained in a cylinder.

Surroundings:

All those things which are outside the system and influence its behavior are known as Surroundings of the System.

Temperature:

The intensity of heat is known as Temperature.

Heat:

Heat is a form of energy which is transferred from one body to other body due to Temperature difference between them.

Thermal equilibrium:

When ever there is no heat exchange between the bodies, the bodies are said to be in Thermal equilibrium.

Internal energy of a system:

The stored energy which is not apparently shown by a system is known as its Internal energy.

Ex: A mixture of H2 and O_2 gas on explosion provides mechanical energy.

Zeroth law of thermodynamics:

When two systems A and B are individually in thermal equilibrium with the third system C then the two systems A and B are in equilibrium with each other ie they are at the same temperature.

First law of thermodynamics:

The amount of heat supplied to a system is equal to the sum of change of internal energy and the work done by the system

i.e., $dQ = dU+dW$

Difference between isothermal and adiabatic process:

Isothermal process	Adiabatic process
(1)It is a process in which a change in pressure and volume takes place keeping the temperature constant.	(1)It is a process in which a change in pressure and volume takes place keeping it thermally insulated from the surroundings.
(2)The gas is enclosed in a good metallic cylinder	(2)The gas is enclosed in a good non-conducting cylinder
(3)It is a slow process	(3)It is a quick process
(4)The temperature of the gas remains constant.	(4)The temperature of the gas does not remains constant
(5)It obeys boyle's law i.e., $PV = \text{constant}$	(5)It obeys poison's law i.e., $PV^{\gamma} = constant$
(6)work done W = $2.303RT \log\frac{V_2}{V_1}$	(6)work done W = $\frac{R}{\gamma-1}\left(T_2 - T_1\right)$
(7)There is an exchange of heat from system to surroundings.	(7)There is no exchange of heat from system to surroundings.

A cycle of processes:

When a system is taken from its initial to final state by one or more process and then back to its initial state by some other one or more processes, the net change in internal energy is zero. ie $dU = 0$

$\therefore dQ = dW$

Reversible process:

A Reversible process is one which can be reversed in such a way that all changes occurring in the direct process are exactly repeated in the opposite order and inverse sense.

If heat is absorbed in the direct process, the same amount of heat should be given out in reverse process. If work is done on the working substance in the direct process, then the same amount of work should be done by the working substance in the reverse process.

Ex: isothermal and adiabatic changes are reversible.

Irreversible process:

Any process which is not reversible exactly is an Irreversible process.

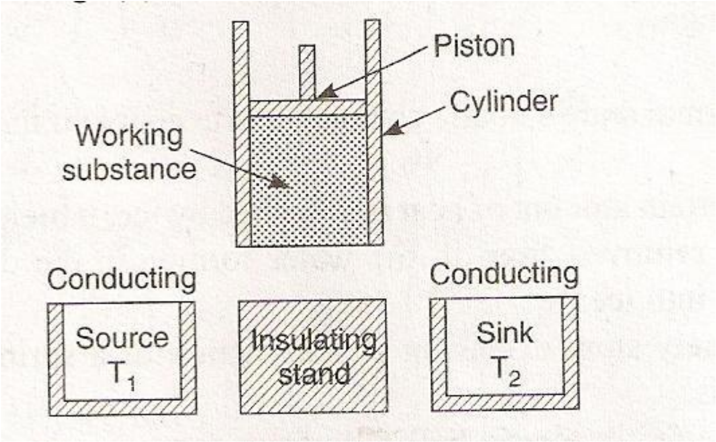
Ex: Conduction, radiation, electrical heating of wire.

CARNOT'S ENGINE:

IN 1824, French engineer Carnot designed an ideal and simple heat engine having the maximum efficiency. It consists of the following parts.

(1) The working substance:

The working substance is an ideal gas enclosed in a cylinder piston arrangement as shown in the fig.



(2) The source of heat:

A hot body of high thermal capacity maintained at a high temperature T_1 K serves as a source. There is no change in temperature if we take some heat from the source.

(3) Sink:

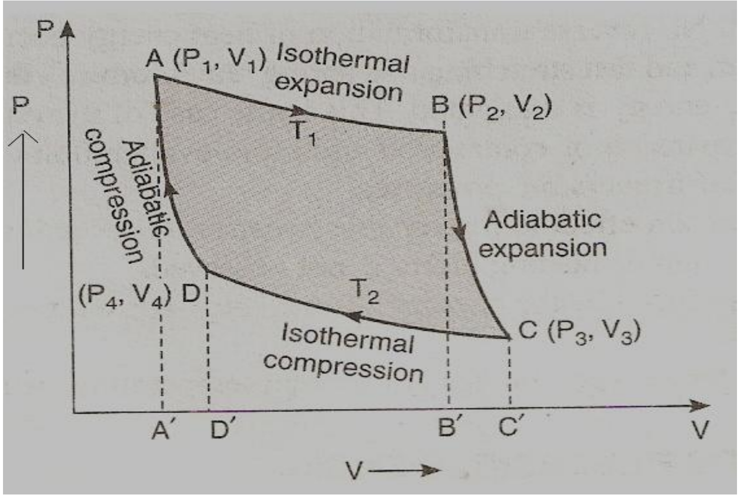
A cold body maintained at a lower temperature T_2 K serves as a sink. If we given some heat to the sink there is no change in the temperature .

(4) Insulating stand:

A perfectly non-conducting platform to serve as a stand for the cylinder.

Carnot's cycle:

The working substance is supposed to undergo the following four operations known as the Carnot's cycle as shown in the fig.



(1) Isothermal expansion:

Let the initial temperature of the gas in the cylinder be T_1 and its state be represented by the point A (P_1, V1) on the indicator diagram. The cylinder is placed on the source and the piston is moved slowly upwards so that the pressure of the gas falls and the volume increases. Hence the fall of temperature is absorbed from the source. The final state of the gas is represented by point B.

Let the quantity of heat absorbed from the source be Q_1. This is equal to the amount of work done W_1 by the gas in the expansion from point A to point B.

$$Q_1 = W_1 = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} RT_1\left(\frac{dv}{V}\right)$$

$$Q_1 = RT_1 \log_e\left(\frac{V_2}{V_1}\right) = area A\ B'A'A ------------(1)$$

(2) Adiabatic expansion:

The cylinder is detached from the source and is placed on the insulating stand. The piston is allowed to move further adiabatically till the temperature of the gas is same as that of the sink (T_2 K). Hence, the gas does external workW_2. In the final state the pressure and volume of the gas are P_3 and V_3 respectively.

$$W_2=\int_{V_2}^{V_3} PdV=\int_{V_2}^{V_3} K\frac{dV}{V^{\gamma}}=K\int_{V_2}^{V_3}\frac{dV}{V^{\gamma}}$$

$$W_2=K\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_2}^{V_3}=K\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_2}^{V_3}$$

$$W_2=\left[\frac{KV_3^{1-\gamma}-KV_2^{1-\gamma}}{1-\gamma}\right]=\left[\frac{P_3V_3-P_2V_2}{1-\gamma}\right]\left(\because K=PV^{\gamma}\ \ \therefore P=\frac{K}{V^{\gamma}}\right)$$

$$W_2=\frac{RT_2-RT_1}{1-\gamma}\left(\because P_2V_2=RT_1\ and\ P_3V_3=RT_2\right)$$

$$W_2=\frac{R(T_1-T_2)}{\gamma-1}=Area\,B\ C'B'B---------------------(2)$$

(3) Isothermal compression:

The cylinder is separated from the insulating stand and placed on the sink at T_2. Now the gas is compressed very slowly till the gas attains the state D where pressure and volume are P_4 and V_4 respectively. Here the developed heat passes to the sink. Let the developed heat be Q_2 which is equal to the work done W_3 on the gas.

$$\therefore Q_2=W_3=\int_{v_3}^{v_4}PdV=RT_2\int_{v_3}^{v_4}\frac{dV}{V}$$

$$=RT_2\left[\log\frac{V_4}{V_3}\right]=-RT_2\log\frac{V_3}{V_4}-----------(3)$$

$$\therefore Q_2=W_3=area\,CC'D'DC$$

(4) Adiabatic compression:

Now the cylinder is separated from the sink and placed on the insulating stand. Now the gas is compressed adiabatically till the state A is reached its temperature rises from T_2 to T_1 .

The work done W_4 on the gas $=\int_{V_4}^{V_1}PdV=-\frac{R(T_1-T_2)}{\gamma-1}=area\ D'A'AD------(4)$

From eq(2) and (4) it is clear that $W_2=W_4$

Net work done by the gas $W = W_1+W_2+W_3+W_4$

$= W_1-W_3$ = area ABCD

$= Q_1-Q_2$

Calculation of the efficiency of the engine:

It is the ratio of the external work done in one cycle to the corresponding amount of heat taken from the source.

