

Unit - 8

# THERMODYNAMICS

Ch-12

Syllabus

Ch-12

Thermal equilibrium & definition of temperature

Zeroth law of thermodynamics, heat, work & internal Energy.

First law of thermodynamics.

Second law of thermodynamics:

gaseous state of matter, change of

Condition of gaseous state, Isothermal,

adiabatic, reversible, irreversible & cyclic

Processes.

**Thermodynamics** - Branch of physics which deals with study of transformation of heat Energy into other forms of Energy & vice-versa.

**Thermal Equilibrium/ Thermodynamical Equilibrium**

Two systems are said to be in thermal equilibrium with each other if they have same temperature.

# **Thermodynamic Equilibrium**

A system is said to be in thermodynamic equilibrium if macroscopic variables like pressure, volume, temperature, mass & composition do not change with time.

Note

**System** - A specified part of Universe which is under observation is known as system.

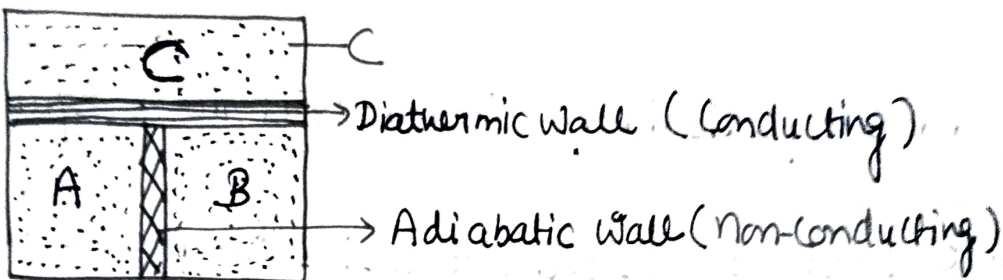
**Surroundings** - Part of Universe other than system is known as surroundings.

OR

Everything outside the system which have a direct effect on system is known as surroundings.

Ques State & explain Zeroth law of thermodynamics  
how does it lead to concept of temperature?

#



Zeroth law of thermodynamics - According to this law if two systems A & B are separately in thermal equilibrium with a third system C, then A & B are also in thermal equilibrium with each other.

$$\Rightarrow A \rightleftharpoons C, \quad B \rightleftharpoons C$$

$$\Rightarrow \boxed{A \rightleftharpoons B}$$

# Concept of Temperature - According to Zeroth law temperature is that physical quantity which have same values for all systems which are in thermal equilibrium with each other.



According to zeroth law of thermodynamics

Temperature is a scalar quantity which is property of all thermodynamic systems, such that equality of temperature is the only condition for thermodynamic systems to be in thermal equilibrium.

\* For Knowledge only

temperature was first defined as degree of hotness & later on the condition for determining the flow of heat.

\* Zeroth law ( $0^{\text{th}}$ ) was formulated after the First & second laws of thermodynamics. But as this law leads to the concept of fundamental quantity temperature, so this law was called Zeroth law.

### Thermodynamic State Variables & eq<sup>n</sup> of state

Thermodynamic state variables are parameters which describe equilibrium states of system

For example - Pressure, Volume, Temperature, mass & Composition (for mixture of gases).



Equation of state represents the connection between State Variables of a system.

$$PV = \mu RT$$

$\mu$  = no of moles of gas

$R$  = gas constant

Thermodynamic State variables are of two types.

- ii Extensive State variable (Volume, mass, internal Energy)
- iii Intensive State variable (Pressure, temp, density)

# extensive State variables change with size of systems; but intensive variables do not

Heat

Heat is mode of Energy transfer that flows from higher temperature to lower temperature

- # This flow is only because of difference in temperatures.
- # When heat is supplied to a gas, its molecules move faster in all directions at random.
- # So heat is a mode of Energy transfer that produces random motion.

Internal Energy:

Internal Energy of a system is total energy possessed by system due to molecular motion & molecular configuration.

$$U = U_k + U_p$$

$U_k =$  Internal Kinetic Energy

# Energy due to molecular motion is known as Internal Kinetic Energy ( $U_k$ )

$U_p =$  Internal Potential Energy

# Energy due to molecular configuration is known as internal potential Energy ( $U_p$ )

$U_p = 0$  for an ideal gas or perfect gas inter-molecular forces are zero so no work is done in changing distance between molecules.

