THERMODYNAMICS

★ root mean square velocity = $C_{rms} = \sqrt{\frac{3RT}{M}}$ → in Kelvin; M → molecular mass

Also, Pressure = $P = f(T, \rho)$

★ Property of System
- Intensive or Intrinsic ⇒ Independent of mass of system eg:- Temp., Pressure, density, velocity, Specific vol., Specific entropy, Specific ethalpy.
- Extensive or Extrinsic ⇒ Depends on mass of the System; eg:- Energy, entropy, volume, enthalpy.

★ Property :- - Point function
- State function
- Independent of Past history
- Exact differential

work or Heat :- - Path function
- Boundary phenom
- Transient pheno.
- Depends on past history
- Inexact differential

★ Continuum concept :- It is valid Till mean free Path is much much lesser then system dimension.

Mean free Path : It is the average distance travelled by the molecule b/w two successive collisions.

★ Thermodynamic equilibrium : Thermal, mechanical, Phase and chemical equilibrium.

⇒ Quasistatic compression or expansion of a gas will be considered as reversible.

⇒ Ideal flow through nozzle & diffuser etc. will be considered as reversible.

★ Pure Substance : Substance is said to be pure if it is of homogenous chemical composition throughout.

eg:- O_2 & N_2 mixture
- water + water vapour
- Ethyle Alcohol + water

★ Azeotrope : The mixture of liquids which behaves as pure substance. [R-500 Series]

★ Gibb's Phase rule : $P + F = C + 2$

P → no. of phase [Solid, liquid, gas]
F → DOF
C → no. of chemical component

★ Zeroth law : If $A \underset{\text{equi.}}{\overset{\text{Thermal}}{\rightleftharpoons}} B \underset{\text{equi.}}{\overset{\text{Thermal}}{\rightleftharpoons}} C$

Then it is sure that $A \underset{\text{equi.}}{\overset{\text{Thermal}}{\rightleftharpoons}} C$

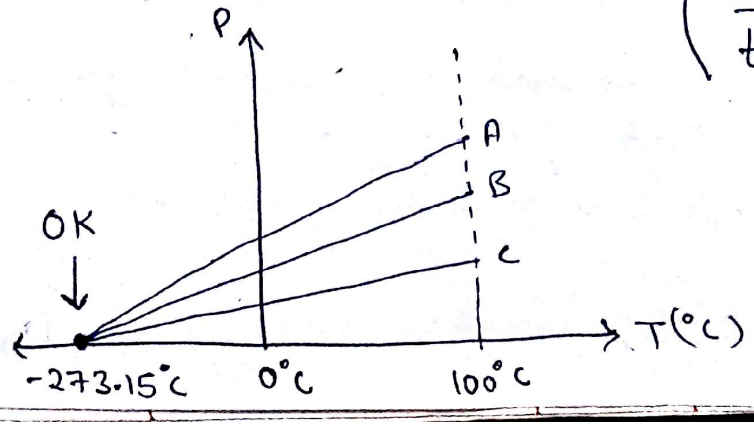
★ Thermometers
- Resistance thermo-meter or thermister ⇒ Resistance
- Thermocouple ⇒ Voltage, Emf
- Const. vol. gas Thermo. ⇒ Pressure
- Const. Pr. gas Thermo. ⇒ Volume

} Thermo metric property.

⇒ Const. Vol. & Const. Pr. gas thermometer
- Both are called ideal gas thermometer as Ideal gas is the material of construction.
- Both are independent of material of construction

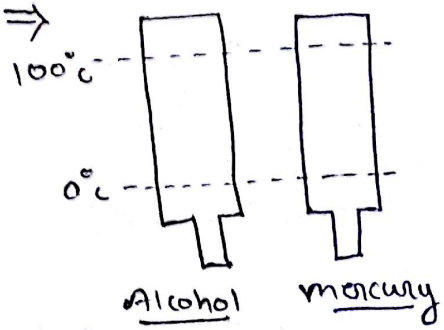
★ Temperature scales :

$$\left(\frac{t - t_i}{t_s - t_i}\right)_{\text{1st scale}} = \left(\frac{t - t_i}{t_s - t_i}\right)_{\text{2nd scale}}$$



H_2O Tripple Point	H_2O critical Point
P = 0.61 KPa	P = 221.2 bar
T = 0.01°C = 273.16 K	T = 374°C

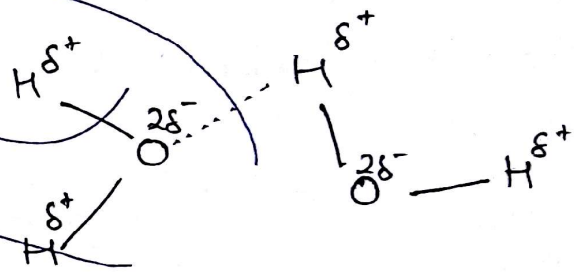
$\Rightarrow 1K = \left(\frac{1}{273.16}\right)$ th of Tripple point of water.



if Both are calibrated (graded) at ice point and steam point & Distance b/w the points are divided into 100 equal parts then they are not guarented to give same reading b/w point of calibration, However they will give same reading at point of calibration.

★ Energy = Microscopic (internal Energy) + macroscopic
- → KE (Bulk motion)
- → PE (Bulk Position)

- → Sensible → Temperature
- → Latent
- → chemical
- → Nuclear



★ methods of energy transfer
- Heat interaction
- work interaction
- mass interaction

★ non flow work or Boundary work or closed System work

$\delta w = P.dv$ T & C :- closed System
- Quasistatic (Reversible)

⇒ Area under P-V diagram represents work interaction for a closed system.

★ non-flow work for various Process

1. constant volume or Isochoric or Isometric

$\delta w = P dv^{\to 0} = 0$

2. Constant Pressure or Isobaric Process

$$\delta w = P dv \Rightarrow w = \int P dv$$

$$\Rightarrow w = P(V_2 - V_1)$$

3. Isothermal Process ($T = const.$, Rectangular hyperbolic curve)

$$w = C \ln\left(\frac{V_2}{V_1}\right) = C \ln\left(\frac{P_1}{P_2}\right) \quad ; \quad T \& C :- \text{Closed sys.}$$

$$C = P_1V_1 = P_2V_2 = mRT$$

- Reversible
- Ideal gas

4. Adiabatic Process ($Q = 0$) [no electric or shaft work]

$$w = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \quad \therefore PV^{\gamma} = const.$$

5. Polytropic process ($PV^n = const.$)

$$w = \frac{P_1V_1 - P_2V_2}{n-1}$$

⇒ Isothermal process can be carried out
- in very slow process
- or when phase transfer (fast process)

⇒ Adiabatic
- very fast
- insulate

} → Two ways to conduct adiabatic process.

