

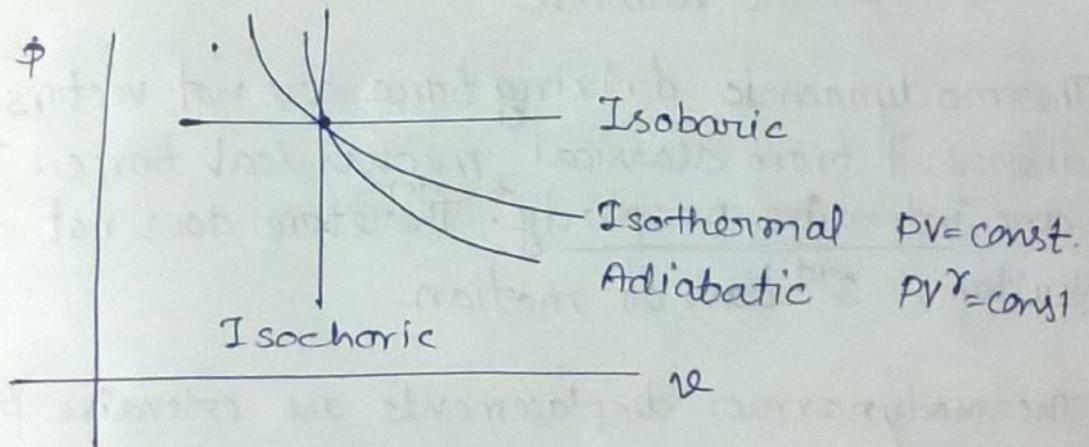
11/01/2017

# Reversible process gives the maximum work output for a certain process.

All the naturally occurring processes can be a series of isobaric and isothermal processes

$$\frac{PV^n = \text{const}}{\text{polytropic process}}$$

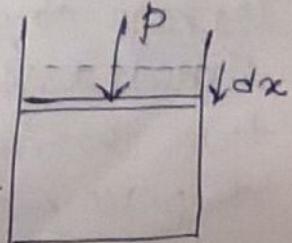
$$\left\{ \begin{array}{l} n=\infty \\ \text{Isochoric } V=\text{const. } PV = dW \\ n=0 \\ \text{Isobaric } P = \text{const. } P(V_2 - V_1) = P/dV \\ n=1 \\ \text{Isothermal process } \int PdV = nRT \ln \frac{V_2}{V_1} \\ n=\gamma \\ \text{Adiabatic process } \Rightarrow PV^\gamma = \text{const} \end{array} \right.$$



Energy is capacity to <sup>indue a</sup> change in that which inherently opposes the change.

- overcome the resistance against change (driving force)
- Thermodynamic displacement i.e. brings in change

P → Thermodynamic driving force

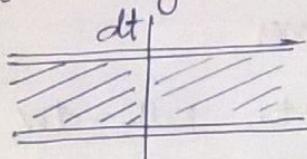


$dV \rightarrow$  Thermodynamic displacement  
(volume change)

For an elastic rubber

Tension  $\rightarrow$  driving force  
displacement  $\rightarrow$  length increased

Flow through a fluid



Flow work

$$= PAU dt$$

$$= P \cancel{A} \overset{Q}{\cancel{U}} dt$$

$$= P Q dt$$

for unit mass, work rate

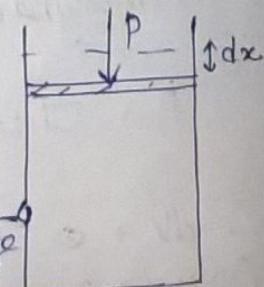
$$= P \times \text{specific volume}$$

Thermodynamic driving force are not vectors, i.e. different from classical mechanical force. These are intensive property of system. Therefore does not obey Newton's 3<sup>rd</sup> Law of motion.

Thermodynamic displacements are extensive property of system.

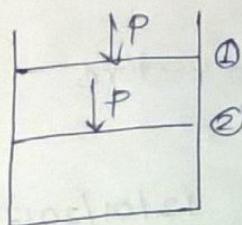
If One driving force brings ~~the~~ only one thermodynamic displacement, then only thermodynamic work done can be calculated

Volume is decreasing as well as leakage of gas is taking place simultaneously. So there are two thermodynamic displacement occurring simultaneously. Thus, thermodynamic work done can not be calculated.



The work done

Energy in transit is a path function



→ Work done (path function)

differential work done is therefore inexact differential

→ System properties Exact differential

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

$$W \neq \int_1^2 dW \neq W_2 - W_1$$

so differential work done can be represented as

$dW$  or  $dW$  and  $dW$  can not be written  
They do not depend on initial and final state.  
instead on path.

Work done

→ Energy in transit

→ Neither the property of system nor surrounding

→ Manifest some change in either system or surrounding or both. But source of change may not be notified

$\Delta T \rightarrow d\bar{U}$

Thermodynamic displacement  $\rightarrow \Delta T \Rightarrow$  Heat

Thermodynamic displacement other than  $\Delta T$   
 $\Rightarrow$  Work

# Selection of system is crucial

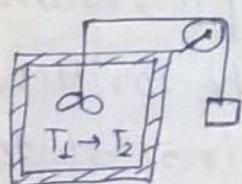
$$\oint dW \neq \oint dQ$$

~~box~~

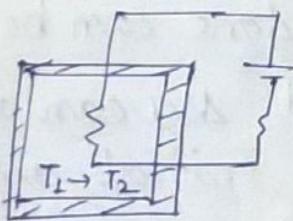
Why heat can not be included in entire domain of work?

12/01/2017

Entire heat can not be transformed in work. Entire portion of heat  $\rightarrow$  is not available. On the other hand entire amount of work can be transformed in to heat. This is corollary from 1<sup>st</sup> law of thermodynamics and Carnot cycle.



paddle wheel



Electrical heating

All processes performed by Joule lead to the conclusion

$$\oint dW \neq \oint dQ$$

$$\oint dW = J \oint dQ$$

In SI units  $J = 1 \frac{\text{N}\cdot\text{m}}{\text{Joule}}$

$$\oint dW = \oint dQ$$

1) Entire cyclic process can not be adiabatic. Some portion of cycle may be adiabatic. 2) The process is not reversible.

3) e.g. If temperature of a body is not increased above ambient temperature, then only work can be extracted from the ball.

① Heat is a path function

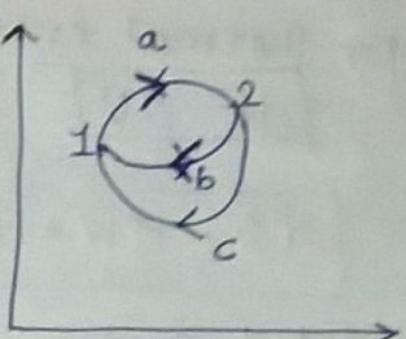
$$\oint dQ = \oint dQ$$

1a2b                  1b2b

$$\oint_{1a2} dQ + \oint_{2b1} dQ = \int_{1a2} dW + \int_{2b1} dW$$

$$\int_{1a2} dQ + \int_{2c1} dQ = \int_{1a2} dW + \int_{2c1} dW$$

-                    -



$$dW = f \cdot r$$

Thermodynamic driving force

Thermo-dynamical displacement

$$\int_{2b1} dQ - \int_{2c1} dQ = \int_{2b1} dW - \int_{2c1} dW \neq 0$$

$$\int_{2b1} dQ \neq \int_{2c1} dQ$$

$$\int_{2b1} dW \neq \int_{2c1} dW$$

$$\int_{2b1} (dQ - dW) = \int_{2c1} (dQ - dW)$$

$$\int_{2b1} (dQ - dW) = \int_{2c1} (dQ - dW)$$

$$(dQ - dW) = dE$$

difference b/w  
two in-exact  
differential

an exact differential  
(State function)

② Energy is state function

$$dE = dU + dE_k + dE_p + \dots$$



For thermal energy dominating

$$dE = dU$$

$$dQ - dW = dU \Rightarrow \text{closed system}$$

isolated system

$$dQ = 0$$

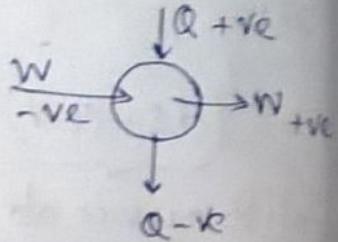
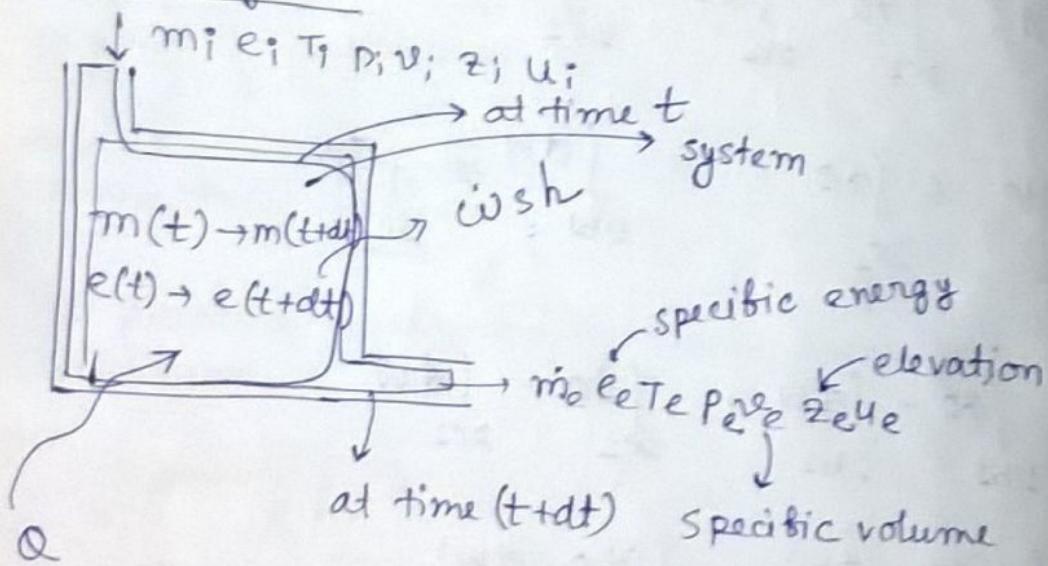
$$dW = 0$$

$$dE = 0$$

$$E_{\text{system}} = \text{constant}$$

$\Rightarrow$  Principle of conservation of energy

For open system



Consider a system so that the mass of the system remains const. during the entire process.

system has variable boundary

at time  $t$ : the mass within container + <sup>mass about to enter in time dt</sup>

$\frac{d}{dt}$  at time  $(t+dt)$ : the mass within the container + mass escaped in time  $dt$

$$m(t) + \dot{m}_i dt = m_e dt + m(t+dt)$$

$$\cancel{m} - \dot{m}_i dt - m_e dt = m(t+dt) - m(t)$$

$$\dot{m}_i - m_e = \lim_{\Delta t \rightarrow 0} \frac{m(t+dt) - m(t)}{\Delta t}$$

$$\cancel{\dot{m}_e} \quad \dot{m}_i - \dot{m}_e = \frac{dm}{dt}$$
$$\cancel{\partial Q - \partial W = dU}$$

$$\dot{m}_i dt e_i + m_e(t) e(t) = \dot{m}_e e_e dt + m(t+dt) e(t+dt)$$

$$\dot{m}_i dt \left( u_i + \frac{v_e^2}{2} + g z_e \right) + m(t) e(t) = \dot{m}_e dt \left( u_e + \frac{v_e^2}{2} + g z_e \right)$$
$$\uparrow W_{sh} dt + \cancel{W_f} dt \quad + m(t+dt) e(t+dt)$$
$$\dot{Q} dt \quad \rightarrow \left( - P_e v_e \dot{m}_i dt + P_e v_e m_e dt \right)$$

#Find 1<sup>st</sup> law for open system

$$\frac{dE}{dt} + m_e e_e - \dot{m}_i e_i = \dot{Q} - W_{sh} - P_e v_e m_e + P_e v_e \dot{m}_i$$

$$\frac{dU}{dt} + \frac{dE_k}{dt} + \frac{dE_p}{dt}$$

$$= \dot{Q} - \dot{W}_{sh} - m_e (U_e + P_e V_e + \frac{V_e^2}{2} + g z_e) + \\ m_i (U_i + P_i V_i + \frac{V_i^2}{2} + g z_i)$$

$$\Delta K.E = \frac{1}{2} m_e U_e^2 - \frac{1}{2} m_i U_i^2$$

$$\Delta P.E \rightarrow m_e g z_e - m_i g z_i$$

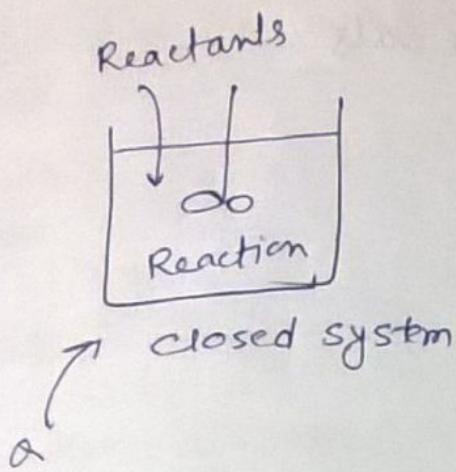
~~APL~~

$$\dot{Q} - \dot{W} = \frac{m_e U_e^2}{2} - \frac{m_i U_i^2}{2} + m_e g z_e - m_i g z_i \\ + m_e P_e V_e - m_i P_i V_i \\ + m_e U_e - m_i U_i$$

$$\dot{Q} - \dot{W} = (\frac{m_e U_e^2}{2} - \frac{m_i U_i^2}{2}) + (m_e g z_e - m_i g z_i \\ + m_e H_e - m_i H_i)$$

where  $H = U + P V$

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$$Q - W = \Delta U = C_V \Delta T$$

$$Q = C_V \Delta T + W = C_V \Delta T + P \Delta V$$

$$= \Delta U + P \Delta V$$

$$= \Delta (U + PV) = \Delta H$$

State $t^n$	Path $t^n$
$\Delta E$	$W$
$\Delta H$	$Q$
$\Delta S$	
$T, P, V$	

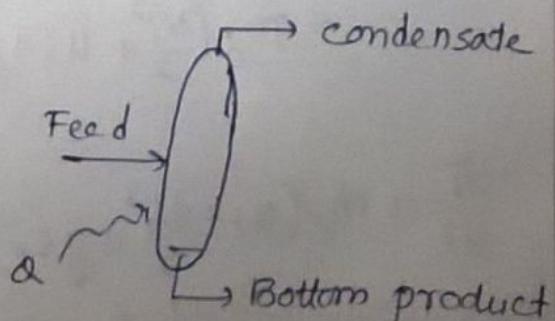
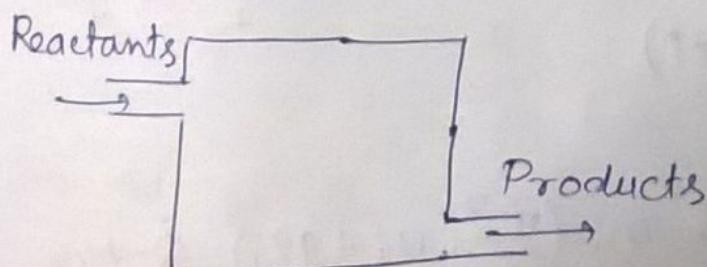
$$Q_p = C_p \Delta T = \Delta H$$

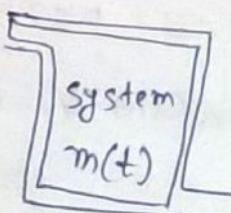
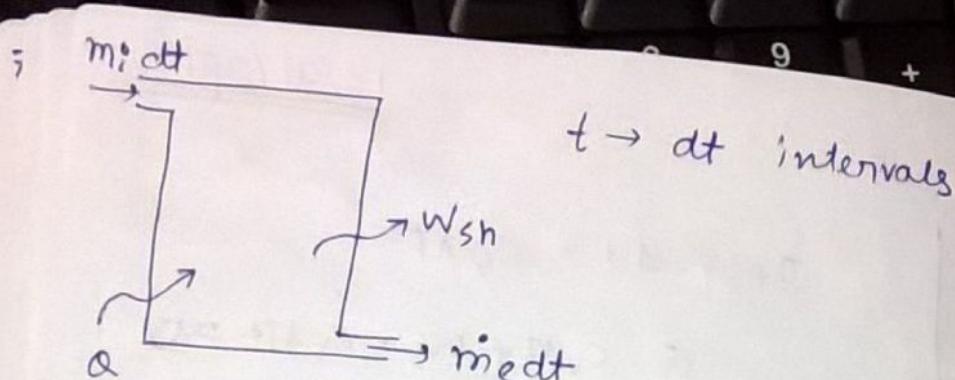
$$Q_v = C_v \Delta T = \Delta U$$

$Q \neq C_p \Delta T$  if pressure is not const.

$Q \neq C_v \Delta T$  if volume is not const.

But  $\Delta U = C_v \Delta T$   
 $\Delta H = C_p \Delta T$  ] for solid, liquid, ideal gases





$$\begin{aligned} m_i dt + m(t) &= m_e dt + m(t+dt) \\ m_i dt - m_e dt &= \frac{dm}{dt} = m_e - m_i \end{aligned}$$

$m_i dt + m(t+dt) = m_e dt + m(t)$   
The system is fixed amount of mass within  
a variable boundary

$$\begin{aligned} \Delta E &= Q - W = \dot{Q} dt + W_{sh} dt + (P_e v_e m_e dt - P_i v_i m_i dt) \\ \Delta E &= E(t+dt) - E(t) + (m_e e dt - m_i e i dt) \\ &= m(t+dt) e(t+dt) - m(t) e(t) + m_e \left( \frac{v_e^2}{2} + u_e + g z_e \right) \\ &\quad - m_i \left( \frac{v_i^2}{2} + u_i + g z_i \right) \end{aligned}$$

$$\begin{aligned} \frac{dE}{dt} + m_e (u_e + \frac{v_e^2}{2} + g z_e) - m_i (\frac{v_i^2}{2} + u_i + g z_i) &= \dot{Q} - W_{sh} \\ &\quad + P_e v_e \end{aligned}$$

$$\frac{dE}{dt} + \dot{m}_e(h_e + \frac{v_e^2}{2} + gz_e) - \dot{m}_i(h_i + \frac{v_i^2}{2} + gz_i) = \dot{Q} - \dot{W}_{sh}$$

$$\frac{dE}{dt} = [\dot{m}_i(h_i + \frac{v_i^2}{2} + gz_i) + \dot{Q}] - [\dot{m}_e(h_e + \frac{v_e^2}{2} + gz_e) + \dot{W}_{sh}]$$

Rate of energy accumulation within the system

$$= (\text{Rate of energy in}) - (\text{Rate of energy out})$$

In flow reactor, usually kinetic, potential energy is neglected as well as shaft work

$$\boxed{\frac{dE}{dt} = \dot{m}_i h_i + \dot{Q} - \dot{m}_e h_e}$$

at steady state

$$\dot{m}_e = \dot{m}_i = \dot{m}; \quad \dot{Q} = \text{const.}$$

$$\frac{dE}{dt} = 0 \quad \dot{W}_{sh} = \text{const.}$$

$$\sum_{\text{effluents}} \dot{m}_e [h_e + \frac{v_e^2}{2} + gz_e] - \sum_{\text{influent}} [h_i + \frac{v_i^2}{2} + gz_i] = \dot{Q} - \dot{W}_{sh}$$

$$\dot{m} [dh + \frac{dv^2}{2} + gdz] = \dot{Q} - \dot{W}_{sh}$$

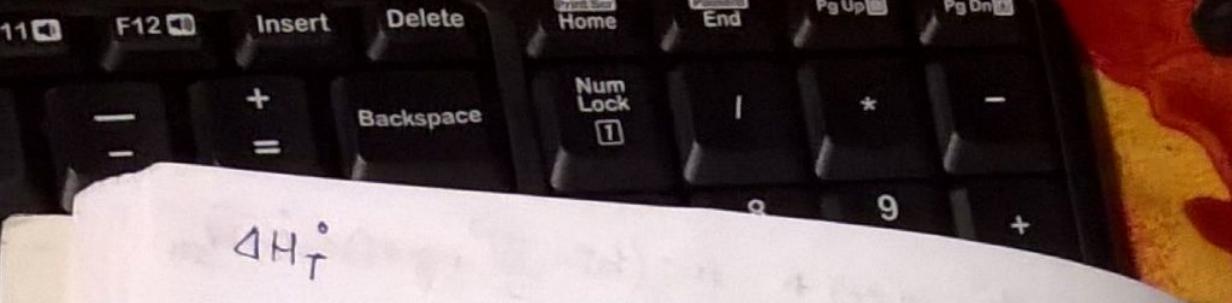
$$\boxed{\dot{Q} = dh + \frac{1}{2} \dot{m} v^2}$$

Standard state

pure gas at 1 atm

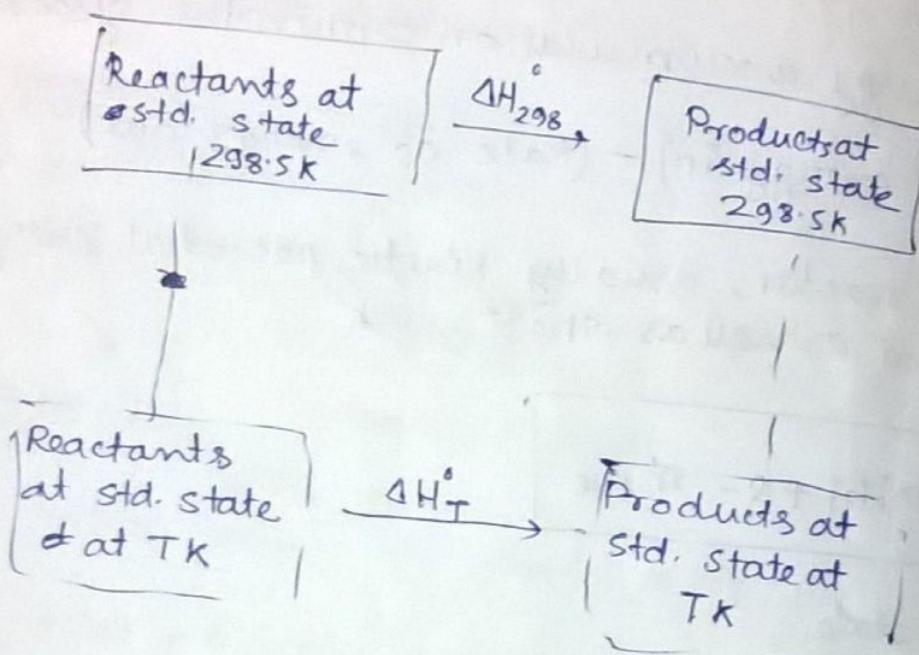
pure liquid at 1 atm

pure solid at its most stable allotropic form at 1 atm



$\Delta H_f^\circ$

$\Delta H^\circ$   
298.15 K

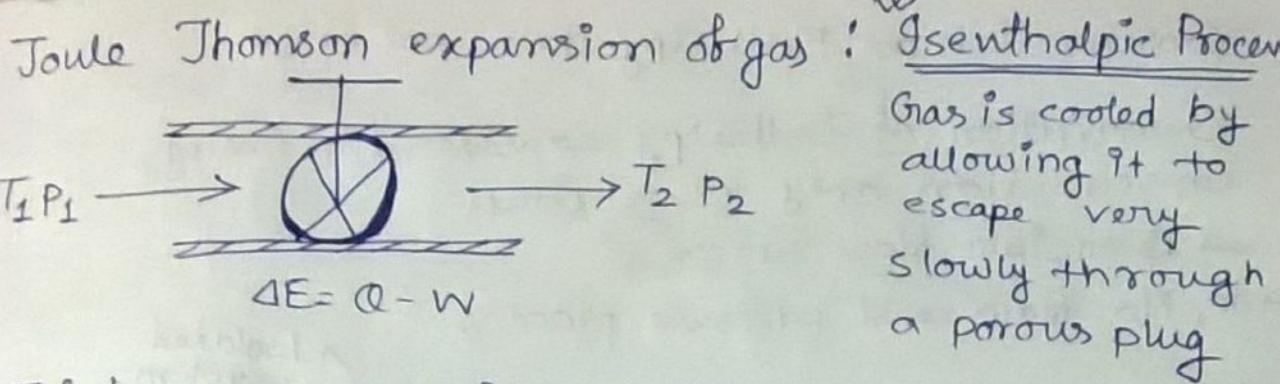


$$* \sum v_i^{\circ} A_i = 0$$

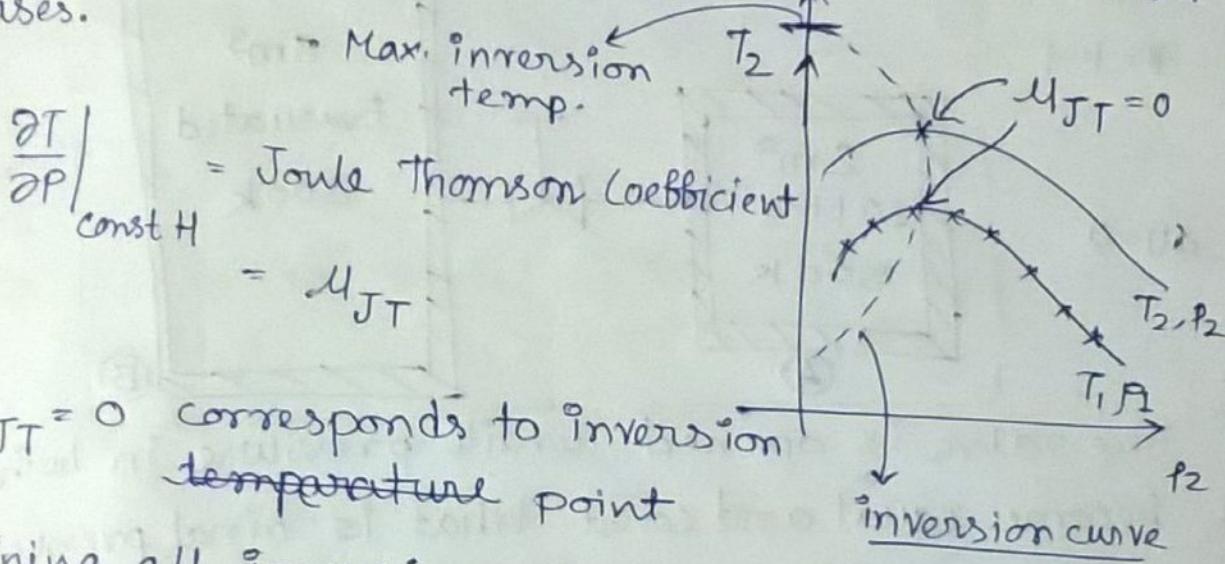
$v_i$  is +ve for product

$v_i$  is -ve in reactant

$$\Delta H_f^\circ = \Delta H^\circ_{298.15 K} + \int_{298.15}^T C_p^\circ dT$$



This happens only for real gas but not for ideal gases.



Joining all inversion points gives inversion curve and cuts the temp. axis at maximum inversion temperature ( $T_{\max \text{ inversion}}$ )

Condition for cooling

$$1) T_2 < T_{\max \text{ inversion}}$$

$$2) \mu_{JT} < 0$$

$\mu_{JT} = \text{slope of isenthalp}$

Temp of downstream beyond the porous plug is  $T_2$

→ Cooling of  $H_2$  and  $He$ , and  $Neon$ , cooling is not possible  
\* by Joule Thomson effect

$(T_{\max \text{ inversion}})_{H_2} < \text{ambient temperature}$

$\Delta H = 0$  → Isenthalpic

Conservation of Enthalpy does not exist

Conservation of Enthalpy considered in Energy conservation only when either

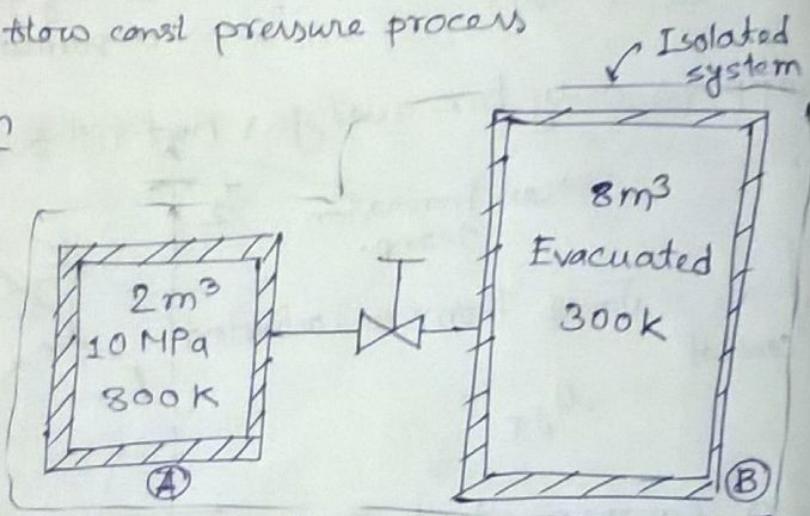
- Reversible flow process
- or, No flow const pressure process

Isolated system

### Problem

$$\gamma = 1.4$$

$$\Delta U = 0$$



The valve is opened until pressure in both become equal and const. What is final pressure and temperature both the tanks

Assumption: Air in tank A undergoes reversible adiabatic expansion

Ex.: Prove the assumption

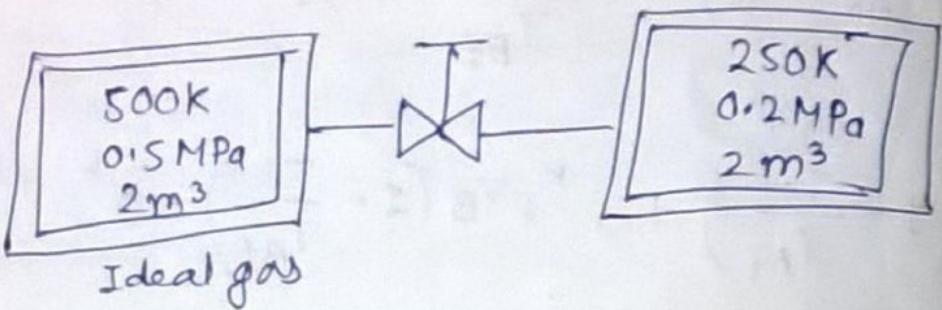
$$N_{A_i} = N_{A_f} + N_{B_f}$$

$$\Delta U = N_{A_f} c_v (T_{A_f} - T_0) + N_{B_f} c_v (T_{B_f} - T_0)$$

$$N_{A_i} = \frac{P_i V_A}{R T_0} = \frac{P_f V_A}{R T_{A_f}} + \frac{P_f V_B}{R T_{B_f}} \quad \text{--- (1)}$$

$$\Delta U = c_v \frac{P_f V_A}{R T_{A_f}} (T_{A_f} - T_0) + c_v \frac{P_f V_B}{R T_{B_f}} (T_{B_f} - T_0) = 0$$

Q.2



Same question as previous

In any polytropic process of  $\nu$  predefined path the specific heat is constant i.e state function.

$$dW = F \, dr$$

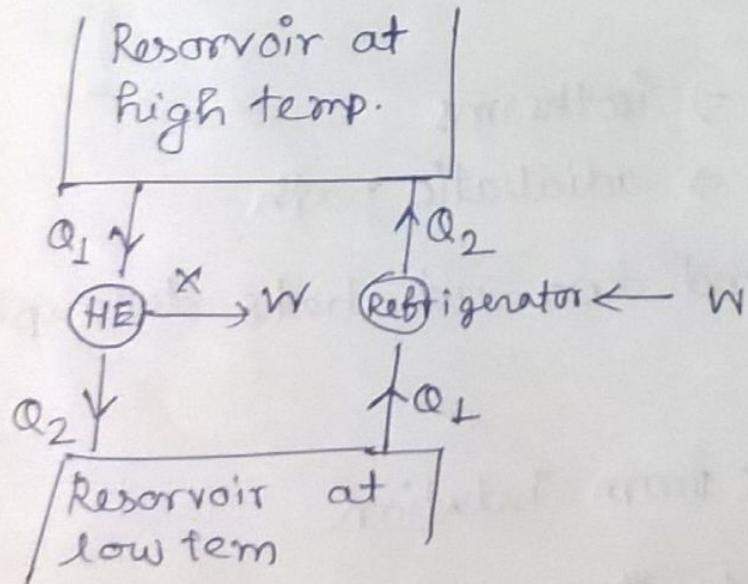
For changing and discharging of a tank

$$\frac{dE}{dt} = m_i h_i + \dot{q} - m_e h_e$$

$$\text{at steady state } \frac{dE}{dt} = 0, \dot{m}_i = m_e$$

$$\Delta H = Q$$

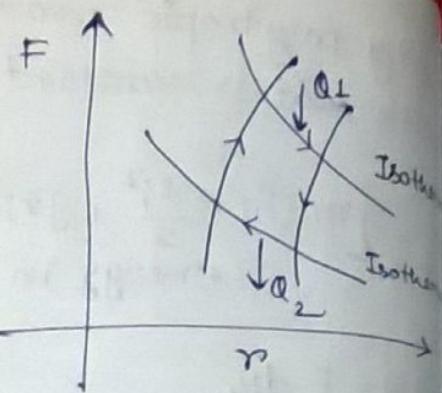
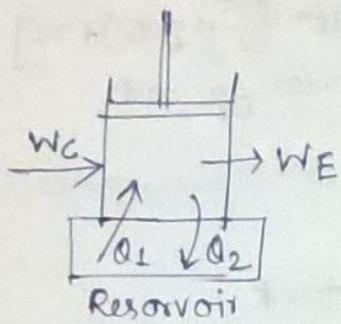
$$\Delta H = m(\dot{h}_e - \dot{h}_i)$$



2<sup>nd</sup> Law: Kelvin statement

# Difference between heat pumps and refrigerators

## Carnot cycle



$$Q_1 - Q_2 = W_E - W_c$$

$$\eta = \frac{\text{Energy effect sought}}{\text{Energy expended}} = \frac{W}{Q_1} \neq 1$$

# highest  $\eta$  is obtained in a reversible process.

# Any particular cycle can not be adiabatic throughout

# For heat interactions to happen there should be an isothermal step in a cycle.

$\Rightarrow$  Heat interaction  $\Rightarrow$  isotherms

Work interaction  $\Rightarrow$  adiabatic path

Two isotherms and two adiabats decouple the heat and work.

# All these laws are from intuition

Postulates of Carnot  $\checkmark$  (Forms basis of Therm)

Theorem 1 : Efficiency of all reversible

$n_{rev} > n_{irrev.}$   $\checkmark$  Prove it

The 2 :  $[n_{rev1} = n_{rev2}] = \text{const}$   $\checkmark$  Prove it

Engines operating between same low and high temp sink and source have same efficiency.

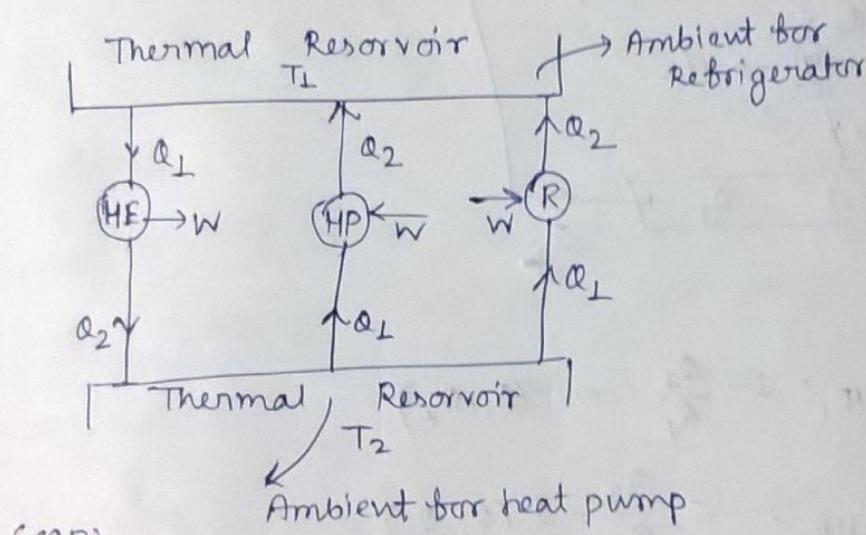
Theorem 3: For ideal gases, on which process is to be performed

$$\eta = 1 - \frac{T_2}{T_1} \quad \boxed{\text{Prove it}}$$

Claussius inequality gives entropy-concept.

19/01/17

Proof Claussius statement & Kelvin Planck statement of 2nd Law of thermodynamics



(COP)

$$\eta_{HE} = 1 - \frac{Q_2}{Q_L} = \frac{W}{Q_L}$$

$$(\text{COP})_{HP} = \frac{Q_L}{W}$$

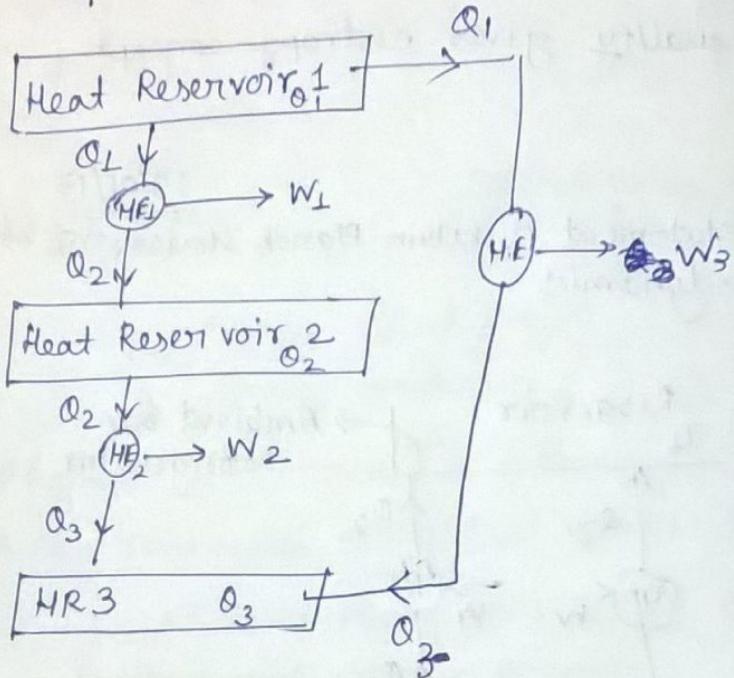
$$(\text{COP})_R = \frac{\text{Energy effect sought}}{\text{Energy expended}}$$

Effectiveness =  $\eta = 1 - \frac{T_2}{T_1}$  for ideal gas scale.

Ax

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

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



$$\eta_{HE_1} = 1 - \frac{Q_2}{Q_1} = f(Q_1, Q_2)$$

$$\eta_{HE_2} = 1 - \frac{Q_3}{Q_2} = f(Q_2, Q_3)$$

$$\eta_{HE_3} = f(Q_1, Q_3)$$

$$\frac{Q_2}{Q_1} = f(Q_2, Q_3)$$

$$\frac{Q_2}{Q_3} = f(Q_2, Q_3)$$

$$\frac{Q_3}{Q_1} = f(Q_1, Q_3)$$

$$\frac{\alpha_1}{\alpha_2} \cdot \frac{\alpha_2}{\alpha_3} = F(\theta_1, \theta_2) F(\theta_2, \theta_3)$$

~~$$\cancel{\frac{\alpha_1}{\alpha_2}} \frac{\alpha_L}{\alpha_3} = F(\theta_1, \theta_3)$$~~

$$F(\theta_1, \theta_2) = \phi(\theta_1) \psi(\theta_2)$$

$$F(\theta_1, \theta_2) = \frac{F(\theta_2, \theta_3)}{\phi(\theta_1) \psi(\theta_2), \phi(\theta_2) \psi(\theta_3), \phi(\theta_1) \psi(\theta_3)}$$

$$\phi(\theta_2) = \frac{1}{\psi(\theta_1)}$$

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

$$\phi(\theta) = \theta$$

$$\boxed{\frac{\alpha_1}{\alpha_2} = \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}}$$

Triple point of water = 273.16 K

# Does not depend on the medium  $\checkmark$   $\eta = 1 - \frac{T_c}{T_H}$

# only uses heat to designate temp.

$$(\alpha_1 - \alpha_2) = (\alpha_2 - \alpha_3) = (\alpha_3 - \alpha_4) = \dots$$

$$\alpha_1 \left(1 - \frac{\alpha_2}{\alpha_1}\right) = \alpha_2 \left(1 - \frac{\alpha_3}{\alpha_2}\right) = \alpha_3 \left(1 - \frac{\alpha_4}{\alpha_3}\right)$$

$$\alpha_1 \left(1 - \frac{T_2}{T_1}\right) = \alpha_2 \left(1 - \frac{T_3}{T_2}\right) = \alpha_3 \left(1 - \frac{T_4}{T_3}\right)$$

$$\frac{\alpha_1}{T_1} (T_1 - T_2) = \frac{\alpha_2}{T_2} (T_2 - T_3) = \frac{\alpha_3}{T_3} (T_3 - T_4)$$

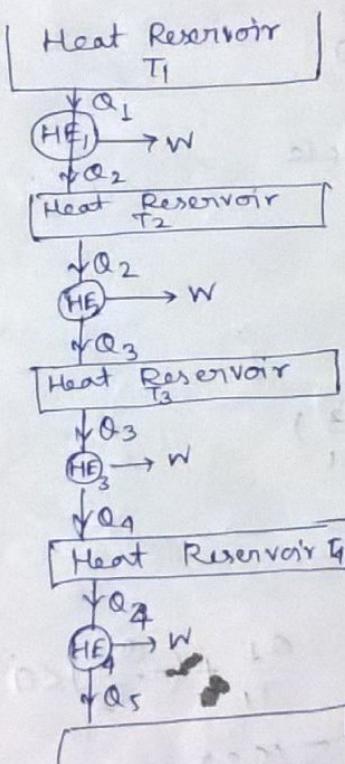
# What is the lowest temp achievable by series of H.E series?

20/01/17

$$\text{1) } \frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}$$

at triple point of water  $T_{tr} = 273.16\text{ K}$

$\theta = T$   
 $\Rightarrow$  These two scales become identical. Thus ~~idea~~  
 absolute temp. is defined by thermodynamic  
 driving force heat, irrespective of working  
 substance.



all the heat engines perform same work

$$Q_1 - Q_2 = Q_2 - Q_3 = Q_3 - Q_4$$

$$\frac{Q_1}{T_1} (T_1 - T_2) = \frac{Q_2}{T_2} (T_2 - T_3) = \frac{Q_3}{T_3} (T_3 - T_4)$$

Lowest temp. conceived by the absolute temp.  
 can only be calculated but can never be attained  
 because of the fact that

to attain such low temp.

$$Q_L = \sum_{i=1}^n w_i$$

But this violates Kelvin Planck statement  
In practical

$Q_L - Q_{n-1}$  = total heat that can be converted to work.

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

For a carnot cycle

$$\sum \frac{Q_i}{T_i} = 0$$

$$n_{irr} < n_R$$

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

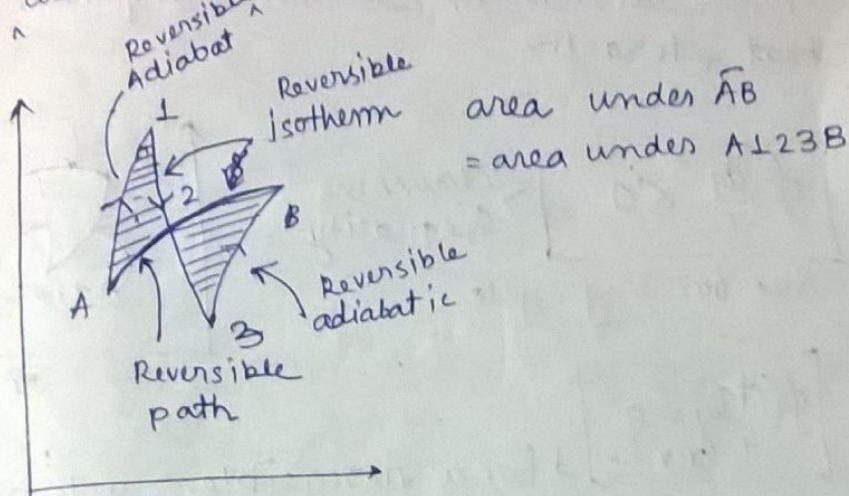
$$-\frac{Q_2}{Q_1} < \frac{T_2}{T_1}$$

$$\frac{Q_2}{T_2} > \frac{Q_1}{T_1} \quad \frac{Q_L}{T_1} + \left(-\frac{Q_2}{T_2}\right) < 0$$

$$\sum \left(\frac{Q_i}{T}\right)_{irreversible} < 0$$

$$\boxed{\sum \left(\frac{Q_i}{T}\right)_{cannot \ cycle} \leq 0}$$

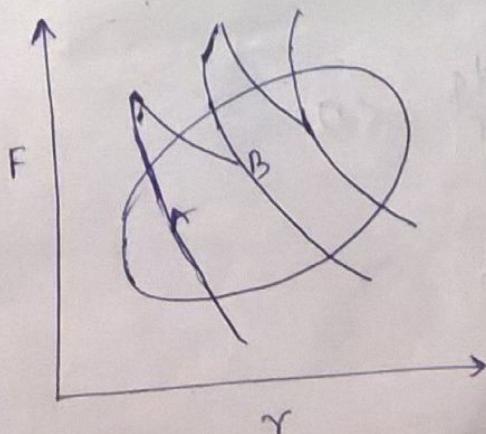
Any reversible process can be expressed as an reversible adiabat, an reversible isotherm and another reversible adiabat



$$\int_{A13B} dW = \int_{AB} dW$$

$$\int_{AB} dU = \int_{A13B} dU$$

$$\int_{A13BA} dQ = \int_{A1}^0 dQ + \int_{13}^0 dQ + \int_{3B}^0 dQ + \int_{BA}^0 dQ - \int_{13}^0 dQ - \int_{BA}^0 dQ$$

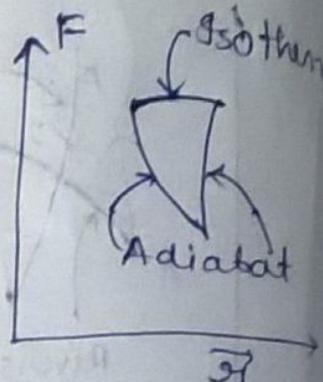


A cyclic reversible process can also be expressed in such a way consisting numerous adiabats joined by numerous isotherms.