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

$$\therefore \eta=1-\frac{Q_2}{Q_1}----------------(5)$$

$$W=Q_1-Q_2=RT_1\log_e\left(\frac{V_2}{V_1}\right)-RT_2\log\left(\frac{V_3}{V_4}\right)----------(6)\because from\,eq(1)\ \&(3)$$

Points B and C lie on the same adiabatic curve

$$\therefore T_1V_2^{\gamma-1}=T_2V_3^{\gamma-1}$$

$$\frac{T_1}{T_2}=\left(\frac{V_3}{V_2}\right)^{\gamma-1}--------------(7)\because PV^{\gamma}=K$$

$$\frac{RT}{V}V^{\gamma}=K$$

$$\because PV=RT$$

$$TV^{\gamma-1}=K$$

Points A and D lie on the same Adiabatic curve

$$\therefore T_1V_1^{\gamma-1}=T_2V_4^{\gamma-1}$$

$$\frac{T_1}{T_2}=\left(\frac{V_4}{V_1}\right)^{\gamma-1}--------------(8)$$

From eq(7)&(8) we get,

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\therefore \frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1} \text{----------------} (9)$$

By substituting the above value in eq(6)we get

$$W = RT_1 \log_e\left(\frac{V_2}{V_1}\right) - RT_2 \log_e\left(\frac{V_2}{V_1}\right)$$

$$W = R(T_1 - T_2)\log_e \frac{V_2}{V_1}$$

$$\therefore \eta = \frac{W}{Q_1} = \frac{R(T_1 - T_2)\log_e \frac{V_2}{V}}{RT_1 \log_e\left(\frac{V_2}{V_1}\right)}$$

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

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

Impracticability of Carnot's engine:

Carnot's engine is an ideal engine and can't be realised in actual practice due to following reasons:

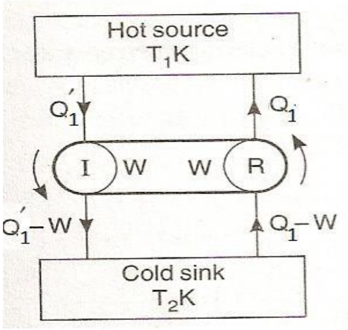
(1)The heat is to be taken and rejected strictly at constant temperature which is practically very difficult to achieve.

(2) The base of cylinder of the engine is assumed to be perfectly conducting and other parts perfectly non-conducting. This is not possible in actual practice.

(3)The engine has very slow working. Therefore it is useless in our daily life.

(4)It is perfectly reversible in its action .But it is not possible in actual practice

Carnot's Theorem



According to this theorem no engine can more efficient than reversible engine working between the same two temperatures.

Proof:

Let us consider a reversible engine R and irreversible engine I working with the same source and sink.

Let engine I absorbs an amount of heat Q_1' from the source, convert a part of it W into work and transfer the balance $Q_1' - W$ to the sink.

$$\therefore efficiency of I = \eta_I = \frac{W}{Q_1'} \text{--------------} (1)$$

Now engine R works as a refrigerator with the work W exerted by the engine I. Hence refrigerator R absorb an amount of heat Q_1-W from the sink and transfer heat Q_1-W+W = Q_1 to the source. If it work as a heat engine then, R absorb an amount of heat Q_1 from the source, but R is reversible engine and hence convert a part of it W into work and transfer the balance Q_1-W to the sink.

$$\therefore efficiency of R = \eta_R = \frac{W}{Q_1} \text{------------} (2)$$

Let us assume that the irreversible engine I is more efficient than reversible engine R

$$\eta_I > \eta_R$$

$$\frac{W}{Q_1'} > \frac{W}{Q_1} \Rightarrow Q_1 > Q_1' \text{---------} (3)$$

$$\therefore (Q_1 - W) > (Q_1' - W) \text{-----------} (4)$$

From eq (3) $Q_1 - Q_1'$ is always +ve and

From Eq (4) $(Q_1 - W) - (Q_1' - W)$ also +ve. Therefore the amount of heat $Q_1 - Q_1'$ is absorbed from the sink and it is given to the source.

From the above discussion it is clear that without any external work heat is absorbed from the cold body and it is supplied to the hot body. According to second law of thermodynamics it is impossible. Hence our assumption is wrong.

$$\therefore \eta_R > \eta_I$$

Second law of thermodynamics:

Kelvin's statement:

When the hot engine absorbs more and more heat from the source, the temperature of the source continuously falls and after some time becomes as that of surroundings [sink]. Hence the engine stops working .The heat engine works only when a source and sink area at higher and lower temperatures respectively.

Statement:

It is impossible to derive a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings.

Clasius Statement:

In refrigerator the transfer of heat takes place from a cold body to a hot body with the aid of an external work. No refrigerator can transfer heat from cold body to a hot body without the aid of an external work

Statement:

It is impossible to transfer heat from cold body to a hot body without the external work.

Thermodynamic or Kelvin scale of temperature:

Lord Kelvin in 1848 started with the result that the efficiency of all reversible engine working between the same two temperatures is a function of two temperatures only and is independent of the nature of working substance. This idea leads to Thermodynamic scale of temperature.

Let Q_1 be the amount of heat absorbed by a reversible engine at temperature T_1 and Q_2 the quantity of heat rejected at temperature T_2 on this scale.

$$\therefore \eta = 1 - \frac{Q_2}{Q_1} = f(T_1, T_2)$$

$$\therefore \frac{Q_2}{Q_1} = 1 - f(T_1, T_2)$$

$$\therefore \frac{Q_1}{Q_2} = \frac{1}{1 - f(T_1, T_2)} = F(T_1, T_2) \text{------------}(1)$$

Where F denotes some new function of T_1 and T_2.

Now we consider another reversible engine absorbing heat Q_2 at temperature T_2 and rejecting heat Q_3 at temperature T_3. Then

$$\frac{Q_2}{Q_3} = F(T_2, T_3) \text{------------------}(2)$$

Similarly for a reversible heat engine working between the temperature T_1 and T_3 we have

$$\frac{Q_1}{Q_3} = F(T_1, T_3) \text{--------------------}(3)$$

Multiplying eqs (1)and(2) we get

$$\frac{Q_1}{Q_2} x \frac{Q_2}{Q_3} = \frac{Q_1}{Q_3} = F(T_1, T_2) x F(T_2, T_3) \text{----------}(4)$$

Comparing eqs (3)and (4) we have

$$F(T_1, T_3) = F(T_1, T_2) X F(T_2, T_3) \text{----------}(5)$$

It is observed from eq (5) that there is no T_2 on left hand side. This is possible if we choose the following function.

$$F(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \text{---------------}(6)$$

$$F(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)} \text{---------------}(7)$$

Where ϕ is another function of temperature.

$$Now F(T_1, T_2) x F(T_2, T_3) = \frac{\phi(T_1)}{\phi(T_2)} . \frac{\phi(T_2)}{\phi(T_3)}$$

$$F(T_1, T_2) x F(T_2, T_3) = \frac{\phi(T_1)}{\phi(T_3)} = F(T_1, T_3)$$

From eq (1) we get

$$\frac{Q_1}{Q_2}=\frac{\phi(T_1)}{\phi(T_2)} \text{------------------}(8)$$

Since Q$_1$>Q$_2$, $\phi(T_1)>\phi(T_2)$ provided T$_1$>T$_2$. Thus $\phi(T)$ is a linear function of T. Let $\phi(T)=\tau$

We have

$$\frac{Q_1}{Q_2}=\frac{\phi(T_1)}{\phi(T_2)}=\frac{\tau_1}{\tau_2} \text{---------------}(9)$$

The above eq defined as Kelvin scale of temperature.

Definition:

The ratio of any two temperatures is the same as the ratio of the heats absorbed and rejected by reversible Carnot engine operating between these two temperatures.

Absolute zero:

We know that

$$=1-\frac{Q_2}{Q_1}=1-\frac{\tau_2}{\tau_1}$$

$$when\,\tau_2=0,\eta=1$$

The temperature at which the reversible engine has efficiency equal to one is known as Absolute zero.

Scale of degree:

In order to fix up the size of the degree, the interval between ice point and steam point is divided into 100 equal parts. Let ice point and steam point are represented by $_o$ and τ_o+100 respectively.

Now if is a reversible engine works between Ice and Steam points then

$$\frac{Q_{100}}{Q_0}=\frac{\tau_0+100}{\tau_0}$$

Thus the Thermodynamic scale is completely defined. If $_2$ is–ve then is greater than one. It is impossible. Hence a -ve temperature is not possible on Absolute scale.

Entropy(S):

In isothermal process the temperature remains constant. In adiabatic process, neither the heat nor the temperature remains constant. Clasius showed that there is something which remains constant during adiabatic process. This constant property is known as entropy.

Entropy is a quantity just like pressure or volume. It is impossible to measure the Absolute Entropy. But we can measure the change in Entropy as the substance moves from one state to another.

Physical significance of Entropy:

By the definition

Change of Entropy = heat energy / temperature

Change of Entropy x temperature = heat energy----------------- (1)

mgh = potential energy

Or mh α P.E ----------------------- (2)

By comparing eq(1)&(2) Entropy may be thought of as a quantity which bears to heat motion a similar relation as mass bears to linear motion. Hence Entropy is also termed as ‘Thermal inertia’.

Entropy is also a measure of randomness or disorder of molecule of a system,. The increase of Entropy implies a transition from a more ordered arrangement of molecules to less ordered arrangement. That is from order to dis-order.

Change in Entropy $ds=\frac{dQ}{T}\because s=\frac{Q}{T}$

Entropy of universe:

We know that Entropy of a system remains constant in a reversible cyclic processes but increases in all irreversible processes. Thus there is no change in the Entropy of universe due to reversible process while the Entropy of the universe increases due to irreversible process. As all actual processes are inherently irreversible, hence the Entropy of universe increases.

