

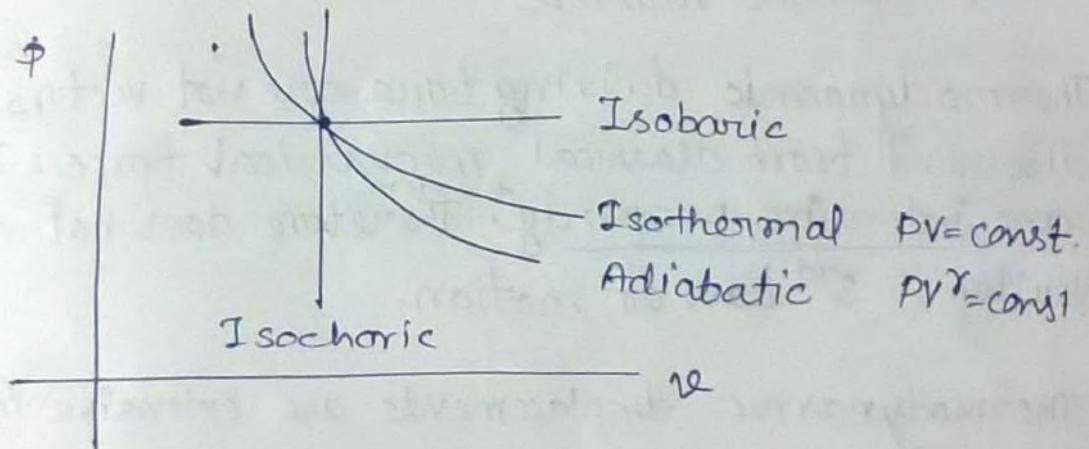
11/01/2017

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

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

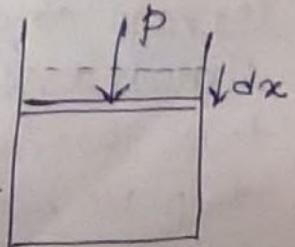
$$\left\{ \begin{array}{l} n=\infty \\ \text{Isochoric } V=\text{const. } PV = dW \\ n=0 \\ \text{Isobaric } P = \text{const. } P(V_2 - V_1) = P[dV] \\ n=1 \\ \text{Isothermal process } \int PdV = nRT \ln \frac{P_2}{P_1} \\ n=\gamma \\ \text{Adiabatic process } \Rightarrow PV^\gamma = \text{const} \end{array} \right.$$



Energy is capacity to ^{induce a} 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

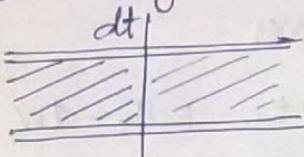


$dV \rightarrow$ Thermodynamic displacement
(volume change)

For an elastic rubber

Tension \rightarrow driving force
displacement \rightarrow length increased

Flow through a fluid



Flow work

$$= PAU dt$$

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

$$= P Q dt$$

for unit mass, work rate

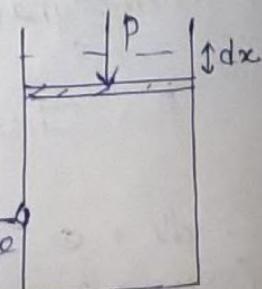
$$= P \times \text{specific volume}$$

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 3rd Law of motion.

Thermodynamic displacements are extensive property of system.

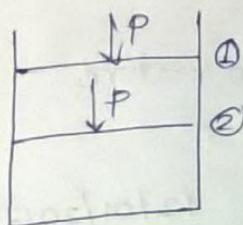
If One driving force brings ~~the~~ only one thermodynamic displacement, then only thermodynamic work done can be calculated

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 ΔW 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 ΔT
 \Rightarrow Work

Selection of system is crucial

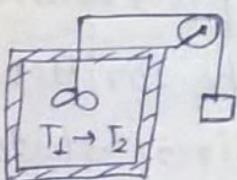
$$\oint dW \neq \oint dQ$$

~~box~~

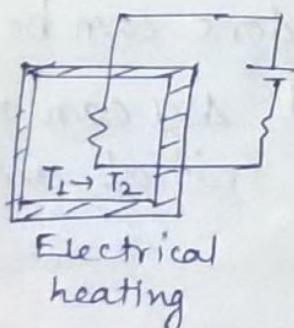
Why heat can not be included in entire domain of work?

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 1st 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

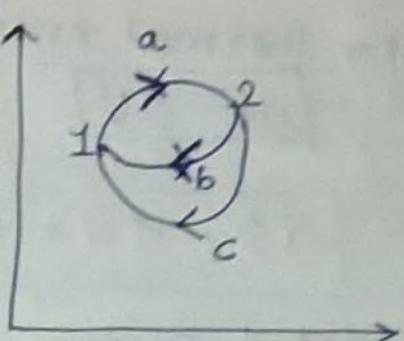
$$\oint dQ = \oint dQ$$

$1a2b$ $1b2b$

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

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

- -



$$dW = f \cdot r$$

Thermodynamic driving force

Thermo-dynamical displacement

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

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

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

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

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

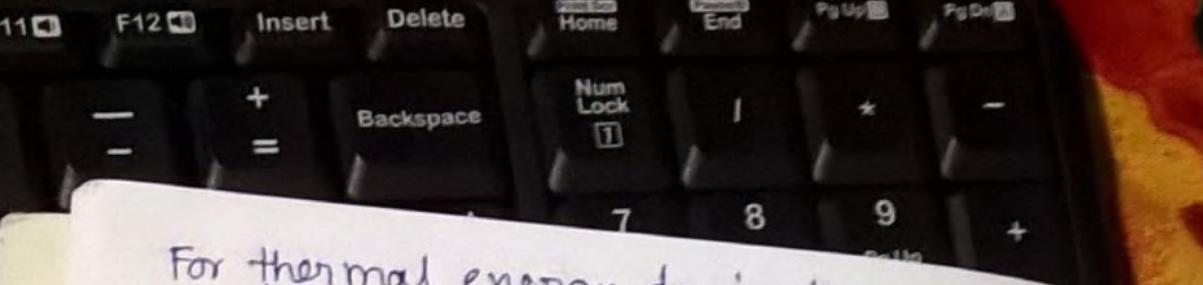
$$(dQ - dW) = dE$$

difference of
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

$$dE = dU$$

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

isolated system

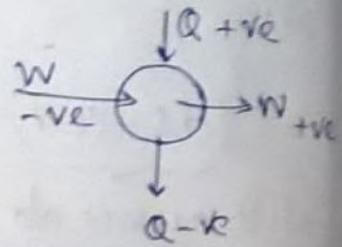
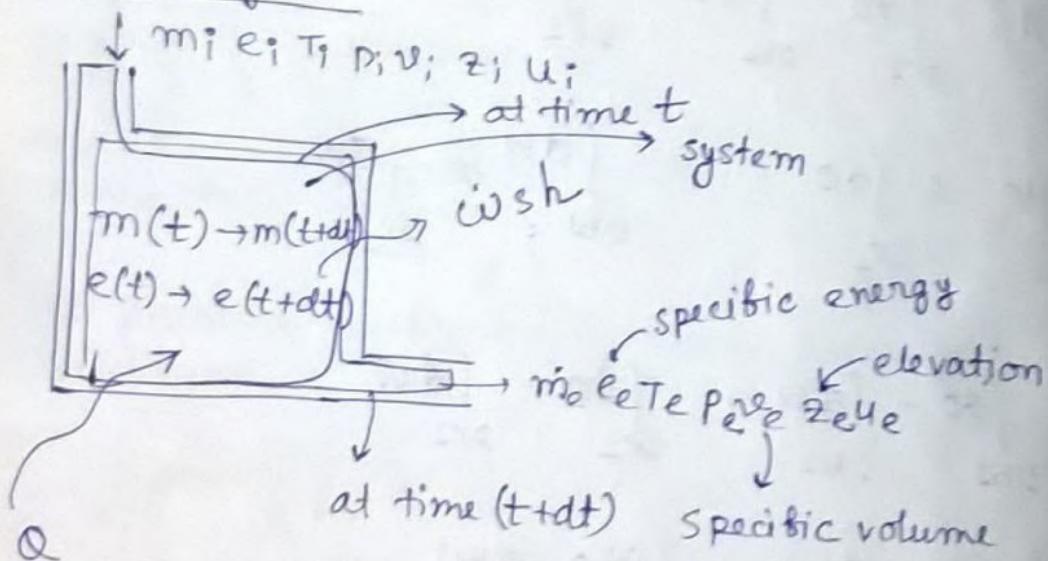
$$dQ = 0$$

$$dW = 0$$

$$dE = 0$$

$$\boxed{E_{\text{system}} = \text{constant}} \Rightarrow \text{Principle of conservation of energy}$$

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 + ^{mass about to enter in time dt}

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

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

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

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

$$\cancel{\dot{m}_e} \quad \dot{m}_e - m_e = \frac{dm_e}{dt}$$
$$\cancel{\dot{Q}} - \cancel{\dot{W}} = dU$$

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

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

Find 1st law for open system

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

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

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

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

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

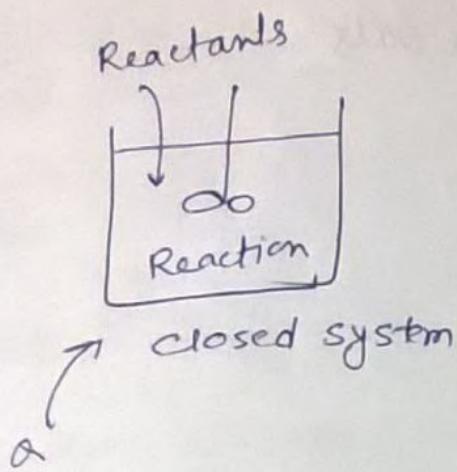
~~APL~~

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

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

where $H = U + P V$

13/01/2017



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

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

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

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

State t^n	Path t^n
ΔE	W
ΔH	Q
ΔS	
T, P, V	

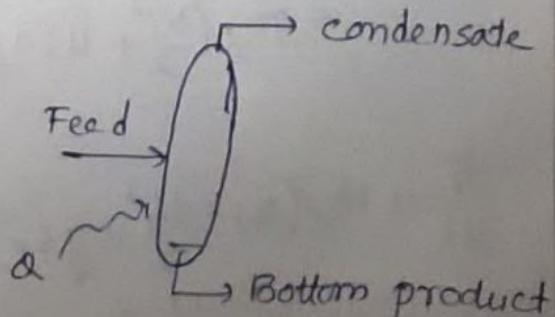
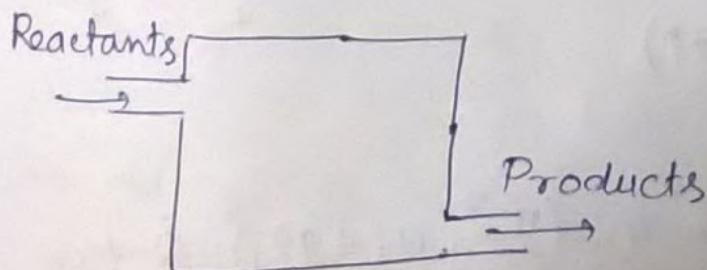
$$Q_p = C_p \Delta T = \Delta H$$

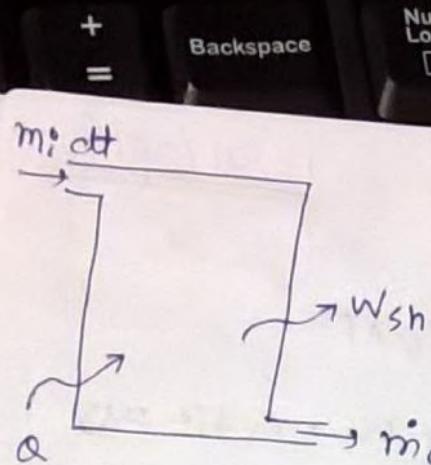
$$Q_v = C_v \Delta T = \Delta U$$

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

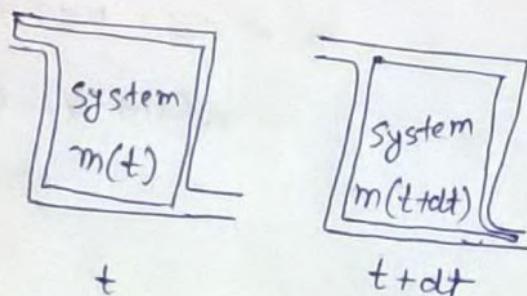
$Q \neq C_v \Delta T$ if volume is not const.

