## Kinetic Theory Of Gases

Gas laws are study of any two of quantities like pressure, volume and temperature, when the third is kept constant

## A. Boyle's law

"At constant temperature, the volume of a given mass of gas is invesely propertional to pressure." Thus $V \square 1 / P$
Or, $\quad \mathrm{PV}=\mathrm{constant}$
If $P_{1}, V_{1}$ are initial pressure and volumes and $P_{2}, V_{2}$ be final values then,

$$
P_{1} V_{1}=P_{2} V_{2}
$$

Graph between $P$ and $V$ at temperature $T_{1}$ and $T_{2}$ such that $T_{1}<T_{2}$ are shown below,


Figure 1
Exp. Curve

-     -         -             - Theoretical curve using eq. 1

Graph above shows that Boyle's law is strictly not obeyed by gases at all values of $P$ and $T$ but it obeys this law only at low pressure and high temperature i.e., at law density

Charle's Law is stated as follows:
"When pressure of a gas is constant the volume of a given mass of gas is directly proportional to its absolute temperature".

$$
\begin{equation*}
\mathrm{V} / \mathrm{T}=\text { Constant } \tag{2}
\end{equation*}
$$

Graph between V and T is


Figure2
This graph shows that experimental graph deviates from straight line. Theoritical and enperimental graphs are in agreement at high temperature.

## 2. Ideal gas equation

We can combine Boyle $\square$ s law eqn (1) and charle $\square$ s law eqn (2) in to a single eqn i.e.,
PV/T = Constant

If n moles is the mass of gas then we write
PV = nRT
where, $n$ is number of moles of gas, $R=N_{A} K_{B}$ is the universal constant known as gas constant and $T$ is the absolute temperature.
A gas satisfying eqn (4) at all values of presserves and temperatures is said to be an ideal gas now no of moles of gas
$n=m / M=N / N_{A}$
where
m - mass of gas containing N molecules
M - molar mass
$\mathrm{N}_{\mathrm{A}}$ - Avagadro $\square$ s number.
From this,
$P=\rho R T / M$
$\rho$ - mass density of gas.

## 3. Moleular nature of matter

We know that molecules which are made up of one or more atoms constitute matter.
In solids these atoms and molecules are rigidly fixed and space between then is very less of the order of few angestrem and hance they can not move.
In liquids these atoms and molecules can more enabeling liquids to flow.
In gases atoms are free to travell without colliding for large distances such that if gases were not enclosed in an enclosure they would disappear.

## 4. Dalton's law of partial pressures :

Consider a mixture of non-interacting ideal gases with $n_{1}$ moles of gas $1, n_{2}$ of gas 2 and so on
Gases are enclosed in an encloser with volume V , temperature T and pressure P .
Equation of state of mixture

$$
\begin{aligned}
& P V=\left(n_{1}+n_{2}\right) R T \\
& \text { or } \quad P=n_{1} R T / V+n_{2} R T / V+--- \\
& =P_{1}+P_{2}+--- \\
& \text { where, } \\
& P_{1}=n_{1} R T / V
\end{aligned}
$$

is pressure the gas 1 would exert at same V and T if no other gases were present in the enclosure. This is know as law of partial pressure of the gases.
The total pressure of mixture of ideal gases is sum of partial pressures of individual gases of which mixture is made of.

## 5. Kinetic Theory of an ideal gas

Following are the fundamental assumptions of kinetic theory of gases.
Gas is composed of large number of tiny invisible particles know as molecules
These molecules are always in state of motion with varying velocities in all possible directions.
Molecules traverse straight line path between any two collisions
Size of molecule is infinitely small compared to the average distance traverse by the molecules between any
two consecutive collisions.
The time of collision is negligible as compared with the time taken to traverse the path.
Molecules exert force on each other except when they collide and all of their molecular energy is kinetic.
Intermolecular distance in gas is much larger than that of solids and liquids and the molecules of gas are free to move in entire space free to them.

## 6. Pressure of gas

Consider a cubical vessel with perfectly elastic walls containing large number of molecules say N let I be the dimension of each side of the cubical vessel.
$v_{1 x}, v_{1 y}, v_{1 z}$ be the $x, y$, and $z$ componenet of a molecule with velocity $v$.
Consider the motion of molecule in the direction perpandicular to the face of cubical vessel.
Molecule strikes the face $A$ with a velocity $\mathrm{v}_{1 \mathrm{x}}$ and rebounds with the same velocity in the backward direction as the collisions are perfectly elastic.


Figure 3
If $m$ is the mass of molecule, the change in momentum during collision is

$$
\begin{equation*}
m v_{1 x}-\left(-m v_{1 x}\right)=2 m v_{1 x} \tag{1}
\end{equation*}
$$

The distance travelled parallel to $x$-axis an is between $A$ to $A^{\prime}$ and when molecule rebounds from $A^{\prime}$ and travel towards $A$ is 2 L

Time taken by molecule to go to face $A^{\prime}$ and then comeback to $A$ is

$$
\Delta t=21 / v_{1 x}
$$

Number of impacts of this molecule with $A$ in unit time is

$$
\begin{equation*}
\mathrm{n}=\mathrm{I} / \Delta \mathrm{t}=\mathrm{v}_{1 \mathrm{x}} / 2 \mathrm{I} \tag{2}
\end{equation*}
$$

Rate of change of momentum is

$$
\begin{aligned}
& \Delta \mathrm{F}=\Delta \mathrm{P} / \Delta \mathrm{t} \\
& =\mathrm{n} \Delta \mathrm{P}
\end{aligned}
$$

from (1) and (2)

$$
\Delta F=m v_{1 x}{ }^{2} / l
$$

this is the force exerted on wall A due to this movecule.
Force on wall A due to all other molecules

$$
\begin{equation*}
F=\Sigma m v_{1 x}{ }^{2} / L \tag{3}
\end{equation*}
$$

As all directions are equivalent
$\Sigma v_{1 x}{ }^{2}=\Sigma v_{1 y}{ }^{2}=\Sigma v_{1 z}{ }^{2}$
$\Sigma v_{1 x}{ }^{2}=1 / 3 \Sigma\left(\left(v_{1 x}\right)^{2}+\left(v_{1 y}\right)^{2}+\left(v_{1 z}\right)^{2}\right)$

$$
=1 / 3 \Sigma v_{1}{ }^{2}
$$

Thus $\quad F=(m / 3 L) \Sigma v_{1}{ }^{2}$
N is total no. of molecules in the container so

$$
F=(m N / 3 L)\left(\Sigma\left(v_{1}\right)^{2} / N\right)
$$

Pressure is force per unit area so

$$
\begin{aligned}
& P=F / L^{2} \\
& =\left(M / 3 L^{3}\right)\left(\Sigma\left(v_{1}\right)^{2} / N\right)
\end{aligned}
$$

where,$M$ is the total mass of the gas and if $\rho$ is the density of gas then

$$
P=\rho \Sigma\left(v_{1}\right)^{2} / 3 N
$$

since $\Sigma\left(v_{1}\right)^{2} / N$ is the average of squared speeds and is written as $v_{m q}{ }^{2}$ known as mean square speed
Thus, $\mathrm{v}_{\mathrm{rms}}=\sqrt{ }\left(\Sigma\left(\mathrm{v}_{1}\right)^{2} / \mathrm{N}\right)$ is known as roon mean squared speed rms-speed and $\mathrm{v}_{\mathrm{mq}}{ }^{2}=\left(\mathrm{v}_{\mathrm{rms}}\right)^{2}$
Pressure thus becomes

$$
\begin{equation*}
P=(1 / 3) \rho v_{m q}{ }^{2} \tag{4}
\end{equation*}
$$

or $\quad P V=(1 / 3) \mathrm{Nmv}_{\mathrm{mq}}{ }^{2}$
from equation (4) rms speed is given as

$$
\begin{align*}
v_{\mathrm{rms}} & =\sqrt{ }(3 \mathrm{P} / \rho) \\
& =\sqrt{ }(3 \mathrm{PV} / \mathrm{M}) \tag{6}
\end{align*}
$$

## 7. Kinetic interpretation of temperature

From equation (5) we have

$$
\mathrm{PV}=(1 / 3) \mathrm{Nmv}_{\mathrm{mq}}{ }^{2}
$$

where N is the number of molecules in the sample. Above equation can also be written as

$$
\begin{equation*}
\mathrm{PV}=(2 / 3) \mathrm{N}(1 / 2) \mathrm{Nmv}_{\mathrm{mq}}{ }^{2} \tag{7}
\end{equation*}
$$