So Internal Energy of an Ideal gas consist only internal kinetic Energy - which depends only on temperature of the gas.

$$U = U_k + 0 \quad \{ \text{for Ideal gas} \}$$

# For real gas - Intermolecular forces are not negligible. Therefore a definite amount of work has to be done in changing distance between molecules

$$\Rightarrow U_p \neq 0$$

so Internal Energy of a real gas is sum of  $\{U_k + U_p\}$ .

## Difference between heat & work

⇒ Heat is a mode of Energy transfer due to temp difference b/w system & surroundings.

# Work is mode of Energy transfer which do not involve temp difference.

⇒ Heat is a mode of Energy transfer that produces random motion

# Work is mode of Energy transfer which produces organised motion.

Sign Conventions Used:

(i) Heat absorbed  $\rightarrow$  +ve  
Heat given out  $\rightarrow$  -ve

(ii) Work done by system  $\rightarrow$  +ve  
Work done on system  $\rightarrow$  -ve

(iii) Increase in internal Energy  $\rightarrow$  +ve  
decrease in internal Energy  $\rightarrow$  -ve.

## For knowledge

In thermodynamics heat & work are not state Variables. These are modes of Energy transfer to a system.



# Thermodynamic Processes

Thermodynamic Processes are those processes which take place when some changes occur in the state of a thermodynamic system. means Thermodynamic parameters change with time.

For eg:-

1. **Isothermal Process**  
 ↓  
 (Constant temp)

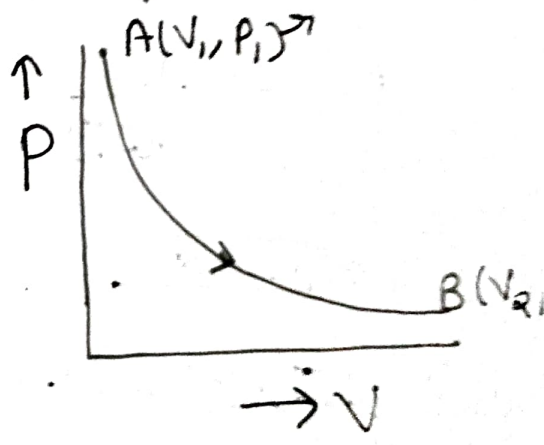
2. **Adiabatic Process**  
 ↓  
 ( $\Delta Q = 0$ )

3. **Isobaric Process**  
 ↓  
 $P = \text{const}$

4. **Isochoric or Isovolume Process**  
 ↓  
 $V = \text{const}$

# Indicator Diagram or P-V diagram

P-V diagram represents variation of volume  $V$  of a system with pressure  $P$  of system.



# Isothermal Change

A change in pressure & volume of a gas without any change in its temperature.

## Two essential conditions for a perfect Isothermal change

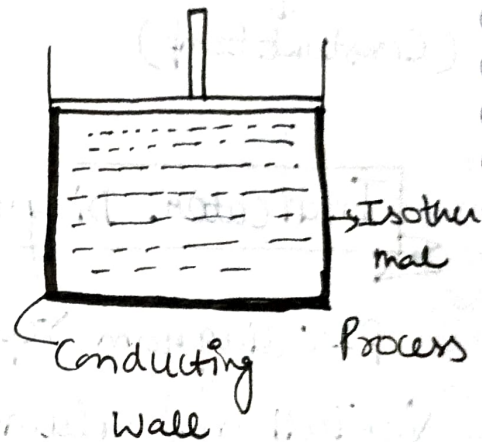
- i) Walls of container must be perfectly conducting to allow free exchange of heat b/w gas & its surroundings.
- ii) Process of compression or expansion should be slow so as to provide time for exchange of heat b/w gas & its surroundings.

\* In an Isothermal change

$$T = \text{const}, \Delta T = 0$$

$$\text{As } C = \frac{\Delta Q}{m(\Delta T)}$$

$$\Rightarrow \boxed{C = \infty}$$



during an Isothermal change specific heat of gas is infinite.