# Such two adiabats never intersect each other because no heat interaction is possible on an adiabat. An isotherm is required for heat interaction

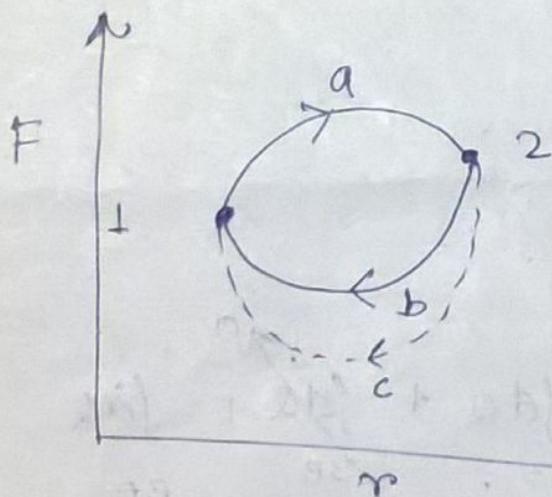
$$\oint \frac{dq}{T} < 0 \Rightarrow \text{ Clausius Inequality}$$

True for any cycle



$$\oint \frac{dq}{T}_{\text{rev}} = 0$$

for a reversible cycle only  
q behaves as state function



$$\oint \frac{dq}{T} = \int_{1a2b1} \frac{dq}{T} + \int_{2b2} \frac{dq}{T} = 0$$

$$\int_{1a2} \frac{dq}{T}_{\text{rev}} - \int_{2b1} \frac{dq}{T} = \int_{1b2} \frac{dq}{T} = \int_1^2 ds = S_2 - S_1 = 45^\circ$$

$$\oint \frac{dq}{T} = \int_{1a2c1} \frac{dq}{T} + \int_{2c1} \frac{dq}{T} < 0$$

$$-\int_{2a1} \frac{dq}{T}_{\text{rev}} + \int_{2c1} \frac{dq}{T}_{\text{irrev.}} < 0$$

each  
possible  
for the

therm

at  
→

only  
ton

$$-\int_2^1 ds + \left(\frac{dq}{T}\right)_{irrev} < 0$$

$$(S_2 - S_1) = \Delta S > \left(\frac{dq}{T}\right)_{irrev}$$

$$\begin{array}{|c|} \hline ds \\ \hline \end{array} \rightarrow \boxed{\begin{array}{l} ds = \left(\frac{dq}{T}\right)_{rev} \\ ds > \left(\frac{dq}{T}\right)_{irrev} \end{array}} \quad \checkmark$$

$$(ds)_\text{isolated}^0$$

Process is reversible. Proceed in both directions

$$(ds)_\text{isolated}^>$$

Spontaneous in forward direction

$$(ds)_\text{isolated}^<$$

process not feasible in forward direction, process  
spontaneous in backward direction.

$$+\int_{2bL}^1 \frac{dq}{T}$$

$$\begin{array}{|c|} \hline ds \\ \hline \end{array} \boxed{ds = \frac{dq}{T} + \underbrace{dS_{irr}}_{\text{Entropy gen. due to irrev. process}}}$$

Adiabatic process:  $\delta Q = 0$

$ds = 0$  for reversible adiabatic process

$ds > 0$  irreversible

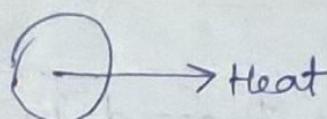
$ds = dS_{irr}$

All reversible adiabatic process is isentropic  
All isentropic processes are rev. and adiabatic  
(not a corollary)

For  $dS=0$

$$-\left(\frac{dq}{T}\right)_{\text{irr}} = +dS_{\text{ex}}$$

An isentropic can neither be reversible nor adiabatic. Entropy generated is equal to heat loss then the process is isentropic.



Heat flows out of the system always in an isentropic process.

Isolated system :  $dW=0$ ,  $dq=0$

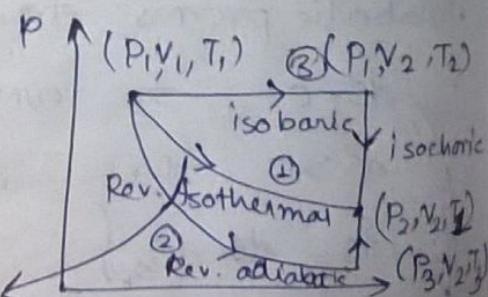
$$(ds)_{\text{isolated}} \geq \left(\frac{dq}{T}\right)_{\text{isolated}} = 0$$

$$(ds)_{\text{isolated}} \geq 0$$

Entropy of the universe is always gradually increasing.

??

Ideal gas / 1 mole



$\Delta S_{\text{rev}} \text{ for } 1, 2, 3$

3  
Pg Dn  
Enter  
Del

1)  $V_1, T, P_1 \rightarrow (V_1 + V_2), T, P$   
Reversible isothermal path

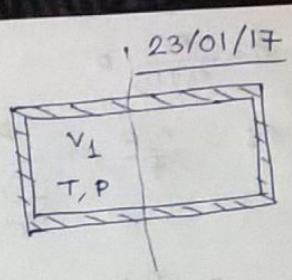
$$dS = \frac{dq_{rev}}{T}$$

$$TdS = dq_{rev} = dU + PdV$$

# Isothermal processes of ideal gases are only of constant energy process.

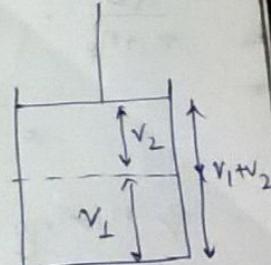
$$ds = \frac{nR}{T} \ln \frac{V_1 + V_2}{V_1} > 0$$

⇒ The process is spontaneous



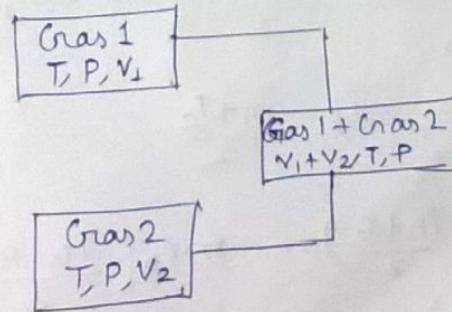
$$2) ds = \frac{nR}{T} \ln \left( \frac{V_1 + V_2}{V_1} \right)$$

$$Q_{\text{sum}} = - nR \ln \left( \frac{V_1 + V_2}{V_1} \right)$$



Rev. isothermal

3)



Gas 1:  $P \rightarrow P_1$

Gas 2:  $P \rightarrow P_2$

$$\begin{aligned} Q &= \underset{\text{rev}}{n_1 R \ln \frac{P}{P_1}} + \underset{2}{n R \ln \frac{P}{P_2}} \\ &= \underset{1}{-n R \ln \frac{P^2}{P_1 P_2}} \end{aligned}$$

$$S = \frac{nR}{T} \ln \frac{n_1 R}{P} \ln \frac{P}{P_1} + \frac{n_2 R}{P} \ln \frac{P}{P_2}$$

$$P_1 = \frac{n_1}{n_1+n_2} P \quad P_2 = \frac{n_2}{n_1+n_2} P$$

$$\Delta S = \frac{n_1 R}{P} \ln \frac{P}{\frac{n_1}{n_1+n_2} P} + \frac{n_2 R}{P} \ln \frac{P}{\frac{n_2}{n_1+n_2} P}$$

$$= \frac{n_1 R}{P} \ln \frac{n_1+n_2}{n_1} + \frac{n_2 R}{P} \ln \frac{n_1+n_2}{n_2}$$

$$= \frac{n_1 R}{P} \ln x_1 + - \frac{n_2 R}{P} \ln x_2$$

$$= -R(x_1 \ln x_1 + x_2 \ln x_2)$$

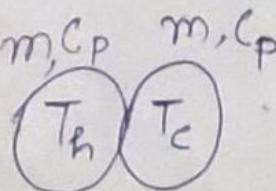
~~$$\frac{\Delta S}{n_1+n_2} = \frac{1}{P} \frac{x_1 R}{x_1} \ln x_1 + \frac{1}{P} \frac{x_2 R}{x_2} \ln x_2$$~~

$$\frac{\Delta S}{n_1+n_2} = -R \sum_{i=1}^N x_i \ln x_i \quad x_i < 0 \\ \ln x_i < 0$$

$$= +ve$$

$\Rightarrow$  Mixing of ideal gases is spontaneous

4) Transfer of heat from hot to cold body.



$$T_f = \frac{T_h + T_c}{2}$$

$$Q_h = -mC_p \left( T_h - \frac{T_h + T_c}{2} \right) = -mC_p \left( \frac{T_h - T_c}{2} \right)$$

$$Q_c = mC_p \left( \frac{T_h - T_c}{2} \right)$$

$$\int_1^2 dS_h = \int_{T_h}^{T_f} \frac{mC_p dT}{T}$$

$$\int_1^2 dS_C = \int_{T_{\text{h}}/T_{\text{c}}}^{T_f/T_{\text{c}}} \frac{mc_p dT}{T}$$

$$\Delta S'_h = +mc_p \ln(T_f/T_h)$$

$$\Delta S_C = +mc_p \ln(T_f/T_c)$$

$$\begin{aligned} \Delta S &= -mc_p \ln \left( \frac{T_h}{T_c} \right) \quad m c_p \ln \left( \frac{T_f/T_c}{T_f/T_h} \right) \\ &= -mc_p \ln \left( \frac{T_h}{T_c} \right) \quad = mc_p \ln \left( \frac{T_f^2}{T_h T_c} \right) \\ &= mc_p \ln \left( \frac{T_c}{T_h} \right) \end{aligned}$$

$$= mc_p \ln \left( \frac{(T_h+T_c)^2}{4T_h T_c} \right)$$

$$T_h > T_c$$

$$T_h - T_c > 0$$

$$(T_h - T_c)^2 > 0$$

$$T_h^2 + T_c^2 - 2T_h T_c > 0$$

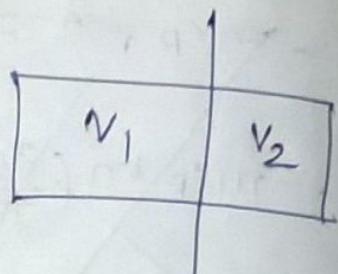
$$(T_h + T_c)^2 > 4T_h T_c \Rightarrow \ln \left( \frac{(T_h + T_c)^2}{4T_h T_c} \right) > 0$$

$$\Rightarrow \Delta S > 0$$

# Thermodynamic probability of a state is determined by entropy.

$$\frac{\text{no. of macro states}}{\text{Total no. of } \overset{\text{possible}}{\text{micro states}}} = \text{Thermodynamic probability}$$

probability of a molecule to stay in volume  $V_1$



$$= \frac{V_1}{V_1 + V_2}$$

Probability of  $N$  molecule to remain in  $V_1$  vol

$$= \left( \frac{V_1}{V_1 + V_2} \right)^N$$

$S \propto W$

$S \propto \ln W$

$$S = K \ln W$$



Boltzmann Const.

Find out the minimum work to separate  $1 \text{ kg}_{\text{mol}}$  of air (ideal) into  $\text{N}_2, \text{O}_2$  at  $0.1 \text{ MPa}$ .

$$[-1281.91 \frac{\text{kJ}}{\text{mol}}]$$

There is a limit to available energy

$$Q = A \cdot E + U \cdot E$$

$$U \cdot E = Q_2 = Q_1 \frac{T_2}{T_1}$$

$$U \cdot E |_{\min} = Q_1 \frac{T_{\text{ambient}}}{T_1}$$

$$A \cdot E |_{\max} = Q_1 \left( 1 - \frac{T_{\text{ambient}}}{T_1} \right)$$

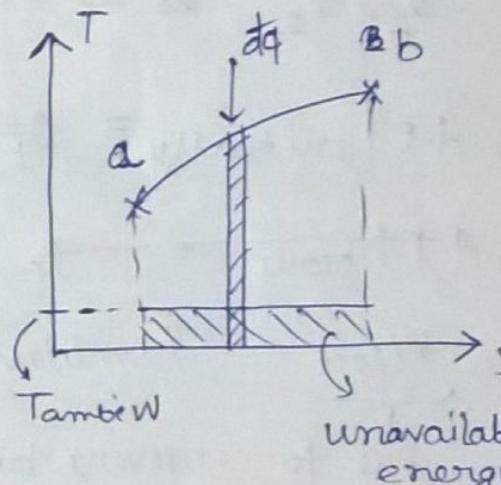
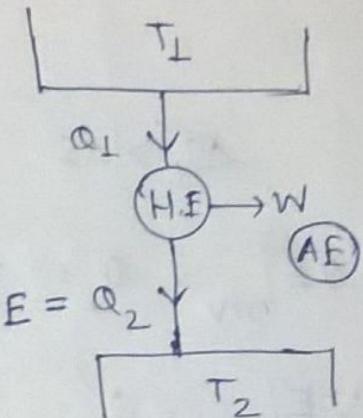
$$\delta W |_{\max} = \delta q_1 \left( 1 - \frac{T_{\text{ambient}}}{T_1} \right)$$

$$W_{\max} = \int_a^b \delta q_1 - \int_a^b \frac{\delta q \cdot T_{\text{ambient}}}{T_1}$$

$$W_{\max} = Q_1 - T_{\text{ambient}} \int_a^b dS$$

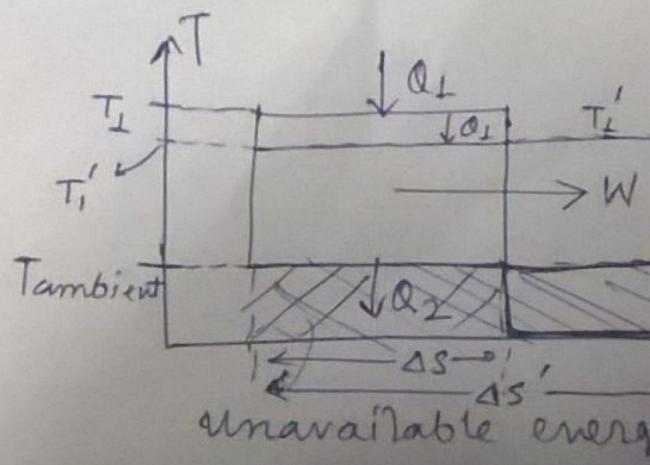
$$= Q_1 - \underbrace{T_{\text{ambient}} (S_b - S_a)}$$

Unavailable energy (U.E)



For a Carnot cycle

$$U.E = T_{\text{ambient}} (\Delta S)$$



Heat interaction occurs across isotherm, and  
work interaction occurs adiabats.

$$Q_1 \Big|_{\text{heat given by source}} = T_1 \Delta S = Q_1 \Big|_{\text{Heat taken by the heat engine.}}$$
$$= T_1' \Delta S'_1$$

$$\Delta S'_1 > \Delta S$$

$$U.E \Big|_{\text{rev}} = Q_2 = T_{\text{amb.}} \Delta S$$

$$U.E \Big|_{\text{now}} = Q'_2 = T_{\text{amb.}} \Delta S'$$

$$Q'_2 > Q_2 \quad \text{as } \Delta S' > \Delta S$$

$$A.E \Big|_{\text{initially}} = \cancel{Q} \Big|_{\pm} (T_1 - T_{\text{ambient}}) \Delta S$$

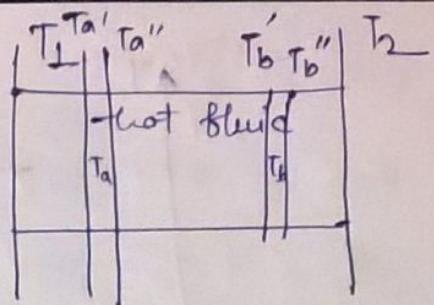
$$A.E \Big|_{\text{now}} = T_f$$

$$W_{\text{lost}} = \underbrace{T_{\text{ambient}}}_{\text{Due to irreversibility of process}} (\Delta S' - \Delta S)$$

Q Taking both input & output <sup>of</sup> heat to be irreversible, find the W<sub>lost</sub>.

$$Q = mc_p(T_a' - T_a'')$$

$$= T_a \Delta S_a ; \quad T_a = \frac{T_a' + T_a''}{2}$$



$$Q = m c_p(T_b' - T_b'')$$

$$= T_b \Delta S_b ; \quad T_b = \frac{T_b' + T_b''}{2}$$

$$A \cdot E_{lost/a} = (Q - T_{ambient} \Delta S_a) \quad \Delta S_b > \Delta S_a$$

$$A \cdot E_{lost/b} = (Q - T_{ambient} \Delta S_b)$$

$$A \cdot E_{lost/a} - A \cdot E_{lost/b}$$

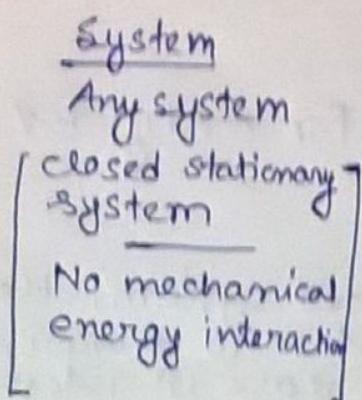
$$= T_{ambient} (\Delta S_b - \Delta S_a)$$

Lossing heat at higher temp give much less in available energy. Thus entropy gives an idea regarding quality of the energy. In Joule Thomson effect, quality of energy is lost by throttling.

25/01/17

$$\delta q = dE + \delta W$$

$$\delta q = dU + \delta W$$



process  
any process

$$\delta q = TdS$$

Any system

Reversible process

$$TdS = dU + pdV$$

only PV work

$$TdS = dH - Vdp$$

→ In case of irreversible processes, the deviation of  $TdS$  from  $\delta q$  and of  $pdV$  from  $\delta W$  are same and hence  $TdS = dU + pdV$  is applicable for any type of process.

### Entropy

- Gives the amount of unavailable energy
- Measure of the quality of work. Same amount of heat at high temp. as compared to that of lower temp.
- Decides feasibility of a process.
- Thermodynamic probability of state of a system.

$S = k \ln W$

$$dS \geq \frac{dT}{T}$$

$$TdS \geq dU + PdV \quad (\text{For only P-V work})$$

$$dU \leq TdS - pdV$$

$$\begin{cases} (dU)_{S,V} \leq 0 \\ (dS)_{S,V} \geq 0 \end{cases}$$

Closed system. Heat should escape from system to surrounding leading to decrease in internal energy of the system.

Isolated system

$$(dS)_{\text{isolated}} \geq 0$$

$$d(U+PV) \leq 0$$

P.S

$$dH \leq TdS + Vdp$$

$$\boxed{(dH)_{S,P} \leq 0}$$

- Heat has to blow out of system to surrounding in order to maintain const. enthalpy, i.e. the system process is isenthalpic.

4 types of interactions between system and surroundings

$$\rightarrow V,S \quad \text{const.}, \quad (dU)_{S,V} \leq 0 \quad \leftarrow$$

$$\rightarrow P,S \quad \text{const.}, \quad (dH)_{P,S} \leq 0 \quad \leftarrow$$

$$\rightarrow T,V \quad \text{const.}, \quad (dA)_{T,V} \leq 0 \quad \leftarrow$$

$$\rightarrow \underset{\text{W}}{\circlearrowleft} T,P \quad \text{const.}, \quad (dG)_{T,P}^{IV} \leq 0 \quad \leftarrow \quad f_{mp}$$

$$TdS \geq dU + pdV$$

$$d(TS) - SdT \geq dU + pdV$$

$$d(U-TS) \leq -SdT - pdV$$

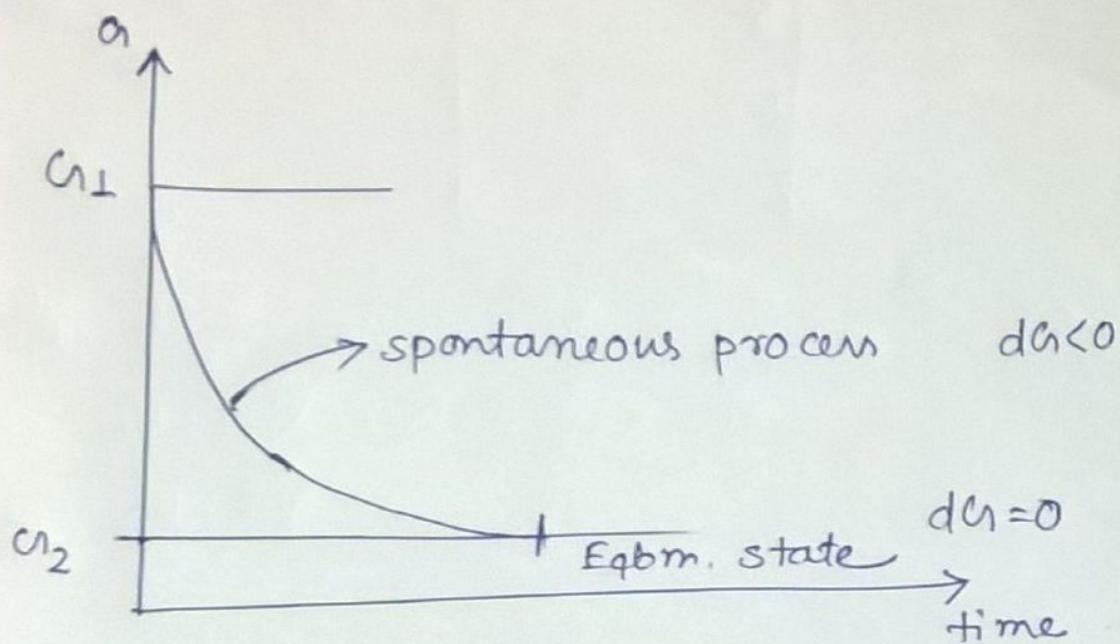
$$\underbrace{d(U-TS)}_{A,T,V} \leq 0$$

$A \rightarrow$  Helmholtz free Energy

$$TdS \geq dU + PdV$$

$$G = H - TS$$

~~$$TdS \geq d(U + PV) - VdP$$~~



If non PV work is also to be included

$$TdS \geq dU + PdV + dW_{\text{non-PV}}$$

$$d(TS) - sdT \geq dU + PdV + dW_{\text{non-PV}}$$

$$d(G - TS) \leq -sdt - PdV + dW_{\text{non-PV}}$$

$$\boxed{(dU)_{S,V} \leq dW_{\text{non-PV}}}$$

$$(dH)_{P,S} \leq dW_{\text{non-PV}}$$

$$(dT)_{T,V} \leq dW_{\text{non-PV}}$$

$$(dU)_{T,P} \leq dW_{\text{non-PV}}$$

27/01/17

$$(dA)_{T,V} < 0$$

↓

Isolated Isothermal

Non spontaneous

+ve H

Spontaneous

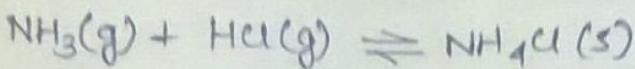
-ve H

$$(dG)_{T,P} < 0$$

-ve S

+ve S

Sobaru's isothermal



$$\Delta H_R |$$

$$1 \text{ bar pressure, } 298.15 \text{ K} = -176.2 \text{ kJ}$$

$$\Delta S_R | \text{ 1 bar pressure } 298.15 \text{ K} = -0.285 \text{ kJ/K}$$

$$\Delta G_R = \frac{\Delta H}{R} - T \Delta S = -176.2 + 0.285 \times 298.15 = -81.27 \text{ kJ}$$



$$\left. \begin{array}{l} \Delta h_{\text{vap}} = 40.64 \text{ kJ/mole} \\ \Delta S_{\text{vap}} = 108.9 \text{ J/Kmole} \end{array} \right\} \text{ at 1 atm } 100^\circ\text{C}$$

$$\Delta G_R |_{100^\circ} = [40.64 - 373 \times 108.9] = 0.0203 \text{ kJ/mole}$$

$$\Delta G_R |_{110^\circ} = [40.64 \times 10^3 - 363 \times 108.9] = -1068.7 \text{ J/mole}$$

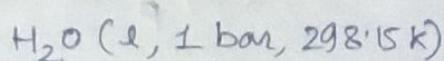
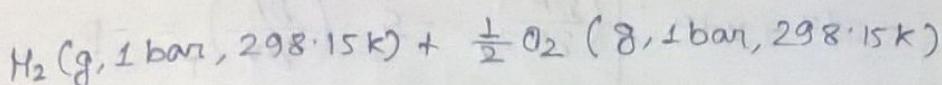
$$\begin{aligned} \Delta G_R |_{90^\circ} &= [40.64 \times 10^3 - 363 \times 108.9] \\ &= 1109.3 \text{ J/mole} \end{aligned}$$

$$(d\alpha)_{T,P} = -dW \text{ non-pv, reversible}$$

$$(dA)_{T,V} = -dW \text{ non-pv, reversible}$$

$$(dH)_{S,P} = -dW \text{ non-pv}$$

$$(dU)_{S,V} = -dW \text{ non-pv}$$



$$\Delta G_{f, H_2O}^{298.15 \text{ K}, 1 \text{ bar}} = -237.1 \text{ kJ/mole}$$

= amount of non-pv  
useful work available in  
the process under those  
conditions.

$$G = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$= (\cancel{\partial U_{rev}} - \cancel{\partial W_{rev}}) + PdV + VdP - TdS - SdT$$

$$= \cancel{VdP} (VdP - SdT) - (\cancel{\partial W_{rev}} - \cancel{PdV})$$

$$dG = (VdP - SdT) - (\cancel{\partial W_{rev}} - \cancel{PdV})$$

Thermodynamic potential gives the useful work available when a system goes from a state to another. These are  $U, H, A, G$ .

→ Decides spontaneity of process under certain conditions

→ Give a measure of the useful work obtained/ to be given to the process

→ Extensive property

→ Thermodynamic potentials and Gibbs' eqns

$$dU = TdS - pdV$$

$$dH = TdS + pdV$$

$$dA = -sdT - pdV$$

$$dG = -sdT + pdV$$

$$\left| \begin{array}{ll} \left(\frac{\partial U}{\partial S}\right)_V = T & \left(\frac{\partial U}{\partial V}\right)_S = -p \\ \left(\frac{\partial H}{\partial S}\right)_P = T & \left(\frac{\partial H}{\partial P}\right)_T = V \\ \left(\frac{\partial A}{\partial T}\right)_V = -S & \left(\frac{\partial A}{\partial V}\right)_T = -p \\ \left(\frac{\partial G}{\partial T}\right)_P = -S & \left(\frac{\partial G}{\partial P}\right)_T = V \end{array} \right.$$

Maxwell's Eqn

$$\cancel{\left(\frac{\partial A}{\partial T}\right)_V} + \cancel{\left(\frac{\partial G}{\partial T}\right)_P} =$$

$$\cancel{\left(\frac{\partial U}{\partial S}\right)_V} = \cancel{\left(\frac{\partial H}{\partial S}\right)_P}$$

$$P = P(x, y)$$

$$dP = Mdx + Ndy$$

$$\left(\frac{\partial H}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$dP =$$

$$\text{Maxwell's Eqn}$$

$$\left(\frac{\partial I}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial U}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$s(P_1, V_1) - s(P_1, V_2) = \left(\frac{\partial S}{\partial V}\right)_P dV = \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$s(P_1, V_1) - s(P_2, V_2) = \cancel{\left(\frac{\partial S}{\partial V}\right)_P dV} + \left(\frac{\partial S}{\partial P}\right)_V dP$$

$$s(P_1, T_2) - s(P_1, T_1) = \left(\frac{\partial S}{\partial T}\right)_P dT$$

$$s(V_1, T_2) - s(V_1, T_1) = \left(\frac{\partial S}{\partial T}\right)_V dT$$

$$s(P_1, T_2) - s(P_1, T_1) = \left(\frac{\partial S}{\partial T}\right)_P dT$$

$$s(P_1, V_2) - s(P_1, V_1) = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$s(P_1, V_1) - s(P_2, V_1) = \int_{P_1}^{P_2} \left(\frac{\partial U}{\partial T}\right)_S dP$$

$$s(P_1, T_2) - s(P_1, T_1) = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_P dT = \int_{T_1}^{T_2} \frac{\left(\frac{\partial h}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial h}\right)_P} dT$$

$$= \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$s(v_1, T_1) - s(v_2, T_2) = \int_{T_1}^{T_2} \left( \frac{\partial S}{\partial T} \right)_v dT = \int_{T_1}^{T_2} \frac{\left( \frac{\partial u}{\partial T} \right)_v}{\left( \frac{\partial u}{\partial S} \right)_v} dT = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

$$s(T, v) \quad ds = \left( \frac{\partial S}{\partial T} \right)_v dT + \left( \frac{\partial S}{\partial v} \right)_T dv$$

$$s(T, P) \quad \boxed{ds = \frac{C_v}{T} dT + \left( \frac{\partial P}{\partial T} \right)_v dv}$$

$$\boxed{Tds = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv}$$

$$ds = \left( \frac{\partial S}{\partial T} \right)_P dP + \left( \frac{\partial S}{\partial P} \right)_T dT$$

$$\boxed{ds = \frac{C_P}{T} dT + \left( \frac{\partial v}{\partial T} \right) dP}$$

$$Tds = C_P dT + T \left( \frac{\partial v}{\partial T} \right) dP$$

$$\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P \quad \kappa = - \frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T$$

$$\left( \frac{\partial P}{\partial T} \right)_v = - \left( \frac{\partial T}{\partial v} \right)_P \cdot \left( \frac{\partial v}{\partial P} \right)_T = -1$$

$$\left( \frac{\partial P}{\partial T} \right)_v = - \left( \frac{\partial v}{\partial P} \right)_T \cdot \left( \frac{\partial P}{\partial v} \right)_T = - \beta / v \cdot \kappa$$

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

$$\boxed{Tds = C_v dT + T \left( -\frac{\beta}{v} \right) dv \cdot \kappa}$$

$$\boxed{Tds = C_P dT - T v \beta dP}$$

$$dU = TdS - \cancel{pdV} p dV$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$dU = T \left( \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \right) dT - \cancel{pdV} p dV$$

$$= C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV - \cancel{pdV} p dV$$

$$= C_V dT + T \left(-\frac{\beta k}{v}\right) dV - \cancel{pdV} p dV$$

$$\cancel{PV=RT} = C_V dT + -dV \left[ \frac{-\beta k T}{v} + p \right]$$

$$\boxed{dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dT}$$

for ideal gas  $PV=RT$

$$\boxed{dU = C_V dT + \left\{ T \left(\frac{\partial P}{\partial T}\right)_V - P \right\} dV}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\frac{\partial U}{\partial P}$$

$$\frac{dP}{dT} = \frac{R}{V}$$

$$\begin{aligned} PV &= RT \\ P &= \frac{RT}{V} \end{aligned}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 + \left\{ T \cdot \frac{R}{V} - P \right\} dV$$

$$= 0 + \{ P - P \} = 0$$

30/01/17

$$\cancel{dU = C_V dT + T \left( \frac{\partial P}{\partial V} \right)}$$

$$dH = C_p dT + [V - T \left( \frac{\partial V}{\partial T} \right)_P] dP = C_p dT + V(1 - \beta_T) dP$$

$$dS = \frac{C_p}{T} dT - T \left( \frac{\partial V}{\partial T} \right)_P dP = C_p dT - \beta V dP$$

$$dU = C_V dT + \left[ T \left( \frac{\partial P}{\partial V} \right)_V - P \right] dV = C_V dT - \left( \frac{\beta_T}{k} + P \right) dV$$

Calculation of  $\Delta H$  for the given P-T diagram following 2 different paths

$$\textcircled{1} \int dH$$

$$= \int \left( \frac{\partial h}{\partial T} \right)_{P=P_1} dT + \int \left( \frac{\partial h}{\partial P} \right)_{T=T_2} dP$$

$$= \int_{T_1}^{T_2} C_P \Big|_{P=P_1} dT + \int_{P_1}^{P_2} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dT$$

$$\textcircled{2}$$

$$\int dH = \int \left( \frac{\partial h}{\partial P} \right)_{T=T_1} dP + \int \left( \frac{\partial h}{\partial T} \right)_{P=P_2} dT \quad [P=0, C_P]$$

$$= \int_{P_1}^{P_2} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP + \int_{T_1}^{T_2} C_P \Big|_{P=P_2} dP$$

# two types of eqn to consider gases that do not behave as ideal gases

# These are :

Cubic eqn of state: Van der Waals eqn

Virial eqn of state:  $\frac{PV}{RT} = 1 + \beta' P + \beta'' P^2 + \dots$

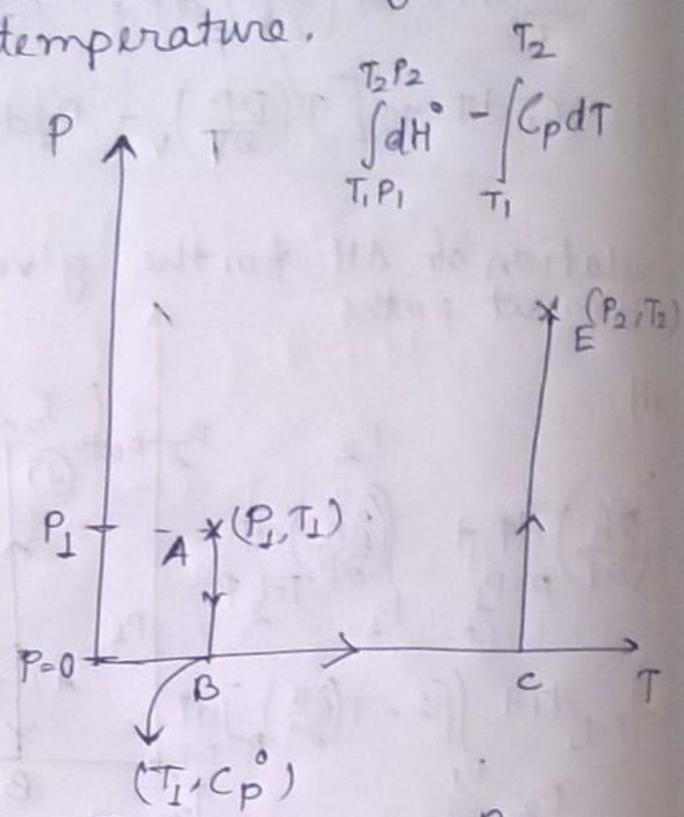
# Three roots of VDW eqn gives

volume of gaseous state, volume of saturated liquid, and a fictitious i.e. unrealistic volume.

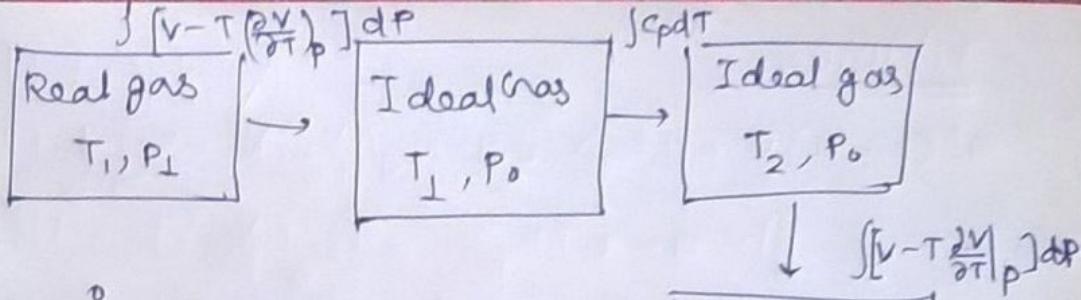
The path that should be considered for calculation of  $\Delta H$  is  $A \rightarrow B \rightarrow C \rightarrow E$

\* Any real gas behaves as an ideal gas at low pressure and high temperature.

$$\begin{aligned} & \int_{T_1, P_1}^{T_2, P_2} dH \\ & = \int_{P_1}^{P_2} \left( \frac{\partial H}{\partial P} \right)_{T=T_1} dP + \int_{T_1}^{T_2} \left( \frac{\partial H}{\partial T} \right)_{P=P_0} dT \\ & + \int_{P_0}^{P_2} \left( \frac{\partial H}{\partial P} \right)_{T=T_2} dP \end{aligned}$$



$$\begin{aligned} & = \int_{P_1}^{P_0} \left[ \nu - T \left( \frac{\partial \nu}{\partial T} \right)_P \right] dP + \int_{T_1}^{T_2} C_p^\circ \Big|_{P=P_0} dT + \int_{P_0}^{P_2} \left[ \nu - T \left( \frac{\partial \nu}{\partial T} \right)_P \right] dP \\ & \quad \underbrace{\qquad \qquad}_{\text{For ideal behavior}} \qquad \qquad \qquad \underbrace{\qquad \qquad}_{\text{Arises due to deviation from ideality}} \qquad \qquad \qquad \underbrace{\qquad \qquad}_{(\text{Residual property})} \end{aligned}$$



$\Delta h^* = h - \bar{h}^*$  = Departure function

= Residual property

correction terms giving deviation from ideal behavior

Very useful tool for binding non-measurable properties of real gases.

$H = H(T)$   
for ideal gases

# Residual amounts are very large for solids and ~~gas~~ liquids.

Find  $\Delta h^*$ ,  $\Delta s^*$  (Assignment)  
 $f^n(T, P)$

Write eqn in pressure explicit form & for a gas that obeys VanDer Wall's eqn.

$$du = Tds - pdv$$

$$dh = Tds + vdp$$

$$da = -sdt - pdv$$

$$dg = -sdt + vdp$$

All Determine the integral energy change associated with <sup>isothermal</sup> extension of liquid film. Also derive an equation relating change in  $T$  with change in surface area under adiabatic condition.

$$du = Tds - \sigma dA$$

$$dh = Tds + Ad\sigma$$

$$da = -sdt - \sigma dA$$

$$dg = -sdt + Ad\sigma$$

$\Gamma \rightarrow T$ . Dynamic driving force

$A \rightarrow T$ . Dynamic displacement

$$\left(\frac{\partial T}{\partial A}\right)_S = -\left(\frac{\partial \sigma}{\partial S}\right)_{\partial A}$$

$$\left(\frac{\partial T}{\partial \sigma}\right)_S = \left(\frac{\partial U}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial A}\right)_T = \left(\frac{\partial \sigma}{\partial T}\right)_{\partial A}$$

$$-\left(\frac{\partial S}{\partial \sigma}\right)_T = \left(\frac{\partial A}{\partial T}\right)_P$$

Need to find

$$\left(\frac{\partial u}{\partial A}\right)_T$$

$$du = c_v dT + \left[\left(\frac{\partial \sigma}{\partial T}\right)_A - \sigma\right] dA$$

$$\left(\frac{\partial u}{\partial A}\right)_T = \left[T \left(\frac{\partial \sigma}{\partial T}\right)_A - \sigma\right]$$

$\sigma \rightarrow$  independent of  $A \Rightarrow \sigma \neq f(A)$

$$\left(\frac{\partial u}{\partial A}\right)_T = \left[T \left(\frac{d\sigma}{dT}\right)_A - \sigma\right]$$

$$\left(\frac{\partial T}{\partial A}\right)_S = - \left(\frac{\partial \sigma}{\partial S}\right)_A$$

$$\left(\frac{\partial T}{\partial A}\right)_S \left(\frac{\partial \sigma}{\partial S}\right)_A \left(\frac{\partial A}{\partial T}\right)$$

$$-\cancel{\left(\frac{\partial \sigma}{\partial S}\right)_A} = \cancel{\left(\frac{\partial A}{\partial T}\right)}$$

$$\left(\frac{\partial T}{\partial A}\right)_S = - \frac{\left(\frac{\partial \sigma}{\partial T}\right)_A}{\left(\frac{\partial S}{\partial T}\right)_A}$$

$$\left(\frac{\partial S}{\partial T}\right)_A = \frac{c_A}{T}$$

$$\left(\frac{\partial T}{\partial A}\right)_S = \frac{T}{c_A} \frac{d\sigma}{dT}$$

$$T > 0, \quad c_A > 0, \quad \frac{d\sigma}{dT} < 0$$

$$\left(\frac{\partial T}{\partial A}\right)_S < 0$$

Collision of droplets leads to decrease in surface area and increase in temp.

Q  
For a paramagnetic solid, determine the i) isothermal heat effect accompanied with increase in intensity of magnetisation ii) the temp. change accompanying adiabatic magnetisation.

$$C_p - C_v = R$$

$$\frac{C_p}{C_v} = \gamma$$

$$U_{JT} = 0$$

ideal gas

$$Td\delta = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv = C_v dT + (\beta/k) T dv$$

$$Td\delta = C_p dT - T \left( \frac{\partial v}{\partial T} \right)_P dp = C_p dT - (\beta v T) dp$$

for ideal gas

$$\beta = \frac{1}{T}, \quad k = \frac{1}{P}$$

$$dH = C_p dT + [v - T \left( \frac{\partial v}{\partial T} \right)_P] dp$$

$$dH = C_p dT + v(1 - \beta T) dp$$

$$(C_p - C_v) dT - T \left( \frac{\partial v}{\partial T} \right)_P dp - T \left( \frac{\partial P}{\partial T} \right)_v dv = 0$$

$$dT = \frac{T \left( \frac{\partial P}{\partial T} \right)_v dv}{C_p - C_v} + \frac{T \left( \frac{\partial v}{\partial T} \right)_P dp}{C_p - C_v}$$

$$dT = \left( \frac{\partial T}{\partial v} \right)_P dv + \left( \frac{\partial T}{\partial P} \right)_v dp$$

$$\left( \frac{\partial T}{\partial v} \right)_P = \frac{T \left( \frac{\partial P}{\partial T} \right)_v}{C_p - C_v} \quad \left| \begin{array}{l} \left( \frac{\partial T}{\partial P} \right)_v \\ = \frac{T \left( \frac{\partial v}{\partial T} \right)_P}{C_p - C_v} \end{array} \right.$$

$$(C_p - C_v) = T \left( \frac{\partial v}{\partial T} \right)_p \left( \frac{\partial P}{\partial T} \right)_v$$

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

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

$$\begin{aligned} (C_p - C_v) &= -T \left( \frac{\partial v}{\partial T} \right)_p \left( \frac{\partial v}{\partial T} \right)_p \left( \frac{\partial P}{\partial v} \right)_T \\ &= -T \left[ \left( \frac{\partial v}{\partial T} \right)_p \right]^2 \left( \frac{\partial P}{\partial v} \right)_T \end{aligned}$$

$$PV = RT$$

$$\therefore v = \frac{RT}{P} \quad \frac{\partial v}{\partial T} = \frac{R}{P} = \frac{R \cdot v}{RT} = \frac{v}{T}$$

$$\frac{\partial P}{\partial v} = -\frac{RT}{v^2}$$

$$= -T \cdot \left( \frac{v}{T} \right)^2 \cdot -\frac{RT}{v^2}$$

$$= + T \cdot \frac{v^2}{T^2} \cdot \frac{RT}{v^2}$$

$$C_p - C_v = R$$

$$c_p - c_v = -T \left( \frac{\partial v}{\partial T} \right)_P^2 \left( \frac{\partial P}{\partial v} \right)_T$$

$$\Rightarrow \frac{T v \beta^2}{\kappa}$$

1)  $c_p > c_v$

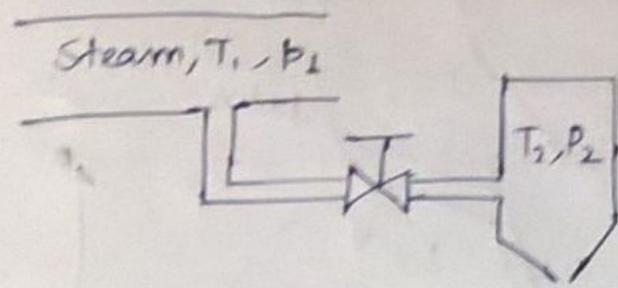
2)  $c_p - c_v = R$  for ideal gas

3)  $c_p = c_v$  at  $T = 0K$

$$\text{or } \beta = 0 \text{ i.e. } \left( \frac{\partial v}{\partial T} \right)_P = 0$$

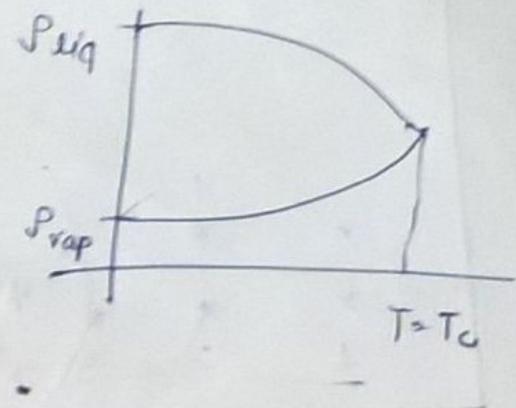
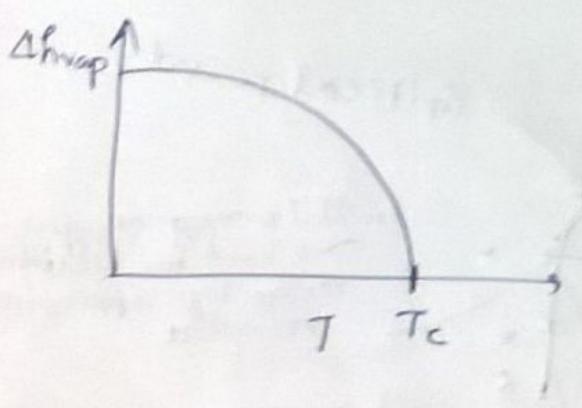
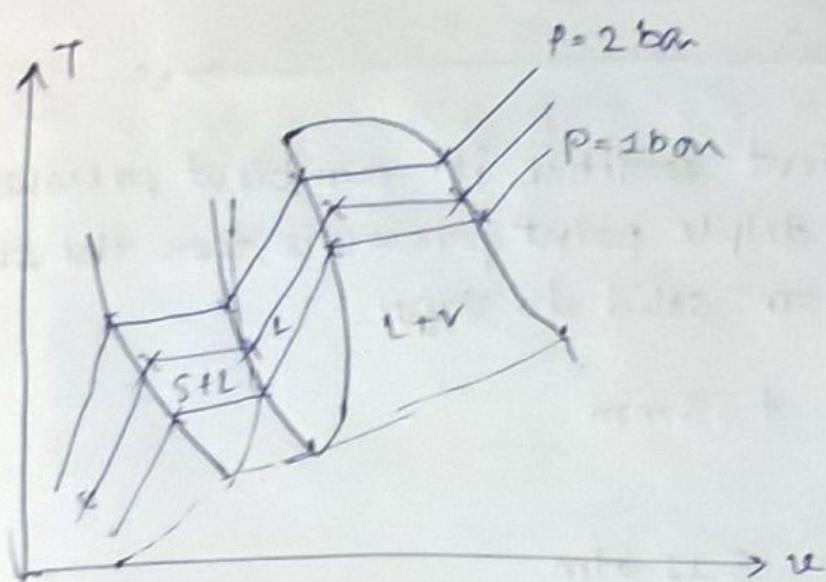
↙  
For solids & liquids

$$\left( \frac{\partial P_{\text{water}}}{\partial T} \right)_P \Big|_{4^\circ C} = 0 \quad \Rightarrow$$



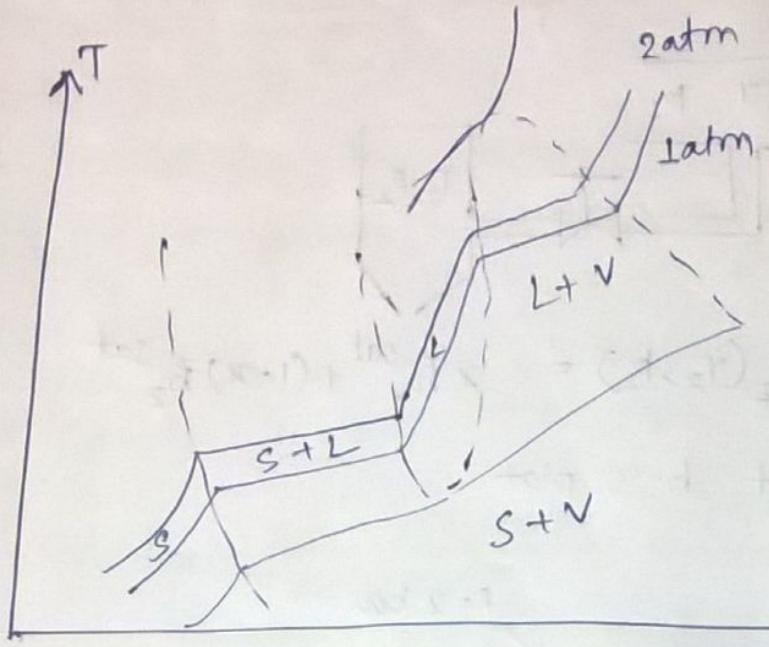
$$h_1 = h_2 = h_2(T_2, P_2) = x h_v^{\text{sat}} + (1-x) h_l^{\text{sat}}$$

Assignment : Plot h-s plot.