The quantity $(1 / 2) \mathrm{Nmv}_{\mathrm{mq}}{ }^{2}$ in equation (7) is the kinetic energy of molecules in the gas. Since the internal energy of an ideal gas is purely kinetic we have,
$\mathrm{E}=(1 / 2) \mathrm{Nmv}_{\mathrm{mq}}{ }^{2}$
Combining equation 7 and 8 we get
$P V=(2 / 3) E$
Comparing this result with the ideal gas equation (equation (4)) we get

$$
\begin{equation*}
\mathrm{E}=(3 / 2) \mathrm{K}_{\mathrm{B}} \mathrm{NT} \tag{9}
\end{equation*}
$$

or, $\quad E / N=(1 / 2) \mathrm{mv}_{\mathrm{mq}}{ }^{2}=(3 / 2) \mathrm{K}_{\mathrm{B}} T$
Where, $K_{B}$ is known as Boltzmann constant and its value is $K_{B}=1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}$
From equation (11) we conclude that the average kinetic energy of a gas molecule is directly proportional to the absolute temperature of the gas and is independent of the pressure, volume and nature of the gas.
Hence average KE per molecule is
$(1 / 2) \mathrm{mv}^{2-}=(3 / 2) \mathrm{K}_{\mathrm{B}}{ }^{\top}$
from this since $v^{2-}=\left(v_{\mathrm{rms}}\right)^{2}$, rms velocity of a molecule is

$$
\begin{equation*}
v_{\mathrm{rms}}=\sqrt{ }\left(3 \mathrm{~K}_{\mathrm{B}} \mathrm{~T} / \mathrm{m}\right) \tag{10}
\end{equation*}
$$

This can also be written as

$$
\begin{align*}
& \mathrm{V}_{\mathrm{rms}}=\sqrt{ }\left(3 K_{B} N T / N m\right) \\
& =\sqrt{ }(3 R T / M) \tag{11}
\end{align*}
$$

where, $\mathrm{M}=\mathrm{mN}$ is the molecular mass of the gas.

Assignment
(1)Gas laws (Boyle's and charle's law) and perfect gas equation can be derived using kinetic theory of gases. try to derive them.

## 7. Law of Equipartition of energy

According to the principle of equipartition of energy, each velocity component has, on the average, an associated kinetic energy (1/2)KT.
The number of velocity components needs to describe the motion of a molecule completely is called the number of degrees of freedom.
For a mono atomic gas there are three degrees of freedom and the average total KE per molecule for any monotomic gas is $3 / 2 \mathrm{~K}_{\mathrm{B}} T$.

## 8. Specific Heat Capacity

## (i) Monoatomic gases :

Monoatemic gas moleules has three translational degrees of freedom.
From law of equipartition of energy average energy of an molecule at temperature $T$ is $(3 / 2) \mathrm{K}_{B} T$
Total internal energy of one mole of such gas is

$$
\begin{align*}
\mathrm{U} & =(3 / 2) \mathrm{K}_{\mathrm{B}} \mathrm{TN} \\
= & (3 / 2) \mathrm{RT} \tag{12}
\end{align*}
$$

If $\mathrm{C}_{\mathrm{V}}$ is melar specific heat at constant volume then

$$
\begin{align*}
& C_{V} \mathrm{~V}=\mathrm{dU} / \mathrm{dT} \\
& =(3 / 2) \mathrm{R} \tag{13}
\end{align*}
$$

now for an ideal gas

$$
C_{P}-C_{V}=R
$$

$C_{P}$ - molar specific heat capacity at constant presseve

$$
\begin{equation*}
C_{P}=5 / 2 R \tag{14}
\end{equation*}
$$

Thus for a monoatomic gas ratio of specific heats is

$$
\begin{equation*}
V_{\text {mono }}=C_{P} / C_{V}=5 / 3 \tag{15}
\end{equation*}
$$

A diatomic gas molecule is treated as a rigid rotator like dumb-bell and has 5 degrees of freedom out of which three degrees of freedom are translatoinal and two degrees of freedom are rotational.
Using law of equipartition of energy the total internal energy of one mole of diatomic gas is

$$
\begin{align*}
& \mathrm{U}=(5 / 2) \mathrm{K}_{\mathrm{B}} \mathrm{TN} \\
& =(5 / 2) \mathrm{RT} \tag{16}
\end{align*}
$$

Specific heats are thus
$C_{V}=(5 / 2) R$
$Y_{\text {dia }}=5 / 7 \quad$ (rigid rotater)
If diatomic molecule is not only rigid but also has an vibrational mode in addition, then

$$
\begin{gathered}
\mathrm{U}=(7 / 2) \mathrm{RT} \\
\text { and } C_{V}=(7 / 2) \mathrm{R} \\
\mathrm{C}_{\mathrm{P}}=(9 / 2) \mathrm{R} \\
\text { and } \mathrm{V}=\mathrm{C}_{\mathrm{P}} / \mathrm{C}_{\mathrm{V}}=9 / 7
\end{gathered}
$$

## 9. Specific heat Capacity of Solids

From law of equipartation of energy we can can also determine specific heats of solids.
Consider that atoms in a solid are vibrating about their mean position at some temperature T .
Oscillation in one dimension has average energy equals $2(1 / 2) K_{B} T=K_{B} T$, as $(1 / 2) K_{B} T$ is $P E$ and $(1 / 2) K_{B} T$ is $K E$ of the atom.
In three dimensions average kinetic energy is $3 \mathrm{~K}_{\mathrm{B}} \mathrm{T}$.
For one mole of solid total energy is

$$
\begin{aligned}
& \mathrm{U}=3 \mathrm{NK}_{\mathrm{B}} \mathrm{~T} \\
& =3 \mathrm{RT}
\end{aligned}
$$

At constant pressure $\Delta Q=\Delta U+P \Delta V=\Delta U$ since for solids $\Delta V$ is negligible hence
$C=\Delta Q / \Delta T=\Delta U / \Delta T=3 R$
This is Dulang and Petit law.
Here we note that predictions of specific heats of solids on the basis of law of equipetation of energy are independent of temperature.
As we go towards low temperatures $T \rightarrow 0$ there is a pronounced departure from the value of specific heat of solids as calculated.
It is seen that specific heats of substance aproaches to zero as $\mathrm{T} \rightarrow 0$.
This result can further be explained using the principles of quantum mechanics which is beyond our scope.

Kinetic Theory Of Gases

## 10. Mean free Path

On the basis of kinetic theory of gases, it is assumed that the molecules of a gas are continously collilding against each other.
Molecules move in straight line with constant speeds between two successive collisions.
Thus path of a single molecule is a series of zig-zag paths of different lengths as shown in fig -.


Figure 4
These paths of different lengths are called free paths of the molecule

Mean Free Path is the averege distance traversed by molecule between two successive collisions.
If $s$ is the Total path travelled in $N_{\text {coll }}$ coilisions, then mean free path

$$
\lambda=\mathrm{s} / \mathrm{N}_{\text {coll }}
$$

Expression for mean free path :
Consider a gas containing $n$ molecules per unit volume.
We assume that only one molecule which is under consideration is in motion while all others are at rest.
If $\sigma$ is the diameter of each molecule then the moving molecule will collide with all these molecules where centers lie within a distance from its centre as shown in fig

$\sigma$
Figure $5 a$


Figure $5 b$

If $v$ is the velocity of the moving molecule then in one second it will collide with all moleculeswith in a distance $\sigma$ between the centres.
In one second it sweeps a volume $\pi \sigma^{2} v$ where any other molecule will collide with it.
If $n$ is the total number of molecules per unit volume, then $n \pi \sigma^{2} v$ is number of collisions a molecule suffers in one second.
If $v$ is the distance traversed by molecule in one second then mean free path is given by
$\lambda=$ total distance traversed in one second /no. of collision suffered by the molecules
$=\mathrm{v} / \pi \sigma^{2} \mathrm{vn}$
$=1 / \pi \sigma^{2} n$
This expression was derived with the assumption that all the molecules are at rest except the one which is colliding with the others.
However this assumption does not represent actual state of affiar.
More exact statement can be derived considering that all molecules are moving with all possible velocities in all possible directions.
More exact relation found using distribution law of molecular speeds is

$$
\lambda=1 /(\sqrt{ } 2) \pi \sigma^{2} n
$$

its derivation is beyond our scope.

