PROPERTIES OF GASES

3.1 DEFINITIONS

Vapour. It may be defined as that state of a pure substance in which the evaporation from its liquid state is incomplete. A vapour consists of a mixture of pure gaseous form and suspended liquid particles. Vapours may exist in three forms : wet, dry and superheated. The vapours are called wet when the dryness fraction is less than one; dry when dryness fraction is unity; and superheated when the temperature of vapours is more than the saturation temperature at the specified pressure. Steam exhibits all the three forms of vapours.

Gas. It is the state of a substance in which the evaporation from the liquid state is complete. Under normal conditions of temperature and pressure, the substances like O_2, H_2, N_2, CO_2 and air are taken as gases.

Perfect Gas. A gas which obeys all the gas laws under all conditions of temperature and pressure is called a perfect gas. In actual practice, no gas behaves like a perfect gas. However, real gases like O_2, H_2, N_2 and air behave like a perfect gas.

3.2 GAS LAWS

There are basically two gas laws : Boyle's law and Charle's law.

3.2.1 Boyle's Law

This law states that the volume of a given mass of a perfect gas varies inversely as the absolute pressure when the temperature remains constant.

Let p = absolute pressure of a gas, Pa

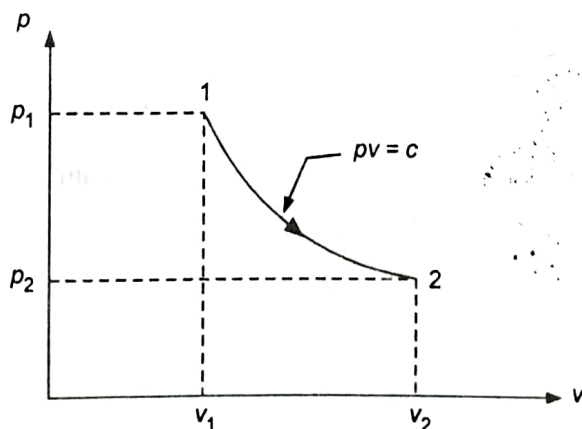V = volume occupied by the gas, m^3

Fig. 3.1 Boyle's law on p-v diagram

Then according to Boyle's law,

$$V \propto \frac{1}{p}$$

or

$$pV = c$$

where
c = constant of proportionality.

For a unit mass, let
v = specific volume of gas.

Then
$$pv = c$$

Let a quantity of gas at pressure p_1 and volume V_1 changes it pressure to p_2 and volume V_2 at constant pressure (Fig. 3.1), then according to Boyle's law, we have

$$p_1 V_1 = p_2 V_2$$

3.2.2 Charle's Law

(a) This law states that if the pressure of a given mass of a gas is kept constant then the volume of the gas varies directly in proportion to its absolute temperature.

Let
V = volume occupied by a given mass of gas, m^3

T = absolute temperature of gas, K

Then according to Charle's law, we have

$$V \propto T \quad \text{when } p \text{ is constant}$$

or

$$\frac{V}{T} = C$$

where
C = a constant of proportionality.

It
V_1, T_1 = initial conditions of volume and absolute temperature at state 1

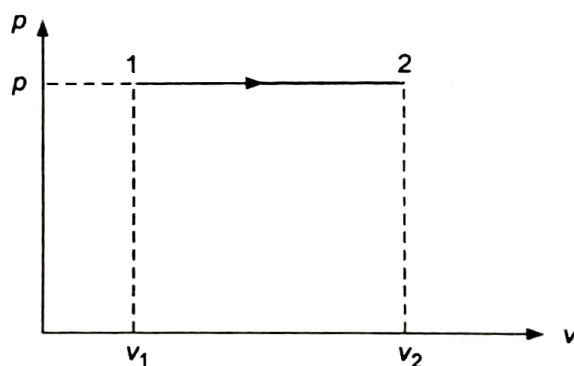V_2, T_2 = final conditions of volume and temperature at state 2 (Fig. 3.2).

