WHAT IS THERMODYNAMICS?

→ Thermodynamics is a branch of science which deals with energy transfer and its effects on properties (physical and chemical) of the substance.

→ Amount of heat (or work) transfer taking place while arriving at one state from another is the main concern of thermodynamics. Units :- J/KJ

SYSTEM AND SURROUNDINGS

System :- It is a fixed mass or region in a space (control volume) where our study is focused.

Surroundings :- Everything external to the system is the surrounding.

(That part of the ~~system~~ surrounding which is affected by the system is called immediate surrounding.)

TYPES OF SYSTEMS :-

(1) Closed system :- It is a type of system in which only energy interactions and no mass interactions take place.

Eg :- Thermo's flask ; Piston - cylinder arrangement without valves ; mass of gas/vapour in engine cylinder

(2) Open system :- It is a type of system in which both energy and mass interactions take place.

Eg :- Piston - cylinder arrangement with valves.

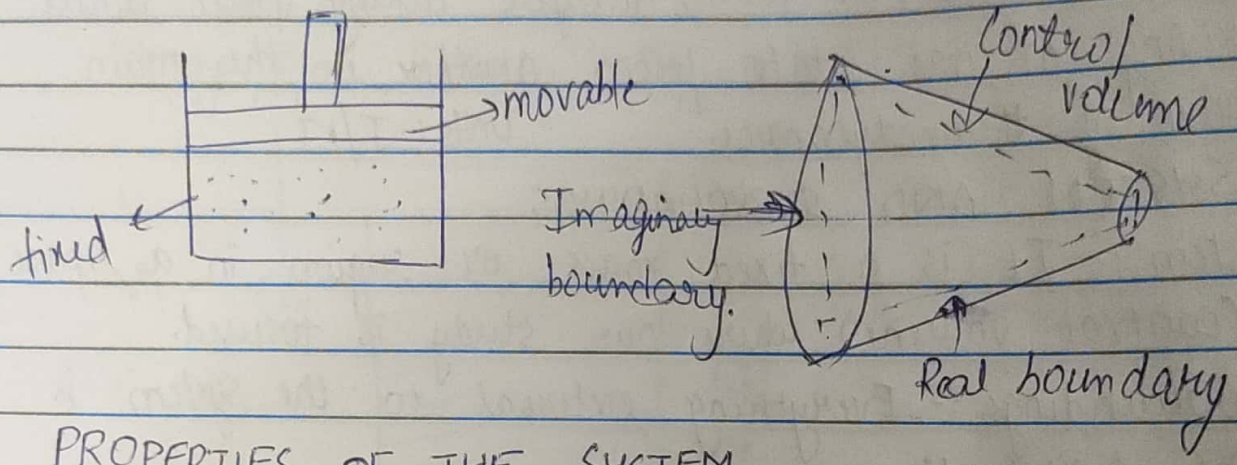
(3) Isolated System :- It is a type of system in which neither energy nor mass interactions take place.

Eg :- Universe

BOUNDARY

→ It is real or imaginary surface that separates system from surroundings.

→ It can be fixed or movable.



PROPERTIES OF THE SYSTEM

Any characteristic of the system is known as the property of the system.

Intensive and Extensive properties

(1) Intensive (or intrinsic) properties:-

Properties which are independent of the mass of the system.

Eg:- Density, temp., pressure etc.

(2) Extensive (or extrinsic) properties:-

Properties which are dependent on the mass of the system.

Eg:- Volume, Enthalpy, Entropy, K.E, P.E etc

* All the specific properties are intensive.

Eg:- Specific volume, specific enthalpy, specific entropy etc.

Mass (M)	Extensive	M/2	M/2
Volume (V)		V/2	V/2
Temp (T)	Intensive	T	T
Pressure (P)		P	P
Density (ρ)		ρ	ρ

Properties which divide when partition is done are called extensive properties.

Key points w.r.t. properties
- They are point functions (Independent of path)
- They are exact differentials
- They are independent of past history.

