

THERMO-DYNAMIC (NOTES)

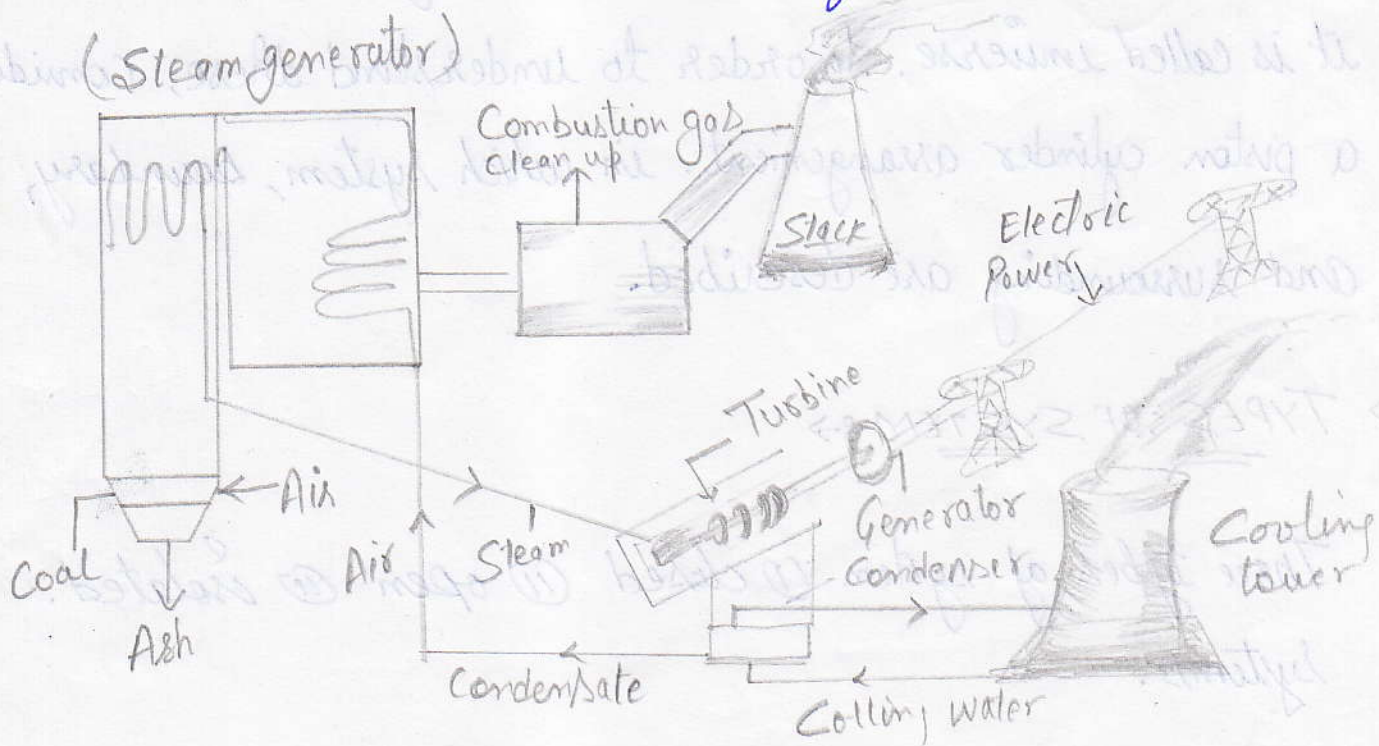
Thermodynamic :-> is the branch of science that deals with energy interactions between material system. In other words it deals with the transformation of energy of all kinds from one form to another.

* The science of thermodynamic is based on the four laws of thermodynamic known as zeroth, first, second and Third law.

Areas of application of Engineering thermodynamic :->

Engineers use principles drawn from thermodynamic and other engineering science such as fluid mechanics and heat and mass transfer.

- (i) Automobile engine
- (ii) Steam and gas turbine etc.



Mass \Rightarrow is the measure of quantity of matter as well as the property called inertia.

Weight \Rightarrow is proportional to mass at a particular location. but the proportionality factor change place to place.

THERMODYNAMIC SYSTEM, SURROUNDING & UNIVERSE...

\Rightarrow System \Rightarrow as a prescribed region or space of finite quantity of matter surrounded by an envelope called boundary.

The boundary may be fixed or it may be moving as when a system containing a gas is compressed expanded.

Surrounding \Rightarrow The space and matter external to the thermodynamic system and outside boundary is called the surrounding.

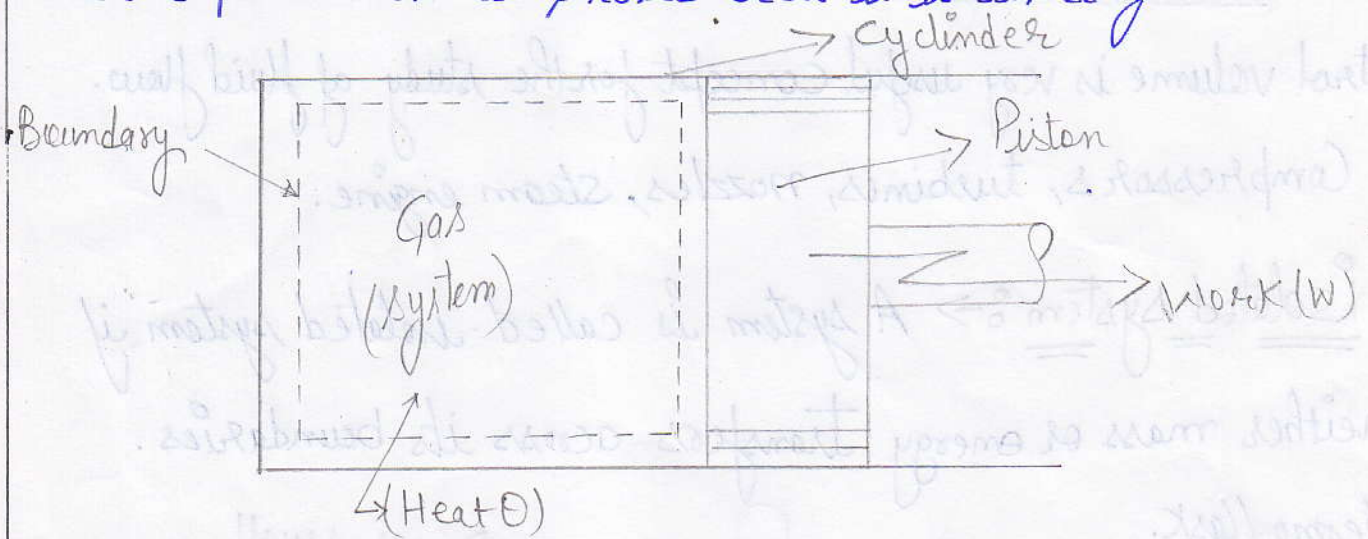
(iii) Universe \Rightarrow When a system and surrounding are put together it is called universe. In order to understand these, consider a piston cylinder arrangement. in which system, boundary and surrounding are described.