Question-1.Let A \& B are two sample of ideal gases of equal mole .let $T$ be the temperature of both the gas
Let $E_{A}$ and $E_{B}$ are there total energy respectively .Let $M_{A}$ and $M_{B}$ are these respective molecular mass which of these is true
$a, E_{A}>E_{B}$
$\mathrm{b}, \mathrm{E}_{\mathrm{A}}<\mathrm{E}_{\mathrm{B}}$
$\mathrm{c}, \mathrm{E}_{\mathrm{A}}=\mathrm{E}_{\mathrm{B}}$
d ,none of these

## Solution:1 <br> $\mathrm{E}_{\mathrm{A}}=3 / 2 \mathrm{nRT}$ <br> $\mathrm{E}_{\mathrm{B}}=3 / 2 \mathrm{nRT}$ <br> ; $\mathrm{E}_{\mathrm{A}}=\mathrm{E}_{\mathrm{B}}$

Question-2. The velocities of the molecules are $\mathrm{v}, 2 \mathrm{v}, 3 \mathrm{v}, 4 \mathrm{v} \& 5 \mathrm{v}$. The rms speed will be a,11v
b, $\mathrm{v}(11)^{1 / 2}$
c, v
d, 3.3 v

## Solution:2

Vrms $=\left(\Sigma \mathrm{V}^{2} / \mathrm{N}\right)^{1 / 2}$
$=\left[\left(\mathrm{V}^{2}+4 \mathrm{~V}^{2}+9 \mathrm{~V}^{2}+16 \mathrm{~V}^{2}+25 \mathrm{~V}^{2}\right) / 5\right]^{1 / 2}$
$=\mathrm{v}(11)^{1 / 2}$

## Question-3:

An ideal gas A is there. Intial temperature is $27^{\circ} \mathrm{C}$. The temperature of the gas is increased to $927^{\circ} \mathrm{C}$. Find the ratio of final $\mathrm{V}_{\mathrm{rms}}$ to the initial $\mathrm{V}_{\mathrm{rms}}$

## Solution-9:

$\mathrm{V}_{\mathrm{rms}}=\sqrt{ } 3 R T / \mathrm{M}$

So it is proportional to Temperature
Now
$\mathrm{T}_{1}=27^{\circ} \mathrm{C}=300 \mathrm{~K}$
$\mathrm{T}_{2}=927^{\circ} \mathrm{C}=1200 \mathrm{~K}$

So intial $V_{\text {rms }}=k \sqrt{ } 300$
Final $V_{\text {rms }}=k \sqrt{ } 1200$
ratio of final to intial=2:1

Question-. 4 Two absolute scales $A$ and $B$ have triple points of water defined as $200 A$ and $350 A$. what is the relation between $T_{A}$ and $T_{B}$

## Solution-4

Given that on absolute scale
Triple point of water on scale $A=200 \mathrm{~A}$
Triple point of water on scale $B=350 B$
Also, triple point of water on Kelvin scale $=273.16 \mathrm{~K}$
Now temperature on scale A and on scale B is equivalent to 273.16 K on absolute temperature scale.
Thus, value of one degree on absolute scale $A=(273.16 / 200) \mathrm{K}$
Or,
Value of temperature $T_{A}$ on absolute scale $A=\left(273.16 X T_{A}\right) / 200$
Similarly value of temperature $T_{B}$ on absolute scale $B=\left(273.16 X T_{B}\right) / 350$

Since $T_{A}$ and $T_{B}$ represent the same temperature
$273.16 \times T_{A} / 200=273.16 \times T_{B} / 350$
Or, $\mathrm{T}_{\mathrm{A}}=200 \mathrm{~T}_{\mathrm{B}} / 350=4 \mathrm{~T}_{\mathrm{B}} / 7$

Question-. 5 . which one is not the assumption in kinetic theory of gases
a.the molecules of the gas are in continual random motion
b. The molecules interact during the collison
c. The molecules are tiny hard sphere undergoing inelastic collision
d. The collison are of short duration

## Solution-5

Answer is c

## Question-.6.

There are two statement
A. Equal volumes of all gases at the same temperature T and pressure P contain an equal no of Molecules
B.the no of molecules in one mole of any gas is $6.0255 * 10^{22}$.
which one of the following is correct
a. A and B both
b. A only
c B only
d. A and B both are incorrect

## Solution-6

Answer is $b$

Question-.7. .There are two statement about Ideal gases
A. The $\mathrm{V}_{\mathrm{rms}}$ of gas molecules depends on the mass of the gas molecule and the temperature
B. The $\mathrm{V}_{\mathrm{rms}}$ is same for all the gases at the same temperature
which one of the following is correct
a. A and B both
b. A only
c B only
d. A and B both are incorrect

## Solution-7

Answer is $b$

Question-.8. .Choose the correct statement of the following
a. The pressure of the gas is equal to the total kinetic energy of the molecules in a unit volume of the gas
b. The product of pressure and volume of the gas is always constant
c. The average kinetic energy of molecule of the gas is proportional to its absolute temperature
d. The average kinetic energy of molecule of the gas is proportional to the square root of its absolute temperature

## Solution-8

Answer is c

Question-.9...which one is true according Vander Waal gas equation
a. The attractive forces between the molecules is not negligible
b Volume of the molecules is negligible as compared to the volume occupied by the gas
c. Volume of the molecules is not negligible as compared to the volume occupied by the gas
d. The attractive forces between the molecules is negligible

## Solution-9

Answer is a,c

Thermodynamics

## 1. Introduction

Thermodynamics is that branch of physics which is concerned with transformation of heat into mechanical work.
It deals with the concepts of heat, temperature and interconversion of heat into other forms of energy i.e., electrical, mechnical, chemical magnetic etc.
Thermodynamics does not take any account of atomic or molecular constitution of matter and it deals with the bulk systems.
State of any thermodynamic system can be described in terms of certain know macroscopic variables known as thermodynamic variables.
Thermodynamic variables determine the thermodynamic behaviour of a system . Quantities like pressure(P), volume $(\mathrm{V})$, and temperature( T ) are thermodynamic variables. Some other thermodynamic variables are entropy, internal energy etc. described in terms of $P, V$ and $T$
A thermodynamic system is said to be in thermal equilibrium if all parts of it are at same temperature.
Thus two systems are said to be in thermal equilibrium if they are at same temperature.

## 2. Concept of Heat

Heat may be defined as energy in transit.
Word heat is used only if there is a transfer of energy from one thermodynamic system to the another.

When two systems at different temperatures are kept in contect with each other then after some time temperatures of both the syatems become equal and this phenomenon can be described by saying that energy has flown from one system to another.
This flow of energy from one system to another on account of temperature difference is called heat transfer.
Flow of heat is a non-mechanical mode of energy transfer.
Heat flow depends not only on initial and find states but also on path it's.

## 3. P-V Indicator Digram

Only two thermodynamic variables are sufficient to describe a system because third vaiable can be calculated from equation of state of the system.
$\mathrm{P}-\mathrm{V}$ Indicator Digram is just a graph between pressure and volume of a system undergoing an operation. When a system undergoes an expansion from state $A\left(P_{1} V_{1}\right)$ to a state $B\left(P_{2} V_{2}\right)$ its indicator digram is shown as follows.


Figure 1
In case of compression system at state $A\left(P_{1} V_{1}\right)$ goes to a state $B\left(P_{2} V_{2}\right)$ its indicator digram is as follows.


Figure 2

Intermediate states of system are represented by points on the curve.
The pressure volume curve for a fixed temperature is called isotherm.

## 4. Work in volume changes

Consider a cylinder filled with gas and equiped with a movable piston as shown in fig below


Figue 3: Force exerted by a system during small exparsion
fig - Force exerted by a system during small expansion.
Suppose,
A - Cross Sectional area of cylinder
P - Pressure exerted by piston at the piston face.
PA - Force exerted by the system.
If piston moves out by a distance dx then work done by this force is dW given by
dW = PAdx

$$
\begin{equation*}
=\mathrm{PdV} \tag{1}
\end{equation*}
$$

since $V=A d x$ and $d V$ is change in volume of the system.
In a finite volume change from $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$

$$
\begin{equation*}
W=\int P d V \tag{2}
\end{equation*}
$$

where limits of integration goes from $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$
Graphically this relationship is shown below


Thus eqn (2) can be interpreted graphically as area under the curve between limits $\mathrm{V}_{1}$ and $\mathrm{V}_{2}$.
If pressure remains constant while the volume changes, then work is

$$
\begin{equation*}
\mathrm{W}=\mathrm{P}\left(\mathrm{~V}_{2}-\mathrm{V}_{1}\right) \tag{3}
\end{equation*}
$$

Work done not only depends on initial and final states but also on the intermediate states i.e., on the path. Learning:Work done in a process is given by area under the process on the PV diagram

## 5. Internal Energy and first law of thermodynamics

Internal energy can be described as the sum of kinetic and potantial energies of individual movecules in the material.