STATE:- Any condition of the system is known as state of the system.
PROCESS:- Change of state is called process.
PROCESS PATH:- The infinite states through which the system passes while going from initial state to the final state is called the process path.

Thermodynamics

Macroscopic	Microscopic
• Classical Thermodynamics	• Statistical Thermodynamics
↓	↓
More number of molecules present	Very few molecules present.

Classification of processes

→ Quasi-static

- It is a kind of process which occurs infinitely slow.
- It is represented by joined lines on property diagrams

→ Non-quasi static

- It is that kind of process which doesn't occur infinitely slow.
- Represented by dashed-lines on property diagrams.

→ Reversible

- It is that kind of a process which can be reversed in direction following the same path and without leaving any effect on system and surroundings.

→ Irreversible

- It is that kind of process which is not reversible.

Some key points:-

- All quasi-static processes are not reversible, but all reversible processes are quasi-static.
- Quasi-static compression and expansion of gas is reversible process.

MACROSCOPIC & MICROSCOPIC ANALYSIS

Macroscopic:- (Pressure, stress)

- In this analysis, average molecular behaviour is taken into consideration.
- This approach is valid till the concept of continuum holds good.

(mean free path << system dimensions)

1 bar = 10^5 Pa ; 1 atm = 101,325 Pa = 1.01325 bars

1 Kgf/cm^2 = 9.807×10^4 Pa = 0.9679 atm = 0.9807 bar

1 atm = 14.696 psi, 1 kgf/cm^2 = 14.223 psi

MICROSCOPIC

- In this analysis, individual molecular behaviour is taken into consideration.
- This approach is valid when system becomes rare. (Mean free path of molecule is of the order of system dimensions).

PRESSURE

Gases:-

- Pressure in gases is due to forces occuring because of colliding molecules with the surface and it acts normal to the surface.
- Pressure is a function of density and temperature.
- Density is directly proportional to the no. of molecules colliding.
- Colliding velocity is directly proportional to temperature

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

Liquid:-

- Pressure in the liquid is due to repulsion of molecules.

THERMODYNAMIC EQUILIBRIUM:-

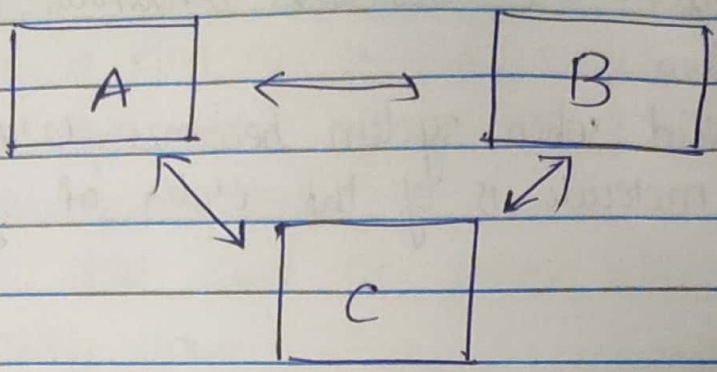
Thermal Eq. → Temp. ~~are~~ is equal

Mechanical Eq. → forces are equal

Chemical Eq → Chemical composition should not change w.r.t. time.

Phase Eq → Mass of each phase should remain cons. w.r.t. time

Zeroth law of thermodynamics



If body A is in thermal equilibrium with C, & B is also in thermal equilibrium with C, then A & B are in thermal equilibrium with each other.

* Study of temperature and its measurement is called thermometry.

Energy and Energy Interactions

Energy → Microscopic + Macroscopic

Microscopic energy is the internal energy.

Macroscopic energy is the bulk kinetic and potential energy.

Internal energy comprises of sensible energy + latent energy + chemical energy + Nuclear energy.

Energy interactions can take place in 3 ways:-

(1) Mass interaction (2) Work interaction

(3) Heat interaction.

IDEAL GAS

Assumptions:-

- Intermolecular forces are negligible.
- Volume occupied by molecules of gas is neglected as compared to the volume of container.

