

## Thermodynamics

"It is a branch of science which deals with the Energy change during a chemical process."

The laws of thermodynamics helps us to predict whether the reaction is carried out or not.

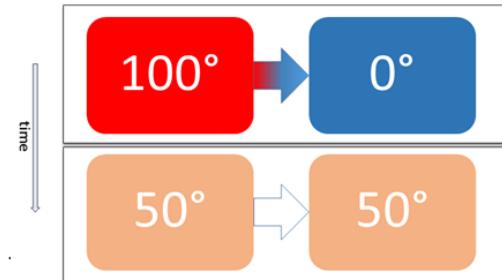
Some basic terms of thermodynamics:

### 1) Thermodynamic Equilibrium

Thermodynamic Equilibrium is the condition or state of a thermodynamic system, the properties of which do not change with time.

Note:- A system is said to be in ~~thermodynamic~~ equilibrium when following three conditions of Equilibrium are satisfied simultaneously.

- I) Mechanical Equilibrium.
- II) Chemical Equilibrium
- III) Thermal Equilibrium.

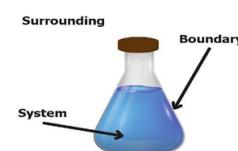


Universe:- Universe is everything in our Existance.

It include Time, Space, Matter, Planets, Stars, galaxies etc.

### Surrounding & System:-

Any part of Universe which is under investigation is called System, and rest of Universe is called Surroundings.



Boundary:- A closed surface surrounding a system through which Energy & Mass may enter or leave the system.

Systems are of three types-

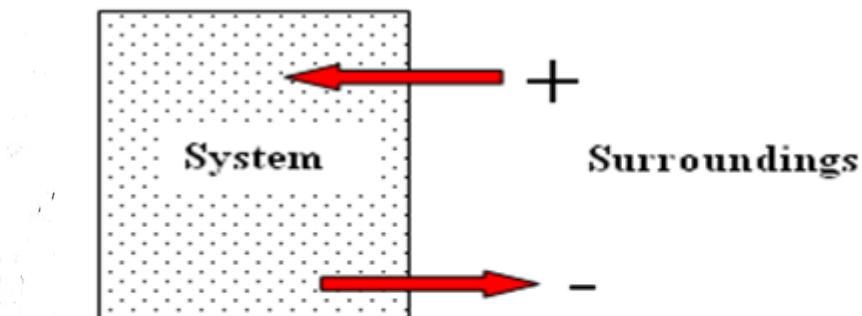
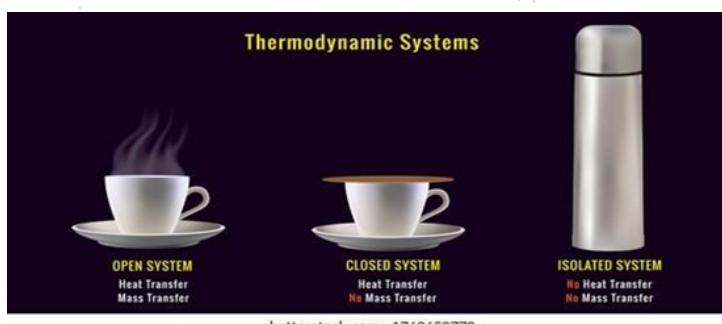
I) Open System- A system is said to be open if it exchange both energy & matter with surroundings. E.g. an open hot cup of tea.

II) Closed System- A system is said to be closed if it exchange only energy but not matter with surroundings.

Eg. Reaction takes place in a closed vessel.

III) Isolated System- A system is said to be isolated if it doesn't exchange both energy and matter with surroundings.

Eg. Reaction takes place in thermoflask.



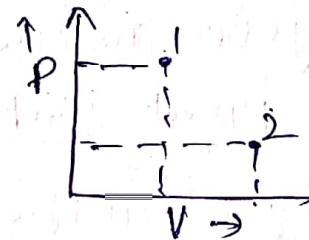
<b>Open system</b>	=	exchange of mass and energy
<b>Closed system</b>	=	exchange of energy but not mass
<b>Isolated System</b>	=	no exchange of mass or energy

# Thermodynamic State Path Process & cycle:-

③

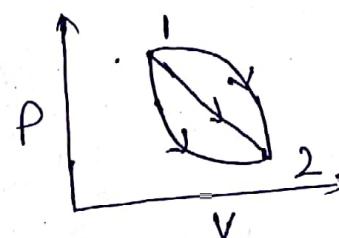
State!:- A state is a condition of a system identified by thermodynamic properties.

Note!:- An operation in which properties of the system change is called change of state.



Path!:- A locus of series of state, from initial to final state is known as Path.

Note: A thermodynamic Property that depends on the path between initial & final state is known as Path function.



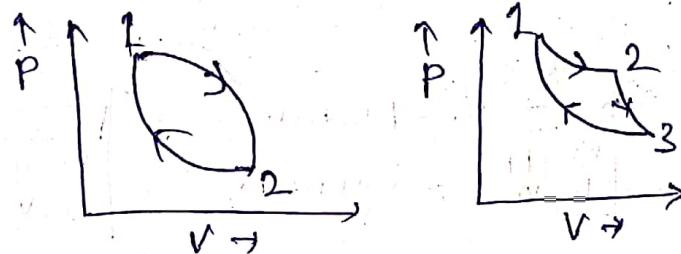
process!:- A complete specification of path from initial state to final state is known as process.

OR It may be defined as a path from one state to another state.

(4)

Cycle:- A thermodynamic cycle is defined as a series of processes such that the system returns to its initial state.

In thermodynamic cycle final state is identical with the initial state.



- In thermodynamic cycle initial state of first process is identical with the final state of second process.
- After completing of cycle initial state restored again.

## Properties of a system - I) Intensive Properties. ⑤

Those properties which don't depend on the Mass and Size of System is called Intensive Properties.