### Examples of Isothermal Change

1. Melting process
2. Boiling process

eq<sup>n</sup> of Isothermal Change  $\boxed{PV = \text{const}}$

$$P_1 V_1 = P_2 V_2$$

### \* Adiabatic change

A change in pressure & volume of a gas when no heat is allowed to enter into or escape from the gas is known as adiabatic change.

### Conditions for perfect adiabatic change

\* Wall of container must be perfectly non-conducting in order to prevent any exchange of heat b/w gas & its surroundings.

\* Process of compression or expansion should be sudden so that there is no time for exchange of heat.

### Examples of adiabatic process

1. Expansion of steam in cylinder of a steam engine.
2. Sudden compression or expansion of a gas in a container with perfectly non-conducting walls.

\* Adiabatic relation b/w P & V for a perfect gas is

$$P V^\gamma = \text{const} = K$$

$\gamma = \frac{\text{specific heat of gas at constant pressure}}{\text{specific heat of gas at constant volume}}$



$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\Rightarrow PV = RT$$

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

$$PV^{\gamma} = K$$

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

$$TV^{\gamma-1} = \frac{K}{R} = \text{another constant}$$

$$TV^{\gamma-1} = \text{Constant}$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

#  $PV^{\gamma} = K$

$$\frac{P R T^{\gamma}}{P^{\gamma}} = K$$

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

$$P^{1-\gamma} T^{\gamma} = \frac{K}{R^{\gamma}} = \text{another constant}$$