⇒ Area enclosed by cycle on P-V diagram is net work done.
- clockwise cycle → work done by system
- anticlockwise cycle → work done on system

⇒ Substance which exists as gases normally considered as ideal gas (eg:- O_2, N_2, CO_2, He, Air, etc.)

⇒ water vapour should be considerd ideal gas.

⇒ Steam should not be considered as ideal gas unless mentioned

⇒ Vapour is special name given to gaseous form of substance when it is close to condensation.

⇒ Steam is special name given to gaseous form of only water, generally at high temperature.

⇒ $PV = n\bar{R}T$; $PV = mRT$

$n\bar{R} = mR$; $R = \frac{\bar{R}}{M}$ → molecular mass

$R_c = \frac{\Sigma mR}{\Sigma m}$

1 mol of O_2 = 32 g

1 K-mol of O_2 = 32 Kg

$\bar{R} = 8.314$ KJ/mol.K

⇒ Const. volume.

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

★ Const. Pressure

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

★ Isothermal $P_1V_1 = P_2V_2$

★ Adiabatic

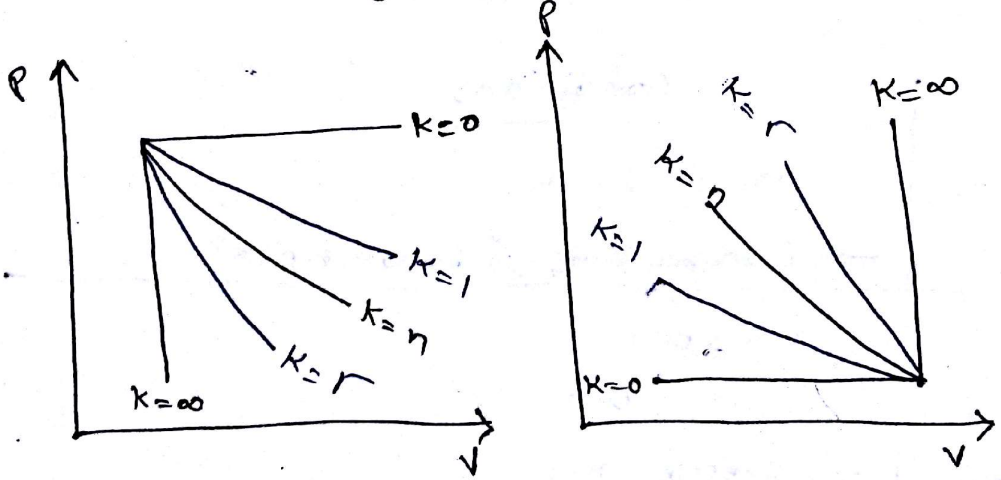
$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \quad ; \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

★ Polytropic

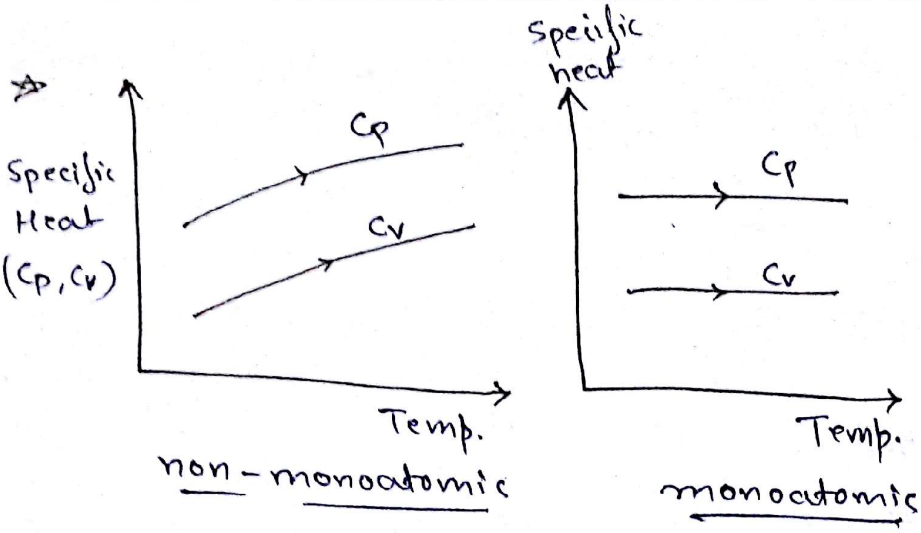
$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} \quad ; \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1}$$

⇒ $P_1V_1^n = P_2V_2^n$ should not be used for calculating 'n' for a process.

★ P-V diagram



K ⇓	Process ⇓
0	const. Pr.
1	isothermal
n	Polytropic
γ	adiabatic
∞	cont.-vol.



$Q \propto m$

$Q \propto dT$

$Q = mCdT$

↓

Specific heat

KJ/kg-K

$C_p \uparrow$, $C_v \uparrow$

$\Rightarrow \gamma \downarrow$

$C_p \Rightarrow$ Const. $\Rightarrow \gamma =$ const.

$C_v =$ const

★ Heat supplied at const pressure is more than Specific heat supplied at const. volume because C_p includes both internal energy as well as boundary work, C_v includes only internal energy.

★ First law of thermodynamics

- Law of conservation of energy, Joule's law

$$\oint \delta Q = \oint \delta W \quad \Rightarrow \text{for a closed cyclic process}$$

- $\delta Q = dE + \delta W$

  - → Ist law of thermodynamics
  - → valid only for closed system
  - → undergoing Process as well as cycle
  - → Both reversible & irreversible

S.no.	Formula	Conditions
1.	$\delta W = P dv$	- closed system - Quasistatic (Reversible)
2.	$PV^\gamma = \text{const.}$ $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$ $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$	- Adiabatic - Reversible - Ideal gas.