But in thermodynamics one should keep in mind that $U$ is simply a macrosopic variable of the system. U is thermodynamic state variable and its value depends only on the given state of the system and not on path taken to arrive the state.
Transfer of heat and performance of work are two mean of adding or subtracting energy from a system. On transfer of energy, system is said to have undergone a change in internal energy.
Thus the sum of heat put into the system plus work done on the system equals increase in internal energy of the system for any process.
if, $U_{1}$ is internal energy of state 1 and $U_{2}$ is internal energy of state 2 than change in internal energy would be

$$
\Delta \mathrm{U}=\mathrm{U}_{2}-\mathrm{U}_{1}
$$

If W is the work done by the system on its surroundings then -W would be the work done on the system by the surroundings .
If $Q$ is the heat put into the system then,

$$
Q+(-W)=\Delta U
$$

usually written as

$$
\begin{equation*}
Q=\Delta U+W \tag{4}
\end{equation*}
$$

Equation (4) is then know as first law of thermodynamics and it can be applied when
$Q, W$ and $U$ are expressed in same units.
Some Imp stuff (1) $Q$ is positive when heat is given to the system and $Q$ is negative when heat is taken from the system
(2) W is positive when system expands and does work on surroundings

Hence we may say that when a certain amount of heat $Q$ is given to the system then some part of it is used in increasing internal energy $\Delta U$ of the system while remaining part leaves the system in form of work done by the system on its surroundings.
From equation 4 we see that first law of thermodynamics is a statement of conservation of energy stated as
' The energy put into the system equals the sum of the work done by the system and the change in internal energy of the system'
If the system undergoes any process in which $\Delta \mathrm{U}=0$ i.e., charge in internal energy is zero then from (4)
$Q=W$
that is heat supplied to the system is used up enterely in doing work on the surroundings.

## 6. Specific heat capacity of an ideal gas

We have defined specific heat capacity and molar specific heat capacity earlier in the previous chapter.
There are two specific heats of ideal gases.
(i) Specific heat capacity at constant volume
(ii) Specific heat capacity at constant pressure
$C_{p}$ and $C_{v}$ are molar specific heat capacities of ideal gas at constant pressure and volume respectively for $C_{p}$ and $C_{V}$ of ideal gas there is a simple relation.

$$
\begin{equation*}
C p-C v=R \tag{7}
\end{equation*}
$$

where R- universal gascontant
This relation can be proved as follows.
from first law of thermaodynamics for 1 mole of gas we have

$$
\begin{equation*}
\Delta Q=\Delta U+P \Delta V \tag{8}
\end{equation*}
$$

If heat is absorbed at constant volume then $\Delta V=0$ and

$$
\begin{equation*}
\mathrm{C}_{\mathrm{V}}=(\Delta \mathrm{Q} / \Delta \mathrm{T})_{\mathrm{V}}=(\Delta \mathrm{U} / \Delta \mathrm{T})_{\mathrm{V}} \tag{9}
\end{equation*}
$$

If $Q$ in absorbed at constant pressure than

$$
\mathrm{C}_{\mathrm{P}}=(\Delta \mathrm{Q} / \Delta \mathrm{T})_{\mathrm{P}}=(\Delta \mathrm{U} / \Delta \mathrm{T})_{\mathrm{P}}+\mathrm{P}(\Delta \mathrm{~V} / \Delta \mathrm{T})_{\mathrm{P}}
$$

now ideal gas equation for 1 mole of gas is

$$
\begin{align*}
& P V=R T \\
& =P(\Delta V / \Delta T)=R \tag{10}
\end{align*}
$$

from (9) and (10)
$\mathrm{C}_{\mathrm{P}}-\mathrm{C}_{\mathrm{V}}=(\Delta \mathrm{U} / \Delta \mathrm{T})_{\mathrm{P}}-(\Delta \mathrm{U} / \Delta \mathrm{T})_{\mathrm{V}}+\mathrm{P}(\Delta \mathrm{V} / \Delta \mathrm{T})_{\mathrm{P}}$
Since internal energy $U$ of ideal gas depands only on temperature so subscripts $P$ and $V$ have no meaning.

$$
\Rightarrow \quad C_{P}-C_{V}=R
$$

## 7. Thermodynamic Processes

a) Quasi static Processes:

In Quasi static process deviation of system from it's thermodynamic equilibrium is infinitesimally small.

All the states through which system passed during a quasi static process may be regarded as equilibrium states.

Consider a system in which gas is contained in a cylinder fitted with a movable piston then if the piston is pushed in a infinitely slow rate, the system will be in quiscent all the time and the process can be considered as quasi-static process.
Vanishingly slowness of the process is an essential feature of quasi-static process.

During quasi-static process system at every moment is infinitesimally near the state of thermodynamic equilibrium. Quasi static process is an idealized concept and its conditions can never be rigoursly satisfied in practice.

## (b) Isothermal Process

In isothermal process temperature of the system remains constant throughout the process.
For an iso-thermal process equation connecting $\mathrm{P}, \mathrm{V}$ and T gives. PV = constant
i.e., pressure of given mass of gas varies inversly with its volume this is nothing but the Boyle's law.
In iso thermal process there is no change in temperature, since internal energy for an ideal gas depends only on temperature hence in iso thermal process there is no change in internal energy. Thus,
$\Delta \mathrm{U}=0$
therefore, $\quad \Delta \mathrm{Q}=\Delta \mathrm{W}$
Thus during iso thermal process
Heat added (or substacted) from the system = wok done by (or on) the system

## (c) Adiabatic Process

Process in which no heat enters or leaves a system is called an adiabatic process

For every adiabatic process $\mathrm{Q}=0$
Prevention of heat flow can be acomplished by surrounding system with a thick layer of heat insulating material like cork, asbestos etc. Flow of heat requires finite time so if a process is perfomed very quickly then process will be pratically adiabatic. On applying first law to adiabatic process we get
$\Delta \mathrm{U}=\mathrm{U}_{2}-\mathrm{U}_{1}=-\Delta \mathrm{W}$
(adiabatic process)

In adiabatic process change in internal energy of a system is equal in magnitade to the work by the system.
If work is done on the system contracts i.e. $\Delta \mathrm{W}$ is nagative then.

## $\Delta \mathrm{U}=\Delta \mathrm{W}$

and internal energy of system increases by an amount equal to the work done on it and temperature of system increases.
If work is done by the system i.e., $\Delta \mathrm{W}$ is negative

$$
\Delta U=-\Delta W
$$

here internal energy of systems decreases resulting a drop in temperature.

## (d) Isochoric process v:

In an isochoric process volume of the system remain uncharged throughout i.e. $\Delta \mathrm{V}=0$.
When volume does not change no work is done ; $\Delta \mathrm{W}=0$ and therefore from first law

$$
U_{2}-U_{1}=\Delta U=\Delta Q
$$

All the heat given to the system has been used to increase the intenal energy of the system.

## (e) Isobaric Process

A process taking place at constant pressure is called isobaric process.

From equation (3) we see that work done in isobaric process is

$$
W=P\left(V_{2}-V_{1}\right) n R\left(T_{2}-T_{1}\right)
$$

where pressure is kept constant.
Here in this process the amount of heat given to the system is partly used in increasing temperature and partly used in doing work.

## 8. Work done in Isothermal process

In an isothermal process temperature remains constant.
Consider pressure and volume of ideal gas changes from $\left(\mathrm{P}_{1}, \mathrm{~V}_{1}\right)$ to $\left(\mathrm{P}_{2}, \mathrm{~V}_{2}\right)$ then, from first law of thermodynamics
$\Delta W=P \Delta V$
Now taking $\Delta \mathrm{V}$ aproaching zero i.e. $\Delta \mathrm{V}$ and suming $\Delta \mathrm{W}$ over entire process we get total work done by gas so we have
$W=\int P d V$
where limits of integration goes from $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$
as $\mathrm{PV}=\mathrm{nRT}$ we have $\mathrm{P}=\mathrm{nRT} / \mathrm{V}$
$\mathrm{W}=\int(\mathrm{nRT} / \mathrm{V}) \mathrm{dV}$
where limits of integration goes from $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$
on integrating we get,
$W=n R T \ln \left(V_{2} / V_{1}\right)$
Where n is number of moles in sample of gas taken.

## 9. Work done in an Adiabatic process

For an adiabatic process of ideal gas equation we have

Where $\gamma$ is the ratio of specific heat (ordinary or molar) at constant pressure and at constant voluume

$$
\mathrm{V}=\mathrm{C}_{\mathrm{p}} / C_{v}
$$

Suppose in an adiabatic process pressure and volume of a sample of gas changs from $\left(P_{1}, V_{1}\right)$ to $\left(P_{2}, V_{2}\right)$ then we have

$$
P_{1}\left(V_{1}\right)^{\mathrm{V}}=\mathrm{P}_{2}\left(\mathrm{~V}_{2}\right)^{\mathrm{Y}}=\mathrm{K}
$$

Thus, $P=K / V Y$
Work done by gas in this process is

$$
\mathrm{W}=\int \mathrm{PdV}
$$

where limits of integration goes from $\mathbf{V}_{1}$ to $\mathbf{V}_{\mathbf{2}}$
Putting for $\mathrm{P}=\mathrm{K} / \mathrm{V}^{\Upsilon}$, and integrating we get,

$$
\begin{equation*}
W=\left(P_{1} V_{1}-P_{2} V_{2}\right) /(\gamma-1) \tag{16}
\end{equation*}
$$

In and adiabatic process if $\mathbf{W}>0$ i.e., work is done by the gas then $T_{2}<T_{1}$ If work is done on the gas $(\mathrm{W}<0)$ then $\mathrm{T}_{2}>\mathrm{T}_{1}$ i.e., temperature of gas rises.