Fig. 3.2 Charle's law on p-v diagram.

Then
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or
$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

(b) The Charle's law may also be stated that if the volume of a given mass of a gas is kept constant then the absolute pressure of the gas varies directly in proportion to its absolute temperature.

$$p \propto T \text{ when } V \text{ is constant}$$

or

$$\frac{p}{T} = \text{const.}$$

$$\therefore \quad \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

3.2.3 Combined Gas Law

A perfect gas obeys Boyle's law as well as Charle's law. These two laws may be combined together to formulate a combined gas law to determine the relation between pressure, temperature and volume. Consider one kg mass of a perfect gas undergoing change from p_1, v_1, T_1 at state 1 to p_2, v_2, T_2 at state 2 by two processes 1-A at constant pressure and A-2 at constant temperature, as shown in Fig. 3.3. Process 1-A obeys Charle's law and process A-2 obeys Boyle's law.

Process 1-A :

$$\frac{v_1}{T_1} = \frac{v_A}{T_A}$$

Fig. 3.3   p-v diagram for combined gas law.

or

$$= \frac{v_1 T_A}{T_1} = \frac{v_1 T_2}{T_1} \quad (\because T_A = T_2) \qquad \qquad \dots(1)$$

Process A-2 :

$$p_A v_A = p_2 v_2$$

or

$$p_1 v_A = p_2 v_2 \qquad (\because p_A = p_1)$$

$$\therefore \qquad v_A = \frac{p_2}{p_1} v_2 \qquad \qquad \dots(2)$$

Comparing Eqs. (1) and (2), we get

$$\frac{v_1 T_2}{T_1} = \frac{p_2}{p_1} v_2$$

or

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

or

$$\frac{pv}{T} = \text{const.} = R$$

or

$$pv = RT$$

where R = characteristic gas constant.

This equation is called the characteristic gas equation.

For a gas having m kg mass,

$$pV = mRT$$

Now

$$R = \frac{pv}{T} = \frac{N}{m^2} \times \frac{m^3}{kg} \times \frac{1}{K} = \frac{N.m}{kg.K} = J/(kg.K)$$

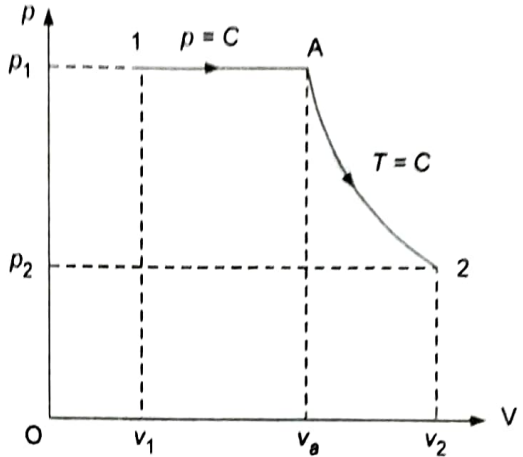Therefore, the S.I. units of R are J/(kg. K)

3.3 AVOGADRO'S HYPOTHESIS

This hypothesis states that equal volumes of all gases at the same temperature and pressure contain equal number of molecules.

<div align="center">OR</div>

Molecular mass of all gases occupy the same volume at N.T.P.

If
$$m = \text{mass of a sample of gas, kg}$$
$$M = \text{molecular mass, kg/kg. mole}$$
$$n = \text{number of moles, kg. mole}$$

Then
$$m = M \times n$$

i.e.,   mass of a gas = molecular mass of a gas × number of moles.

kg-mole or kmol. It is the unit of mass. A kg. mole of any gas has a mass equal to its molecular weight. For example : one kg mole of O_2 has a mass of 32 kg.

N.T.P. — Normal temperature and pressure corresponds to $p = 101.325 \, kPa$ and $T = 273.15K$ or $t = 0°C$.