\Rightarrow TYPES OF SYSTEM \Rightarrow

Three types of system (i) closed (ii) open (iii) isolated systems.

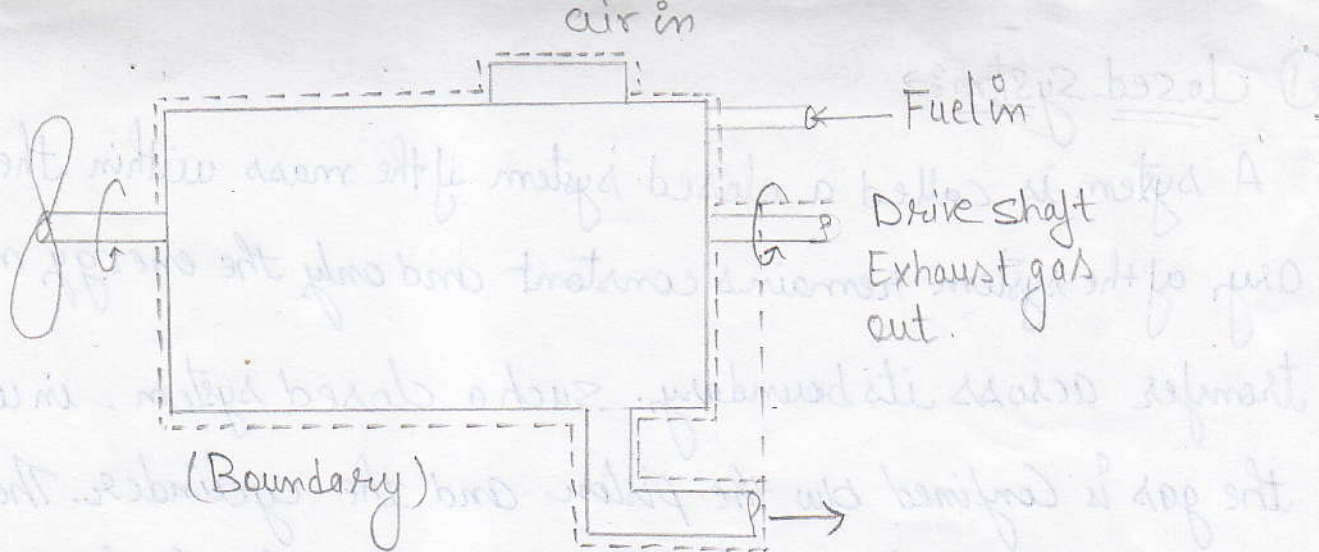
① closed system :->

A system is called a closed system if the mass within the boundary of the system remains constant and only the energy may transfer across its boundary. Such a closed system, in which the gas is confined b/w the piston and the cylinder. The mass of the gas is constant within the system even though the gas may be expanded or compressed bec'z it is closed from all sides.



(Closed system)

② open system :-> A system is called an open system if the mass as well as the energy transfer across its boundaries. Such as open system in which the gas is entering and coming out of the system while transfer of heat and work energy is also taking place. The net amount of mass within the system may also vary with time.



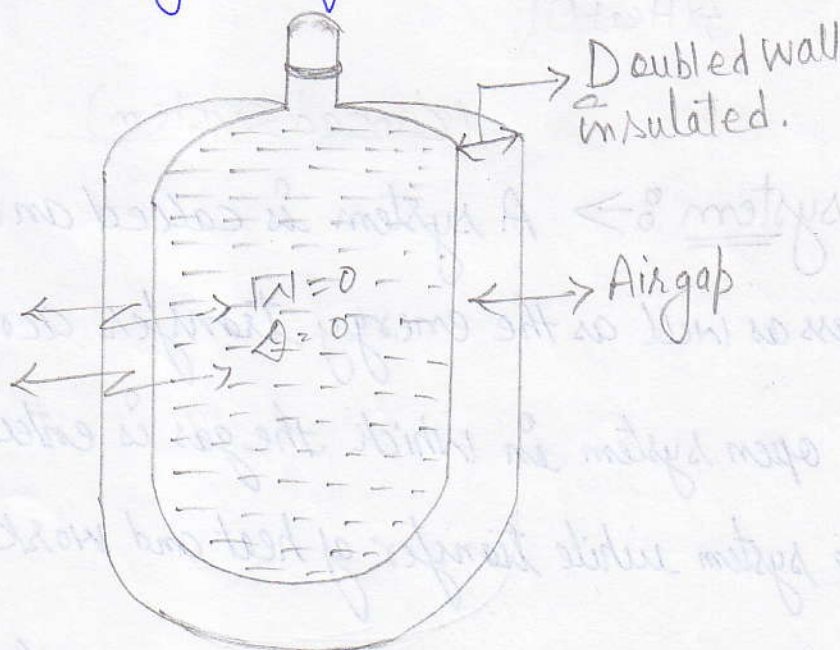
(Automobile Engine)

Control volume is very useful concept for the study of fluid flow.