3.	$\delta Q = dE + \delta W$	- closed system
4.	$\delta Q = dU + \delta W$	- closed system & $\Delta KE = \Delta PE = 0$
5.	$\delta Q = dU + PdV$	- closed system - $\Delta KE = 0 = \Delta PE$ - Quasistatic (Reversible)

★ Consequencies of 1st law of thermodynamics

- Heat transfer is a Path function
- $\delta Q - \delta W = dE \Rightarrow dE$ is a property [internal Energy]
- Energy of an isolated system is constant
- PMM-I is impossible (m/c working without E_{input})

★ 1 atm = 101.325 KPa = 1.01325 bar

1 bar = 100 KPa

⇒ Pressure is not Energy, it only tells energy per unit volume (energy concentration)

★ Heat transfer in various process

1. Const volume

$\delta Q = dU + PdV$ (PdV → 0)

$\delta Q = dU$

$dU = mC_v dT$

→ Const. vol., any Substance

→ ideal gas, any process

2. Const. Pressure

$\delta Q = dU + PdV$

$\delta Q = dU + dPV$

$\delta Q = d(U + PV)$

$\delta Q = dH$

$dH = mC_p dT$

→ Const. Pr., any Substance

→ ideal gas, any Process

3. Isothermal Process

$\delta Q = \delta W + dU$ (dU → 0)

$\delta Q = \delta W = C \ln\left(\frac{P_1}{P_2}\right) = C \ln\left(\frac{V_2}{V_1}\right)$

4. Adiabatic Process $\quad \delta Q = 0$

5. Polytropic Process

$$\left(\delta Q\right)_{poly} = \left(W_{poly}\right) \times \left(\frac{\gamma - n}{\gamma - 1}\right)$$

⇒ For a constant Pressure process the maximum Boundary work for a given amount of heat is obtained when gas is monoatomic

$$\text{work ratio} = 1 - \frac{C_v}{C_p} = 1 - \frac{1}{\gamma}$$

$\gamma = 1.67 \Rightarrow$ monoatomic
$\gamma = 1.4 \Rightarrow$ diatomic
$\gamma = 1.33 \Rightarrow$ Polyatomic

★ Meyer's equation ⇒ $C_p - C_v = R$

$$C_v = \frac{R}{\gamma - 1} \quad ; \quad C_p = \frac{\gamma R}{\gamma - 1}$$

★ Polytropic specific heat is -ve for, $1 < n < \gamma$, because eventhough heat is added to the gas temperature of gas decreases, since the work done by gas is more than the heat supplied.

$$\frac{Q_{poly}}{m(T_2 - T_1)} = -C_v\left(\frac{\gamma - n}{n - 1}\right)$$

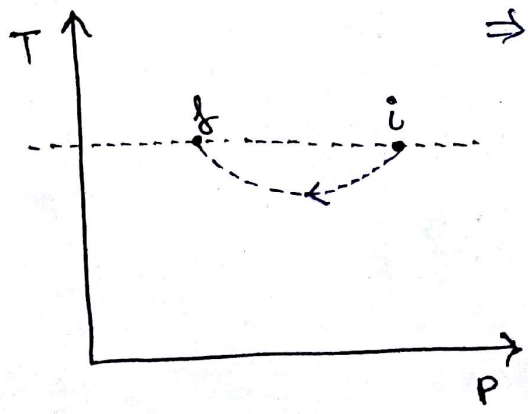
★ Free expansion $\quad \delta Q^{\circ} = dU + \delta W^{\circ}$

$$\Rightarrow dU = 0$$

$$mC\,dT = 0 \Rightarrow dT = 0 \Rightarrow T_i = T_f$$

$$P_i V_i = P_f V_f$$

⇒ Process is not isothermal as temperature decreases in between



★ Steady flow energy equation

KJ/kg

$$h_1 + \frac{c_1^2}{2} + gz_1 + q = h_2 + \frac{c_2^2}{2} + gz_2 + w_{c.v.}$$

J/kg [so multiplied by 10^{-3}]

↳ 1st law of thermodynamics for an open system working under steady state.

★ For ideal gas

$U = mC_vT$ & $H = mC_pT$

★ SFEE applied on various device

1. nozzle: - Steady flow
   - $\Delta PE = 0$
   - Adiabatic ($q=0$)
   - $w_{c.v.} = 0$

   $\Rightarrow h_1 + \frac{c_1^2}{2} = h_2 + \frac{c_2^2}{2}$

   if - $c_1 << c_2 \Rightarrow c_2 = \sqrt{2(h_1 - h_2)}$

2. Diffuser: - Steady flow
   - $\Delta PE = 0$
   - Adiabatic ($q=0$)
   - $w_{c.v.} = 0$

   $\Rightarrow h_1 + \frac{c_1^2}{2} = h_2 + \frac{c_2^2}{2}$

   If - $c_2 << c_1 \Rightarrow c_1 = \sqrt{2(h_2 - h_1)}$

3. Turbine: - Steady flow
   - $\Delta PE = 0 = \Delta KE$
   - $q = 0$

   $\Rightarrow w_{c.v.} = h_1 - h_2$

4. Compressor: - Steady flow
   - $\Delta KE = 0$
   - $\Delta PE = 0$
   - $q = 0$

   $\Rightarrow w_{c.v.} = h_2 - h_1$

5. Throttling device : - Steady flow
- $\Delta KE = 0 = \Delta PE$
- $w_{c.v.} = 0$
- $q = 0$ (adiabatic)

$\Rightarrow h_1 = h_2$

$\Rightarrow$ - Isenthalpic
- highly irreversible

☆ Unsteady state Analysis

1. Conservation of mass

$$\left(\frac{dm}{dt}\right)_{c.v.} = \dot{m}_i - \dot{m}_e$$

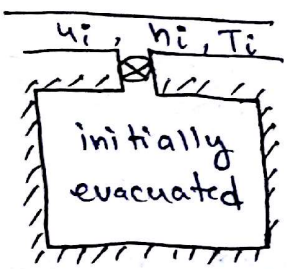
2. Conservation of Energy

$$\left(\frac{dE}{dt}\right)_{c.v.} = \dot{m}_i\left(h_i + \frac{c_i^2}{2} + gz_i\right) + \dot{Q} - \dot{m}_e\left(h_e + \frac{c_e^2}{2} + gz_e\right) - \dot{W}_{c.v.}$$

if $\Delta KE = 0 = \Delta PE$

$$\left(\frac{du}{dt}\right)_{c.v.} = \dot{m}_i h_i + \dot{Q} - \dot{m}_e h_e - \dot{W}_{c.v.}$$

$\Rightarrow$



$u_2 = h_i$

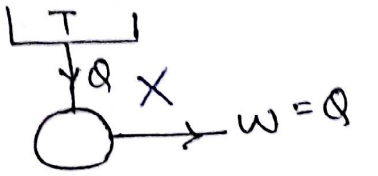
& $T_2 = \gamma T_i$

☆ Energy Quality

- Low grade → Heat
  - Available energy
  - unavailable energy $\propto$ Entropy.
- High grade
  - → work
  - → KE
  - → PE

★ 2nd Law of thermodynamics

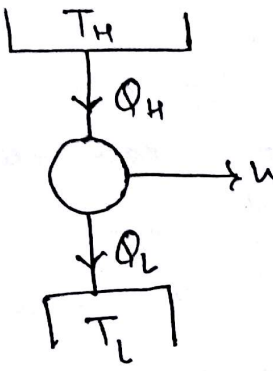
- Kelvin Plank: It is impossible to develop a cyclic device which develops work while exchanging energy with a single reservoir. Also an engine can never have 100% efficiency.