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

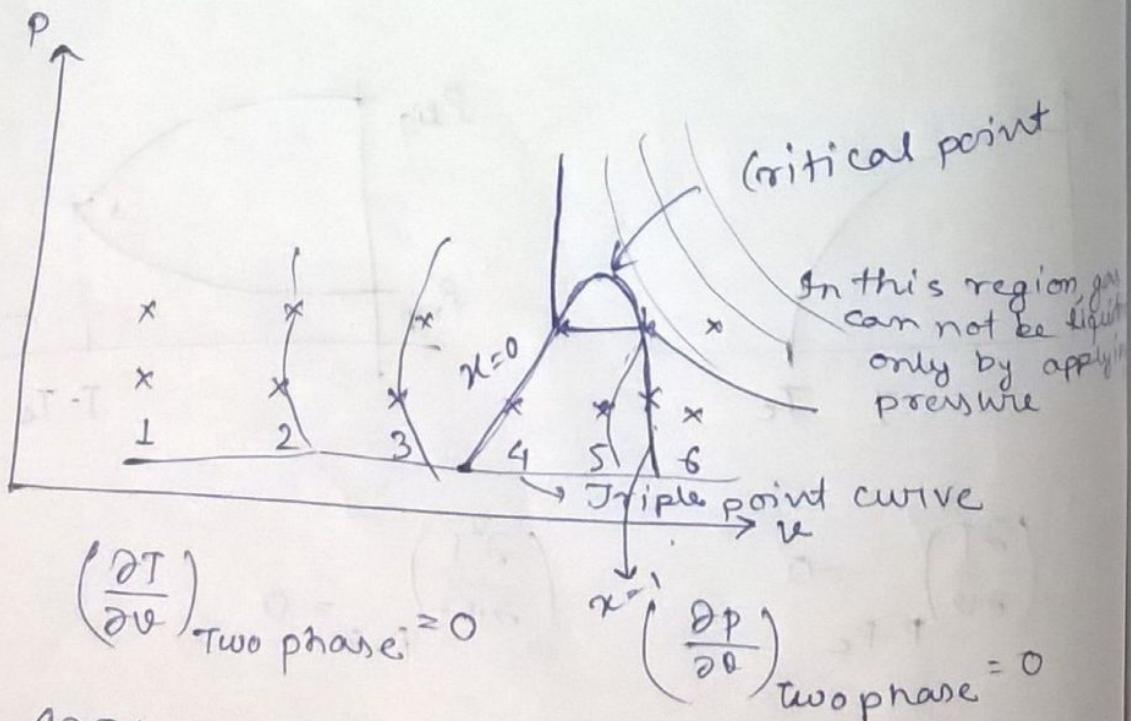
$$\left(\frac{\partial^2 T}{\partial v^2}\right)_{P=P_c} = 0$$



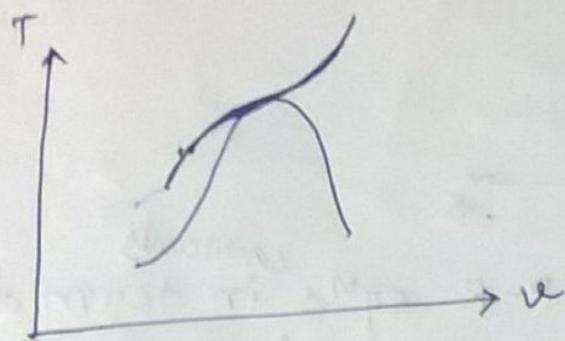
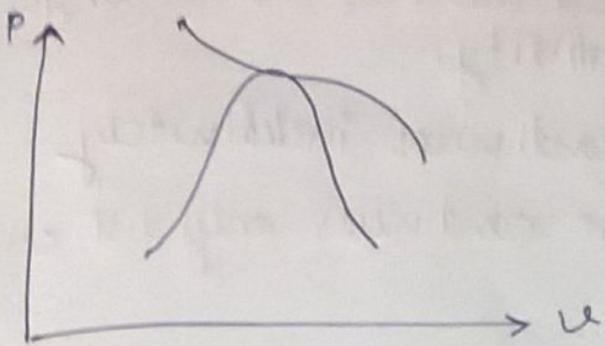
Under ambient condition, if ambient pressure is lower than triple point pressure, then the substance sublimes from solid to vapor.

$$P_{\text{triple}}|_{H_2O} = 4.58 \text{ mm}$$

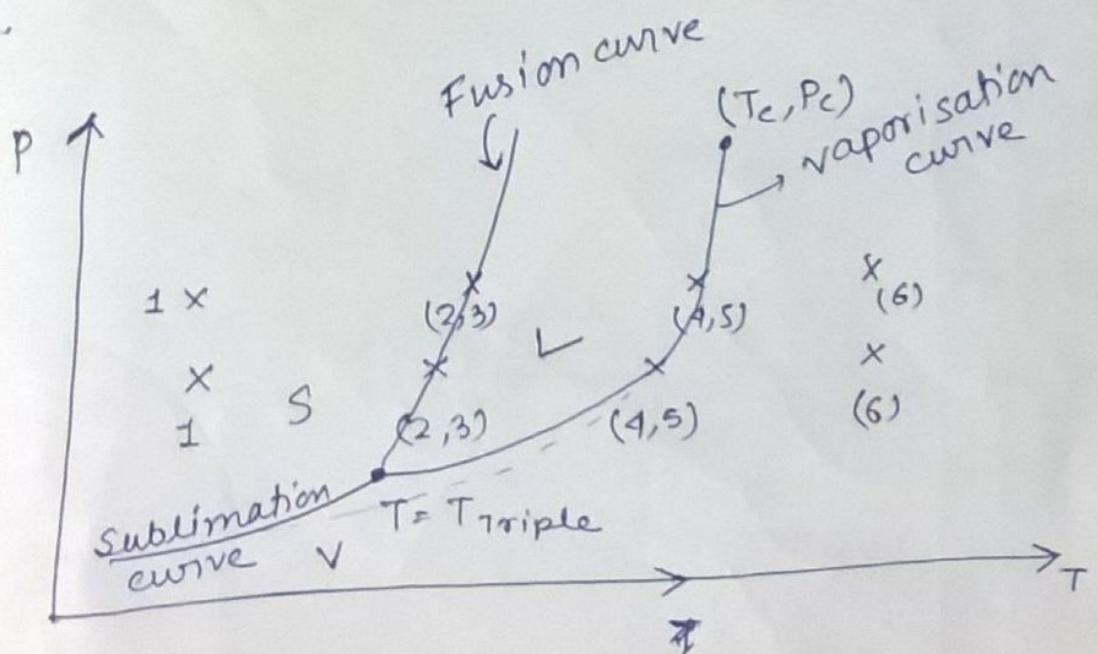
$$P_{\text{triple}}|_{CO_2} = 5.11 \text{ atm}$$



$$\left(\frac{\partial T}{\partial v}\right)_{P=P_c} = 0 \quad \left(\frac{\partial^2 T}{\partial v^2}\right)_{P=P_c} = 0 \quad \left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0 \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0$$



For two phase, only  $P$  or  $v$  can not define a state, we need to know either quality or specific volume.

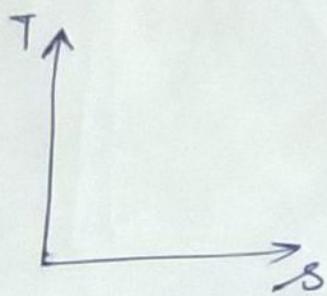


Vapor pressure curve of pure substance

→ Beyond critical point gas can not be liquified applying pressure alone  
→

At transition state, there is a change in molecular arrangement & mobility.

## Home work :

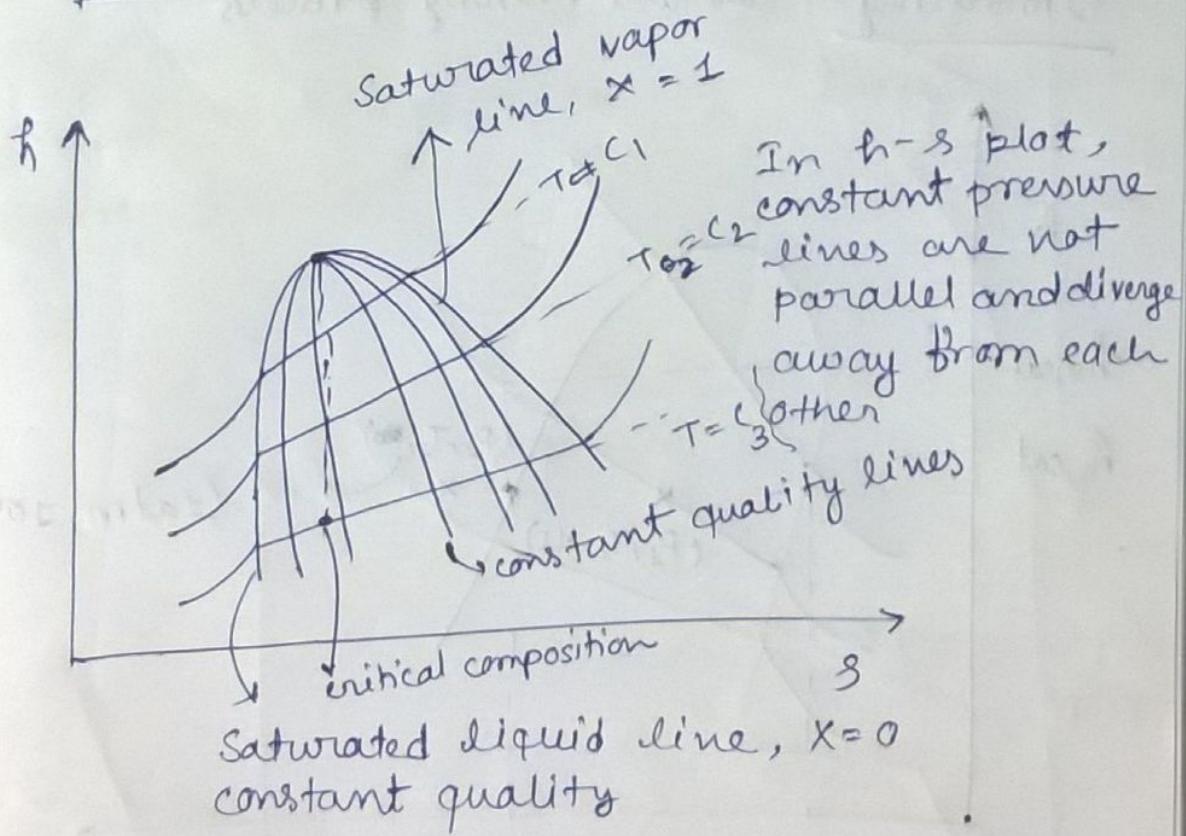
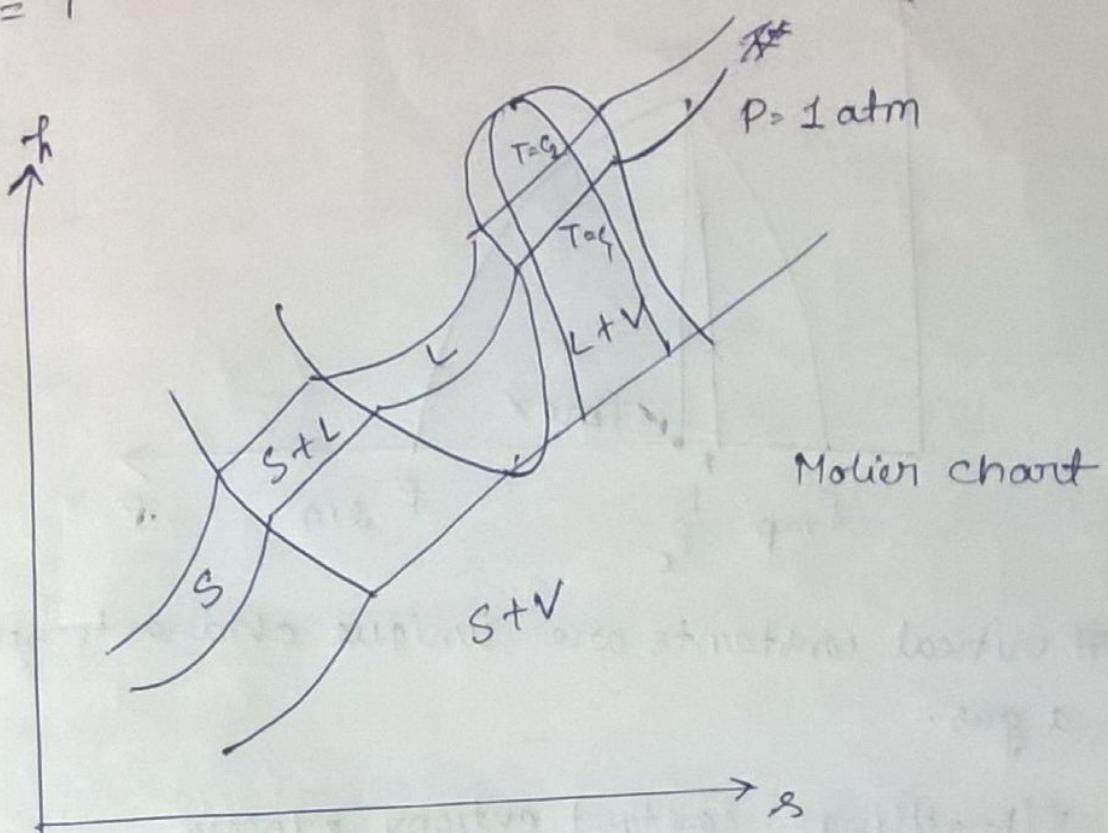


Express VDW, R-K, P-R eqns, constants in term of  $s$

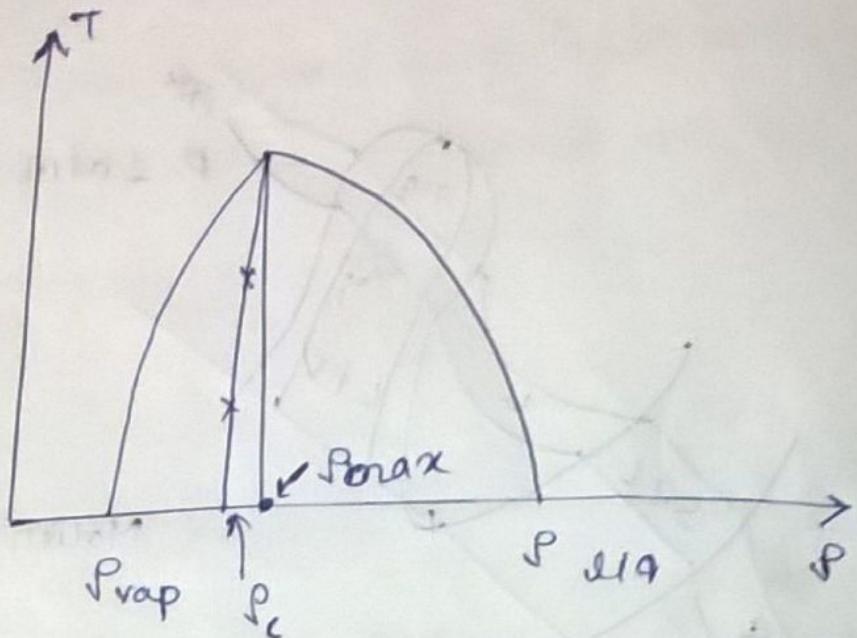
A decorative border element consisting of a stylized, multi-layered rectangular frame.

$$dH = Tds + vdp$$

$$\left(\frac{\partial H}{\partial s}\right)_P = T$$

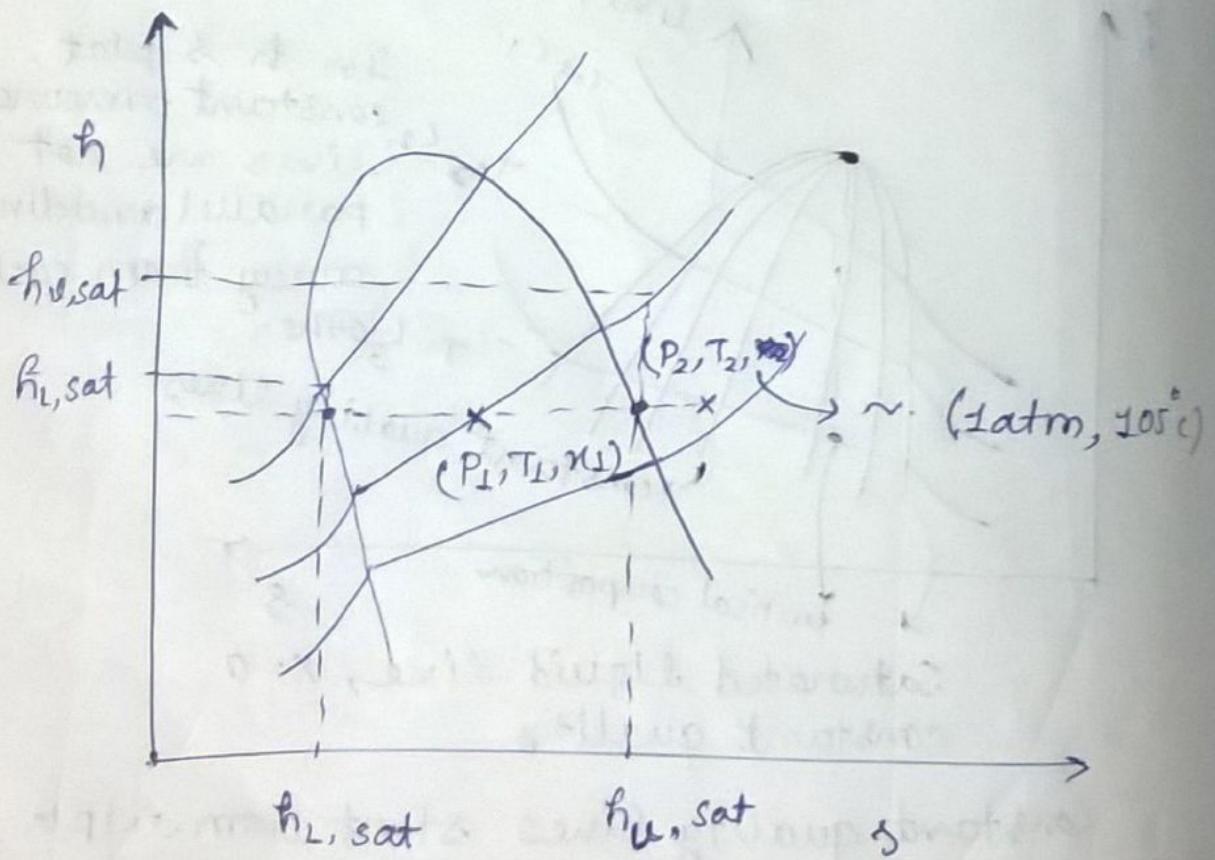


Constant quality lines start from triple point and end\* at critical point



# critical constants are unique characteristics of a gas.

Throttling: constant entropy process



Q1

The initial pressure  $P_1 = 1.5 \text{ MPa}$ .

During 5 minutes, the moisture collected in separator  
is  $0.15 \text{ L}$  at  $70^\circ\text{C}$ . Steam condensed in 5 minutes  
is ~~3.8 kg~~  $3.24 \text{ kg}$

$P_1 = 0.1 \text{ MPa}$ ,  $T_1 = 110^\circ\text{C}$

Find quality of steam in pipeline.

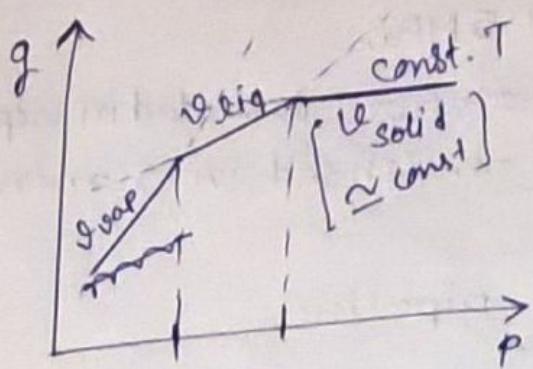
Hint:  $m_1 h_{1f} + q = m_2 h_2$

[Throttling calorimeter]

Q2 Steam flows in a pipeline at  $1.5 \text{ MPa}$ . After  
throttling to  $0.1 \text{ MPa}$ , temperature is  $120^\circ\text{C}$ .

Find quality of steam in the pipeline

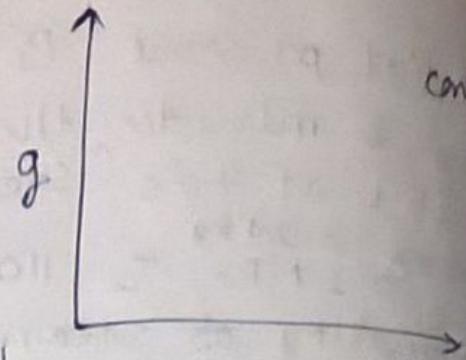
→ what is the maximum moisture content at  
 $1.5 \text{ MPa}$ , that can be determined in this setup  
it atleast  $5^\circ$  of superheat is required for the  
throttling process.



$$T_{\text{triple}} > T > T_{\text{critical}}$$

$$dG = vdp - sdt$$

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



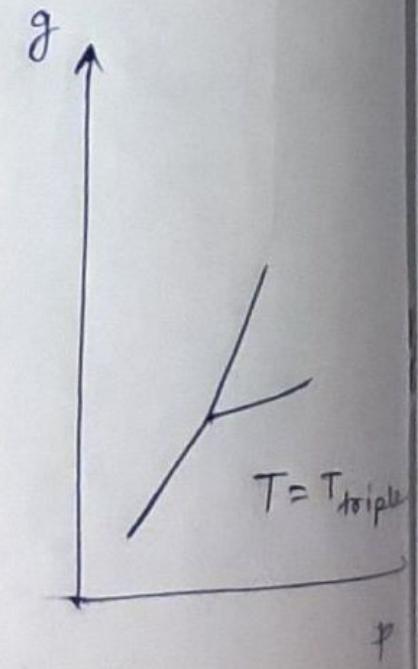
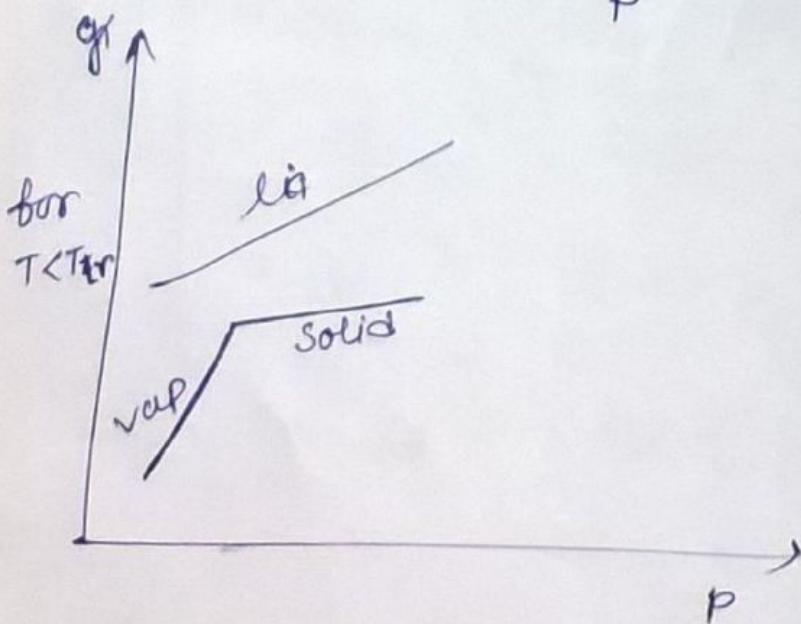
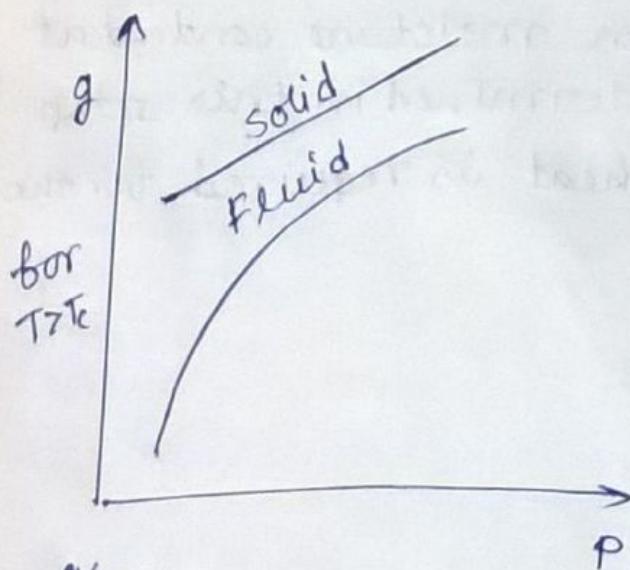
$$\left(\frac{\partial g}{\partial T}\right)_P = -s$$

$$g = h - Ts$$

$$\frac{g}{T} \approx \frac{h}{T} - s$$

$$\frac{\partial}{\partial T} \left( \frac{g}{T} \right) = \frac{\partial}{\partial T} \left( \frac{h}{T} \right) -$$

$$-\frac{1}{T^2} \left( \frac{\partial g}{\partial T} \right) = -\frac{1}{T^2} \left( \frac{\partial h}{\partial T} \right)_P$$



$$\frac{\partial}{\partial T} \left(\frac{\partial f}{\partial T}\right) = \frac{1}{T} \left( \frac{\partial^2 f}{\partial T^2} \right)_P - \frac{h}{T^2} - \left( \frac{\partial s}{\partial T} \right)_P \xrightarrow{C_P/T}$$

$$\boxed{\frac{\partial}{\partial T} \left(\frac{\partial f}{\partial T}\right) = - \frac{h}{T^2}} \quad \Rightarrow \text{Gibbs-Helmholtz's eqn}$$

according to VDW eqn

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

$$\Rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{--- } \textcircled{A}$$

At critical point

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

$$\Rightarrow \left(\frac{\partial P}{\partial v}\right)_T \Big|_{\substack{\text{critical} \\ \text{point}}} = - \frac{RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0$$

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

again,

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T \Big|_{\substack{\text{critical} \\ \text{point}}} = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0$$

$$\Rightarrow \frac{2RT}{(v_c - b)^3} = \frac{6a}{(v_c)^4} \quad \text{--- } \textcircled{II}$$

Dividing  $\textcircled{II}$  by  $\textcircled{I}$

$$\frac{(v_c - b)}{2} = \frac{v_c}{3}$$

$$3v_c - 3b = 2v_c$$

$$\boxed{b = \frac{v_c}{3}} \quad \boxed{v_c = 3b} \quad \text{--- } \textcircled{III}$$

substituting  $v_c = 3b$  in eqn ①

$$\frac{RT_c}{4b^2} = \frac{2q}{27Rb}$$

$$\boxed{T_c = \frac{8q}{27Rb}} \quad | \quad b = \frac{8q}{27RT_c} \quad - \textcircled{IV}$$

substituting  $v_c$  and  $T_c$  in eqn ④

$$P_c = \frac{RT_c}{v_c - b} - \frac{q}{v_c^2}$$

$$P_c = \frac{\cancel{RT_c}}{\cancel{2b} \frac{8q}{27Rb}} - \frac{a}{\cancel{27} 9b^2}$$

$$P_c = \frac{8q}{54b^2} - \frac{a}{9b^2} = \frac{8q - 6a}{54b^2}$$

$$\boxed{P_c = \frac{a}{27b^2}} \quad | \quad a = 27P_c b^2 \quad \textcircled{V}$$

from ③, ④ & ⑤

$$\frac{T_c}{P_c} = \frac{8q}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

∴

$$\boxed{b = \frac{RT_c}{8P_c}} \quad - \quad \textcircled{VI}$$

$$T_c^2 = \frac{64a^2}{729b^2 R^2} ; \quad \frac{T_c^2}{P_c} = \frac{64a^2}{729b^2 R^2} \cdot \frac{24b^2}{27} = \frac{64a^2}{27R^2}$$

∴

$$\boxed{a = \frac{27R^2 T_c^2}{64P_c}} \quad - \quad \textcircled{VII}$$

08/02/2015

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

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP = \beta v dT - k v dP$$

$$\frac{dv}{v} = \beta dT - k dP$$

$$\ln\left(\frac{v_2}{v_1}\right) = \beta(T_2 - T_1) - k(P_2 - P_1)$$

Eq's of state

Cubic Eq's of state

Nernst eqn

$$\frac{PV}{RT} = 1 + B_1 P + B_2 P^2$$

$$= 1 + \frac{C_1}{V} + \frac{C_2}{V^2}$$

Applicable  
moderate tem  
& pressure

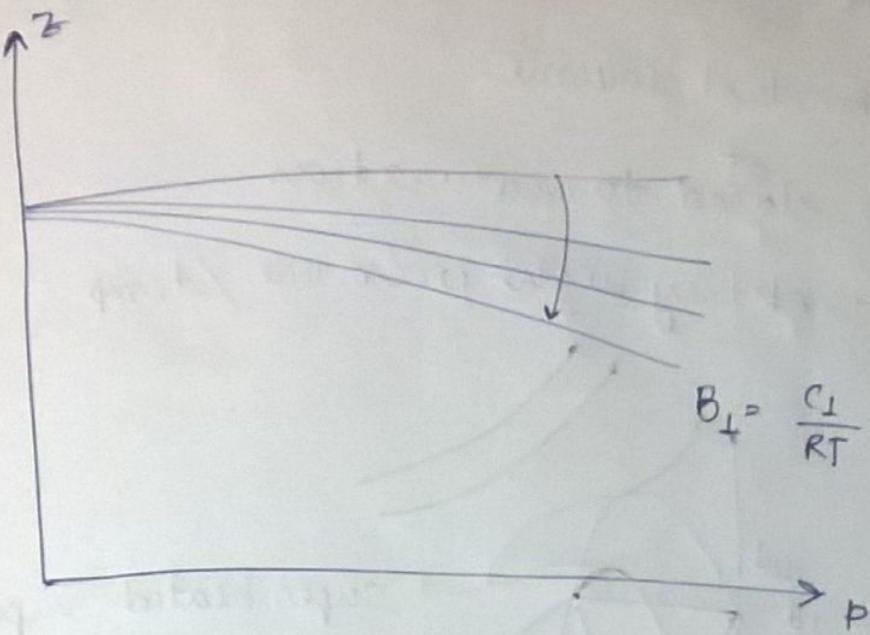
$$1 + B_1 P = 1 + \frac{C_1}{V}$$

$$\boxed{B_1 = \frac{C_1}{PV} = \frac{C_1}{RT}}$$

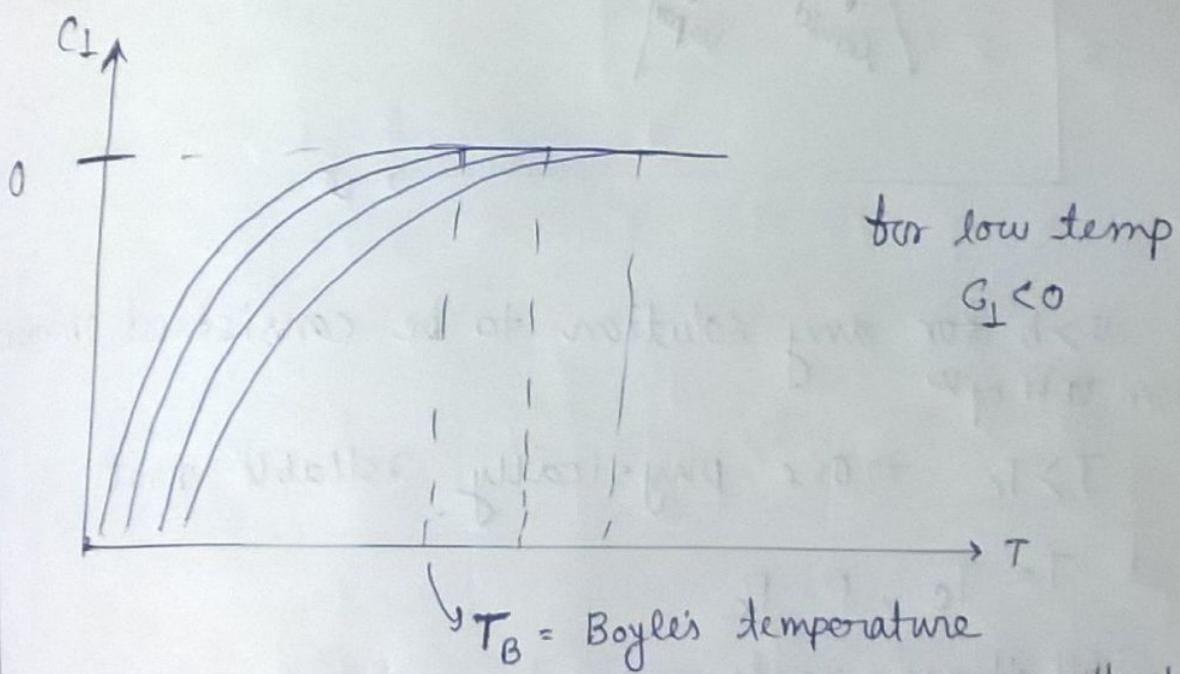
$$B_1 \rightarrow f(T)$$

$$C_1 \rightarrow f(T)$$

$$\left(\frac{\partial Z}{\partial P}\right)_T = B_1$$



$$B_{\perp} = \frac{C_{\perp}}{RT}$$



$\downarrow T_B$  = Boyle's temperature

[Real gases act as ideal gases because attractive & repulsive force among the molecules cancel each other out at  $T = T_B$ ] -

$$\chi = 1 + B_{\perp} P$$

$$= 1 + \frac{C_{\perp}}{v}$$

$$\frac{PV}{RT} = 1 + \frac{C_{\perp} P}{RT} = 1 + B_{\perp} P$$

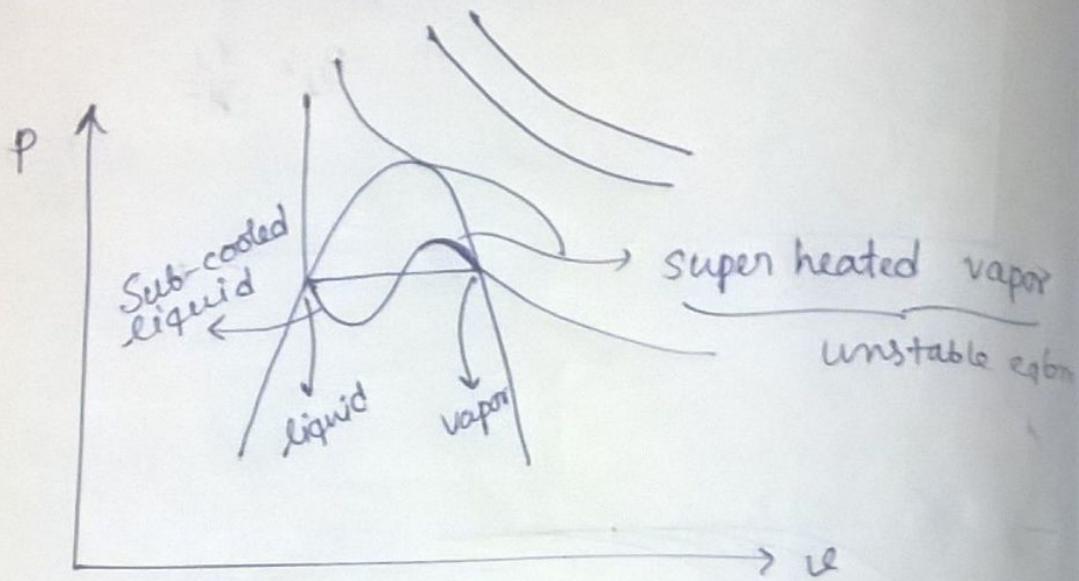
$$v = \frac{RT}{P} + C_{\perp} \Rightarrow v = v_0 + \zeta$$

$$G_1 = \delta v^*$$

↓ residual volume

$P - R \xrightarrow{eq^n}$  closed to saturation

$R - K \xrightarrow{eq^n}$  at very high pressure / temp



$v > b$  for any solution to be consistent, obtained from VDW eq<sup>n</sup>

$T > T_c \Rightarrow$  one physically reliable root

at  $T = T_c, P = P_c$

All three roots are same

$$\frac{\partial P}{\partial T} \quad \left( \frac{\partial P}{\partial v} \right)_T > 0 \quad \underbrace{\text{Not possible}}$$

The state is unrealizable  
physical conditions

$$T < T_c$$

$$P = P_{sat} \quad \left. \begin{array}{l} 3 +ve \text{ roots} \\ \downarrow \text{highest} \rightarrow \text{sat. vapor} \\ \downarrow \text{lowest} \rightarrow \text{sat. liquid} \\ \downarrow \text{Middle one} \rightarrow \text{not realisable} \end{array} \right\}$$

highest  $\rightarrow$  sat. vapor

lowest  $\rightarrow$  sat. liquid

Middle one  $\rightarrow$  not realisable

cons. of all cubic eqn of states  
 → can not predict behavior of the pure substance  
 in liquid-vapor dome.

$$(P_c + 3v_c P_c) \left(v - \frac{8}{3} \frac{v_c}{3}\right) = RT_c$$

$$(P + 3v_c P_c) \left(v - \frac{v_c}{3}\right) = RT$$

$$(P + 3v_c P_c) \frac{2}{3} v_c = RT$$

$$\left(\frac{P}{P_c} + 3 \frac{v_c^2}{V_0^2}\right) \left(\frac{v}{v_c} - \frac{1}{3}\right) = RT$$

$$= \frac{RT}{P_c v_c}$$

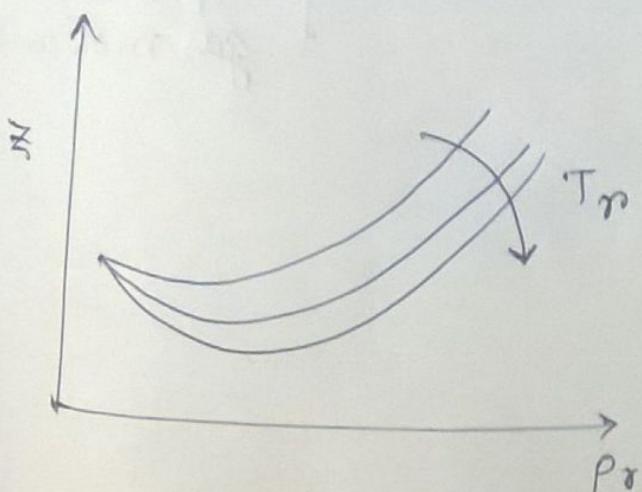
$$\left(\frac{P}{P_c} + 3 \frac{v_c}{V_0}\right) \frac{2}{3} = \frac{RT/T_c}{P_c v_c / T_c}$$

$$\boxed{(P_r + 3/v_r^2) (v_r - \frac{1}{3}) = \frac{8}{3} T_r}$$

$$v_r = v_r(T_r, P_r)$$

Law of corresponding  
States

$$z = z_r(T_r, P_r)$$



$$\left( P_r + \frac{3}{v_r^2} \right) \left( v_r - \frac{1}{3} \right) = \frac{8}{3} T_r$$

$$Z = \frac{3 v_r}{3 v_r - 1} - \frac{9}{8 T_r v_r}$$

$$0.23 \leq Z_c \leq 0.32$$

$$Z_c \approx 0.27$$

$$Z = Z(T_r, P_r, \omega)$$

Acentric factor  $\geq_{\text{vapor}}^{\text{reduced}}$

Three parameter law of corresponding states

$$\omega = - \log_{10} P_r^{\text{sat}} \quad \Rightarrow \text{Particularly for}$$

$$\omega = - \log_{10} P_r^{\text{sat}} \Big|_{T_r=0.7} - 1.00 \quad \text{for perfect spherical gas molecules}$$

# Thermodynamics of Multiphase - Multi component

22/02/17

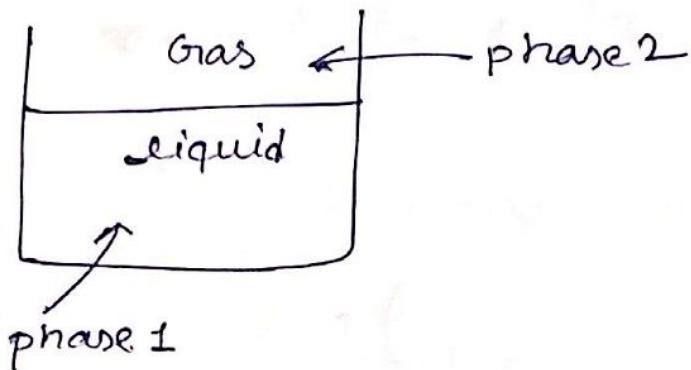
- 1) Single phase - Multiple component /  
2) Single component - Multiphase      } Non reactive  
3) Multiphase - Multi component  
4) Reactive

End sem → only the portion covered after midsem

P.A. Dashpande ⇒ Google + page ⇒ Assignments

## Phase vs. States of Matter

→ homogeneity of property in space → phase



→ In majority of cases phase coincides with physical state

→ Solid with different phases

e.g. Steel → Mardenite  
→ Ferrite  
→ Acemenite  
→ Pearlite



Component: Chemically distinct species.

Multi component: ortho-xylene, meta-xylene, para-xylene  
Mixture

Postulates : Theory, proposed



without proof

statement which is supported by observations, experiments. This is not contradicted by any observation

Postulate 1: In all processes for which net effect on surroundings is zero, all systems have a tendency to evolve a unique state.



Egbm state

Due to rate of rkn. If a reaction is very slow, e.g. rusting, then the system may not attain egbm. during the period of observation.