S.T.P. — Standard temperature and pressure corresponds to $p = 101.325 \, kPa$ and $T = 288.15K$ or $t = 15°C$.

Molecular volume. It is the volume occupied by a gas at N.T.P. This volume is same for all gases at N.T.P. The volume of a gas at N.T.P. whose mass is equal to its kg. mole is 22.4136 m^3/kg. mole.

3.4 UNIVERSAL GAS CONSTANT

If we multiply both sides of the characteristic gas equation by the molecule mass of the gas, then
$$M \, pv = MRT$$

Now
$$Mv = v_{mole} = \text{molar volume of gas, i.e., the volume occupied by one mole of gas.}$$

∴
$$pv_{mole} = MRT$$

Let
$$R_0 = MR$$

According to Avogadro's hypothesis, V_{mole} is same for all gases. Therefore, R_0 must also be same for all gases. Thus R_0 is known as the Universal gas constant.

∴
$$pv_{mole} = R_0T$$

∴
$$R_0 = \frac{101.325 \times 10^3 \times 22.4136}{273.15} = 8314.3 \text{ J/(kg. mole-K)}$$

The values of characteristic gas constant for various gases is given in Table 3.1.

N.T.P. ⇒ Normal temp. and pressure
$$P = 101.325 \, kPa \quad \text{and} \quad t = 0°C$$

S.T.P. ⇒ standard temp. and pressure
$$P = 101.325 \, kPa \quad \& \quad t = 15°C$$

* **Molecular Volume:**

It is the volume occupied by a gas at N.T.P.
This volume is equal for all gases at N.T.P.

* **Molecular Mass of O_2**

- $V = 22.4136 \, m^3$
  $P = 1.01325 \, bar$
  $T = 273 \, K = 0°C \quad (\text{at N.T.P.})$
  $R = 260 \, J/kg \, K \quad \text{for } O_2$

  $PV = RT$
  $P \times V \times m = mRT$
  $\quad PV = mRT \quad \text{But } m = n \times M$

∴ $PV = n \times M \times R.T$

- ∴ $1.01325 \times 10^5 \times 22.4136 = 1 \times M \times 260 \times 273$

  ∴ $M = 31.978 \cong 32 \, kg/kg \, mol$

∴ $\underline{M_{O_2} = 32 \, kg/kg\text{-mol}}$

---

specific heat at constant Volume (C_v)
$$\delta q = du + \cancel{Pdv}^{\,0}$$
∴ $C_v dT = du \quad \rightarrow \quad C_v = \left(\dfrac{du}{dT}\right)_v$

Specific heat at constant pressure (C_p)
$$C_p = \left(\dfrac{dh}{dT}\right)_p$$
$$C_p dT = du + Pdv$$
$$= du + d(Pv) - \cancel{Vdp}^{\,0}$$
$$= d(u + Pv) - Vdp$$
$$\underline{C_p dT = dh}$$

Relation between C_p, C_v & R

For 1 kg of gas and at constant Pressure

Initial condition of Gas

$$P V_1 = M R T_1 \qquad \text{But } m = 1 \text{ kg}$$

$$\therefore \quad P V_1 = R T_1 \qquad \qquad - ①$$

For final condition of gas

$$P V_2 = M R T_2$$

$$\therefore \quad P V_2 = R T_2 \qquad \qquad - ②$$

eqn ① − eqn ②

$$\therefore \quad P(V_2 - V_1) = R (T_2 - T_1) \qquad \left.\begin{array}{l} \\ = \text{change in } W \cdot D. \\ = \delta w \end{array}\right\} - ②a$$