## 10. Heat Engine and efficiency

Any device which convents heat continously into mechenical work is called a heat engine.
For any heat engine there are three essential requirements.
(i) SOURCE : A hot body at fixed temperature $T_{1}$ from which heat engine can draw heat (ii) Sink: A cold body, at a fixed lower temprature $T_{2}$, to which any amount of heat can be rijectd.
(iii) WOEKING SUBTANCE : The material, which on being supplied with heat will do mechanical work.

In heat engine, working substances, could be gas in cylinder with a moving piston. In heat engine working substance takes heat from the sorce, convents a part of it into mechanical work, gives out rest to the sink and returns to the initial state. This series of operations constitutes a cycle.
This cycle is represented in fig below


Figure 5
Work from heat engine can be continously obtained by performing same cycle again and again.

Consider,
Q1 - heat absorbed by working substance from sorce
$\mathrm{Q}_{2}$ - heat rejected to the since
W - net amount of work done by working substance
$\mathrm{Q}_{1}-\mathrm{Q}_{2}$ - net amount of heat absorbed by working substance.
$\Delta U=0$ since in the cycle Working Substance returns to its initial condition.
So on application of first law of thermodynamics
$Q_{1}-Q_{2}=W$
Thermal efficiency of heat engine
$\eta=$ work output in energy units / Heat input in same energy units
$=W / Q_{1}=\left(Q_{1}-Q_{2}\right) / Q_{1}$
Or, $n=1-\left(Q_{2} / Q_{1}\right)$
from this equation it is clear that
$Q=1$ for $Q_{2}=0$
and there would be $100 \%$ conversion of heat absorbed into work but such ideal engines are not possible in practice.

## 11. Principle of a Refrigerator

Refrigerators works in reverse direction of heat engines.
In refrigerators working substance extracts heat $Q_{2}$ from sink at lower temperature $T_{2}$
Some external work is performed by the compressor of refrigerator and then heat $Q_{1}$ is rejected to the source, to the radiator of the refrigerator.


Figure 6
Coefficent of performance :
$\beta=$ Amount of heat absorbed from the cold reservoir / work done in running the mechinery
$Q_{2}$ - heat absorbed from cold reservoir.
$Q_{1}$ - heat rejected to hot reservoir during one complete cycle
$\mathrm{W}=\left(\mathrm{Q}_{1}-\mathrm{Q}_{2}\right)$ is the work done in running the machinery
thus,

$$
\begin{equation*}
\beta=Q_{2} / W=Q_{2} /\left(Q_{1}-Q_{2}\right) \tag{18}
\end{equation*}
$$

Like heat engines refrigerators can not work without some external work done on the system. Hence coefficent of performance can not be infinite.

## 12. Second law of thermodynamics

First law of thermodynamics states the equivalance of heat and energy.
It does not state anything about the limitation in the conversion of heat into work or about the condition necessary for such conversion.

Second law of thermodynamics is generalization of certain experience and observation and is concerned with tine direction in which energy flow takes place.
This law can be stated in number of ways. Although differently said, they are essentially equvalent.
(i)Kelvin Plank Statment :
"It is impossible to construct a device which, operating in a cycle, has a sole effect of extracting heat from a reservoir and performing an equivalent amount of work".
(ii)Clasius Statement :
"It is impossible for a self acting machine, unaided by enternal agency, to transfer heat from a colder body to a hotter body".
It can ne proved that these two statements of second law are completely equivalent and voilation of Kelvin Plank statement leads to voilation of Clasius statement and vice-versa.

## 13. Reversibility and irreversibility

Reversible process is the one which can be retraced in opposite order by changing external conditions slightly. Those processes which can not be retraced in opposite order by reversing the controling factors are known as irreversible process.
It is a consequence of second law that all the natural processes are irreversible process. Conditions for reversibility of a process are
(i) Process is performed quasi-statically
(ii) it is not accompained by any dissipative effects.

It is impossible to satisfy these two conditions perfectly, thus requessible process is purely an ideal abstraction.

## 14. Carnot's Heat Engine

According to second law of thermodynamics, no heat engine can have $100 \%$ efficiency
Carnot $\square$ s heat engine is an idealized heat engine that has maximum possible efficiency consistent with the second law.
Cycle through which working substance passed in Carnot $\square$ s engine is known as Carnot $\square$ s Cycle.
Carnot's engine works between two temperatures
$\mathrm{T}_{1}$ - temperature of hot reservoir
$\mathrm{T}_{2}$ - temperature of cold reservoir
In a Complete Carnot's Cycle system is taken from temperature $T_{1}$ to $T_{2}$ and then back from temerature $\mathrm{T}_{2}$ to $\mathrm{T}_{1}$.
We have taken ideal gas as the working substance of cornot engine.
Fig below is an indicator digram for Cornot Cycle of an ideal gas


## Figure 7

(i) In step $\mathrm{b} \rightarrow \mathrm{c}$ iso thermal esepansion of gas taken place and thermodynamic variables of gas changes from $\left(\mathrm{P}_{1}, \mathrm{~V}_{1}, \mathrm{~T}_{1}\right)$ to $\left(\mathrm{P}_{2}, \mathrm{~V}_{2}, \mathrm{~T}_{1}\right)$
If $Q_{1}$ is the amount of heat absorbed by working substance from the source and $W_{1}$ the work done by the gas then from eqn (13)

$$
\begin{equation*}
Q_{1}=W_{1}=n R T 1 \ln \left(V_{2} / V_{1}\right) \tag{19}
\end{equation*}
$$

as process is iso thermal.
(ii) Step $\mathrm{c} \rightarrow \mathrm{d}$ is an adiabatic expension of gas from $\left(\mathrm{P}_{2}, \mathrm{~V}_{2}, \mathrm{~T}_{1}\right)$ to $\left(\mathrm{P}_{3}, \mathrm{~V}_{3}, \mathrm{~T}_{2}\right)$. Work done by gas in adiabatic esepansion is given by eqn (16)

$$
\begin{equation*}
W_{2}=n R\left(T_{1}-T_{2}\right) /(\gamma-1) \tag{20}
\end{equation*}
$$

(iii)Step $d \rightarrow a$ is iso-thermal compression of gas from $\left(P_{3}, V_{3}, T_{2}\right)$ to $\left(P_{4}, V_{4}, T_{2}\right)$. Heat $Q_{2}$ would be released by the gas to the at temperature $\mathrm{T}_{2}$
Work done on the gas by the environment is

$$
\begin{align*}
W_{3} & =Q_{2} \\
& =n R T_{2} \ln \left(V_{3} / V_{4}\right) \tag{21}
\end{align*}
$$

(iv)Step $\mathrm{a} \rightarrow \mathrm{b}$ is adiabatic compression of gas from $\left(\mathrm{P}_{4}, \mathrm{~V}_{4}, \mathrm{~T}_{2}\right)$ to $\left(\mathrm{P}_{1}, \mathrm{~V}_{1}, \mathrm{~T}_{1}\right)$

Work done on the gas is

$$
\begin{equation*}
\mathrm{W}_{4}=\mathrm{nR}\left(\mathrm{~T}_{1}-\mathrm{T}_{2}\right) /(\mathrm{\gamma}-1) \tag{22}
\end{equation*}
$$

Now total work done in one complete cycle is

$$
W=W_{1}+W_{2}-W_{3}-W_{4}
$$

$$
\begin{equation*}
=n R T_{1} \ln \left(V_{2} / V_{1}\right)-n R T_{2} \ln \left(V_{3} / V_{4}\right) \tag{23}
\end{equation*}
$$

as $W_{2}=W_{4}$

Efficency of carnot engine

$$
\begin{align*}
& \eta=W / Q_{1}=1-\left(Q_{2} / Q_{1}\right) \\
& =1-\left(T_{2} / T_{1}\right) \ln \left(V_{3} / V_{4}\right) / \ln \left(V_{2} / V_{1}\right)  \tag{24}\\
& \text { or } \quad \eta=1-\left[T_{2} \ln \left(V_{3} / V_{4}\right) / T_{1} \ln \left(V_{2} / V_{1}\right)\right] \tag{25}
\end{align*}
$$

Since points $b$ and $c$ lie on same iso thermal

$$
\begin{equation*}
P_{1} V_{1}=P_{2} V_{2} \tag{26}
\end{equation*}
$$

also points $c$ and $d$ lie on same adiabatic

$$
\begin{equation*}
P_{2}\left(V_{2}\right)^{\mathrm{V}}=\mathrm{P}_{3}\left(\mathrm{~V}_{3}\right)^{\mathrm{V}} \tag{27}
\end{equation*}
$$

also points $d$ and a lie on same iso thermal and points $a$ and $b$ on sum adiabatic thus,

$$
\begin{align*}
& \mathrm{P}_{3} \mathrm{~V}_{3}=\mathrm{P}_{4} \mathrm{~V}_{4}  \tag{28}\\
& \mathrm{P}_{4}\left(\mathrm{~V}_{4}\right)^{\mathrm{Y}}=\mathrm{P}_{2}\left(\mathrm{~V}_{1}\right)^{\mathrm{Y}} \tag{29}
\end{align*}
$$

multiplying all the above four eqns me get

$$
\begin{equation*}
V_{3} /_{4}=V_{2} / V_{1} \tag{30}
\end{equation*}
$$

Putting this in equation (25) we get

$$
\begin{equation*}
\eta=1-\left(T_{2} / T_{1}\right) \tag{31}
\end{equation*}
$$

From above eqn we can draw following conclusions that efficency of Carnot engine is
(i) independent of the nature of working substance
(ii) depend on temperature of source and sink

## 15. Carnot Theorem

Carnot Engine is a reversible engine.
Carnot $\square$ s theorem consists of two parts
(i) no engine working between two given temperatures can be more efficent than a reversible Carnot engine working between same source and sink.
(ii) all reversible engines working between same source and sink (same limits or temperature) have the same efficiency irrespective the working substance.