$$P^{1-\gamma} T^{\gamma} = \text{const}$$

$$P_1^{1-\gamma} T_1^{\gamma} = P_2^{1-\gamma} T_2^{\gamma}$$

# Slope of Isothermal & Adiabatic curves

Slope of an Isothermal or adiabatic curve is  $\frac{dP}{dV}$

for an Isothermal change  $PV = K$

$$PV = K$$

$$P dV + V dP = 0$$

$$V dP = -P dV$$

$$\boxed{\frac{dP}{dV} = -\frac{P}{V}}$$

# For an Adiabatic change.

$$PV^\gamma = K$$

$$\gamma PV^{\gamma-1} dV + V^\gamma dP = 0$$

$$V^\gamma dP = -\gamma PV^{\gamma-1} dV$$

$$\frac{dP}{dV} = -\frac{\gamma PV^{\gamma-1}}{V^\gamma} = -\frac{\gamma P}{V}$$

$$\boxed{\frac{dP}{dV} = -\frac{\gamma P}{V}}$$

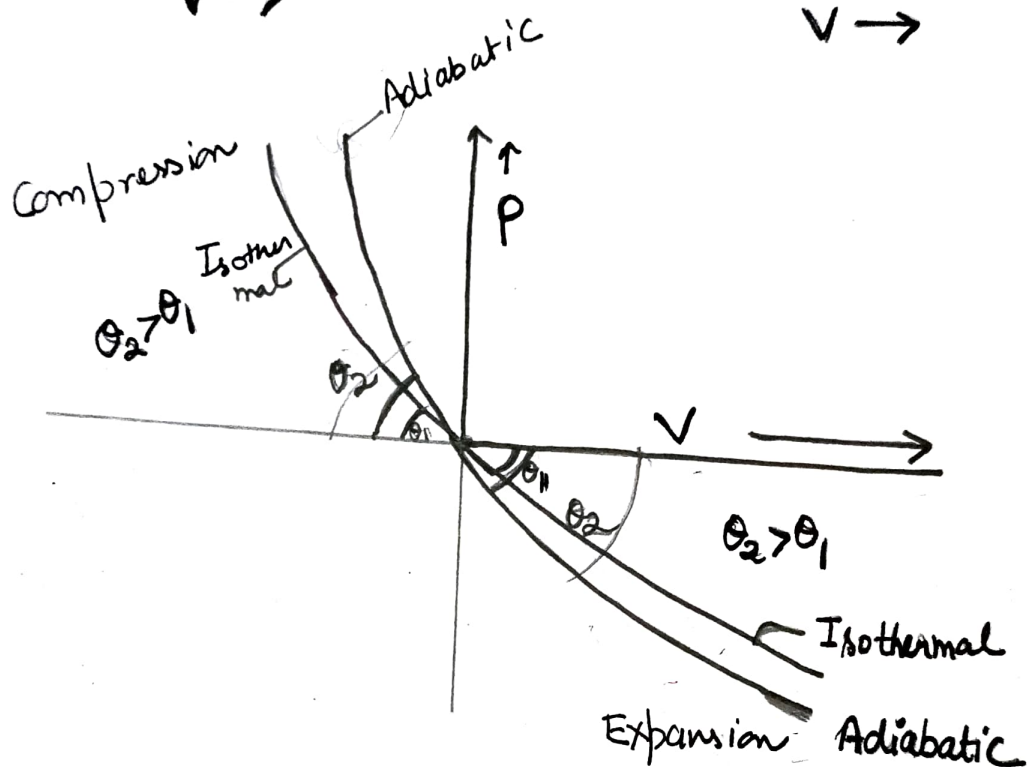
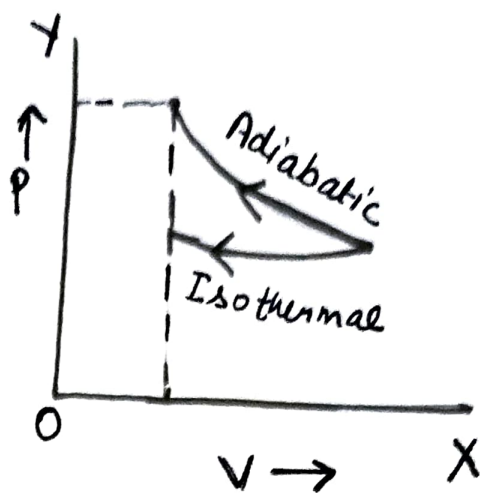
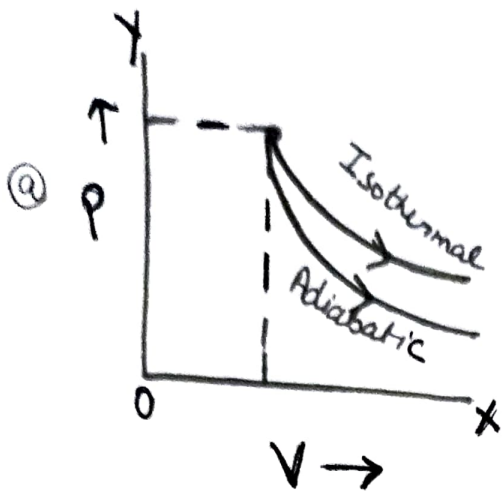
# Slope  $\frac{dP}{dV}$  of an adiabatic curve is  $\gamma$  times

the slope  $\frac{dP}{dV}$  of an Isothermal curve.

# as  $\gamma > 1$ , adiabatic curve is steeper than the Isothermal Curve.

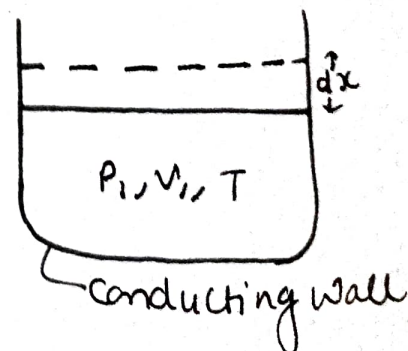
# In case of expansion Isothermal curve lies above adiabatic curve.

# In case of compression Isothermal curve lies below adiabatic curve. because adiabatic curve is steeper than Isothermal curve.



### Work done in an Isothermal Expansion

Consider one gram mole of an ideal gas enclosed in a cylinder with conducting walls & fitted with a frictionless & conducting piston.





Internal Energy is a State function does not depend upon path followed by object.



Let  $\left. \begin{matrix} P_1 \\ V_1 \\ T \end{matrix} \right\}$  Initial pressure, volume & Temperature of gas.