From 1st law of thermodynamics, for unit mass

$$\delta q = \delta u + \delta w$$
$$\delta q = du + \delta w \qquad \qquad - ③$$

for $p = $ const

$$\delta q = C_p (T_2 - T_1) \qquad \qquad \therefore ④$$

for $v = $ const, $\delta w = 0$

$$\delta q = du = C_v (T_2 - T_1) \qquad - ⑤$$

Using eqn ③, ②a, ④ & ⑤

$$C_p (T_2 - T_1) = C_v (T_2 - T_1) + R (T_2 - T_1)$$

$$\therefore \quad \boxed{C_p - C_v = R} \qquad \text{Mayer's eqn}$$

Flow and Non flow Processes

- State
- → p~v diagram change of State
- → Flow process
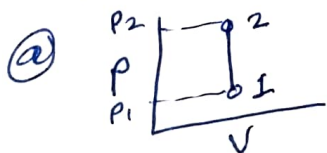- → Non flow processes
- → Steady flow process. eg. Turbine

Different types of Non flow Process

① Constant Volume process
② Constant Pressure process
③ Isothermal Process
④ Adiabatic process
⑤ Polytropic process

We find the following for all above listed Processes

ⓐ Represent it on p-v diagram
ⓑ Work done during the process
ⓒ Relation between P, V and T
ⓓ Change in internal energy
ⓔ Heat Transferred
ⓕ change in enthalpy.

Constant volume process

ⓐ

$$P_2 \vdash \quad 2$$

P

$$P_1 \vdash \quad 1$$

V

ⓑ
$$W.D. = P \times (a \times l)$$
$$= P \times (a \times dl)$$
$$= P \cdot dV$$

Total W.D.
$$= \int_{V_1}^{V_2} P \, dV$$
$$dV = 0$$
$$\therefore W.D. = 0$$

Relation bet'n P, V & T

$V = C$

∴ $P \propto T$ $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

④ change in Internal Energy

$du = Cv (T_2 - T_1)$

$du = m Cv (T_2 - T_1)$

∴ $du = m Cv \displaystyle\int_{T_1}^{T_2} dT$ J

⑤ Heat Transferred

$\delta Q = \delta W + du$

$\delta Q \overset{0}{=} du = m Cv (T_2 - T_1)$

⑥ change in Enthalpy

$H = U + PV$ J

$\Delta H = H_2 - H_1$

$= (U_2 - U_1) + (P_2 V_2 - P_1 V_1)$
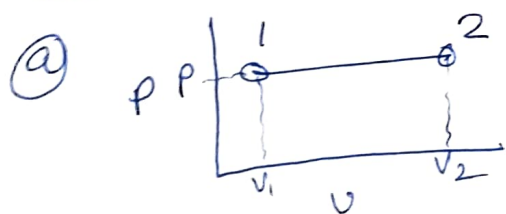
$= m Cv (T_2 - T_1) + mR (T_2 - T_1)$

∴ $R = Cp - Cv$

$\Delta H = m Cv (T_2 - T_1) + m(Cp - Cv)(T_2 - T_1)$

$\Delta H = m Cp (T_2 - T_1)$ J

Constant Pressure Process

@

$$W.D. = \int_{V_1}^{V_2} p \, dv$$

$$= P(V_2 - V_1) \, J$$

ⓒ Relation between P, V and T

$$(P = c)$$

$$\therefore \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

ⓓ change in I.E.