Eg Compressors, turbines, nozzles, steam engine.

(iii) Isolated system \Rightarrow A system is called isolated system if neither mass or energy transfers across its boundaries.

(Thermoflask)



Isolated system

Macroscopic and Microscopic Point of view :->

If the analysis of a thermodynamic system is explained by the measurable properties such as pressure, volume etc. of the system.

It is termed as macroscopic point of view. The microscopic point of view focus on the statistical behaviour of mass consisting of numerous individual molecules and correlates macroscopic properties of matter with molecular configuration and with intermolecular forces.

macroscopic characteristics

- > They don't explain the structure of system.
- > They are readily measurable.
- > only a few co-ordinates are sufficient to describe the system.

Density :-> (ρ) The average density of a system is the ratio of its total mass to its total volume.

$$\rho = \frac{\Delta m}{\Delta V} = \text{Kg/m}^3$$

Specific weight :-> (ρ_w) is the weight per unit volume. It may be expressed in N/m^3 . It is also known as weight density.

Specific volume \Rightarrow is defined as the volume per unit mass and may be expressed in m^3/kg , reciprocal of the density.

$$v = \frac{1}{\rho} = \text{m}^3/\text{kg}.$$

Pressure \Rightarrow is defined as the force exerted normal to unit area of the boundary. When a fluid is contained within a vessel, the pressure exerted on the vessel is equal to the mean change of momentum of the molecules exerted \perp to the confining boundary per unit area.

$$P = \frac{\Delta F}{\Delta A} = \text{N}/\text{m}^2.$$

(a) Atmospheric pressure \Rightarrow The pressure exerted by the atmospheric air. The standard atmospheric pressure is defined as the pressure produced by a column of mercury 760 mm high, the mercury density $13.5951 \text{ kg}/\text{m}^3$.

Gauge pressure \Rightarrow The pressure measured from the gauge and instrument such as Bourdon and manometers is called gauge pressure. The gauge actually measures the difference b/w the fluid pressure and the pressure of atmosphere surrounding.

(4)

Absolute pressure \Rightarrow The pressure measured from the level of absolute zero pressure is called absolute pressure. Absolute zero pressure will only occur when the molecular momentum of the fluid is zero.

$$P_{abs} = P_{atm} + P_{gauge} = N/m^2.$$

Vacuum pressure \Rightarrow If the pressure of fluid to be measured is less than atmospheric pressure, the gauge will read on the negative side of the atmospheric pressure. Which is known as Vacuum.

$$P_{abs, vacuum} = P_{atm} - P_{vac, gauge} = N/m^2.$$

THERMODYNAMIC EQUILIBRIUM \Rightarrow

A system is said to be in a state of thermodynamic equilibrium if the value of the property is the same at all points in the system.

Consider an isolated system. An isolated system always reaches in course of time a state of thermodynamic equilibrium.

(i) Mechanical Eq. (ii) Chemical Eq... (iii) Thermal eq...

(iv) Electrical equilibrium.

Mechanical Eq... $\circ \rightarrow$ A system is said to be in a state of mechanical Equilibrium if there exists no unbalanced force either in the interior of the system or b/w the system and surrounding.

Chemical Eq... $\circ \rightarrow$ A system is said to be in a state of Chemical Equilibrium if there exist no chemical reaction or transfer of matter from one part of the system to another.

Thermal Eq... $\circ \rightarrow$ When a system existing in mechanical and chemical equilibrium is separated from its surrounding by a diathermic wall and if there is no spontaneous change in the property of the system. is said to be exist in thermal Equilibrium.

Electrical Equilibrium $\circ \rightarrow$ A system is said to be in a state of electrical equilibrium if there exists an uniformity of Electrical potential throughout the system.

Property $\circ \rightarrow$ of a system is its measurable characteristics describe the system. The measurable characteristics are mass, physical composition, temp, pressure, volume etc.

(1) Intensive properties \Rightarrow if the value of the property does not depend upon the mass of the system it is called an intensive property. Eg \Rightarrow pressure, temperature, velocity, density. 15)

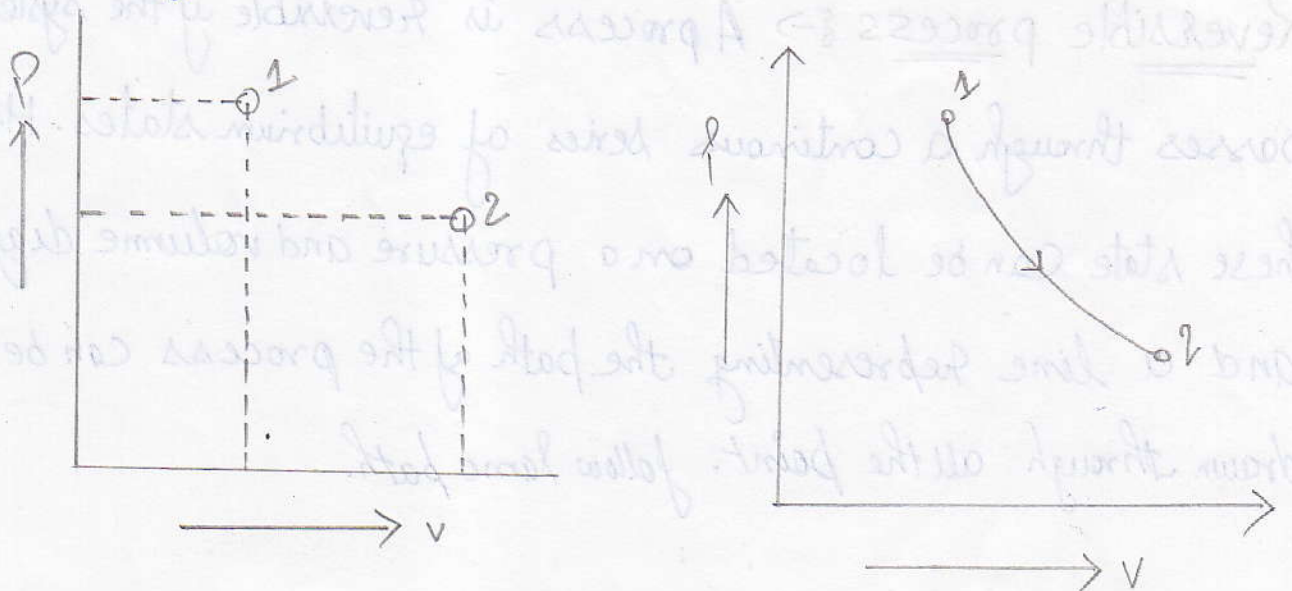
(II) Extensive property \Rightarrow if the value of the property depend upon the mass of the system it is called an extensive property. Eg, volume, surface area, internal energy, potential energy.