Question-1. What is true of Isothermal Process
a, $\Delta T>0$
b, $\Delta \mathrm{U}=0$
c $\Delta Q=\Delta W$
d $\mathrm{PV}=$ constants

## Solution-1:

In an Isothermal Process
Temperature remains constant $\Delta T=0$
Since Internal energy depends on the temperature
$\Delta U=0$

From first law of Thermodynamics
$\Delta U=\Delta Q-\Delta W$
Since $\Delta U=0$
$\Delta Q=\Delta W$

Also PV=nRT
As T is constant
PV= constant

Question-. 2 Two absolute scales A and B have triple points of water defined as 200A and 350A. what is the relation between $T_{A}$ and $T_{B}$

## Solution-2

Given that on absolute scale
Triple point of water on scale A $=200 \mathrm{~A}$
Triple point of water on scale $B=350 \mathrm{~B}$
Also, triple point of water on Kelvin scale $=273.16 \mathrm{~K}$
Now temperature on scale $A$ and on scale $B$ is equivalent to 273.16 K on absolute temperature scale.
Thus, value of one degree on absolute scale $A=(273.16 / 200) \mathrm{K}$ Or,
Value of temperature $\mathrm{T}_{\mathrm{A}}$ on absolute scale $\mathrm{A}=\left(273.16 \mathrm{X} \mathrm{T}_{\mathrm{A}}\right) / 200$
Similarly value of temperature $T_{B}$ on absolute scale $B=\left(273.16 X T_{B}\right) / 350$
Since $T_{A}$ and $T_{B}$ represent the same temperature
$273.16 \times T_{A} / 200=273.16 \times T_{B} / 350$
Or, $\mathrm{T}_{\mathrm{A}}=200 \mathrm{~T}_{\mathrm{B}} / 350=4 \mathrm{~T}_{\mathrm{B}} / 7$

Question 3:A gas is contained in a cylinder with a moveable piston on which a heavy block is placed. Suppose the region outside the chamber is evacuated and the total mass of the block and the movable piston is 102 kg . When 2140 J of heat flows into the gas, the internal energy of the gas increases by 1580 J . What is the distance $s$ through which the piston rises?

## Solution:3

Total heat supplied =Workdone + Change in internal energy
So work done=2140-1580=560 J

Let s be the distance moved then
the workdone is given by $=\mathrm{Fs}$
$\mathrm{Fs}=560$
$\mathrm{s}=560 / \mathrm{F}$
$=560 / 102 * 10$
$\mathrm{s}=.54 \mathrm{~m}$

Question-4: At $27^{\circ} \mathrm{C}$,two moles of an ideal monoatomic gas occupy a volume V.The gas is adiabatically expanded to a volume 2 V .
Calculate the ratio of final pressure to the intial pressure
Calculate the final temperature
Change in internal energy
Calculate the molar specific heat capacity of the process

## Solution-4

Given
$\mathrm{n}=2 \mathrm{~T}=27^{\circ} \mathrm{C}=300 \mathrm{~K}, \mathrm{~V}_{1}=\mathrm{V}, \mathrm{V}_{2}=2 \mathrm{~V}$

Now $\mathrm{PV}^{\mathrm{y}}=$ constant
$\mathrm{P}_{1} \mathrm{~V}_{1} \mathrm{y}=\mathrm{P}_{2} \mathrm{~V}_{2} \mathrm{y}$
$P_{2} / P_{2}=\left(V_{1} / V_{2}\right)^{y}$
$=.5^{5 / 3}$

ALso
$\mathrm{T}_{1} \mathrm{~V}_{1}^{\mathrm{y}-1}=\mathrm{T}_{2} \mathrm{~V}_{2}^{\mathrm{y}-1}$
or $T_{2}=300 / 2^{5 / 3}=189 \mathrm{~K}$

Change in internal energy $=n C_{v} \Delta T$
For monoatomic gas $\mathrm{C}_{\mathrm{v}}=3 \mathrm{R} / 2$
Substituting all the values
Change in internal energy==-2764J
As in adiabatic process $\Delta Q=0$, molar specific heat capacity $=0$

## Question-5

An ideal gas heat engine operates in Carnot cycle between $227^{\circ} \mathrm{C}$ and $127^{\circ} \mathrm{C}$. It absorbs $6^{*} 10^{2}$ cal of heat at the higher temperature. Calculate the amount of heat supplied to the engine from the source in each cycle

## Solutions-5:

$\mathrm{T}_{1}=227^{\circ} \mathrm{C}=500 \mathrm{~K}$
$\mathrm{T}_{2}=127^{\circ} \mathrm{C}=400 \mathrm{~K}$

Efficiency of the carnot cycle is given by

$$
=1-\left(T_{2} / T_{1}\right)=1 / 5
$$

Now also efficency =Heat supplied from source/Heat absorbed at high temperature so Heat supplied from source $=6 * 10^{2 *}(1 / 5)==1.2^{*} 10^{2}$ cal

## THERMODYNAMICS

- Thermal Equilibrium:- Two systems are said to be in thermal equilibrium with each other if they have the same temperature.
- Thermo dynamical system:- An assembly of large numbers of particles having same temperature, pressure etc is called thermo dynamical system.
- Thermodynamic variables :- The variables which determine the thermodynamic behavior of a system are called thermodynamic variables
- Zeroth law of Thermodynamics :- IT states that if two system $A$ and $B$ are in thermal equilibrium with a third system $C$, then the two system $A$ and $B$ are also in thermal equilibrium with each other.
- Thermodynamic Process :- A thermodynamic process is said to be taking place, if the thermodynamic variable of the system change with time.
- Types of thermodynamic Process:-
(1) Isothermal process - process taking place at constant temperature.
(2) Adiabatic process - process where there is no exchange of heat.
(3) Isochoric process - process taking place at constant volume
(4) Isobaric process -Process taking place at constant Pressure.
(5) Cyclic process:- Process where the system returns to its original state.
- Equation of state : A relation between pressure, volume and temperature for a system is called its equation of state .
- Indicator diagram (P-V diagram) :- The graphical representation of the state of a system with the help of two thermodynamical variables is called indicator diagram of the system.
- Internal energy of a gas :- It is the sum of kinetic energy and the intermolecular potential energy of the molecules of the gas. Internal energy is a function of temperature.
- First law of Thermodynamics :- It states that if an amount of heat dQ I added to a system, a part of heat is used in increasing its internal energy while the remaining part of heat may be used up as the external work done dW by the system.

$$
d Q=d U+P d V .
$$

- Work done during expansion / compression of gas:- When the volume of gas changes from $V_{1}$ to $V_{2}$, the work done is given by $W=\oint_{V 1}^{V 2} P d V=$ Area under the $\mathrm{P}-\mathrm{V}$ diagram.
- Thermodynamical operations are
(1) Isothermal process : A thermodynamic process that takes place at constant temperature is called an isothermal process.
- Equation of state for isothermal process : PV = constant.
- Work done during an isothermal process

$$
W_{\text {iso }}=R T \log _{e} \frac{\mathrm{~V}_{2}}{\mathrm{~V}_{1}}=2.303 R T \log _{\mathrm{e}} \frac{\mathrm{~V}_{2}}{\mathrm{~V}_{1}}
$$

(2) Adiabatic process : A thermodynamic process that takes place in such a manner that no heat enters or leaves the system is called adiabatic process
$\rightarrow$ Equation of state for adiabatic process
(i) $\mathrm{PV}^{\mathrm{V}}=$ constant (ii) $\mathrm{TV}^{\mathrm{V}-1}=$ constant

$$
\frac{\mathrm{p}^{\gamma-1}}{\mathrm{~T}^{\gamma}}=\text { constant }
$$

$\rightarrow$ Work done during adiabatic change

$$
\mathrm{W}_{\mathrm{adia}}=\frac{R(T 1-T 2)}{(\gamma-1)}
$$

- Reversible process :- It is a process in which the system can be retraced to its original state by reversing the condiditions.
- Irreversible process:- It is a process in which the system cannot be retraced to its original state by reversing the conditions.
- Second law of thermodynamics:
$\rightarrow$ Kelvin's statement of second law - It is impossible to derive a continous supply of work by cooling a body to a temperature lower than that of the coldest of its surrounding.
$\rightarrow$ Clausius statement of second law - It is impossible for a self -acting machine unaided by any external agency to transfer heat from a body to another body at higher temperature.
- Heat Engine - a heat engine is a device for converting heat energy continuously into a mechanical work.
$\rightarrow$ Component of heat engine- (i) source of heat (ii) Sink (iii) Working substance
- Efficiency of heat Engine :-It is defined as the ratio of the external work obtained to the amount of heat energy absorbed from the heat source.