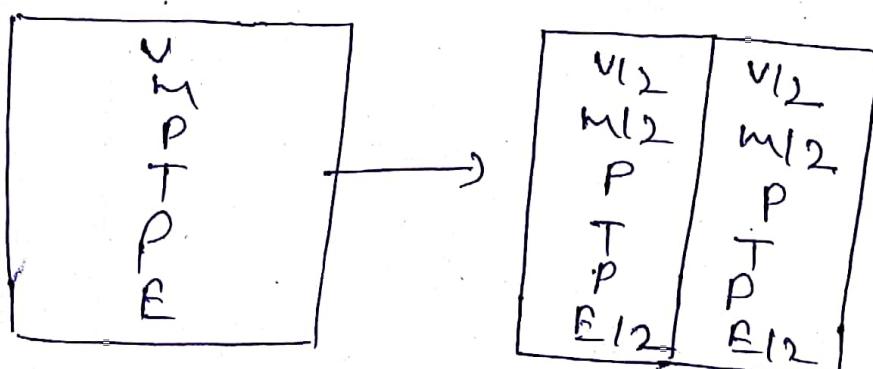
Eg. Pressure, Temperature, Density, conductivity, viscosity etc.

## II) Extensive Properties:-

Those properties which depend on the Mass and Size of System is called Extensive Properties.

Eg. volume, mass, Energy, Entropy, Enthalpy.

Example! - Considering Intensive and Extensive properties before and after partition inside a room.



Intensive  $\rightarrow$  T, P, P

Extensive  $\rightarrow$  V, M, E

Note! - I) Ratio of two extensive Properties gives Intensive Properties.

(Intensive)  $\leftarrow P = \frac{M}{V} \rightarrow$  Extensive.

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

II) If we want to check whether the property

Is intensive or Extensive decide the size of system  
(or make partition).

- If Property change wrt size called Extensive Property.
- If Property don't change wrt size called Intensive Property

Note - Specific Properties are always Intensive Properties.

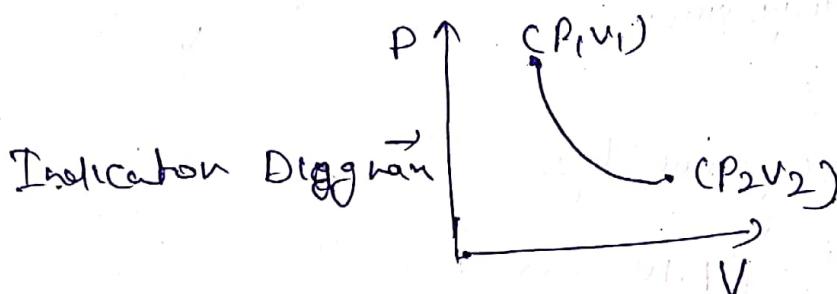
E.g. Specific Enthalpy.

(when Enthalpy is divided by mass ( $m$ ) then Specific Enthalpy is obtained).

## INDICATOR DIAGRAM

The variation of one thermodynamic variable with respect to another is necessary to analyse a thermodynamic process. Such plot is known as Indicator Diagram.

Eg.



## THERMODYNAMIC PROCESS

i) Isobaric Process:- A change in thermodynamic coordinates of a thermodynamic system bring about a change in the state of the system and is called thermodynamic process.

Following are some of the important thermodynamic processes

ii) Isobaric Process:- (constant pressure process).

Isobaric process is that which occurs at constant pressure

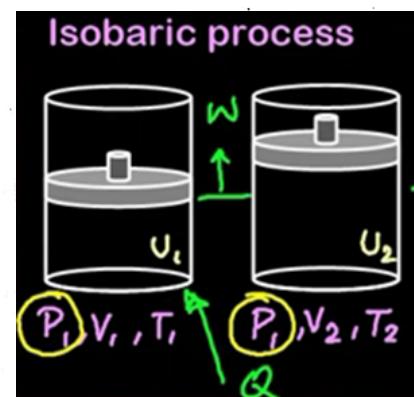
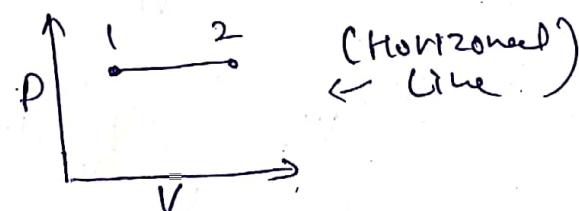
The work done for very small change in volume  $dV$

$$dW = PdV$$

When gas expand from  $V_1$  to  $V_2$

$$W = \int_{V_1}^{V_2} PdV$$

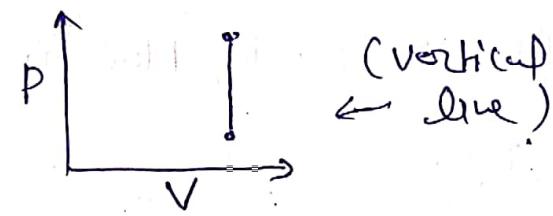
$$W = P(V_2 - V_1)$$



## Isochoric Process (constant volume process)

Isochoric Process is that which occurs at constant volume.

Isochoric Process is represented by line parallel to pressure axis on PV diagram.

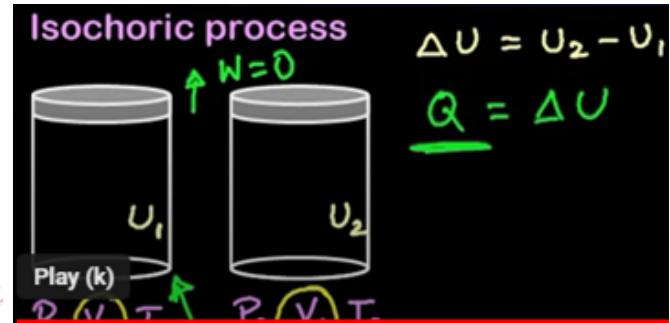


$$\text{As } dV = 0$$

work done is given by

$$W = \int_{V_1}^{V_2} P dV = 0$$

$[W=0]$



## Isothermal Process (constant Temperature Process)

Isothermal Process is that which occurs at constant temperature.