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





$t \rightarrow dt$ intervals



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

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

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

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

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

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

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

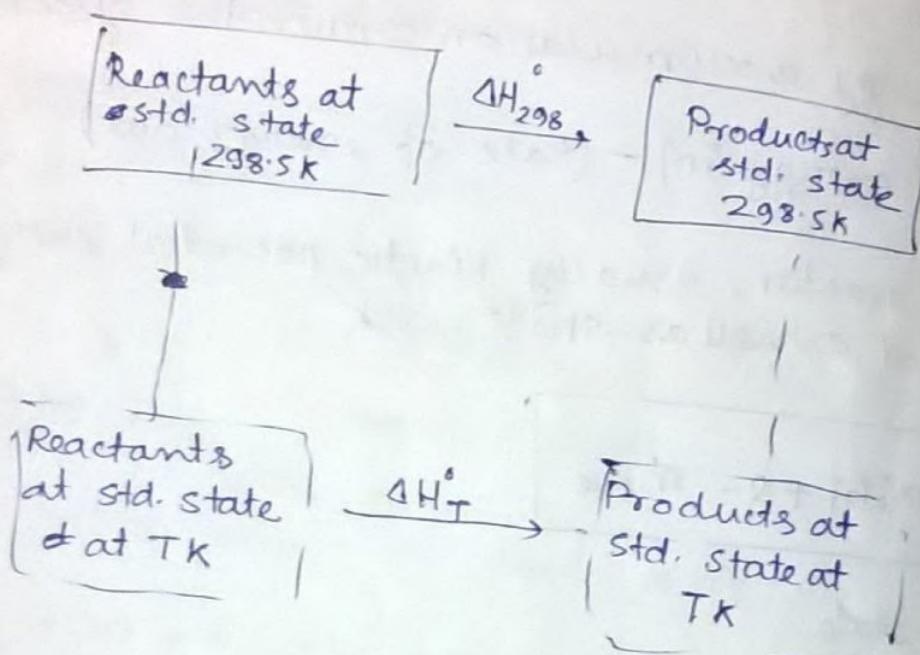
pure liquid at 1 atm

pure solid at its most stable allotropic form at 1 atm



ΔH_f°

ΔH°
298.15 K

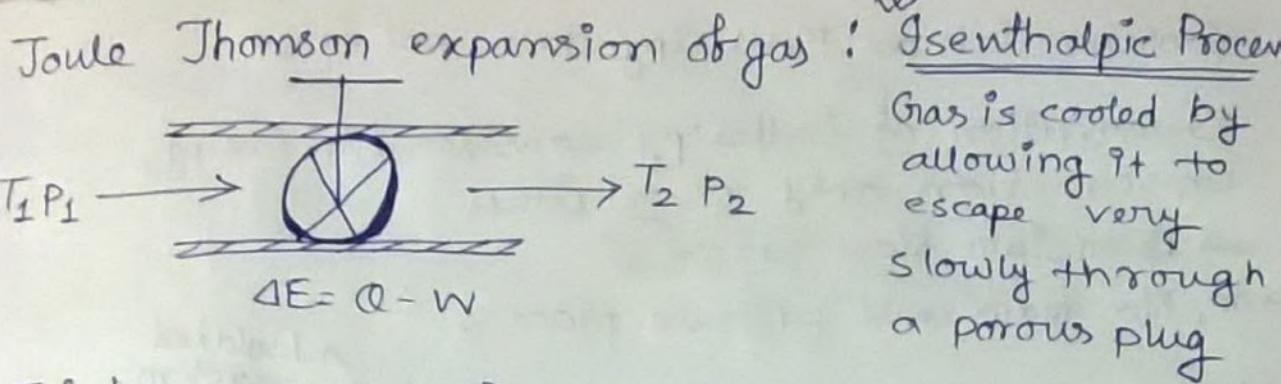


* $\sum v_i^\circ A_i = 0$

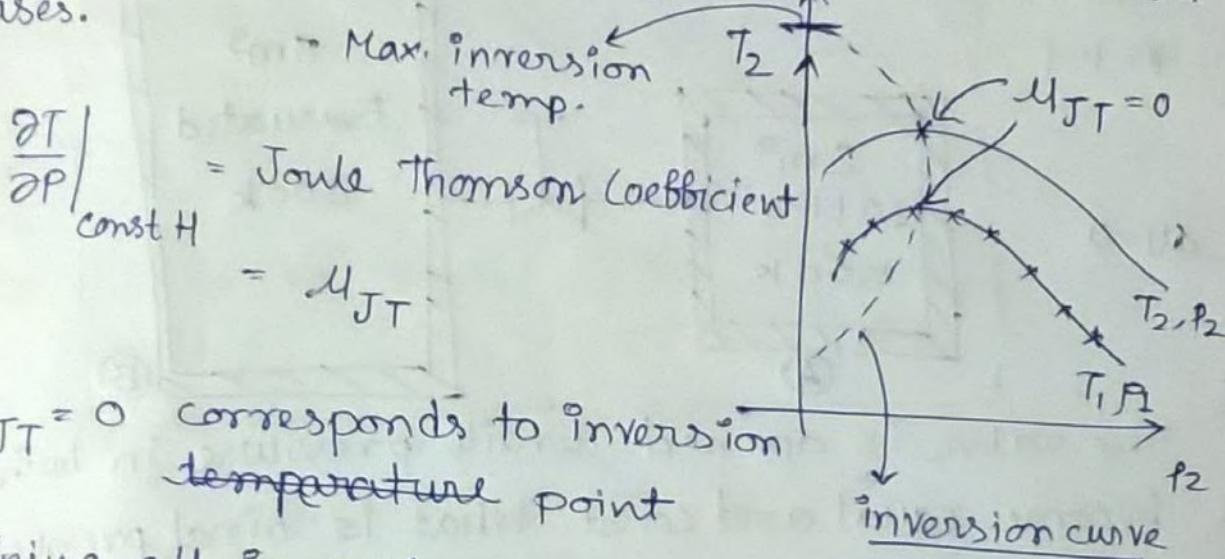
v_i is +ve for product

v_i is -ve in reactant

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



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

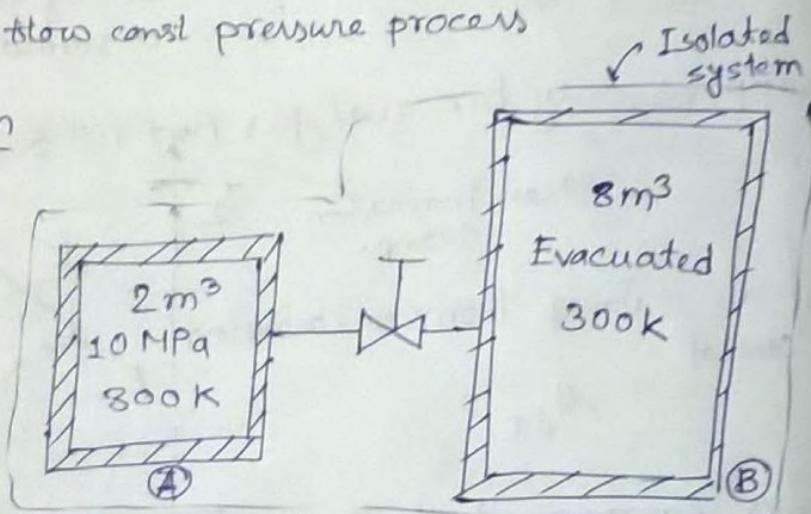
Conservation of Enthalpy does not exist

Conservation of Enthalpy considered in Energy conservation only when either
→ Reversible flow process
→ or, No flow const pressure process

Problem

$$\gamma = 1.4$$

$$\Delta U = 0$$



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

Assumption: Air in tank A undergoes reversible adiabatic expansion

Ex: Prove the assumption

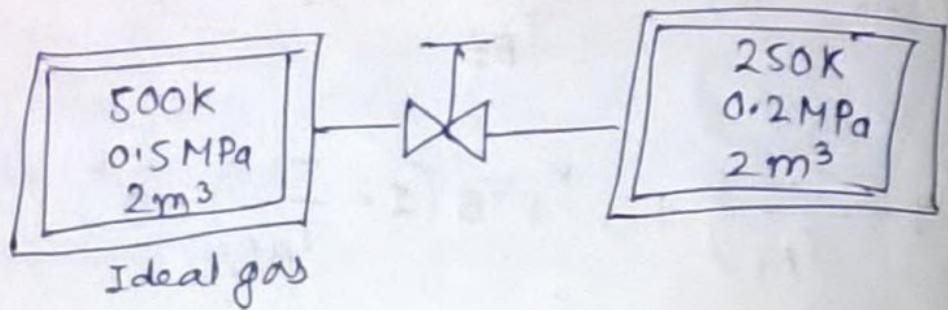
$$N_{A_f} = N_{A_i} + N_{B_f}$$

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

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

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

Q.2



Same question as previous

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

$$dW = F \, dr$$

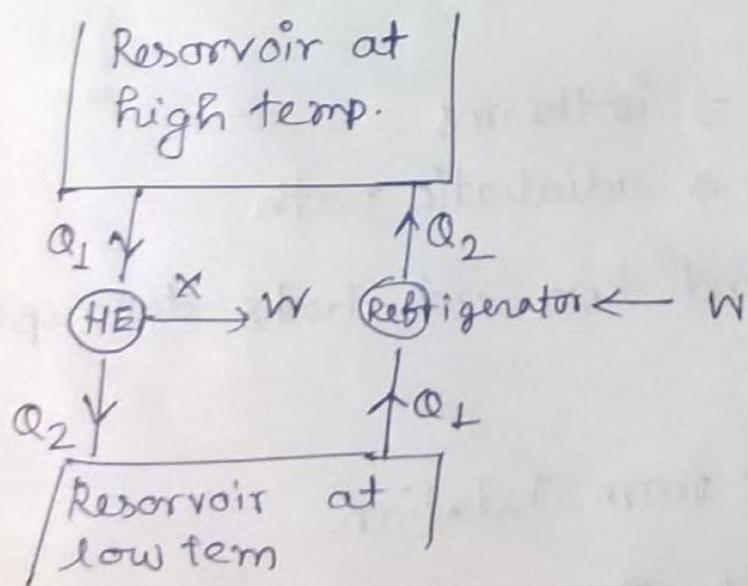
For changing and discharging of a tank

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

at steady state $\frac{dE}{dt} = 0$, $m_i = m_e$

$$\Delta H = Q$$

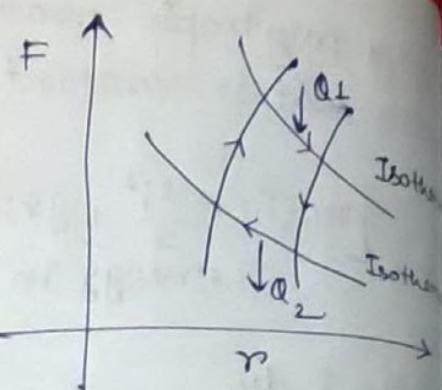
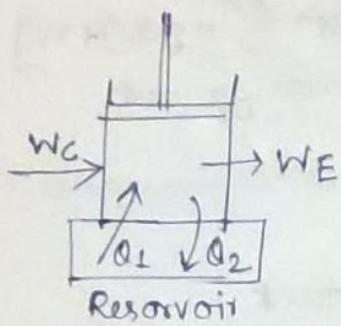
$$\Delta H = m(\bar{h}_e - \bar{h}_i)$$



2nd 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 η 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 heat and work.

All these laws are from intuition

Postulates of Carnot ∇ (Forms basis of Therm)

Theorem 1 : Efficiency of all reversible

$n_{rev} > n_{irrev.}$ ∇ Prove it

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

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

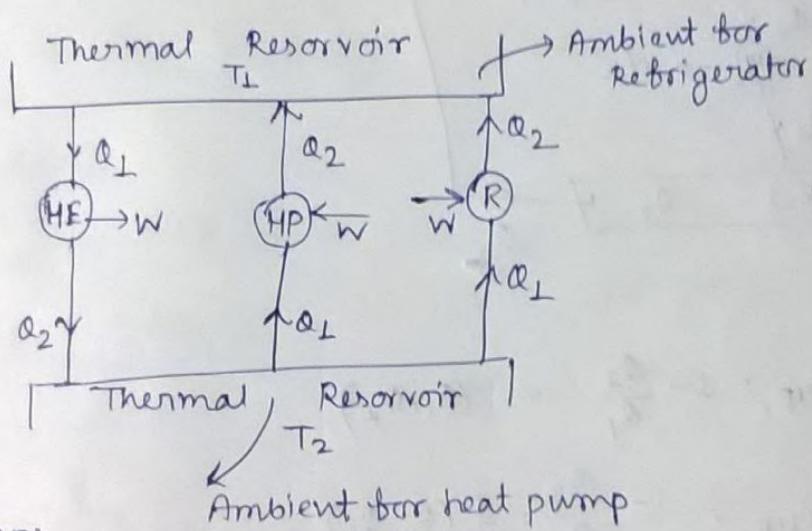
Theorem 3: For ideal gases, on which process is to be performed

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

Claussius inequality gives entropy-concept.