State \Rightarrow The state is a unique condition of the system.

Broadly speaking state is the equilibrium of a system at an instant of time described by its property such as pressure temperature density etc.

(I) A variable is a property, and only, if it has a single value at each equilibrium state.

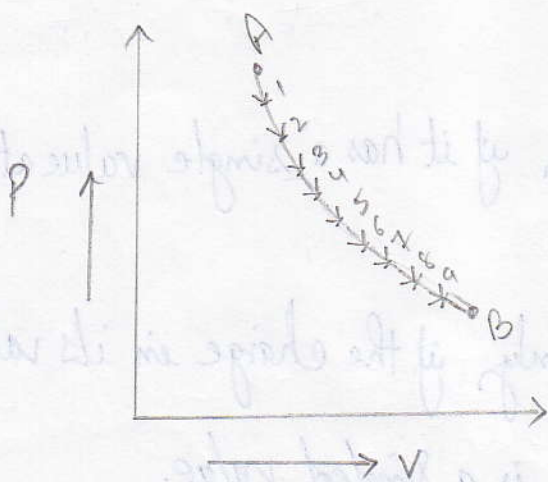
(II) A variable is a property, and only, if the change in its value between any two equilibrium state is a single value.



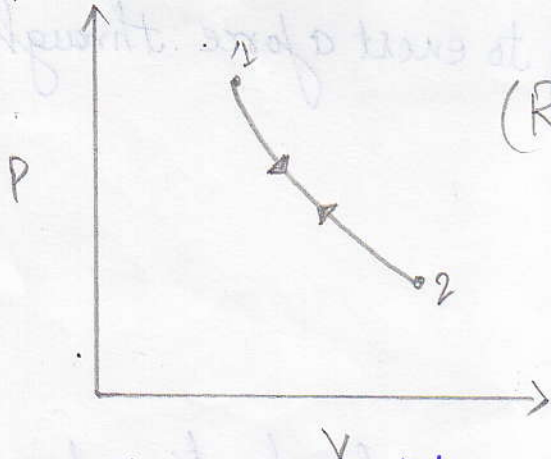
Path \Rightarrow A thermodynamic system passing through a series constitutes a path.

Process \Rightarrow A process is defined as a transition in which a system changes from one initial state to a final state.

Quasi-static (Quasi-Equilibrium) process \Rightarrow A quasi static process is one in which the system deviates from one equilibrium state by only infinitesimal amount throughout the entire process. A process closely approximating to a succession of equilibrium states is known as equilibrium.



Reversible process \Rightarrow A process is reversible if the system passes through a continuous series of equilibrium states. Hence these state can be located on a pressure and volume diagram and a line representing the path of the process can be drawn through all the point. follow same path.



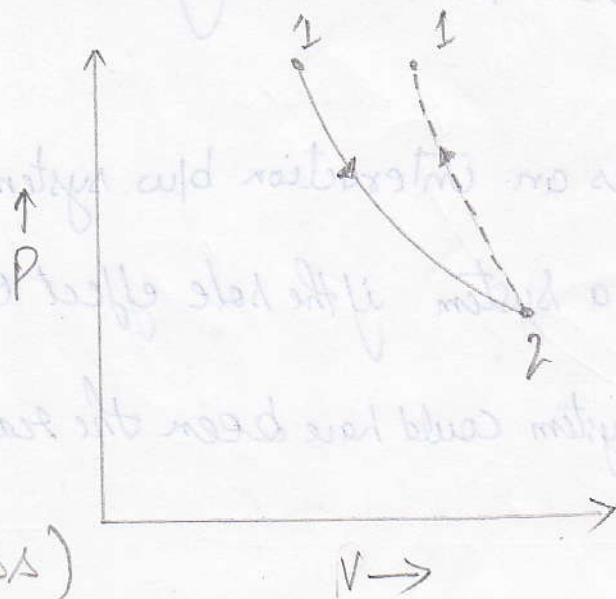
(Reversible process)

- Frictionless relative motion.
- frictionless adiabatic expansion or compression of fluid.
- Extension or compression of a fluid.
- Electrolysis
- Isothermal expansion or compression.

Irreversible process → A process is irreversible if a system passes through a sequence of non equilibrium states.

These states cannot be located on any property diagram becz each property does not have a unique value in the entire system.

- ① fluid flow with friction.
- ② Diffusion of gases.
- ③ Throttling
- ④ Heat transfer
- ⑤ Adiabatic mixing.



(Irreversible Process)

Energy \Rightarrow is defined as the capacity to exert a force through a distance i.e. capacity to do work.

$$[MLT^{-2}]$$

Unit of joule = (J)

(P.E) \Rightarrow is the energy due to position and the elevation of mass with respect to the earth. A force f is exerted on a mass m due to gravitational attraction $F = mg$.