Let gas expand to a vol  $V_2$ , when pressure reduces to  $P_2$ .

if  $A =$  Area of cross-section of piston

Force exerted by gas on piston =  $P \times A$

Small amount of work during expansion

$$dW = F dx = P \times A \times dx$$

$$dW = P dV$$

$$\boxed{A dx = dV}$$

Total work done by gas in expansion from initial vol  $V_1$  to final volume  $V_2$  is  $W = \int_{V_1}^{V_2} P dV$

$$P V = R T$$

$$P = \frac{R T}{V}$$

$$W = \int_{V_1}^{V_2} \frac{R T}{V} dV = R T \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$W = R T \left\{ \log_e V \right\}_{V_1}^{V_2}$$

$$W = RT \{ \log_e v_2 - \log_e v_1 \}$$

$$W = RT \log_e \frac{v_2}{v_1}$$

$$W = 2.3026 RT \log_{10} \frac{v_2}{v_1}$$

as  $W = 2.3026 RT \log_{10} \frac{P_1}{P_2}$

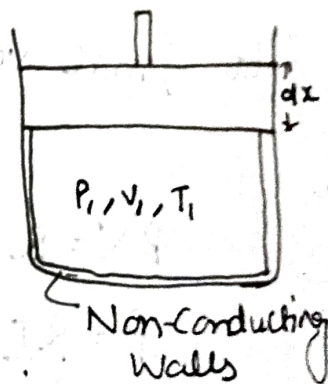
$$P_1 v_1 = P_2 v_2$$

$$\frac{P_1}{P_2} = \frac{v_2}{v_1}$$

$$H = \frac{W}{J} = 2.3026 \frac{RT}{J} \log_{10} \left( \frac{v_2}{v_1} \right)$$

### Work done in an Adiabatic Expansion

Consider one gram mole of an ideal gas enclosed in a cylinder with perfectly non-conducting walls & fitted with a perfectly frictionless non-conducting piston.



Let  $P_1, V_1, T_1$  be initial pressure, volume & temp of gas.

Force exerted by gas on piston =  $P \times A$

Small amount of work done during expansion =  $dW = F dx = P \times A dx = P dv$



Total work done by gas in adiabatic expansion from volume  $V_1$  to  $V_2$  is

$$W = \int_{V_1}^{V_2} p dV$$

Eq<sup>n</sup> of adiabatic change  $PV^{\gamma} = \text{Constant} = K$

$$\gamma = \frac{C_p}{C_v} = \frac{\text{sp. heat of gas at constant pressure}}{\text{sp. heat of gas at constant volume}}$$

$$P = \frac{K}{V^{\gamma}} = K V^{-\gamma}$$

$$W = \int_{V_1}^{V_2} K V^{-\gamma} dV = K \left[ \frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2}$$

$$W = \frac{K}{1-\gamma} \left[ V_2^{1-\gamma} - V_1^{1-\gamma} \right]$$

$$W = \frac{1}{1-\gamma} \left[ K V_2^{1-\gamma} - K V_1^{1-\gamma} \right]$$

as  $P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = K$

$$W = \frac{1}{1-\gamma} \left[ P_2 V_2^{\gamma} V_2^{1-\gamma} - P_1 V_1^{\gamma} V_1^{1-\gamma} \right]$$

$$W = \frac{1}{1-\gamma} \left[ P_2 V_2 - P_1 V_1 \right]$$

$$\boxed{P_1 V_1 = R T_1} \quad , \quad \boxed{P_2 V_2 = R T_2}$$

$$W = \frac{1}{1-\gamma} (RT_2 - RT_1)$$

$$W = \frac{R}{1-\gamma} (T_2 - T_1)$$

Amount of heat spent in adiabatic expansion

$$H = \frac{W}{J} = \frac{R(T_2 - T_1)}{(1-\gamma)J}$$

### Difference between Isothermal & Adiabatic change

#### Isothermal Changes

1. Temperature remains constant  $\Delta T = 0$
2. System is thermally conducting to surroundings
3. Isothermal changes occur slowly
4. Internal Energy = Const  
 $\Delta U = 0$
5. Specific heat becomes  $\infty$   
 $C = \frac{\Delta Q}{m \Delta T} = \infty$   
as  $\Delta T = 0$

#### Adiabatic changes

- Heat remains constant  $\Delta Q = 0$
2. System is thermally insulated from surroundings
  3. Adiabatic changes occur suddenly
  4.  $U \neq \text{Const}$   
 $\Delta U \neq 0$
  5.  $C = \frac{\Delta Q}{m \Delta T}$   
as  $\Delta Q = 0$   
 $C = 0$

6. Isothermal eq<sup>n</sup>  
 $PV = \text{const}$

6. Adiabatic eq<sup>n</sup>  $PV^\gamma = \text{const}$

7. Slope of Isothermal  
 Curve,  $\frac{dP}{dV} = -\frac{P}{V}$

7. Slope of adiabatic  
 Curve  $= -\frac{\gamma P}{V}$

## First law of Thermodynamics

According to First law Whenever heat is added  
to a system, it transforms to an equal amount  
of energy in some other form.