● $du = m \, c_v \, (T_2 - T_1)$

ⓔ Heat Transferred

$$\delta Q = \delta W + du$$

$$= P(V_2 - V_1) + m \, C_v \, (T_2 - T_1)$$

$$= m R (T_2 - T_1) + m C_v (T_2 - T_1)$$

$$= m (C_p - C_v)(T_2 - T_1) + m C_v (T_2 - T_1)$$

● $\delta Q = m \, C_p \, (T_2 - T_1) \, J$

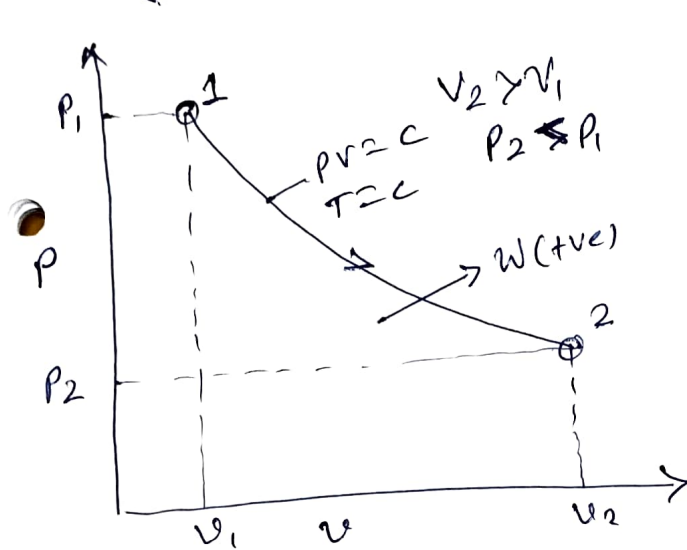ⓟ change in enthalpy

$$\Delta H = m \, C_p \, (T_2 - T_1)$$

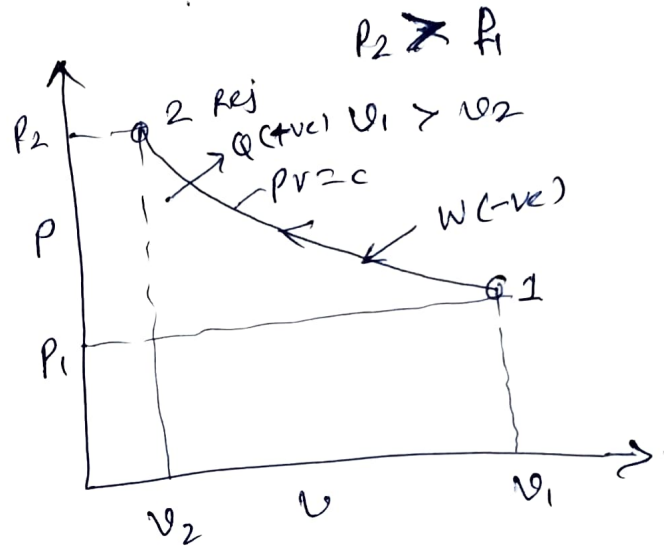## Isothermal Process $(T = const.)$

$$P \propto \frac{1}{V}$$

$$\boxed{PV = C}$$

Also known as hyperbolic process or const. internal energy Process

① **Representation on P-v diagram:**

$P_2 \neq P_1$

(a) Expansion

(b) compression

② **W.D. during the process**

$$W.D. = \int_{V_1}^{V_2} dV \cdot P. \quad (\text{area below the curve})$$

Since $PV = C$, $P = \frac{C}{V}$

$$\therefore \quad W.D. = \int_{V_1}^{V_2} \frac{C}{V} dV = C \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= C \ln \frac{V_2}{V_1}$$

Now $C = PV = P_1 V_1 = P_2 V_2$

$$\therefore \quad W.D. = P_1 V_1 \ln \frac{V_2}{V_1} = P_2 V_2 \ln \frac{V_2}{V_1} \quad J$$

$$= P_1 V_1 \ln \ell = P_2 V_2 \ln \ell$$

where $\dfrac{V_2}{V_1} = \ell =$ Ratio of expansion

$$\therefore \; W.D. = m RT_1 \ln \ell = MRT_2 \ln \ell$$

③ Relation between P, V & T

$$\therefore \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad \text{But } T_1 = T_2$$

$$\therefore \quad \boxed{P_1 V_1 = P_2 V_2}$$

④ change in Internal energy

$$\Delta u = du = m C_v (T_2 - T_1)$$

But $T_1 = T_2$

$$\therefore \quad \Delta u = du = 0$$

⑤ Heat Transferred

$$\delta Q = \delta u + \delta w$$

$$\overset{0}{}$$

$$\therefore \quad \delta Q = P_1 V_1 \ln \ell = P_1 V_1 \ln \frac{V_2}{V_1}$$

$$= P_1 V_1 \ln \frac{P_1}{P_2}$$

⑥ change in Enthalpy

$$\Delta h = m C_p \Delta T$$

$$= m C_p (T_2 - T_1)$$

$$\Delta T = 0$$

$$\therefore \quad \boxed{\Delta h = 0}$$

Adiabatic Process $(PV^\gamma = Const)$

$\delta q = \delta w + du$ (From 1st law)