work done for a very small change in volume  $dV$

$$dW = P dV$$

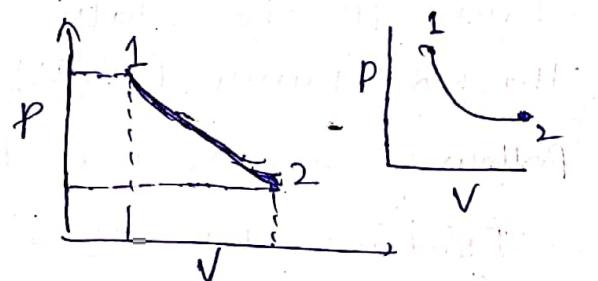
$$W = \int_{V_1}^{V_2} P dV$$

$$W = \int_{V_1}^{V_2} \frac{RT}{V} dV$$

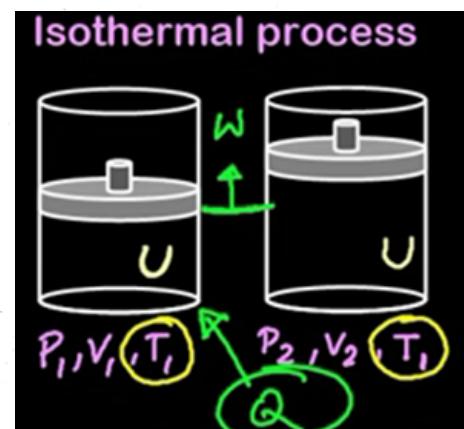
$$= RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$W = 2.3026 RT \log_e \frac{V_2}{V_1}$$

$$W = 2.3026 RT \log_{10} \frac{V_2}{V_1}$$



( we have )  
 $PV = RT$   
 $P = \frac{RT}{V}$



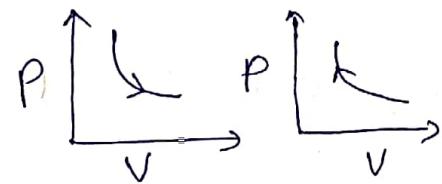
## ADIABATIC PROCESS:-

A process in which no heat Enter or leave the system thermodynamic system during change.

for Adiabatic Process

$$PV^r = \text{constant} = k.$$

( $r_2$  Adiabatic Index)



$$P = kV^{-r} \quad \text{(1)}$$

$$dW = PdV$$

$$W = \int_{V_1}^{V_2} pdV$$

$$= \int_{V_1}^{V_2} KV^{-r} dV$$

$$= K \int_{V_1}^{V_2} V^{-r} dV$$

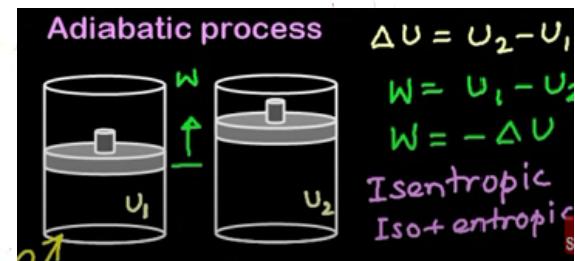
$$= K \left[ \frac{V^{-r+1}}{-r+1} \right]_{V_1}^{V_2}$$

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

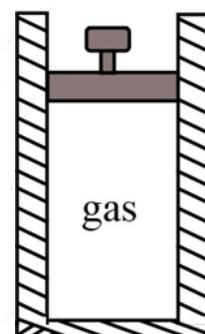
$$\Rightarrow \frac{1}{1-r} \left( KV_2^{-r} V_2 - KV_1^{-r} V_1 \right)$$

Using (1)

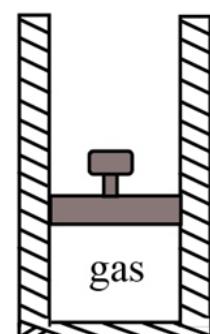
$$\Rightarrow \boxed{\frac{1}{1-r} (P_2 V_2 - P_1 V_1)} \quad \text{work done}$$



Adiabatic piston



Initial state



Final state

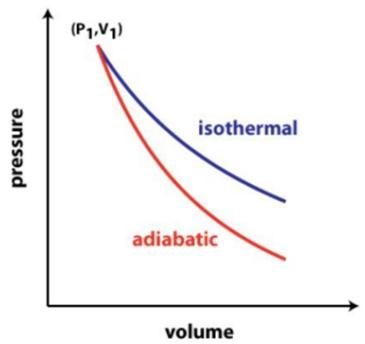
Note:-  $Q = W + \Delta U$

$$Q = W + \Delta U$$

$$W = -\Delta U$$

(10)

## Comparison between Adiabatic & Isothermal curve



Slope of adiabatic is  $\gamma$  than the Isothermal curve  
we have

For Adiabatic

$$PV^\gamma = C$$

Taking log both side

$$\log P + \gamma \log V = \log C$$

Differentiating both sides

$$\frac{1}{P} dP + \frac{\gamma}{V} dV = 0 \quad \text{---(1)} \Rightarrow \frac{dP}{dV} = -\gamma \frac{P}{V}$$

For Isothermal

$$PV = C$$

Taking log

$$\log P + \log V = \log C$$

on Differentiating

$$\frac{1}{P} dP + \frac{1}{V} dV = 0$$

$$\frac{dP}{P} = -\frac{dV}{V} \Rightarrow \frac{dP}{dV} = -\frac{P}{V} \quad \text{---(2)}$$

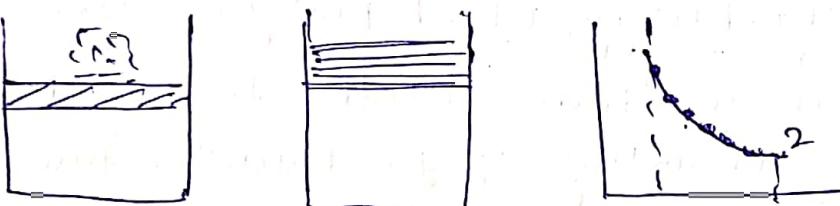
Dividing (1) by (2)

$$\frac{\left(\frac{dP}{dV}\right)_{\text{adiabatic}}}{\left(\frac{dP}{dV}\right)_{\text{iso}}} = \frac{-\gamma \frac{P}{V}}{-\frac{P}{V}} = \gamma$$

$\Rightarrow$  Slope of Adiabatic  $\left(\frac{dP}{dV}\right) = \gamma$  (Slope of Isothermal  $\left(\frac{dP}{dV}\right)$ )

## Quasi static process

The word quasi means almost, so it is almost static process. Quasi static Process is almost slow process in such a ~~process~~ way that each and every intermediate state is in Equilibrium.