19/01/17

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



(COP)

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

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

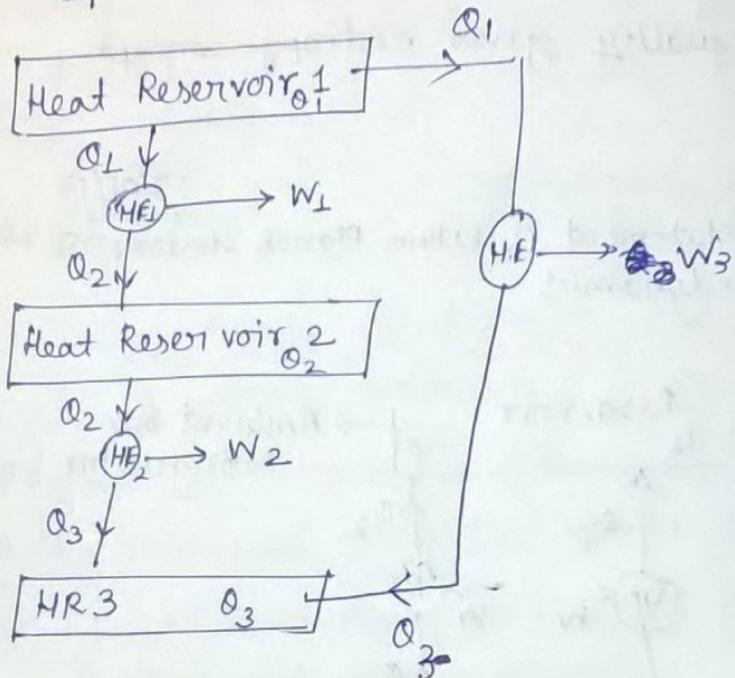
$$(\text{COP})_R = \frac{\text{Energy effect sought}}{\text{Energy expended}}$$

Ax

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

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

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

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

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

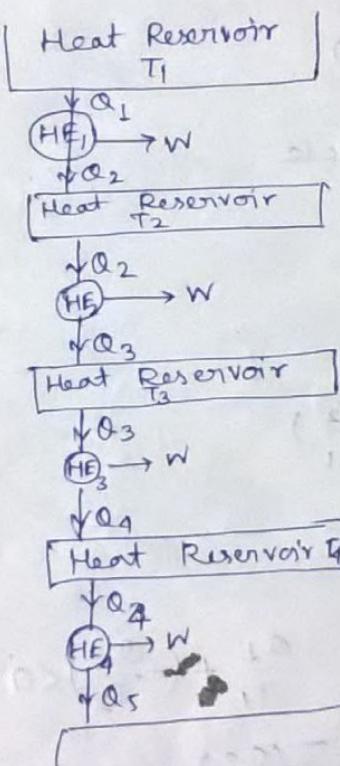
What is the lowest temp achievable by series of H.E series?

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

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

$$n_{irr} < n_R$$

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

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

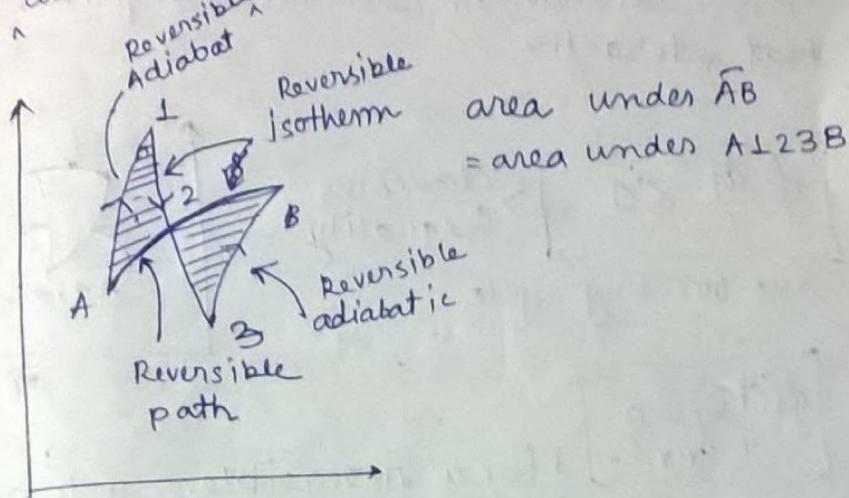
$$\frac{Q_2}{T_2} > \frac{Q_1}{T_1} \quad \frac{Q_1}{T_1} + \left(-\frac{Q_2}{T_2}\right) < 0$$

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

cannot cycle

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

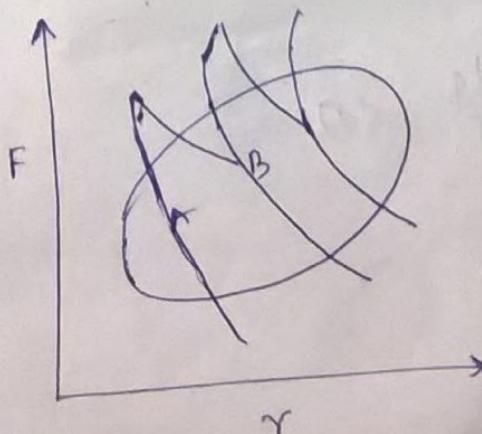
Any reversible process can be expressed as an reversible adiabat, an reversible isotherm and another reversible adiabat



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

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

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

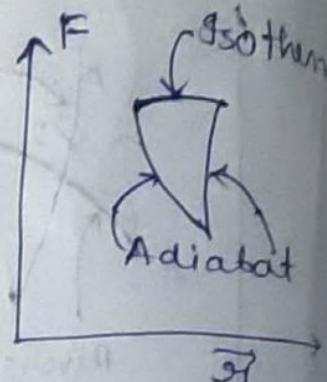


A cyclic reversible process can also be expressed in such a way consisting numerous adiabats joined by numerous isotherms.

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

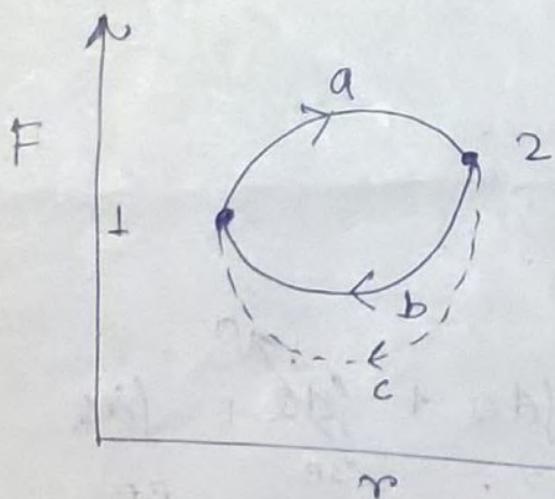
$$\phi \frac{dq}{T} \leq 0 \quad \Rightarrow \text{ Clausius Inequality}$$

True for any cycle



$$f\left(\frac{dq}{T}\right)_{rev} = 0$$

for a reversible cycle only
 q behaves as state function



$$\phi\left(\frac{dq}{T}\right) = \int \frac{dq}{T} + \int \frac{dq}{T}$$

1a2b₁ 1a₂ 2b₁

= 0

$$\int_{1a_2}^{\left(\frac{d_2}{T}\right)} = - \int_{2b_1}^{\frac{d_2}{T}} = \int_{1b_2}^{\frac{d_2}{T}} = \int_1^2 ds = S_2 - S_1 = 4$$

$$\oint \frac{dq}{T} = \int_{12} \frac{dq}{T} + \int_{21} \frac{dq}{T} < 0$$

$$\left[-\int \frac{dq}{T} + \int \frac{dq}{T} \right] < 0$$

(2a) rev (2c) irrev.

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

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

$$\begin{aligned} \cancel{\frac{ds}{dt}} &\rightarrow ds = \left(\frac{dq}{T}\right)_{rev} \\ &ds > \left(\frac{dq}{T}\right)_{irrev.} \end{aligned} \quad \boxed{\quad} \quad \checkmark$$

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

Process is reversible. Proceed in both directions

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

Spontaneous in forward direction

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

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

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

$$ds = \frac{dq}{T} + \cancel{dS_{irr}}$$

Entropy gen. due to irrev. process

Adiabatic process: $\cancel{dq} = 0$

$ds = 0$ for reversible adiabatic process

$ds > 0$ irreversible

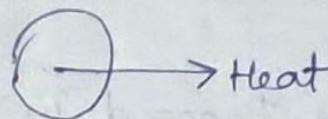
$$ds = \cancel{dS_{irr}}$$

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 : $dW=0$, $dq=0$

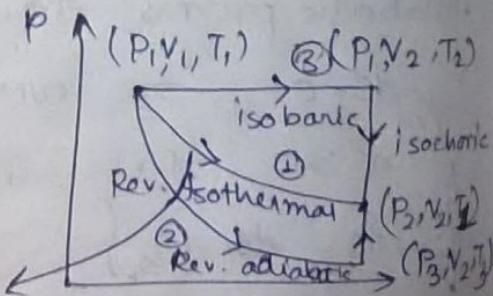
$$(ds)_{\text{isolated}} \geq \left(\frac{dq}{T}\right)_{\text{isolated}} = 0$$

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

Entropy of the universe is always gradually increasing.

??

Ideal gas / 1 mole



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

Enter

3
Pg Dn

Del

23/01/17

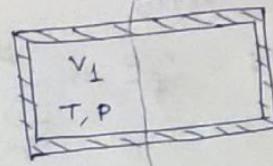
$$1) V_1, T, P_1 \rightarrow (V_1 + V_2), T, P$$

reversible isothermal path

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

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

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

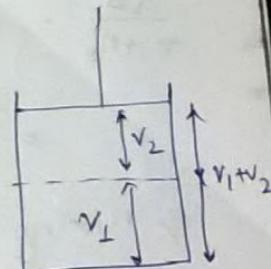


$$ds = \frac{nR}{T} \ln \left(\frac{V_1 + V_2}{V_1} \right) > 0$$

⇒ The process is spontaneous

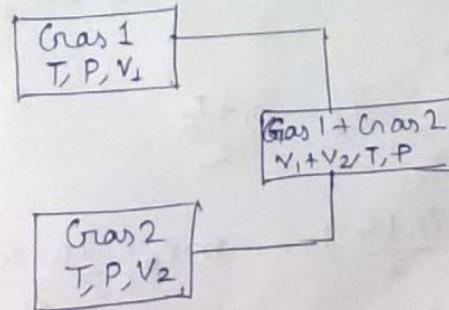
$$2) ds = \frac{nR}{T} \ln \left(\frac{V_1 + V_2}{V_1} \right)$$

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



Rev. isothermal

3)



$$\text{Gas 1: } p \rightarrow p_1$$

$$\text{Gas 2: } p \rightarrow p_2$$

$$Q = \frac{nR}{T} \ln \frac{P}{P_1} + \frac{nR}{T} \ln \frac{P}{P_2}$$

$$= \frac{nR}{T} \ln \frac{P^2}{P_1 P_2}$$

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

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

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

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

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

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

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

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

$$= +ve$$

\Rightarrow Mixing of ideal gases is spontaneous

4) Transfer of heat from hot to cold body.

$$mC_p \quad mC_p$$

$$(T_h) \quad (T_c)$$

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

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

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

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

$$\int_1^2 dS_C = \int_{T_h}^{T_f} \frac{mc_p dT}{T}$$

$$\Delta S'_h = +mc_p \ln\left(\frac{T_f}{T_h}\right)$$

$$\Delta S_C = +mc_p \ln\left(\frac{T_f}{T_c}\right)$$

$$\Delta S = -mc_p \ln\left(\frac{T_h}{T_c}\right) \quad \cancel{+ mc_p \ln\left(\frac{T_f}{T_h}\right)}$$

$$= -mc_p \ln\left(\frac{T_h}{T_c}\right)$$

$$= mc_p \ln\left(\frac{T_c}{T_h}\right)$$

$$= mc_p \ln\left(\frac{T_c}{T_h}\right)$$

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

$$T_h > T_c$$

$$T_h - T_c > 0$$

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

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

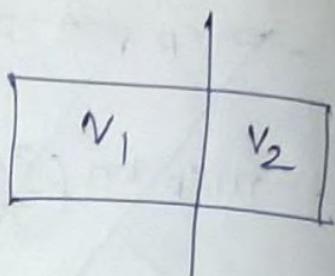
$$(T_h + T_c)^2 > 4T_h T_c \Rightarrow \ln\left(\frac{(T_h + T_c)^2}{4T_h T_c}\right) > 0$$

$$\Rightarrow \Delta S > 0$$

Thermodynamic probability of a state is determined by entropy.