Postulate 2: All systems can be completely defined by two independently variable properties and moles/masses of all components

e.g. ① Pure ideal gas

Components = 1

To be specified  $\Rightarrow$  Property 1  
Property 2

No. of moles ( $n$ )

$$\check{p}\check{V} = \check{n}\check{R}\check{T}$$

Property B, no. of moles

$$B = f(x, y, n_1, n_2, \dots, n_N)$$

No. of components

$$dB = \left( \frac{\partial f}{\partial x} \right)_{y, n_1, n_2, \dots, n_N} dx + \left( \frac{\partial f}{\partial y} \right)_{x, n_1, n_2, \dots, n_N} dy$$

$$+ \sum_{i=1}^N \left( \frac{\partial f}{\partial n_i} \right)_{x, y, n_i^*} dn_i$$

$n_i^*$  → every  $n$  excluding  $n_i$

$$x = s, y = v$$

$$dB = \left( \frac{\partial f}{\partial s} \right)_{v, n_1, \dots, n_N} ds + \left( \frac{\partial f}{\partial v} \right)_{s, n_1, n_2, \dots, n_N} dv$$

$$+ \sum_{i=1}^N \left( \frac{\partial f}{\partial n_i} \right)_{s, v, n_i^*} dn_i$$

When  $x \equiv s$   
 $y \equiv v$   
 $f = U$

$$\Rightarrow dU = \left( \frac{\partial U}{\partial s} \right)_{v, n_1, \dots, n_N} ds + \left( \frac{\partial U}{\partial v} \right)_{s, n_1, \dots, n_N} dv$$

$$+ \sum_{i=1}^N \left( \frac{\partial U}{\partial n_i} \right)_{s, v, n_i^*} dn_i$$

$$\left(\frac{\partial U}{\partial S}\right)_{V, n_1, n_2, \dots, n_N} = T$$

$$\left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_N} = -P$$

$$\left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_1^*, \dots} = \mu_i$$

↓  
Chemical potential of  $i^{th}$  component

Conclusion

$$dU = Tds - pdV + \sum_{i=1}^N \mu_i dn_i$$

① Fundamental eqn

② Chemical potential of  $i^{th}$  component =  $\left(\frac{\partial U}{\partial n_i}\right)_{S, V}$

③  $T \rightarrow$  intensive  
 $P \rightarrow$  intensive }  $\Rightarrow \mu_i \rightarrow$  intensive

$\Rightarrow T-S, P-V, \mu_i - n_i$

Thermodynamic conjugates

(pair of intensive and extensive properties)

One of the properties is derivative of another

Quiz on sheet 1 → next week

23/02/2017

## Change of Natural coordinates

$$dU = Tds - pdv + \sum_{i=1}^N u_i dn_i$$

$$\left(\frac{\partial U}{\partial s}\right)_{v, n_1, \dots, n_N} = T$$

$$U = U(s, v, n_1, \dots, n_N)$$

n+3 dimensional system

$$\left(\frac{\partial U}{\partial v}\right)_{s, n_1, \dots, n_N} = -P$$

$$\left(\frac{\partial U}{\partial n_i}\right)_{s, v, n_i^*} = u_i$$

$$U = U(s, v, n_1, \dots, n_N)$$

Natural coordinates for  $U$

$$f = f(T, v, n_1, \dots, n_N)$$

$$f = \left[ \left( \frac{\partial U}{\partial s} \right)_{v, n_1, \dots, n_N}, n_1, n_2, \dots, n_N \right]$$

's' has been changed with  $\frac{\partial U}{\partial s}$

$$y = f(x) \quad \leftarrow \text{have}$$

$$y = g\left(\frac{dy}{dx}\right) \quad \leftarrow \text{want}$$

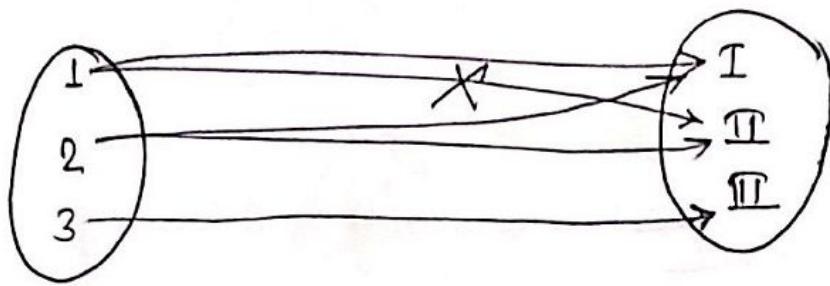
$$\frac{\partial U}{\partial s} = T$$

$x^2 y^2 \rightarrow 2x$

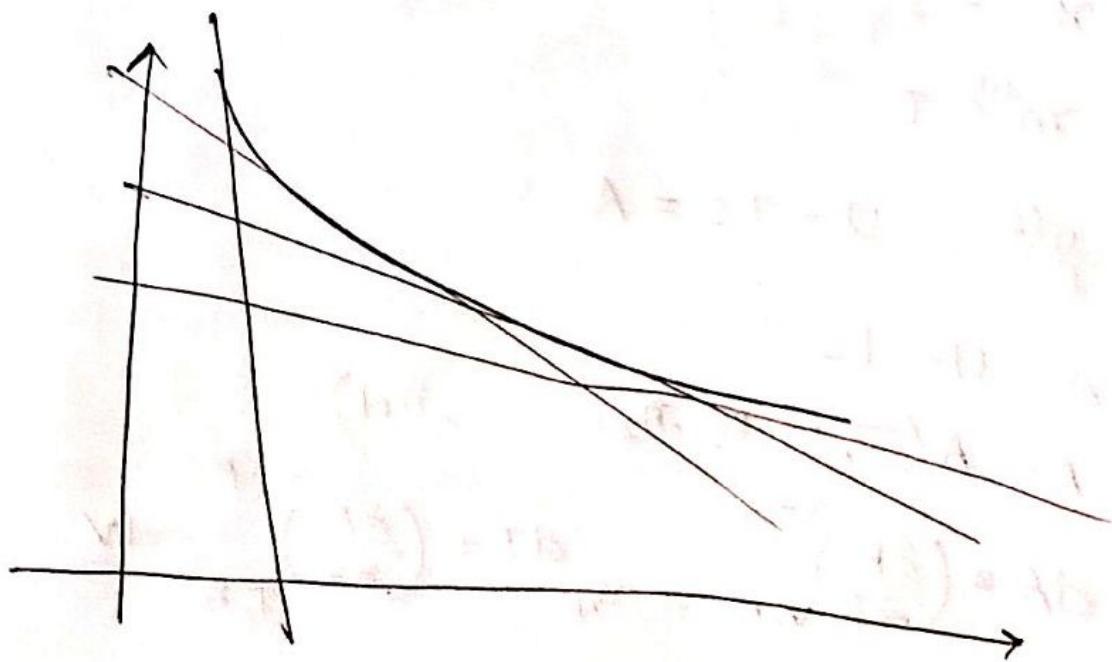
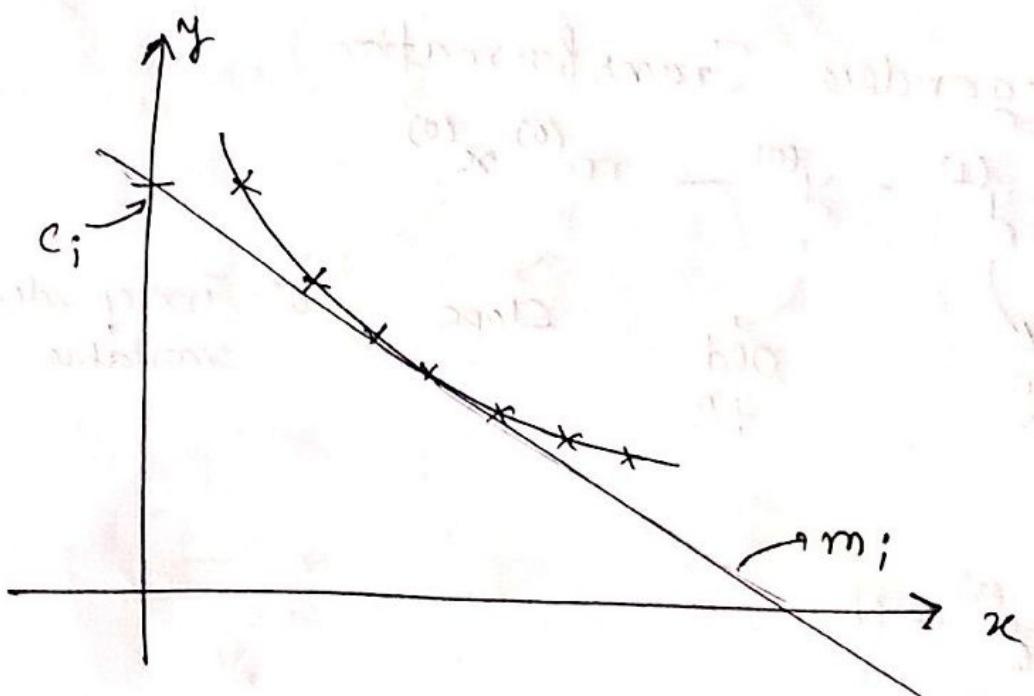
$x$	$y$	$\frac{dy}{dx}$	$y = g\left(\frac{dy}{dx}\right)$
1	1	2	1
2	4	4	4
3	9	6	9

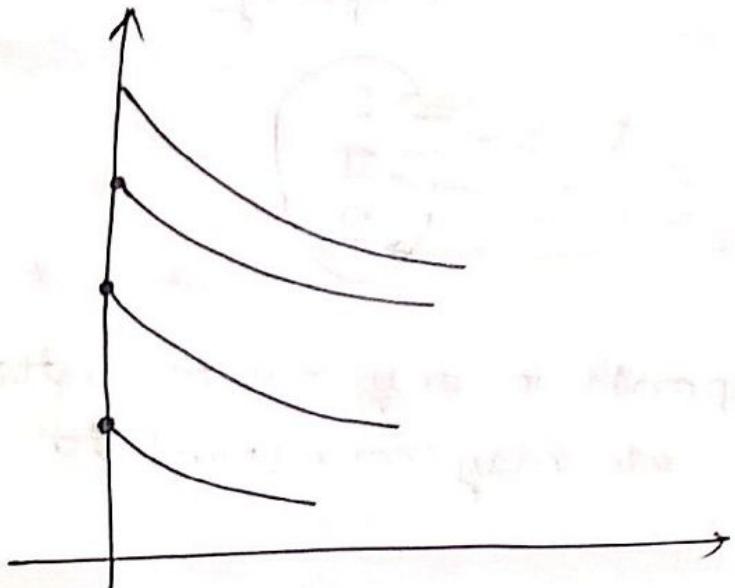
state

Property



- ⇒ One state corresponds to only one properties  
⇒ More than one state may correspond to same property.





# Legendre Transformation

$$y^{(1)} = y^{(0)} - m^{(0)} x^{(0)}$$

↙ New  $f^n$       ↘ Old  $f^n$       ↗ slope      ↗ old independent variable.

$$y^{(0)} = U$$

$$x^{(0)} = S$$

$$m^{(0)} = T$$

$$y^{(1)} = U - TS = A$$

$$A = U - TS$$

$$A = A(T, V, n_1, n_2, \dots, n_N)$$

$$\begin{aligned}
 dA &= \left( \frac{\partial A}{\partial T} \right)_{V, n_1, \dots, n_N}^{-S} dT + \left( \frac{\partial A}{\partial V} \right)_{T, n}^{-P} dV \\
 &\quad + \sum_{i=1}^N \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_i} dh_i
 \end{aligned}$$

$$u_i^{\circ} = \left( \frac{\partial u}{\partial n_i} \right)_{S, V, n_i^*}$$

$$u_i = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_i^*}$$

$$U = U(S, V, n_1, n_2, \dots, n_N)$$

↓  
P

$$y^{(0)} = U$$

$$y^{(1)} = y^{(0)} - m^{(0)} x^{(0)}$$

$$m^{(0)} = -P$$

$$x^{(0)} = V$$

$$y^{(1)} = U + PV = H$$

$$H = H(S, P, n_1, \dots, n_N)$$

$$dH = \left( \frac{\partial H}{\partial S} \right)_{P, n}^T dS + \left( \frac{\partial H}{\partial P} \right)_{S, n}^V dP + \sum_{i=1}^n \left( \frac{\partial H}{\partial n_i} \right)_{S, P, n_i^*} dn_i$$

$$dH = T dS + V dP + \sum_{i=1}^n u_i dn_i$$

$$u_i^{\circ} = \left( \frac{\partial H}{\partial n_i} \right)_{S, P, n_i^*}$$

$$U = U(S, V, n_1, n_2, \dots, n_N)$$

↓      ↓  
T      P

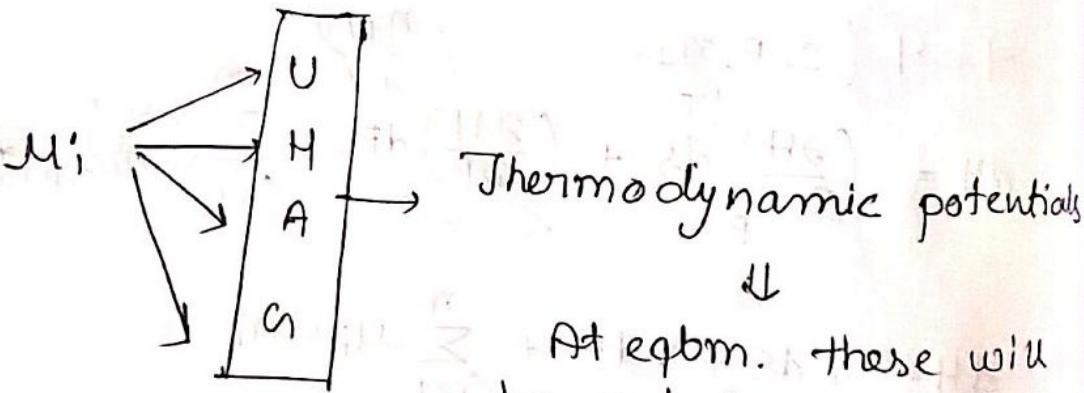
$$y^{(2)} = y^{(0)} - \sum_{i=1}^2 m^{(i)} x^{(i)}$$

$$y^{(2)} = U - TS + PV = G$$

$$G = (T, P, n_1, \dots, n_N)$$

~~$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, \dots, n_N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n} dP + \sum_{i=1}^n \mu_i dn_i$$~~

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_i^*}$$



At eqbm. these will be minimum when natural co-ordinates are changed only

$\mu_i \rightarrow$  change in thermodynamic potential with  $m$  no. of moles of components, under certain constraints.

## partial molar property

$$\overline{B}_i = \left( \frac{\partial B}{\partial n_i} \right)_{T, P, n_j \neq i}$$

$$\overline{g}_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq i} = g_i = \text{partial molar gibbs potential}$$

$$= \mu_i$$

## Partial molar property

$$\bar{B}_i = \left( \frac{\partial B}{\partial n_i} \right)_{T, P, n_i^*}$$

$$\bar{G}_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_i^*} = \sigma_i = \text{partial molar gibbs potential}$$

$$= \mu_i$$

24/02/17

Integration of Fundamental eq<sup>n</sup> thermodynamic conjugate

$$dU = Tds - pdV + \sum_{i=1}^N \mu_i dn_i \quad \textcircled{1}$$

$$dH = Tds + Vdp + \sum_{i=1}^N \mu_i dn_i \quad \textcircled{2}$$

$$dA = -sdt - pdV + \sum_{i=1}^N \mu_i dn_i \quad \textcircled{3}$$

$$dG = -sdt + Vdp + \sum_{i=1}^N \mu_i dn_i \quad \textcircled{4}$$

$\textcircled{1}$ T-S	$\textcircled{1}$ Tds/sdT
$\textcircled{2}$ P-V	$\textcircled{2}$ pdV/Vdp
$\textcircled{3}$ $\mu_i - n_i$	$\textcircled{3}$ $\mu_i dn_i / n_i d\mu_i$

Rule

$\textcircled{1}$  change the sign when you change the differential

## Classical Thermodynamics

- No details required at molecular level
- continuum hypothesis (Applicable for all practical purpose)

## Statistical Thermodynamics $\Rightarrow$

$$U = TS - PV + \sum_{i=1}^N u_i n_i$$

$$H = TS + PV + \sum_{i=1}^N u_i n_i$$

X X } all three are inconsistent

$$H - U = 2PV \quad X$$

$$H - U = PV \quad W$$

## Euler Integration

$$f(x, y, a, b)$$

$$\longleftrightarrow I \longleftrightarrow J$$

$x \rightarrow kx$   
 $y \rightarrow ky$  } changes  $f(x, y, a, b)$  to same other  
 $a \rightarrow a$   
 $b \rightarrow b$

$$f(kx, ky, a, b) = k^h f(x, y, a, b)$$

↓

→ Homogeneous function

→ Order of dependence = "h"

$$hf = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y}$$

$$U = U(S, V, n_1, n_2, \dots, n_N)$$

$$U(2S, 2V, 2n_1, 2n_2, \dots, 2n_N) = \underline{\underline{2}} U(S, V, n_1, n_2, \dots, n_N)$$

↓  
order of dependence  
is ±

$$\Rightarrow U = TS - PV + \sum_{i=1}^N n_i u_i$$

$$H = \mathcal{H}(S, P, n_1, n_2, \dots, n_N)$$

$P \rightarrow$  intensive variable

$$H = TS + \sum_{i=1}^N \mu_i n_i$$

$$H - U = PV$$

$$A = -PV + \sum_{i=1}^N \mu_i n_i \quad T \rightarrow \text{intensive}$$

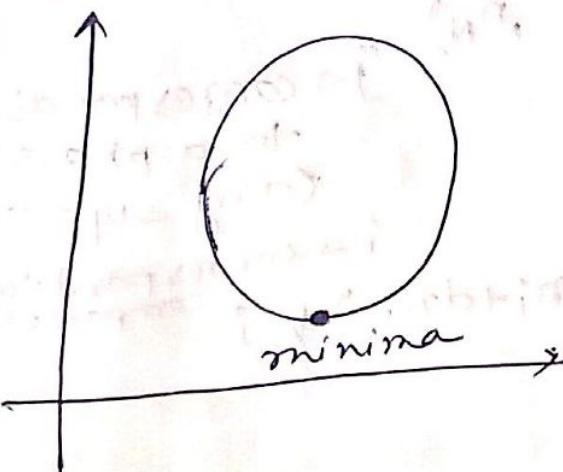
$$G = \sum_{i=1}^N \mu_i n_i \quad T, P \rightarrow \text{both intensive}$$

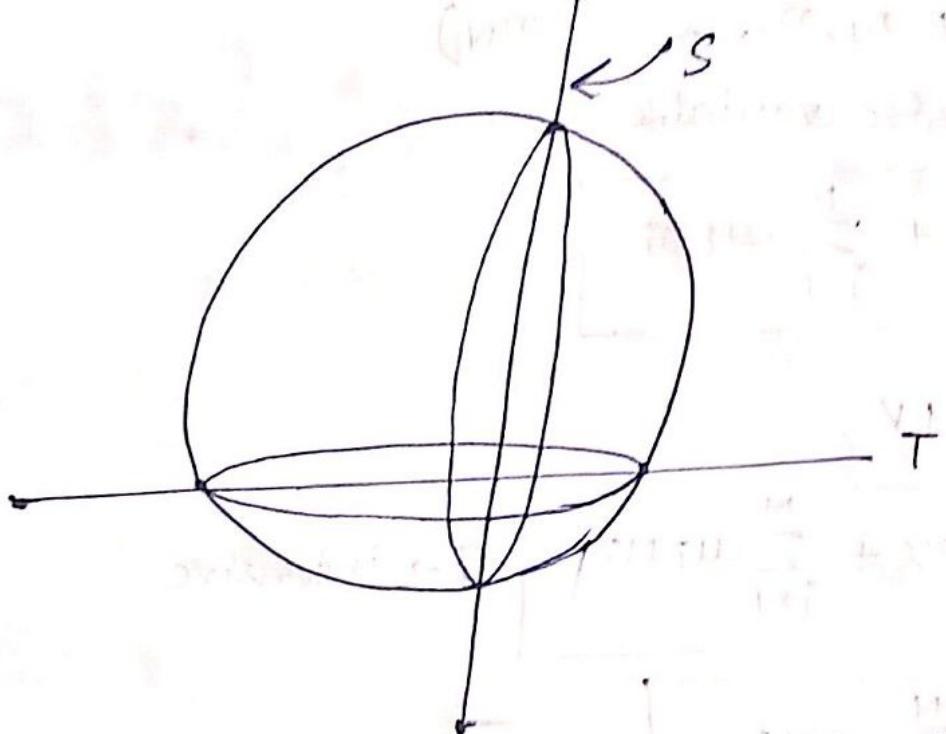
# order of dependence for intensive variable  
= 0, zero

In thermodynamics,

minima  $\rightarrow$  T, D potentials

maxima  $\rightarrow$  Entropy





⇒ Requires correct conditions to define a system.

# Driving force for any mass transfer operations is called chemical potential

N - components

$\Pi \rightarrow$  phases

$$S^j = S^j(U, V, n_1, n_2, \dots, n_N)$$

$j \rightarrow$  corresponds to a phase  
(any superscript)

$$S^j + dS^j = S^j(U+dU, V+dV, n_i+dn_i) - \mu_i^j$$

$i \rightarrow$  corresponds to component

$$ds^j(U+dU, V+dV, n_i+dn_i) \quad \forall i$$

$$= s^j(U, V, n_i) + \left(\frac{\partial s}{\partial U}\right)_{V, n_i}^j dU^j + \left(\frac{\partial s}{\partial V}\right)_{U, n_i}^j dV^j + \sum_{i=1}^N \left(\frac{\partial s}{\partial N_i}\right)_{U, V, n_i}^j dn_i^j$$

$$ds^j = \frac{1}{T^j} dU^j + \left(\frac{P^j}{T^j}\right) dV^j - \left(\frac{u_i^j}{T^j}\right) dn_i^j \quad \forall i$$

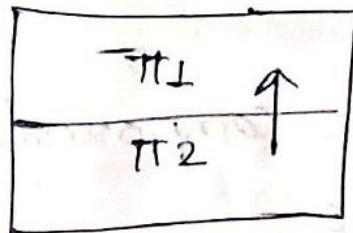
$$ds^{\text{system}} = \sum_{j=1}^N ds^j$$

For a binary system at eqbm.

$$\cancel{\left[ \frac{1}{T^1} dU^1 + \frac{P^1}{T^1} dV^1 \right]} + \left[ \frac{1}{T^1} dU^1 + \frac{1}{T^2} dU^2 \right] + \left[ \frac{P^1}{T_1} dV^1 + \frac{P^2}{T^2} dV^2 \right] - \sum_{i=1}^N \left[ \frac{u_i^1}{T^1} + \frac{u_i^2}{T^2} \right] dN_i^i = 0$$

$$(ds_{\text{system}})_{\text{eqbm.}} = 0$$

For an isolated system



$$dU = dU^1 + dU^2$$

$$dU^1 = -dU^2$$

$$dV^1 = -dV^2$$

$$dn_i^1 = -dn_i^2$$

conditions  
of isolation

$$\left[ \frac{1}{T_1} - \frac{1}{T_2} \right] dU + \left[ \frac{P_1}{T_1} - \frac{P_2}{T_2} \right] dV$$

$$+ \sum_{i=1}^N \left( \frac{\mu_i^1}{T^1} - \frac{\mu_i^2}{T^2} \right) dn_i = 0$$

$$T^1 = T^2$$

$$P^1 = P^2$$

$$\Rightarrow \frac{1}{T_1} - \frac{1}{T_2} = 0$$

$$\frac{P_1}{T_1} - \frac{P_2}{T_2} = 0$$

$$\frac{\mu_i^1}{T^1} - \frac{\mu_i^2}{T^2} = 0$$

$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \mu_i^4 = \mu_i^5 = \dots = \mu_i^\pi$$

$$T^1 = T^2 = T^3 = \dots = T^\pi$$

$$P^1 = P^2 = P^3 = \dots = P^\pi$$

chemical potential of a given component  
are equal in all the phases

# Tutorial Sheet-1

$$\left(\frac{\partial T}{\partial n_i}\right)_{S, V, n_i^*} = \left(\frac{\partial u_i}{\partial s}\right)_{V, n_1, n_2, \dots, n_N}$$

$$dU = Tds - Pdv + \sum_{i=1}^N u_i dn_i$$

Maxwell reciprocity

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

$$\left(\frac{\partial U}{\partial s}\right)_{V, n_1, n_2, \dots, n_N} = T$$

$$\left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_i^*} = u_i$$

$$\left(\frac{\partial^2 U}{\partial n_i \partial s}\right)_{S, V, n_i^*} = \left(\frac{\partial T}{\partial n_i}\right)_{S, V, n_i^*}$$

$$\left(\frac{\partial^2 U}{\partial s \partial n_i}\right)_{V, n_1, n_2, n_3, \dots, n_N} = \left(\frac{\partial u_i}{\partial s}\right)_{V, n_1, n_2, \dots, n_N}$$

using Maxwell Reciprocity

$$\left(\frac{\partial^2 U}{\partial n_i \partial s}\right)_{S, V, n_i^*} = \left(\frac{\partial u_i}{\partial s}\right)_{V, n_1, n_2, \dots, n_N}$$

$$\frac{\partial f}{\partial u_i} \left. \right|_{S, P, M_i^*} = - \left( \frac{\partial n_i}{\partial S} \right)_{P, M_1, M_2, \dots, M_N}$$

$$dH = TdS + VdP + \sum_{i=1}^N \mu_i dn_i$$

$$U = U(S, V, \overset{\mu_1}{n_1}, \overset{\mu_2}{n_2}, \dots, \overset{\mu_N}{n_N})$$

$$y^{(N+1)} = y_0 - \sum_{i=1}^N \mu_i n_i$$

$$df_L = TdS + VdP - \sum_{i=1}^N n_i d\mu_i$$

$$\left( \frac{\partial f_L}{\partial S} \right)_{P, M_1, M_2, \dots, M_N} = T$$

$$\left( \frac{\partial f_L}{\partial \mu_i} \right)_{S, P, n_i^*} = n_i$$

$$\left(\frac{\partial T}{\partial \mu_i}\right)_{S, V, \text{el}^*} = - \left(\frac{\partial \mu_i}{\partial S}\right)_{V, u_1, u_2, \dots, u_N}$$

$$df = Tds + -pdV - \sum_{i=1}^N n_i du_i$$

$$\left(\frac{\partial f}{\partial \mu_i}\right)_{V, n_i}$$

useful Relations

$$1) \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

$$2) \frac{\partial y}{\partial x} = \pm 1 / (\partial x / \partial y)$$

$$3) \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$4) \left(\frac{\partial y}{\partial x}\right) \left(\frac{\partial x}{\partial z}\right) = \left(\frac{\partial y}{\partial z}\right)$$

Book: Hogen, Watson, Ragatz

part II - Thermodynamics

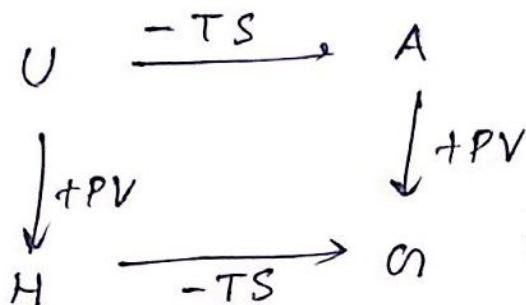
Q.3 Eq<sup>n</sup> of state

$$P = f_1(C - \dots)$$

$$T = f_2(C - \dots) \quad \text{B.T.} + 267$$

$$\mu = f_3(C - \dots)$$

Q.5



Q.4

reverse of ③

Find a fundamental eq<sup>n</sup>

Q.6

Important

$$\frac{\partial U}{\partial T^2} = - \frac{d}{dT} \left( \frac{A}{T} \right)_{V,n}$$

$$A = U - TS \Rightarrow U = A + TS, \quad S = \frac{\partial A}{\partial T}$$

$$\frac{A}{T^2} = \frac{U}{T^2} - \frac{S}{T}$$

Conditions of Equilibrium

$$T^1, T^2 = \dots$$

$$P^1, P^2 = \dots$$

$$\mu_1^1 = \mu_1^2 = \dots \quad \Delta \mu$$

Driving force for mass transfer is difference of chemical potential.

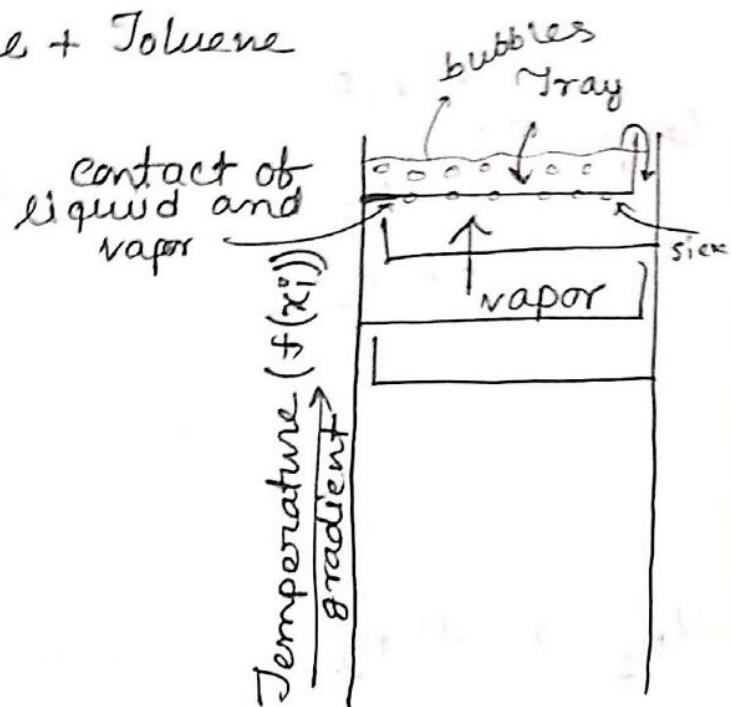
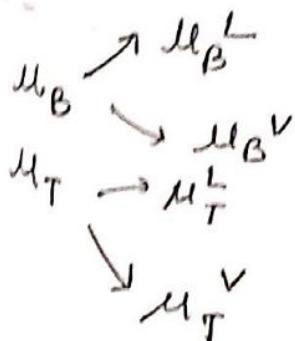
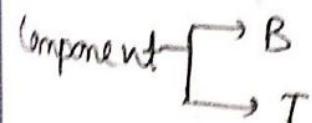
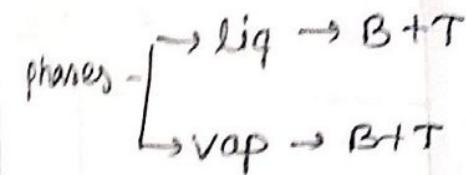
1) Distillation

2) Adsorption

3) Leaching and extraction

Species should be allowed to move between phases.

1) Distillation: Benzene + Toluene



at eqbm.

$$\left. \begin{array}{l} \mu_B^V = \mu_B^L \\ \mu_T^V = \mu_B^L \end{array} \right\}$$

Such relations are exactly same as no. of trays

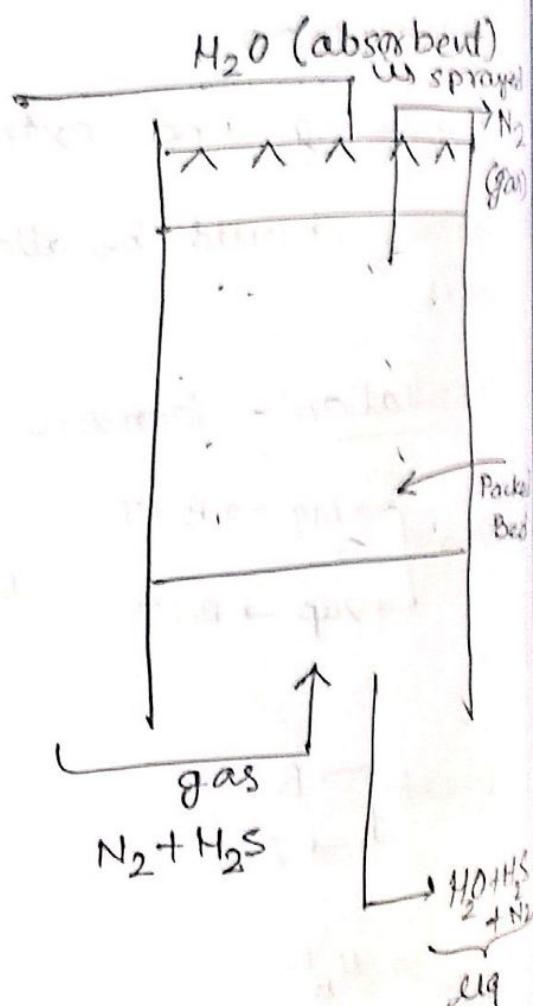
Temp. gradient  $\rightarrow f(x_i)$

$$\mu = \mu^\circ + RT \ln P$$

2) Absorption:  $H_2S$

Phases -  $\begin{cases} \text{liq} \\ \text{gas} \end{cases}$

Component -  $\begin{cases} H_2O \\ N_2 \\ H_2S \end{cases}$



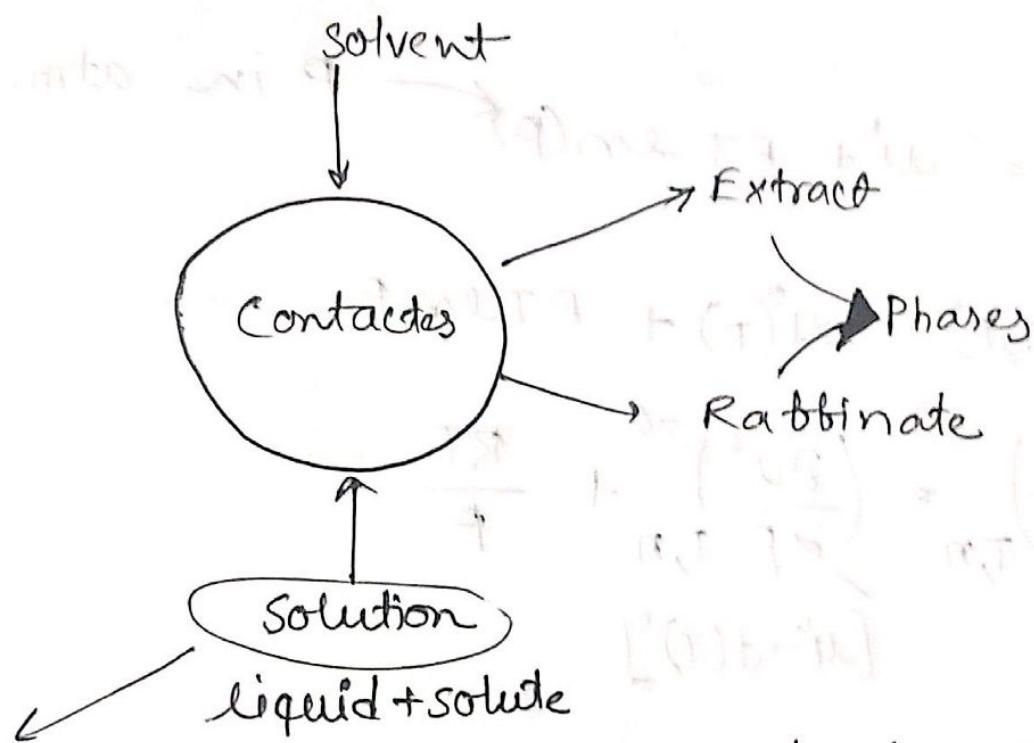
$$\mu_{N_2}^L = \mu_{N_2}^G$$

$$\mu_{H_2O}^L \quad \mu_{H_2O}^G$$

$$\boxed{\mu_{H_2S}^L = \mu_{H_2S}^G}$$

i) Tea

solid  $\rightarrow$  Inert + Solute ]  $\leftarrow$  Leaching  
liquid  $\rightarrow$  liquid + solute ]  $\leftarrow$  Extraction



Not considered as phase as at eqbm extract and raffinate is only obtained.

### The gas phase

- i) Pure Ideal gas
- ii) Pure non-ideal gas
- iii) mixture of ideal gases
- iv) mixture of non-ideal gases.

## Pure Ideal gas

$$\mu = \mu^0 + RT \ln(P/P_0)$$

$P \rightarrow \text{in atm}$   
 $P_0 = 1 \text{ atm}$

↓ chem potential  
 chem potential at std. state  
 at temp T

$$\mu = \mu^0 + RT \ln(P) \quad P \text{ in atm.}$$

$$\mu(T, P) = \mu^0(T) + RT \ln P$$

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \cancel{\left(\frac{\partial \mu^0}{\partial P}\right)_{T,n}^0} + \frac{RT}{P}$$

$[\mu^0 \rightarrow f(T)]$

$$dG = -SdT + VdP + \mu dn$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,n} = V$$

$$G = \sum \mu_i n_i = n\mu$$

$$\Rightarrow \frac{\partial \mu}{\partial P} = \frac{V}{n}$$

$$\frac{V}{n} = \frac{RT}{P} \quad \Rightarrow PV = nRT$$

$$\left(\frac{\partial \mu}{\partial T}\right)_{P,n} = \left(\frac{\partial \mu^0}{\partial T}\right)_{P,n} + R \ln P$$

$$-\frac{S}{n} = \left(\frac{\partial \mu^0}{\partial T}\right)_{P,n} + R \ln P$$

$$-S = -n \left(\frac{\partial \mu^0}{\partial T}\right)_{P,n} + nR \ln P$$

$$H = G - TS$$

$$h = \mu + TS$$

$$\cancel{s = \left(\frac{\partial \mu^0}{\partial T}\right)} \quad h = \mu^0 + \cancel{RT \ln P} - T \left(\frac{\partial \mu^0}{\partial T}\right)_{P,n} + \cancel{R \ln P}$$

$$h = \mu^0 - T \left(\frac{\partial \mu^0}{\partial T}\right)_{P,n}$$

$\downarrow$                        $\downarrow$   
 $f(T)$                        $f(T)$

$$h = \mu^0(T) - f(T) \quad \left. \begin{array}{l} h = h(T) \\ u = u(T) \end{array} \right\}$$

$$u = h - PV = h - RT$$

$$\mu = \mu^\circ + RT \ln f \quad \text{--- Non-ideal}$$

↑  
Fugacity

$\left(\frac{f}{P}\right) \rightarrow 1$  as  $P \rightarrow 0$  i.e. gas tends to behave ideally.

↓  
fugacity coefficient → indicator of non-ideal behavior of system.

$$PV = nRT$$

$$PV = z nRT$$

$\frac{f}{P} \rightarrow 1$  as  $P \rightarrow 0$  i.e. gas tends to behave ideally.

Fugacity coefficient → indicator of non-ideality of system.

$$PV = nRT$$

$$PV = z nRT$$

### Mixture of Gas

02/03/17

$$\mu = \mu^\circ + RT \ln P \rightarrow \text{ideal gas}$$

$$\mu = \mu^\circ + RT \ln f \rightarrow \text{non-ideal}$$

$f/P \rightarrow$  fugacity coefficient

as  $P \rightarrow 0$ ,  $f/P \rightarrow 1$

$$\mu = \mu^\circ + RT \ln f$$

$$\left( \frac{\partial \mu}{\partial P} \right)_{T,n} = \frac{V}{n}$$

$$d\mu|_{T,n} = \left( \frac{V}{n} \right) dP|_{T,n}$$

$$d(\mu^{\circ} + RT \ln f) \Big|_{T,n} = \left(\frac{V}{n}\right) dP \Big|_{T,n}$$

- Fugacity coefficient has physical interpretation
- Fugacity coefficient gives fugacity.

$$RT d(\ln f) \Big|_{T,n} = \left(\frac{V}{n}\right) dP \Big|_{T,n}$$

$$RT d(\ln f) = RT d(\ln P) \Big|_{T,n}$$

$$= \left(\frac{V}{n}\right) dP \Big|_{T,n} - RT \ln(P) \Big|_{T,n}$$

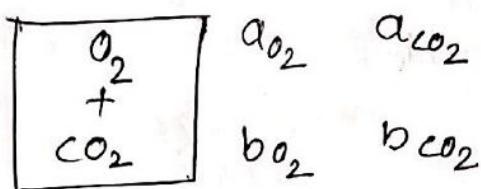
$$RT d[\ln(f/P)] \Big|_{T,n} = \left(\frac{V}{n} - \frac{RT}{P}\right) dP \Big|_{T,n}$$

$$d[\ln(f/P)] \Big|_{T,P} = \left(\frac{V}{nRT} - \frac{1}{P}\right) dP \Big|_{T,n}$$

$$\ln(f/P) = \int_0^P \left(\frac{V}{nRT} - \frac{1}{P}\right) dP$$

\* To determine fugacity coefficients, numerical method is employed to integrate the  $\left(\frac{V}{nRT} - \frac{1}{P}\right)$  at different temperatures, pressures.

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$



Averaging / Mixing rule.

$$a_m = \frac{a_{CO_2} + a_{O_2}}{2}$$

Mixture

$$b_m = \sqrt{b_{CO_2} \cdot b_{O_2}}$$

$$\mu = \mu^\circ + RT \ln P; P = \text{total pressure}$$

ideal gas

$$\mu_i = \mu_i^\circ + RT \ln p_i; p_i = \text{partial pressure of } i^{\text{th}} \text{ component in an ideal gas mixture}$$

$$\mu_i^\circ = \mu_i^\circ + RT \ln f_i$$

$$\frac{f_i}{p_i} \rightarrow 1 \text{ as } P \rightarrow 0$$

Pressure of total gas tends to zero; i.e. the entire gas mixture behaves ideally.

$$\mu_i^\circ = \mu_i^\circ + RT \ln p_i$$

$$\mu_i^\circ = \mu_i^\circ + RT \ln y_i + RT \ln P$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1^*, n_2^*, \dots, n_N^*} = \frac{RT}{P} = \bar{V}_i^*$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, n_2, \dots, n_N} = \bar{V}_i^*$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j^*}$$

$$\begin{aligned} \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, \dots, n_N} &= \frac{\partial}{\partial P} \left[ \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j^*} \right]_{T, n_1, n_2, \dots, n_N} \\ &= \frac{\partial}{\partial n_i} \left[ \left(\frac{\partial G}{\partial P}\right)_{T, P, n_j^*} \right] \\ &= \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j^*} = \bar{V}_i^* \end{aligned}$$

$$P \bar{V}_i^* = RT \quad \text{--- ideal gas mixture}$$

$$\sum_{i=1}^N n_i \bar{V}_i^* = V_T$$

$$G = \sum \mu_i n_i = \sum \bar{G}_i^* n_i$$

$$\sum_{i=1}^N n_i^* \frac{RT}{P} = V_T$$

$$\frac{RT}{P} \sum_{i=1}^N n_i^* = V_T$$

$$\frac{n_r RT}{P} = V_T$$

$$PV_T = n_T RT$$

$$(\Delta V_{\text{mixing}})_{\text{ideal}}^{\circ} = 0$$

Apparantly it's not possible to determine whether the system is single component or multi component.

$$\mu_i^{\circ} = \bar{\mu}_i + RT \ln y_i + RT \ln P$$

$$\Rightarrow \frac{\mu_i^{\circ}}{T} = \frac{\bar{\mu}_i}{T} + R \ln y_i + R \ln P.$$

$$\left[ \frac{\partial}{\partial T} \left( \frac{\mu_i}{T} \right) \right]_{P, n_1, \dots, n_N} = \left[ \frac{\partial}{\partial T} \left( \frac{\bar{\mu}_i}{T} \right) \right]_{P, n_1, \dots, n_N} + 0 + 0$$

$$\overline{\sigma}_i = \bar{H}_i - T \bar{S}_i$$

$$\sigma_i = H_i - TS_i$$

$$\downarrow \quad \downarrow \quad * \downarrow$$

$$\overline{\sigma}_i = \bar{H}_i^{\circ} - T \bar{S}_i^{\circ}$$

~~$$\mu_i^{\circ} = \bar{\mu}_i^{\circ}$$~~      
$$\mu_i^{\circ} = \bar{H}_i^{\circ} - T \bar{S}_i^{\circ}$$

$$\bar{H}_i^{\circ} = \mu_i^{\circ} + T \bar{S}_i^{\circ}$$

$$\frac{\bar{H}_i^{\circ}}{T^2} = \frac{\mu_i^{\circ}}{T^2} + \frac{\bar{S}_i^{\circ}}{T} = \frac{\mu_i^{\circ}}{T^2} - \frac{1}{T} \left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_1, \dots, n_N}$$

$$\frac{\bar{H}_i^{\circ}}{T^2} = -\frac{\partial}{\partial T} \left( \frac{U_i^{\circ}}{T} \right)_{P,n}, \dots$$

$$\frac{\bar{H}_i^{\circ}}{T^2} = -\frac{\partial}{\partial T} \left( \frac{U_i^{\circ}}{T} \right)_{P,n}, \dots$$

$$\bar{H}_i^{\circ} = -T^2 \frac{\partial}{\partial T} \left( \frac{U_i^{\circ}}{T} \right)_{P,n}, \dots$$

$(\Delta H_{\text{mixing}})^{\text{ideal}} = 0$  provided Temp. is const.

$(\Delta V_{\text{mix}})^{\text{ideal}} = 0$

→ Gives important conclusion.  $\Rightarrow$  Interactions in ideal gases is zero  
Non ideality effect

1) Finite size

2) Finite interaction

03/03/17

### Liquid vs. Gases

Ideal gases - No interactions

Ideal gas mixtures  $\rightarrow \Delta H_{\text{Mix}}^{\circ} = 0$   
 $\Delta V_{\text{Mix}} = 0$

### Condition for Ideality of gas

- Particles that constitute the gas, do not interact
- The size of the particle is negligible

03/03/17

## Liquid vs. Gases

Ideal gases - No interactions

Ideal gas mixtures  $\rightarrow \Delta H^{\text{Mix}} = 0$   
 $\Delta V^{\text{Mix}} = 0$

### Condition for Ideality of gas

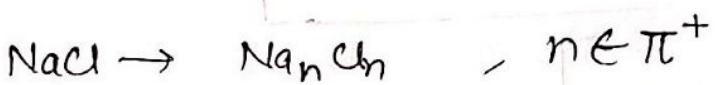
- Particles that constitute the gas, do not interact
- The size of the particle is negligible

when compared to vessel volume.

## Ideal liquid mixture

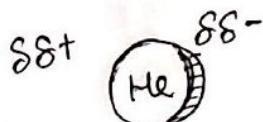
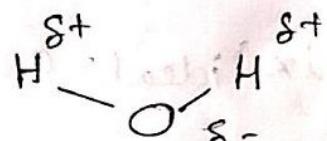
No interactions  $\rightarrow$  fundamentally impossible.

Solids  
+ liquids } condensed matter phase

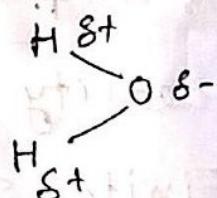


Interactions in a system

1) Electrostatic



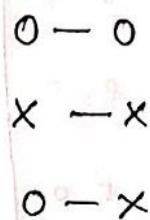
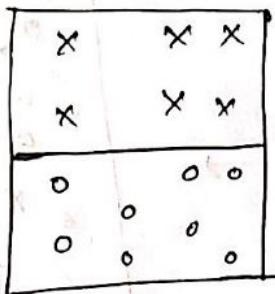
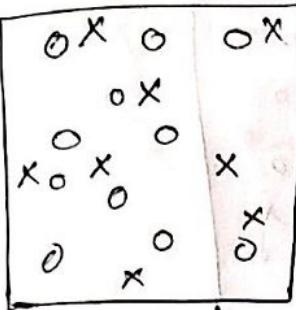
Time fluctuating dipole moment



2) gravitational

3) Weak Force

4) Strong Force } in the nucleus



Ideality is defined in terms of interactions between molecules.

→ If  $O-X$  is similar to  $O-O$  and  $X-X$ , then the sol<sup>n</sup> is ideal.

- 1) Do gases always mix? → Yes
- 2) Do liquids always mix? → No

$$G = H - TS$$

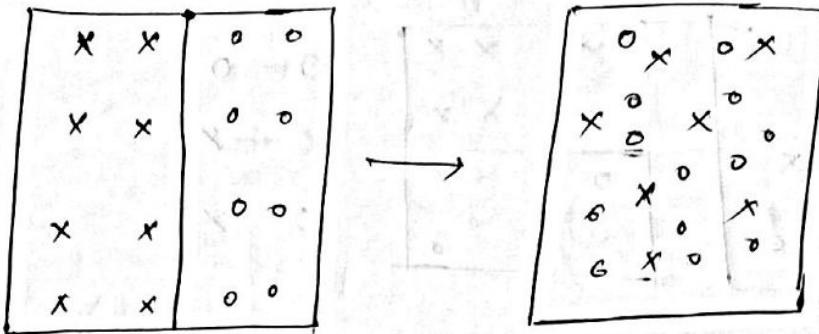
$$\Delta G = \Delta H - T\Delta S$$

Enthalpic contribution      Entropic contribution

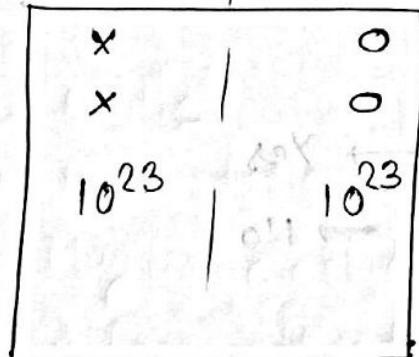
When a process is occurring:-

→ Enthalpically Favoured  
or,

→ Entropically Favoured



### Mixing of gas

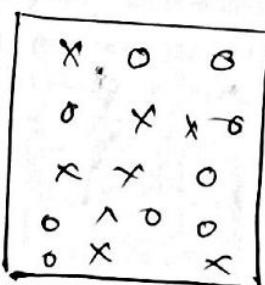


$$P_1 = \frac{1}{2^{10^{23}}} \approx 0$$

$$\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2^2} \quad \frac{1}{2^4}$$

For practical purposes

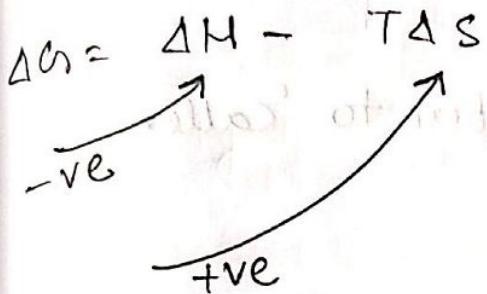
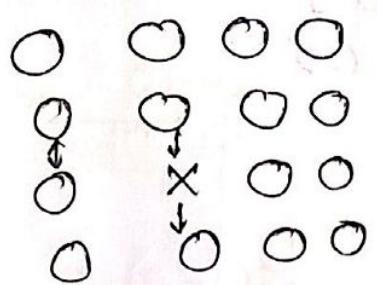
highly improbable



$$P_2 \approx \frac{1}{2}$$

$\Rightarrow$  Entropy facilitates to mix

# For gases under normal condition, only entropic contribution is considered. If there is high degree of non ideality, both entropic and enthalpic contribution should be considered



In liquid, both the contributions are considered.