Entropy and disorder:

We know that solid state is an orderly state as the arrangement of molecules can be specified. When a substance is converted from solid form to gaseous form, the dis-order increases. At the same time, we find that in the process of change of state the Entropy increases. Thus with dis-order, Entropy increases. The converse of the above is also true, i.e., when the substances are converted into water and then into ice the Entropy and dis-order of the molecules decreases.

Temperature Entropy diagram:[T-S diagram]

A graph is drawn by taking Temperature on Y-axis and Entropy on X-axis is known as T-S diagram

Uses of T-S diagram:

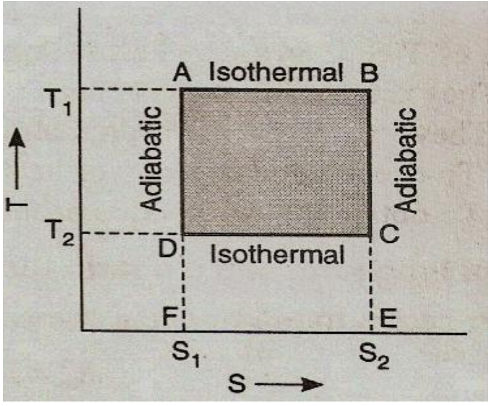
1. They are used in meteorology.
2. They are used in predicting defects in the performance of engine.
3. They are used to check the efficiency of heat engine.
4. They are used to obtain the work value of the fuel used.

Efficiency of Carnot engine:

The working substance undergoes the following operations:

1. Isothermal expansion at the temperature T_1 of the source.
2. Adiabatic expansion when the temperature falls from T_1 to T_2.
3. Isothermal compression at temperature T_2 of the sink.
4. Adiabatic compression that the temperature rises from T_2 to T_1

The above operations are shown on T-S diagram.



From the fig it is clear that Entropy changes linearly in an Isothermal process while it remains constant in adiabatic process.

During Isothermal expansion AB at constant temperature T_1 the Entropy increases from S_1 to S_2. During Adiabatic expansion BC and Adiabatic compression DA the Entropy is constant. During Isothermal compression CD at constant temperature T_2, the Entropy decreases from S_2 to S_1. the rectangular area of the cycle of T-S diagram gives the available thermal energy for useful work in a Reversible process.

Let S_1 and S_2 be the entropies at A and B respectively. During Isothermal change AB the increase in entropy = S_2-S_1, Let Q_1 be the amount of heat absorbed by the working substance in Isothermal expansion and Q_2 be the heat rejected in Isothermal compression CD. Then

$Q_1 = T_1 (S_2-S_1)$

$Q_1 = AFxAB$

$Q_1 =$ area of ABEF

And $Q_2 = T_2 (S_2-S_1)$

= area DCEF

Available energy per cycle converted into useful work

$= Q_1-Q_2$

= area ABEF- area DCEF

= area ABCD

$$The\ \ efficiency\ \eta = \frac{Q_1 - Q_2}{Q_1} = \frac{ABxAD}{ABxAF}$$

$$= \frac{AD}{AF} = \frac{T_1 - T_2}{T_1}$$

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

Thus the ratio of $\frac{AD}{AF}$ on T-S diagram gives the efficiency.

Entropy of a perfect gas:

Consider a mole of a perfect gas at a pressure P, temperature T and volume V. If dQ be the amount of heat given to the gas then the increase in Entropy is given by,

$$dS = \frac{dQ}{T} \text{ - - - - - - - - - - - - - - - -}(1)$$

According to first law of thermodynamics

$$dQ = dU + dW \qquad \because\ dU = C_V dT$$

$$dQ = C_V dT + PdV \text{ ----------}(2) \qquad dW = PdV$$

$$\therefore dS = C_V \frac{dT}{T} + \frac{PdV}{T} \text{ ----------}(3)$$

$$but\ \ P = \frac{RT}{V}$$

$$\therefore dS = C_V \frac{dT}{T} + \frac{RT}{V}\frac{dV}{T} = C_V \frac{dT}{T} + R\frac{dV}{V} \text{ ----------}(4)$$

The change in entropy can be calculated by integrating eq (4) within proper limits

$$S_f - S_i = \int_{T_i}^{T_f} C_V \frac{dT}{T} + R\int_{V_i}^{V_f} \frac{dV}{V} = C_V \log_e\left(\frac{T_f}{T_i}\right) + R\log_e\left(\frac{V_f}{V_i}\right)$$

$$S_f - S_i = 2.303\left[C_V \log_{10}\left(\frac{T_f}{T_i}\right) + R\log_{10}\left(\frac{V_f}{V_i}\right)\right] \text{ ------------}(5)$$

To express the entropy in terms of T and P ,we eliminate Vor dV from eq (3)

$$dS = C_V \frac{dT}{T} + P\frac{dV}{T}$$

PV = RT

PdV+VdP = RdT

$$dV = \frac{RdT - VdP}{P}$$

$$dS = C_V \frac{dT}{T} + P\left(\frac{RdT - VdP}{PT}\right)$$

$$dS = C_V \frac{dT}{T} + R\frac{dT}{T} - V\frac{dP}{T}$$

$$dS = C_V \frac{dT}{T} + \left(C_P - C_V\right)\frac{dT}{T} - V\frac{dP}{T}$$

$$\because\ PV = RT$$

$$\therefore V = \frac{RT}{P}$$

$$dS = C_V \frac{dT}{T} + C_P\frac{dT}{T} - C_V\frac{dT}{T} - V\frac{dp}{T}$$

$$dS = C_P \frac{dT}{T} - V\frac{dP}{T}$$

$$dS = C_P \frac{dT}{T} - \frac{RT}{P}\frac{dP}{T}$$

$$dS = C_P \frac{dT}{T} - R\frac{dP}{P}$$

Integrating the above eq we get

$$S_f - S_i = C_P\int_{T_i}^{T_f} \frac{dT}{T} - R\int_{P_i}^{P_f} \frac{dP}{P}$$

$$S_f - S_i = C_P \log_e\left(\frac{T_f}{T_i}\right) - R\log_e\left(\frac{P_f}{P_i}\right)$$

$$S_f - S_i = 2.303\left[C_P \log_{10}\left(\frac{T_f}{T_i}\right) - R\log_{10}\left(\frac{P_f}{P_i}\right)\right] \text{ ----------}(6)$$

To express the entropy in terms of P and V ,we eliminate T from eq (3)

$$dS = C_V \frac{dT}{T} + \frac{PdV}{T}$$

$$dS = C_V\left[\frac{PdV + VdP}{RT}\right] + \frac{PdV}{T}$$

$$dS = C_V \frac{dV}{V} + C_V\frac{dP}{P} + \frac{RT}{V}\frac{dV}{T}$$

$$\therefore PV = RT$$

$$PdV + VdP = RdT$$

$$\therefore dT = \frac{PdV + VdP}{R}$$

$$dS = C_V \frac{dV}{V} + C_V\frac{dP}{P} + R\frac{dV}{V}$$

$$dS = C_V \frac{dV}{V} + C_V\frac{dP}{P} + \left(C_P - C_V\right)\frac{dV}{V}$$

$$dS = C_V \frac{dP}{P} + C_P\frac{dV}{V}$$

By integrating the above eq we get

$$S_f - S_i = C_V \int_{P_i}^{P_f} \frac{dP}{P} + C_P \int_{V_i}^{V_f} \frac{dV}{V}$$

$$S_f - S_i = 2.303\left[C_V \log_{10}\left(\frac{P_f}{P_i}\right) + C_P \log_{10}\left(\frac{V_f}{V_i}\right)\right]$$

<u>Change of entropy when ice changes into steam:</u>

Let us consider m gram of ice at T_1 K changes into steam at T_2 K. let L_1 and L_2 be the latent heats of fusion and vaporization respectively.

Change in entropy can be calculated as follows.

(1) First ice T_1 K changes into water at T_1 K

Change in entropy is given by $\Delta S_1 = \frac{mL_1}{T_1}$ ---------- (1)

(2) Secondly water at T_1 K changes into water at T_2 K

Change in entropy is given by $\Delta S_2 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_3} \frac{mcdT}{T} = mc\log_e\left(\frac{T_2}{T_1}\right)$ ---------- (2)

(3) Water at T_2 K changes into steam at T_2 K.

Change in entropy is given by $\Delta S_3 = \frac{mL_2}{T_2}$ ----------------(3)

The total change in entropy when it is convertible in to steam is given by

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S = \frac{mL_1}{T_1} + mc\log_e\left(\frac{T_2}{T_1}\right) + \frac{mL_2}{T_2}$$

$$\Delta S = \frac{mL_1}{T_1} + 2.303mc\log_{10}\left(\frac{T_2}{T_1}\right) + \frac{mL_2}{T_2} \text{ ---------------- (4)}$$

THERMO DYNAMIC POTENTIALS AND MAXWELL'S EQUATIONS

<u>**Thermo dynamic potentials**</u>**:** Thermo dynamical state of a system may be represented in terms of certain selected variables like pressure, volume, temperature and entropy. For the complete description of the system certain other relations are required. For this purpose we use certain energy terms of variables P,V,T and S which are known as thermo dynamical functions. The thermodynamical potentials are (1) Internal energy [U] (2) Helmholtz function (F) (3) Enthalpy (H)(4)Gibbs function(G) The above quantities are known as Thermodynamic potentials.