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

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 kg of air (ideal) into N_2, O_2 at 0.1 MPa.

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

There is a limit to available energy

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

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

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

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

$$dW_{\max} = d\bar{q}_1 \left(1 - \frac{T_{\text{ambient}}}{T_1} \right)$$

$$W_{\max} = \int_a^b d\bar{q}_1 - \int_a^b \frac{d\bar{q} \cdot T_{\text{ambient}}}{T_1}$$

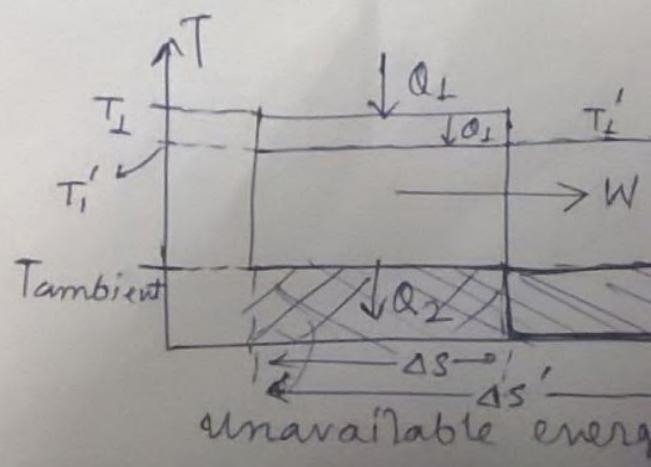
$$W_{\max} = Q_1 - T_{\text{ambient}} \int_a^b dS$$

$$\Rightarrow Q_1 - \underbrace{T_{\text{ambient}} (S_b - S_a)}_{\text{Unavailable energy (U.E)}}$$

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.

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

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

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

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

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

$$A.E \Big|_{\text{initially}} = \cancel{Q_1} \rightarrow (T_1 - T_{\text{ambient}}) \Delta S$$

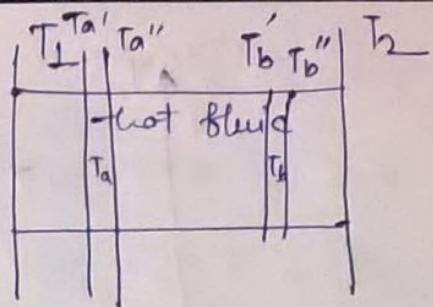
$$\cancel{A.E \Big|_{\text{now}}} = T_f$$

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

Q Taking both input & output ^{of} heat to be irreversible, find the W_{lost}.

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

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



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

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

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

$$\Delta S_b > \Delta S_a$$

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

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

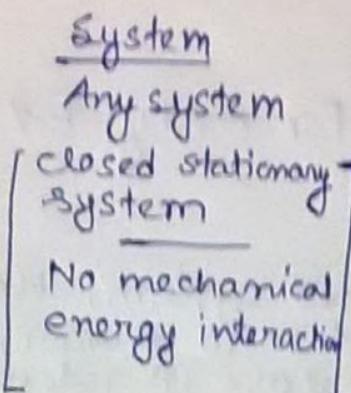
$$= T_{ambient} (\Delta S_b - \Delta S_a)$$

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

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

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



$$\delta q = TdS$$

Any system

Reversible process

$$TdS = dU + pdV$$

only PV work

$$TdS = dH - Vdp$$

- In case of irreversible processes, the deviation of TdS from δq and of pdV from δW 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.

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

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

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

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

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

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

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

$$TdS \geq dU + pdV$$

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

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

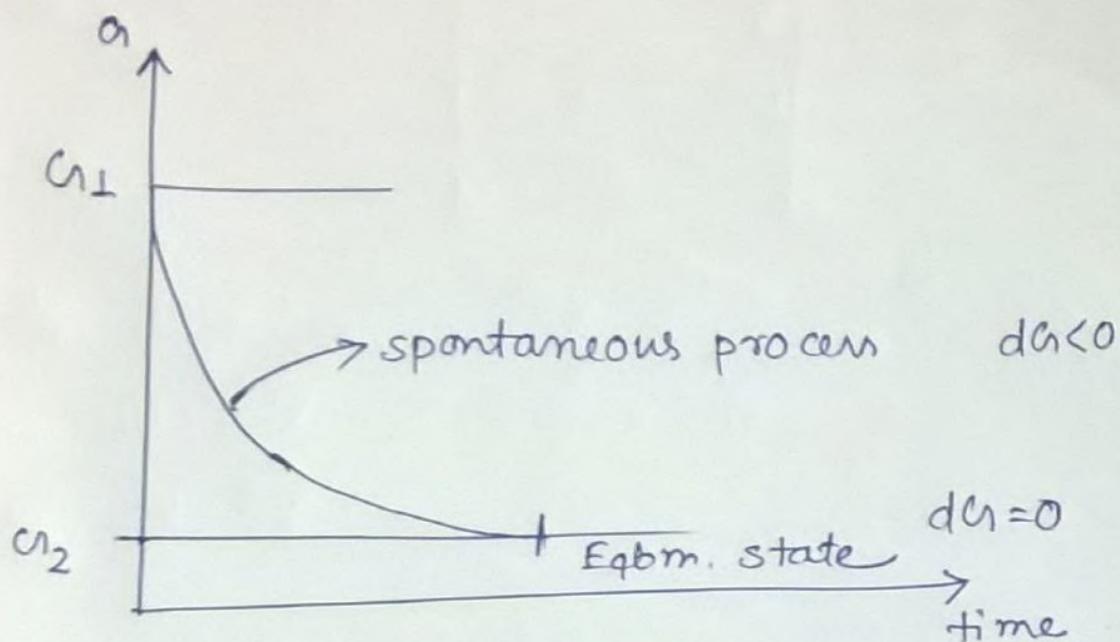
$$\underbrace{d(U-TS)}_{A,T,V} \leq 0$$

$A \rightarrow$ 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

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

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

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

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

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

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

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

27/01/17

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

↓

Isolated Isothermal

Non spontaneous

+ve H

Spontaneous

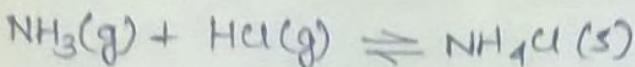
-ve H

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

-ve S

+ve S

Sobaru's isothermal



$$\Delta H_R |$$

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

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

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



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

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

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

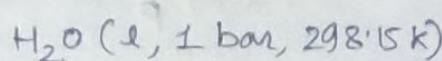
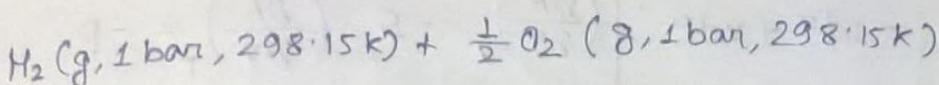
$$\begin{aligned} \Delta G_R |_{90^\circ} &= [40.64 \times 10^3 - 363 \times 108.9] \\ &= 1109.3 \text{ J/mole} \end{aligned}$$

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

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

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

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



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

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

$$G = U + PV - TS$$

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

$$= (\cancel{\partial A}_{rev} - \cancel{\partial W}_{rev}) + PDV + VdP - T\cancel{\partial S} - SdT$$

$$= \cancel{VdP} (VdP - SdT) - (\cancel{\partial W}_{rev} - \cancel{pdV})$$

$$dG = (VdP - SdT) - (\cancel{\partial W}_{rev} - \cancel{pdV})$$

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 diff' 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

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

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

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

$$dP = Mdx + Ndy$$

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

$$dP =$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$s(v_1, T_2) - s(v_1, T_1) = \int_{T_1}^{T_2} \frac{(\partial u)}{(\partial v)}_v dT = \int_{T_1}^{T_2} \frac{(\partial u)_v}{(\partial s)_v} dT = \int_{T_1}^{T_2} \frac{c_v}{T} dT$$

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

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

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

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

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

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

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

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

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

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

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

$$\boxed{T ds = c_p dT - T v \beta dP}$$

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

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

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

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

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

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

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

for ideal gas $PV=RT$

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

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

$$\frac{\partial V}{\partial P}$$

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

$$PV = RT$$

$$P = \frac{RT}{V}$$

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

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

30/01/17

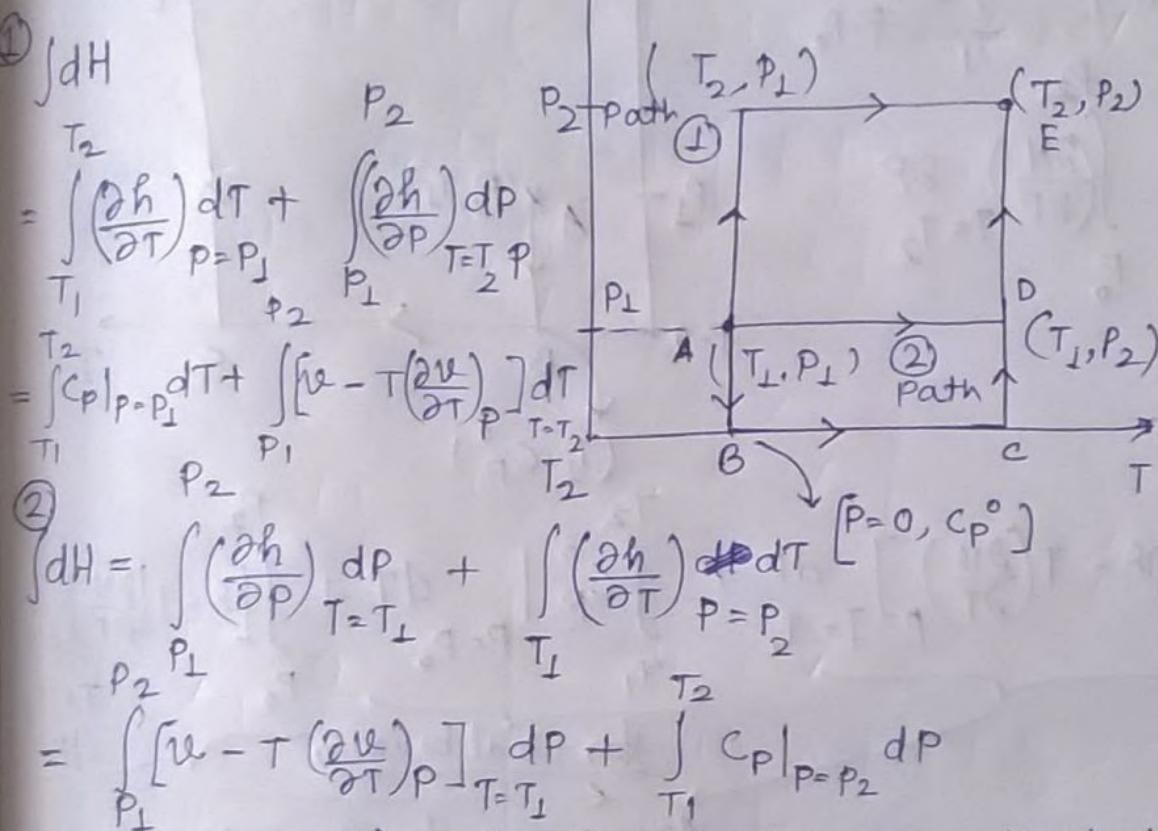
$$dU = C_V dT + T \left(\frac{\partial P}{\partial V} \right) dP$$

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

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

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

Calculation of ΔH for the given P-T diagram following 2 different paths



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

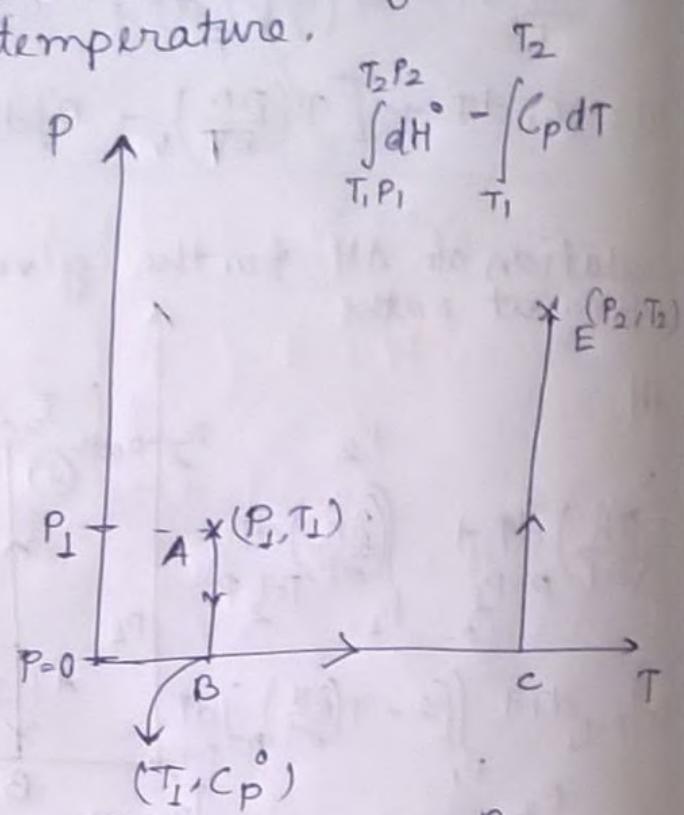
Three roots of VDW eqn gives volume of gaseous state, volume of saturated liquid, and a fictitious i.e. unrealistic volume.