Mathematically

$$
\mathrm{\eta}_{\mathrm{b}}=\frac{W}{\mathrm{Q} 1}=\frac{\mathrm{Q} 1-\mathrm{Q} 2}{\mathrm{Q} 1}=1-\frac{\mathrm{Q} 2}{\mathrm{Q} 1}
$$

- Carnot's heat Engine :- it is an ideal heat Engine which is based on carnot's reversible cycle.

Efficiency of carnot's heat Engine

$$
\eta_{0}=1-\frac{\mathrm{Q} 2}{\mathrm{Q} 1}=1-\frac{\mathrm{T} 2}{\mathrm{~T} 1}
$$

- Refrigerator or Heat pump:- it is heat engine working backward.
- Co-efficient of performance : It is the ratio of heat absorbed from cold body to the work done by the refrigerator.

Mathematically $\quad \beta=\frac{\mathrm{Q} 2}{W}=\frac{\mathrm{Q} 2}{\mathrm{Q} 1-\mathrm{Q} 2}=\frac{\mathrm{T} 2}{\mathrm{~T} 1-\mathrm{T} 2}$

## All Questions with **(mark) are HOTs Question

Q1 Which Thermodynamical variable is defined by the first law of thermodynamics?

Ans: Internal energy

Q2 What is the amount of work done in the Cyclic process? 1

Ans:It is numerically equal to the area of the cyclic process.

Q3 Out of the parameters- temperature, pressure,work and volume, which parameter does not

Characterize the thermodynamics state of matter?
Ans: Work

Q4 What is the nature of P-V diagram for isobaric and isochoric process?
Ans: The P-V diagram for an isobaric process is a straight line parrel to the volume axis while that

For an isochoric process is a straight line parallel to pressure axis.
Q5 On what factors does the efficiency of Carnot engine depends? 1

Ans: Temperature of the source of heat and sink.
** Q6 Can we increase the temperature of gas without supplying heat to it? 1

Ans: Yes, the temperature of gas can be by compressing the gas under Adiabatic condition.

Q7 Why does the gas get heated on compression?1

Ans: Because the work done in compressing the gas increases the internal energy of the gas.

Q8 Which thermodynamic variable is defined by Zeroth law of thermodynamics?

Ans: Temperature

Q9 Can the whole of work be converted into heat? 1

Ans: Yes ,Through friction.
Q10 In a Carnot engine, temperature of the sink is increased. What will happen to its efficiency? 1

Ans: We know $\boldsymbol{\eta}=1-\frac{\mathrm{T} 2}{\mathrm{~T} 1}$
On increasing the temperature of the sink $\left(T_{2}\right)$, the efficiency of the Carnot engine will decrease
${ }^{* *}$ Q11 If hot air rises, why is it cooler at the top of mountain than near the sea level? 2

Ans: Since atmospheric pressure decreases with height, pressure at the top of the mountain is lesser. When the hot air rises up,it suffer adiabatic expansion at the top of the mountain.For an adiabatic change,first law of thermodynamics may be express as

$$
\begin{array}{ll}
d U+d W=0 & (d Q=0) \\
d W=-d U &
\end{array}
$$

Therefore work done by the air in rising up (dW =+ve ) result in decrease in the internal

Energy of the air (dU = -ve) and hence a fall in the temperature.
Q12 What happen to the internal energy of a gas during (i) isothermal expansion (ii) adiabatic Expansion?

Ans: In isothermal expansion ,temperature remains constant.Therefore internal energy which is a function of temperature will remain constant.
(ii)for adiabatic change dQ $=0$ and hence first law of thermodynamics becomes

$$
0=d U+d W
$$

$$
d W=-d U
$$

During expansion, work is done by the gas i.e. dW is positive. Hence ,dU must be negative.

Thus, in an adiabatic expansion , the internal energy of the system will decrease.

Q13.Air pressure in a car increases during driving. Explain Why?
Ans: During driving as a result of the friction between the tyre and road ,the temperature of

The tyre and the air inside it increases. Since volume of the tyre does not change, due to increase in temperature , pressure of the increases (due to pressure law ).

Q14 The efficiency of a heat engine cannot be $100 \%$. Explain why? 2
Ans: The efficiency of heat engine $\boldsymbol{\eta}=1-\frac{\mathrm{T} 2}{\mathrm{~T} 1}$
The efficiency will be $100 \%$ or 1 , if $\mathrm{T}_{2}=0 \mathrm{~K}$.
Since the temperature of 0 K cannot be reached, a heat engine cannot have $100 \%$ efficiency.

Q15 In an effort to cool a kitchen during summer, the refrigerator door is left open and the kitchen door and windows are closed. Will it make the room cooler?

Ans: The refrigerator draws some heat from the air in front of it. The compressor has to do some

Mechanical work to draw heat from the air at lower temperature. The heat drawn from the air together with the work done by the compressor in drawing it, is rejected by the refrigerator with the help of the radiator provided at the back to the air. IT follows that in each cycle, the amount of heat rejected to the air at the back of the refrigerator will be greater than that is drawn from the air in front of it. Therefore temperature of the room will increase and make hotter.

Q16 Why cannot the Carnot's engine be realised in practice?
Ans: Because of the following reasons The main difficulty is that the cylinder should come in contact with the source,sink and stand again and again over a complete cycle which is very difficult to achieve in practice.
(ii) The working substance should be an ideal gas however no gas fulfils the ideal gas behaviour.
(iii) A cylinder with a perfectly frictionless piston cannot be realised

Q17 A slab of ice at 273K and at atmospheric pressure melt.(a) What is the nature of work done on

The ice water system by the atmosphere?(b)What happen to the internal energy of the ice- Water system?

Ans: (a) The volume of the ice decreases on melting. Hence the work done by the atmosphere on The ice - water system is positive in nature.
(b) Since heat is absorbed by the ice during melting, the internal energy of the icewater system increases.

Q18 Why is the conversion of heat into work not possible without a sink at lower temperature? 2

Ans:For converting heat energy into work continuosly, a part of the heat energy absorbed from the source has to be rejected. The heat energy can be rejected only if there is a body whose

Temperature is less than that of the source. This body at lower temperature is called sink.
** Q19 Can water be boiled without heating ? 2
Ans:Yes, water can be boil without heating. This is done by increasing the pressure on the surface of water inside a closed insulated vessel. By doing so, the boiling point of the water decreases to the room temperature and hence starts boiling.

Ans: The limitations are --- (i) It does not tells us the directions of heat transfer
(iii)it does not tell us under what conditions heat is converted into work.

## **Q21 Calculate the fall in temperature when a gas initially at $72^{\circ} \mathrm{C}$ is expanded suddenly to eight times its original volume. Given $\gamma=5 / 3$.

Ans: Let $V_{1}=x c c \quad V_{2}=8 x c c$

$$
\mathrm{T}_{1}=273+72=345 \mathrm{~K} \quad \neq=5 / 3, \quad \mathrm{~T}_{2}=?
$$

Using the relation $T_{1} V_{1}^{¥-1}=T_{2} V_{2}^{¥-1}$

$$
\text { Therefore } \begin{aligned}
T_{2} & =T_{1}\left(V_{1} / V_{2}\right)^{¥-1} \\
& =345 \times(1 / 8)^{2 / 3}
\end{aligned}
$$

Taking log of both sides, we get

$$
\begin{aligned}
\log T_{2}= & \log 345-2 / 3 \log 8 \\
& =2.5378-2 / 3(0.9031) \\
& =2.5378-0.6020=1.9358
\end{aligned}
$$

$$
\text { Or } \quad \mathrm{T}_{2}=86.26 \mathrm{~K}
$$

Therefore the fall in temperature $=345-86.26258 .74 \mathrm{~K}$
Q22 A Carnot engine whose source temperature is at 400 K takes 100 Kcal of heat at this temperature in each cycle and gives 70 Kcal to the sink. Calculate (i) the temperature of the sink
(ii) the efficiency of the engine.