- Note:-
- \* All the reversible processes are quasi-static
  - \* But all quasi-static processes are not reversible always. (It must be frictionless for being reversible).

Reversible Process:- The process is said to be reversible if it follows the same path as that of forward path without affecting the system and surroundings. (It is frictionless process)

Irreversible Process:- A process in which system & surroundings do not return to their original conditions.

Note:- Friction is the main cause of irreversibility.

Endothermic Process:- (Absorb heat)

Exothermic Process:- (Release heat)

Spontaneous Process! - Spontaneous process are those which takes place of its own without any External Energy or Effort.

They Process only in Single direction and proceeds till Equilibrium is Achieved.

Eg. If we take a cap of tea in Open room then it Starts losing Energy (heat Energy) itself and this Process continue until the temperature of both tea and surrounding is in Equilibrium.

Note! Generally Spontaneous Process tends to occur to Minimise their Potential Energy.

### CONTINUUM MODEL!

If is a concept in which Molecular gaps or voids are neglected.



Note! In case of liquid and solid Continuum is always valid, but in case of gas it is not always true.

To check whether Continuum is valid or not

Knudsen Number ( $Kn$ ) is used.

$$Kn = \frac{\text{mean free Path}}{\text{Characteristic Dimension}}$$

Condition for ( $Kn$ ) to be satisfy continuum.

$$Kn \leq 0.01 < \frac{1}{100}$$

## Equation of State

The equation of state relates the pressure  $P$ , volume  $V$  and temperature  $T$  of a physically homogeneous system to the state state of thermodynamic Equilibrium

$$f(P, V, T)$$

Suppos we have Thermodynamic Potential as -

$$\text{Thermodynamic Potential} = H, G, A, U$$

(  $H$ - Enthalpy,  $G$ - Gibbs Energy  
 $A$ - Area,  $U$ - Internal Energy )

4 Thermodynamic Variables =  $S, P, V, T$

(  $S$ - Entropy,  $P$ - Pressure  
 $V$ - Volume,  $T$ - Temperature )

So Equation of ~~State~~ State represent the variation in thermodynamic variables on thermodynamic Potential.

## First Thermodynamic Equation of State:-

1) we have  $dU = TdS - PdV$

$$\Rightarrow \boxed{\left( \frac{dU}{dV} \right)_T = T \left( \frac{dS}{dV} \right)_T - P}$$

First Equation of State.

(14) (i) For Ideal gas ( $C_P V = RT$ )

we have -  $\left(\frac{dU}{dV}\right)_T = 0$

(ii) For 1 mole of van der waal's gas Equation

$$\left(\frac{dU}{dV}\right)_T = \frac{q}{V^2}$$

(iv) For n mole of van der waal's gas Equation

$$\left(\frac{dU}{dV}\right)_T = \frac{qn^2}{V^2}$$

## INTERNAL ENERGY!

The energy content of a system is called Internal Energy. Internal Energy is the sum of following forms of energy of the system.

- (I) Kinetic Energy due to translational, rotational and vibrational motion of molecule, all of which depend on the temperature.
- (II) Potential Energy due to intermolecular forces, which depends on the separation between the molecule.

OR

Internal Energy of a System is the Energy Posses by the System due to Molecular Motion and Molecular Configuration.

- Energy due to Molecular Motion is called Internal Kinetic Energy.
- Energy due to Molecular configuration is called Internal potential Energy ( $U_p$ )

$$U = U_k + U_p$$

\* Internal Energy is Path Independent

Path Function! There are certain quantities like heat & work that can't be located on a graph by a point but they are represented by area. Such quantities are called Path Function

E.g. work (W), Heat (H)

### Point Functions

When two coordinates are located on a graph, they define a point and two properties on graph define state.

These Properties are (P,V,T) and called Point Function.

Graphs of these functions can be plotted with respect to time.

Graphs independent of time represent stationary states.

Independent variables will not change with time.

Dependent variables will change with time.

Time dependent functions are called Transient.

Time independent functions are called Stationary.

Stationary states are independent of time.

Transient states are dependent on time.

Stationary states are independent of time.

Transient states are dependent on time.

Stationary states are independent of time.

Transient states are dependent on time.

Stationary states are independent of time.

Transient states are dependent on time.

## First law of thermodynamics:

"Energy can neither be created nor be destroyed it change only its form"

(It is based on law of conservation of Energy).

When a certain amount of heat  $dQ$  is supplied to a system which does external work  $W$  in passing from state 1 to 2, amount of heat is equal to sum of increase in internal energy of the system and External work done by the System.

Mathematically

$$\boxed{dQ = (U_2 - U_1) + dW}$$

In differential form -

$$dQ = dU + dW \quad (\text{for very small change}).$$

Note:-  $dU$  is a perfect differential because  $U$  is a function of state system.

- This law is restatement of the Principle of conservation of Energy as applied to heat Energy.

## Sign conventions:-

- I) When heat is supplied to the system  $dQ$  is taken as positive. (Endothermic)
- II) Heat removed / released -  $dQ$  negative. (Exothermic)
- III) Temperature increased -  $dU$  positive
- IV) Temperature Decrease -  $dU$  negative

v) work done by the system -  $dW$  positive  
(Expansion)

vi) work done by the system -  $dW$  Negative  
(compression)

Note:- First law of thermodynamics introduce the concept of internal Energy.