### Books

0. Prausnitz
1. Hougen-Watson
2. Kyle
3. Tester-Modell
4. callen
5. Denbigh
6. Smith-van Ness

1. Distillation
2. Absorption
3. Adsorption
4. leaching
5. Extraction
6. Drying
7. Humidification
8. Membrane separation
9. crystallization

→ "Hougen-Watson" Tutorial-1  
for Q2

Q.7 & Q.3 are inverse

$$\left(\frac{\partial U}{\partial S}\right)_{V, n_1, \dots} = T$$

$$\left(\frac{\partial S}{\partial U}\right)_{V, n_1, \dots} = \frac{1}{T}$$

Refer to 'Callen'

# ① Elastic

② Electrostatic

③ Magnetic effect

④ Surface effect

$$dU = TdS - pdV + \sum_{i=1}^N u_i dn_i + \sigma dA$$

$$\left(\frac{\partial S}{\partial \sigma}\right)_{T, V, n_1, \dots, n_N}$$

$$df = TdS - pdV + \sum_{i=1}^N u_i dn_i - Ad\sigma$$

$$df_2 = -sdT - pdV + \sum_{i=1}^N u_i dn_i - Ad\sigma$$

## Tutorial-2

$$1) \frac{\text{Gibbs-Duhem eqn}}{-SdT + VdP - \sum_{i=1}^N n_i d\mu_i} = 0$$

$$dG = TdS - pdV + \sum_{i=1}^N \mu_i dn_i \quad \dots \quad (1)$$

$$U = TS - PV + \sum \mu_i n_i \quad \dots \quad (2)$$

$$dU = TdS + SdT - pdV + VdP + \sum \mu_i dn_i + \sum n_i d\mu_i \quad \dots \quad (3)$$

Subtracting (1) from (3)

$$0 = -SdT + VdP - \sum_{i=1}^N n_i d\mu_i$$

$$2) \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{T, P, n_1, \dots, n_N} = \bar{\mu}_i$$

$$\bar{B}_i = \left( \frac{\partial B}{\partial n_i} \right)_{T, P, n_1, \dots}$$

$$B = B(T, P, n_1, \dots, n_N)$$

$$B = \sum_{i=1}^N n_i \bar{B}_i$$

$$B = \left( \frac{\partial B}{\partial T} \right)_{P, n_1, \dots, n_N} + \left( \frac{\partial B}{\partial P} \right)_{T, n_1, \dots, n_N} + \sum_{i=1}^N n_i \left( \frac{\partial B_i}{\partial n_i} \right)_{T, P}$$

$$dB = \sum n_i d\bar{B}_i + \sum \bar{B}_i dn_i \quad \dots \quad (1)$$

$$dB = \left( \frac{\partial B}{\partial T} \right) dT + \left( \frac{\partial B}{\partial P} \right) dP + \sum_{i=1}^N \left( \frac{\partial B}{\partial n_i} \right) dn_i \quad \dots \quad (2)$$

$$3) U = U(S, V, n_1, \dots, n_N)$$

$$y^{n+2} = y^0 - \sum_{i=1}^{n+2} m_i x_i$$

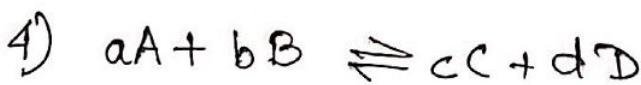
$$= U - [TS - PV + \sum_{i=1}^N u_i n_i]$$

$$= U - TS + PV - \sum_{i=1}^N u_i n_i$$

$$dy^{n+2} = 0 \quad \text{at eqbm.}$$

$$dU - Tds - sdT + PdV + VdP - \sum_{i=1}^N u_i dn_i - \sum_{i=1}^N n_i du_i$$

$$-sdT + Vdp - \sum_{i=1}^N n_i du_i = 0$$



$$cC + dD - aA - bB = 0$$

$$\sum_{i=1}^N \gamma_i c = 0$$

$\gamma \rightarrow -ve$  for reactant  
 $+ve$  in product

$$u_i^A = u_i^B \quad \forall i$$

For non-reactive system

$$S = S(U, n_1, n_2, \dots, n_N)$$

$Adx + Bdy + cdz = 0 \Rightarrow$  not applicable  
for reactive system

$$\sum_{j=1}^N \nu_j \mu_j^\circ = 0$$

For reaction eqbm:

$$\sum (E) \text{ all reactants} = \sum (E) \text{ all products}$$

⑥ combination of  
 ① Gibbs-Duhem eq<sup>n</sup>  
 +

$$② \sum \nu_j \mu_j^\circ = 0$$

⑥ condition of eq<sup>bm</sup>

$$P^1 = P^2$$

$$T^1 = T^2$$

$$\mu_i^1 = \mu_i^2 + i -$$

N <sub>2</sub>	1
O <sub>2</sub>	1
He	1
CO <sub>2</sub>	1
NO <sub>x</sub>	1
CO	1

$$d\bar{\mu}_i = -S_i dT + V_i dP + \sum_{j=1}^N \left( \frac{\partial \mu_j}{\partial n_j} \right)_{T, P, n_i^*, dn_i} dn_j$$

↗

$$d\mu = -SdT + VdP + \sum \mu_i dn_i$$

$$\frac{\partial n_i}{\partial n_j} = \delta_{ij} \rightarrow \text{dirac delta}$$

$$= 0 \quad \text{for } i \neq j$$

$$= 1 \quad \text{for } i = j$$

08/03/17

Lewis Randall Rule

$$\mu_i = \mu_i^\circ + RT \ln p_i$$

$$\mu_i = \mu_i^\circ + RT \ln f_i$$

$$\mu = \mu^\circ + RT \ln f$$

↑ Pure component fugacity

$$\ln \left( \frac{f}{P} \right) = \int_0^P \left( \frac{V}{nRT} - \frac{1}{P} \right) dP$$

$$\mu_i = \mu_i^\circ + RT \ln P + RT \ln y_i$$

$$\begin{matrix} \uparrow & \uparrow \\ f(T) & g(T, P) \end{matrix}$$

$$\mu_i = \mu_i^*(T, P) + RT \ln y_i \quad \dots \textcircled{1}$$

$$\mu_i = \mu_i^\circ(T) + RT \ln f_i \quad \dots \textcircled{2}$$

$$\underbrace{\mu_i^\circ(T) - \mu_i^*(T, P)}_{\text{fugacity of } T, P} = -RT \ln \left( \frac{f_i}{y_i} \right)$$

Should be composition independent

$$f_i = y_i f_i^{\text{pure}}$$

$$\frac{f_i}{y_i} = \frac{f_i(y_i)}{y_i(y_i)}$$

$f_i(y_i=1)$

= pure component fugacity

$$= f_i^{\text{pure}}$$

$$\frac{f_i}{y_i} = f_i^{\text{pure}}$$

$$\boxed{f_i = y_i f_i^{\text{pure}}}$$

Lewis Randall Rule

## Intuitive vs. non-intuitive quantities

$$\mu_i = \overline{G}_i$$

Gibbs-Duhem eq<sup>n</sup>

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\Rightarrow n_1 d\mu_1 = -n_2 d\mu_2$$

$$\Rightarrow d\mu_1 = -\left(\frac{n_2}{n_1}\right) d\mu_2$$

$$\lim_{n_2 \rightarrow 0} d\mu_1 = -\infty$$

$$\mu = \mu_i^\circ + RT \ln f_i$$

$$\mu = \mu^\circ + RT \ln f$$

Vapor liquid eqbm.  $\rightarrow \mu^V, \mu^L$

$$\mu^V = \mu_i^{\circ V} + RT \ln f^V$$

$$\mu^L = \mu_i^{\circ L} + RT \ln f^L$$

$$\Rightarrow \boxed{f^L = f^V}$$

$$\text{or, } f_i^{\circ L} = f_i^{\circ V}$$

$$\mu_i = \mu_i^\circ + RT \ln p_i \xrightarrow[p_i \rightarrow x_i]{} \text{ideal gas mixture}$$

$$\mu_i = \mu_i^\circ + RT \ln x_i \xrightarrow{} \text{ideal liquid mixture}$$

depends on composition too

$$\mu_i = \mu_i^\circ + RT \ln f_i \quad (\leftarrow \text{Non ideal gas mixture})$$

$$\mu_i = \mu_i^* + RT \ln a_i \quad (\rightarrow \text{non ideal liquid mixture})$$

↑

Activity

↓  
Molecular models

$$\mu_i = \mu_i^* + R + \ln(\gamma_i x_i)$$

↓

~~compressibility~~ Activity coefficient

### Molecular Models

- ① NRTL → Non random two liquid model
- ② UNIQUAC → Universal quasi chemical model
- ③ UNIFAC → UNIQUAC functional group activity coefficient model

① Excess function

② Mixing function

$$B^{Ex} = B - B^{\text{Ideal}} \quad \text{at same } T, P, x_i$$

$$B^{\text{Mix}} = \sum_{i=1}^N n_i B_i^{\text{Mix}} - \sum_{i=1}^N n_i B_i^{\text{Pure}}$$

$B^{\text{Mix}}$  vs.  $B^{\text{Ex.}}$

Lewis - Randall Mixture → A mixture which behaves as a single component mixture

$$\Delta V^{\text{Mix}} = \Delta V^{\text{Ex.}}$$

$$\Delta H^{\text{Mix}} = \Delta H^{\text{Ex.}}$$

$$\Delta U^{\text{Mix}} = \Delta U^{\text{Ex.}}$$

~~But not~~

but not  
 $\Delta G_{\text{mix}}$  and  $\Delta G^{\text{Ex}}$   
 $\Delta A_{\text{mix}}$  and  $\Delta A^{\text{Ex}}$  } need  
 not equal  
 ↓  
 Entropy dependent

### 1. Ideal solution behavior

### 2. Regular sol<sup>n</sup> behavior

→ ~~if~~ system has difference in interaction between different molecules. Enthalpic contribution dependent

### 3. Athermal sol<sup>n</sup> behavior

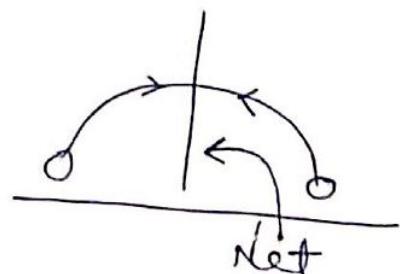
→ Interactions are similar but depends on entropy also. Both ~~enthalpic and~~ Entropic contribution is dependent.

### # Reversibility

#### Macroscopic reversibility

Newton's Laws of motion are time reversible, macroscopically reversible.

⇒ Direction of interaction can not be distinguished



## Multiphase Systems

$$U = U(S, V, n_1, n_2, \dots, n_N) \leftarrow N+2$$

↑ in a "given" phase

Single phase-multiphase systems

$$U^1 = U(S^1, V^1, n_1^1, \dots, n_N^1) \quad \dots \quad (N+2) \text{ variables}$$

$$U^2 = U(S^2, V^2, n_1^2, \dots, n_N^2) \quad \dots \quad (N+2) \text{ variables}$$

$(2N+4)$

$$A^1 = A(T^1, V^1, n_1^1, n_2^1, \dots, n_N^1) \quad \dots \quad (N+2)$$

$$A^2 = A(T^2, V^2, n_1^2, n_2^2, \dots, n_N^2) \quad \dots \quad (N+2)$$

$\left. \begin{array}{l} T^1 = T^2 \\ 2N+4 \end{array} \right\}$

1) Equal across the phases -  $T, P, u_i$

2) Differ in different phases -  $S, V, H, U$  ← order parameters

can not be used  
to distinguish  
between phases

vary across phases

Intensive vs. Extensive variables

Indensity

Extent

Description of a system can be measured/explained in terms of a combination of intensive and extensive properties

How many intensive variables are allowed to be specified?

$$b = b(c_1, c_2, c_3, \dots, c_{N+1}, n_T)$$

$$db = \sum_{i=1}^{N+1} \left( \frac{\partial b}{\partial c_i} \right) dc_i + \boxed{\left( \frac{\partial b}{\partial n_T} \right) dn_T} \xrightarrow{c_i \rightarrow 0}, \text{ as } b \rightarrow \text{intensive}$$

$$b = b(c_1, c_2, \dots, c_{N+1})$$

any intensive property can be expressed as  $(N+1)$  independent variable intensive properties within a phase.

component,  $\pi$ -phase system  
of variables to be specified in  $\pi$  phase =  $\pi(N+1)$

$$T^1 = T^2 = T^3 = \dots = T^\pi \Rightarrow (\pi-1) \text{ relationships}$$

$$P^1 = P^2 = P^3 = \dots = P^\pi \rightarrow (\pi-1)$$

$$U_i^1 = U_i^2 = U_i^3 = \dots = U_i^\pi \rightarrow N(\pi-1); \forall i$$

---

Total number of equilibrium  
relationships =  $(N+2)(\pi-1)$

$$y = mx + c$$



One variable  
is allowed  
to be specified

$$z = 4y + 3x + 2$$



Two variables  
are allowed

$$\text{degree of Freedom } (f) = \overbrace{\pi(N+1)}^{\text{No of known}} - \overbrace{(N+2)(\pi-1)}^{\text{No of relationships}} = N+2-\pi$$

$$= \pi - \cancel{\pi}$$

$$\boxed{\pi + f = N+2} \quad \leftarrow$$

Gibbs Phase Rule

In a  $(N-\pi)$  system      ↗ For non-reactive system

$$\text{Max \# of intensive variable} = N - \pi + 2$$

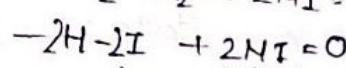
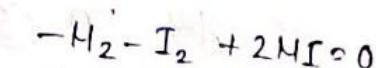
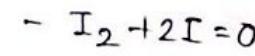
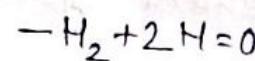
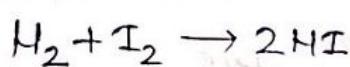
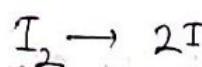
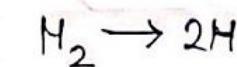
$$\text{total \# of variable (Int + extensive)} = \pi(N+2)$$

Non reactive system ( $N-\pi$ )

$$f = n - \pi + 2$$

Reactive system with "R" number of independent reaction

$$f = n - \pi + 2 - R$$



can be obtained from rest three

Stoichiometric Matrix

species	H <sub>2</sub>	H	I <sub>2</sub>	I	HI
H <sub>2</sub> , I <sub>2</sub> , H, I, HI	-1	+2	0	0	0
H <sub>2</sub> , I <sub>2</sub> , H, I, HI	0	0	-1	+2	0
H <sub>2</sub> , I <sub>2</sub> , H, I, HI	-1	0	-1	0	+2
H <sub>2</sub> , I <sub>2</sub> , H, I, HI	0	-2	0	-2	+2

$$\begin{array}{l} R_1 \\ R_2 \\ R_3 \\ R_4 \end{array} \left[ \begin{array}{ccccc} H_2 & H & I_2 & I & HI \\ -1 & +2 & 0 & 0 & 0 \\ 0 & 0 & -1 & +2 & 0 \\ -1 & 0 & -1 & 0 & +2 \\ 0 & -2 & 0 & -2 & +2 \end{array} \right] = A$$

Elementary-Row operation

→ Non zero rows

→ Rank of the matrix

4th reaction as a linear combination of other reactions

$$P(A) = R$$

↑ no. of independent reaction

$$f = N - \pi + 2 - R$$

difference

Why R?

Why -ve?

We can not change no. of moles independently in a reactive system.

① Pure gas,  $N = 1$

$$\pi = 1$$

$f = 2 \rightarrow$  bivariant system

$$PV = nRT$$

$$PV = RT$$

gas in eqbm. with its liquid state is called vapor

② Vapor-liquid,  $N = 1$

$$\pi = 2$$

$f = 1 \rightarrow$  univariant system

③ Vapor-liquid-solid eqbm.

$$N = 1$$

$$\pi = 3$$

$f = 0 \rightarrow$  invariant system

- ① Region
- ② lines
- ③ points

## Q Ternary distillation of ortho, meta, para xylene

$$\pi = 2$$

$$N = 3$$

Only temperature can be adjusted and rest other changes automatically. The engineer suspect that the walls are acting as catalyst for isomerization. How to establish that the engineer is correct or not?

$$\underline{\underline{Sol^n}} \quad f = 1$$

$$f_{NR} = N - \pi + 2$$



$$f_R = N - \pi + 2 - R$$

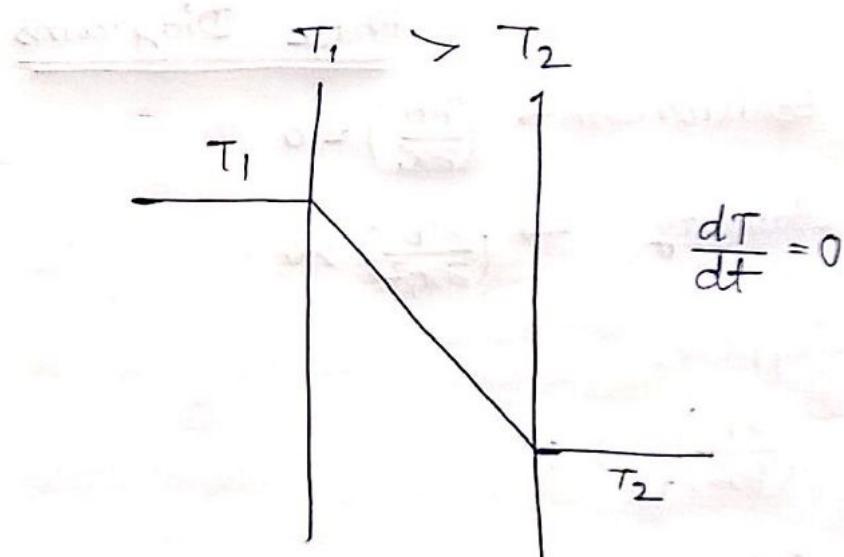
$$f_{NR} = 3 - 2 + 2 = 3$$

$$f_R = 3 - 2 + 2 - 2 = 1$$

## Eqbm. & stability

→ at eqbm,

$$\text{net flux} = 0$$



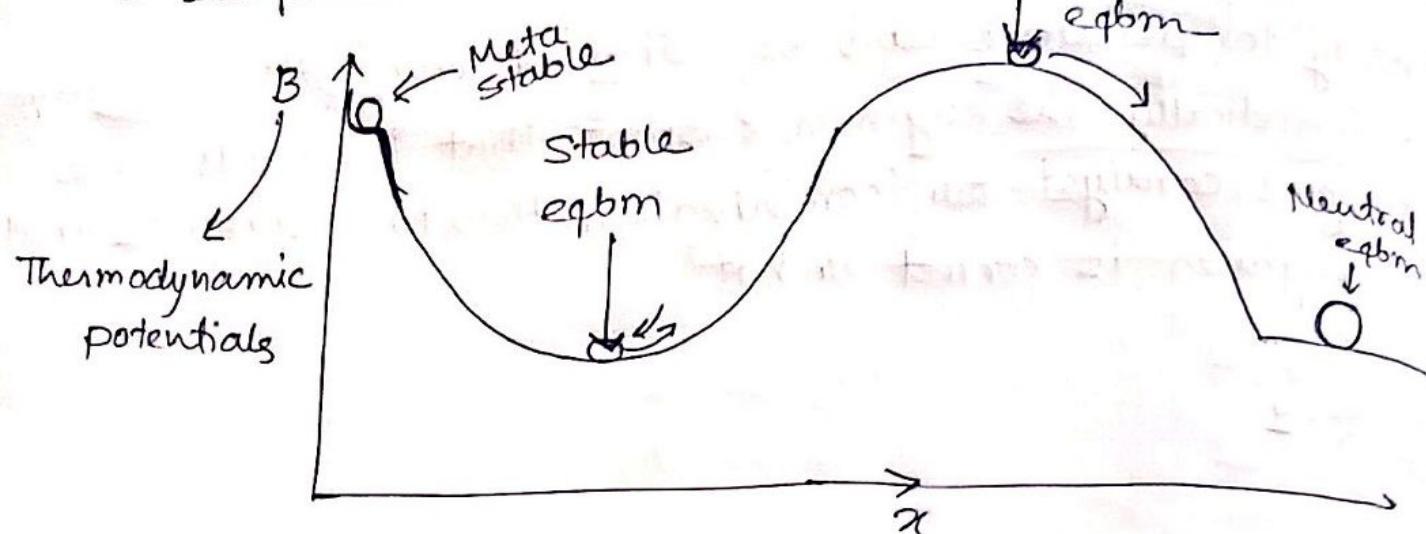
→ Steady state

→ Net flux ≠ 0

→ Not in eqbm.

$$\frac{\partial B}{\partial x} = 0 \text{ at eqbm}$$

↓ Independent variable



$$\frac{\partial^2 B}{\partial x^2} < 0 \rightarrow \text{unstable}$$

$$\frac{\partial^2 B}{\partial x^2} > 0 \rightarrow \text{stable}$$

Meta stable  $\Rightarrow$  conditional eqbm.

Crystallisation occurs at meta stable condition

### Phase Diagrams

$$\text{Equilibrium} \rightarrow \left( \frac{\partial B}{\partial x_i} \right) = 0$$

$$\text{Stability} \rightarrow \left( \frac{\partial^2 B}{\partial x_i^2} \right) > 0$$

Suppose,

$$\left( \frac{\partial^2 A}{\partial V^2} \right)_{T,n} > 0$$

$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial V} \right)_{T,n} \right]_{T,n} > 0$$

$$\boxed{\left( \frac{\partial P}{\partial V} \right)_{T,n} < 0} \rightarrow \text{stability criterion}$$

or

criterion for mechanical  
Stability

(IX)

- \* Tutorial 3 Solutions  
— Refer Dembigh

### Phase diagrams

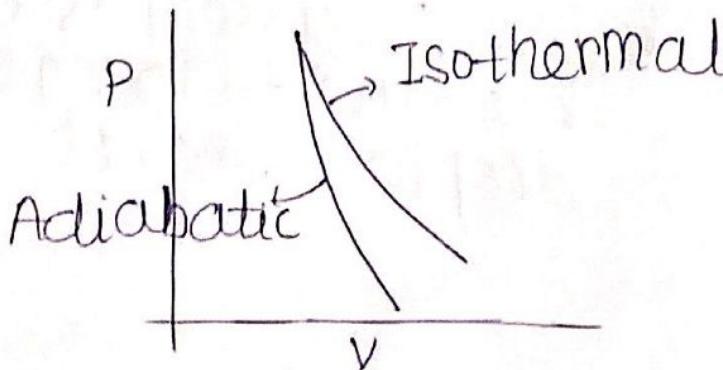
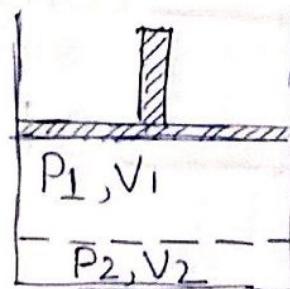
#### VLE systems

Equilibrium  $\rightarrow \frac{\partial B}{\partial x_i} = 0$

Stability  $\rightarrow \frac{\partial^2 B}{\partial x_i^2} > 0$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T, n} > 0$$

(stability criteria)



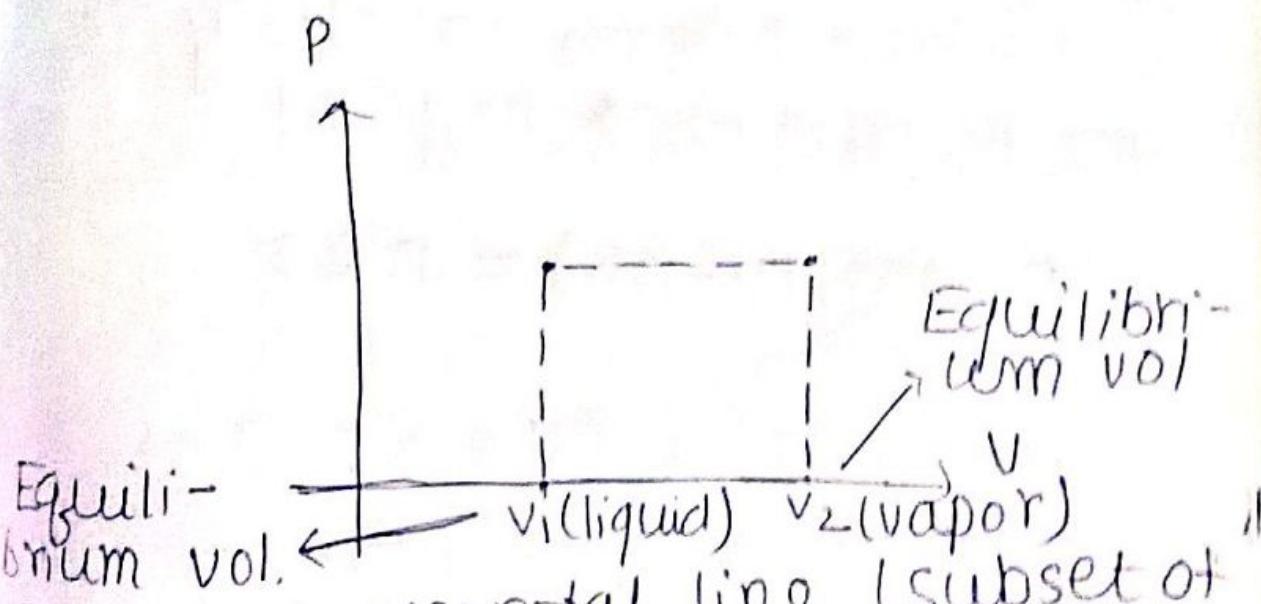
$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial V} \right) \right]_{T,n} > 0$$

$$\Rightarrow \boxed{\left( \frac{\partial P}{\partial V} \right)_{T,n} < 0} \rightarrow \text{stability criteria}$$

criterion for mechanical stability of a system

\*Importance of stability criterion:

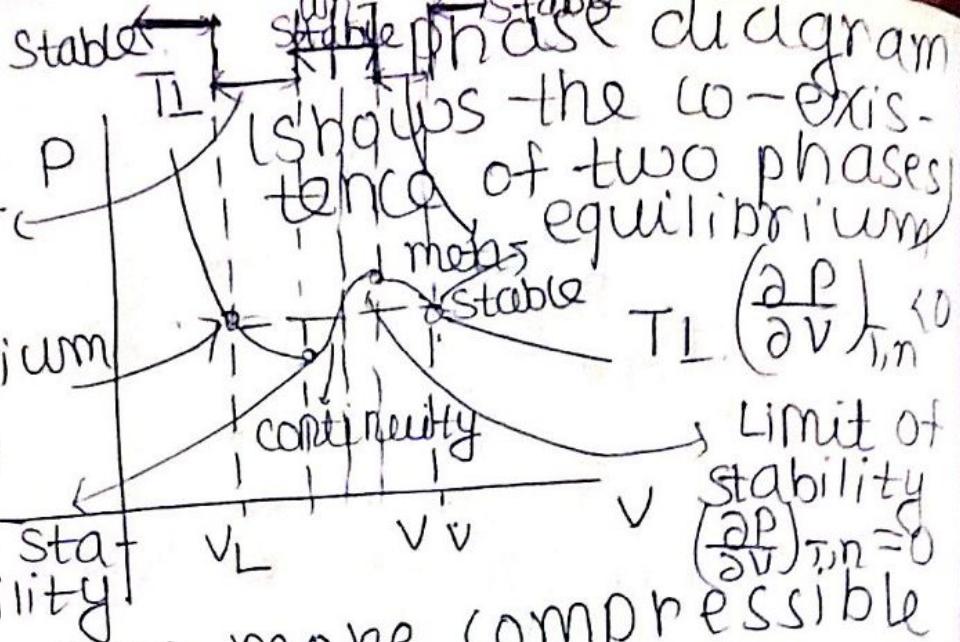
① coordinates of phase diagram



Every horizontal line (subset of them) corresponds to an equilibrium state due to

$$\left( \frac{\partial A}{\partial V} \right)_{T,n} = 0$$

$$\rightarrow \underline{\underline{P = 0}}$$



Gases are more compressible than liquids.

(stability is necessary for us to observe a system).

(Experiment should be performed very carefully in the metastable region)

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$\alpha V^3 + \beta V^2 + \gamma V + \delta = 0 \rightarrow V_1$$

$$\alpha x^3 + b x^2 + cx + d = 0. \quad V_2$$

↓

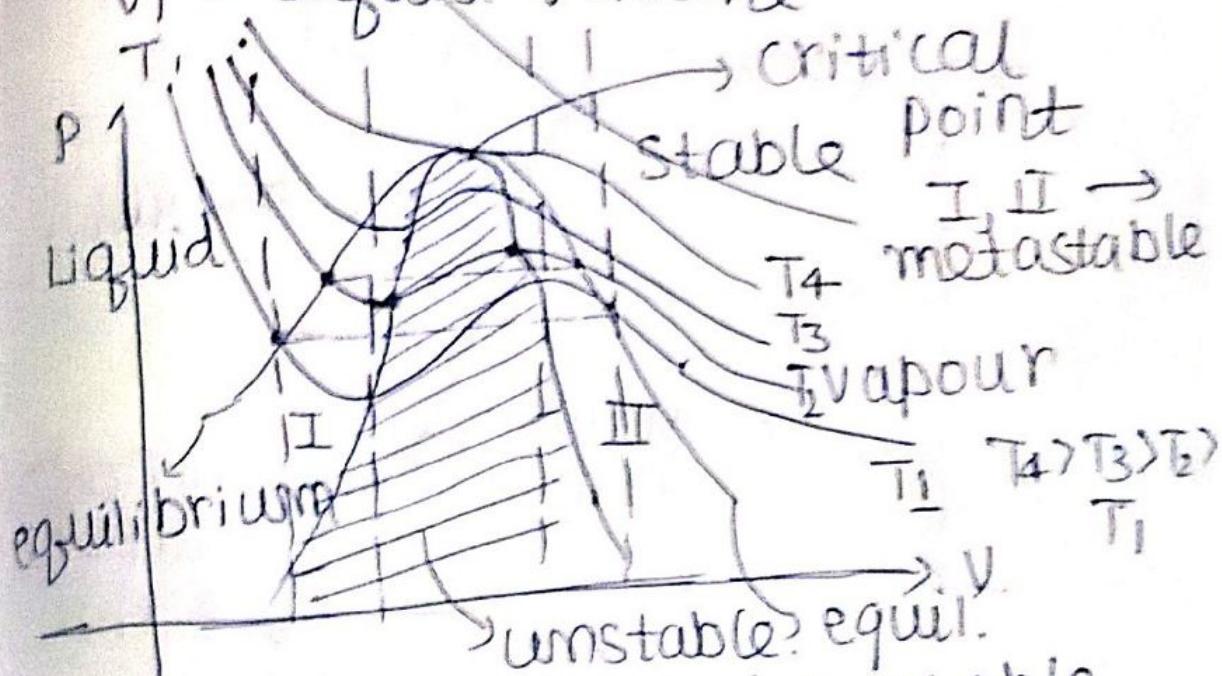
3 solutions

$\left. \begin{matrix} V_1 \\ V_2 \\ V_3 \end{matrix} \right\}$  Let All are real solutions  
(positive)

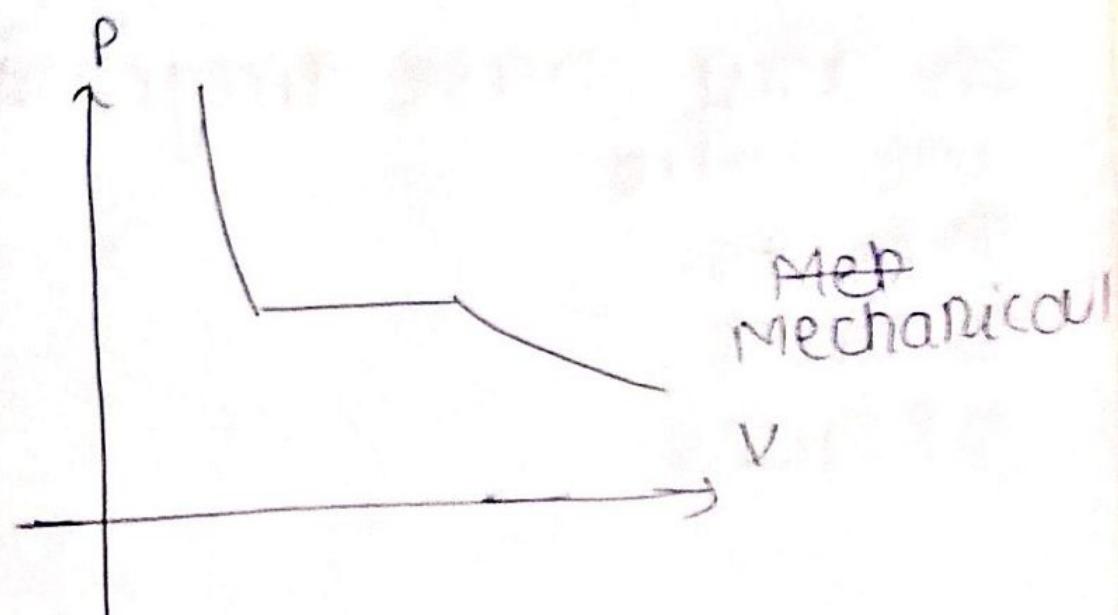
Let  $V_3 > V_2 > V_1$

$V_3$  = Vapor volume

$V_1$  = Liquid volume

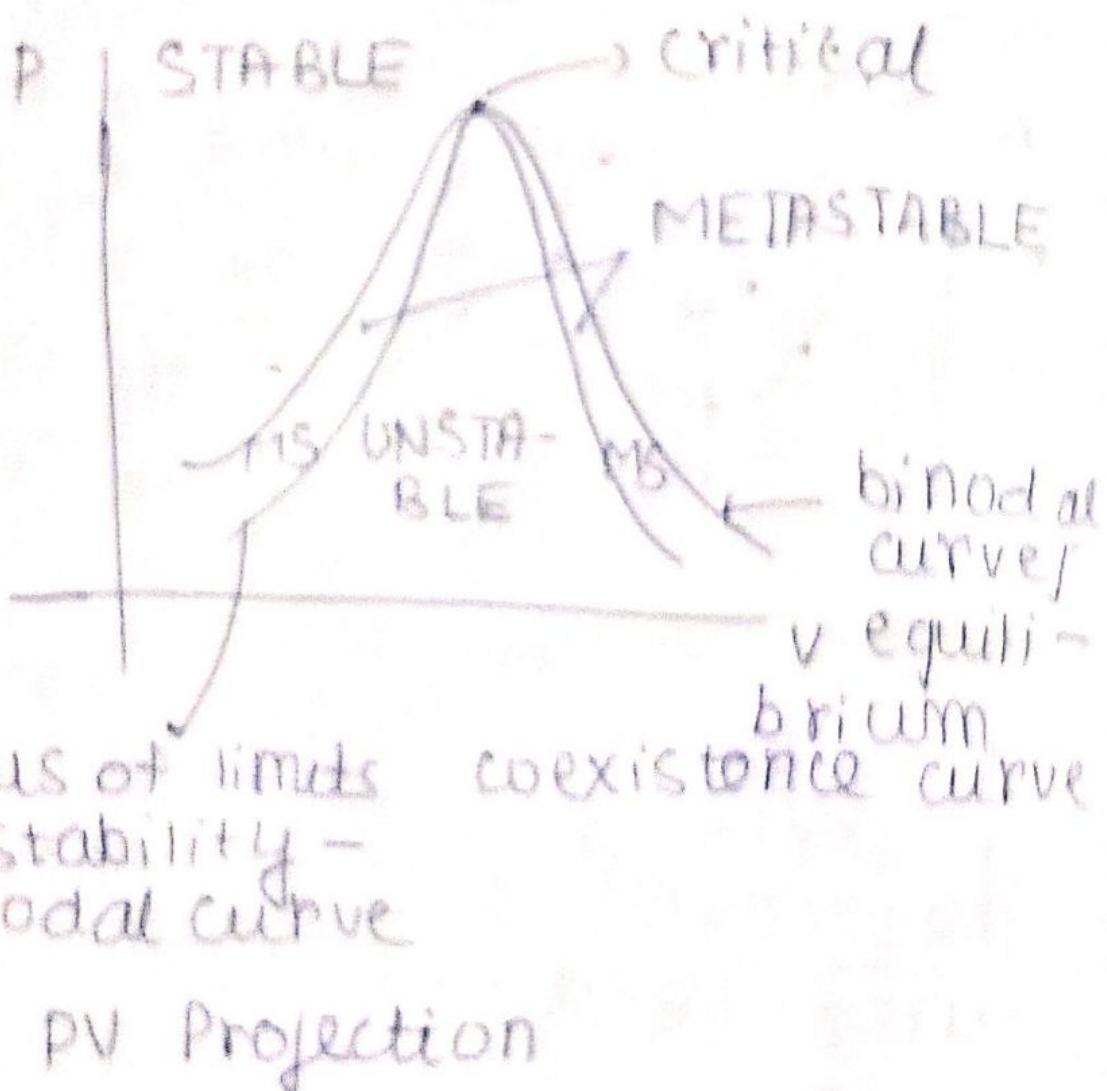


The system will be stable in the region which is on the convex side of the curve (bell shaped)



Above the critical point, we can approximate gas as the ideal one, and we can use the ideal gas equation

$$PV = NRT$$



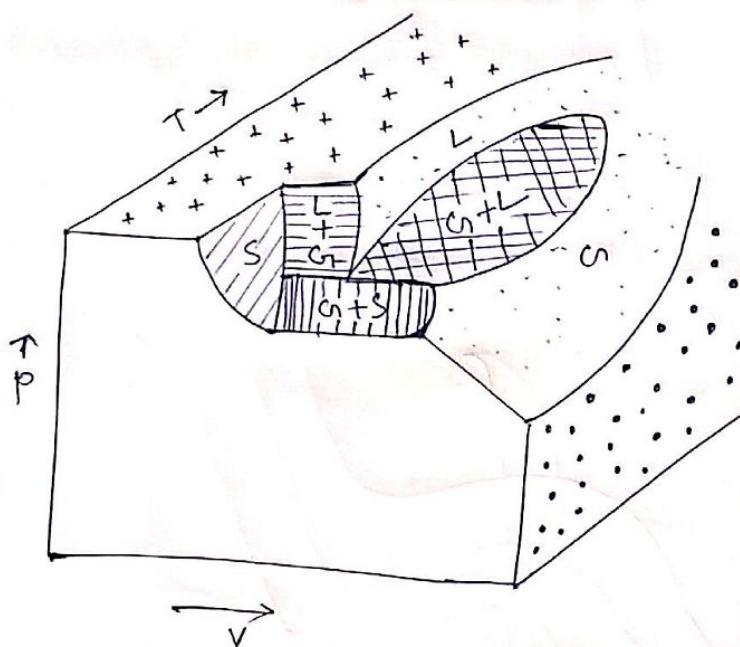
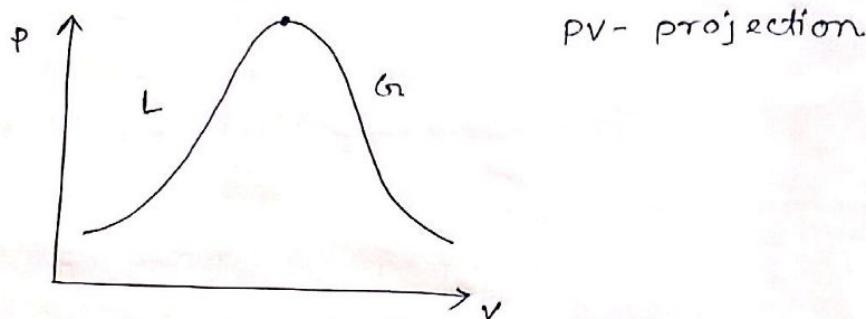
PV Projection

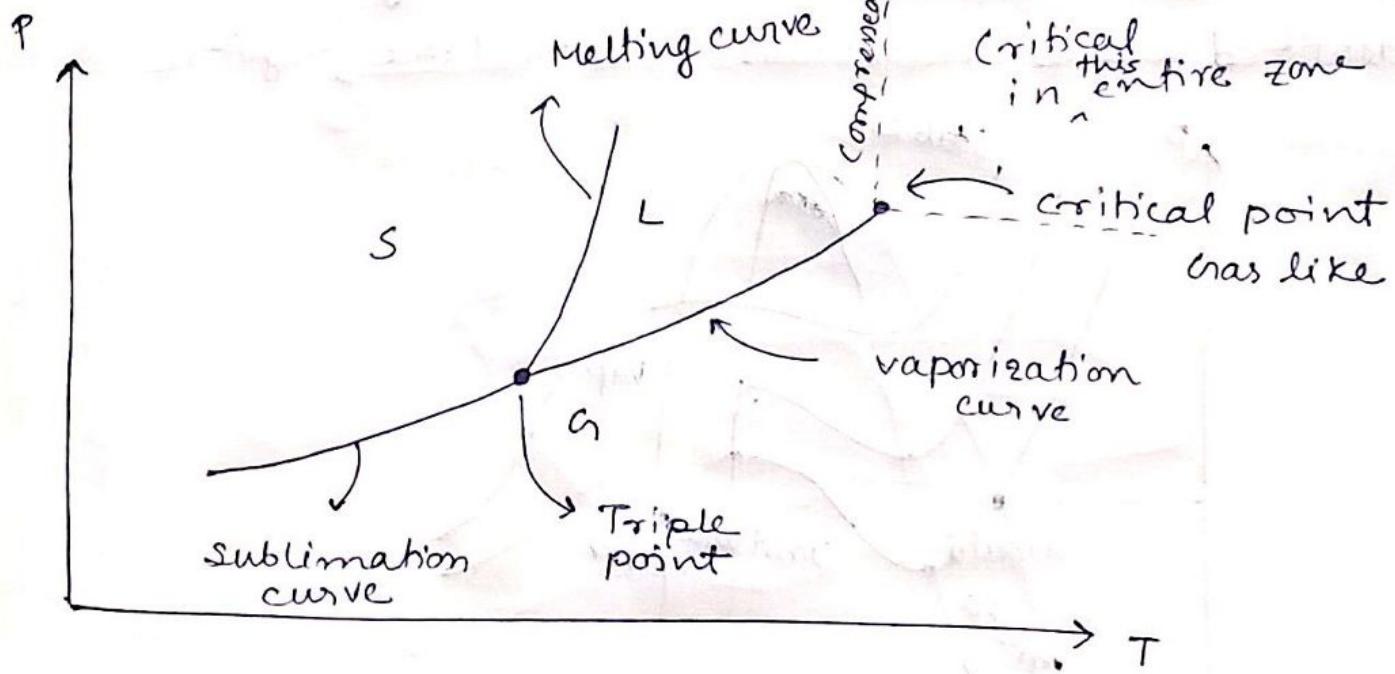
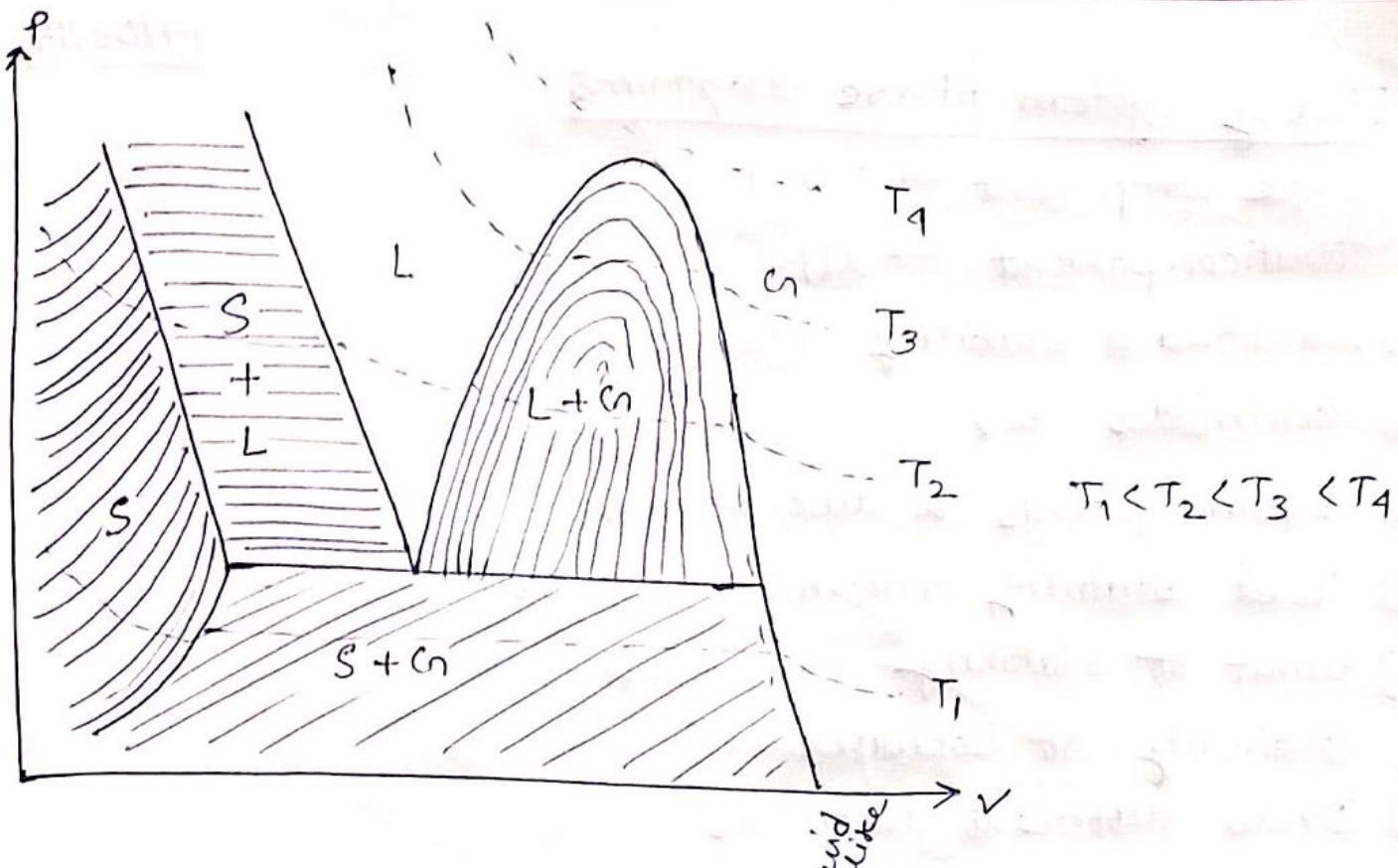
In any phase diagram,  
we have

- ① Points
- ② Curves
- ③ Regions

16/03/17

P-V-T diagram





Gas, liquid eqbm curve does not exist beyond critical point.