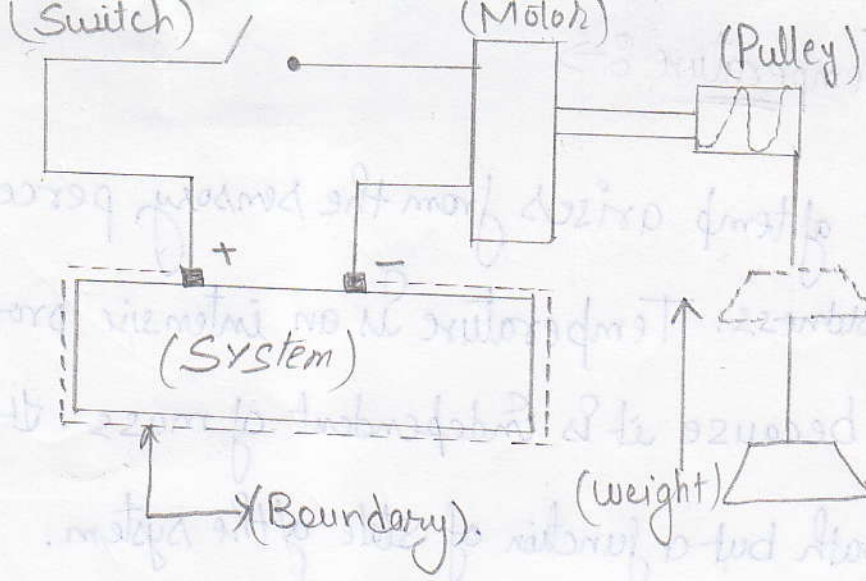
(K.E) \Rightarrow is defined as the energy created from the motion of a mass.

$$(K.E)_c = \frac{mc^2}{2}$$

Work \Rightarrow is defined as the energy transferred, without transfer of mass across the boundary of a system because of an intensive property difference other than temperature that exists b/w system and surrounding.

OR

Work is an interaction b/w system and surrounding and is done by a system if the sole effect external to the boundaries of the system could have been the raising of a weight.



Concept of Work

Power :-> Power may be defined as rate of doing work

$$\Rightarrow P = \frac{\text{Workdone}}{\text{time}} = \frac{W}{t} ; \text{J/s or watt.}$$

(1 watt = 1 joule)

Sign Convention of various Energies on their Algebraic sense :->

Heat received by system : Q is +ve.

Heat rejected by system = Q is -ve.

Heat neither received nor rejected = $Q = 0$.

Internal energy inc = ΔU is positive

Internal energy dec = ΔU is -ve.

Workdone by system = W is positive.

Workdone on system = W is negative.

No workdone on or by system = $W = 0$.

Concept of temperature $\circ \rightarrow$

The concept of temp arises from the sensory perception of hotness of coldness. Temperature is an intensive property of the system because it is independent of mass. It is not a function of path but a function of state of the system.

Zeroth law of Thermodynamic $\circ \rightarrow$

Consider three systems A, B and C as shown. perfectly insulated from surrounding and apply the equality of temp. If A and C are brought into good contact energy in the form of heat will transfer from the body at a higher temperature to the body at a lower temperature. After a certain time they will be in thermal equilibrium. If B and C are brought into good contact after some time, these two will be in thermal equilibrium. Now if A and B are brought in good contact they will be also in thermal equilibrium.

"If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other. This statement is known as the Zeroth law of Thermodynamic."

Liquid Thermometers (Mercury) \Rightarrow Out of many liquid thermometers ^⑧

the mercury thermometer is the most commonly used in scientific work for ordinary temperature. This is because of the fact that mercury has many advantages as the thermometric fluid over other fluids.

Concept of an Ideal Gas (Macro Analysis) \Rightarrow

As long as a fluid remains homogeneous in composition and chemical form, and retains its chemical identity it is termed as a pure substance.

If the working fluid (system) condenses or evaporates during the thermodynamic process it is called vapour.

* Many gases which do not change their phase during a thermodynamic process and obey a set of common rules governing change of their properties are called ideal gases or perfect gases.

There exists a relationship b/w pressure (P) specific volume (v) and temperature (T) of a substance

$$F(p, v, t) = 0$$

$$= P = f(v, t)$$

$$= P = f(v, T)$$

applies widely for gases because in gaseous state where there is a change in pressure, there is an appreciable change in specific volume.

$$PV = (RT)_{P \rightarrow 0, \text{ real gas.}}$$

$$P = \left(\frac{RT}{V}\right)_{P \rightarrow 0, \text{ real gas.}}$$

① An ideal gas obeys the law $PV = RT$.

② The internal energy is a function of temp alone $U = f(T)$.

Those gas which follow all path and there is no force of attraction b/w molecules.

* Gas having no force of inter molecular attraction.

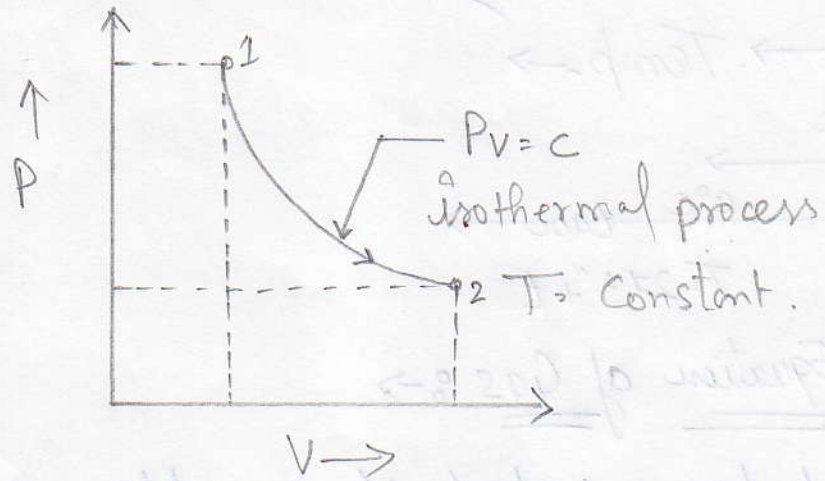
* The gas which follow the gas law at all stages or ranges like pressure and temp are considered as ideal gas.

Boyle's law \rightarrow Robert Boyle in 1662 A.D.