Limitations :- It doesn't say how much heat Energy can be converted to work.

## Applications of 1st Law of thermodynamics.

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### I) Isothermal Process

In Isothermal process as there is no change in temperature, there will be no change in Internal Energy.

$$dU = 0$$

According to First law of thermodynamics

$$dQ = dU + dW$$

$$\boxed{dQ = dW}$$

$\Rightarrow$  Heat added or subtracted = External work done

### II) Isobaric Process

In Isobaric process, as the pressure remains constant the amount of heat supplied is used in doing external work and in increasing volume  $dV$ .

$$\text{External work } dW = PdV$$

According to First law of thermodynamics

$$dQ = dU + dW$$

$$\boxed{dQ = dU + PdV}$$

### III) Isochoric Process

In Isochoric process since volume of system remains constant ~~is known as~~ then  $dV = 0$

$$\boxed{dW = PdV = 0}$$

According to First law of thermodynamics

$$dQ = dU + dW$$

$$\boxed{dQ = dU}$$

(20)

Hence whole heat supplied to system is used in increasing its internal Energy only.

### d) Adiabatic Process:-

In adiabatic process as no heat enter or leave the system, but when a gas is allowed to expand it does external work and heat energy of gas decrease.

Similarly when a gas is compressed work is done & due heat energy of gas increase.

According to first law of thermodynamics

$$dQ = dU + dW$$

(since no heat enter or leave the system  $dQ=0$ )

$$\Rightarrow \boxed{0 = dU + dW}$$

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

Increase in Internal Energy  $\approx$  External work done on (or by) the gas.

## Adiabatic Equation of State:

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Consider a gas compressed adiabatically, so that the piston moves inward through a distance ( $x$ ). Let pressure, volume & temperature be  $P, V \& T$  respectively.

Then work done by the piston

$$W = \text{Force} \times \text{distance}$$

$$= P \times A \times dx$$

$$\int dW = PdV$$

According to First law of thermodynamics

$$dQ = dU + dW$$

$$\text{for Adiabatic } dQ = 0$$

$$0 = dU + dW$$

$$0 = dU + PdV \rightarrow ①$$

As the gas is compressed heat  $C_V = \frac{dU}{dT}$

$$dU = C_V dT \rightarrow ②$$

Put ② in ①

$$C_V dT + PdV = 0 \rightarrow ③$$

Now we have

$$PV = RT$$

on differentiating

$$PdV + VdP = RdT$$

$$dT = \frac{PdV + VdP}{R} \rightarrow ④$$

Substituting ④ in ③

$$C_V \frac{PdV + VdP}{R} + PdV = 0$$

$$C_V PdV + C_V VdP + RPdV = 0$$

$$C_V PdV + RPdV + C_V VdP = 0$$

$$(C_V + R)PdV + C_V VdP = 0$$

We know that  $C_P - C_V = R \Rightarrow \boxed{C_V + R = C_P}$

$$\Rightarrow C_P PdV + C_V VdP = 0 \quad \text{--- (5)}$$

Dividing (5) by  $C_V PV$

$$\Rightarrow \frac{C_P PdV}{C_V PV} + \frac{C_V VdP}{C_V PV} = 0$$

$$\Rightarrow \frac{C_P}{C_V} \frac{dV}{V} + \frac{dP}{P} = 0$$

We know that  $\boxed{\frac{C_P}{C_V} = r}$

$$\Rightarrow r \frac{dV}{V} + \frac{dP}{P} = 0 \quad \text{--- (6)}$$

Integrating Eqn (6)

$$\Rightarrow r \log V + \log P = \text{constant}$$

$$\Rightarrow r \log PV = \text{constant}$$

$$\Rightarrow \log PV^r = \text{constant}$$

$$\boxed{PV^r = K}$$

$$\Rightarrow \boxed{P_1 V_1^r = P_2 V_2^r}$$

Case I

$$PV^r = \text{const}$$

(23)

$$PV = RT$$

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

$$\Rightarrow \left( \frac{RT}{V} \right) V^r = \text{const}$$

$$\boxed{RTV^{r-1} = \text{const}}$$

Case II

$$PV^r = \text{const.}$$

$$PV = RT$$

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

$$P \left( \frac{RT}{P} \right)^r = \text{const.}$$

$$\frac{P^r T^r}{P^r} = \frac{\text{const}}{R}$$

$$\Rightarrow \frac{T^r}{P^{r-1}} = \text{const.}$$

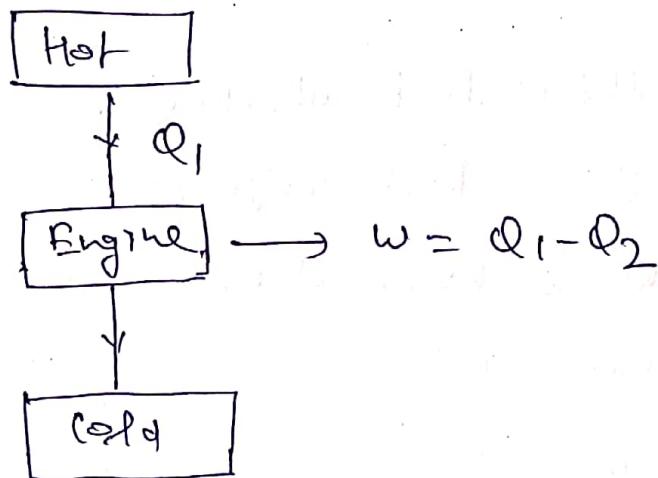
$$\text{or } \boxed{\frac{P^{r-1}}{T^r} = \text{const}}$$

## Heat Engine:-

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A machine that can convert heat into work is said to be a Heat Engine.

Heat Engine must operate continuously, It absorb heat at higher temperature and reject it at lower temperature.



The material used in the operation of Engine is called working substance.