\* Although latest experiment shows existence of the curve

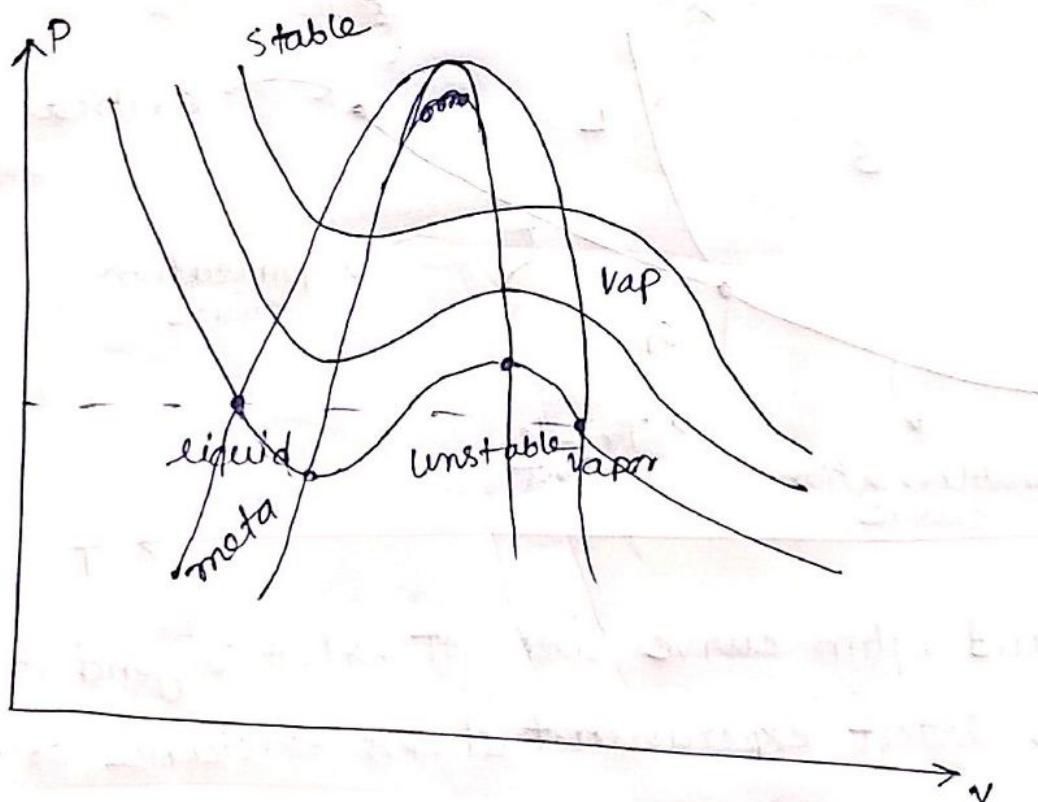
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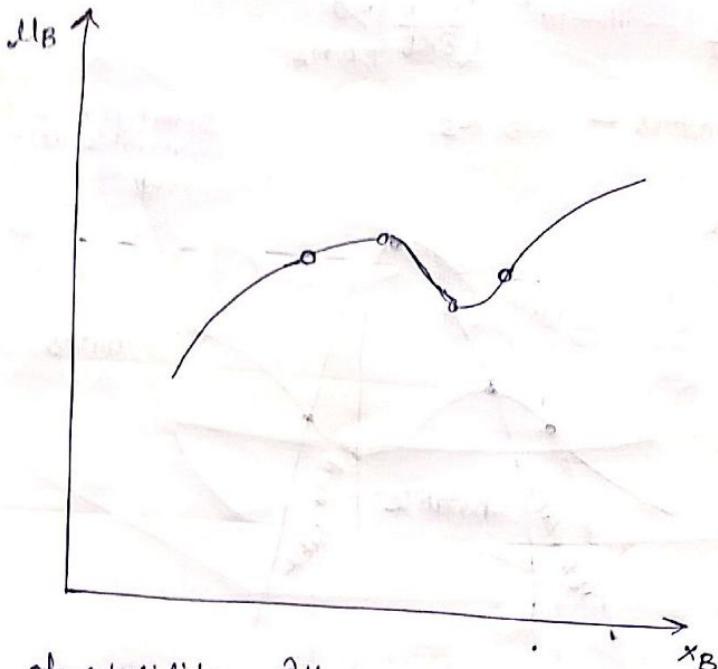
## Binary system phase diagrams

Pure component  $\rightarrow P, V, T$

Multicomponent  $\rightarrow \mu_i$

- 1) Identified a stability criterion.
- 2) coordinates  $P-V$
- 3) Eqbm. points & two phases
- 4) Used stability criterion to draw isocurves
- 5) limit of stability
- 6) continuity of isocurves
- 7) Drew different isocurves
- 8) Loci of eqbm points and limits of stability
- 9) Identified stable, metastable and unstable region





At limit of stability  $\frac{\partial \mu_B}{\partial x_B} = 0$   
here  $\frac{\partial \mu_i}{\partial x_i} = 0$

$\frac{\partial \mu_i}{\partial x_i}$  either  $> 0$   
~~or~~  $< 0$  for stability

Which potential relates to  $\mu_i$ ?

$$\underbrace{\frac{\partial}{\partial x_i} \left( \frac{\partial G_i}{\partial n_i} \right)}_{P, T, n_i} > 0 \Rightarrow \frac{\partial \mu_i}{\partial x_i} > 0$$

Gives constant composition curves

$$\Rightarrow \text{limit of stability} \rightarrow \left( \frac{\partial \mu_B}{\partial x_B} \right) = 0$$

$$\mu_B = \left( \frac{\partial G_B}{\partial n_B} \right)_{T, P, n_A}$$

$$\left( \frac{\partial \mu_B}{\partial x_B} \right)_{T, P, n_A} = \frac{\partial}{\partial x_B} \left[ \left( \frac{\partial G}{\partial n_B} \right)_{T, P, n_A} \right]_{T, P, n_A} > 0$$

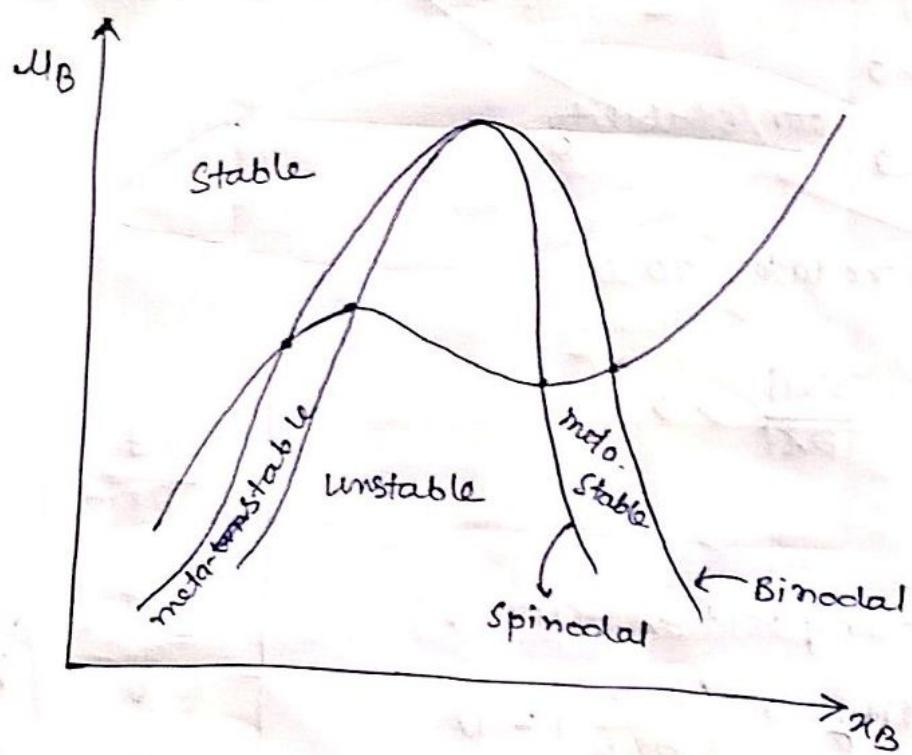
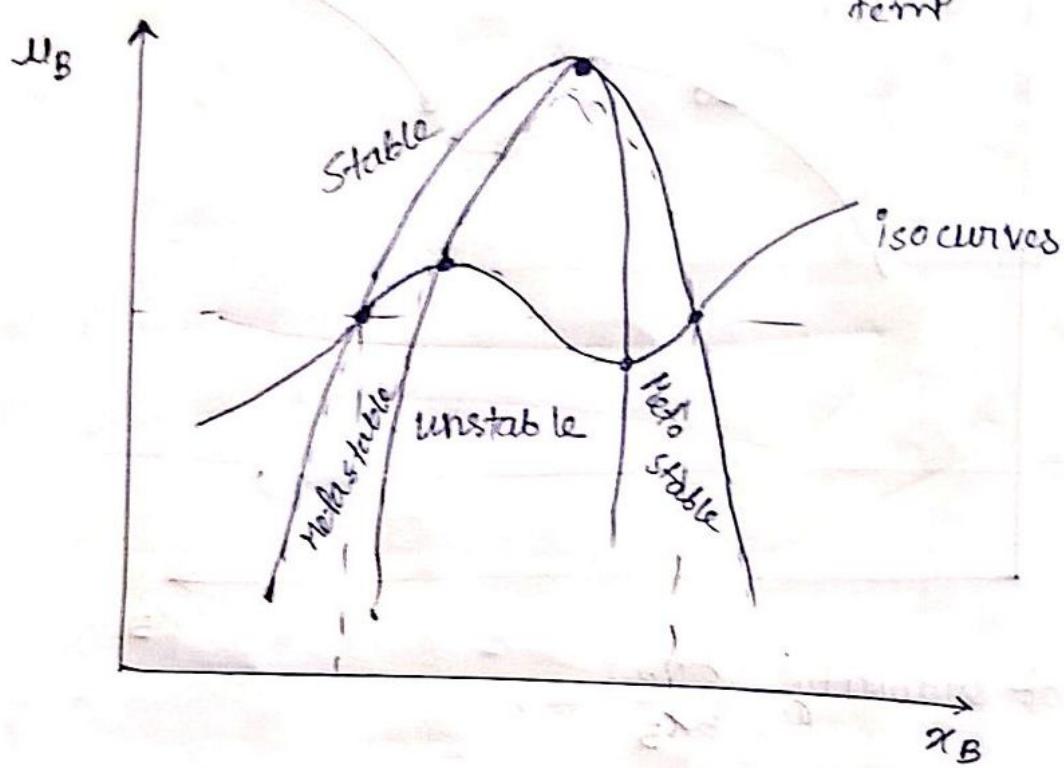
$\frac{\partial^2 f}{\partial x^2}$   
 $\frac{\partial^2 f}{\partial y^2}$   
 $\frac{\partial^2 f}{\partial x \partial y}$

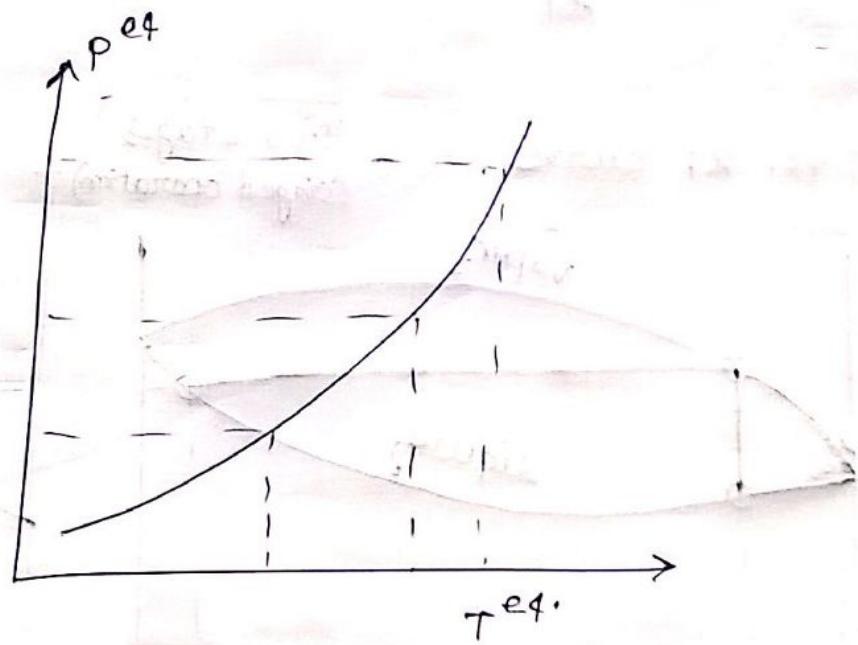
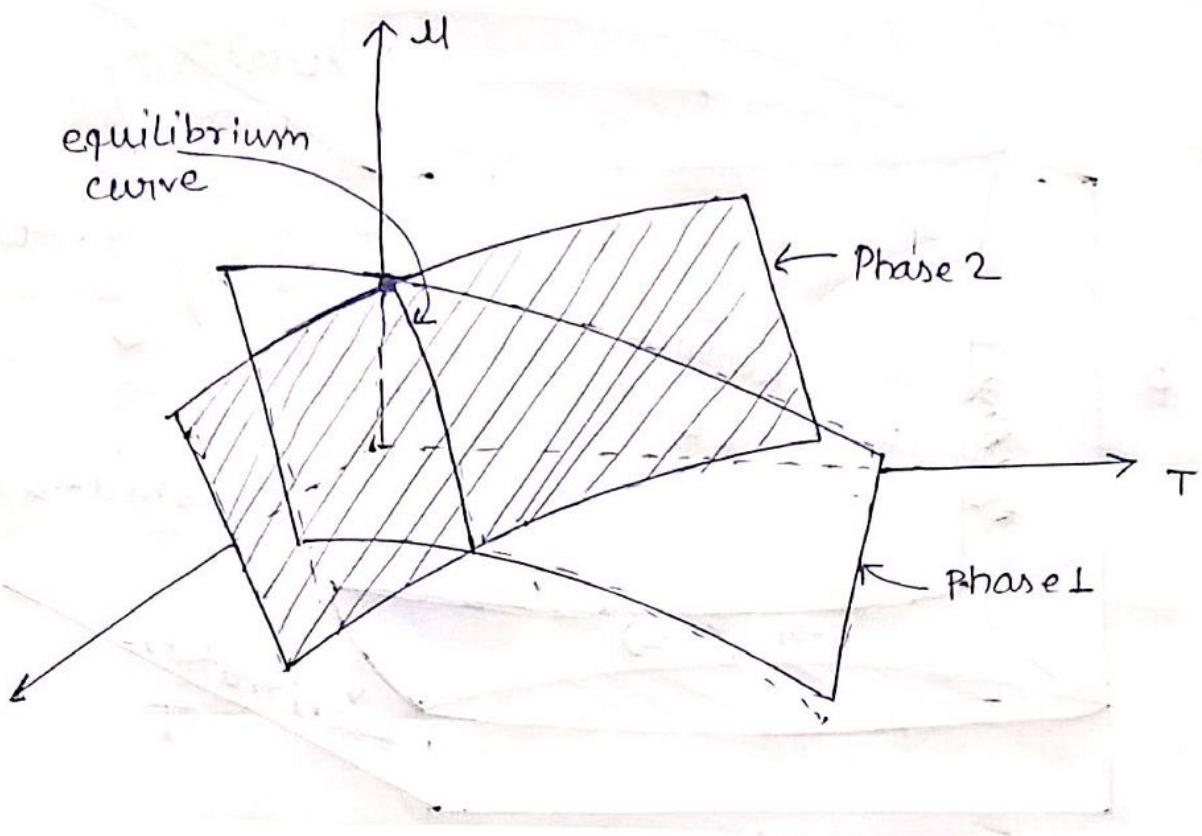
} all can  
be used  
as stability  
criterion

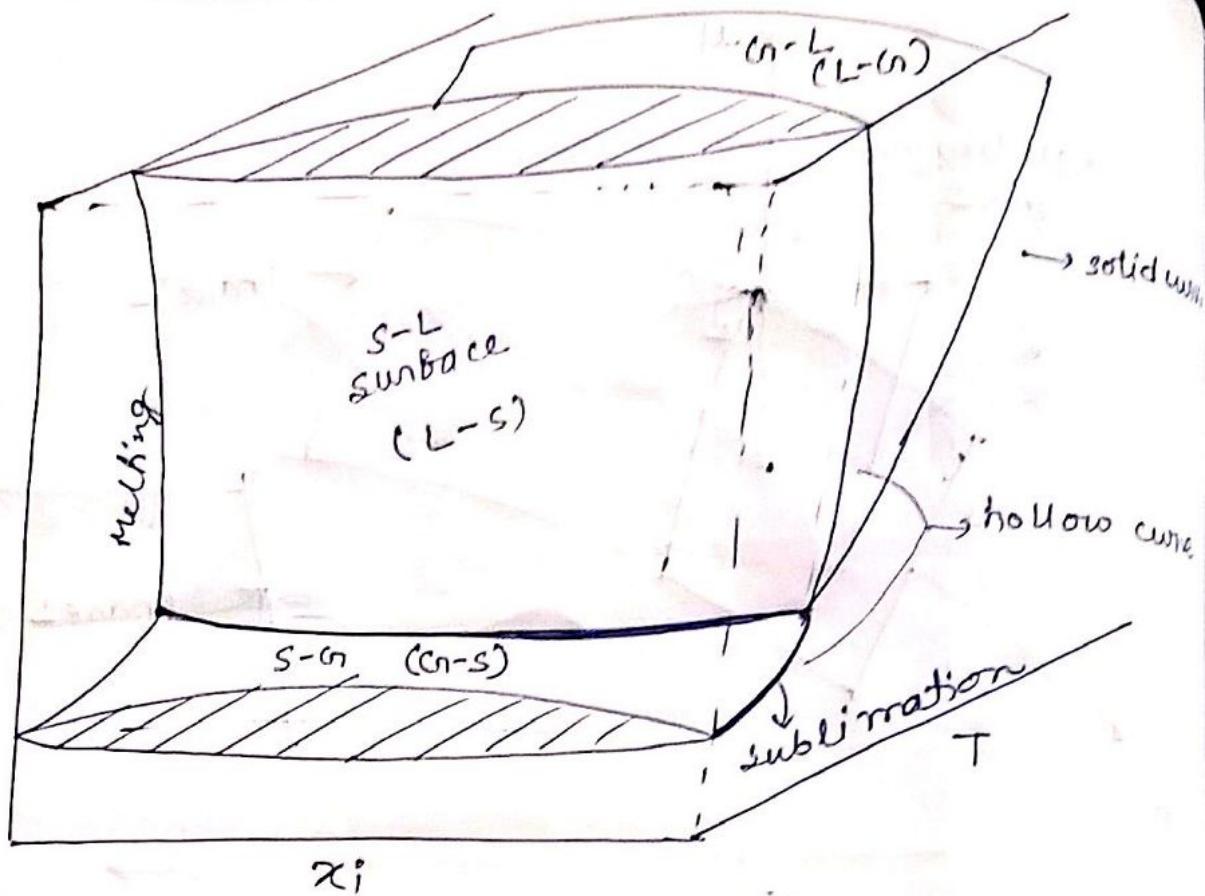
① Stability criteria:  $\left(\frac{\partial \mu_B}{\partial x_B}\right)_{T, P, n_A} > 0$

② Co-ordinates  $\rightarrow \mu_B, x_B$

Difference in independent variable decreases with temp

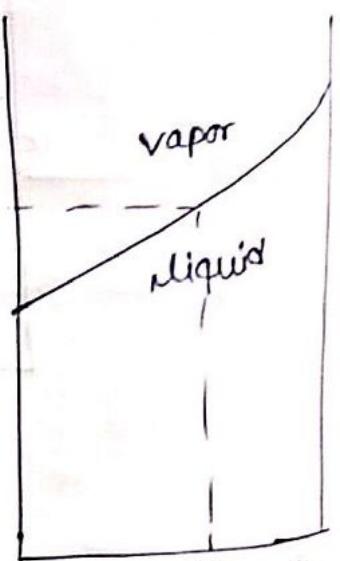
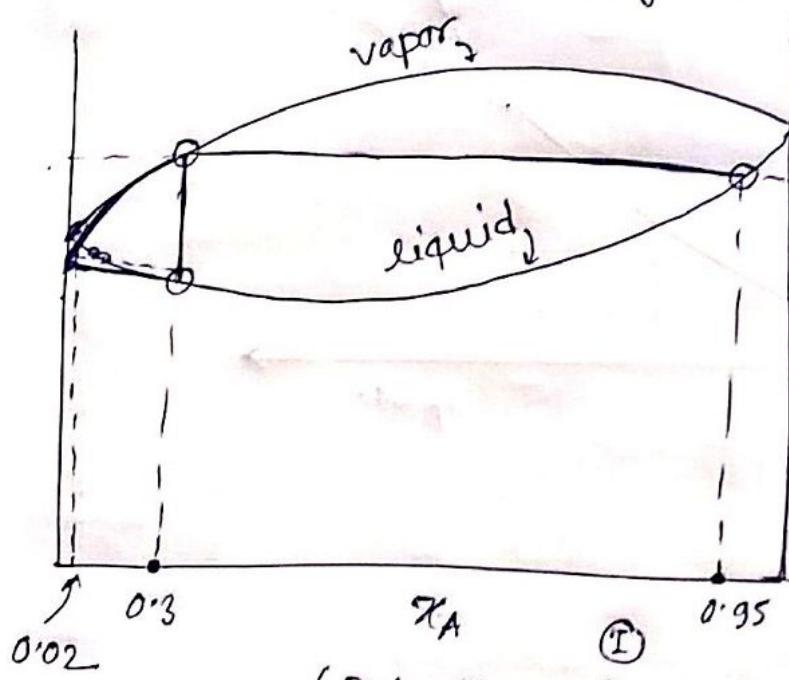






cal  $T$  vs.  $x_i$  curve

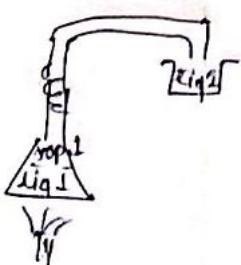
Two stages  
(staged operation)  $T$



(Projection of  
binary phase  
diagram)

(lets assume)  
this happen

distillation

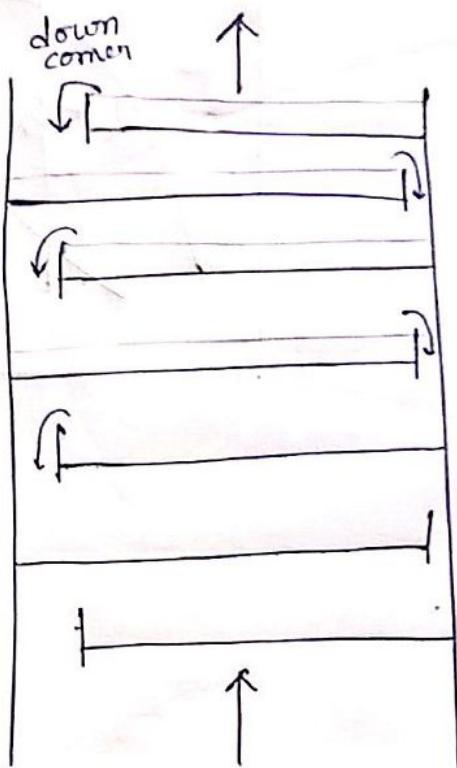


composition of liquid 2

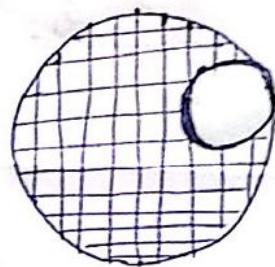
= composition of vapor 1

for case ① distillation simply fails as

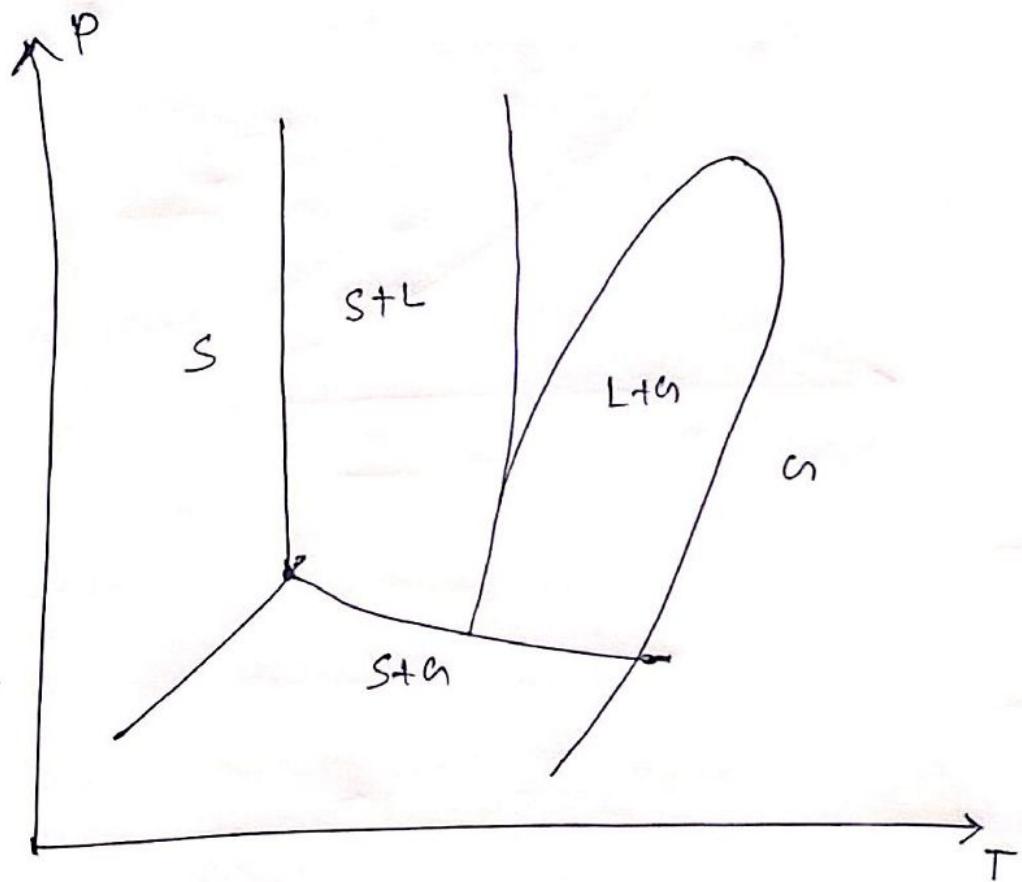
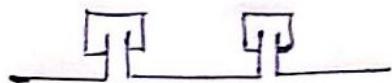
composition of liquid 1 = composition of liquid 2

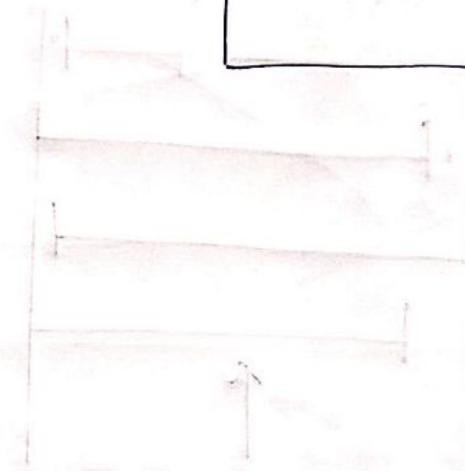
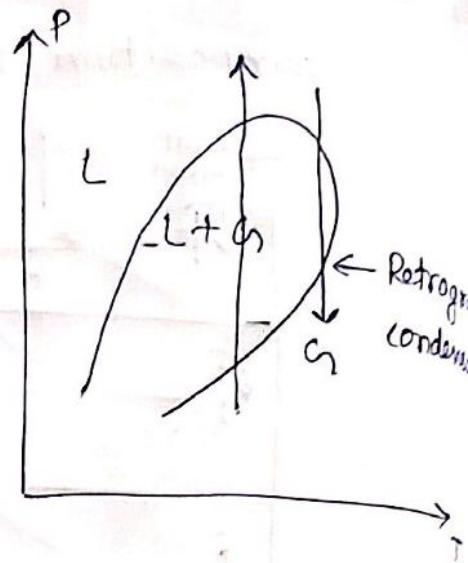
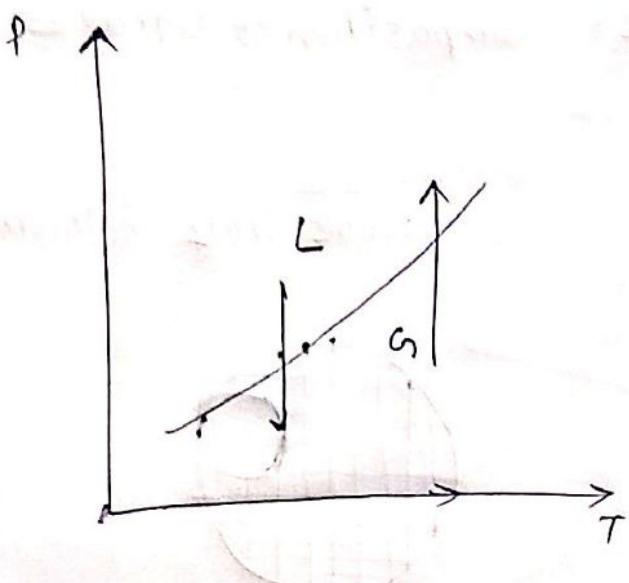


sieve-tray column



Bubble capped column





## Critical Phenomenon

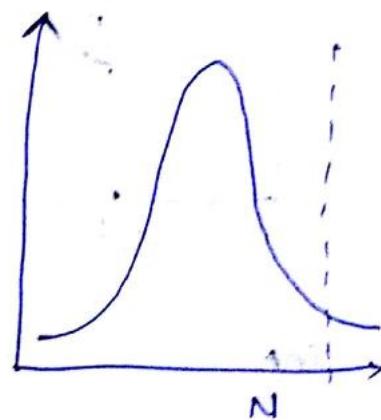
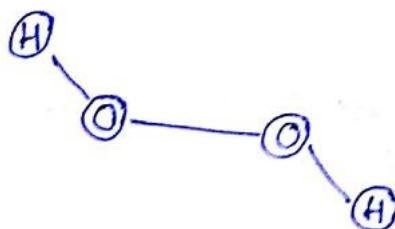
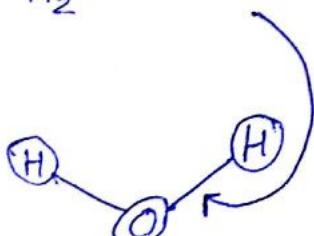
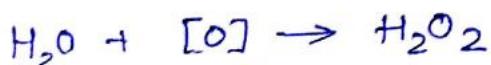
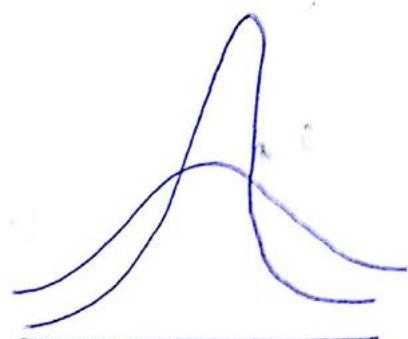
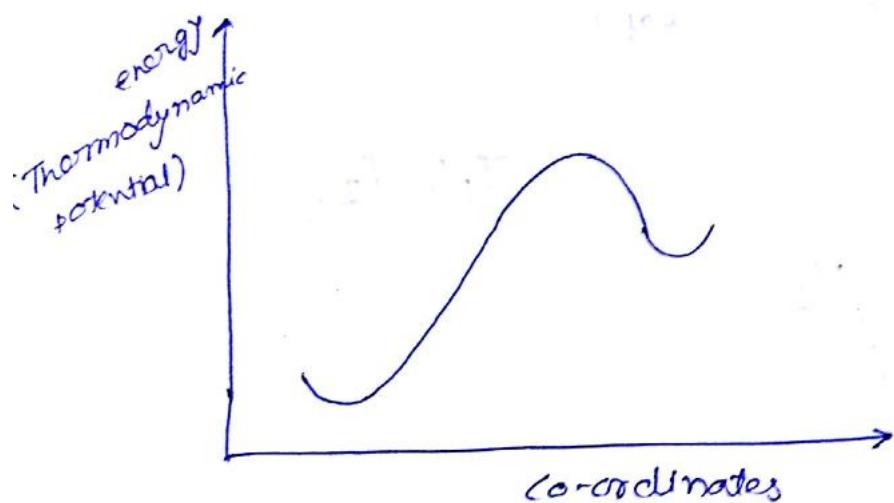
Landau theory ← Lev Landau

①  $P - V - T$ ,  $\mu - P - T$

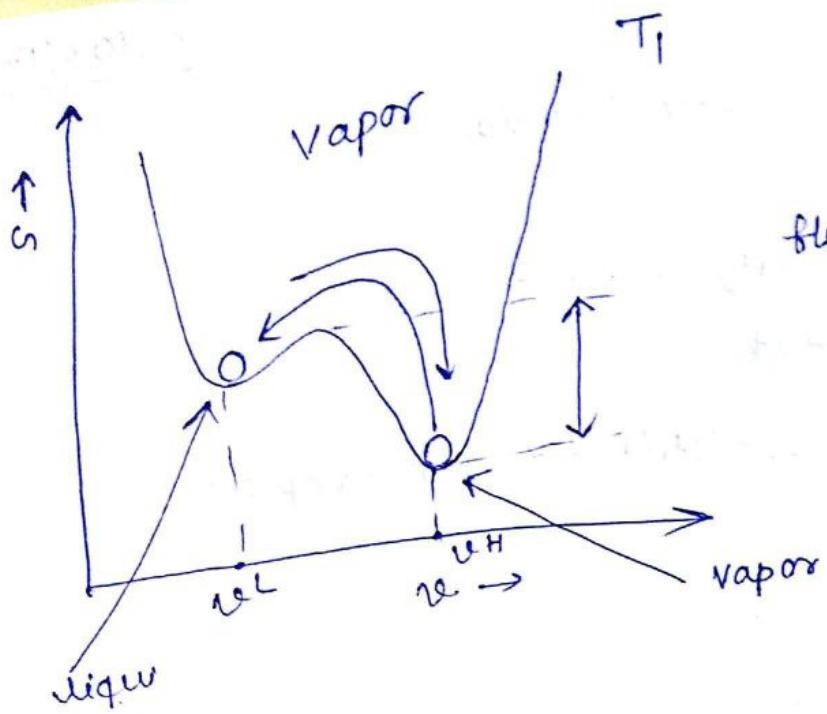
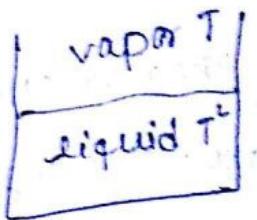
② Projections - stability criteria

③ Super critical state

Energy landscape & distribution of properties

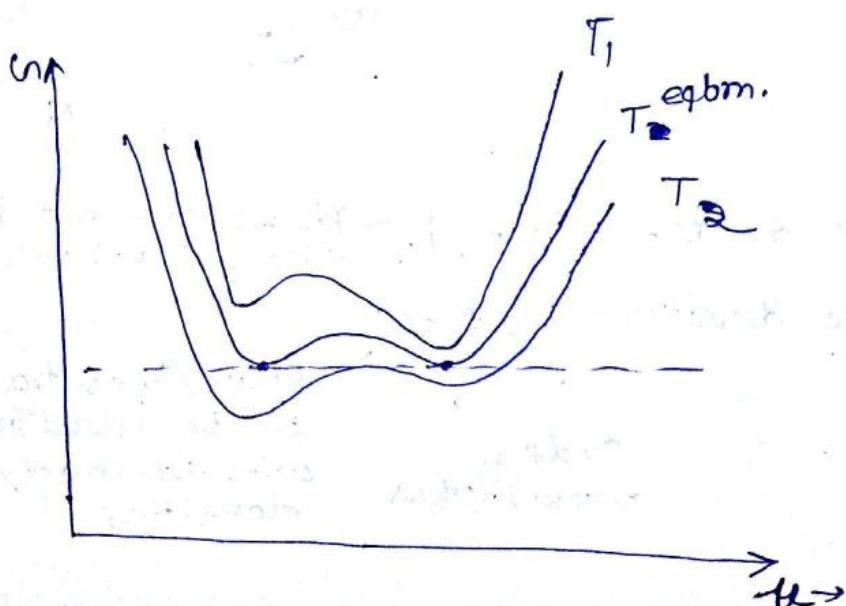
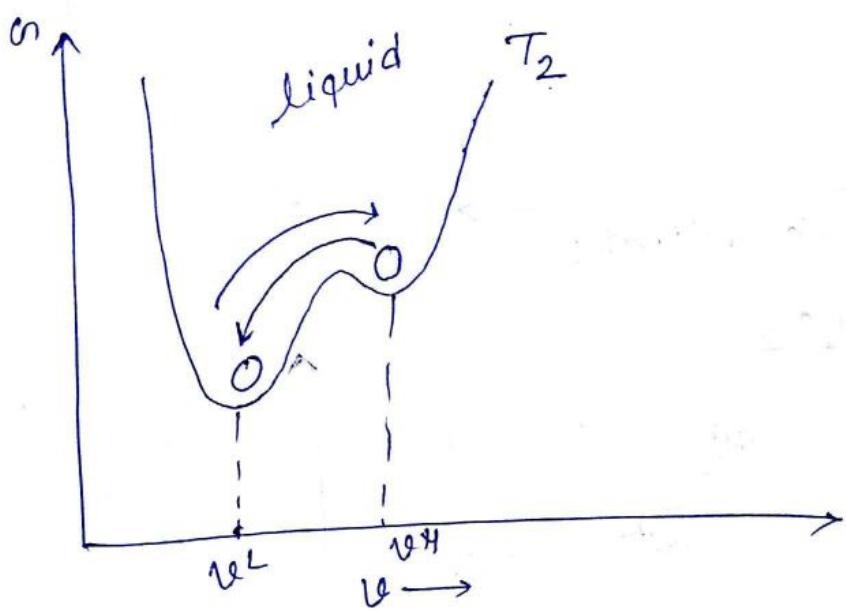


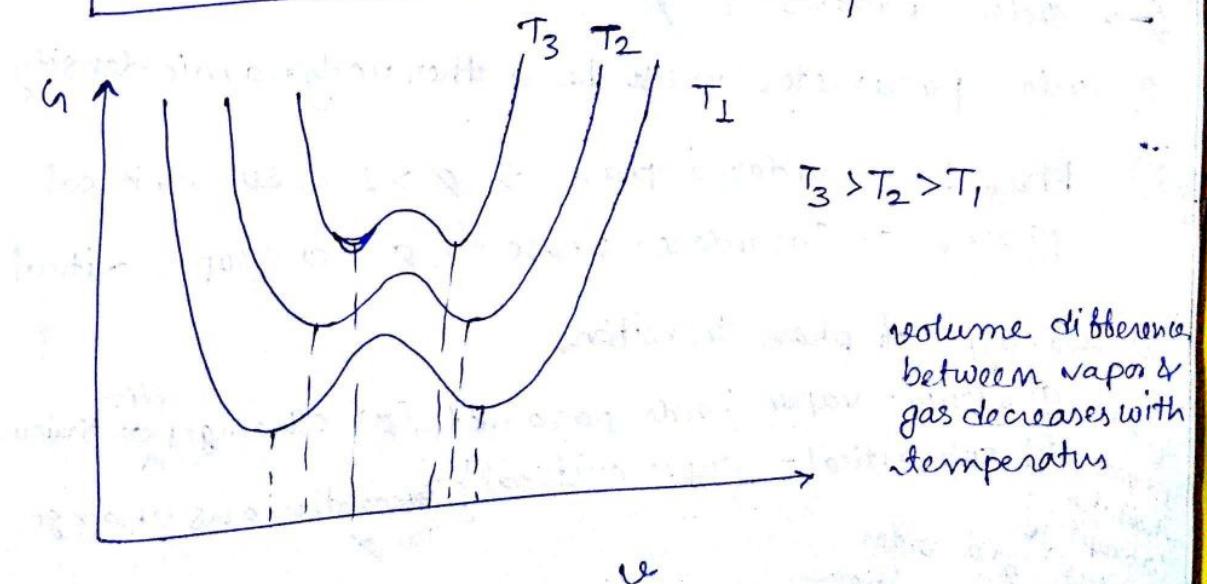
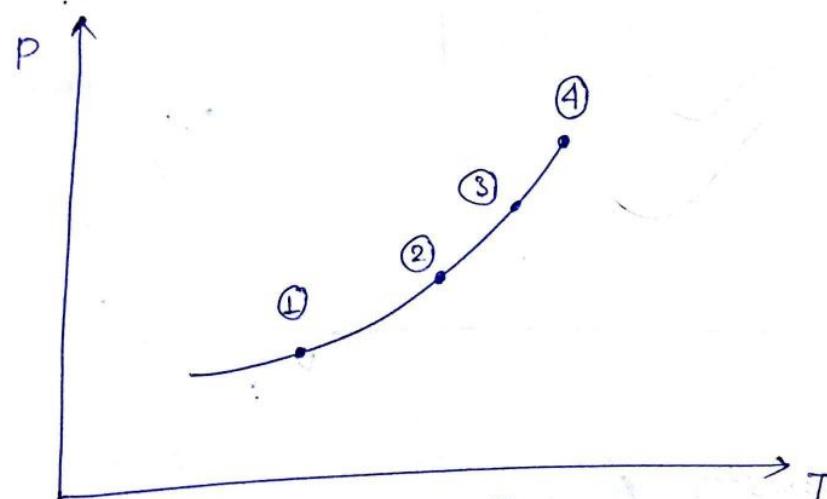
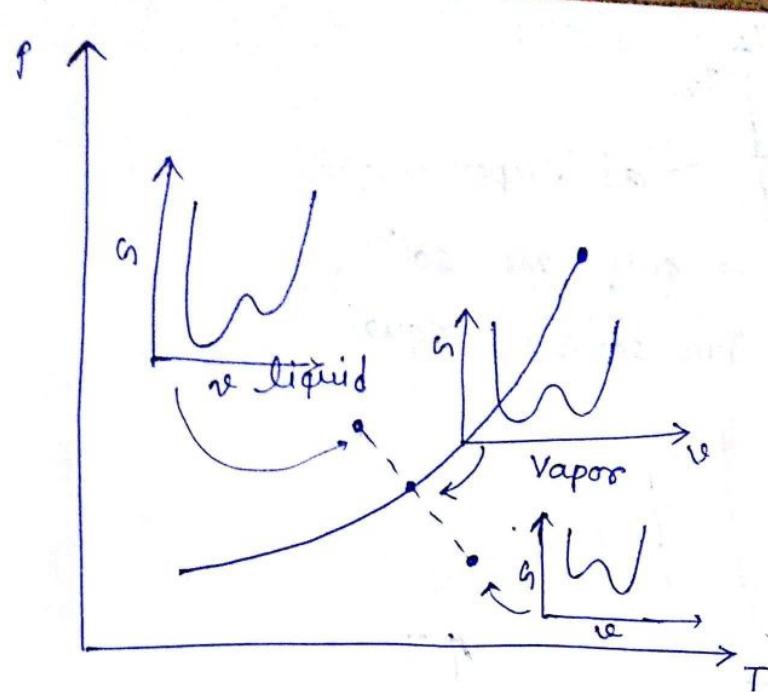
- Thermodynamic fields -  $(T, P, \mu)$  → phases can not be distinguished with Th. fields
- Thermodynamic densities -  $(\rho, h, v)$  → Phase/Phase transition can be identified with thermodynamic densities  
Order parameters