When temperature remains constant, the volume of a perfect gas is inversely proportional to the absolute pressure.

- p = absolute pa.
- V = volume of gas at pa.
- T = absolute temp. of gas

$$V \propto \frac{1}{P} \quad T = \text{constant}$$



Charles law :-> Charles in 1887 A.D. It may be stated that

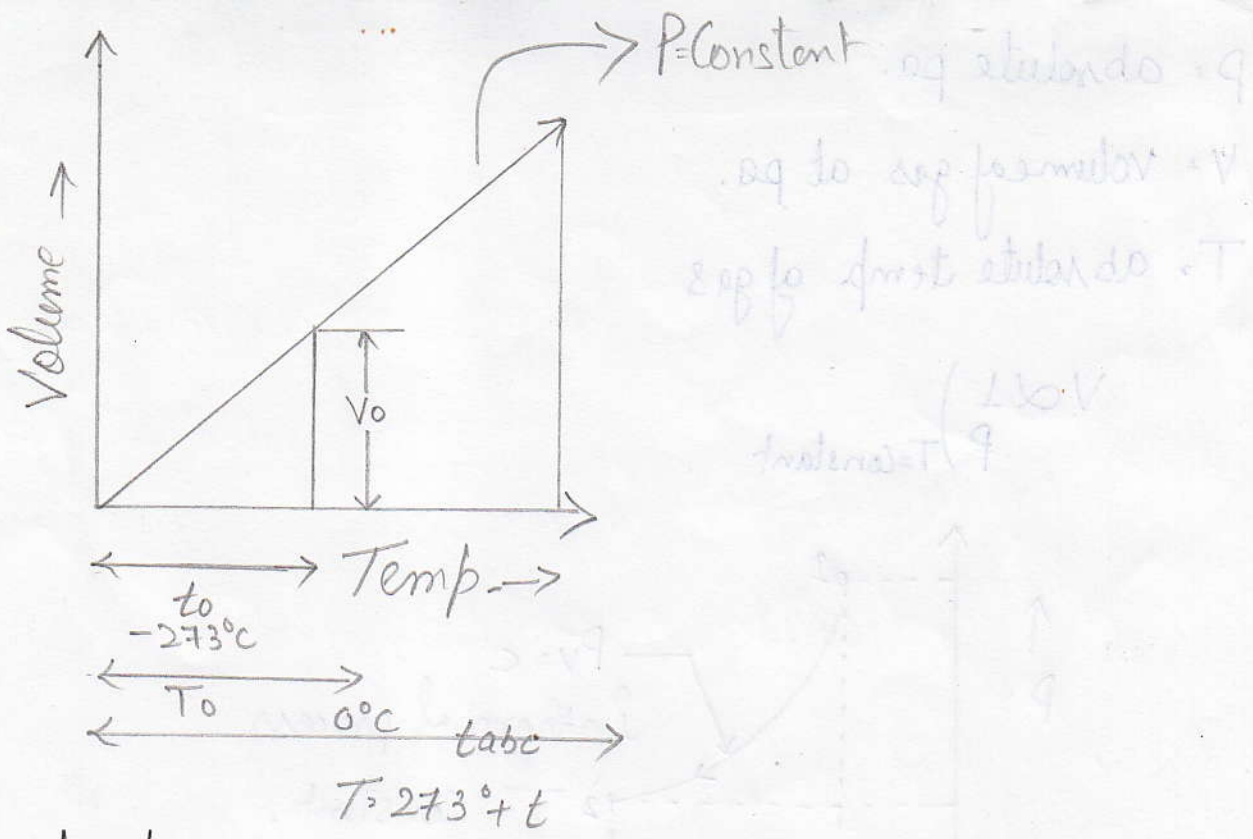
in two ways

(a) if pressure remains constant the volume of a given mass of gas varies directly as the absolute temperature.

$$V \propto (T) \quad p = \text{constant}$$

$$= \frac{V}{T} = \text{constant}$$

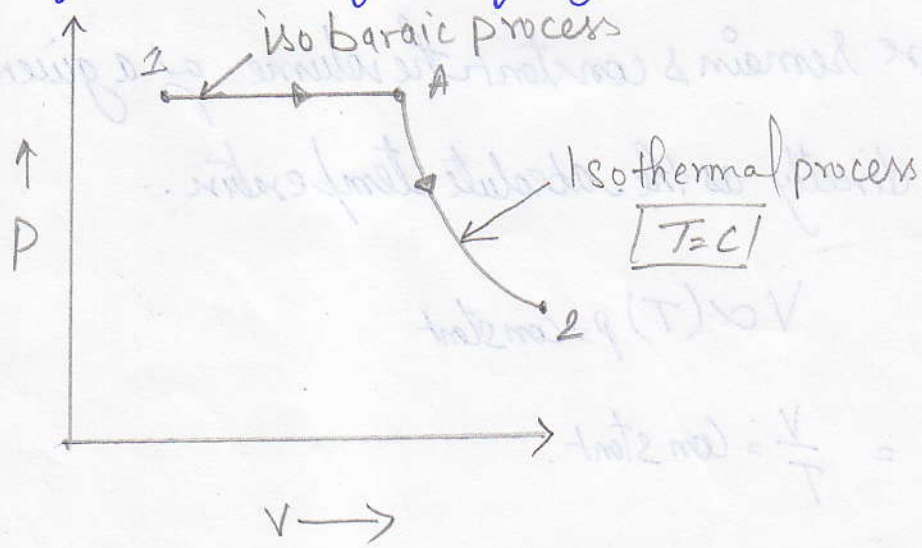
(b) If the volume remains constant the pressure of a given mass of gas varies directly with temperature $P \propto (T) \quad V = \text{constant}$



Characteristics Equation of Gas :->

By combining Boyle's and Charles' law a relation between pressure, temperature and volume may be found. The resulting

equation may be equation of state for gas



Derivation of characteristics Gas equation.

During constant pressure volume changes from V_1 to V_2 and during constant temperature volume changes from V_1 to final volume V_2 applying Charles law.