When we supply some heat energy to a  
 system it may do one or both of the two  
 things.

- i) Increase in Internal Energy
- ii) do the external work if it leaves the system.

$$\text{Heat given to a System} = \text{Increase in internal Energy} + \text{external work done by system.}$$

$$dQ = dW + dU$$

$dQ$  = Small amount of heat supplied to system

$dW$  = Small amount of work done by system

$dU$  = Small change in internal energy.

Sign-Conventions

1.  $dQ$  - heat supplied to system (+ve)  
 $dQ = -ve$  heat is drawn from system..

2. When a gas expands, Work is done by gas  
 $dW = +ve$

When a gas is compressed, work is done on the gas  
 $dW = -ve$

3. When temp of a gas increases  
 $dU = \uparrow$  → sign +ve

When temp of a gas decreases  
 $dU = \downarrow$  sign → -ve

### Applications of First law of Thermodynamics

(a) Isothermal Process

$$T = \text{const}$$

$$U = \text{const}$$

$$dU = 0$$

$$dQ = dU + dW$$

$$dQ = 0 + dW$$

$$dQ = dW$$

i.e. heat supplied in an Isothermal process is used entirely to do work against external surroundings.



(b) Adiabatic Process  $dQ = 0$

I law of thermodynamics

$$dQ = dU + dW$$

$$0 = dU + dW$$

$$\boxed{dU = -dW}$$

When a gas expands  $dW = +ve$   
 $\boxed{dU = -ve}$

means internal energy of system would decrease  
 & gas will be cooled & vice-versa.

(c) Isochoric Process  $dV = 0$

$$dQ = dU + dW$$

$$dQ = dU + PdV$$

$$\boxed{dQ = dU}$$

if heat is absorbed by a system at constant volume,  
 its internal energy increases by same amount & vice versa

(d) Isobaric Process In an Isobaric process, pressure  
 is kept constant.

for example When a liquid boils, its pressure & temp  
 remain constant till whole of liquid is converted  
 into vapours

$V_i =$  initial volume of liquid

$V_f =$  final vol of vapours.

$P$  = Constant pressure at which liquid converts into vapours.

$$\text{Workdone} = P \cdot dV = P (V_f - V_i)$$

$$dQ = mL$$

$$dQ = dU + dW$$

$$dQ - dW = dU$$

$$\Rightarrow \boxed{mL - P(V_f - V_i) = dU}$$

Change in internal Energy of liquid on vaporisation.

(e) Cyclic Process

→ Such process in which system returns to its initial state after no. of changes.

as Internal Energy is a State Variable

∴ Therefore there is no change in internal Energy of system. i.e.  $dU = 0$ .

I law of thermodynamics

$$dQ = dU + dW$$

$$\boxed{dQ = dW}$$

∴ Net work done during a cyclic process exactly equals the amount of heat energy transferred.

## (f) Melting Process

When a substance melts change in its vol is very small & therefore it can be neglected

$$dW = PdV = P \times 0 = 0$$

So  $dQ = dU + dW$

$$dQ = mL, \quad mL = dU + 0$$

$$\boxed{dU = mL}$$

↑ in internal Energy during melting process is at constant temperature. Therefore it will increase internal potential Energy ( $U_p$ ).

# Internal kinetic Energy ( $U_k$ ) remains constant.

## (g) Boiling Process

In boiling, a liquid changes into vapours at constant temperature & pressure.

Suppose  $m$  = mass of a liquid at its boiling point

$V_1$  = volume of liquid

$P$  = constant pressure at which boiling occurs

$V_2$  = Vol. of same liquid in the vapour form Under the same pressure.

$L$  = Latent heat of vaporisation of liquid.

∴ Work done in expansion,  $dW = P \cdot dV = P(V_2 - V_1)$

Heat absorbed by liquid in boiling process,  $dQ = mL$

According to I law of Thermodynamics

$$dQ = dU + dW$$

$$dU = dQ - dW$$

$$dU = mL - P(V_2 - V_1)$$

Increase in internal energy of the liquid in the boiling process is due to increase in internal potential energy.