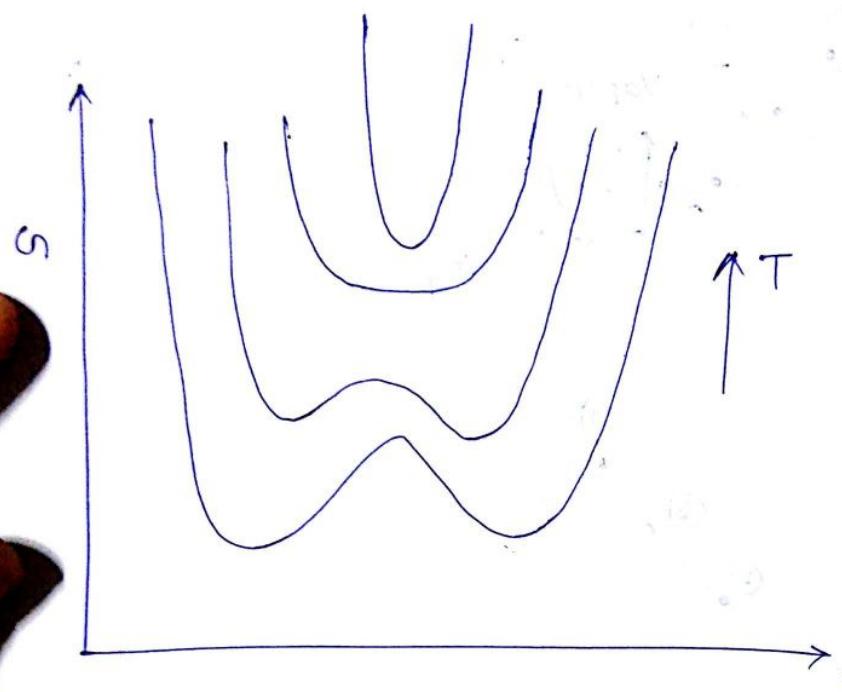
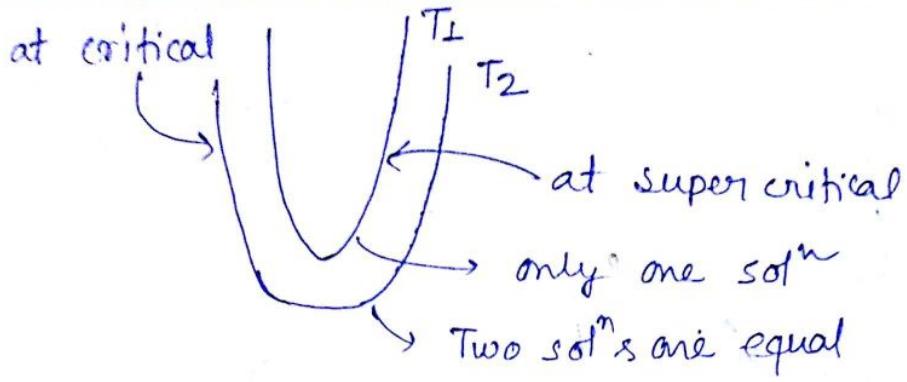


fluctuation - non-systematic disturbance

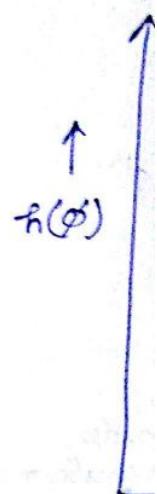
$$T_1 > T_2$$







5) Landau



Thermodynamics

1) order parameter  $\phi$

2) order parameter must be a thermodynamic density

3) Phase 1  $\rightarrow$  ordered phase  $\rightarrow \phi > 1 \Rightarrow$  sub critical

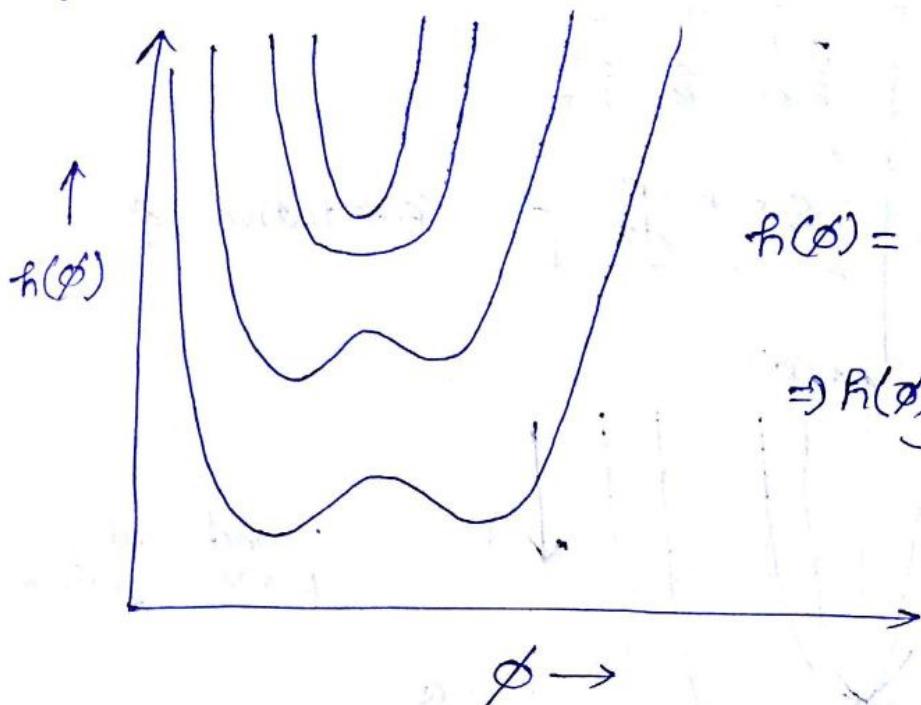
phase 2  $\rightarrow$  Disordered phase  $\rightarrow \phi = 0 \Rightarrow$  super critical

4) Two types of phase transitions

- a) liquid - vapor { order parameter ( $\phi$ ) changes continuously}
  - b) subcritical - supercritical } discontinuous change in  $\phi$
- 1st order transition (abrupt change)  $\downarrow$
- 2nd order transition

### 5) Landau Potential

$$f(x) = ax^2 + bx^4$$



$$f(\phi) = a + b\phi + c\phi^2 + d\phi^3 + e\phi^4$$

*weights*

$$\Rightarrow f(\phi) = \underbrace{a + b\phi^2 + c\phi^4}_{\text{only even powers of } \phi} + \dots$$

Thermodynamics

Now we want to calculate

the resulting energy  
in terms of the magnetic  
field applied parallel  
to the direction of motion

and also the effect of  
the magnetic field on  
the minimum of the potential

## Super critical state

24/03/17

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

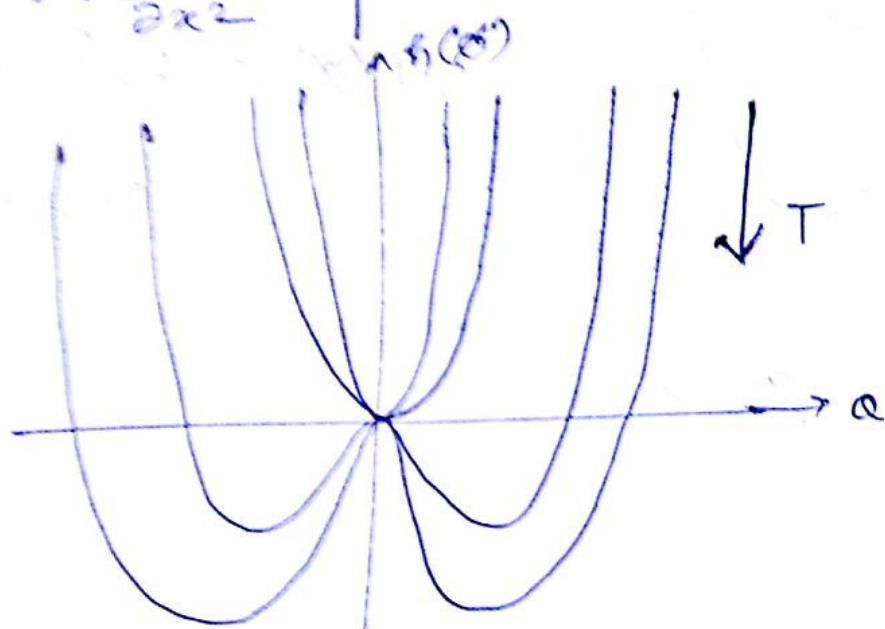
$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial \rho}{\partial t} = \gamma \frac{\partial^2 \rho}{\partial x^2}$$

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t}$$

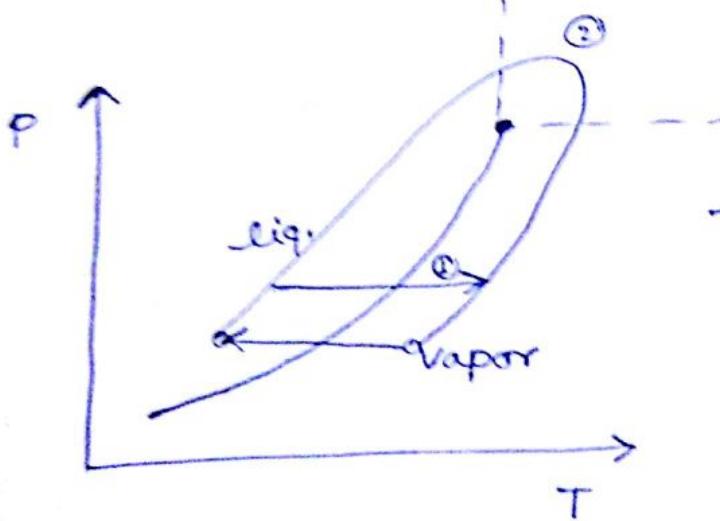
$$\sigma = K \frac{dT}{dx}$$

← constitutive eqn



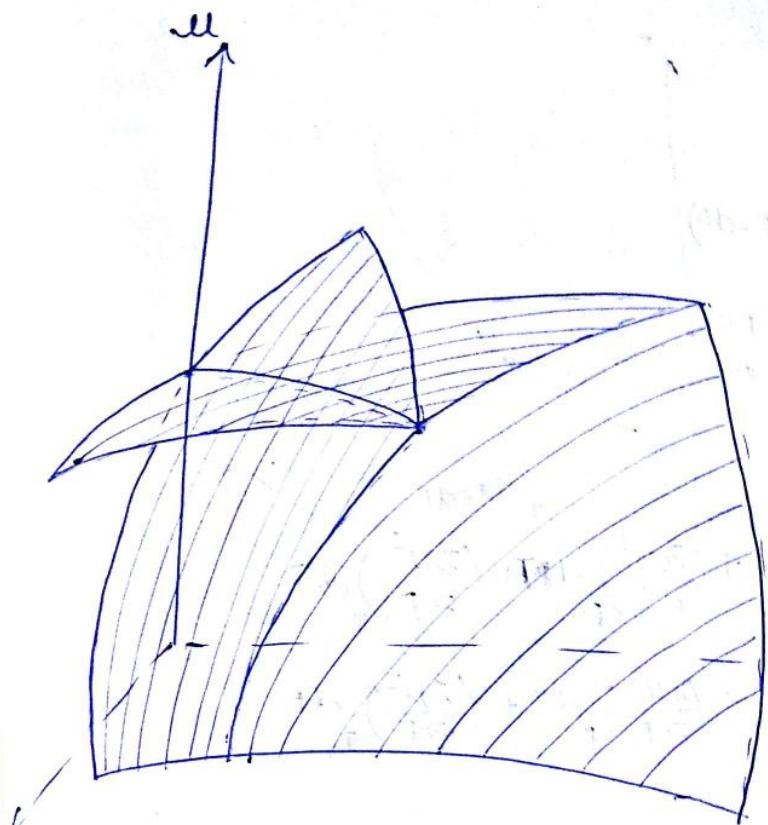
second order  
phase transform

← direction of phase transformation

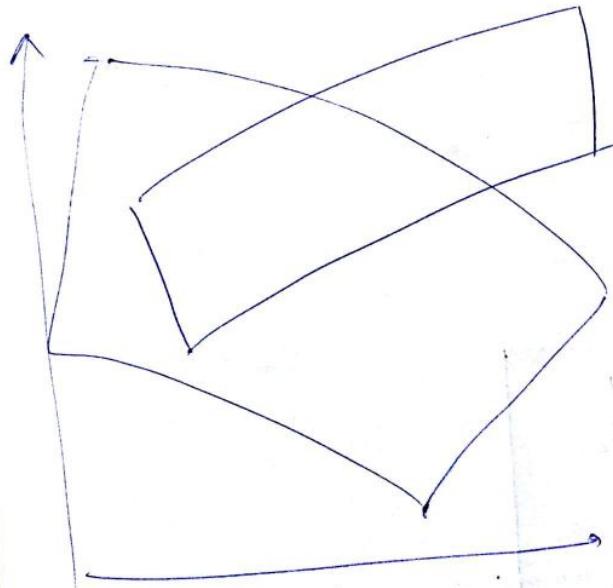


→ When we go from liquid to vapor via path ① there is abrupt change in specific volume.

→ But if we go via path ②, we skip the eqbm plain. So, there is no clue to what happens at eqbm



- phase diagram changes at super critical state
- geometry of planes start merging at these conditions

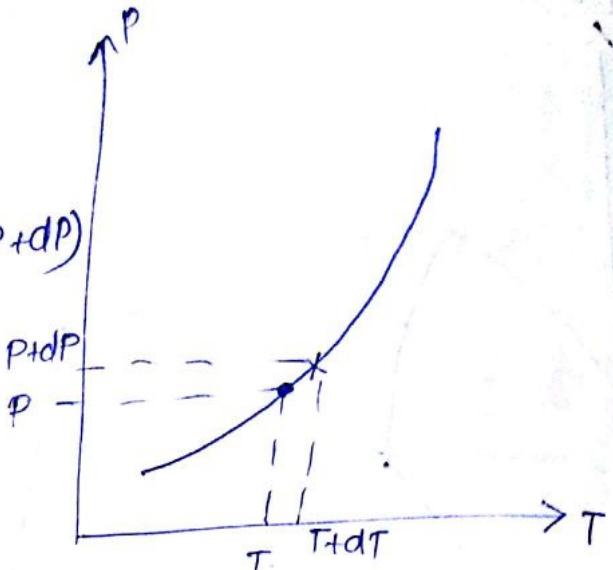


phase diagram  
normally (not under  
super critical state)

P-T projections

$$\mu^1(T, P) = \mu^2(T, P)$$

$$\mu^1(T+dT, P+dP) = \mu^2(T+dT, P+dP)$$



$$\mu^1(T+dT, P+dP) = \mu^1(T, P) + \left(\frac{\partial \mu^1}{\partial T}\right)_P dT + \left(\frac{\partial \mu^1}{\partial P}\right)_T dP$$

$$\mu^2(T+dT, P+dP) = \mu^2(T, P) + \left(\frac{\partial \mu^2}{\partial T}\right)_P dT + \left(\frac{\partial \mu^2}{\partial P}\right)_T dP$$

$$\frac{dP}{dT} = \frac{\left(\frac{\partial \mu^1}{\partial T}\right)_P - \left(\frac{\partial \mu^1}{\partial T}\right)_P}{\left(\frac{\partial \mu^1}{\partial P}\right)_T - \left(\frac{\partial \mu^2}{\partial P}\right)_T}$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -s$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \nu$$

$$\boxed{\frac{dP}{dT} = \frac{-s^2 + s^1}{\nu^1 - \nu^2} = \frac{s^1 - s^2}{\nu^1 - \nu^2}}$$

H vapor liquid eqbm.  $1 \equiv \text{vap.}$   $2 \equiv \text{liq.}$

$$\left(\frac{dP}{dT}\right)_{VLE} = \frac{\Delta s}{\Delta \nu}$$

at eqbm

$$\Delta G = \Delta H - T \Delta S$$

$$\boxed{\left(\frac{dP}{dT}\right)_{VLE} = \frac{L}{T_1 \nu_1 - T_2 \nu_2}} \quad \begin{array}{l} \text{Clausius} \\ \text{Clapeyron eqn} \end{array}$$

$$(\Delta H)_{\text{phase transition}} = \frac{\Delta H}{\Delta \nu}$$

$$\left(\frac{dP}{dT}\right)_{V,L,E} = f(T)$$

Phases -  $\alpha$  and  $\beta$

Components - A and B

$$T^\alpha = T^\beta \quad \left| \begin{array}{l} \mu_A^\alpha = \cancel{\mu_B^\alpha} \mu_A^\beta \\ \mu_B^\alpha = \mu_B^\beta \end{array} \right. \quad \left| \begin{array}{l} \ln f_A^\alpha = \ln f_A^\beta \rightarrow f = f(T, P, x_A) \\ \ln f_B^\alpha = \ln f_B^\beta \end{array} \right.$$

$$d(\ln f_A^\alpha) = \left( \frac{\partial \ln f_A^\alpha}{\partial T} \right)_{P, x_A} dT + \left( \frac{\partial \ln f_A^\alpha}{\partial P} \right)_{T, x_A} dP + \left( \frac{\partial \ln f_A^\alpha}{\partial x_A} \right)_{T, P} dx_A^\alpha$$

$$d(\ln f_A^\alpha) = \left( \frac{\bar{H}_A^\alpha - H_A'}{RT^2} \right) dT + \left( \frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP + \left( \frac{\partial \ln f_A^\alpha}{\partial x_A} \right)_{T, P} dx_A^\alpha$$

$H_A'$  = partial molar enthalpy of first component when system acts ideally

$\bar{H}_A$  = partial molar enthalpy

$$= \left( \frac{\bar{H}_A^\alpha - \bar{H}_A^\beta}{RT^2} \right) dT + \left( \frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP + \frac{\partial}{\partial x_A^\alpha} (\ln f_A^\alpha)_{T, P} dx_A^\alpha = 0$$

$$-\frac{\partial}{\partial x_A^\beta} (\ln f_A^\beta)_{T, P} dx_A^\beta = 0$$

$$-\left( \frac{\bar{H}_A^\alpha - \bar{H}_A^\beta}{RT^2} \right) dT + \left( \frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP - \dots \quad ①$$

$$-\left( \frac{\bar{H}_A^\alpha - \bar{H}_A^\beta}{RT^2} \right) dT + \left( \frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP$$

$$+ \frac{\partial}{\partial x_A^\alpha} (\ln f_A^\alpha)_{T, P} dx_A^\alpha - \frac{\partial}{\partial x_A^\beta} (\ln f_A^\beta)_{T, P} dx_A^\beta = 0 \quad ②$$

$$x_A^\alpha \left( \frac{\partial \ln f_A^\alpha}{\partial x_A^\alpha} \right) + x_B^\alpha \left( \frac{\partial \ln f_B^\alpha}{\partial x_B^\alpha} \right) = 0$$

$$\left( \frac{\partial P}{\partial T} \right)_{x_A^\beta} = \frac{1}{T} \left\{ \frac{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^\beta) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^\beta)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)} \right\}$$

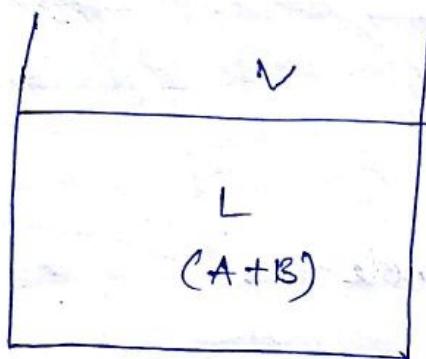
$$\left( \frac{\partial P}{\partial x_A^\beta} \right)_T = RT \left\{ \frac{(x_A^\alpha - x_A^\beta x_B^\alpha / x_B^\beta) (\partial \ln f_A^\beta / \partial \ln x_A^\beta)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)} \right\}$$

$$\left( \frac{\partial T}{\partial x_A^\beta} \right)_P = -RT^2 \left\{ \frac{(x_A^\alpha - x_A^\beta x_B^\alpha / x_B^\beta) (\partial \ln f_A^\beta / \partial x_A^\beta)}{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^\beta) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^\beta)} \right\}$$

29/03/17

## Binary Vapor - Liquid eqbm. systems

liquid  $\rightarrow$  A + B

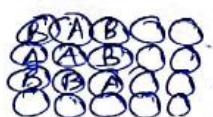
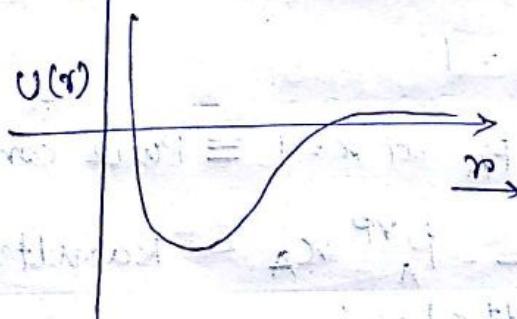
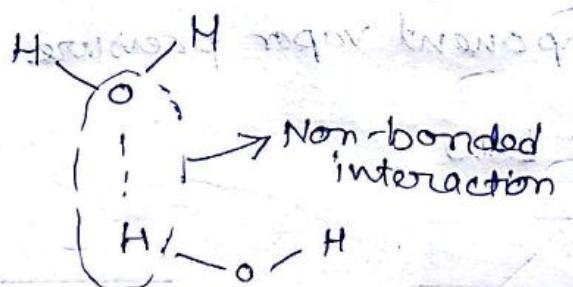
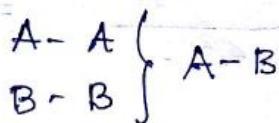


Spatial distribution of molecules of A & B?

boiling  $\rightarrow$  bulk phenomena

1. Similarity of shape & size

2. Similarity of interactions (non-bonded)



- Ideal :  $A-A \approx B-B \approx A-B$  for liquids

$A-A = B-B = A-B = 0$  for ideal gases.

$\rightarrow$  composition at surface = composition of liquid bulk

$P(A) = x_A \rightarrow$  mole fraction of A in liquid phase  
 probability of a molecule sampled from surface to be A

$$p(A) \propto P(A)$$

Pressure exerted by A-type molecule

$$p_A \propto x_A$$

Liq phase

Vapor phase

$$p_A = k x_A$$

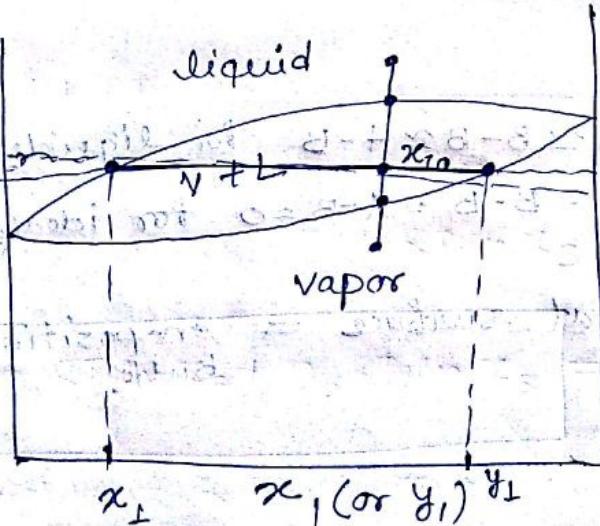
$$x_A = 1$$

$k = p_A^{\circ}$  at  $x=1 \equiv$  Pure component vapor pressure

$$p_A = p_A^{\circ} x_A \rightarrow \text{Raoult's Law}$$

Raoult's Law:

$$p_i = x_i p_i^{\circ}$$



$$x_1 = \frac{n_1^L}{n_1^L + n_2^L} = \frac{n_1^L}{n_T^L} \quad \text{--- } ①$$

$$y_1 = \frac{n_1^V}{n_1^V + n_2^V} = \frac{n_1^V}{n_T^V} \quad \text{--- } ②$$

Total mole balance for component 1

$$x_{1a} = \frac{n_1^L + n_1^V}{n_T^L + n_T^V} \quad \text{--- } ③$$

$$x_{1a}(n_T^L + n_T^V) = x_1 n_T^L + y_1 n_T^V$$

$$x_{1a} n_T^L + x_{1a} n_T^V = x_1 n_T^L + y_1 n_T^V$$

$$(x_{1a} - x_1) n_T^L = (y_1 - x_{1a}) n_T^V$$

$$\left[ \frac{n_T^L}{n_T^V} = \frac{y_1 - x_{1a}}{x_{1a} - x_1} \right] \rightarrow \text{Lever Rule}$$

$$P_{\text{ambient}} = \underbrace{P_1^{VP} x_1}_{\bar{P}_1} + \underbrace{\bar{P}_2^{VP} x_2}_{\bar{P}_2} \quad \sum \bar{P}_i$$

$$P_{\text{amb}} = P_1^{VP} x_1 + P_2^{VP} (1-x_1)$$

$$\Rightarrow P_{\text{amb}} - P_2^{VP} = (P_1^{VP} - P_2^{VP}) x_1$$

$$\Rightarrow x_1 = \frac{P_2^{VP} - P_{\text{amb}}}{P_1^{VP} - P_2^{VP}}$$

$$\text{Composition} = f(P, P_i^{\text{NP}}) \quad i$$

$$P_i^{\text{VP}} = g(T)$$

$$\log(P_i^{\text{NP}}) = A - \frac{B}{T+C} \quad \leftarrow \text{Empirical Correlation}$$

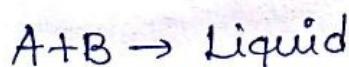
Relation vs. Correlation

$$S = ut + \frac{1}{2} at^2 \quad \text{— Relation}$$

$$S = f(u, a, t)$$

30/03/17

Ideal Solutions



$$\Delta G = G_A^{\text{soln}} + G_B^{\text{soln}} - G_A^{\text{pure}} - G_B^{\text{pure}}$$

$$G_A^{\text{pure}} = n_A \mu_A^{\text{pure}}$$

$$G_B^{\text{pure}} = n_B \mu_B^{\text{pure}}$$

$$G_A^{\text{soln}} = n_A \mu_A^{\text{soln}}$$

$$G_B^{\text{soln}} = n_B \mu_B^{\text{soln}}$$

$$\Delta G = n_A \mu_A^{\text{soln}} + n_B \mu_B^{\text{soln}} - n_A \mu_A^{\text{pure}} - n_B \mu_B^{\text{pure}}$$

$$\mu_i^{\circ} = \mu_i^* + RT \ln x_i$$

~~$$\mu_A^{\text{pure}} = \mu_A^{\text{soln}} + RT \ln x_A$$~~

$$\mu_B^{\text{soln}} = \mu_B^{\text{pure}} + RT \ln x_B$$

$$\Delta G = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Rightarrow \Delta G < 0$$

$$n_i^{\circ} \rightarrow +\text{ve}, \quad R \rightarrow +\text{ve}, \quad T \rightarrow +\text{ve}, \quad x_i \rightarrow +\text{ve} < 1$$

$$\Delta G = \Delta H - T \Delta S \quad +ve$$

↑                      ↑  
Enthalpic    Entropic  
(~0)            (increased)



$$dS = -\left(\frac{\partial G}{\partial T}\right)_{P,n}$$

$$\Delta S = -(n_A R \ln x_A + n_B R \ln x_B) \Rightarrow S > 0$$

$$\Delta H = \Delta G + T \Delta S$$

$$\Delta H = 0$$

$$\Delta V = \left(\frac{\partial \Delta H}{\partial P}\right)_{S,x}^0 = 0$$

$$\Delta V = 0$$

1. Similarity of shapes and sizes of molecules of different kinds

2. Similarity of interactions:  $A-A \approx B-B \approx A-B$

3.  $\Delta G < 0$

4.  $\Delta V = 0$

5.  $\Delta H = 0$

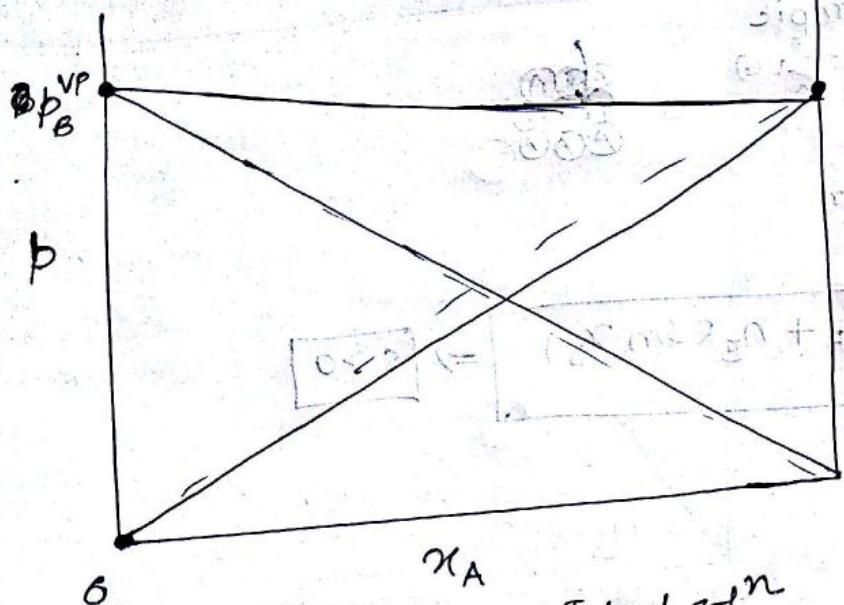
6.  $\Delta S > 0$

7. Follows Raoult's Law.

$$P_i = P_i^{vap} x_i$$

$$P_A = P_A^{vap} x_A$$

$$P_B = P_A^{vap} x_B$$



Raoult's Law - Ideal sol'n

Find all possible examples

A-A - very strong - Ethanol

B-B - weak -  $S = C_2H_5$

$A+B \rightarrow A-A + B-B$

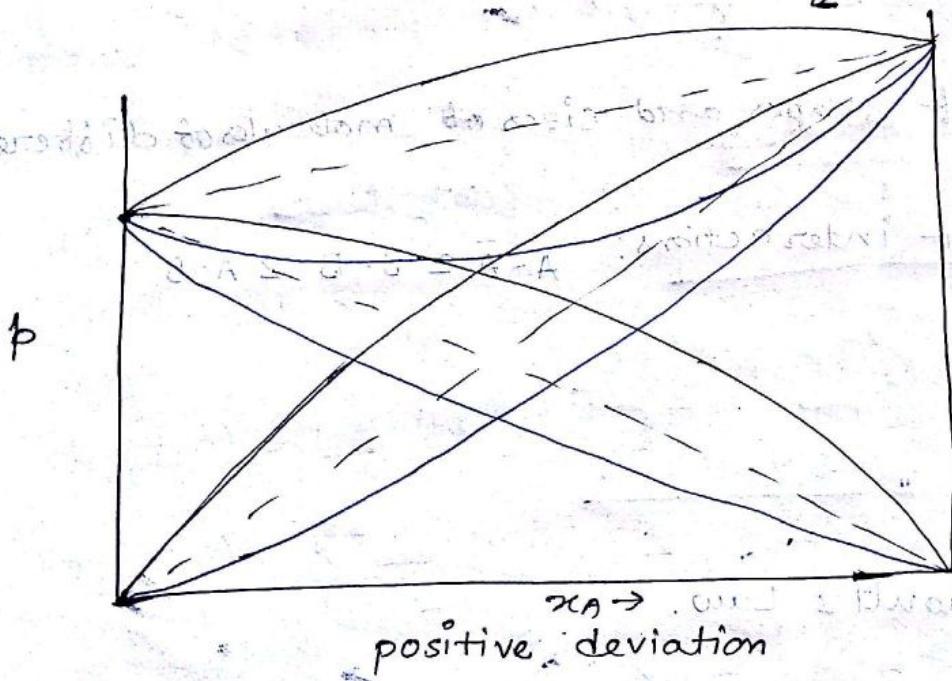
$A-B < A-A$

$p_A + p_B = p_{total}$

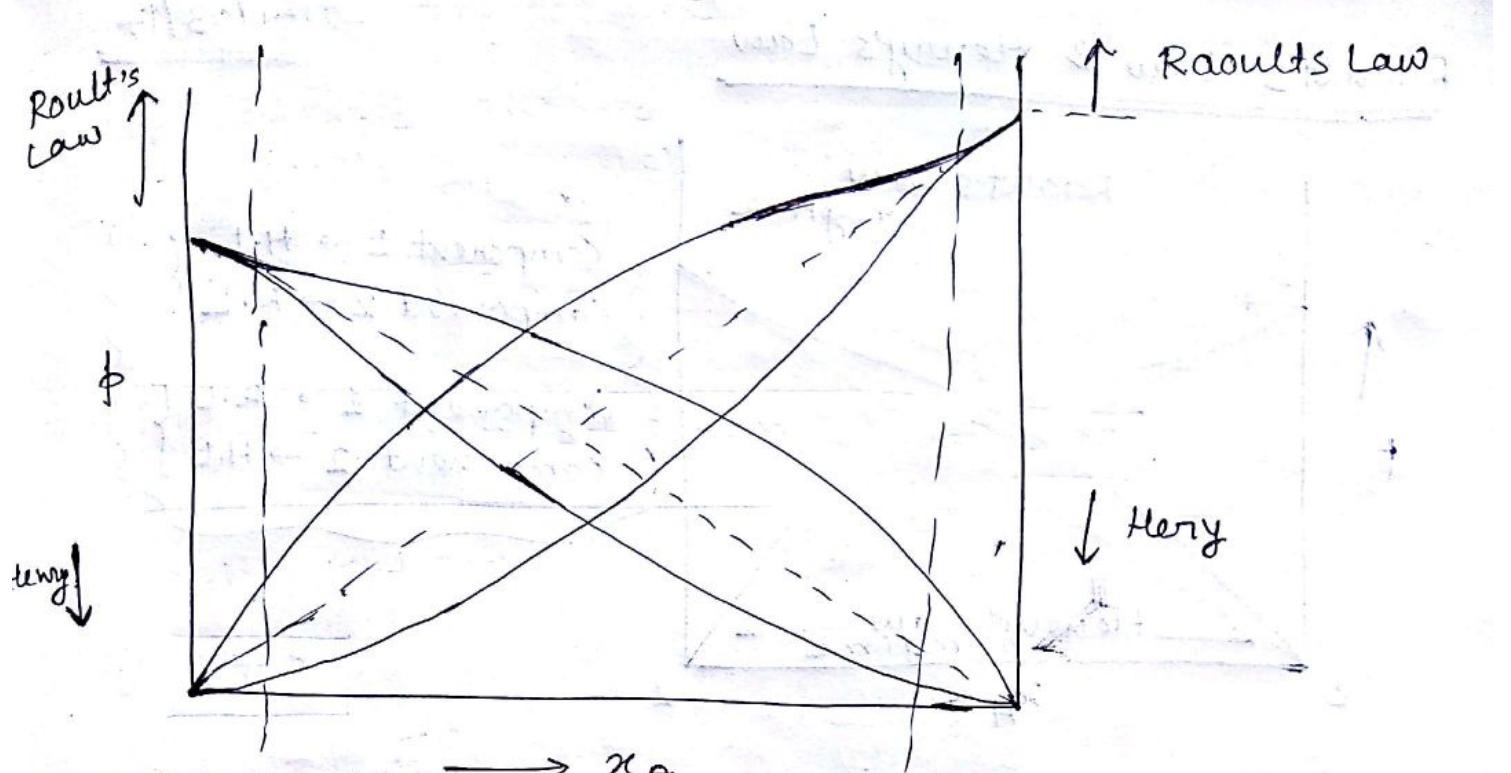
1

-ve deviation  
+ve deviation

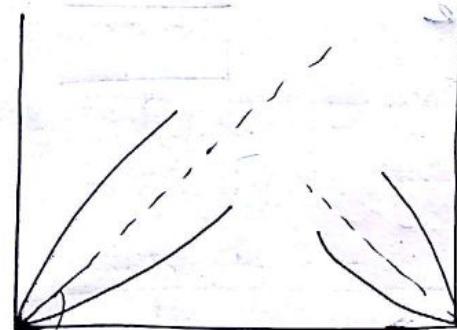
$C = VL$



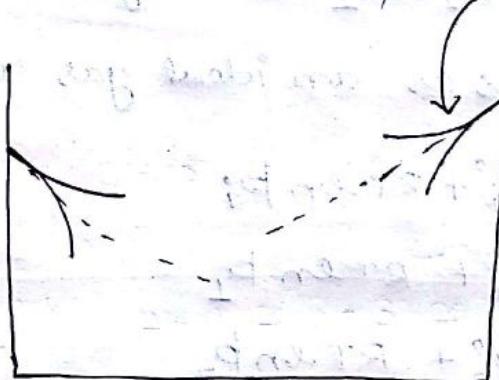
$x_A \rightarrow 0$  and  $1$  B shows curved S



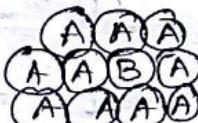
A-B interaction



A-A interaction

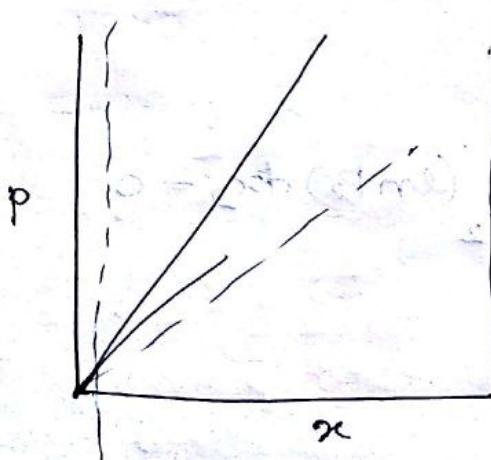


Asymptotically reaches  
Raoult's Law behavior



System behaves  
like this at  $\infty$ -dilution

A-A' interaction



Sparingly soluble

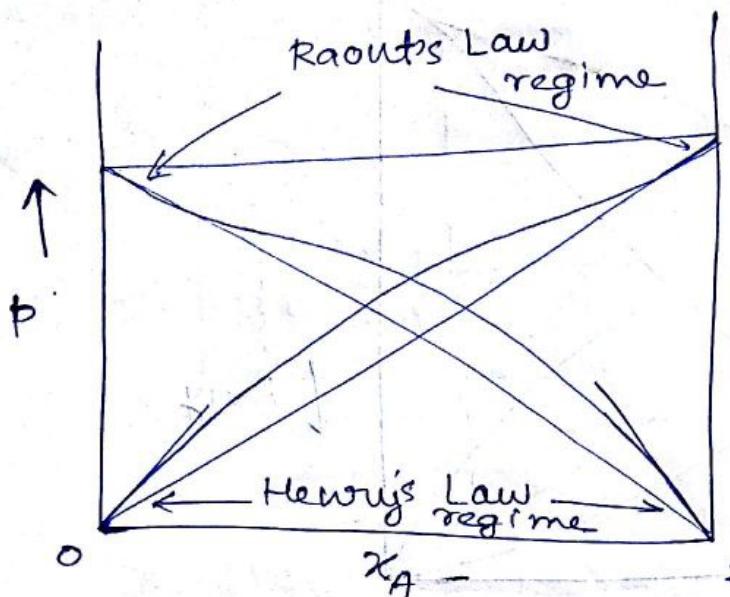
$$P = K_H x$$

const.

Henry's Law const.

# Raoult's Law & Henry's Law

31/08/17



Component 1  $\rightarrow$  H.L  
 Component 2  $\rightarrow$  R.L

Component 1  $\rightarrow$  R.L  
 Component 2  $\rightarrow$  H.L

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad - \text{Gibbs-Duhem eqn} \quad (\text{at const. } T, P)$$

Assumption  
Vapour acts as an ideal gas mixture

$$\mu_i^\circ = \mu_i^\circ + RT \ln p_i$$

$$\mu_1 = \mu_1^\circ + RT \ln p_1$$

$$\mu_2 = \mu_2^\circ + RT \ln p_2$$

$$d\mu_1(T, P) = RT \frac{\partial}{\partial x_1} (\ln p_1) dx_1$$

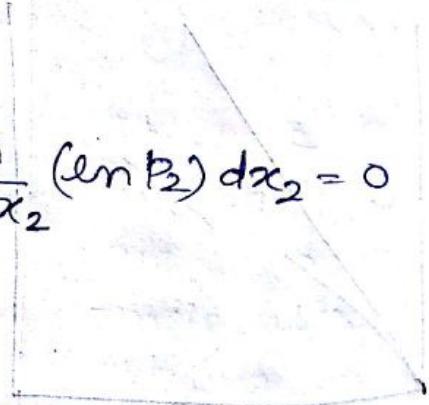
$$d\mu_2(T, P) = RT \frac{\partial}{\partial x_2} (\ln p_2) dx_2$$

$$x_1 RT \frac{\partial}{\partial x_1} (\ln p_1) dx_1 + x_2 RT \frac{\partial}{\partial x_2} (\ln p_2) dx_2 = 0$$

$$x_1 + x_2 = 1$$

$$dx_1 = -dx_2$$

$$x_1 \frac{\partial (\ln p_1)}{\partial x_1} = x_2 \frac{\partial (\ln p_2)}{\partial x_2}$$



If, component 1 follows Raoult's Law

$$p_1 = x_1 p_1^{\text{VP}}$$

$$\cancel{x_1} \frac{p_1^{\text{VP}}}{x_1} = x_2 \frac{\partial(\ln p_2)}{\partial x_2}$$

$$\frac{x_1}{x_2} p_1^{\text{VP}} = \frac{\partial(\ln p_2)}{\partial x_2}$$

$$\cancel{x_1} p_1^{\text{VP}} \ln x_2 = \ln p_2$$

$$x_2 e^{\cancel{x_1} p_1^{\text{VP}}} = \cancel{\ln} p_2$$

$$p_2 = k_H x_2$$

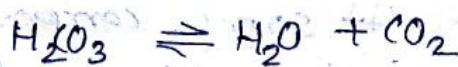
⇒ In cold drinks  $\text{CO}_2$  is dissolved. Mole fraction of  $\text{CO}_2$  in that  $\sim 0$  as  $\text{CO}_2$  is sparingly soluble

$$p_2 = k_H x_2$$

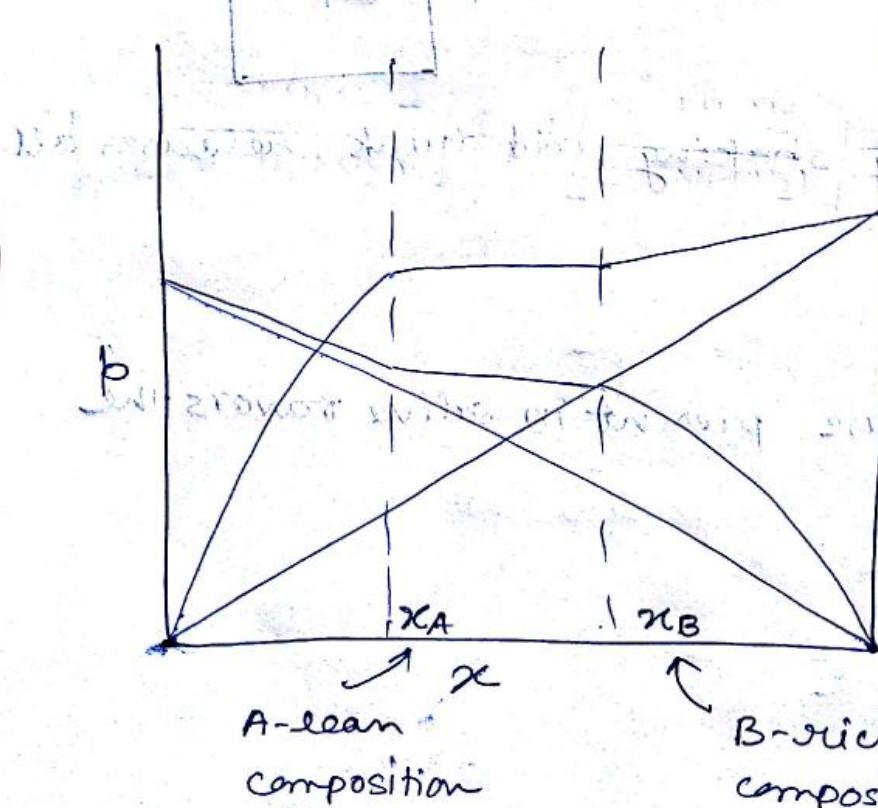
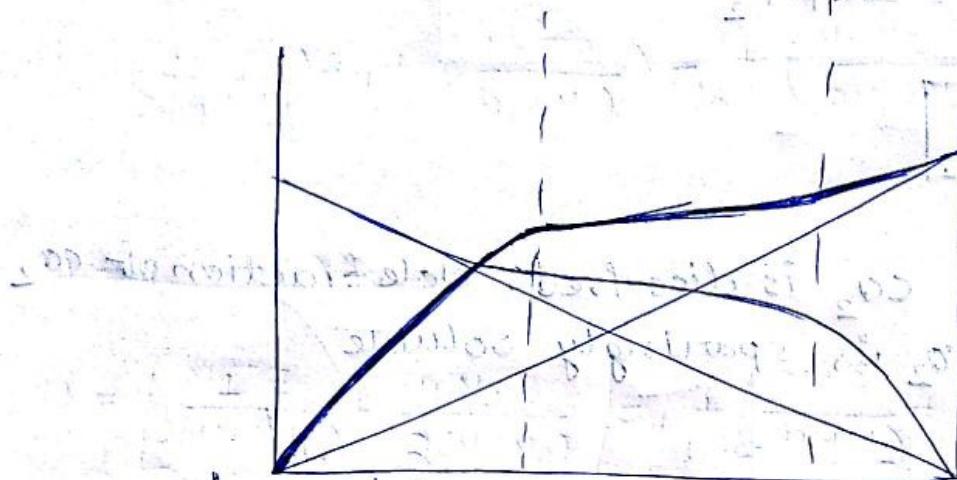
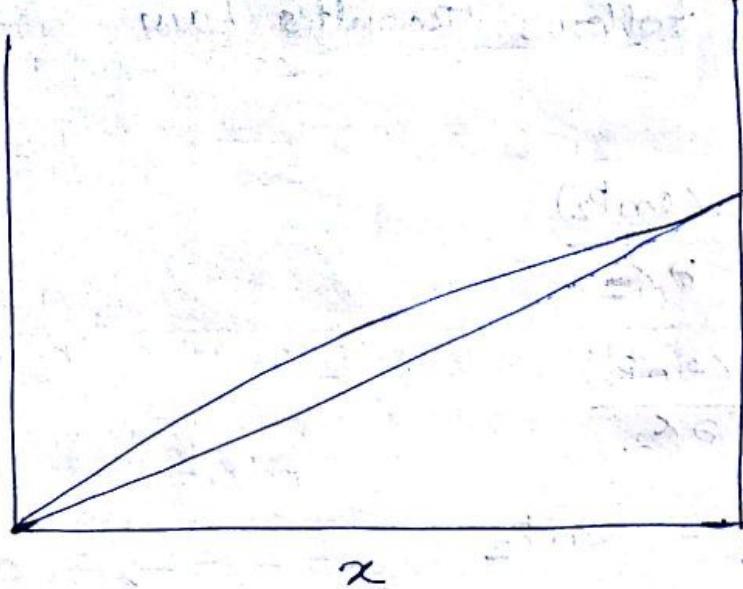
↑  
Henry's Law



Why mechanically shaking cold drink, releases all  $\text{CO}_2$ ?