According to first law of thermodynamics

dQ = dU+dW ------------(1)

Second law can be written as

dQ = TdS---------------- (2)

From eqs (1) and (2) we have

Tds =dU+dW

dU =TdS-PdV -----------(3) (dW=PdV)

This is the basic eqn. connecting the first and second laws of thermodynamics.

<u>**(1) INTERNAL ENERGY**</u>**:** The energy which it possesses due to its molecular constitution and motion is known as internal energy (U) .

(or)

The stored energy which is not apparently shown by a system is known as its internal energy.

<u>(2) Enthalpy</u>(H):Mathematically Enthalpy can be expressed as

H=U+PV.....................(4)

Differentiating the above equation we get

dH=dU+PdV+VdP

=TdS-PdV+PdV+VdP Since dU=TdS-PdV

dH=TdS+VdP----------- 5

(3) <u>Helmholtz function</u>: Mathematically Helmholtz function can be expressed as

F=U-TS.....................(6)

Differentiating the above equation we get

dF=dU-TdS-SdT

dF=TdS-PdV-TdS-SdT Since du=Tds-pdv

dF= -SdT-PdV --------- (7)

(4)Gibbs function : Gibbs function can be expressed as

G=H-TS---------(8)

Differentiating the above equn. we get

dG=dH-TdS-SdT

=TdS+VdP-TdS-SdT

dG=VdP-SdT------- (9)

Maxwell's equations:

(1) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(2) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(3) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(4) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Derivation of relations: According to the definition of first law of thermodynamics

du=Tds-pdv-------------- (1)

According to the definition of enthalpy

dH=TdS+VdP-------------(2)

According to the def of Helmholtz function

dF= -SdT-PdV ------------ (3)

According to the def of Gibbs function

dG= -SdT+Vdp ---------- (4)

If there exists any relation among x,y,z then we can write Z as the function x,y. dz= $\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy ------(5)$

let $\frac{\partial z}{\partial x} = M$ and $\frac{\partial z}{\partial y} = N$

Then equ (5) can be written as

dz=Mdx+Ndy ---------------- (6)

We can derive the following equations from partial derivatives

$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial^2 Z}{\partial x \partial y}$ and ∵ M= $\frac{\partial z}{\partial x}$

$\left(\frac{\partial N}{\partial x}\right)_Y = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial^2 Z}{\partial x \partial y}$ ∵ N= $\frac{\partial z}{\partial y}$

From above two equations

$\left(\frac{\partial M}{\partial Y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y ------(7)$

By comparing eqs (1) and (6) we have

M------- → T

x----- →S

N-----→-P

y------ → V

Substituting the above values in equation (7) we get

$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ ———(8)

This is Maxwell's first thermodynamic relation

Comparing equ (2) and (6) we have

M------ →T

x------ → S

N----→V

y----- →P

Substituting the above values in equation (7) we get

$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p -----(9)$

This is Maxwell's second thermodynamic relation

Comparing eqs (3) and (5) we have

M------ →-S

x------- →T

N------- →-P

y ------ →V

Substituting the above values in eq (7) we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

This is Maxwell's third thermodynamic relation

Comparing eqs (4) & (5) we get

M -----→-S
x----- →T
N ----→V
y ----→P

Substituting the above values in equ (7) we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

This is Maxwell's fourth thermodynamic relation.

Derivation of Clausius – Clapeyron's equation using Maxwell's equation: The CLAUSIUS – CLAPEYRON'S latent heat equation relates the change in melting point or boiling point with change in pressure .The equation can be derived from Maxwell's second Thermodynamic relation which is expressed as

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

Multiplying both sides by T we get

$$T\left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial V}\right)_T$$

$$= \left(\frac{T\partial S}{\partial V}\right)_T \qquad \text{T= constant}$$

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial V}\right)_T \qquad \because \partial Q = T\partial s$$

here ∂Qrepresents the heat absorbed at constant temperature i.e. $\partial Q$is latent heat.

Let unit mass of a substance under constant temperature is converted from one state to another state absorbing an amount of heat L. Suppose specific volumes in the first and second states be V_1 and V_2 then $\partial V = V_2 - V_1$ then

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{L}{V_2 - V_1}\right)_T$$

$$T\left(\frac{\partial P}{\partial T}\right) = \frac{L}{V_2 - V_1}$$

$$\therefore \frac{\partial P}{\partial T} = \frac{L}{T(V_2 - V_1)}$$

This is clausius clapeyron latent heat equation

Ratio of specific heats:

Specific heat:

The amount of heat required to raise the temperature of unit mass of the substance through 1^0c is known as specific heat of the substance.

In case of gases heat is supplied under

(1) At constant volume
(2) At constant pressure

Hence there are two specific heats in case of gases

They are

(1) Specific heat at constant volume Cv and specific heat at constant pressure Cp

Derivation of ratio of specific heats: $\left[\frac{c_p}{C_v}\right] = \gamma$

The adiabatic elasticity Es= $-V\left(\frac{\partial p}{\partial V}\right)_s$ ------------(1)

The isothermal elasticity E_T= $-V\left(\frac{\partial P}{\partial V}\right)_T$ ------------(2)

Dividing eq(1) by eq(2) we get

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{\left(\frac{\partial P}{\partial T}\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\frac{\partial S}{\partial V}\right)_T}$$

$$= \frac{\left(\frac{\partial P}{\partial T}\right)_s \left(\frac{\partial T}{\partial V}\right)_s}{\left(\frac{\partial P}{\partial S}\right)_t \left(\frac{\partial S}{\partial V}\right)_T}$$

Substituting the values of Maxwell's equ we get

$$\frac{E_s}{E_T} = \frac{\left(\frac{\partial S}{\partial V}\right)_p \left(\frac{\partial P}{\partial S}\right)_v}{\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial P}{\partial T}\right)_v} = \left[\frac{\frac{\partial S}{\partial V}}{\frac{\partial T}{\partial V}}\right]_p \left[\frac{\frac{\partial P}{\partial s}}{\frac{\partial P}{\partial T}}\right]_v$$

$$= \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial S}\right)_v$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_v}$$

Multiplying numerator and denominator by T we get

$$\frac{E_S}{E_T} = \frac{T\left(\frac{\partial S}{\partial T}\right)_p}{T\left(\frac{\partial S}{\partial T}\right)_v} = \frac{\left(\frac{\partial Q}{\partial T}\right)_p}{\left(\frac{\partial Q}{\partial T}\right)_v} = \frac{C_p}{C_v} = \gamma$$

$$\therefore \frac{C_p}{C_v} = \gamma = \frac{E_S}{E_T}$$

DIFFERENCE OF TWO SPECIFIC HEATS:

The molar specific heats at constant pressure and at constant volume are expressed as

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \quad , \quad C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

$$C_P - C_V = \left(\frac{\partial Q}{\partial T}\right)_P - \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_P - C_V = T\left[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V\right] - - - - - - - - (1)$$

Let entropy be a function of independent variable V and T then

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

differentiating the above equation with respect to T at constant pressure we get

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_T \left(\frac{\partial V}{\partial T}\right)_P - - - - (2)$$

From eqn (1) and (2) we get

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P - - - - - - - - - - (3)$$

For perfect gas of one mole PV=RT

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad and \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

By

Substituting the above values in eq (3) we get

$$C_P - C_V = T\left(\frac{R}{V}\right)\left(\frac{R}{P}\right) = \frac{TRR}{PV} = \frac{TRR}{RT} = R$$

$$C_P - C_V = R$$

<u>For Vander wall's gas</u>:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Where a, b are constants

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{V - b}$$

Differentiating with respect to T at constant volume

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \text{ ----------(4)}$$

Differentiating with respect to T at constant pressure

$$-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{R}{V-b} \quad =>$$

$$\left(\frac{\partial V}{\partial T}\right)_p\left[\frac{RT}{(V-b)^2} - \frac{2a}{v^3}\right] = \frac{R}{V-b}$$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{\frac{R}{v-b}}{\left[\left\{\frac{RT}{(V-b)^2}\right\} - \left\{\frac{2a}{v^3}\right\}\right]} \text{ --------------(4)}$$

By substituting the above values in eq (3) we get

$$C_p - C_v = T\left[\frac{R}{V-b}\right]\frac{\frac{R}{V-b}}{\left[\left\{\frac{RT}{(V-b)^2}\right\} - \left\{\frac{2a}{v^3}\right\}\right]} = \frac{RTR}{(V-b)^2\left[\frac{RT}{(V-b)^2} - \frac{2a}{v^3}\right]}$$

Dividing numerator and denominator by RT wege

$$= \frac{R}{1-\left(\frac{2a}{v^3}\right)\frac{(v-b)^2}{RT}}$$

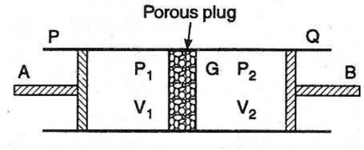
Since v>>b, we can replace (v-b) by v

$$\therefore C_p - C_v = \frac{R}{1-\frac{2a\,v^2}{v^3\,RT}} = \frac{R}{1-\frac{2a}{RTv}} = R\left[1-\frac{2a}{RTv}\right]^{-1}$$

$$\therefore C_p - C_v = R\left[1+\frac{2a}{RVT}\right]$$

Neglecting higher powers after expanding the term.

JOULE-KELVIN EFFECT:[POROUS PLUG EXPERIMENT]:



When a gas under a constant high pressure is passed through a porous plug to a region of constant low pressure then there is a change in it's temperature . This is called joule-Kelvin effect.