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

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

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

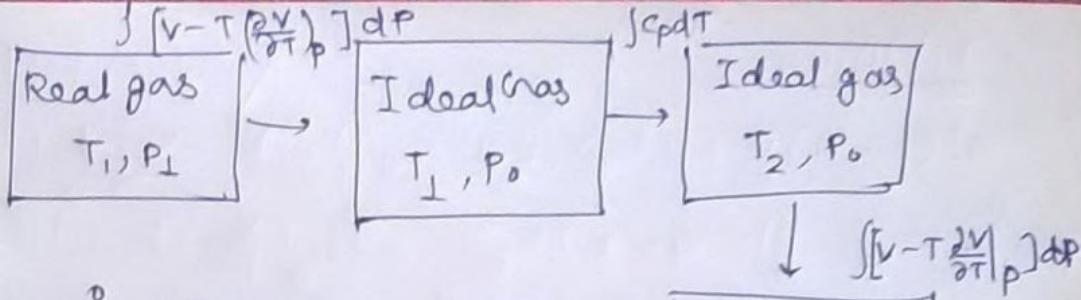
$$= \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T=T_2} dP + \int_{P_0}^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T=T_2} dP$$



$$= \int_{P_1}^{P_0} \left[\nu - T \left(\frac{\partial \nu}{\partial T} \right)_P \right] dP + \int_{T_1}^{T_2} C_p^{\circ} \Big|_{P=P_0} dT + \int_{P_0}^{P_2} \left[\nu - T \left(\frac{\partial \nu}{\partial T} \right)_P \right] dP$$

for ideal behavior

Arises due to deviation from ideality
(Residual property)



$\Delta h^* = h - \bar{h}^*$ = 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 Δh^* , Δs^* (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 ^{isothermal} extension of liquid film. Also derive an equation relating change in T with change in surface area under adiabatic condition.

$$du = Tds - \sigma dA$$

$$dh = Tds + Ad\sigma$$

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

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

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

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

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

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

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

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

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

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

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

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

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.

$$\left. \begin{array}{l} C_p - C_v = R \\ \frac{C_p}{C_v} = \gamma \\ U_{JT} = 0 \end{array} \right\} \text{ideal gas}$$

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

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

for ideal gas

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

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

$$dH = C_p dT + V(1 - \beta T) dP$$

$$(C_p - C_v) dT - T \left(\frac{\partial V}{\partial T} \right)_P dP - T \left(\frac{\partial P}{\partial T} \right)_V dV = 0$$

$$dT = \frac{T \left(\frac{\partial P}{\partial T} \right)_V dV}{C_p - C_v} + \frac{T \left(\frac{\partial V}{\partial T} \right)_P dP}{C_p - C_v}$$

$$dT = \left(\frac{\partial T}{\partial V} \right)_P dV + \left(\frac{\partial T}{\partial P} \right)_V dP$$

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

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

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

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

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

$$PV = RT$$

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

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

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

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

$$C_p - C_v = R$$

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

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

1) $c_p > c_v$

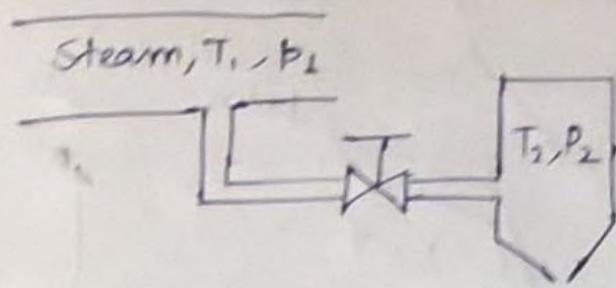
2) $c_p - c_v = R$ for ideal gas

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

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

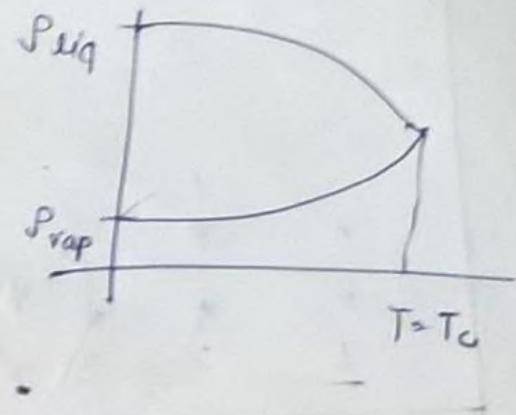
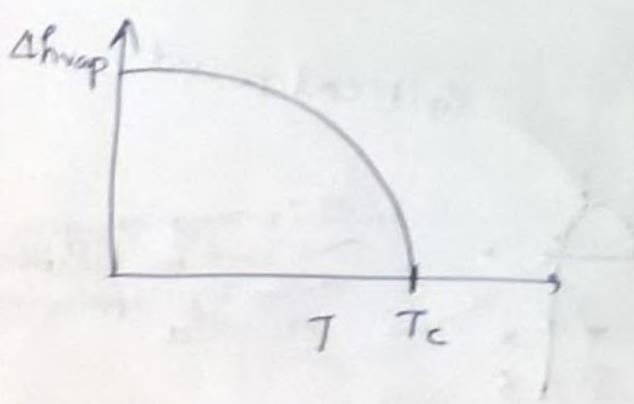
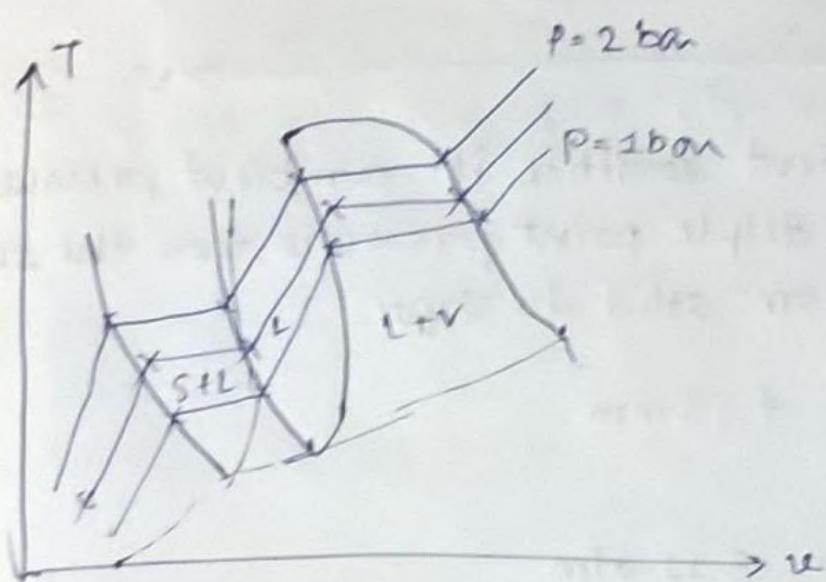
↙
For solids & liquids

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



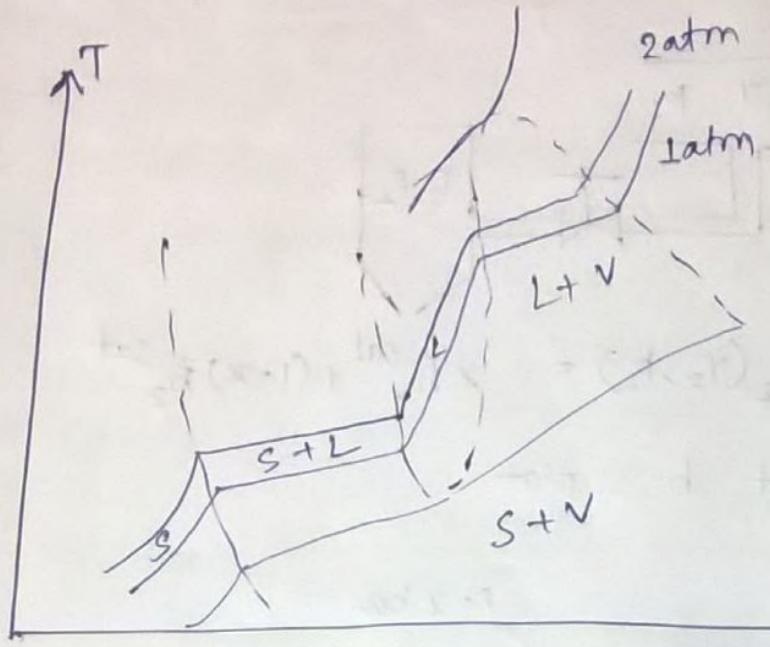
$$h_1 = h_2 = h_2(T_2, P_2) = x h_{v_1}^{\text{sat}} + (1-x) h_{l_2}^{\text{sat}}$$

Assignment : Plot h-s plot.



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

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

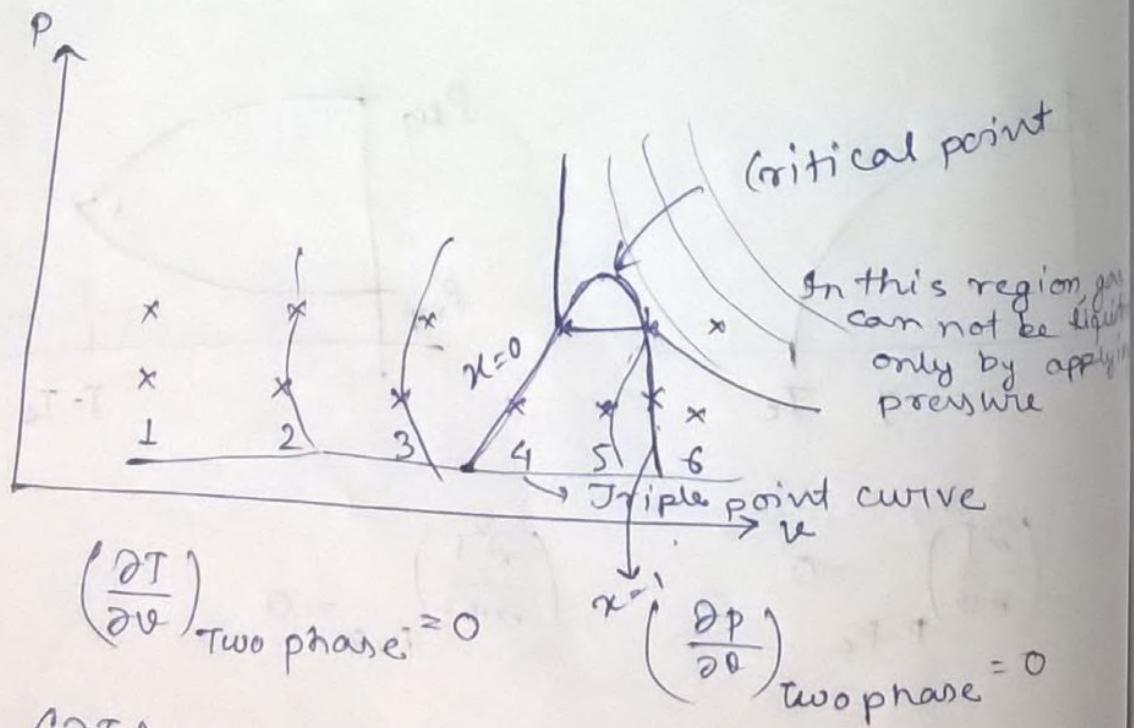


06/02/14

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

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

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



$$\left(\frac{\partial T}{\partial v}\right)_{\text{Two phase}} = 0$$

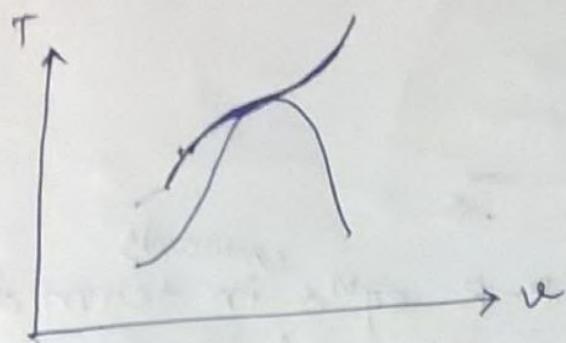
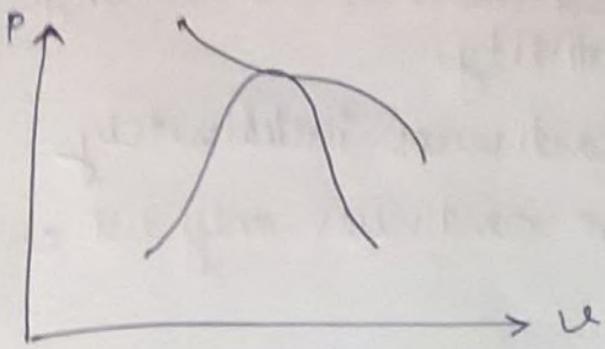
$$\left(\frac{\partial P}{\partial v}\right)_{\text{Two phase}} = 0$$