Conditions:-

- Pressure should be less.
- Temperature should be high.

Key points w.r.t. ideal gas

- All the substances which are gases in normal conditions will always be taken as ideal gases.
  Eg:- O_2, N_2, CO_2 etc.
- Water vapour will be taken as ideal gas till mentioned.
- Steam will never be taken as ideal gas till mentioned

GAS CONSTANT

$PV = mRT$; where R = characteristic gas constant
$= 0.287$ KJ/Kg-K (KJ/Kg-K)

$PV = n\bar{R}T$; where $\bar{R}$ = universal gas constant (KJ/Kmol-K)
$= 8.314$ KJ/Kmol-K

$R = \bar{R}/M$

Ideal gas equation for various processes

$PV = mRT$

Since m & R are constant

$$\frac{PV}{T} = \text{constant} \Rightarrow \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

where T is absolute temp. and P is absolute pressure

IDEAL GAS EQUATIONS FOR VARIOUS PROCESSES

(1) Constant volume (isochoric) → $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

(2) Constant pressure (isobaric) → $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

(3) Constant temp. (isothermal) → $P_1V_1 = P_2V_2$

(4) Adiabatic → PV^γ = constant

(No heat transfer) $P_1V_1^\gamma = P_2V_2^\gamma$ (or) $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ $\gamma = C_p/C_v$

(5) Polytropic → PV^n = constant

$P_1V_1^n = P_2V_2^n$ (or) $T_1V_1^{n-1} = T_2V_2^{n-1}$

Slope of Isothermal and Adiabatic curve on P-V Diagram for Ideal Gas

Slope of adiabatic > slope of isothermal

Isothermal

PV = constant

$PdV + VdP = 0$

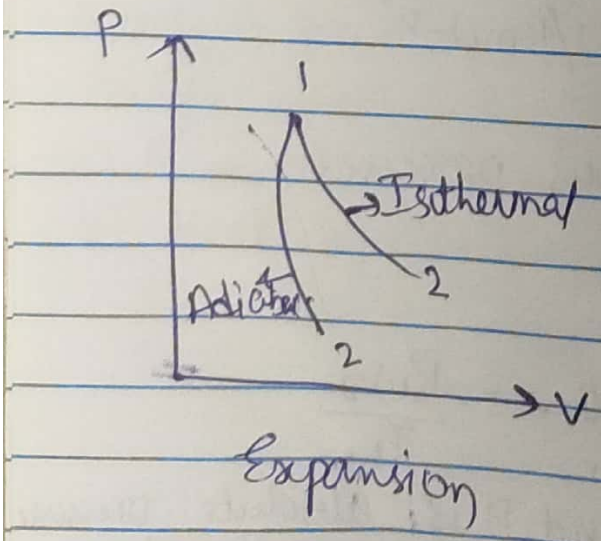
$\text{Slope} = \frac{dP}{dV} = \frac{-P}{V}$