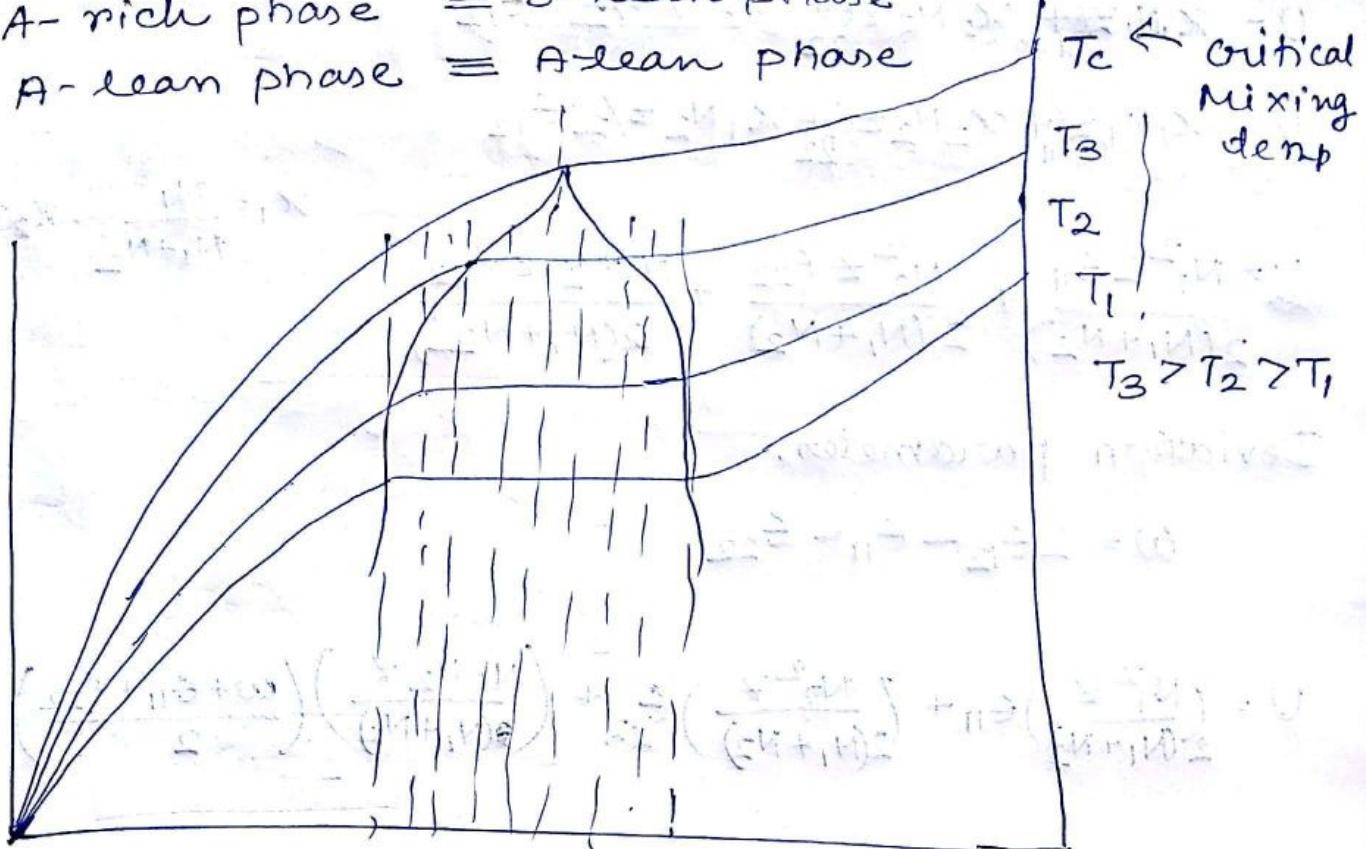
Carbonic anhydrase present in saliva favors the dissociation.



Partially-miscible system

At some compositions interactions between one component molecules are so strong, so that they don't allow other component molecules leading to phase separation.

A-rich phase  $\equiv$  B-lean phase  
 A-lean phase  $\equiv$  A-lean phase



From this diagram it is evident any liquid is miscible in one any other subject to fact that they are liquid at higher temperature beyond critical mixing temperature.

$$\mu_i = \mu_i^* + RT \ln \chi_i$$

A+B,

∴ There are no entropic barriers

$$U = N_{11}\epsilon_1 + N_{22}\epsilon_2 + N_{12}\epsilon_{12}$$

$N \rightarrow$  number of particles

$\epsilon \rightarrow$  interaction energy

$$N_{11} = x_1 N_1 \approx \frac{z}{2} \leftarrow \text{co-ordination no.}$$

$$N_{22} = x_2 N_2 \approx \frac{z}{2}$$

$$N_{12} = x_1 N_2 \approx \frac{z}{2} = x_2 N_1 \approx \frac{z}{2}$$

$$U = x_1 N_1 Z \epsilon_{11} + x_2 N_2 Z \epsilon_{22} + x_2 N_1 Z/2 \cdot \epsilon_{12}$$

$$\bar{U} = x_1 N_1 Z \epsilon_{11} + x_2 N_2 Z \epsilon_{22} + x_1 N_2 Z/2 \cdot \epsilon_{12}$$

$$U = \frac{N_1^2 Z \epsilon_{11}}{2(N_1 + N_2)} + \frac{N_2^2 Z \epsilon_{22}}{2(N_1 + N_2)} + \frac{N_1 N_2 Z \epsilon_{12}}{2(N_1 + N_2)}$$

$$x_1 = \frac{N_1}{N_1 + N_2} - x_2$$

Deviation parameter.

$$\omega = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$$

$$U = \left( \frac{N_1^2 Z}{2(N_1 + N_2)} \right) \epsilon_{11} + \left( \frac{N_2^2 Z}{2(N_1 + N_2)} \right) \epsilon_{22} + \left( \frac{N_1 N_2 Z}{2(N_1 + N_2)} \right) \left( \frac{\omega + \epsilon_{11} + \epsilon_{22}}{2} \right)$$

~~$U = (\quad) \epsilon_1 +$~~

$$U = \left[ \frac{N_1^2 Z}{2(N_1 + N_2)} + \frac{N_1 N_2 Z}{2(N_1 + N_2)} \right] \epsilon_{11} + \left[ \frac{N_2^2 Z}{2(N_1 + N_2)} + \frac{N_1 N_2 Z}{2(N_1 + N_2)} \right] \epsilon_{22} + \left( \frac{N_1 N_2 Z}{2(N_1 + N_2)} \right) \omega$$

$$U = \left[ \frac{(N_1^2 + N_1 N_2) Z}{2(N_1 + N_2)} \right] \epsilon_{11} + \left[ \frac{N_2^2 + N_1 N_2}{2(N_1 + N_2)} \right] \epsilon_{22} + \left[ \frac{N_1 N_2 Z}{2(N_1 + N_2)} \right] \omega$$

$$U = U_{\text{Id}}^{\text{Id}} + \left[ \frac{N_1 N_2 Z}{2(N_1 + N_2)} \right] \omega$$

For ideality  $\omega = 0$

$$c_v = c_v^{\text{Id}} + \left[ \frac{N_1 N_2 Z}{2(N_1 + N_2)} \right] \omega$$

For sol's where entropy does not play a major role

$$u_i^{\text{Id}} = u_i^{\text{*Id}} + RT \ln x_i$$

$$c_v = c_v^{\text{Id}} + \left[ \frac{n_1 n_2 N_A V Z}{2(n_1 + n_2)} \right] \omega$$

$$u_1 = \left( \frac{\partial c_v}{\partial n_1} \right)_{T, P, n_2}$$

$$u_1 = u_1^{\text{Id}} + \left( \frac{N_A Z \omega}{2} \right) \frac{\partial}{\partial n_1} \left( \frac{n_1 n_2}{n_1 + n_2} \right)_{T, P, n_2}$$

$$= u_1^{\text{Id}} + \left( \frac{N_A Z \omega}{2} \right) \left[ \frac{n_2}{n_1 + n_2} - \frac{n_1 n_2}{(n_1 + n_2)^2} \right]$$

$$= u_1^{\text{Id}} + \frac{N_A Z \omega}{2} \cdot \frac{n_2^2}{(n_1 + n_2)^2}$$

$$u_1 = u_1^{\text{Id}} + \frac{N_A Z \omega}{2} x_2^2$$

$$u_1 = u_1^{\text{*Id}} + RT \ln x_1 + \left( \frac{N_A Z \omega}{2} \right) x_2^2 \rightarrow \text{non ideal}$$

$$u_1 = u_1^{\text{*}} + RT \ln x_1 \rightarrow \text{ideal}$$

$$u_1 = f(x_1) \rightarrow \text{ideal soln}$$

$$u_1 = g(x_1, x_2) \rightarrow \text{non ideal soln}$$

$$U_i = U_i^{\circ, \text{Id}} + RT \left[ x_1 \exp \left( \frac{NAZ\omega x^2}{2RT} \right) \right] \quad \text{non ideal}$$

$$U_i = U_i^* + RT \ln x_i \quad \text{ideal} \rightarrow \alpha \quad \text{determined experimentally}$$

$$\Rightarrow U_i = U_i^* + RT \ln \alpha_i \quad \text{non ideal}$$

$$\alpha_i = x_1 \exp \left( \frac{NAZ\omega}{2RT} x^2 \right) = x_1 e^{\alpha x_2^2 + \beta x_2^3 + \gamma x_2^4 + \dots}$$

$$\ln \left[ \frac{x_1}{x_1^*} \exp \left( \frac{NAZ\omega}{2RT} x^2 \right) \right] = \frac{NAZ\omega}{2RT} x^2$$

$$\ln \left[ \frac{x_1}{x_1^*} \right] + \frac{NAZ\omega}{2RT} x^2 = \frac{NAZ\omega}{2RT} x^2$$

$$\ln \left( \frac{x_1}{x_1^*} \right) = \frac{NAZ\omega}{2RT} x^2 + \frac{NAZ\omega}{2RT} x^3 + \frac{NAZ\omega}{2RT} x^4 + \dots$$

$$\ln \left( \frac{x_1}{x_1^*} \right) = \frac{NAZ\omega}{2RT} x^2 + \frac{NAZ\omega}{2RT} x^3 + \dots$$

$$\frac{\partial \ln \left( \frac{x_1}{x_1^*} \right)}{\partial x^2} = \frac{NAZ\omega}{2RT} + \frac{NAZ\omega}{2RT} x^2 + \dots$$

$$\frac{\partial \ln \left( \frac{x_1}{x_1^*} \right)}{\partial x^2} = \frac{NAZ\omega}{2RT} + \frac{NAZ\omega}{2RT} x^2 + \dots$$

both terms -  $\frac{\partial \ln \left( \frac{x_1}{x_1^*} \right)}{\partial x^2} = \frac{NAZ\omega}{2RT} + \frac{NAZ\omega}{2RT} x^2 + \dots$

both terms -  $\frac{\partial \ln \left( \frac{x_1}{x_1^*} \right)}{\partial x^3} = \frac{NAZ\omega}{2RT} + \frac{NAZ\omega}{2RT} x^3 + \dots$

for both  $\frac{\partial \ln \left( \frac{x_1}{x_1^*} \right)}{\partial x^2} = \frac{NAZ\omega}{2RT} + \frac{NAZ\omega}{2RT} x^2 + \dots$

for both  $\frac{\partial \ln \left( \frac{x_1}{x_1^*} \right)}{\partial x^3} = \frac{NAZ\omega}{2RT} + \frac{NAZ\omega}{2RT} x^3 + \dots$

$$\mu_i = \mu_i^{\circ, \text{Id}} + RT \left[ x_1 \exp \left( \frac{NA^2 \omega x^2}{2RT} \right) \right]$$

non ideal

$$\mu_i = \mu_i^* + RT \ln x_1$$

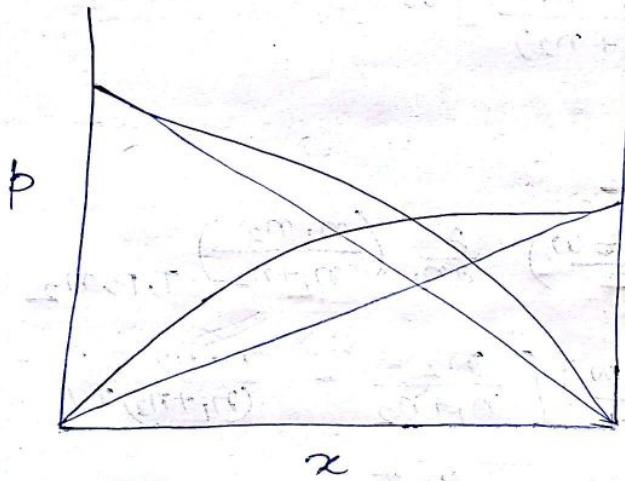
ideal

$$\mu_i = \mu_i^* + RT \ln x_1 - \text{non ideal}$$

determined experimentally

$$x_1 = x_1 \exp \left( \frac{NA^2 \omega}{2RT} x^2 \right) = x_1 e^{\alpha x_2^2 + \beta x_2^3 + \gamma x_2^4 + \dots}$$

05/04/17



1) Binary - A+B

2) A - ideal  $\Rightarrow$  Raoult's Law

A Ideal  $\Leftrightarrow$  B Ideal

Gibbs-Duhem eqn

1)  $x_1 d\mu_1 + x_2 d\mu_2 = 0$  - constant T, P

2) Component 1 - Raoult's Law

$$\mu_1 = \mu_1^* + RT \ln x_1$$

$$\mu_1^* = \mu_1^* + RT \ln x_1^*$$

$$x_1 d(\ln a_1) + x_2 d(\ln a_2) = 0$$

$$x_1 d(\ln x_1) + x_2 d(\ln x_2) = 0$$

It,  $a_2 = x_2$  (to be proved)

then component 2 also follows Raoult's law.

$$d \ln(a_2) = -\frac{x_1}{x_2} d(\ln x_1)$$

~~$$d \ln(a_2) = -\frac{x_1}{x_2} d(\ln(1-x_1))$$~~

~~$$d \ln(a_2) = -\frac{x_1}{x_2} \left(\frac{1}{x_1}\right) (-dx_1)$$~~

$$d \ln(a_2) = -\frac{x_1}{x_2} d \frac{1}{x_1} dx_1$$

$$d \ln(a_2) = \frac{dx_2}{x_2} = d(\ln x_2)$$

~~$$\ln a_2 = \ln x_2$$~~

$$d(\ln a_2) = d(\ln x_2)$$

$$\underline{a_2 = x_2}$$

ii) when component 1 follows Raoult's law, component 2 follows Henry's Law

iii) when component 1  $\rightarrow$  ideal  
component 2  $\rightarrow$  ideal

system is either ideal or non ideal with respect to both component

iv) Both the components either show ~~or~~ +ve or -ve deviation.

$$\mu_i = \mu_i^* + RT \ln(a_i)$$

$$\Delta G =$$

1. Completely miscible liquid liquid mixture

$$\mu_i = \mu_i^* + RT \ln x_i$$

$$x_i = p_i / p_i^{vp}$$

$$\mu_i^o = \mu_i^* + RT \ln \left( \frac{p_i}{p_i^{vp}} \right)$$



$x_i^o \rightarrow 1$  ← Raoult's Law  
standard state

$$\mu_1^s$$

$$\mu_2^s$$

$$\Delta H =$$

$$\Rightarrow \frac{\Delta H^M}{R}$$

$$a_i =$$

$$\frac{\Delta G}{T}$$

2. Sparingly soluble → solute + solvent

$$\mu_i = \mu_i^* + RT \ln \left( \frac{p_i}{p_i^{vp}} \right)$$

$$p_i = K_H \cancel{x_i} x_i$$

$$\mu_i = \mu_i^* + RT \ln \left( \frac{K_H x_i}{p_i^{vp}} \right) \rightarrow \text{when the system has deviated from ideality}$$

Dissimilar interaction

$$\mu_i = \left[ \mu_i^* + RT \ln \left( \frac{K_H \cancel{x_i}}{p_i^{vp}} \right) \right] + RT \ln \left( \cancel{\frac{x_i}{K_H}} \right) \rightarrow \text{similar interaction}$$

$$\boxed{\mu_i = \mu_i^* + RT \ln(a_i)}$$

At std. state,  $x_i^o \rightarrow 0$

Non i

concentration → change initial value and add C initial

$$\Delta G = (n_1 \mu_1^{\text{sol}} + n_2 \mu_2^{\text{sol}}) - (n_1 \mu_1^{\text{pure}} + n_2 \mu_2^{\text{pure}})$$

$$\mu_1^{\text{sol}} = \mu_1^{\text{pure}} + RT \ln a_1$$

$$\mu_2^{\text{sol}} = \mu_2^{\text{pure}} + RT \ln a_2$$

$$\Delta G = n_1 RT \ln a_1 + n_2 RT \ln a_2$$

$$\Rightarrow \frac{\Delta G_{\text{Molar}}}{RT} = x_1 \ln a_1 + x_2 \ln a_2$$

$$a_i = \gamma_i x_i$$

$$\frac{\Delta G_{\text{Molar}}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_1 \ln x_1 + x_2 \ln x_2$$

$\gamma_i = 1$  for ideal systems

$$\frac{\Delta G_{\text{Molar}}}{RT} = \left[ \frac{\Delta G_{\text{molar}}}{RT} \right]_{\text{ideal}} + x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\frac{\Delta G_{\text{molar}}}{RT} = \left[ \frac{\Delta G_{\text{Molar}}}{RT} \right]_{\text{ideal}} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\frac{1}{RT} \Delta G_{\text{excess}}^{\text{Molar}} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

Nonideal

$$a_i = \gamma_i x_i$$

$$a_1 = \gamma_1 x_1 e^{\alpha x_2^2}$$

$$a_2 = \gamma_2 x_2 e^{\alpha x_1^2}$$

$$\frac{\Delta G_{\text{Molar}}}{RT} = x_1 \ln a_1 + x_2 \ln a_2$$

$$= x_1 \ln \gamma_1 + x_1 \ln x_1 + \alpha x_2^2 x_1 + x_2 \ln \gamma_2 + x_2 \ln x_2 + \alpha x_1^2 x_2$$

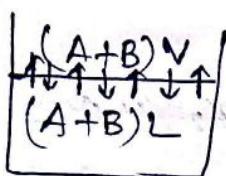
$$\frac{\Delta G_i}{RT}^{\text{Molar}} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2$$

$$\frac{\Delta G_i}{RT}^{\text{Molar excess}} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + \alpha x_1 x_2$$

07/04/17

### Solid- liq Equilibrium

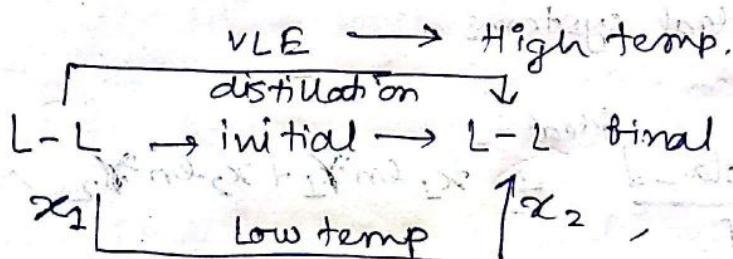
VLE  $\rightarrow$  2 phases  $\rightarrow$  V + L



2 components  $\rightarrow$  A + B

liquid A + liquid B

distillation  $\rightarrow$  enrichment



liquid  $\rightarrow$  possible to obtain vapor  $\rightarrow$  separation

For crude oil, required temp. for distillation  $\sim 100^\circ\text{C}$

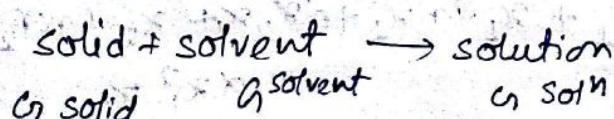
liquid  $\rightarrow$  possible to obtain solid

1) Why do solids dissolve in liquids?

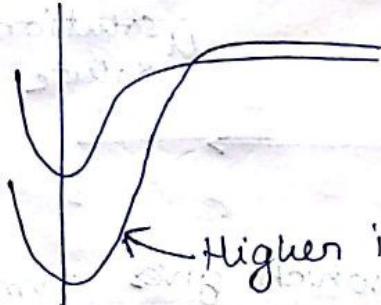
2) Under what condition will a solid dissolve in a liquid?

$$\Delta G = \Delta H - T \Delta S \quad \text{at const. } T, P$$

↑ maintained  
 ↓  
 -ve Enthalpic Entropic



- solution results in minimization of free energy of system.
- Entropy increases in sol<sup>n</sup>  $\Rightarrow$  more entropic contribution
- Enthalpic contribution depends on molecular interaction
- A system with larger interaction has lower free energy.



Dissolution depends on enthalpic barrier & entropic contribution

for  $\text{SiO}_2$  in water

$$\Delta G^\circ = \Delta H - T\Delta S$$

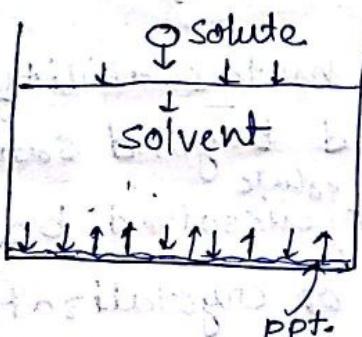
↑                      ↑  
inhibits      Favors

3. How much solid can be dissolved in a given amount of a liquid?

→ saturation is not the cause, it is the result

→  $\Delta H$

→  $\mu$



$$\mu_{\text{solute}}^{\text{solution}} = \mu_{\text{solute}}^{\text{pure solid}}$$

at const. T, P

Phase 1  $\rightarrow$  sol<sup>n</sup> (liquid)

Phase 2  $\rightarrow$  solute (solid)

$$\mu \rightarrow f(T, P)$$

pure solid  
 $\mu_{\text{solute}}$

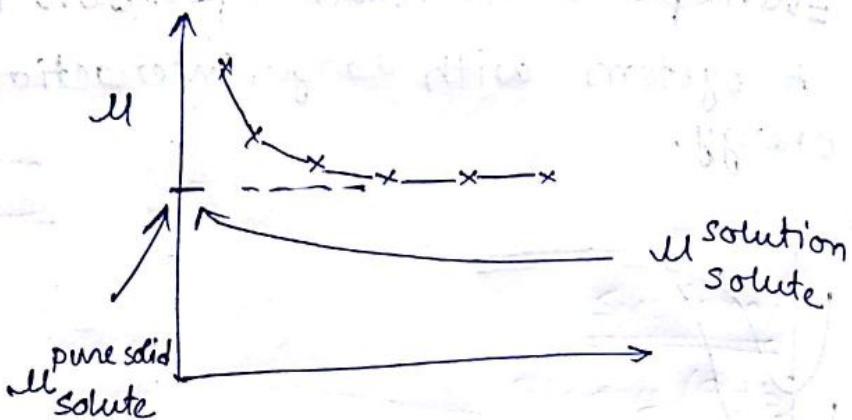
??

Is it const. at given T, P?

$$G_1 = n\mu$$

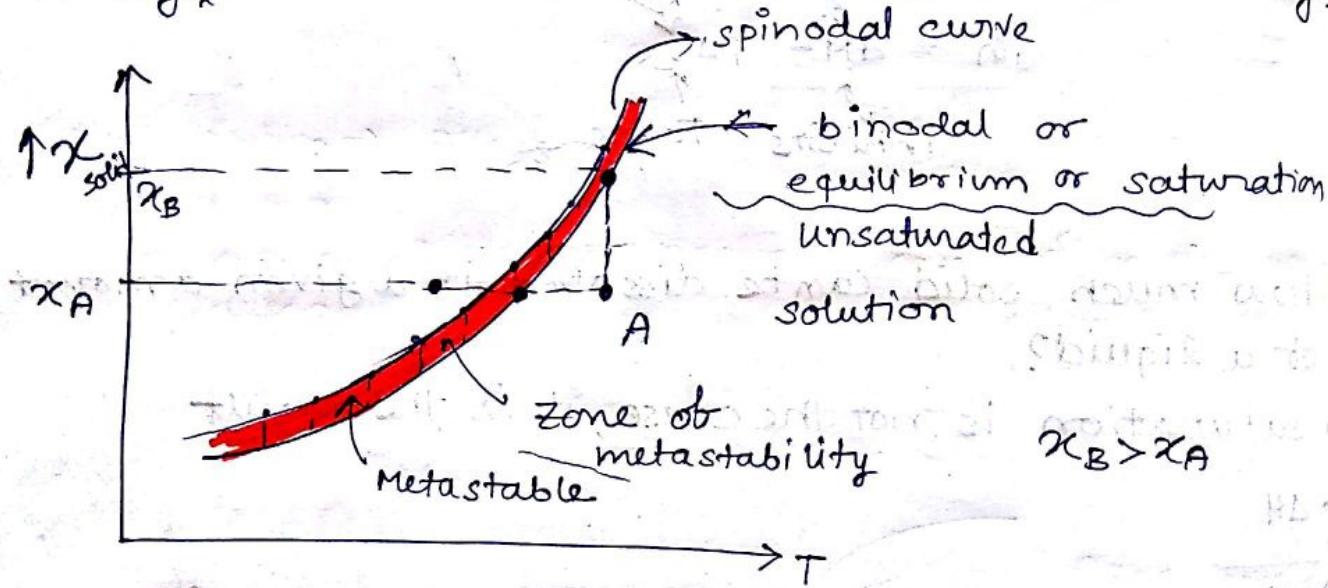
$$\mu = G_1/n$$

Molar quantity

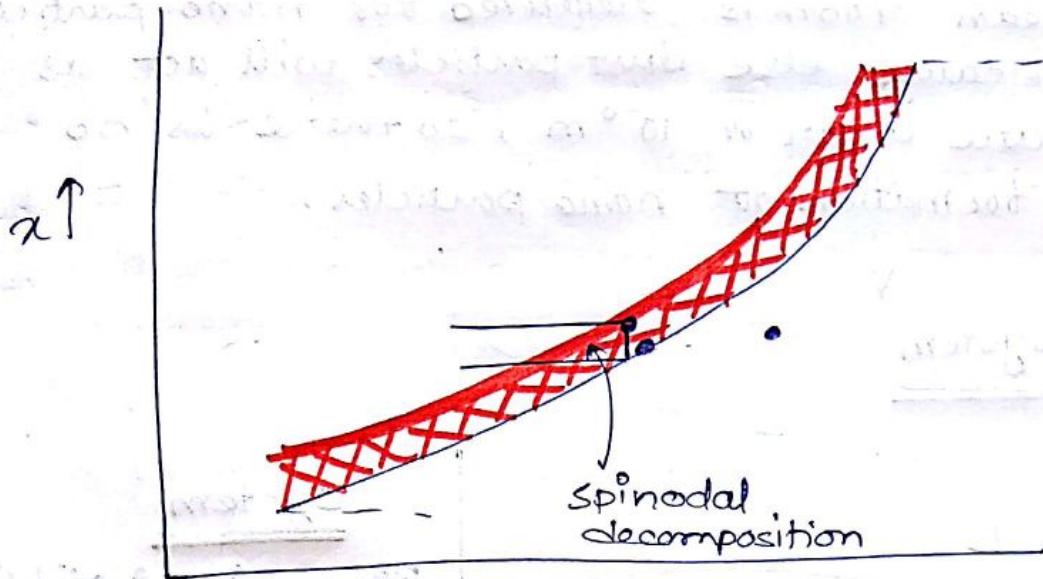


→ The amount of solid in solution which gives same molar gibbs energy of solute can be dissolve in soln at max.

\* Why in different solvents, solute has different solubility?



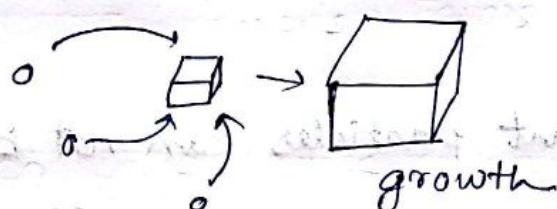
→ Thickness of zone of metastability gives the amount of extra solid dissolved beyond saturation. Thus, more the amount of dissolved beyond saturation more the amount of crystallization



Crystal Formation: 1) size, 2) size distribution

- 1) Nucleation
- 2) Growth

Smallest possible aggregate - nuclei embryos  $\xrightarrow{\infty}$  Better product



3) Breakage

4) Coalescence (Reverse of breakage)

\* 5) Seed  $\rightarrow$  May bring change in energy to start nucleation. External agent to induce nucleation, this is called heterogeneous nucleation.

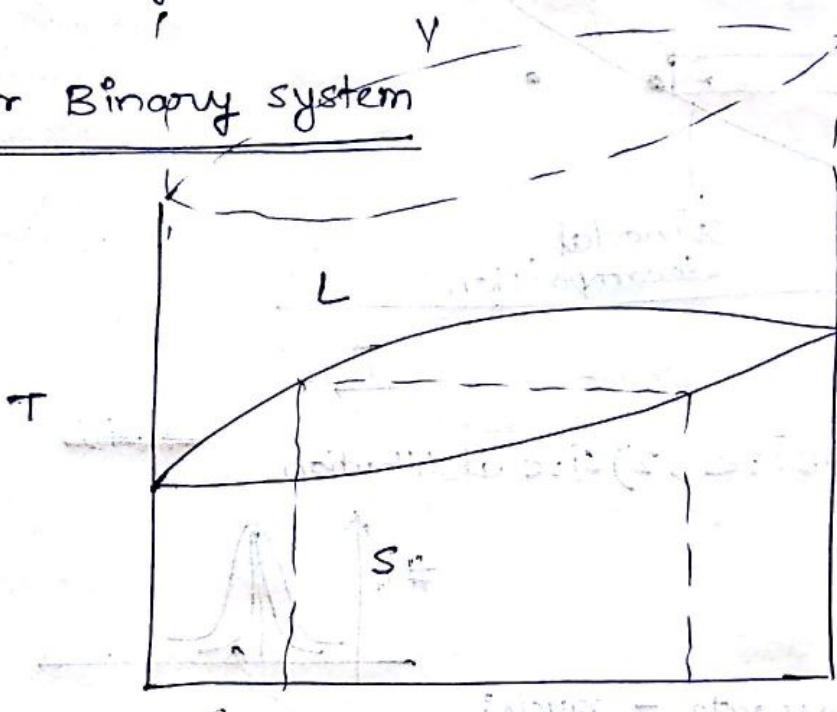
$$\sum (m_i \times n_i) = m_T = \text{const} \quad \leftarrow \text{total mass of mother liquor}$$

$$\sum m_i = m_T \quad \begin{matrix} \uparrow \\ \text{mass of particles} \end{matrix} \quad \begin{matrix} \uparrow \\ \text{No. of particles} \end{matrix}$$

For creating nano particle, required. Clean room is synthesis because else seeds, which are order or possibility of formation of nano particles.

~~homogeneous~~ nucleation is required for nano particle dust particles will act as  $10^{-6}$  m, so there is no possibility of formation of nano particles.

For Binary system



### System

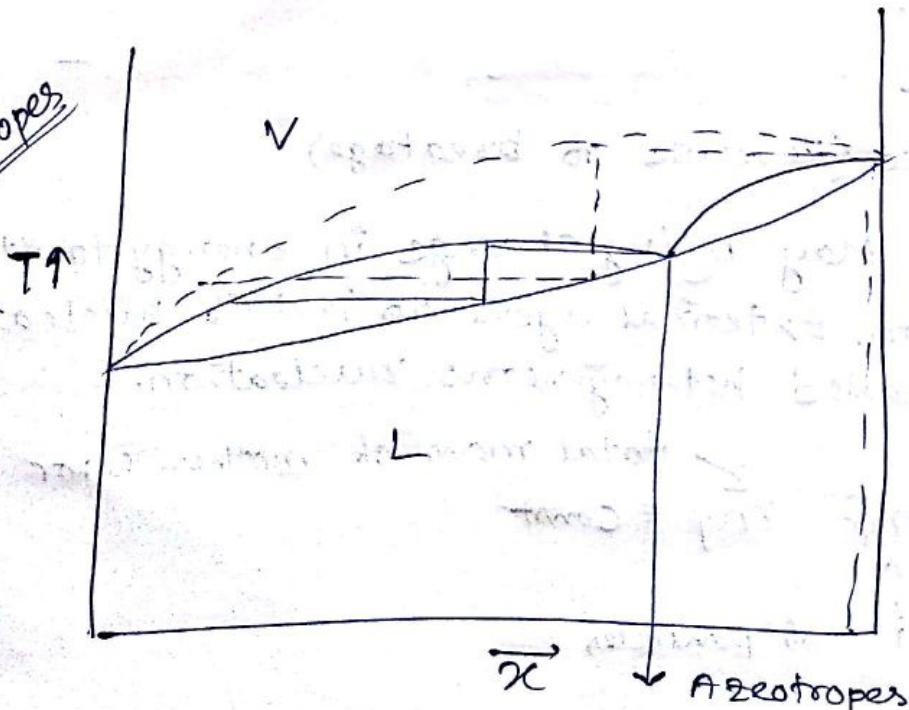
Binary (A+B) solidly soluble in "all" proportions in liquid phase

Solid solution  $\rightarrow$  Alloys

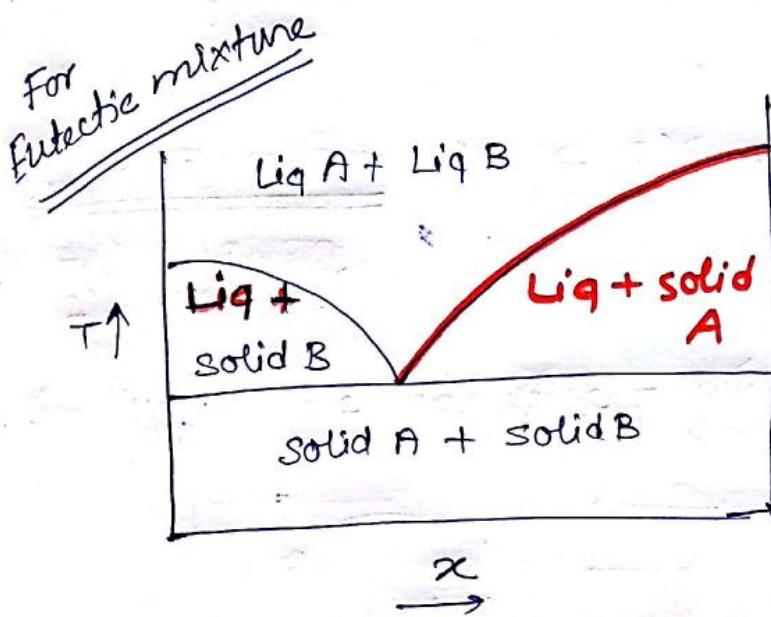
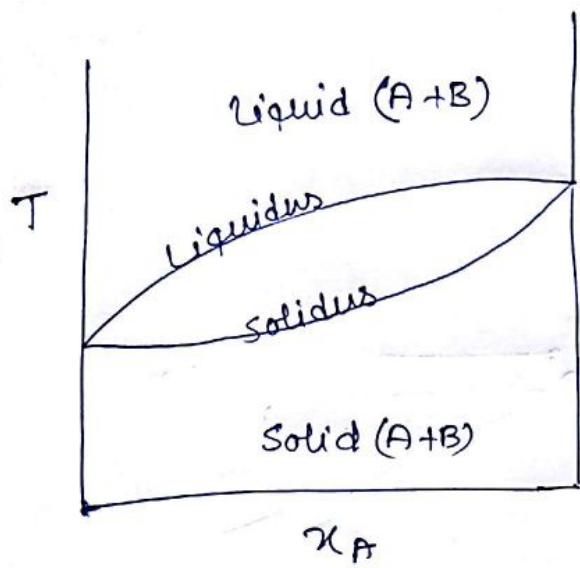
$\begin{matrix} \textcircled{1} & \textcircled{2} & \textcircled{3} \\ \textcircled{4} & \times & \textcircled{5} \\ \textcircled{6} & \textcircled{7} & \textcircled{8} \end{matrix}$

Different particles can not be distinguished

For azeotropes



Azeotropes can not be enriched in 1 phase component. They can not be distilled due to presence of minimum & maximum.



Eutectic behavior

# Reactive systems

12/01/17

Two fundamental questions

1) Condition for reaction eqbm.  $\sum n_i M_i = 0$

2) Reactive phase rule  $\rightarrow f = N - P + 2 - R$

1) Run fast Run far:

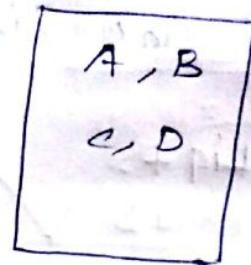
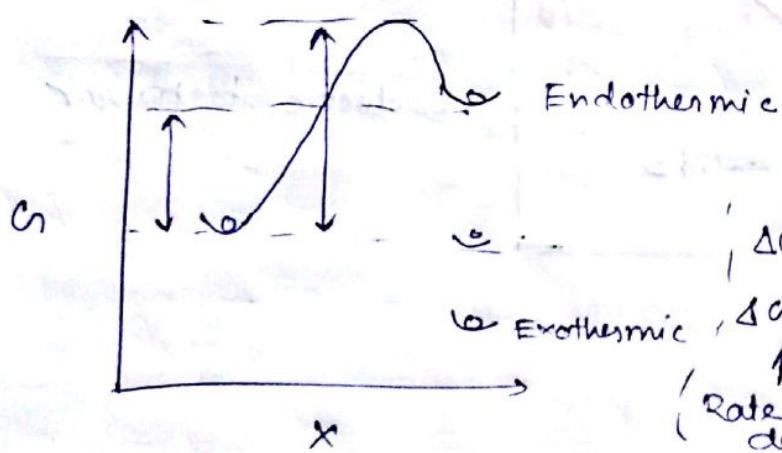
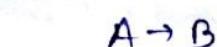
Reaction must take place at a high rate



governs  
time      size of  
the vessel

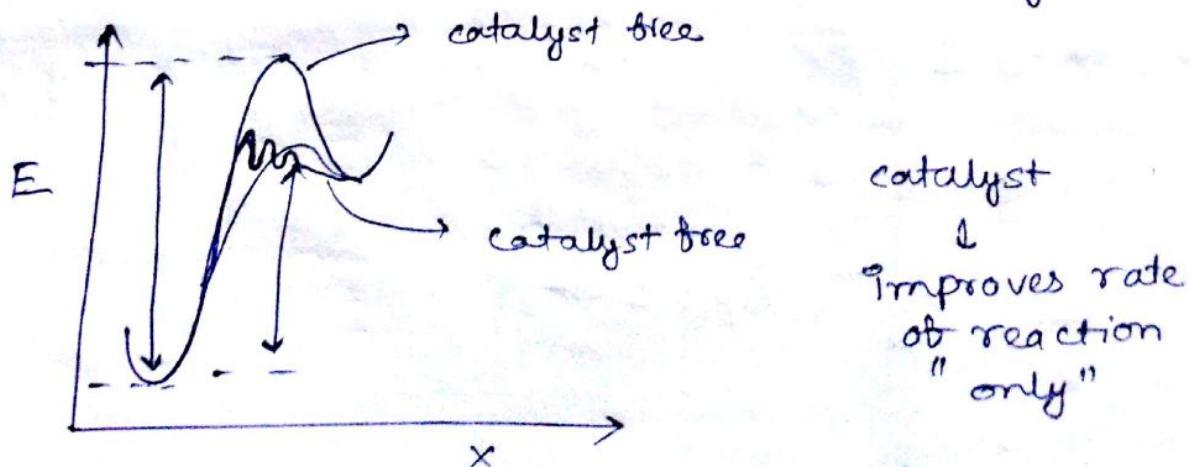
→ Chemical Reaction Engineering

→ Eqbm. conversion can be attained at max.



ΔH<sub>R</sub>  
 ΔG<sup>act</sup>  
 ΔH<sub>R</sub>, ΔG<sup>act</sup>  
 Rate of reaction depends

catalyst → rate of reaction improves due to decrease in activation energy



catalyst  
 ↓  
 improves rate  
 of reaction  
 "only"

$$\sum \gamma_i u_i = 0$$

Assume ideal gas mixture of reactants and products

$$\sum_{i=1}^N \gamma_i u_i = 0$$

$$u_i^\circ = u_i^\circ + RT \ln p_i$$

$$\sum_{i=1}^N (\gamma_i u_i^\circ + \gamma_i RT \ln p_i) = 0$$

$$-RT \sum_{i=1}^N \ln \boxed{p_i^{\gamma_i}} = \boxed{\sum_{i=1}^N u_i \gamma_i}$$

$\uparrow$                              $\uparrow$   
K                             $\Delta G^\circ$

$$\boxed{-RT \ln K_p = \Delta G^\circ} \quad \rightarrow \text{For ideal } \underline{\text{gas}}$$

$$K_p = \frac{p_c^c \cdot p_d^d \cdots}{p_A^a \cdot p_B^b \cdots}$$

$$\Delta G^\circ = \sum \gamma_i u_i^\circ \leftarrow f(T)$$

If, the reaction mixture acts as an ideal gas mixture, then  $K_p$  is a function of T only.

$$\sum \gamma_i u_i = 0$$

$$u_i^\circ = u_i^\circ + RT \ln(f_i)$$

$$\sum_{i=1}^N (\gamma_i u_i^\circ + \gamma_i RT \ln f_i) = 0 \Rightarrow RT \ln K_f = \sum \gamma_i u_i^\circ$$

$$K_f = \frac{f_c^c \cdot f_d^d \cdots}{f_A^a f_B^b} = g(T) \neq$$

- ideal gas mixture  $\rightarrow k_p = g(T)$   
 non-ideal  $n \rightarrow k_f = g(T)$   
 non-ideal gas  $n \rightarrow k_p = g(T, P, x)$

$$-RT \cdot \ln K_p = \sum n_i \mu_i^\circ$$

$$\ln K_p = -\frac{1}{R} \sum n_i (\mu_i^\circ / T)$$

$$\frac{d}{dT} (\ln K_p) = -\frac{1}{R} \sum n_i \frac{d}{dT} (\mu_i^\circ / T)$$

$$\frac{d}{dT} (\ln K_p) = \frac{\Delta H_{\text{Reaction}}}{RT^2} \quad \text{--- Van't Hoff eqn}$$

Van't Hoff eqn

$$\ln \left( \frac{K_{P_2}}{K_{P_1}} \right) = \frac{\Delta H_{\text{Reaction}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Eqbm const.

Independent of catalyst.

Arrhenius eqn

$$k = A_0 e^{-E_a/RT}$$

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

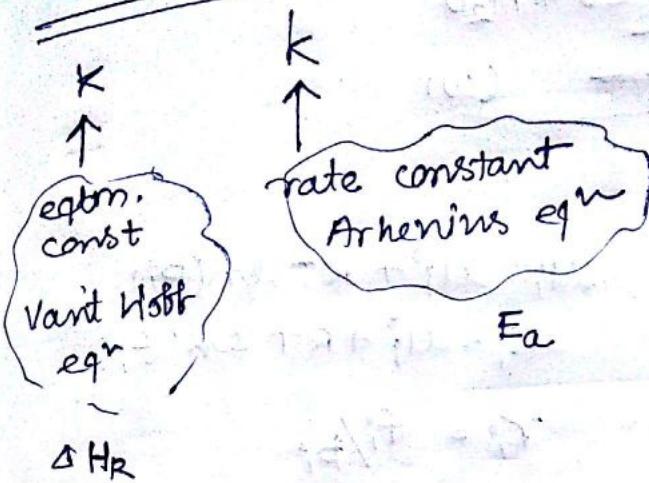
Rate const.

Van't Hoff eqn  $\rightarrow$  used to know the eqbm conversion

Arrhenius eqn  $\rightarrow$  in  $\ln v \propto \ln k$   $\propto$  rate const.

# Calculation of Eqbm. Composition

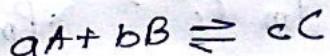
13/04/17



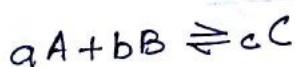
$k \rightarrow$  no fixed units (hence unit)

$$r = -k_1 C_A^\alpha C_B^\beta + k_2 C_C^\gamma$$

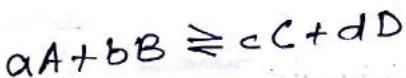
$$\frac{dc}{dt} = \text{mol/L.s}$$



$$\alpha = \beta = \gamma = 1 \Rightarrow r = -k_1 C_A C_B + k_2 C_C$$



$$k_{P_1} = \frac{P_C^c}{P_A^a P_B^b}$$



$$k_{P_2} = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

$$\mu = \mu^\circ + RT \ln(P/P^\circ)$$

$$\mu_i^\circ = \mu_i^\circ + RT \ln(P_i^\circ/P) \rightarrow \text{gases}$$

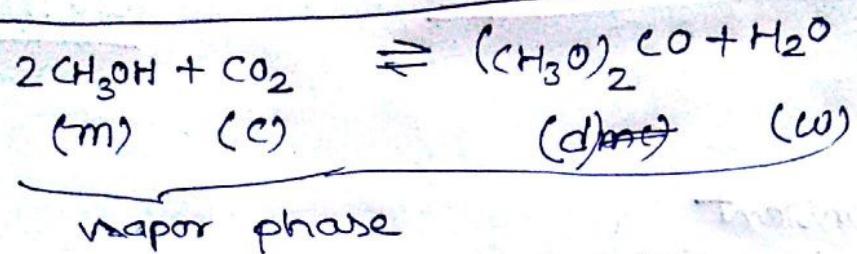
$$\mu_i = \mu_i^\circ + RT \ln x_{ii} \rightarrow \text{liq}$$

\* Industrial and Engineering chemistry Research 2015,

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## Calculation of eqbm. composition



$$K_f = \frac{f_d f_w}{f_m^2 f_c}$$

$$\mu_i^\circ = \mu_i^\circ + RT \ln(p_i^\circ)$$

$$\mu_i^\circ = \mu_i^\circ + RT \ln(f_i)$$

$$\gamma_i^\circ = f_i^\circ / p_i^\circ$$

$$K_f = \left( \frac{\gamma_d \gamma_w}{\gamma_m^2 \gamma_c^\circ} \right) \left( \frac{p_d p_w}{p_m^2 p_c} \right)$$

$$K_f = [ \quad ] \cdot \left( \frac{p_d \cdot p_w}{p_m^2 p_c} \right)$$

Fugacity Coefficients



$$\begin{array}{cccc} 1 & 0 & 0 & 0 \\ (1-x) & (0-\frac{x}{2}) & \frac{x}{2} & \frac{x}{2} \end{array} \quad \text{--- at eqbm.}$$

$$\text{total no. of moles at eqbm} = 1+0-\frac{x}{2}$$

$$y_m^{eq} = \frac{1-x}{1+0-\frac{x}{2}}$$

$$y_c^{eq} = \frac{0-\frac{x}{2}}{1+0-\frac{x}{2}}$$

$$y_d^{eq} = \frac{\frac{x}{2}}{1+0-\frac{x}{2}}$$

$$y_w^{eq} = \frac{\frac{x}{2}}{1+0-\frac{x}{2}}$$

$$K_f = \left[ \begin{matrix} \checkmark \\ \checkmark \end{matrix} \right] \frac{1}{P} \left[ \begin{matrix} \cancel{(x_{11}^{\alpha_1})} (1 + \checkmark - x_{12}^{\alpha_2}) \\ \cancel{(1 - x_{11}^{\alpha_1})} (1 - \checkmark - x_{12}^{\alpha_2}) \end{matrix} \right]$$

$$K_f = g(x^{eq})$$

$$x^{eq} = g^{-1}(K_f)$$

$\text{en}(b_i)$

$\text{en}(f_i)$

$$x^{eq} + c \geq d + w$$

$$(1-x)^{eq} (0 - \frac{x^{eq}}{2}) \quad \frac{x^{eq}}{2} \quad \frac{x^{eq}}{2}$$

— X —