The working substance in a Steam Engine is Steam(water)

## Efficiency:-

The efficiency of an Engine is defined as the ratio of net work done to the heat absorb during one complete cycle.

$$\eta = \frac{\text{Useful work done}}{\text{Heat absorb}}$$
(1)

After one complete cycle, the Engine return to its initial state. Therefore change in internal Energy is zero ( $\Delta U=0$ )

From first law

$$Q_1 - Q_2 = \Delta U + W$$

$$\Delta U = (Q_1 - Q_2) - W$$

$$0 = (Q_1 - Q_2) - W$$

$$\boxed{W = Q_1 - Q_2} \quad \text{---(2)}$$

Where

$Q_1$  is heat absorbed.

$Q_2$  is heat rejected.

$W$  is work done

From eqn (1) & (2)

$$\begin{aligned} n &= \frac{W}{Q_1} \\ &= \frac{Q_1 - Q_2}{Q_1} \end{aligned}$$

$$\boxed{n = 1 - \frac{Q_2}{Q_1}}$$

∴  $n$  is always less than unity.

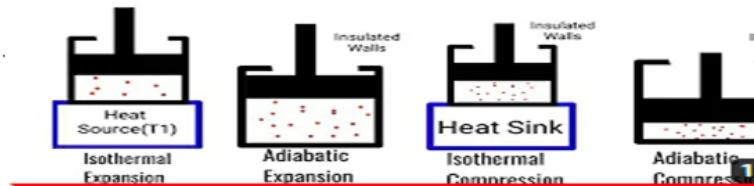
## Carnot Engine and Carnot Cycle! -

Carnot heat Engine is an ideal heat Engine and it is impossible to achieve ideal Engine in real situations. But it is important in Thermodynamics.

Carnot cycle consist of four stages!

- I Isothermal Expansion
- II Adiabatic Expansion
- III Isothermal Compression
- IV Adiabatic Compression

### Carnot's Engine



### Isothermal Expansion!

The cylinder first placed on the source, and let the gas undergo reversible Isothermal Expansion.

Let the working substance undergo during Isothermal Expansion goes from its initial state A ( $P_1, V_1, T_1$ ) to final state B ( $P_2, V_2, T_2$ ) at constant temperature  $T_1$  along AB. In this process, the substance absorb heat  $Q_1$  from the source at  $T_1$  and does work  $W_1$ , gives -

$$Q_1 - W_1 = \int_{V_1}^{V_2} P dV = R T_1 \log_e \frac{V_2}{V_1}$$

From Isothermal Process

$$\Delta U = 0$$

A.T. First law of thermodynamics -

$$Q_1 = W_1$$

## Adiabatic Expansion!

The cylinder is now removed from the source and is placed on the insulating stand. Now the gas is allowed to undergo reversible adiabatic expansion.

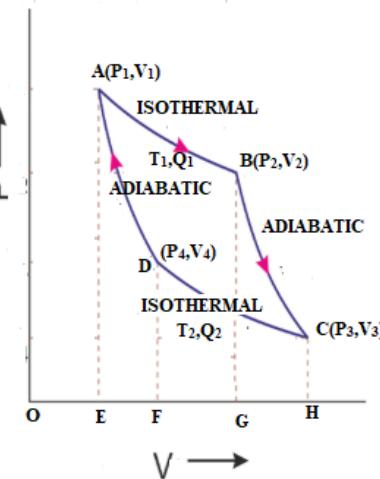
The temperature falls from  $T_1$  to  $T_2$ .

In this process there is no transfer of heat, the temperature of substance falls to  $T_2$  and it does some external work  $w_2$

$$w_2 = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$

$$= \frac{RT_2 - RT_1}{1-\gamma}$$

$$w_2 = \frac{R(T_1 - T_2)}{\gamma - 1}$$



Note:- Gas is now at low pressure to be used in cyclic processes/other, it has to be stored to its initial state. To this effect gas is compressed in two stages.

## Isothermal compression!

The cylinder is now removed from the insulating stand and is placed on the sink which is at temperature  $T_2$ . Now piston moves inward so that the work is done on the gas. Now temperature tend to increase due to heat produced by compression. Since the conducting base of cylinder is in contact with the sink and temp of gas remaining constant at  $T_2$ .

(29)

In this process the system rejects heat  $\text{Q}_2$  to the sink at  $T_2$  & work  $W_3$  is done by the system -

$$\begin{aligned} Q_2 &= W_3 = \int_{V_3}^{V_4} P dV \\ &= RT_2 \log_e \frac{V_4}{V_3} \end{aligned}$$

Note :-  $V_4$  is less than  $V_3$

$W_3 = -\text{ve}$  ( work is done on the system/gas )

$$( W_3 = -RT_2 \log_e \frac{V_3}{V_4} )$$

### Adiabatic compression:-

The cylinder is now removed from sink and again placed on the insulating stand. The piston is slowly moved inwards so that the gas is adiabatically compressed and temp rises.

The adiabatic compression is continued till the gas comes back to its original condition. Thus completing full cycle.

$$\begin{aligned} W_u &= \int_{V_4}^{V_1} P \cdot dV \\ &= \frac{R(T_2 - T_1)}{r-1} \\ &= -\frac{R(T_1 - T_2)}{r-1} \end{aligned}$$

(-ve sign indicate work done on the gas)

Net effect of the cycle:-

(25)

Total work done by engine is -

$$W_2 \int pdV = W_1 + W_2 - W_3 - W_4$$

$$= RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_3}{V_4}$$

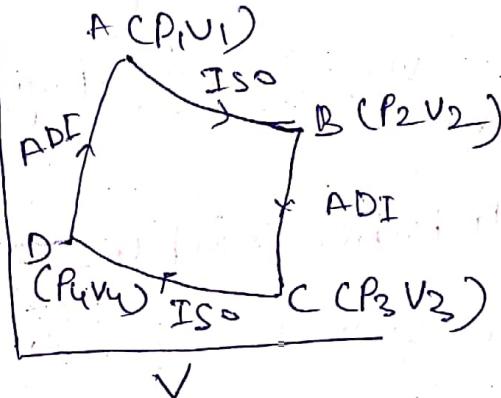
$$W = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_3}{V_4}$$