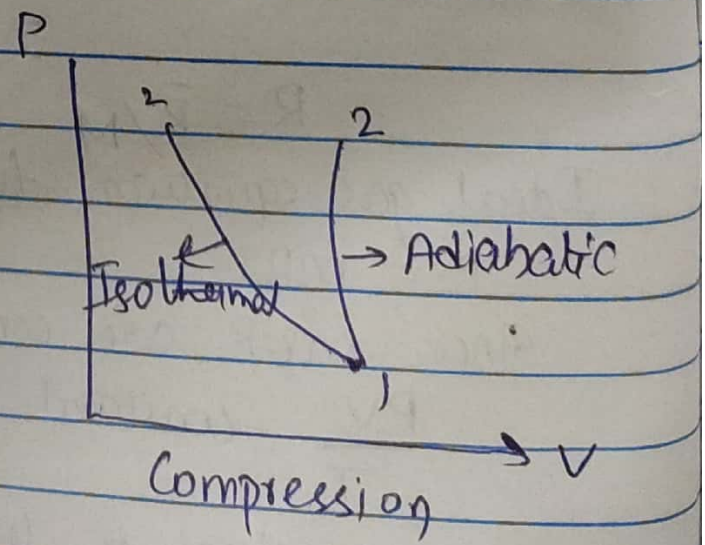
Adiabatic

PV^γ = constant

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

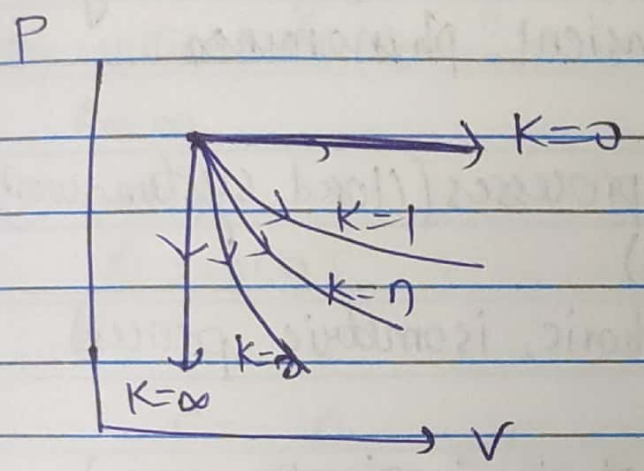
$\text{Slope} = \frac{dP}{dV} = \frac{-\gamma P}{V}$



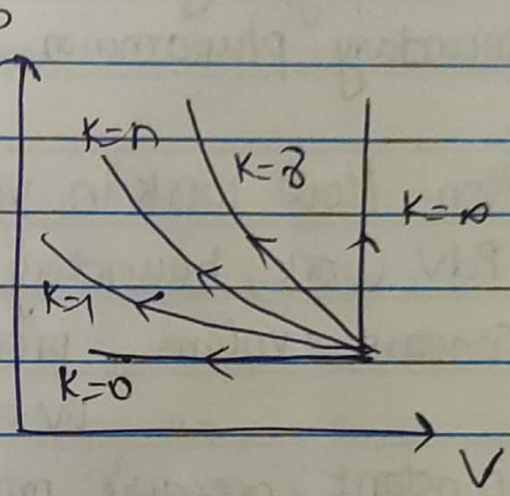


PV^K = constant

Value of K	Process
0	Isobaric
1	Isothermal
n	Polytropic
γ	Adiabatic
∞	Isochoric



Expansion



Compression

WORK

When a body is displaced with the application of force, work is said to be done.

$$\vec{\delta W} = \vec{F} \cdot \vec{dr}$$

- It depends upon direction of force as well as displacement.
- If displacement is zero, work is not necessarily zero.
- If displacement is zero, work is zero for conservative forces.

CLOSED SYSTEM ANALYSIS

Area under the P-V diagram when projected on the volume axis is gives the work interaction for the closed system.

$$\vec{\delta W} = P \cdot \vec{dV}.$$

$$\text{Pressure} = \frac{F}{A}$$

Conditions :-

- Closed system
- Quasi-static or pressure close to the piston system

IMPORTANT POINTS w.r.t. WORK and HEAT

- Path function
- Not a property
- Boundary phenomenon
- Inexact differential
- Dependent on past history
- Transient phenomenon

Non-flow work in various processes (Closed system work, PdV work, boundary work)

1. Constant volume process (isochoric, isometric process)

$$W = 0$$

2. Constant pressure process (isobaric, isopiestic process)

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

3. Constant temperature process (isothermal process)

$$W = C \ln \frac{V_2}{V_1}, \quad W = C \ln \frac{P_1}{P_2},$$

where $C = P_1V_1 = P_2V_2 = nRT$

4. Adiabatic process ($PV^{\gamma} = \text{constant}$)

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

5. Polytropic process ($PV^n = \text{constant}$)

$$W = \frac{P_1V_1 - P_2V_2}{n-1}; \quad n \neq 1$$

$1 < n < \gamma \rightarrow$ general

$-\infty < n < \infty \rightarrow$ ideal

* Quasi-static expansion or compression process is the most efficient process. Work obtained during quasi-static expansion is maximum and work required during quasi-static compression is minimum.