$\delta q = Pdv + Cv\,dT$ $(\because m = 1\,kg)$

for adiabatic Process $\delta q = 0$

$\therefore \quad Pdv + Cv\,dT = 0$ —————— ①

$PV = RT$ (Ideal gas eq^n for $m=1\,kg$)

$\therefore$ Differentiating both side

● $Pdv + vdP = RdT$

$\therefore \quad dT = \dfrac{Pdv + vdP}{R}$ —————— ②

from eq^n ① & ②

$$Pdv + Cv\left[\dfrac{Pdv + vdP}{R}\right] = 0$$

● $$Pdv + Cv\left[\dfrac{Pdv + vdP}{Cp - Cv}\right] = 0$$

$\therefore \quad P \cdot Cp \cdot dv - Cv\,Pdv + Cv\,Pdv + Cv\,vdP = 0$

$\therefore \quad Cp\,Pdv + Cv\,vdP = 0$ —————— ③

Dividing eq^n ③ by $Cv\,PV$

$\therefore \quad \dfrac{Cp\,Rdv}{Cv\,PV} + \dfrac{Cv\,vdP}{Cv\,PV} = 0$

$\gamma\,\dfrac{dv}{v} + \dfrac{dP}{P} = 0$

$$\int \frac{dP}{P} + \gamma \int \frac{dv}{v} = 0$$
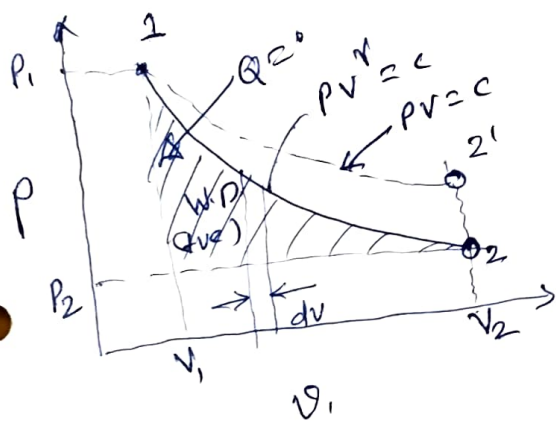
$$\ln P + \gamma \ln v = \ln C$$
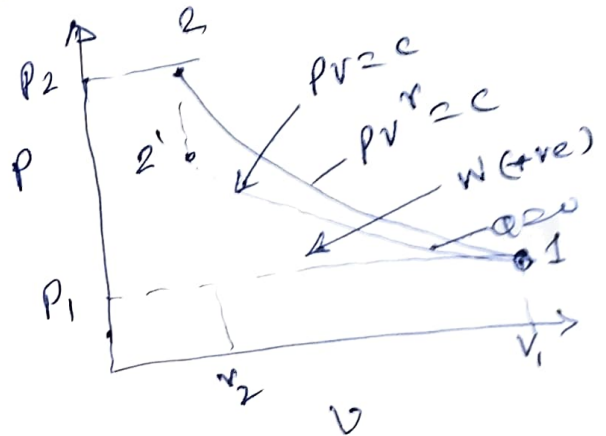
$$\therefore \boxed{P v^\gamma = C}$$