The following point's are observed :

1. (1) At ordinary temperatures all gases except hydrogen and helium suffer a fall in temperature ,while hydrogen and helium suffer a slight rise in temperature .
2. (2) The change in temperature is directly proportional to the pressure difference on the two sides of the plug.
   (3) If the initial temperature of the gas rises then the cooling effect decreases. At a certain initial temperature, known as "inversion temperature", the cooling effect is changed into heating effect.

EXPRESSION FOR JOULE – KELVIN COEFFICIENT:

When a gas suffers Joule-Kelvin effect the total enthalpy of the gas remains constant.

H =U+PV =CONSTANT

or dU+ PdV +VdP =0 --------------(1)

We know that TdS=dU +PdV---------------- (2)

By substituting equ(2) in equ (1) we get

TdS + VdP =0----------(3)

Let us consider s is a function of P and T then change is entropy

$$dS = \left(\frac{\partial s}{\partial p}\right)_T dp + \left(\frac{\partial s}{\partial T}\right)_P dT$$

By substituting the above value in equ (3) we get

$$\left[T\left(\frac{\partial S}{\partial P}\right)_T dp + T\left(\frac{\partial S}{\partial T}\right)_P dt\right] + vdp = o \text{ ------------- (4)}$$

But T $\left(\frac{\partial S}{\partial T}\right)_P = \left(T\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$

$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ ∵ Maxwell's fourth equation

Substituting the above values in eqn. (4) we get

$$-T\left(\frac{\partial V}{\partial T}\right)_P dp + C_p dT + VdP = 0$$

$$C_P\, dT = T\left(\frac{\partial V}{\partial T}\right) dP - Vdp$$

$$C_P\, dT = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \text{dp}$$

$$\frac{dT}{dP} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

or $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \quad (5)$

Here $\left(\frac{\partial T}{\partial P}\right)_H =$ which is known as joule Kelvin coefficient

$$\therefore \mu = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \quad (6)$$

The following important points are observed .

(1) If $\left(\frac{\partial T}{\partial P}\right)_H$ is positive then there is a cooling effect.

(2) If $\left(\frac{\partial T}{\partial P}\right)_H$ is negative then there is a heating effect.

(3) If $\left(\frac{\partial T}{\partial P}\right)_H = 0$ then there is neither cooling nor heating.

The corresponding temperature is known as inversion temperature.

Joule-Kelvin effect for a perfect gas :

For a perfect gas PV=RT

V=RT/P

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Substituting the above value in equation (5) we get

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{R}{P}\right) - V\right] = \frac{1}{C_P}\left[\frac{TR}{P} - V\right] = 0$$

Hence joule-Kelvin effect for a perfect gas is zero.

Joule-Kelvin effect for vanderwall's gas:

For vanderwall's gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Differentiating the above equation with respect to T and taking P constant then we get.

$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R(V-b)}{\left[RT - \frac{2a}{V}\right]}$ (neglecting b^2 and 2Vb in comparison with V^2)

Now T $\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT(V-b)}{\left(RT - \frac{2a}{v}\right)}$

T $\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b$ (neglecting $\frac{2ab}{VRT}$)

Substituting the above values in equ (5) we get

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$$

Where $\frac{2a}{RT} = b$ then $\frac{\partial T}{\partial P} = 0$ the corresponding temperature is known as inversion temperature Ti.

$$T_i = \frac{2a}{bR}$$

If the initial temperature of the gas T is less than Ti then the gas suffers cooling and if The initial temperature of the gas is greater than Ti then it suffers heating.

LOW TEMPERATURE PHYSICS

INTRODUCTION:

Scientists have achieved the lowest temperature -273^{0}C or 0K. This is known as the absolute zero of temperature. Low temperatures can be achieved by the following methods.

(1) FREEZING MIXTURES:

When common salt is mixed with ice, some of the ice melts in cooling the salt to 0^{o}C .The salt readily dissolves in the water formed from the melting ice . Heat is absorbed while salt is dissolving in water and further ice will melt absorbing latent heat of fusion of ice. Hence it gives -22^{o}C.

(2) EVAPORATION OF LIQUIDS:

When a liquid evaporates it draw the latent heat of evaporation from the surroundings.

By reducing the pressure on the liquid surface the liquid can be made to boil at the room temperature. The latent heat necessary for boiling is taken from the liquid itself and consequently the temperature of the liquid falls.

Ex: boiling NH_3 gives -33.4^{o}C

(3) Still lower temperatures were obtained by the liquefaction of permanent gases. Liquid H_2 gives -253^{o}C

(4) 1^{o}K is obtained by adiabatic de magnetization of paramagnetic salts.

JOULE -KELVIN EFFECT:

When a gas under constant pressure is passed through porous plug to a region of lower constant pressure, the gas suffers a change in temperature. This effect is known as joule Thomson effect.

POROUS PLUG EXPERIMENT:

Description: As shown in the fig. PQ is thermally insulated cylinder containing porous plug G (silk or cotton wool placed between two perforated brass plates). PQ is devided in to two parts using two nonconducting pistons A and B.

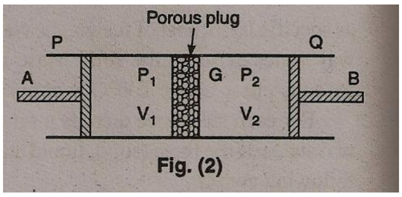


Fig. (2)

Let the gas is compressed to a high pressure P_1on oneside.The gas then passes through the porous plug on the other side which is at constant low pressure P_2.Then there is a change in temperature called as Joule-Kelvin effect.

The following important points are observed:

(1) At sufficiently low temperatures all gases show a cooling effect. But at ordinary temperature hydrogen, helium show heating effect.

(2) The fall in temperature is proportional to the difference of pressure on the two sides of the plug.

(3) If the initial temperature raises then the cooling effect decreases, at particular temperature called Inversion temperature the effect is zero. It differs from one gas to another gas.

(4) Any gas below its temperature of inversion will cool in passing through the plug.

Explanation:

At the temperature of inversion the cooling is due to intermolecular attraction is just balanced by the heating due to the external work done on the gas. Above the temperature of inversion the heating due to the external work done on the gas will be greater than the cooling due to the inter molecular attraction. Hence heating is produced. Below the temperature of inversion the cooling due to intermolecular attraction and cooling due to external work done by the gas is produced.

Inversion temperature of H_2 is -51^{o}C and for He is -239^{o}C which is low temperature than normal temperature. Hence it will show heating effect in Joule Kelvin expansion.

DIFFERENCES BETWEEN JOULE-KELVIN EXPANSION AND ADIABATIC EXPANSION:

JOULE KELVIN EXPANSION	ADIABATIC EXPANSION
(1)The cooling is mainly due to internal work done by the gas against inter molecular forces of attraction.	(1) The cooling of gas is mainly due to the external work done by the gas.
(2) For perfect gas there is no cooling.	(2)For any gas we can observe cooling effect
(3) For a real gas there is cooling effect, when its initial temperature is below its temperature of inversion.	(3) There is no such heating effect.
(4)There will be heating effect if the gas is initially above its inversion temperature.	(4)There is always cooling effect.
(5)It is always irreversible.	(5)It is reversible.

EXPRESSION FOR JOULE-THOMSON COOLING:

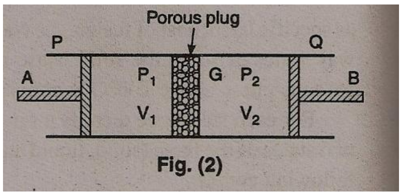


Fig. (2)

Consider a thermally insulated cylinder PQ divided into two compartments by a porous plug G. let $V_1$and V_2 be the volumes of gas before and after passing through the porous plug respectively.

External work done on the gas by the piston A = P_1V_1
External work done by the gas on the piston B= P_2V_2
Net external work done by the gas = $P_2V_2-P_1V_1$

If we assume the gas to obey vanderwall's equation, the attraction between the molecules is equivalent to an internal pressure $\left(\frac{a}{V^2}\right)$ where 'a' is a constant and 'v' is the volume occupied by the gas. Hence the internal work done against these forces when 1 g. mole expands from volume V_1 to volume V_2 is

$$\int_{V_1}^{V_2}\left(\frac{a}{v^2}\right)dV=\frac{a}{V_1}-\frac{a}{V_2}$$

The total work done W = $P_2V_2-P_1V_1 + \frac{a}{V_1}-\frac{a}{V_2}$ ---------- (1)

According to vanderwall's equation, we have

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

$$PV+\frac{a}{V}-Pb-\frac{ab}{V^2}=RT$$

As a, b are small quantities, $\frac{ab}{v^2}$ can be neglected.

$$PV+\frac{a}{V}-Pb=RT$$

$$PV=RT-\frac{a}{V}+Pb$$

Now $$P_1V_1=RT-\frac{a}{V_1}+P_1b$$

$$P_2V_2=RT-\frac{a}{V_2}+P_2b$$

$$(P_2V_2-P_1V_1)=a\left(\frac{1}{V_1}-\frac{1}{V_2}\right)-b(P_1-P_2) \text{ ---------- } (2)$$

Substituting eq (2) in eq (1) we get

$$W=a\left(\frac{1}{V_1}-\frac{1}{V_2}\right)-b(P_1-P_2)+\frac{a}{V_1}-\frac{a}{V_2}$$

$$W=2\left(\frac{a}{V_1}-\frac{a}{V_2}\right)-b(P_1-P_2) \text{ ------------- } (3)$$

Since $\frac{a}{V_1} and \frac{a}{V_2}$ are small quantities we can use the approximate relation

PV=RT

i.e $\frac{a}{V_1}=\frac{P_1a}{RT} and \frac{a}{V_2}=\frac{P_2a}{RT}$

Now eq (3) becomes

$$W=2\left(\frac{P_1a}{RT}-\frac{P_2a}{RT}\right)-b(P_1-P_2)$$

$$W=\frac{2a}{RT}(P_1-P_2)-b(P_1-P_2)$$

$$W=(P_1-P_2)\left[\frac{2a}{RT}-b\right]$$

As the system is thermally insulated, this work is drawn from the internal energy of the gas. Hence the gas cools.