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

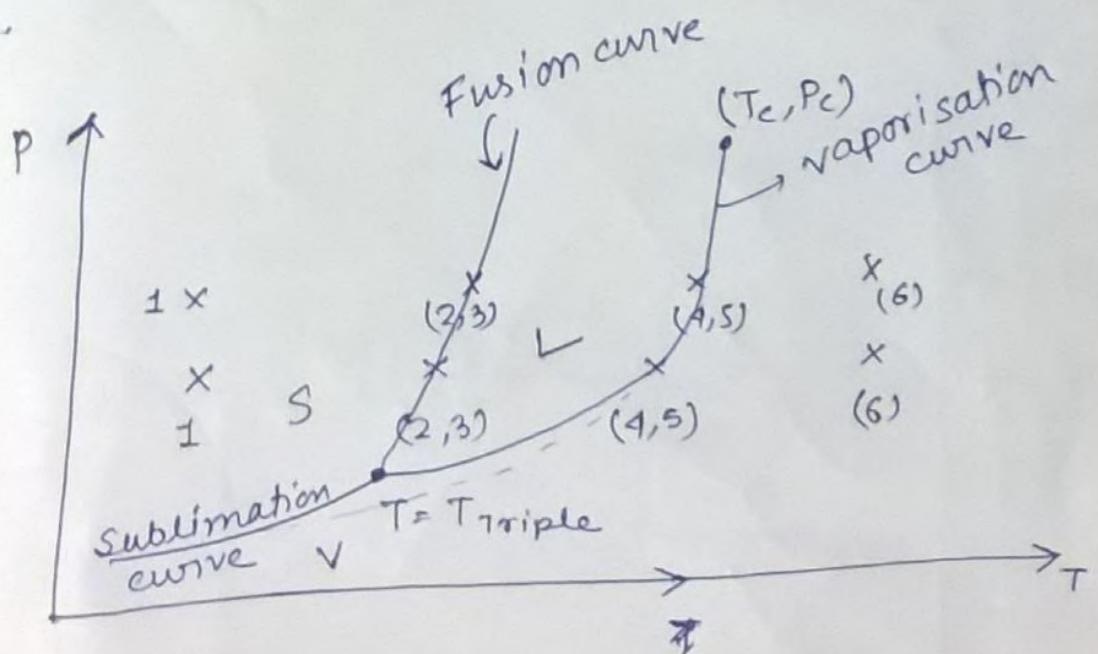
$$\left(\frac{\partial^2 T}{\partial v^2}\right)_{P=P_c} = 0$$

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

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



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

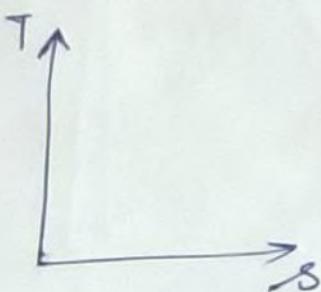


Vapor pressure curve of pure substance

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

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

Home work :

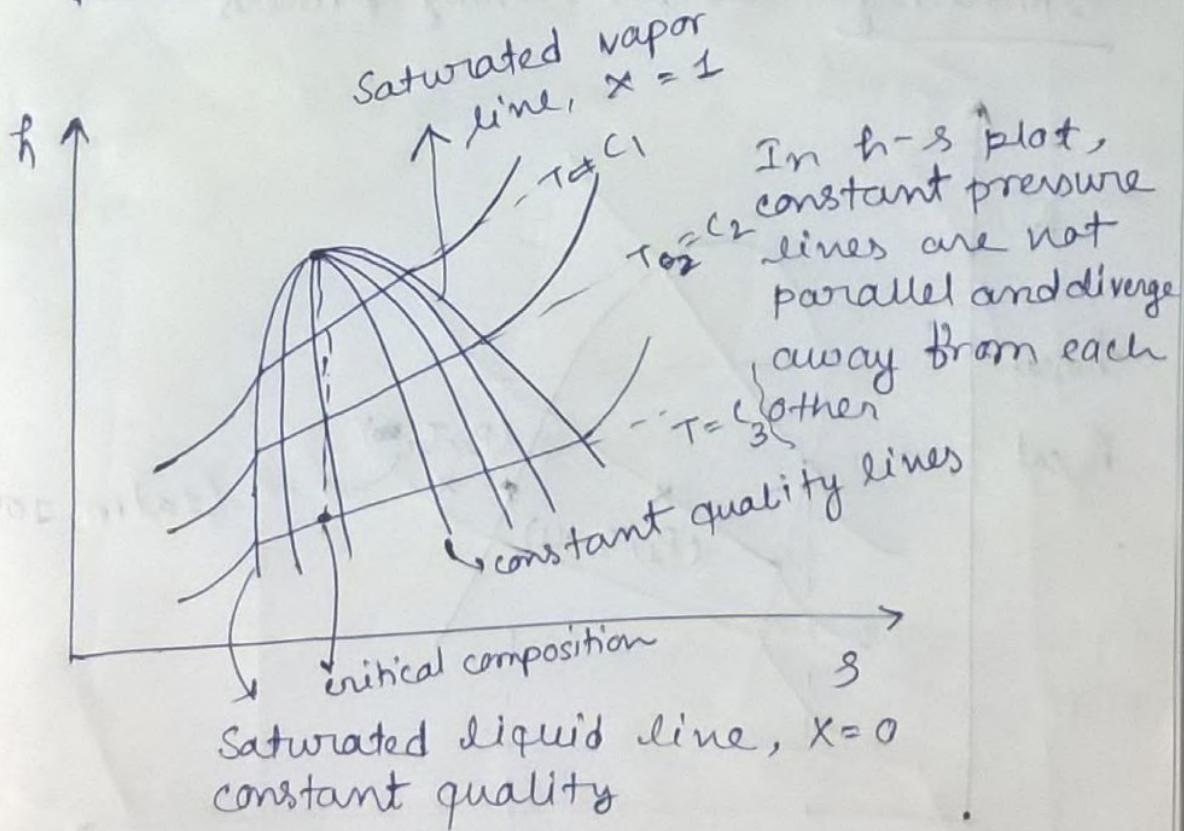
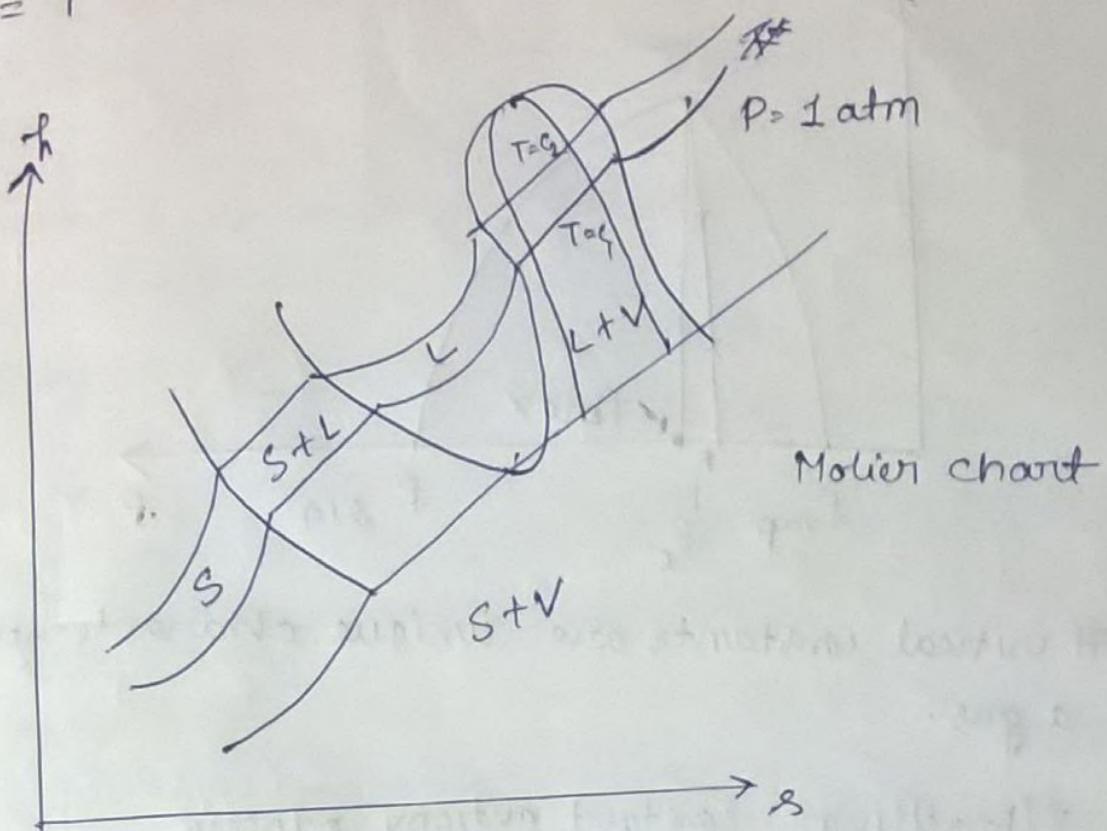