⇒ PMM-II is impossible

- Clausius: It is impossible to develop a cyclic device which transfer energy from lower temperature to higher temperature without any external energy input. Also, COP of a device can never be infinity.

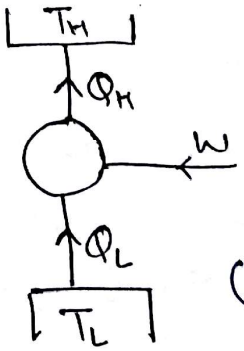
★ Violation of Kelvin plank statement leads to violation of Clausius statement and vise-versa. Hence these two statement are called parallel statement of 2nd Law of thermodynamics.



$$\eta = \frac{W}{Q_H}$$

$$\eta = \frac{Q_H - Q_L}{Q_H}$$

$$\eta = 1 - \frac{T_L}{T_H}$$

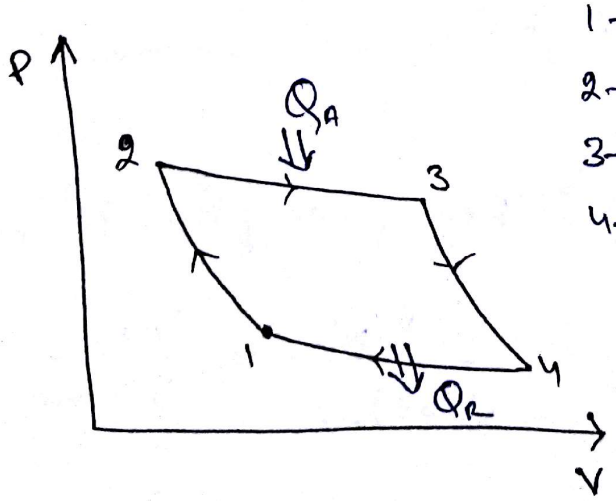


$$(COP)_{Ref.} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L}$$

$$(COP)_{H.P.} = \frac{Q_H}{Q_H - Q_L} = \frac{T_H}{T_H - T_L}$$

$$(COP)_{HP} = (COP)_{Ref.} + 1 = \frac{1}{\eta_E}$$

★ Carnat Cycle



1-2 ⇒ adiabatic compression
2-3 ⇒ Isothermal heat addition
3-4 ⇒ adiabatic Expansion
4-1 ⇒ Isothermal heat rejection.

★ All process are reversible

Carnot Principle

1st : $\eta_{irreversible} < \eta_{reversible}$

2nd : $(\eta_1)_{rev.} = (\eta_2)_{rev} = (\eta_3)_{rev} \cdots$

* above 2 principles are valid till the engines are working b/w same temp. limits.
* $\eta_{rev.}$ is independent of working fluid.

* Clausius Inequality

$$\oint \frac{\delta Q}{T} \leq 0 \; ;$$

Reversible $\Rightarrow \oint \frac{\delta Q}{T} = 0$

irreversible $\Rightarrow \oint \frac{\delta Q}{T} < 0$

impossible $\Rightarrow \oint \frac{\delta Q}{T} > 0$

$\Rightarrow$ whenever a device is shown exchanging heat from more than 2 reservoirs it can be a case of combination of cycles, hence clausius inequality should be used.

$\Rightarrow$ Temp. Appearing in Expression are temp. of working fluid

$\Rightarrow \eta = 1 - \frac{T_L}{T_H}$ & $(COP)_R = \frac{T_L}{T_H - T_L}$ & $(COP)_{HP} = \frac{T_H}{T_H - T_L}$ are only valid if - cycle is reversible
- Heat addition & rejection are isothermal.

* 2nd law Efficiency (η_{II})

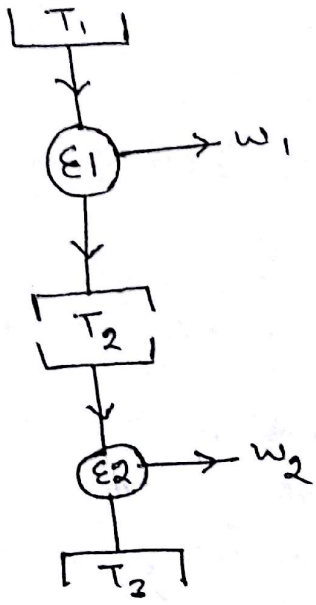
for engine

$$\eta_{II} = \frac{\eta_{actual}}{\eta_{reversible}} = \frac{W_{actual}}{W_{max.}}$$

for Refrigerator / Heat Pump

$$\eta_{II} = \frac{(COP)_{actual}}{(COP)_{rev.}} = \frac{W_{min}}{W_{actual}}$$

★ 2 Heat Engines in Series



⇒ overall efficiency of arrangement = η

$$\eta = \eta_1 + \eta_2 - \eta_1 \times \eta_2$$

⇒ If, work is same ; $W_1 = W_2$

then, $T_2 = \frac{T_1 + T_3}{2}$

⇒ If, $\eta_1 = \eta_2$; then $T_2 = \sqrt{T_1 T_3}$

★ ENTROPY

- for a reversible process, $\left(\frac{\delta Q}{T}\right)_{\substack{\text{inter} \\ \text{rev.}}} = ds$
- for a irreversible process, $\left(\frac{\delta Q}{T}\right)_{\substack{\text{inter} \\ \text{irrev.}}} + (\delta s)_{gen} = ds$
- Entropy is a property
  - → Point function
  - → state function
  - → Exact differential
- Entropy generation (δS_{gen}) is not a property.
- A process is said to be internally reversible if no entropy generation takes place inside the system during the process.
- Entropy generation represents degradation of energy.