If C_p be the specific heat at constant pressure then the amount of heat that must be supplied to restore the original temperature will be $-C_p\,dT$ J ergs.

Where $-dT$ = fall in temperature. Hence

$$-C_p\,dTJ=(P_1-P_2)\left[\frac{2a}{RT}-b\right]$$

$$dT=-\frac{(P_1-P_2)}{C_pJ}\left[\frac{2a}{RT}-b\right] \text{ ----------- } (5)$$

From the above eqs the following important points are noted.

(1) At any temperature cooling is directly proportional to pressure difference.

(2) For a given pressure difference (P_1-P_2) cooling is greater for lower initial temperature.

(3) If $\frac{2a}{RT} - b$ is +ve ,then dT will be –ve therefore gas will be cooled .

(4) If $\frac{2a}{RT} - b$ is –ve , then dT will be +ve . Therefore gas will be heated.

(5) If $\frac{2a}{RT} - b$ becomes zero i.e $T = \frac{2a}{Rb}$ then dT = 0.In this case the temperature of the gas remains unchanged.

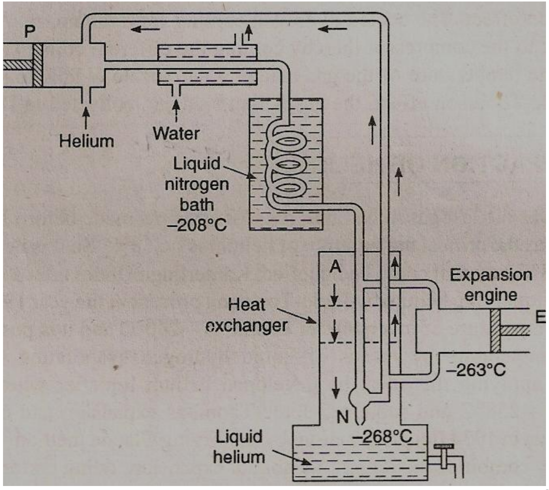
This particular temperature T_i is known as temperature of inversion.

$$T_i = \frac{2a}{Rb}$$

Clearly every gas above its temperature of inversion would show a heating effect while below its temperature of inversion will show cooling effect.

The temperatures of inversion of hydrogen and helium are as low as -80°C and -240°C respectively. Hence they show heating effect at ordinary temperatures.

LIQUEFACTION OF HELIUM : [KAPITZA'S METHOD]



The experimental set up is as shown in the fig. pure and dry helium is compressed to 30 atmospheres by compressor P. Heat of compression is removed by flowing water in a jacket surrounding a portion of the tube. The gas is then pre-cooled by passing it through a bath of liquid nitrogen boiling under reduced pressure. The pre-cooled gas is divided into two parts at A in the heat exchanger. One part passes to the expansion engine E. Due to adiabatic expansion of the gas it cools to -263°C. This cooled gas rises up in the heat exchanger and cools the second part coming towards the nozzle N. The second part is now so cooled that after the expansion at nozzle N, it is liquefied. The liquefied portion is collected in Dewar flask and the remaining part goes back to the compressor through the heat exchanger.

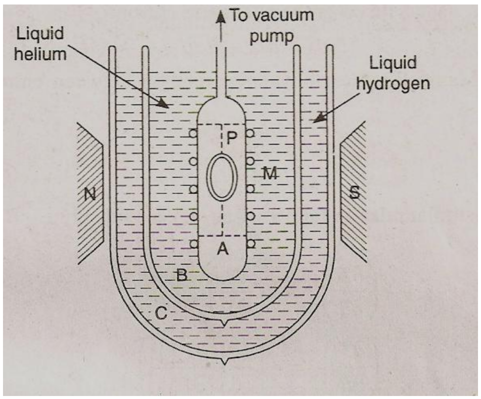
ADIABATIC DE-MAGNETISATION:

In 1926 Debye and Giauque reached the lowest temperature by adiabatic de magnetization.

PRINCIPLE:

When a paramagnetic substance already magnetised is suddenly demagnetised adiabatically then a slight fall in temperature of the substance , due to work is done by the substance. This is known as adiabatic de-magnetisation.

METHOD:



The experimental arrangement is as shown in fig. The paramagnetic substance like Gadolinium sulphate is suspended in a vessel A which is connected to a vacuum pump. The vessel A is surrounded by liquid helium at 1K placed in a Dewar flask C containing liquid hydrogen .A strong magnetic field is applied to magnetise the paramagnetic material. The coils M round A are used to measure the temperature by susceptibility measurements.

First of all A is filled with helium gas so that the paramagnetic substance P comes in thermal contact of liquid helium and cooled to 1K. Now the magnetising field is switched on. The paramagnetic substance becomes warmed but the heat flows through the helium gas into the liquid helium. The temperature of the substance again falls to 1K.Now helium gas is pumped out from the vessel A so that the paramagnetic substance becomes thermally insulated. Then the magnetic field is switched off. Due to adiabatic de magnetisation the temperature of the substance falls. The fall in temperature is detected by susceptibility measuring coils. In this way they reached a temperature of 0.25K

THEORY:

According to curie law, the paramagnetic susceptibility χ is inversely proportional to the absolute temperature T

$$\therefore \chi \propto \frac{1}{T}$$

$$\chi = \frac{C}{T} ------------(1)$$

Where c = curie constant

We know that $\chi = \frac{I}{B}$ -------------(2)

From eq (1) and eq (2)

where I = intensity of magnetization

B = intensity of magnetizing field

$$\frac{C}{T} = \frac{I}{B}$$

$$\therefore I = \frac{CB}{T} ---------(3)$$

We know that the fall in temperature

$$\partial T = \frac{-T}{mC_B}\left(\frac{\partial I}{\partial T}\right)_B \partial B --------(4)$$

$$\therefore \partial T = \frac{-T}{mC_B}\left[\frac{\partial}{\partial T}\left(\frac{CB}{T}\right)\right]\partial B$$

Let T_i and T_f be the initial and final temperatures of the substance corresponding to the initial and final magnetic flux densities B_i and B_f respectively.

$$T_f - T_i = \frac{-T}{mC_B}\int_{B_i}^{B_f}\left\{\frac{\partial}{\partial T}\left(\frac{CB}{T}\right)\right\}\partial B$$

On simplifying we get

$$T_f - T_i = \frac{-C}{2mC_BT}\left(B_f^2 - B_i^2\right)$$

$$T_f - T_i = -\frac{kB_i^2}{2C_BT}$$

Where k = (C/m) called as curie constant per unit mass .When magnetic field is switched off then $B_f = 0$

The –ve sign indicates a fall in temperature. Using above eq. we can calculate the fall in temperature of the paramagnetic substance.

APPLICATION OF LOW TEMPERATURES:

(1) Liquid air, liquid oxygen etc.., are used in calorimeters.
(2) Liquid oxygen is used for respiration and also in the manufacture of explosives.
(3) Liquid ammonia, liquid sulphurdioxide, Freon are used in refrigerators and air conditioners.
(4) Using liquefied gases we can obtain vacuum of higher order.
(5) The properties of super fluidity and super conductivity of matter can be used for the advantage in electrical conduction.
(6) Low temperature physics is used in cryogenic engineering.
(7) It is used to preserve animal life and vegetable matter.

Quantum theory of radiation

Introduction:

The transfer of heat by conduction and convection requires the presence of a material medium. But the transfer of heat without material medium is known as radiation. For example we receive heat from the sun without material medium. The radiant energy is transported by electromagnetic waves because these waves can travel through vacuum.

The radiation emitted by the body by virtue of its temperature is known as thermal radiation.

Prevost's law:

Every body emits and absorbs radiant energy continuously as long as its temperature is above O^0K.

Emissive power:

The emissive power of a body at a given temperature and for a given wavelength is defined as the radiant energy emitted per second by unit surface area of the body per unit wavelength range.

Absorptive power:

The absorptive power of a body, at a given temperature and for a given wavelength is defined as the ratio of the radiant energy absorbed per second by unit surface area of the body to the total energy falling per second on the same area.

Black body:

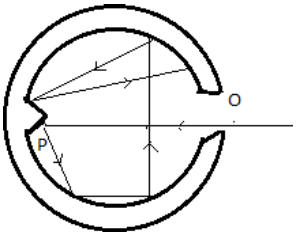
Black body is that which absorbs all the incident radiation and doesn't reflect the ray's incident on it. The absorbing and emissive power is about 100%but the reflecting power is almost zero. Hence it appears dark when it is cold and bright when it is hot.