Express VDW, R-K, P-R eqns, constants in term of ϵ & σ

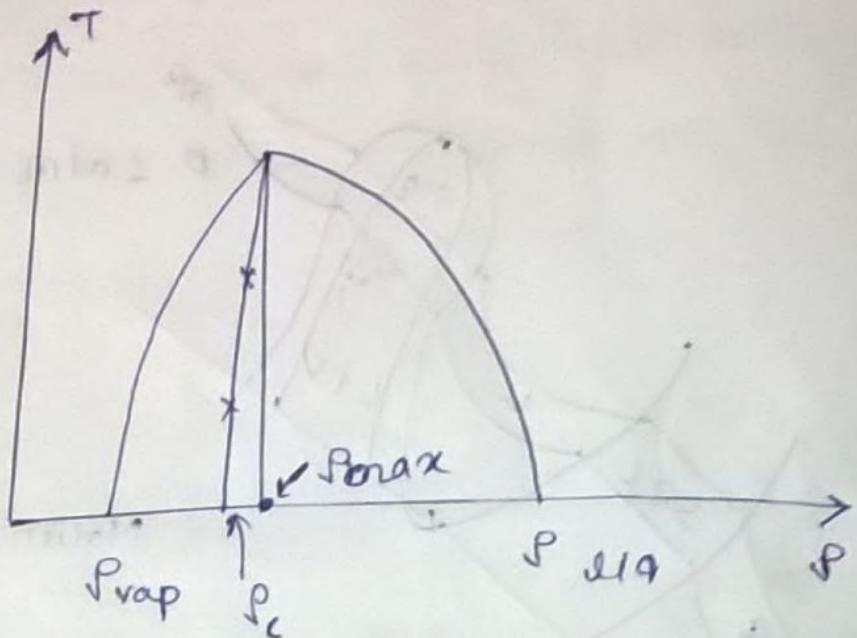
四

$$dH = Tds + vdp$$

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

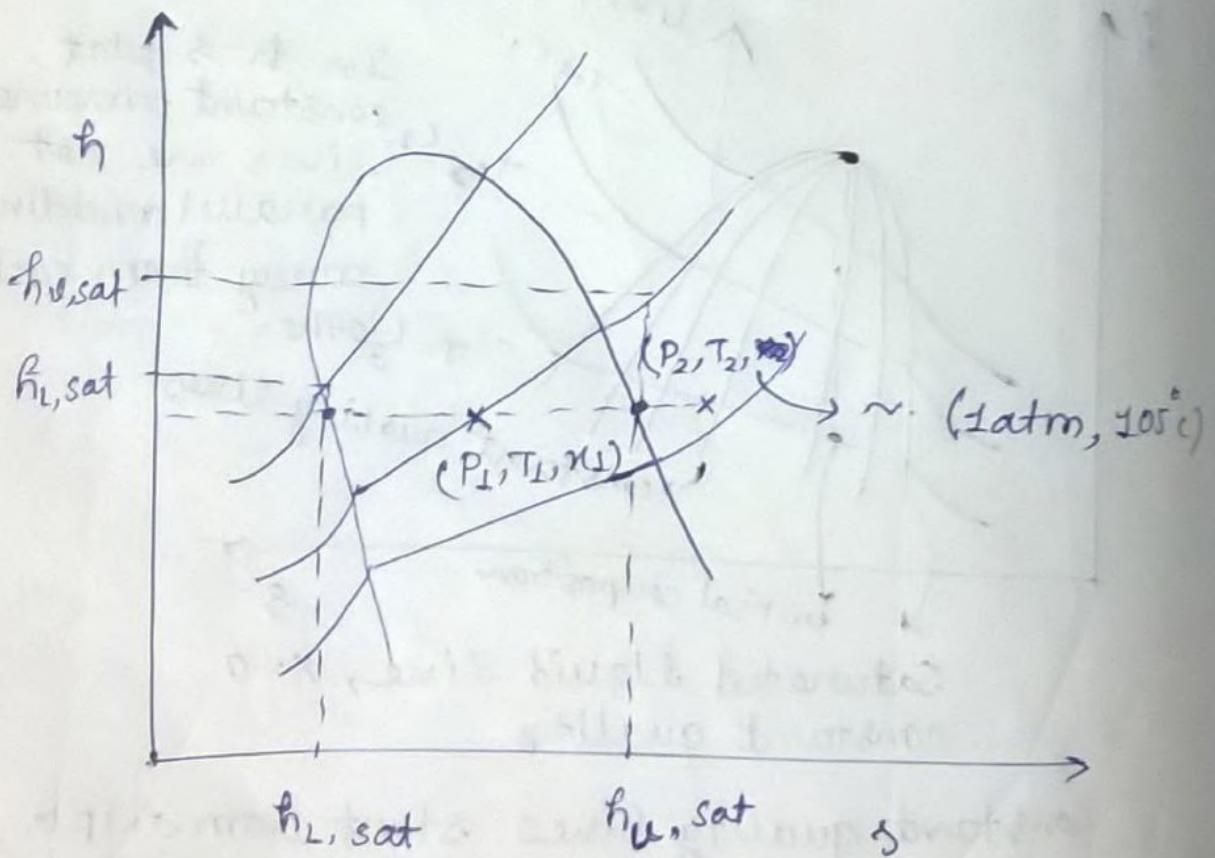


Constant quality lines start from triple point and end* at critical point



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 L at 70°C . Steam condensed in 5 minutes is 3.8 kg 3.24 kg

$$P_1 = 0.1 \text{ MPa}, T_2 = 110^\circ\text{C}$$

Find quality of steam in pipeline.

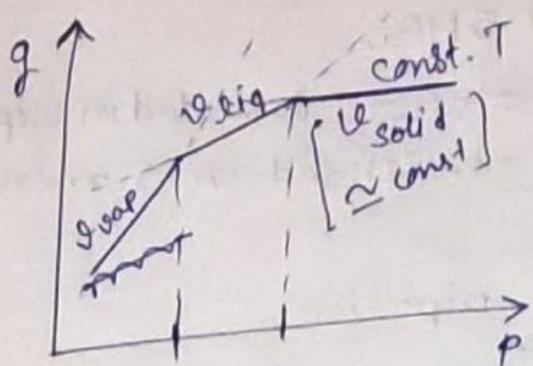
Hint: $m_1 h_1 + q = m_2 h_2$

[Throttling calorimeter]

Q2 Steam flows in a pipeline at 1.5 MPa . After throttling to 0.1 MPa , temperature is 120°C .

Find quality of steam in the pipeline

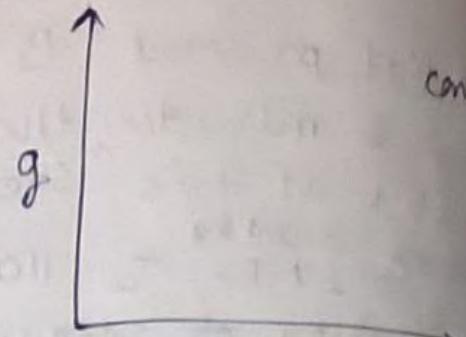
→ what is the maximum moisture content at 1.5 MPa , that can be determined in this setup
it atleast 5° of superheat is required for the throttling process.



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

$$dG = v dP - s dT$$

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



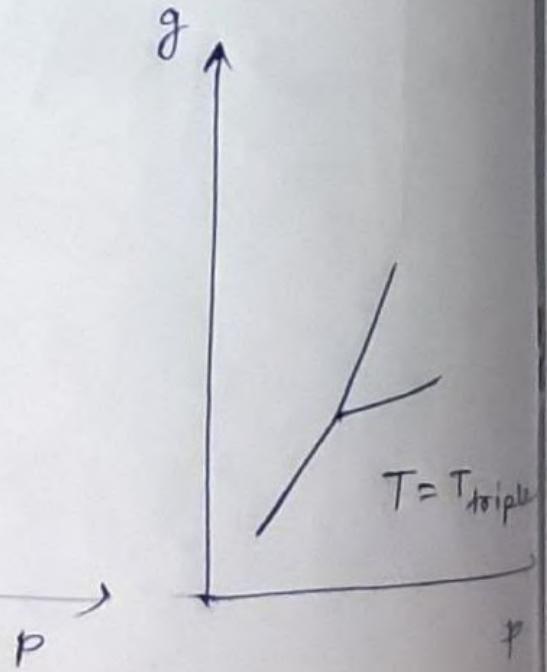
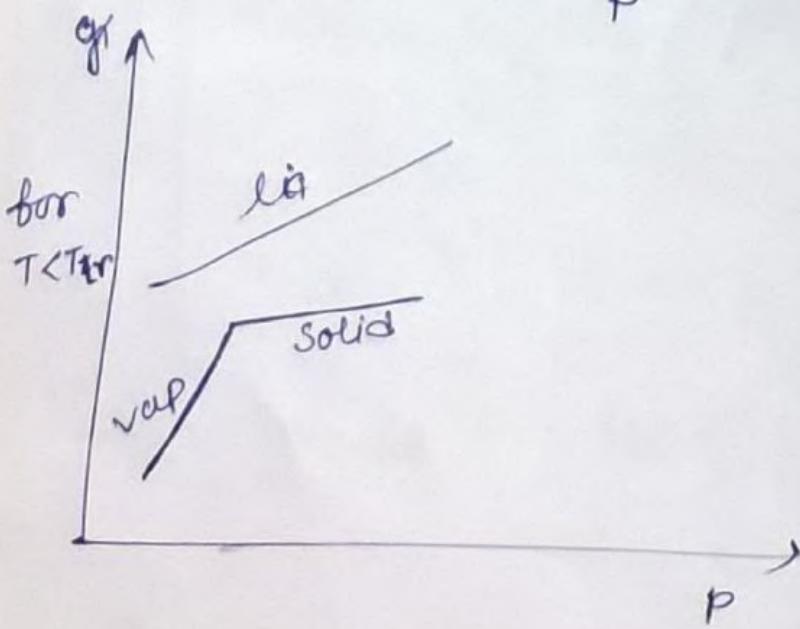
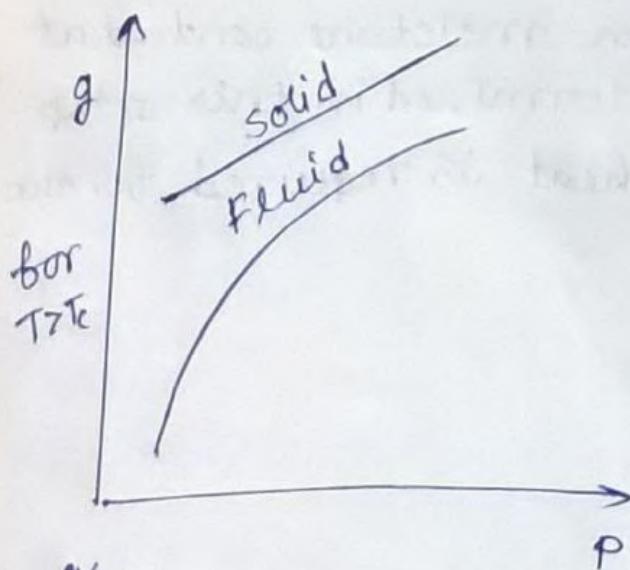
$$\left(\frac{\partial g}{\partial T}\right)_P = -s$$