★ for a cyclic device

$$\oint ds = 0 \; ; \; [\text{for both reversible \& irreversible}]$$

★ Entropy can change by 3 methods

1. Heat interaction
2. mass interaction [External interaction]
3. Entropy generation [internal interaction]

★ Fixed mass Entropy analysis :

A) Reversible $[\delta S_{gen} = 0]$

$$ds = \left(\frac{\delta Q}{T}\right) + \cancel{\delta S_{gen}}$$

1. Heat addition

$$ds = \left(\frac{\delta Q}{T}\right)^{+ve} = +ve$$

2. Heat rejection

$$ds = \left(\frac{\delta Q}{T}\right)^{-ve} = -ve$$

3. Adiabatic

$$ds = \left(\frac{\delta Q}{T}\right)^{0} = 0$$

↳ isentropic

B) Irreversible

$$ds = \left(\frac{\delta Q}{T}\right) + (\delta S)_{gen}$$

1. Heat addition

$$ds = \frac{\delta Q}{T}^{+ve} + \delta S_{gen} = +ve$$

2. Heat rejection

$$ds = \frac{\delta Q}{T}^{-ve} + \delta S_{gen} = +ve, -ve,$$

isentropic ← 0

3. Adiabatic

$$ds = \frac{\delta Q}{T}^{0} + \delta S_{gen} = +ve$$

★ Entropy of universe :

⇓

isolated ; $\delta Q^{0} = dU + \delta W^{0}$

$dU = 0$ ⇒ Energy remains constant.

$$ds = \frac{\delta Q}{T}^{0} + \delta S_{gen} = +ve \Rightarrow \text{Entropy} \geq 0$$

- ∴ entropy of universe can increase or remain constant but can never decrease. This is called as increase in entropy principle.

★ If we talk about same amount of energy then entropy associated is higher at lower temperature and lower at higher temperature.

- If mass is same then Entropy is higher at higher temp. & lower at lower temp. bcz total energy is also different.

★ Area under curve on T-S diagram represents heat interaction for a reversible process.

- Area enclosed by reversible cycle on T-S diagram represents net heat transfer which is equal to net work transfer.
- All clockwise cycle ⇒ Power producing device
  All anticlockwise cycle ⇒ Power consuming device

★ Combined 1st law & 2nd law equations

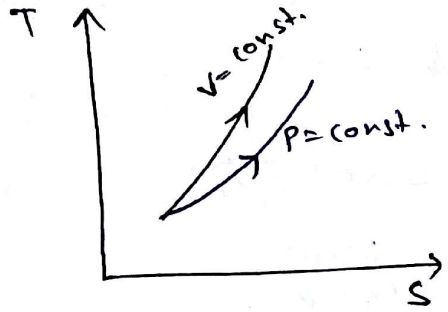
or

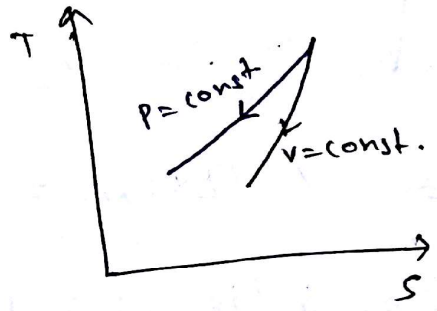
Tds equations

① $Tds = dU + PdV$ ② $Tds = dh - vdP$

- These equations are valid for all processes.

★ Const. Pr. & const. vol. T-S diagram





$$\left(\frac{dT}{ds}\right)_v = \frac{T}{C_v}$$

$$\left(\frac{dT}{ds}\right)_P = \frac{T}{C_P}$$

- Const. vol. process is more steeper.

★ Entropy calculation

→ Thermal Reservoir or Phase change

$$ds = \frac{Q}{T}$$

→ Solid or liquid of finite mass

$$\Delta S = S_2 - S_1 = mc \ln\left(\frac{T_2}{T_1}\right)$$

→ Gas → Real gas (T.D. relations)

→ Ideal gas ($Pv = RT$)

kJ/kgK

1. $\Delta S = S_2 - S_1 = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$
2. $\Delta S = S_2 - S_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$
3. $\Delta S = S_2 - S_1 = C_v \ln\left(\frac{P_2}{P_1}\right) + C_p \ln\left(\frac{V_2}{V_1}\right)$

★ Control volume Entropy Analysis :-

- Steady state

$(\Delta E)_{c.v.} = 0$

$(\Delta m)_{c.v.} = 0$

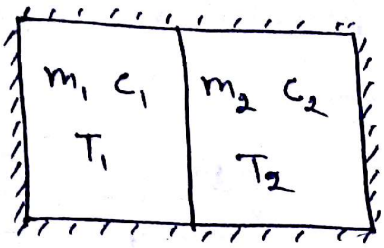
$(\Delta S)_{c.v.} = 0$

$(\Delta S)_{c.v.} = \dot{S}_{entry} - \dot{S}_{exit} + \delta\dot{S}_{gen}$

$0 = \dot{S}_{entry} - \dot{S}_{exit} + \delta\dot{S}_{gen}$

$\Rightarrow \boxed{\delta\dot{S}_{gen} = \dot{S}_{exit} - \dot{S}_{entry}}$

★ mixing of two incompressible fluids (liquid) or two solids :-



$$T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2}$$

$$(\Delta S)_{uni.} = m_1 c_1 \ln\left(\frac{T_f}{T_1}\right) + m_2 c_2 \ln\left(\frac{T_f}{T_2}\right)$$

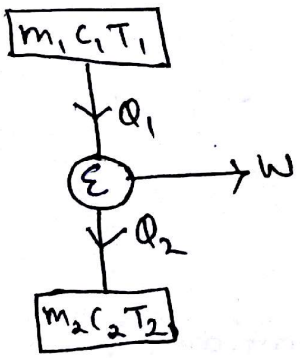
if $m_1 = m_2 = m$ & $c_1 = c_2 = c$

$$T_f = \frac{T_1 + T_2}{2} \quad \& \quad (\Delta S)_{uni.} = 2mc \ln\left(\frac{AM}{GM}\right)$$

(AM → of temp., GM → of temp.)

for, n bodies $\Rightarrow (\Delta S)_{uni} = n\,mc \ln\left(\frac{AM}{GM}\right)$

★ Maximum obtainable work when two finite body are allowed to exchange heat through reversible engine.