(h) Free Expansion-

Free expansion consist of adiabatic processes in which no transfer of heat occur b/w system & surroundings & no work is done on or by the

system i.e  $dQ = 0$  &  $dW = 0$ .

According to first law of Thermodynamics,

$$dU = dQ - dW = 0$$

Relation Between two principal specific heat of a gas (Mayer's Formula)

Consider one gram mole of an ideal gas enclosed in a cylinder with a piston, which is perfectly frictionless.



Let  $P, V, T$  be the Initial Pressure, Volume & temperature of the gas.

Let the gas be heated at constant volume through a small range of temp  $dT$ .

∴ Amount of heat energy supplied to gas

$$dQ = C_v \cdot l \cdot dT$$

$C_v$  = molar specific heat of gas at constant volume.

as volume remains constant,  $dV = 0$

$$\therefore dQ = dU + dW$$

$$dQ = dU + PdV$$

$$dQ = dU + 0$$

$$dQ = C_v dT = dU$$

# Let gas be now heated at constant Pressure through same range of temperature  $dT$

Amount of heat Energy Supplied to gas

$$dQ' = C_p \cdot l \cdot dT$$

if  $dU'$  is increase in internal energy, then according to First law of thermodynamics -

$$dQ' = dU' + dw'$$

$$C_p dT = dU' + PdV$$

as rise in temp of gas in two cases is (same = dT)  
 therefore increase in its internal energy (which depends only on temperature in case of ideal gas) must be same in two cases

$$dU' = dU$$

$$dU' = dU = C_v dT$$

$$C_p dT = C_v dT + PdV$$

$$\Rightarrow C_p dT - C_v dT = PdV$$

$$(C_p - C_v) dT = PdV$$

According to gas eq<sup>n</sup>  $PV = RT$

$$VdP + PdV = R dT$$

at constant pressure  $dP = 0$

$$PdV = R dT$$

$$(C_p - C_v) dT = R dT$$

$$C_p - C_v = R$$

# LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

1. First law does not indicate the direction in which the change can occur.

# When two bodies at different temperatures are put in thermal contact with each other, heat flows from body at higher temp to body at lower temperature.

But heat can not flow from body at lower temperature to body at higher temperature, although first law of thermodynamics is not violated.

2. First law gives no idea about extent of change.

# There is no restriction on conversion of mechanical work into heat. But there are restrictions on reverse process i.e. conversion of heat energy into mechanical energy.

3. First law of thermodynamics gives no information about source of heat i.e. whether it is a hot or a cold body.



# Cyclic & Non-cyclic Processes

A cyclic process consist of a series of changes which return the system back to its initial state.

for example- suppose a system consist of a gas at pressure P, volume V & temperature T.

Let system be subjected to a number of changes including; Isothermal, adiabatic expansions & Compressions, & if in the final state system has same pressure P, same volume V & same Temp T Then process is said to be cyclic process.

For cyclic process  $\Rightarrow$  Internal energy of system remains unchanged  
ie  $dU=0$

## Non-cyclic Process

In a Non-cyclic process, series of changes involved do not return the system back to its initial state.

# Work done in a non-cyclic process depends upon the path chosen or series of changes involved

## Second law of Thermodynamics

(a) Kelvin Planck Statement

It is impossible to construct a heat engine which would absorb heat from a reservoir and convert



100% of the heat absorbed into work.

(b) Clausius Statement

It is Impossible to design a self acting machine unaided by any external agency, which would transfer heat from a body at a lower temperature to another body at a higher Temp.

Reversible & Irreversible processes

Reversible process - A thermodynamical process is said to be reversible process if system & surrounding return to their original states.

For eg:- for a process to be reversible, following conditions must be satisfied.

(i) Process should proceed at an extremely slow rate.

(ii) System should be free from dissipative force like friction, inelasticity, viscosity etc.

\* No process in nature is truly reversible.

Irreversible process - Processes which do not come back to their original state or which does not satisfy even one of the conditions for reversible process.

- for eg:-
1. Rusting of Iron
  2. Mixing of two different substances like water & alcohol.