CONCEPT OF TEMPERATURE \Rightarrow The concept of Temperature arise from the sensory preception of hotness and coldness.

Equality of Temperature \Rightarrow In order to understand equality of temperature is a method of defining and measuring temp, Consider two system A and B perfectly insulated from the surrounding. Both them are brought in good contact, the energy in the form of heat will transfer from the body at a higher temperature to the body at lower temperature. After some time is elapsed the bodies A and B will approach a state at which no further change is observed. The two bodies are then in a state of thermal equilibrium.

Zeroth law of thermodynamic \Rightarrow Consider three systems A, B and C perfectly insulated from surrounding and apply the equality of temperature. If A and C are brought into good contact energy in the form of heat will transfer from the body at a higher temperature to the body at a lower temperature.

After a certain time they will be in thermal equilibrium if B and C are brought into good contact. After these two will be in thermal equilibrium. Now if A and B are brought in good contact they will be also in thermal equilibrium.

"If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other. This statement is known as zeroth law of thermodynamics.

Characteristics Equation of gas \Rightarrow

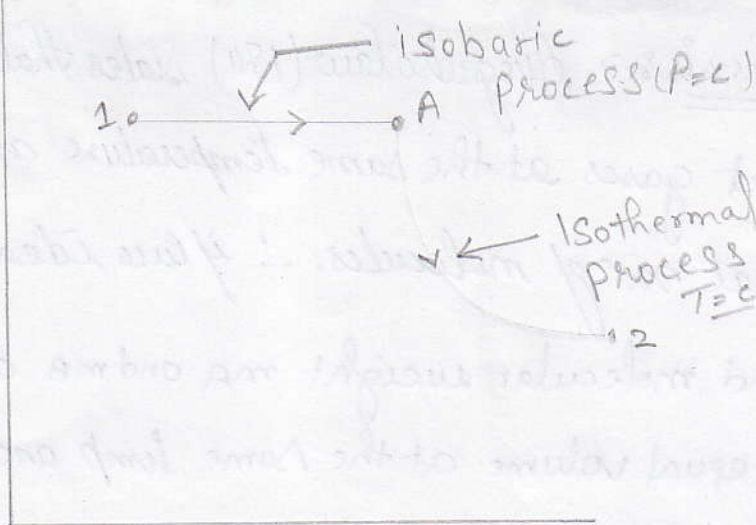
By combining Boyle's and Charles's law a relationship between pressure, temperature and volume may be found

The resulting equation must be an equation of state for gas. Consider 1 kg of mass changes from state P_1, V_1, T_1 to another state P_2, V_2, T_2 by the two processes namely constant pressure and constant temperature. During constant pressure volume changes from V_1 to V_A and during constant temp...

Vol change from V_A to final volume V_2 . Applying Charles law

$$= \frac{V_1}{T_1} = \frac{V_A}{T_A}$$

$$V_A = \frac{V_1}{T_1} T_A = \frac{V_1 T_2}{T_1} \quad (\text{Since } P_A = P_1)$$



For Constant temp process A-2 boyles law.

$$= V_1 P_1 = V_2 P_2$$

$$= V_1 = V_2 \frac{P_2}{P_1} = V_2 \frac{P_2}{P_1} \text{ (Since } P_1 = P_2 \text{)}$$

Equation of .

$$V_1 \frac{T_2}{T_1} = V_2 \frac{P_2}{P_1} \text{ or } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{Pv}{T} = \text{Constant} = R$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R$$

where R is constant and called the characteristic gas constant.

$$R = \frac{Pv}{T} = \frac{N}{m^2} \times \frac{m^3}{kg \cdot K} = J/kgK.$$

P_2 Pressure N/m^2

V_2 Specific volume m^3/kg

T_2 Temperature. K.

$$\bar{R} = 8.314 \text{ KJ/Kgmole}$$

$$K = 8.314 \text{ J/mole K.}$$

Avogadro's Hypothesis \Rightarrow Avogadro law (1811) states that equal volume of all perfect gases at the same temperature and pressure contain an equal no. of molecules. \therefore if two ideal gas having mass m_A and m_B and molecular weight M_A and M_B and contained in two vessel of equal volume at the same temp and pressure hence each gas contain equal no. of molecules.

$$= m_A = n M_A = \frac{N}{A} M_A \quad \text{and} \quad m_B = n M_B = \frac{N}{A} M_B$$

$$\frac{m_A}{m_B} = \frac{M_A}{M_B}$$

But $m = \rho v$ where volume v is the same for both gases. ρ is density.

$$= \frac{\rho_A}{\rho_B} = \frac{v_B}{v_A} = \frac{m_A}{m_B}$$

$$= m_A v_A = m_B v_B = v_{\text{mole}} = \text{Constant}$$

\rightarrow value is 6.02×10^{26} molecules in a Kgmole.

Critical State \Rightarrow The limiting state at which no discontinuities are noticeable between liquid and vapour phase of a pure substance is called the critical state

Equation of state \Rightarrow Properties such as pressure temperature specific volume, internal energy, electrical resistance etc.

$$f(P, v, T) = 0$$

it is to be noted that all of these properties are not independent

Vander waal's Equation of state (1873) :-

(125)

In 1873 Vander waal's proposed an equation of state which was an attempt to correct the ideal gas equation of states so that it would be applicable to real gases.

While deriving the ideal gas equation of state on the basis of kinetic theory in which it was assumed that (i) there is no intermolecular force between particles (ii) the volume of the molecules is negligible in comparison with gas.

Correction for finite size of molecules :- The 2nd correction is due to the size of the molecule. To account for the volume occupied by molecule, Vander waal's proposed that the specific volume in the ideal gas equation of state V must be replaced by the term $(V-b)$ where the constant b accounts for the reduction in volume due to finite size of the molecule of a real gas.

Thus Vander waal's realising the behaviour of real gas and its deviation from the perfect gas proposed the following

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Where a and b are specific constants and depends upon

The nature of the substance v represents the molar volume and R is the universal gas constant.