Ans: Here $T_{1}=400 \mathrm{~K}, Q_{1}=100 \mathrm{Kcal} \quad, Q_{2}=70 \mathrm{Kcal}$

$$
\mathrm{T}_{2}=? \quad, \pi=?
$$

(i) $\quad Q_{1} / Q_{2}=T_{1} / T_{2}$

$$
\text { Or } \quad T_{2}=\left(Q_{2} / Q_{1}\right) T_{1}
$$

$$
\text { Or } \quad T_{2}=70 / 100 \times 400
$$

$$
\text { Or } \mathrm{T}_{2}=280 \mathrm{~K}
$$

(ii) $\quad \eta=1-T_{2} / T_{1}$

$$
=1-0.7=0.3
$$

Or \% of $\eta=0.3 \times 100=30 \%$
Q23 If at $50^{\circ} \mathrm{C}$ and 75 cm of mercury pressure, a definite mass of gas is compressed (i)slowly
(iii) suddenly, then what will be the final pressure and temperature of the gas in each case, if the final volume is one fourth of the initial volume? Given $y=1.5$

Ans:(I) When the gas is compressed slowly, the change is isothermal.

$$
\text { Therefore } \quad \begin{aligned}
P_{2} V_{2} & =P_{1} \vee_{1} \\
P_{2} & =P_{1} \bigvee_{1} / V_{2} \\
& =\left(75 \times \bigvee_{1} / \vee_{1}\right) \times 4=300 \mathrm{~cm} \text { of mercury }
\end{aligned}
$$

Temperature remains constant at $50^{\circ} \mathrm{C}$
(ii)When the gas is compressed suddenly, the change is adiabatic

$$
\begin{aligned}
& \text { As per } P_{2} V_{2}^{V}=P_{1} V_{1}{ }^{\vee} \\
& P_{2}=P_{1}\left(V_{1} / V_{2}\right)^{V} \\
& =75 \times(4)^{1.5}=600 \mathrm{~cm} \text { of } \mathrm{Hg} \\
& \text { Also } T_{2} V_{2}^{*-1}=T_{1} V_{1}^{*-1} \\
& T_{2}=T_{1}\left(V_{1} / V_{2}\right)^{\neq-1}=323 \times(4)^{(1.5-1)}=646 \mathrm{~K} \\
& =646-273=373^{\circ} \mathrm{C}
\end{aligned}
$$

Q24 Two engines $A$ and $B$ have their sources at 400 K and 350 K and sink at350K and 300 K

Respectively. Which engine is more efficient and by how much?
Ans: For engine $A \quad T_{1}=400 \mathrm{~K}, T_{2}=350 \mathrm{~K}$
Efficiency $\eta_{A}=1-T_{2} / T_{1}$

$$
\begin{aligned}
& =1-350 / 400=1 / 8 \\
& \% \text { of } \eta_{A}=1 / 8 \times 100=12.5 \%
\end{aligned}
$$

$$
\begin{aligned}
\text { For Engine } B \\
\text { Efficiency } \begin{aligned}
T_{1} & =350 \mathrm{~K}, \quad T_{2}=300 \mathrm{~K} \\
& =1-T_{2} / T_{1} \\
& =1-300 / 350=1 / 7 \\
\% \text { of } \eta_{B} & =1 / 7 \times 100=14.3 \%
\end{aligned}
\end{aligned}
$$

Since $\eta_{B}>\eta_{A}$ so engine $A$ is much more efficient than engine $B$ by (14.3\% $12.5 \%$ ) $=1.8 \%$
** Q25 Assuming a domestic refrigerator as a reversible heat engine working between melting point

Of ice and the room temperature at $27^{\circ} \mathrm{C}$, calculate the energy in joule that must be supplied to freeze 1 Kg of water at $0^{\circ} \mathrm{C}$. 3

Ans: Here $\mathrm{T}_{1}=27+273=300 \mathrm{~K}, \mathrm{~T}_{2}=0+273=273$

Mass of water to be freezed, $M=1 \mathrm{Kg}=1000 \mathrm{~g}$

Amount of heat that should be removed to freeze the water

$$
\begin{aligned}
& Q_{2}=M L=1000 \times 80 \mathrm{cal} \\
& =1000 \times 80 \times 4.2=3.36 \times 10^{5} \mathrm{~J}
\end{aligned}
$$

$$
\text { Now } Q_{1}=\left(T_{1} / T_{2}\right) \times Q_{2}=(300 / 273) \times 3.36 \times 10^{5}=3.692 \times 10^{5} \mathrm{~J}
$$

Therefore energy supplied to freeze the water

$$
\begin{aligned}
W & =Q_{1}-Q_{2}=3.693 \times 10^{5}-3.36 \times 10^{5} \\
& =3.32 \times 10^{5} \mathrm{~J}
\end{aligned}
$$

** Q26 A refrigerator freezes 5 Kg of water at $0^{\circ} \mathrm{C}$ into ice at $0^{\circ} \mathrm{C}$ in a time interval of 20 minutes. Assume that the room temperature is $20^{\circ} \mathrm{C}$, calculate the minimum power needed to accomplish it.

Ans: Amount of heat required to convert water into ice at $0^{\circ} \mathrm{C}$,

$$
=400 \mathrm{Kcal}
$$

$$
\begin{aligned}
& \text { Now } T_{1}=20^{\circ} \mathrm{C}=273+20=293 \mathrm{~K} \\
& \mathrm{~T}_{2}=0^{\circ} \mathrm{C} 0+273=273 \mathrm{~K} \\
& \text { We know that } \mathrm{Q}_{2} \mathrm{~W}=\mathrm{T}_{2} /\left(\mathrm{T}_{1}-\mathrm{T}_{2}\right) \\
& \text { Or } \begin{aligned}
\mathrm{W} & =\mathrm{Q}_{2} \times\left(\mathrm{T}_{1}-\mathrm{T}_{2}\right) / \mathrm{T}_{2} \\
& =400 \times(293-273) / 273 \\
& =29.3 \mathrm{Kcal}=29.3 \times 4.2 \times 10^{3} \mathrm{~J} \\
& =123 \times 10^{3} \mathrm{~J}
\end{aligned}
\end{aligned}
$$

$$
\text { Time } \mathrm{t}=20 \mathrm{~min}=20 \times 60=1200 \mathrm{~s}
$$

$$
\text { Power needed } \quad P=W / t \quad=123 \times 10^{3} / 1200
$$

$$
=102.5 \mathrm{~W}
$$

${ }^{* *}$ Q27 The temperature $T_{1}$ and $T_{2}$ of two heat reserviour in an ideal carnot engine are $1500^{\circ} \mathrm{C}$ and
$500^{\circ} \mathrm{C}$. Which of this increasing the temperature $\mathrm{T}_{1}$ by $100^{\circ} \mathrm{C}$ or decreasing $\mathrm{T}_{2}$ by $100^{\circ} \mathrm{C}$ would result in greater improvement of the efficiency of the engine?

Ans: Using $\mathbb{T}=1-T_{2} / T_{1}=\left(T_{1}-T_{2}\right) / T_{1}$
(1)increasing $T_{1}$ by $100^{\circ} \mathrm{C} \quad \Pi_{1}=(1600-500) /(1600+273)$

$$
=1100 / 1873=59 \%
$$

(ii) Decreasing $T_{2}$ by $100^{\circ} \mathrm{C} \quad T_{2}=1500-(500-100) /(1500+273)$

$$
=1100 / 1773=67 \%
$$

Therefore decreasing $\mathrm{T}_{2}$ by $100^{\circ} \mathrm{C}$ results in greater improvement of efficiency.

Q28 State the first law of thermodynamics and discussed the application of this law to the boiling process. 3

## Q29 What is thermodynamic system ? Prove that work done by thermodynamic system is equal to the area under $\mathrm{P}-\mathrm{V}$ diagram. 3

30 Prove that $C_{p}-C_{v}=R$, for an ideal gas . 3
Q31 What is isothermal process / State two essential conditions for such a process to takes place. Show analytically that the work by one mole of an ideal gas during volume expansion from $\mathrm{V}_{1} \mathrm{~V}_{2}$ at temperature T is given by $\mathrm{W}=\mathrm{RT} \log _{\mathrm{e}} \mathrm{V}_{2} / \mathrm{V}_{1}$ 5

Q32 Define an adiabatic process. State two essential conditions for such a process to takes place.Derive an expression for adiabatic process to takes place. 5

Q33 Discuss the four steps of Carnot's cycle and show that the efficiency is given by $\quad \boldsymbol{I}=1-T_{2} / T_{1}$, Where $T_{1}$ and $T_{2}$ are the temperature of the source and sink respectively. 5

Q34 Describe the working of refrigerator as heat pump. Derive the expression of its coefficient of performance. If the door of a refrigerator is kept open for a long time ,will it make the room warm or cool? 5

Q35 What is the need of introducing the second law of thermodynamics? State the Kelvin -Planck and Claussius statement of second law of thermodynamics and show that both the statement are equivalent.