Now

for B to C line on the same adiabatic curve

$$T_1 V_2^{r-1} = T_2 V_3^{r-1}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{r-1} \quad \text{--- (1)}$$



For A and D points.

$$T_1 V_1^{r-1} = T_2 V_4^{r-1}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_4}\right)^{r-1} \quad \text{--- (2)}$$

From (1), (2)  $\therefore \frac{V_1}{V_4} = \frac{V_2}{V_3} \Rightarrow \left[ \frac{V_2}{V_1} = \frac{V_3}{V_4} \right]$

From Above Eqn

$$W_2 = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_3}{V_4}$$

$$\Rightarrow \boxed{W_2 = R(T_1 - T_2) \log_e \frac{V_2}{V_1}}$$

$$\text{Hence} \quad \left( \text{Efficiency } \eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \right)$$

As there is no heat interaction along reversible adiabatic process b-C and d-q and application of first law of thermodynamics gives -

$$dW = dQ$$

Now Efficiency of heat ~~engine~~ Engine

$$\begin{aligned} \eta &= \frac{W}{Q_1} = \frac{W}{W_1} \\ &= \frac{R(T_2 - T_1) \log \frac{V_2}{V_1}}{RT_1 \log \frac{V_2}{V_1}} \\ &= \frac{T_2 - T_1}{T_1} = 1 - \frac{T_2}{T_1} \end{aligned}$$

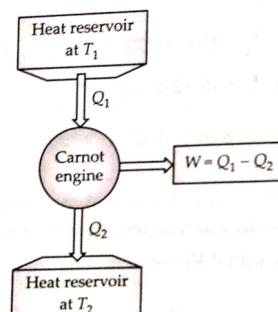
$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$

## Carnot Engine & Carnot Refrigerator

(22)

Carnot cycle is perfectly reversible. It can work as a heat engine also as a refrigerator.

- I) When it is operated as a heat engine, it absorb heat  $Q_1$  from the source at Temperature  $T_1$ , and does work  $W$  and reject heat  $Q_2$  to the sink at Temperature  $T_2$  ( $T_2 < T_1$ )

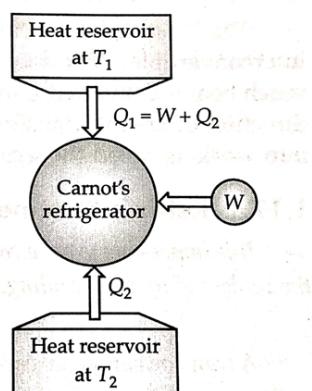


A Carnot's engine.

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- II) When it is operated as refrigerator it absorb heat  $Q_2$  from the sink at Temperature  $T_2$ . Work is done by external means and reject heat  $Q_1$  to the source at temperature  $T_1$  ( $T_1 > T_2$ ).

\* Note In this case work done on the system  $W$  and output is heat  $Q_2$  removed from lower temperature reservoir.



A Carnot's refrigerator.

CS Scanned with CamScanner

A Refrigerator therefore Rated by its Coefficient of Performance  $B$  defined as -

$$B = \frac{\text{Heat output}}{\text{Workdone}}$$

$$\therefore B = \frac{Q_2}{W}$$

$$\therefore B = \frac{Q_2}{W} = \frac{Q_2}{\frac{Q_1 - Q_2}{\eta}} = \frac{Q_2 \eta}{Q_1}$$

$$\text{or } B = \eta \frac{T_2}{T_1 - T_2}$$

For ideal gas

$$\left( \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \right)$$

## Concept of Entropy:-

The entropy is defined as the measure of molecular disorder. It means greater is the molecular disorder more is the entropy. Represented by  $S$ .

A change in order is a change in number of ways of arranging the particles and it is a key factor in determining the direction of any process.

Solid  $\rightarrow$  liquid  $\rightarrow$  gas

more order  $\longrightarrow$  less order

When a body absorb or reject a small amount of heat energy at Temp  $T_1$ , the change  $dS$  in entropy of body is -

$$dS = \frac{dq}{T} \quad (\text{calories}/^\circ\text{C or JK}^{-1})$$

It is difficult to define absolute value of entropy in passing from one adiabatic ( $A_1$ ) to other ( $A_2$ ) is -

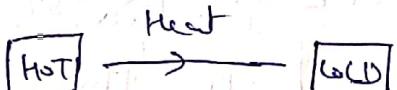
$$S_2 - S_1 = \int_{A_1}^{A_2} dS = \int_{A_1}^{A_2} \frac{dq}{dT}$$

for Adiabatic  $\frac{dq}{dT} = 0$

Thus along adiabatic there is no change in entropy or we can say that adiabatic are curves of constant entropy. Entropy is path independent function

## Second Law of Thermodynamics!

(35)

- 1) The entropy of Universe is increasing continuously as a result of Spontaneous process.  
(All spontaneous process are irreversible)
- 2) Without the help of external Agency the spontaneous process can't be reversed.
- 3) Clausius Statement! It is impossible to spontaneous flow of heat from colder body to hot body  
(Heat always flows from hot to cold body).  


```
graph LR; A[Hot] -- Heat --> B[Cold]
```
- 4) Kelvin Planck! It is impossible to construct a machine which has 100% efficiency  
(convert 100% heat to work)
- 5) Kelvin Statement! It is impossible to obtain work by cooling a body below its lower temperature.

## Third law of thermodynamics!

- 1) It state that as the temperature of a system approached absolute zero, its entropy becomes constant or change in entropy (ΔS) is zero.
- 2) Third law of thermodynamics also called Herbst law.

Absolute zero! - The coldest possible temperature

$$\begin{aligned} \text{is } 0\text{K} \\ 0\text{K} &= -273^\circ\text{C} \\ &= -459.67^\circ\text{F} \end{aligned}$$

Example At absolute zero temperature the entropy of a perfectly crystalline substance becomes zero.

$$\begin{aligned} \Delta S &= 0 \\ \text{Temp} &= 0\text{K} \quad (\text{crystalline solid}) \end{aligned}$$

# At 0K the entropy of ideal gas becomes zero.

Liquid  $\longrightarrow$  Solid (0K)

### Zeroth law of Thermodynamics:

If two systems A & B ~~are not~~ separately are in thermal equilibrium with a third system C then A & B will be thermal equilibrium or all (A, B, C) will be in thermal equilibrium.