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

$$\therefore \quad P V^\gamma = m^\gamma \cdot C = C$$

$$\boxed{P V^\gamma = C} \qquad \text{Poisson's Law}$$

① Representation on P-v diagram

$$V_2 > V_1, \ P_2 < P_1, \ T_2 < T_1$$

@ Expansion

ⓑ compression

② W.D. during the adiabatic process. (for expansion process)

$$W.D = \int_{v_1}^{v_2} P dv$$

$$P v^\gamma = \text{constant}$$

$$P_1 v_1^\gamma = P_2 v_2^\gamma = P v^\gamma = C$$

$$P = \frac{C}{V^\gamma}$$

$\therefore$ Work done $= \displaystyle\int_{V_1}^{V_2} \frac{Cdv}{V^\gamma} = C \displaystyle\int_{V_1}^{V_2} \frac{dv}{V^\gamma}$

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

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

Now $\quad C = P_1 V_1^\gamma = P_2 V_2^\gamma$

$\therefore \quad W \cdot D \cdot = \dfrac{1}{-\gamma+1} \left[P_2 V_2^\gamma \cdot V_2^{-\gamma+1} - P_1 V_1^\gamma V_1^{-\gamma+1} \right]$

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

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

OR $\quad \delta q = \delta W + du$

$\quad O$

$\therefore \quad \boxed{\delta W = -du}$

③ Relation between P, V and T

$$PV^\gamma = C \quad\quad\quad - \quad\quad ⓐ$$

$$\frac{PV}{T} = C \quad\quad\quad - \quad\quad ⓑ$$

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

$$\therefore \boxed{\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma} \quad\longrightarrow\quad \text{ⓒ}$$

Dividing eqⁿ ⓐ by ⓑ

$$\frac{P V^\gamma \times T}{P V} = C$$

$$V^{\gamma-1} . T = C$$

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

$$\therefore \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad\longrightarrow\quad \text{ⓓ}$$
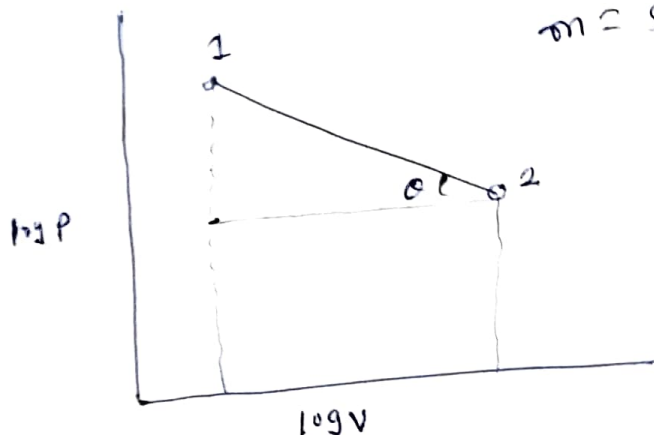
From eqⁿ. ⓒ $\qquad \dfrac{V_1}{V_2} = \left(\dfrac{P_2}{P_1}\right)^{1/\gamma}$

$$\therefore \quad \boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}} \quad\longrightarrow\quad \text{ⓔ}$$