HEAT

Heat is a form of energy which is transferred by the virtue of temperature difference.

$Q \propto m$

$Q \propto dT$

$Q = mc\,dT$

$c \rightarrow$ specific heat

$mc \rightarrow$ heat capacity

$$C = \frac{Q}{m\,dT} \text{ KJ/kg-K} \quad (\text{or}) \text{ KJ/kg-°C}$$

$C_p \rightarrow$ specific heat capacity at cons. pressure

$C_v \rightarrow$ " " " " " volume

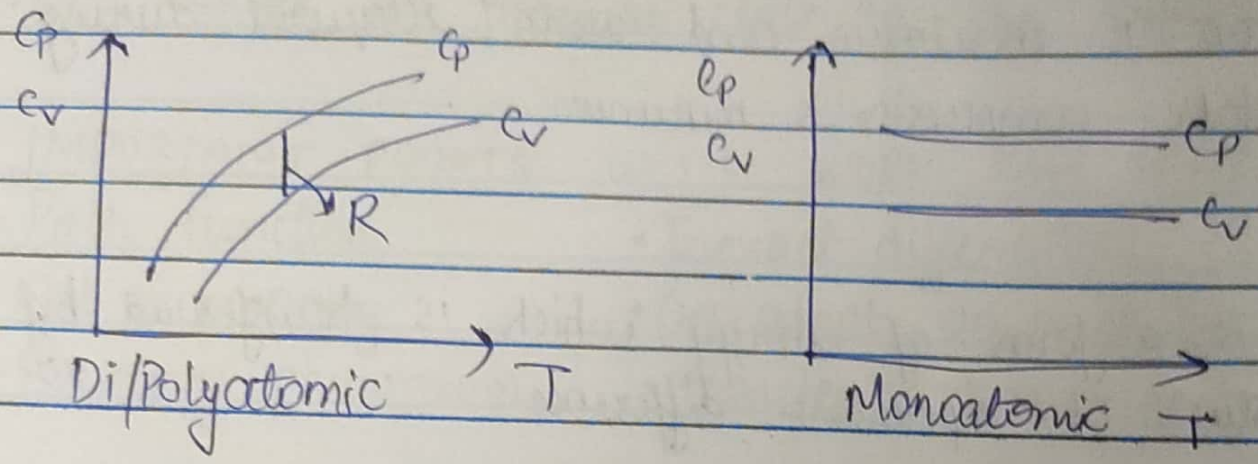
Specific heat is the amount of energy required to raise the temperature of unit mass of a substance by unit degree.

Specific heat at constant pressure (C_p) is greater than specific heat at constant volume (C_v) because C_p includes both internal energy as well as boundary work whereas C_v includes only internal energy.

As temperature increases

Both C_p and C_v increases but γ decreases for polyatomic gases.

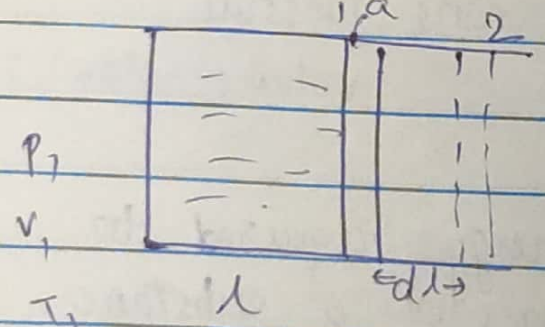
For mono-atomic gases both C_p and C_v remains constant; hence $\gamma \rightarrow$ constant.



Sign conventions for heat & work.

HEAT → given to system (+ve)
taken from system (-ve)

WORK → Done by system (+ve)
Given to system (-ve)



$dw = F \times dl$

$dw = P a dl$

$\int dw = \int P dv$

$W = \int_{1}^{2} P dv.$