$(\Delta S)_1 + (\Delta S)_E + (\Delta S)_2 = 0$; [for max. work] ($(\Delta S)_E = 0$: cyclic)

$$m_1 c_1 \ln\left(\frac{T_f}{T_1}\right) + 0 + m_2 c_2 \ln\left(\frac{T_f}{T_2}\right) = 0$$

if $m_1 = m_2 = m$ & $c_1 = c_2 = c$

$$T_f = \sqrt{T_1 T_2}$$

$$W_{max.} = 2mc(AM - GM)$$

for n bodies; $W_{max.} = n\,mc(AM - GM)$

★ Reversible work in a steady flow process

assumptions – 1. Steady flow

2. $\Delta KE = 0 = \Delta PE$

3. reversible

$$W_{c.v.} = -\int v\,dp$$

★ In a gas cycle for non adiabatic process ($PV^n = c$) the

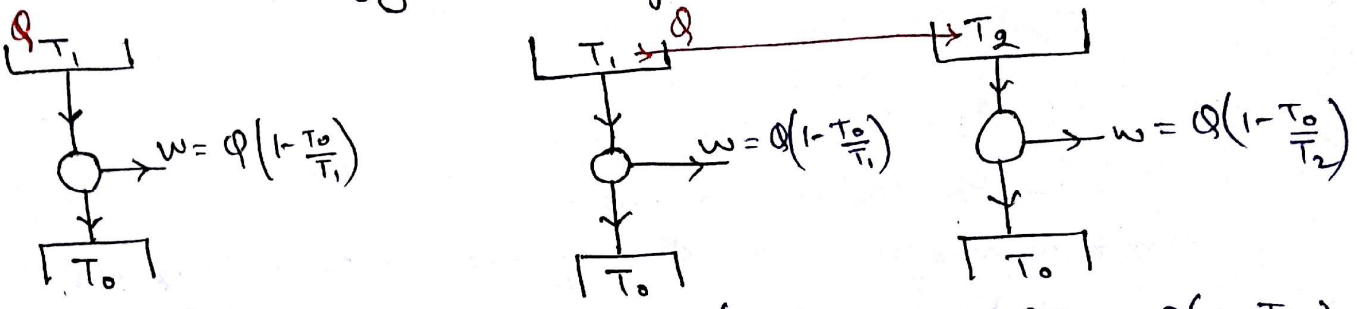
$W_{c.v.} = -\int v\,dp$ or $W_{c.v.} = \left(\frac{n}{n-1}\right)(P_1V_1 - P_2V_2)$

⇒ **Available Energy or Exergy or Availability**

Available energy is the maximum useful work which can be obtained in a process in which system attains dead state.

→ Available energy is a function of – Energy of system
– State of system
– State of surroundings

① **Thermal energy at a single temperature**



$A\mathcal{E}_1 = Q\left(1 - \frac{T_0}{T_1}\right)$

$A\mathcal{E}_1 = Q\left(1 - \frac{T_0}{T_1}\right)$ $\quad A\mathcal{E}_2 = Q\left(1 - \frac{T_0}{T_2}\right)$

$\Delta A\mathcal{E} = A\mathcal{E}_1 - A\mathcal{E}_2$

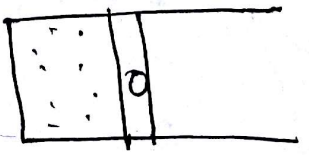
② **Thermal energy with a given mass of solid or liquid**

$\boxed{\phi = u - T_0 s}$; $\phi_1 = u_1 - T_0 s_1$ | $\Delta\phi = \phi_1 - \phi_2$

$\phi_2 = u_2 - T_0 s_2$ | $= (u_1 - u_2) - T_0(s_1 - s_2)$

③ **Non-flow gases**

$\boxed{\phi = U - T_0 S + P_0 V}$



$\Delta\phi = \phi_1 - \phi_2 = (U_1 - U_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2)$

$(U_1 - U_2) - T_0(S_1 - S_2)$ ⇓ max. work

$P_0(V_1 - V_2)$ ⇓ $W_{atm.}$

⇓ max. useful work

④ **flowing fluids**

$\boxed{\phi = h - T_0 s}$

★ Since K.E & P.E. are totally available energy hence they can be directly added in the available energy expressions.

Irreversibility (I)

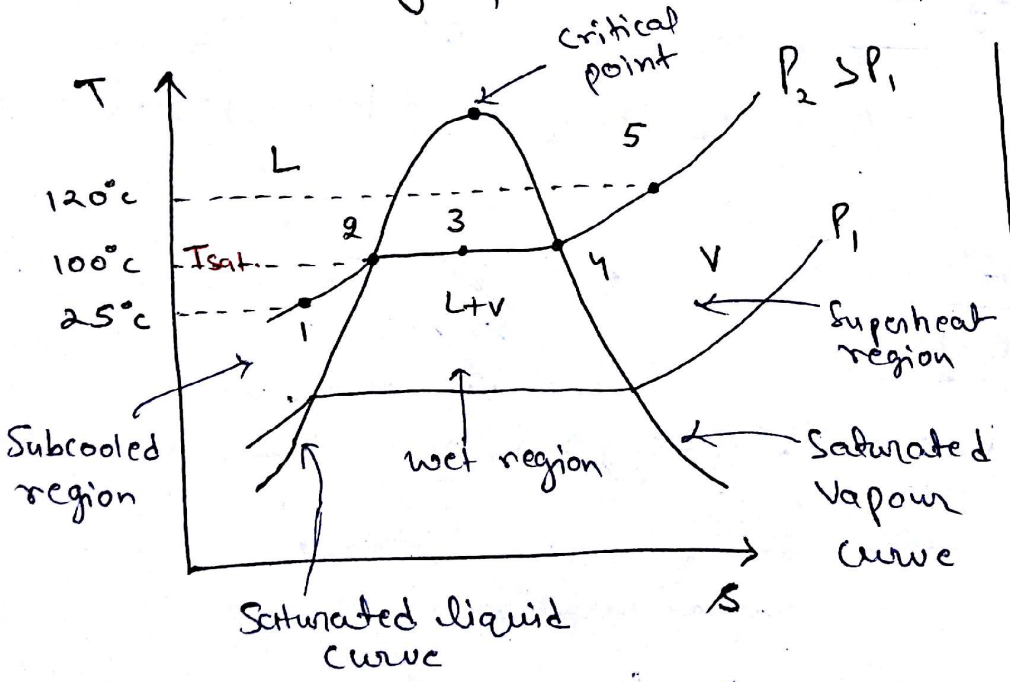
I = Loss of A.E.
= increase in U.A.E
= $W_{max.} - W_{actual}$

★ Gouy - Stodala theorm

$$I_{total} = T_0 (\Delta S)_{uni.}$$

- Causes of irreversibility
  - Conversion of High grade energy into low grade energy
    - friction
    - viscous forces
    - Electric resistance
    - Inelastic collision
  - Heat transfer through finite temp. differences.
  - Free Expansion
  - mixing of fluids.