# (T-S) Diagram (Temperature Vs Entropy).

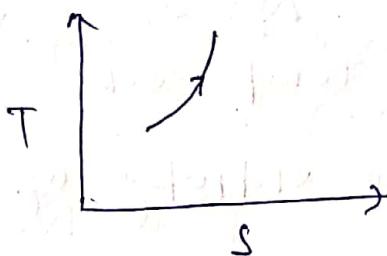
## D) Iso baric Process ( $P = \text{constant}$ )

$$\frac{dT}{dS} = \frac{T}{C_p}$$



## II) Iso choric Process ( $V = \text{constant}$ )

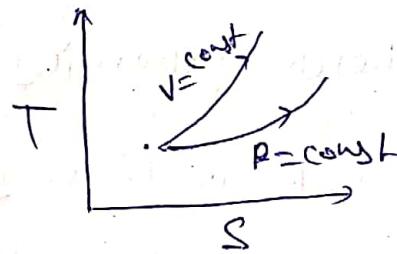
$$\frac{dT}{dS} = \frac{T}{C_V}$$



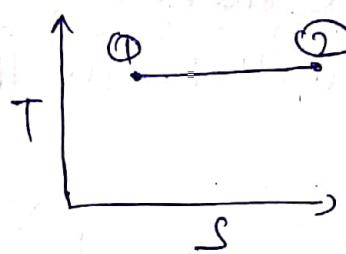
On comparing Iso baric & Iso choric

AS

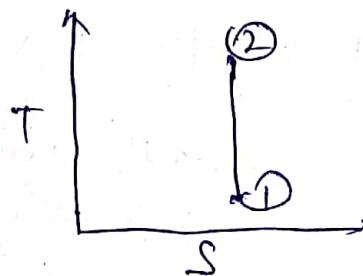
$$(C_p - C_V = R \Rightarrow)$$



## III) Iso thermal process ( $T = \text{constant}$ )



## IV) Adiabatic Process ( $PV^r = \text{constant}$ )



## Entropy change during irreversible process.

Let us consider an engine performing irreversible cycle of change in which the working substance absorb heat  $Q_1$  at temperature  $T_1$  from the source and reject heat  $Q_2$  to the sink at temp  $T_2$ .

Then

Efficiency of irreversible cycle.

$$\eta' = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad \text{--- (1)}$$

Efficiency of reversible cycle.

$$\eta = 1 - \frac{T_2}{T_1} \quad \text{--- (2)}$$

According to Carnot theory, Efficiency of irreversible engine should be less than efficiency of reversible cycle

$$\eta' < \eta$$

$$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

$$\text{or } \frac{Q_2}{T_2} > \frac{Q_1}{T_1} \text{ or } \boxed{\frac{Q_2}{T_2} - \frac{Q_1}{T_1} > 0}$$

Thus there is an increase in entropy of system during an irreversible process.

This is known as law of increase of entropy.

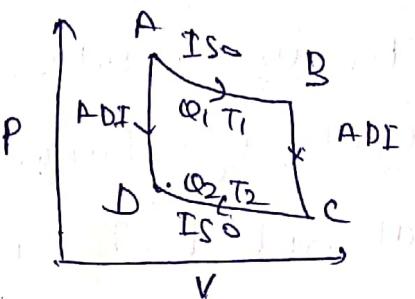
\* All natural process in Universe are irreversible.

## (34)

### Change in Entropy in Reversible Process (Carnot Theory)

Consider a complete Reversible Carnot Cycle as shown in Figure

formed by two Isothermal & two adiabatic process.

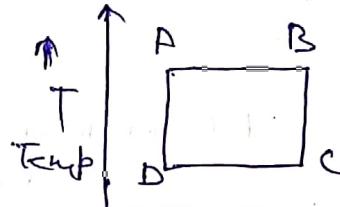


#### I) Isothermal Expansion AB :-

Let  $Q_1$  is the heat absorbed at Temp.  $T_1$

The increase in enthalpy of the working substance is -

$$B \int_A^B dS = \frac{Q_1}{T_1}$$



S (Entropy)

#### II) Adiabatic Expansion BC :-

BC - Adiabatic Expansion.  
during this process

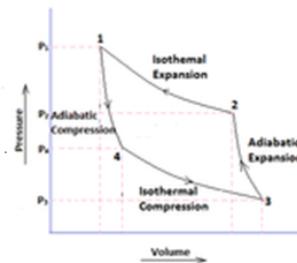
$$C \int_B^C dS = 0$$

#### III) Isothermal compression CD :-

CD - Isothermal compression.

Working substance rejects heat  $Q_2$  to the sink at Temp  $T_2$ . The entropy of the working substance decrease and change in entropy is given by -

$$D \int_C^D dS = -\frac{Q_2}{T_2}$$



P-v and T-s Diagrams of a Carnot

## V) Adiabatic compression DA-

DA - Adiabatic

$$\text{then change in Entropy } \int_B^A dS = 0$$

Thus Net gain in entropy

$$= \int_A^B dS + \int_B^C dS + \int_C^D dS + \int_D^A dS$$

$$= \frac{Q_1}{T_1} + 0 + \left( -\frac{Q_2}{T_2} \right) + 0$$

$$\oint dS = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \quad \text{--- (1)}$$

Substituting for reversible cycle cannot cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Substituting Eqn (1)

$$\Rightarrow \oint dS = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

Thus in Reversible cycle the Entropy of the system remains Unchanged.

Statement of Carnot theorem A reversible Engine operating between two given reservoirs (Carnot Engine) is most efficient that can operate between these reservoirs. OR

No engine operating between two given temperature is more efficient than Carnot Engine.