P = Pressure N/m^2 v = molar volume m^3/kg , T = Temperature.

R = gas constant, a = Constant, b = constant.

(a) A new term (a/v^2) has been added to the term pressure

P

(b) a new term b has been subtracted from the volume term v .

It is to be noted that as the pressure approaches zero and the specific volume approaches infinity the correction term (a/v^2) and b are negligible and the equation reduce to $Pv = RT$.

At low p_a where the mean free path is large in comparison to the molecule's dimension, the quantity b in Vander Waals equation may be neglected.

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

$$= Pv = RT - \frac{a}{v}$$

States that Pv is less than RT for shape of curve at low pressure. Similarly at high p_a . the term a/v^2 can be neglected compared to p and Vander Waals equation reduces.

$$= P(v-b) = RT$$

$$= Pv - Pb = RT$$

$$= Pv = RT + Pb$$

is known as Clausius equation of state. It is obvious that the product Pv is greater than RT and increases linearly with pressure. (13)

Vander waal equation

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0$$

The above equation suggest that Vander waal's equation of state is cubic in volume.

Determination of Constant a and $b \Rightarrow$ The Vander waal's equation though widely used for the real gases has a fundamental weakness that the Constant a and b actually vary with Temperature.

Hence their values should be determined empirically for particular regions of pressure and temperature.

$$\left(\frac{\partial P}{\partial v}\right)_c = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_c = 0$$

where subscript c denotes critical point Vander waal's equation at the critical temp

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \quad \text{--- (1)}$$

This equation represents the curve PMD . Differentiating w.r. to V_c and noting that T_c is a constant.

$$\left(\frac{\partial P}{\partial v}\right)_C = -\frac{RT}{(v_c-b)^2} + \frac{2a}{v_c^3} = 0$$

$$= RT_c = \frac{2a}{v_c^3} (v_c-b)^2 \quad \text{--- (2)}$$

Again

$$\left(\frac{\partial^2 P}{\partial v^2}\right) = \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0$$

$$= RT_c = \frac{3a}{v_c^4} (v_c-b)^3$$

$$= v_c = 3b \quad \text{--- (3)}$$

Putting the value of v_c in equation.

$$T_c = \frac{a}{27Rb} \quad \text{--- (4)}$$

Putting the value v_c and T_c in equation - (1)

$$P_c = \frac{a}{27b^2} \quad \text{--- (5)}$$

The equation (3), (4), (5) show the critical properties in term of constant a and b for a particular gas given by Vanderwaal equation.

(a) if the critical points for a particular gas are known, the constants for the vander waals equation of state may be calculated. As the critical volume is difficult to measure experimentally the constants a and b .

with the help of (4) and (5)

$$a = \frac{27RT_c^2}{64 P_c}$$

$$b = \frac{RT_c}{8P_c}$$

Reduced coordinates \rightarrow

(19)

Reduced Coordinates are the non-dimensional coordinates which are obtained by dividing the coordinates with the corresponding coordinates of the critical states.

$$P_r = \frac{P}{P_c} \text{---(1)} \quad V_r = \frac{V}{V_c} \text{---(2)} \quad T_r = \frac{T}{T_c} \text{---(3)}$$

are termed as the reduced coordinates. It means that the reduced pressure, P_r , reduced volume V_r and reduced Temperature T_r at a given state are obtained by dividing the pressure, volume V , temperature T at the state by the value of the same property at the critical state.

$$V_r = 3b, \quad T_c = \frac{8a}{27Rb}, \quad P_c = \frac{a}{27b^2}$$

with the help of (1) (2) and (3)

$$= V = V_r V_c = 3b V_r \text{---(4)}$$

$$= T = T_r T_c = \frac{8a}{27Rb} T_r \text{---(5)}$$

$$\Rightarrow P = P_r P_c = \frac{a}{27b^2} P_r \text{---(6)}$$

= Vander waal equation \rightarrow

$$= \left(P_r + \frac{3}{V_r} \right) \left(V_r - \frac{1}{3} \right) = \frac{8}{3} T_r$$

Compressibility \Rightarrow for real gases, especially at high pressure and low temperature the ideal gas equation of state is not a good approximation. It is because of the fact that at high p and low temperature, the specific volume become very large. The departure of real gas behaviour from that of ideal gas is frequently characterised by a compressibility factor z .

$$z = \frac{pv}{RT}$$

Since RT/p is the ideal gas specific volume (v_{ideal}) of a gas the compressibility factor may be considered a measure of the ratio of the actual specific volume to the ideal gas specific volume.

$$z = \frac{v_{actual}}{v_{ideal}}$$

Law of corresponding states \Rightarrow Though specific compressibility

charts are different for different substances but they have the same trends is common. Thus it is possible to determine

value of z from the properties of a gas based on only limited amount of data by taking the help of common trends of gases. These common trends when stated in the form of law is called the law of corresponding states.

Basic Concept of thermodynamic.

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ KPa} = 0.1 \text{ MPa}$$

$$1 \text{ atm} = 101.325 \text{ KPa}$$

Power $\Rightarrow 1 \text{ W} = 1 \text{ J/s} = 1 \text{ N/s}$

ideal gas equation of state = $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$. at very low pressure or density all gases and vapour approach ideal gas behaviour.

$$R_{O_2} = \frac{8.3143}{32} = 0.262 \text{ KJ/kgK}$$

$$R_{air} = \frac{8.3143}{28.96} = 0.287 \text{ KJ/kgK}$$

\rightarrow Avogadro 6.023×10^{23} molecules in a g mol
A. 6.023×10^{26} molecules / kg mol.

\rightarrow First law of thermodynamic ($dd = du + dw$) ($dw < dd$)

\rightarrow The internal energy of an ideal gas depends on temperature

$$\rightarrow \text{Van der Waal's equation} \rightarrow \left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$\rightarrow \text{Work done} = dw = PdV$$

work = (change in volume)