Properties of pure substance



Degree of subcooling
$= T_{sat.} - T_1$

Degree of superheating
$= T_s - T_{sat.}$

Dryness fraction (x)

$$x = \frac{m_v}{m_l + m_v}$$

m_v = mass of vapour
m_l = mass of liquid

★ As the pressure increase latent heat of vapourisation decreases and boiling point increases. L.H. becomes zero at critical Point
★ At critical point Dryness fraction is undefined & DOF = 0
★ only vapour exists above critical point.

- During phase change pressure & temp. are dependent property.

Expressions for wet region

$$h = h_f + x\,h_{fg}$$
$$v = v_f + x\,v_{fg}$$
$$s = s_f + x\,s_{fg}$$
$$u = u_f + x\,u_{fg}$$
$$\frac{1}{\rho} = \frac{1}{\rho_f} + x\left(\frac{1}{\rho_g} - \frac{1}{\rho_f}\right)$$

$$h_1 = h_f - C_{p_l}(T_{sat.} - T_1)$$
$$h_s = h_g + C_{p_v}(T_s - T_{sat.})$$
$$s_1 = s_f - C_{p_l}\ln\left(\frac{T_{sat.}}{T_1}\right)$$
$$s_s = s_g + C_{p_v}\ln\left(\frac{T_s}{T_{sat.}}\right)$$

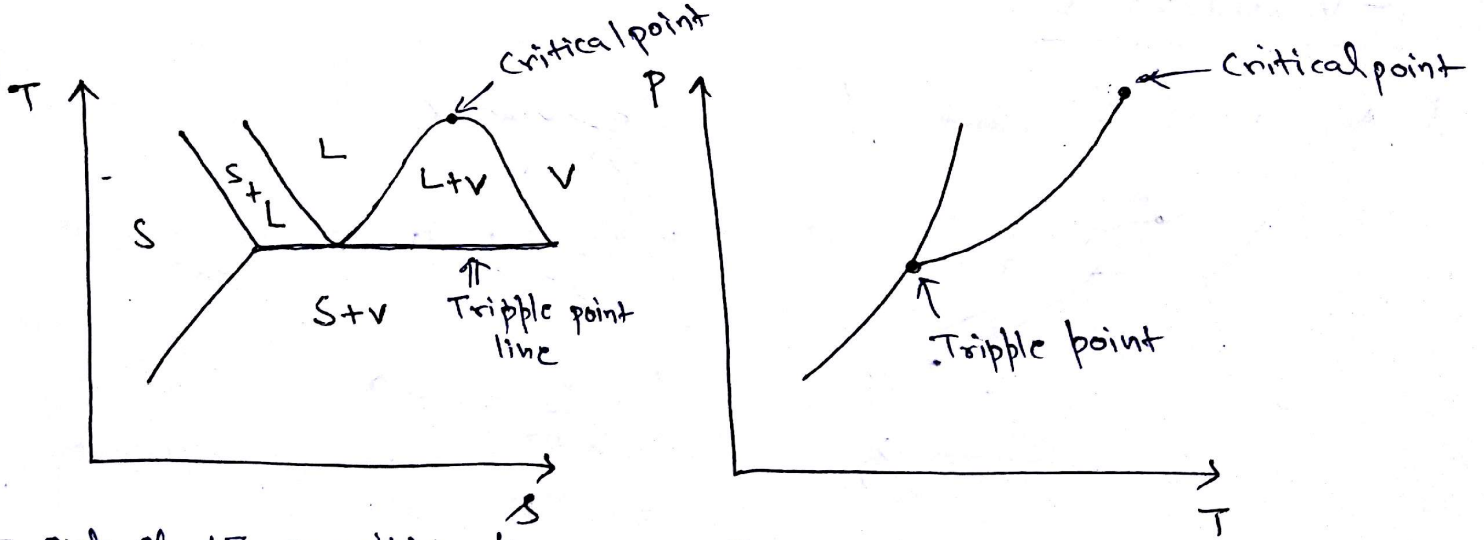
★ Heat supplied at const. Pressure is change in enthalpy. Heat supplid at const. volume is change in internal energy.

★ If steam is heated in rigid container then energy supplied is change in internal energy, not enthalpy.

★ A common mistake is not multiplying by mass. ($m = \frac{V}{v}$)

★ In steam table reference point is tripple point of water & $u = 0$, $s = 0$ considered.

Pressure temp. diagram

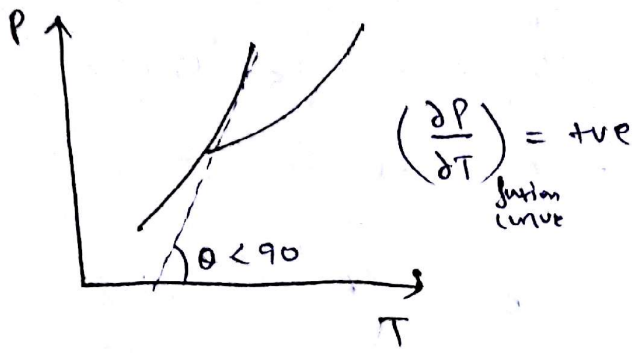


- out of 15 possible diagrams [P, V, T, U, H, S ; ${}^6C_2 = 15$] if diagram is P-T then phase change region is abscent and tripple point is a point.
- on all other diagram phase change region is present and tripple point is line
- Critical point is a point on all diagram.

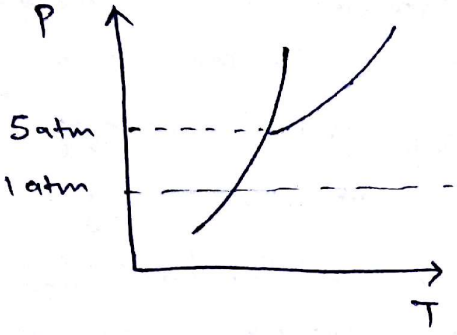
General Substance

$S \rightarrow L \Rightarrow$ Expand

$L \rightarrow S \Rightarrow$ contract



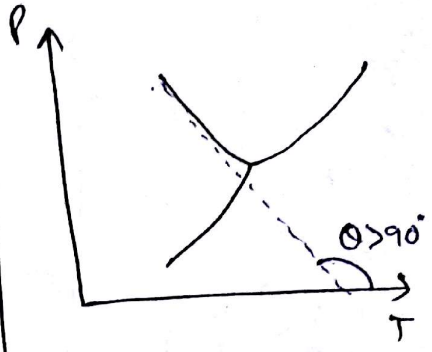
eg:- CO_2 [dry ice.]