$\therefore$ from eqⁿ ⓒ, ⓓ & ⓔ

$$\boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

Polytropic Process

$m = \text{slope} = \dfrac{\log P}{\log v}$

$y = mx + c$

$pv^n = c$

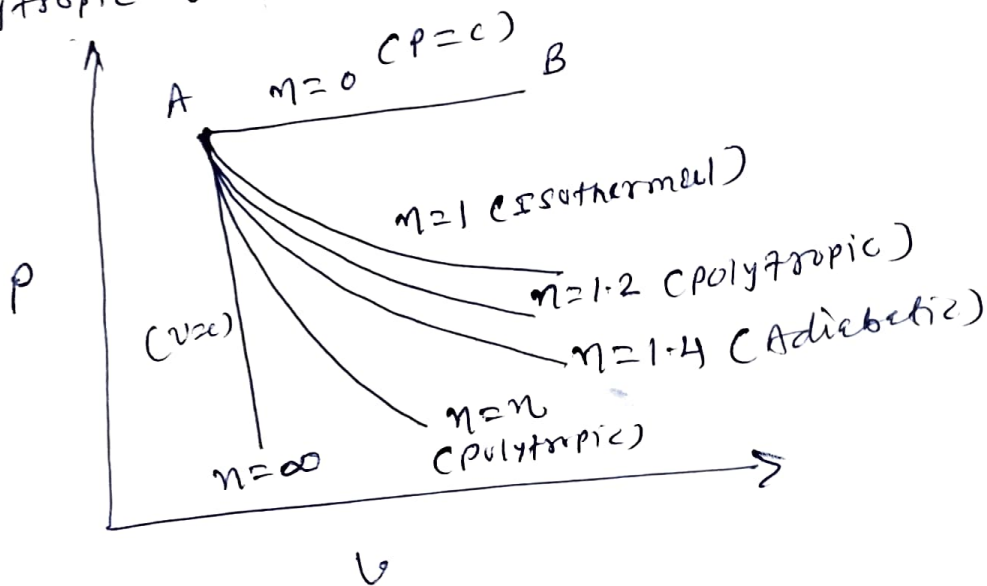$\log p + n \log v = \log c$

$\log p = -n \log v + \log c$

$\therefore\ y = \log P,\quad m = -n,\quad x = \log v$

$c = \text{const} = \log c$

$n \Rightarrow 1 \text{ to } 1.7$

$pv^n = c$

Draw p-v diagram for quasistatic process with polytropic index $n = 0, 1, 1.4 \,\&\, \infty$.

$m = 0 \ (P = c)$

$m = 1 \ (\text{isothermal})$

$n = 1.2 \ (\text{polytropic})$

$n = 1.4 \ (\text{Adiebatic})$

$n = n \ (\text{polytropic})$

$n = \infty$

$(v = c)$

→ Heat Transferred

$$\delta Q = \delta u + \delta W$$

$$\delta W = \dfrac{P_1 v_1 - P_2 v_2}{n-1},$$

$$\delta u = m \, C_v \,(T_2 - T_1)$$

$$\therefore \quad \delta Q = \frac{P_1 V_1 - P_2 V_2}{n-1} + m c_v (T_2 - T_1)$$

But
$$C_p - C_v = R$$

$$\frac{C_p}{C_v} - 1 = \frac{R}{C_v} \quad (\text{divide by } C_v)$$

$$\gamma - 1 = \frac{R}{C_v} \Rightarrow \therefore C_v = \frac{R}{\gamma - 1}$$

$\therefore \quad \delta Q = \text{Heat Transfered} =$

$$\frac{P_1 V_1 - P_2 V_2}{n-1} + \frac{m \cdot R}{\gamma - 1}(T_2 - T_1)$$

$$= \frac{P_1 V_1 - P_2 V_2}{n-1} + \frac{m R T_2 - m R T_1}{\gamma - 1}$$

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

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

$$= \frac{(P_1 V_1 - P_2 V_2)\left[\gamma - 1 - n + 1\right]}{(n-1)(\gamma - 1)}$$

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

$$\delta Q = \left[\frac{\gamma - n}{\gamma - 1}\right] \times W \cdot D, \text{ during the polytropic process}$$

Theoretical Determination of Polytropic Index n

$$P_1 V_1^n = P_2 V_2^n$$

$$\ln P_1 + n \ln V_1 = \ln P_2 + n \ln V_2$$

$$\therefore \quad \ln P_1 - \ln P_2 = n\left(\ln V_2 - \ln V_1\right)$$

$$\therefore \quad n = \frac{\ln P_1 - \ln P_2}{\ln V_2 - \ln V_1}$$

$$\therefore \quad n = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{V_2}{V_1}\right)} \quad \boxed{\text{or}}$$

$$n = \frac{\log_{10}\left(\frac{P_1}{P_2}\right)}{\log_{10}\left(\frac{V_2}{V_1}\right)}$$