There is no perfect black body in nature. The nearest approach is lamp black or platinum black. A perfectly black body is a good absorber as well as good radiator. So if it is heated to a suitable high temperature, it emits radiation of all wavelength's which is known as black body radiation.

Ferry,s black body:As shown in the fig. it contains double walled conducting sphere.To prevent conduction and convection losses the interspace between the walls is evacuated.

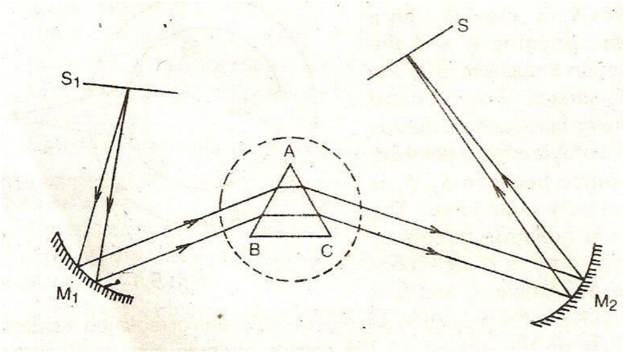
It has a small hole 'O' and a conical projection 'P'. Inner surface is coated with lamp-black outter surface is polished with nickel.

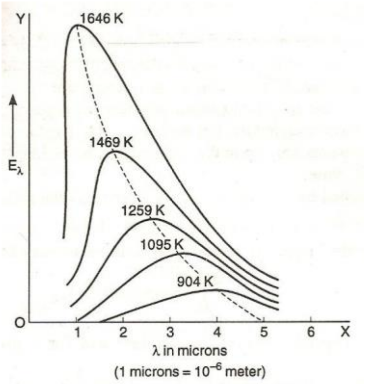
When the radiation is incident on the hole, it passes inside the enclosure. The radiation suffers multiple reflections inside enclosure and is compleetely absorbed.Conical projection 'P' prevents reflection of radiation.



ENERGY DISTRIBUTION IN BLACK BODY RADIATION

IN 1899 lummer and pring sheim determined experimentally the distribution of energy in black body radiation for different wave lengths and at various temperatures .The experimental arrangement is as shown in the fig.1.They used the black body as electrically heated chamber with a narrow slit whose temperature was recorded by a thermo couple.





The radiations from the black body pass through the slit S_1 and fall on the reflector M_1. After reflection the parallel beam of radiation fall on a fluorescent prism ABC placed on the turn table of the spectrometer. The emergent light is focused by the reflector M_2 on a line bolometer placed behind the slit S_2 . The bolometer is connected to a sensitive galvanometer. The turn table is rotated slowly so that different parts of the radiation spectrum successively fall on the bolometer circuit are read. The sensitivity of each line is proportional to the deflection of the galvanometer. Then a curve is drawn between intensity and wavelength.

Then the body is heated to different temperatures and drawn for various temperatures. The curves are shown below.

The experimental results are shown below

1. At a given temperature the energy is not uniformly distributed in the radiation spectrum of a black body.
2. The intensity of radiation increases with increase of wavelength and becomes maximum at a particular wavelength. After that the intensity decreases.
3. An increase in temperature causes a decrease in λ_m .[$\lambda_m T = 0.02896 cmK = constant$]
4. An increase in temperature causes an increase in energy emission for all wavelengths.
5. The area under each curve represents the total energy emitted by the body at a particular temperature for the range of wavelengths .this area increases with increase of temperature. It is found that $E \alpha T^4$ which is Steffen's law

Wein's law:

The product of the wavelength corresponding to maximum energy λ_m and the absolute temperature T is constant i.e.

$$\lambda_m T = constant$$

$$= 0.2896 cmK = 0.2896 x 10^{-2} mk$$

Wein's displacement law:

The maximum energy emitted by a black body is proportional to the fifth power of its absolute temperature.

i.e., $(E_\lambda)_{\max} \alpha T^5 or \frac{(E_\lambda)\max}{T^5} = constant$

Rayleigh –Jean's law:

According to Rayleigh-jean's law, the energy distribution in the thermal spectrum is given by

$$E_\lambda = \frac{8\pi kT}{\lambda^4} \qquad \text{Where K=boltz Mann constant}$$

Quantum theory of radiation:

In 1900, Max Planck proposed quantum theory of radiation

Planck's hypothesis:

(1) A black body radiator contains simple harmonic oscillators of possible frequencies

(2) The oscillators cannot emit or absorb energy continuously. This is contrary to E.M theory.

(3)Emission or absorption of energy takes place in discrete amounts of energy which is equal to $nh\upsilon$

Where n=0, 1, 2

i.e., E= $nh\upsilon$ where h= Planck's constant

The small unit of energy $h\upsilon$ is known as quantum or photon

Derivation of Planck's law:

Let N be the total number of Planck's oscillators and E be this total energy. Then the average energy per Planck's oscillator $\bar{E}$ is given by

$$E = \frac{E}{N} - (1)$$

Let there be N_0, N_1, N_2………N_r …etc Oscillators having energy 0, E,2E, 3E………..rE………..

$$N=N_o+N_1+N_2+\dots\dots+N_r+ ------------------ (2)$$

And $E= 0+EN_1+2EN_2+3EN_3+\dots\dots rEN_r+$ ----------------------- (3)

According to Maxwell's distribution formula

$$N_r = N_o e^{-\frac{rE}{kT}} ———————————(4)$$

Where K= boltz Mann constant

Substituting the values of N_1, N_2, N_3 from eq (4) in eq (2) we get

$$N = N_o + N_0 e^{\frac{-E}{Kt}} + N_o e^{\frac{-2E}{kT}} + - - + N_o e^{\frac{-re}{kT}} + - - - - - - - -$$

$$= N_o\left[1+e^{\frac{-E}{kT}}+e^{\frac{-2E}{kT}} ++ e^{\frac{-rE}{kT}} +\dots\dots\right] - - - - - - - - - - (5)$$

$$= \frac{N_0}{1-e^{\frac{-E}{kT}}}$$

…

Substituting the values of N_1, N_2, N_3 from eq (4) in eq (3) we get

$$E = (N_0 X 0) + EN_0 e^{\frac{-E}{kT}} + 2EN_0 e^{\frac{-2E}{kT}} + \dots\dots + rEN_0 e^{\frac{-rE}{kT}} + \dots\dots$$

$$= N_0 E e^{\frac{-E}{kT}} [1+ 2e^{\frac{-E}{kT}} + \dots\dots + re^{\frac{-(r-1)E}{kT}}$$

$$= N_0 E e^{\frac{-E}{kT}} \left[\frac{\square 1}{\left\{1-e^{\frac{-E}{kT}}\right\}^2} \right] - - - - - - - - - (6) \because 1+2x+3x^2+ - - - rx^{r-1} = \frac{1}{(1-x)^2}$$

….(7)

We know that number of oscillations per unit volume in frequency range υ and $+d\upsilon$ Is given by

$$f = \frac{8\pi\upsilon^2}{c^3} dv - - - - - - - - - - (8)$$

Multiplying eq (8) with eq (7) we get the total energy per unit volume belonging to the range $d\upsilon$

$$E_\upsilon d\upsilon = \frac{8\pi\upsilon^2}{c^3} d\upsilon \frac{h\upsilon}{e^{\frac{h\upsilon}{KT}}-1}$$

$$E_\upsilon d\upsilon = \frac{8\pi h\upsilon^3}{c^3}\frac{d\upsilon}{e^{\frac{h\upsilon}{KT}}-1} ----------(9)$$

This is called Planck’s radiation law

The energy density $E_\lambda d$ belongs to the range $d\lambda$ can be obtained by using the relation $= \frac{c}{\lambda}$

$$\therefore E_\lambda d\lambda = \frac{8\pi h c^3}{c^3 \lambda^3}\left[\frac{\square 1}{e^{\frac{hc}{\lambda KT}}-1}\right]\left[\frac{c}{\lambda^2}d\lambda\right] \qquad \therefore \left|d\upsilon\right| = \frac{c}{\lambda^2}d$$

$$\therefore E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{\square 1}{e^{\frac{hc}{\lambda KT}}-1}\right]d\lambda -----------(10)$$

This is Planck’s radiation law in terms of wavelength.

<u>Deduction of wein’s law from Planck’s law:</u>

For shorter wavelength λ is very small

$$e^{\frac{hc}{\lambda KT}} >> 1$$

According to Planck’s law

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda KT}}-1}d$$

For shorter wavelength

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda KT}}}d\lambda$$

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}e^{\frac{-hc}{\lambda KT}}d\lambda$$

Putting $8\pi hc = A, \frac{hc}{K} = B$ then we have

$$E_\lambda d\lambda = \frac{A}{\lambda^5}e^{\frac{-B}{\lambda T}}d\lambda = A\lambda^{-5}e^{\frac{-B}{\lambda T}}d\lambda$$ Wein’s law = $E_\lambda = C_1\lambda^{-5}e^{-c_2}$

This is wein’s law which agrees with the experimental values with shorter wave length

<u>Deduction of Rayleigh-jeans law from Planck’s law:</u>

For longer wavelength $\frac{hc}{\lambda KT}$ is very mall

$$\therefore e^{\frac{hc}{\lambda KT}} = 1 + \frac{hc}{\lambda KT} + \frac{h^2c^2}{\lambda^2K^2T^2} + ---$$

$$= 1 + \frac{hc}{\lambda KT}$$ Neglecting higher powers

$$\therefore E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{1+\frac{hc}{\lambda KT}-1}$$

$$= \frac{8\pi hc\lambda KT}{\lambda^5 hc}d$$

$$\therefore E_\lambda d\lambda = \frac{8\pi KT}{\lambda^4}d$$

This is Rayleigh-jeans law which agrees with experimental values at longer wave length.