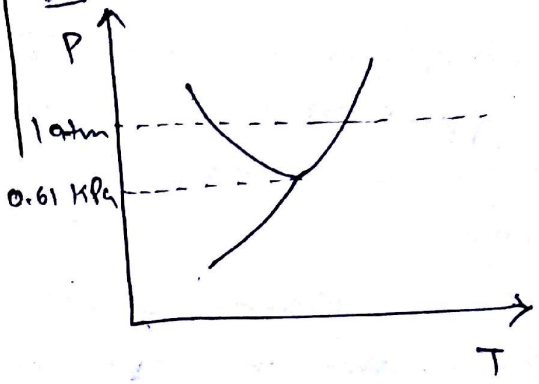
Water (H_2O)

$S \rightarrow L \Rightarrow$ contract

$L \rightarrow S \Rightarrow$ Expand

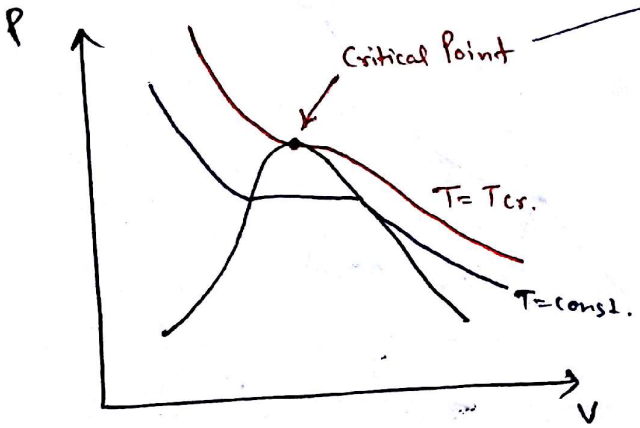


H_2O



- If Substance is kept below tripple point ~~temperature~~ Pressure then it will directly convert to vapour (from solid) on heating.

P-V diagram



$\left(\frac{\partial P}{\partial v}\right) = 0$

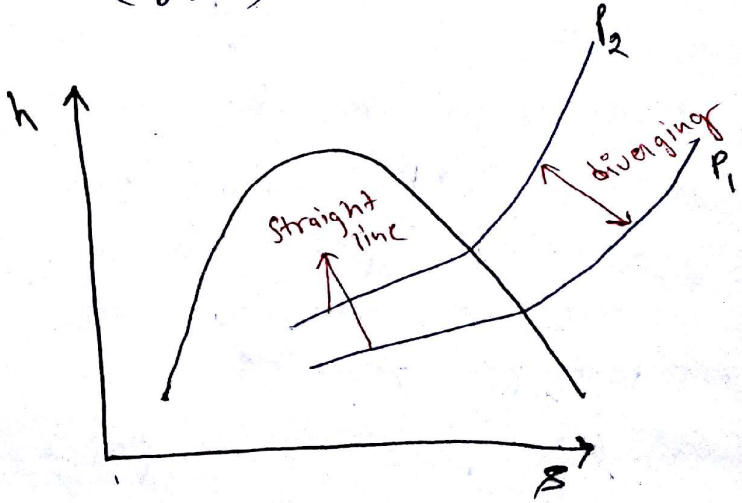
$\left(\frac{\partial^2 P}{\partial v^2}\right) = 0$

$\left(\frac{\partial^3 P}{\partial v^3}\right) < 0$

Mollier diagram

$\left(\frac{dh}{ds}\right)_P = T$

Slope = T



Real Gases

* compressibility factor = $Z = \frac{v_a}{v_i}$

→ $Z = 1 \Rightarrow$ real gas behaving as ideal gas

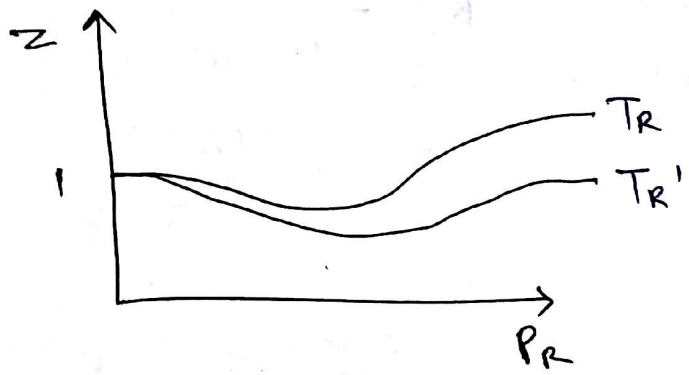
→ $Z > 1 \Rightarrow v_a > v_i \Rightarrow$ repulsion dominate $\Rightarrow$ Difficult to compress as compared to ideal gas

→ $Z < 1 \Rightarrow v_a < v_i \Rightarrow$ attraction dominate $\Rightarrow$ easier to compress as compared to ideal gases.

* Different Gases behaves differently at same temperature and Pressure but there behaviour is almost same at same Reduced Pressure & Reduced temperature.

$$P_R = \frac{P}{P_{cr.}} \qquad T_R = \frac{T}{T_{cr.}}$$

⇒ compressibility chart



$T_R > T_R'$

⇒ Vander waal's equation

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = n\bar{R}T$$

for $n = 1$

$$\left(P + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T$$

$\bar{v} = m^3/mol.$

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

$v = m^3/Kg$

$$a = \frac{27 R^2 T_{cr}^2}{64 P_{cr.}} \qquad b = \frac{RT_{cr.}}{8 P_{cr.}}$$

Thermodynamic Relations

- Gibb's function ⇒ $G = H - TS$
- Helmonth's function ⇒ $F = U - TS$

Maxwell's equation

T	P	$\left(\frac{\partial P}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s$	$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$
v	s	$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T$	$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$

Tds Partial differential Equⁿ

1. $Tds = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$
2. $Tds = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$

Clapeyron equation

$$\frac{dP}{dT} = \frac{L.H.}{T_{sat.}(V_g - V_f)}$$

Mayer's Equation

$$C_p - C_v = -T\left(\frac{\partial P}{\partial v}\right)_T \left[\left(\frac{\partial v}{\partial T}\right)_P\right]^2$$

$$K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

$$C_p - C_v = \frac{T v \beta^2}{K_T}$$

Energy equation

$$dU = C_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

Clausius clapeyron eqn

$$\frac{dP}{dT} = \frac{L.H. \cdot P_{sat}}{T_{sat}^2 \times R}$$

$$\int \frac{dP}{P} = \frac{LH}{R} \int \frac{dT}{T^2}$$

Joule thomson coefficient (μ)

$$dh = C_p dT - \left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right] dP$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right] = 0 \text{ for ideal gas}$$