Pyrometer:

It is an instrument which is used for measurements of high temperatures. The gas thermometers, thermoelectric thermometers and resistance thermometers are used to measure high temperatures. These thermometers have to be put in contact with the hot body. These thermometers become useless for the measurement of high temperatures. In the case of radiation pyrometers, they need not be put in contact with the hot body.

Advantages:

(1) They can be used to measure very high temperatures.

(2) They need not be put in contact with the hot body
(3) There is no difficulty in extra polation because radiation laws are valid at all temperatures.

Disadvantages:

(1) Their range roughly begins at 600^0c and so temperatures below this limit can't be measured
(2) The temperatures obtained by these pyrometers are always less than the actual temperature of the source, because there is no perfect black body in nature.

Types of pyrometers:

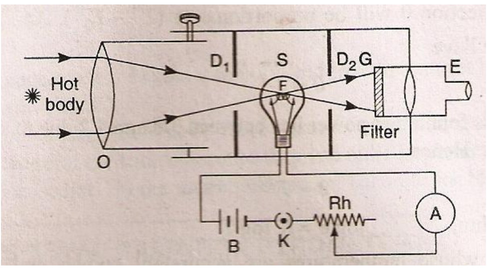
(1) Total radiation pyrometers:

The instruments that measure total radiation emitted by the body under test are called as total radiation pyrometers. The temperature is determined by making the use of stefen's law.

(2) Optical pyrometer: The Optical pyrometers compare the intensity of radiation of a certain wavelength emitted by the body with that of the radiation of same wavelength emitted by a standard body at a known temperature. The temperature of the body is obtained by applying wein's displacement law (or) Planck's law.

Dis appearing filament optical pyrometer:

Construction:



This device was invented by Morse. Further it was improved by Holborn and Kurlbaum.
This type of pyrometer consists of a telescope fitted with an objective O at one end and eye-piece E at the other end. The distance between objective and eye-piece can be adjusted rack and pinion arrangement. The cross wire of the telescope are replaced by an electric lamp S. The filament Fof the lamp is connected to a battery B, Rheostat R_h and ammeter A in series. The filament is heated by the electric current flowing through it and its temperature can be changed by adjusting the current in the circuit. The current is recorded by the ammeter D_1 and D_2 are the two diaphragms which limit the cone of radiation entering the telescope. A red glass fitter G is placed before eye-piece E.

Working:

The objective of the pyrometer is directed towards the hot body whose temperature is to be measured. With the help of rack and pinion arrangement, the position of the objective is so adjusted that the image of hot body is focused on the filament F. The image is viewed with the help of eye-piece E. The image of the filament superimposed with the illuminated red background. The current is so adjusted that the filament become disappears against the background. The current (I) in the ammeter is recorded.

The temperature of the filament T can be calculated from the formula

$I= a+bT+cT^2$

Where a, b, and c, are constants.

Using various bodies whose temperatures are known accurately, the corresponding ammeter readings are recorded when filament disappears. Using the above equation and solving it for three readings we can calculate the constants a, b, and c.

The instrument is suitable for measuring temperatures from 600^0c to 2700^0c.

Merits:

(1) It is more accurate than total radiation pyrometer.
(2) It is easily portable.

De-merits:

(1) It cannot be used to measure the continuous variation of temperature of a hot body.
(2) It needs some little settings.

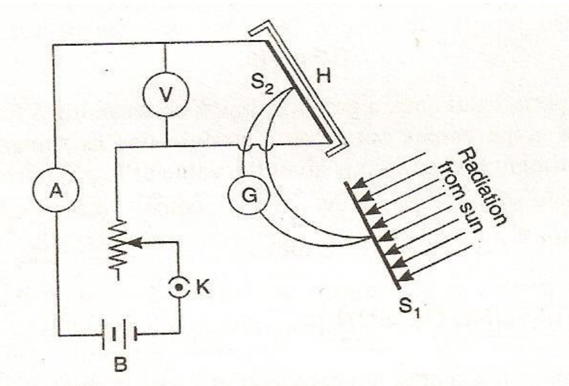
Solar-constant:

Sun is radiating energy in all directions by virtue of its temperature. The earth receives only a fraction of this energy. The amount of solar radiation received by he surface of the earth depends on the location, the time of the day, the time of the year, the weather and the tilt of the surface to sun's rays.

Definition: The rate which solar energy received by a black surface per unit area placed normal to the sun rays at the mean distance of the earth from the sun in the absence of earth's atmosphere. It's value is $1340 Wm^{-2}$

Angstroms pyrheliometer : [determination of solar constant]

Construction:



As shown in the fig Angstroms pyrheliometer consists of two thin exactly similar blackened stripes of platinum or constantan S_1 and S_2. The two stripes are

arranged such that one is open to receive radiation from the sun normally .While the other is protected by a doubled walled shield H. The backs of S_1 and S_2 are connected to two junctions of a thermocouple consisting of copper and constantan wire through galvanometer G. The strip S_2 is heated electrically with the help of electric circuit .

Working:

When both S_1 and S_2 are at the same temperatures then there is no deflection in the galvanometer. When S_1 exposed to radiation from the sun its temperature rises and galvanometer shows some deflection. Now current is passed through strip S_2 and its strength is so adjusted that the galvanometer shows no deflection. Now the temperatures of S_1 and S_2 are the same. The heat energy supplied to strip S_2 can be calculated from the known values of the current and voltage in the circuit. If 'A' be the area of cross section of the strip and 'a' its absorption co-efficient, then energy absorbed per minute per square centimeter is —— Cal cm^{-1} mm^{-1}

Solar constant S=—— Cal cm^{-1} mm^{-1}

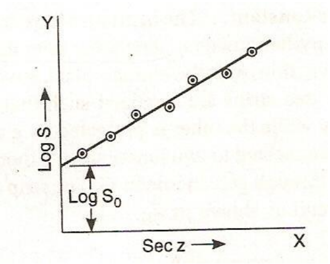
The experiment was performed several times on the same day under constant sky conditions with different evolutions of the sun. The average value of solar constant was then calculated by performing the experiment throughout the year.

The observed value of solar constant S and the true value of solar constant S_0 are connected by the relation

$$S = S_0\,\tau^{\sec z}$$

Where τ is the transmission co-efficient of the atmosphere and Z is the Zenith distance of the sun [angular altitude].by taking logarithms we have

$$\log S = \log S_0 + \sec z \log \tau$$



A graph is drawn between log S and sec z. The graph is a straight line and the intercept of the straight line on y-axis gives the value of $\log S_0$. From this the value of S_0 can be calculated. The value of S_0=1340wm^{-2}

Determination of temperature of the Sun: Let R be the radius of the photosphere of the sun .Then its surface area is .If T be the absolute temperature of the sun, according to Stefan's law the amount of energy emitted by the Sun is given by

Where = Stefan's constant.

Let us concider a sphere of radius r concentric with the Sun.the radiated energy will be spread over the surface

If S is the Solar constant , the energy received by the surface per min is..............Hence

= .

1. Calculate the change in entropy when 1kg of water at 0^{0}C is mixed with 1kg of water at100^{0}C.

   A) Let Tbe the common temperature of the mixture.

   Heat lost by the hot water= Heat gained by the cold water

   1000 x 1 x (100-T) = 1000 x 1 x (T-0)

   Therefore T= 50^{0}C

   Increase in entropy of cold water S_1 = ms 2.303 log(T_2/T_1)

   = 1000 x 1 x 2.303 log(273+50/273+0)

   = 1000 x 1 x 2.303 log(323/273)

   = 1000 x 1 x 0.0731 = 168.4 cal/K

   Decrease in entropy of hot water S_2 = ms 2.303 log(T_2/T_1)

   = 1000 x 1 x 2.303 log(273+100/273+50)

   = 1000 x 1 x 2.303 log(373/323)

   = 1000 x 1 x 0.0614 = 141.5 cal/K

   Increase in entropy = S_1 –S_2=168.4 - 141.5 =26.9 cal/K

2. Carnot engine has an efficiency of 30%, when the temperature of the sink is 27^{0}C. What must be the change in temperature of the source so as to make the efficiency 50%.

   A)Given T_2=27+273= 300K

   η_1= 30%= 0.3

   T_1=?

   We know that

   =

   η_2= 50%= 0.5

   T_2=27+273= 300K

   T_1^1= ?

   =

3. Calculate the efficiency of a reversible engine that operate betweenthe temperatures 200^{0}C and 120^{0}C.

   A) Given T_2=120+273= 393K

   T_1=200+273=473K

   η_1= ?

   We know that

4. The efficiency of a Carnot engine is 25%. On reducing the temperature of the sink by 50 K, the efficiency is 50%. What are the initial temperatures of source & sink.

   A) Given η= 25%

   When T'_2 = T_2-50 η= 50%=0.5

   0.25 =50

5. The rms speed of Hydrogen molecule is 1.84 km/sec .what will be the rms speed of Oxygen molecule at the same temperature.

A) Given

=?