$$g = h - T s$$

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

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

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



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

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

according to VDW eqn

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

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

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}

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

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

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

substituting $v_c = 3b$ in eqⁿ ①

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

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

substituting v_c and T_c in eqⁿ ④

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

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

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

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

from ③, ④ & ⑤

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

∴

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

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

∴

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

08/02/2014

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

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

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

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

Eq's of state

Cubic Eq's of state

Nernst eqn

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

$$= 1 + \underbrace{\frac{C_1}{V}}_{B_1} + \underbrace{\frac{C_2}{V^2}}_{B_2}$$

Applicable
moderate tem
& pressure

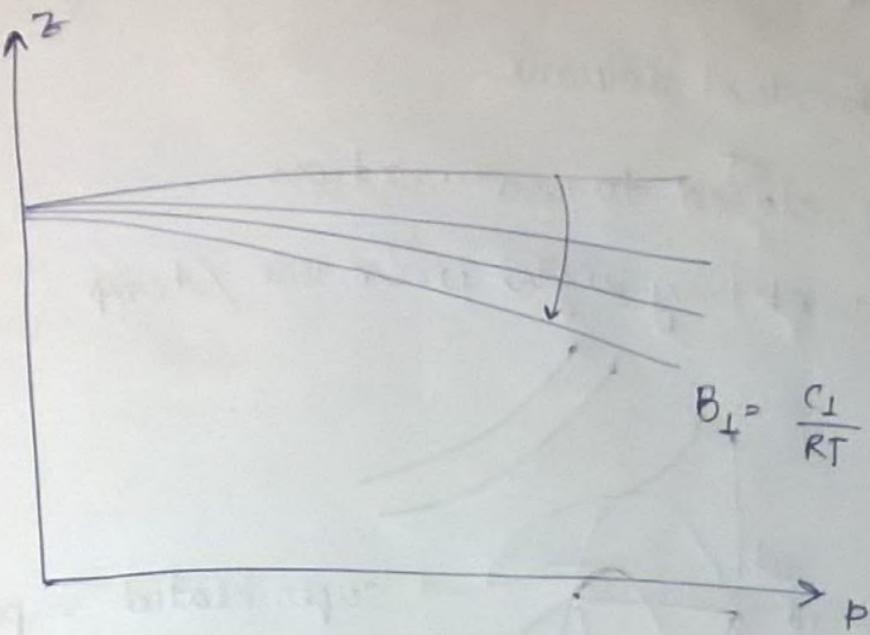
$$1 + B_1 P = 1 + \frac{C_1}{V}$$

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

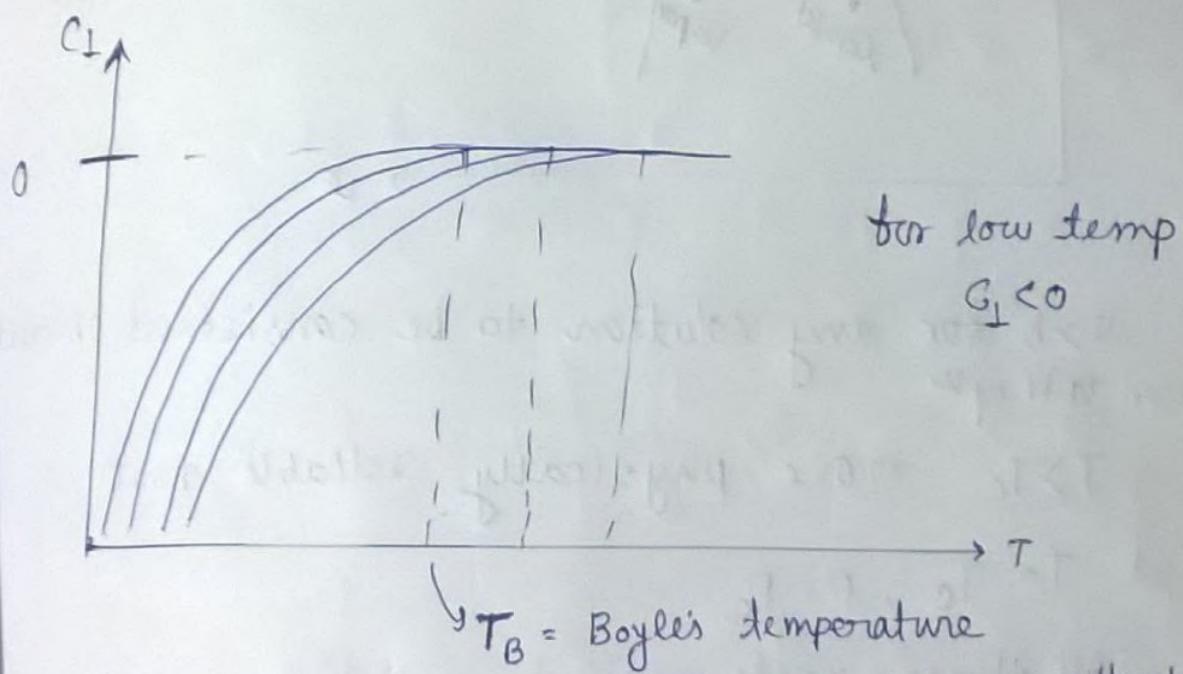
$$B_1 \rightarrow f(T)$$

$$C_1 \rightarrow f(T)$$

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



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



for low temp
 $C_{\perp} < 0$

T_B = Boyle's temperature

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

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

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

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

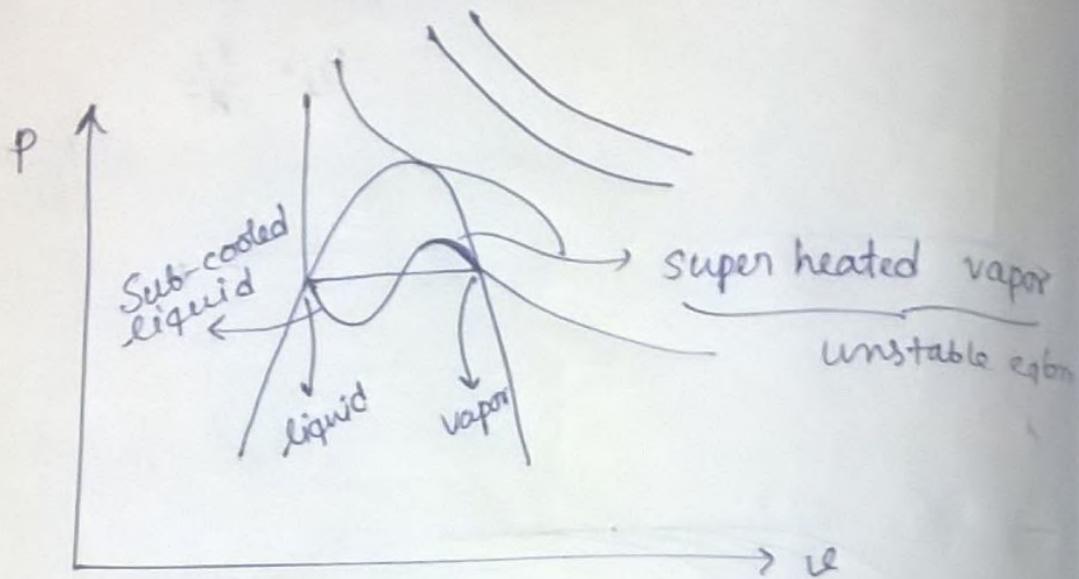
$$v = \frac{RT}{P} + C_{\perp} \Rightarrow v = v_0 + C$$

$$C_1 = \alpha v^*$$

↓ 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 eqⁿ

$T > T_c \Rightarrow$ 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 condition

$$T < T_c$$

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

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

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

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

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

$$\left(\frac{P}{P_c} + 3\frac{v_c}{P_c}\right) \frac{2}{3} = R T / P_c v_c$$

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

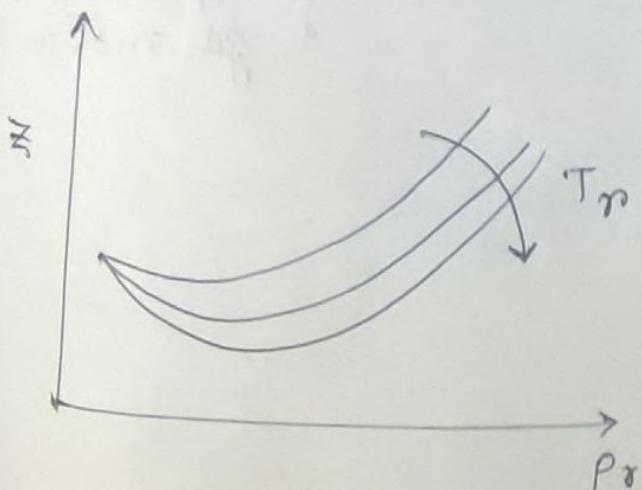
$$\left(\frac{P}{P_c} + 3\frac{v_c}{P_c}\right) \frac{2}{3} = \frac{RT/T_c}{P_c v_c / T_c}$$

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

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

Law of corresponding
States

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



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

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

$$0.23 \leq Z_c \leq 0.32$$

$$Z_c \approx 0.27$$

$$Z = Z(T_r, P_r, w)$$

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

Three parameter law of corresponding states

$$w = - \log_{10} P_r^{\text{sat}} \Big|_{T_r=0.7} \Rightarrow \text{Particularly for}$$

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

Thermodynamics of Multiphase - Multi component

22/02/17

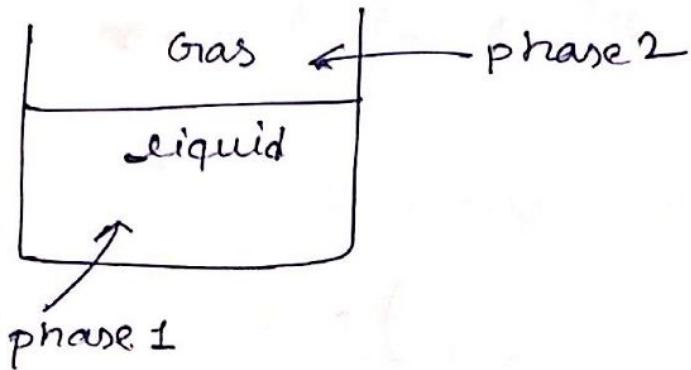
- 1) Single phase - Multiple component /
2) Single component - Multiphase } Non reactive
3) Multiphase - Multi component
4) Reactive

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

$$x = s, y = v$$

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

$$+ \sum_{i=1}^N \left(\frac{\partial f}{\partial n_i} \right)_{s, v, n_i^*} dn_i \quad \begin{array}{l} \text{When } x \equiv s \\ y \equiv v \\ f = U \end{array}$$

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

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

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

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

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

↓
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

Change of Natural coordinates

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

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

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

$n+3$ dimension system

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

Natural coordinates for U

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

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

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

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

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

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

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

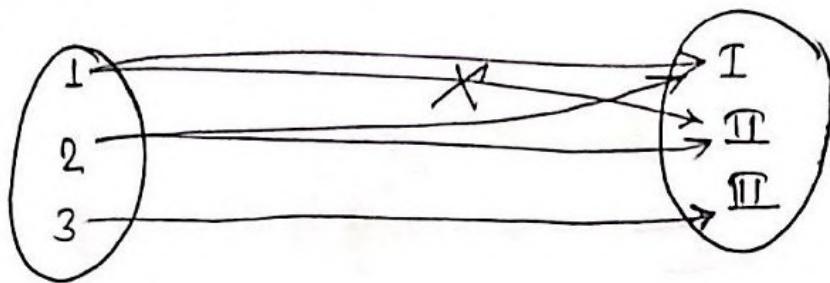
x	y	$\frac{dy}{dx}$	$y = g\left(\frac{dy}{dx}\right)$
1	1	2	1
2	4	4	4
3	9	6	9

$$x^2 y^2$$

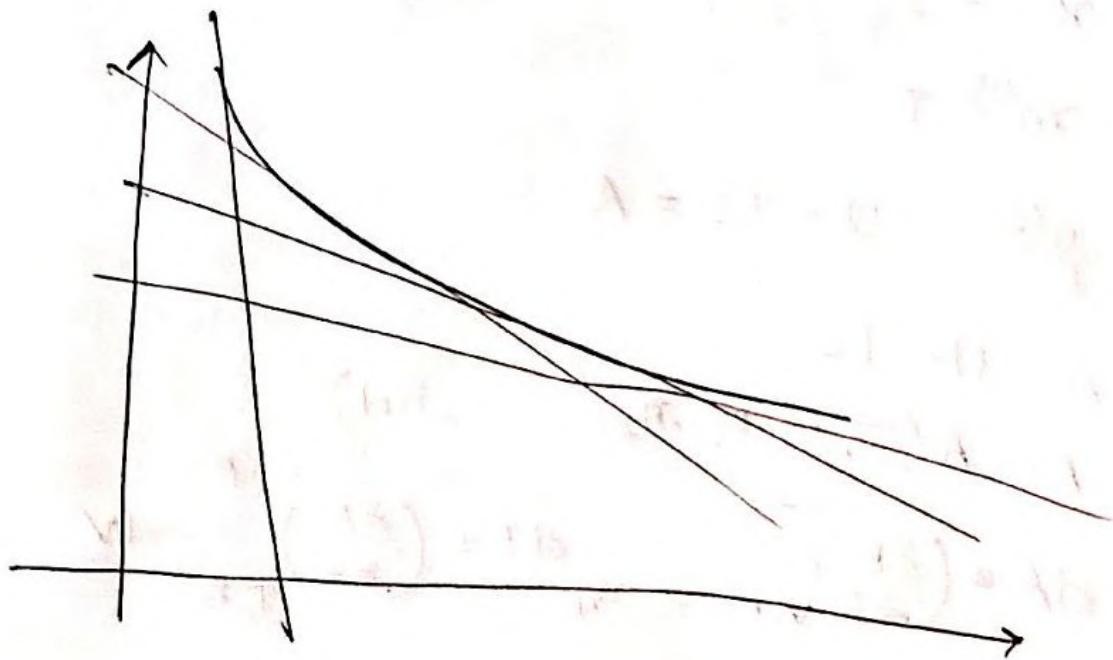
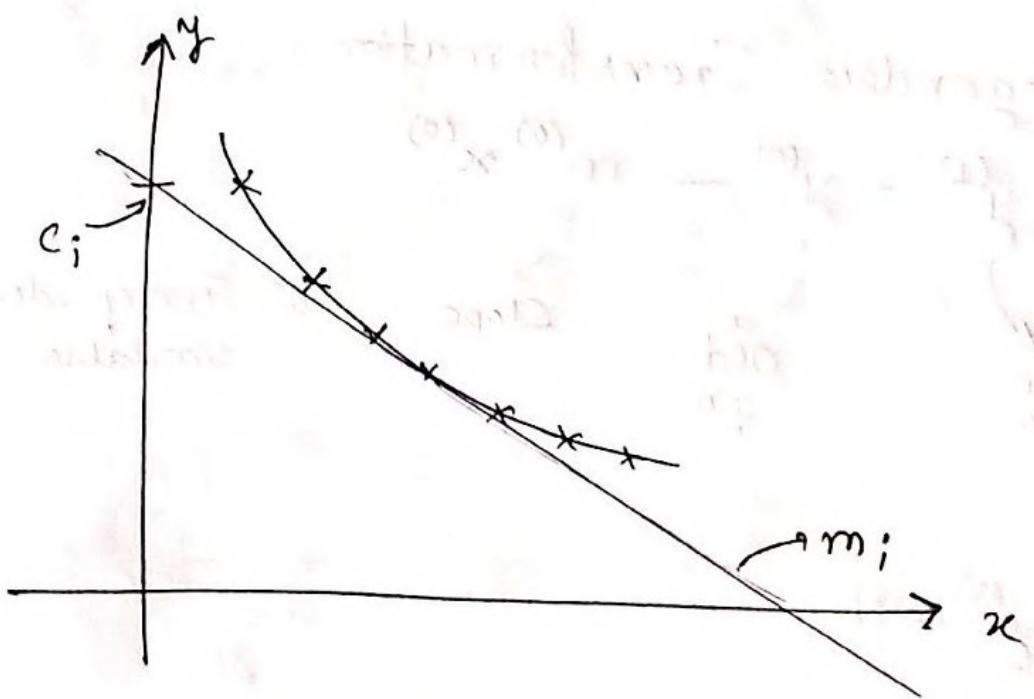
$$2x$$

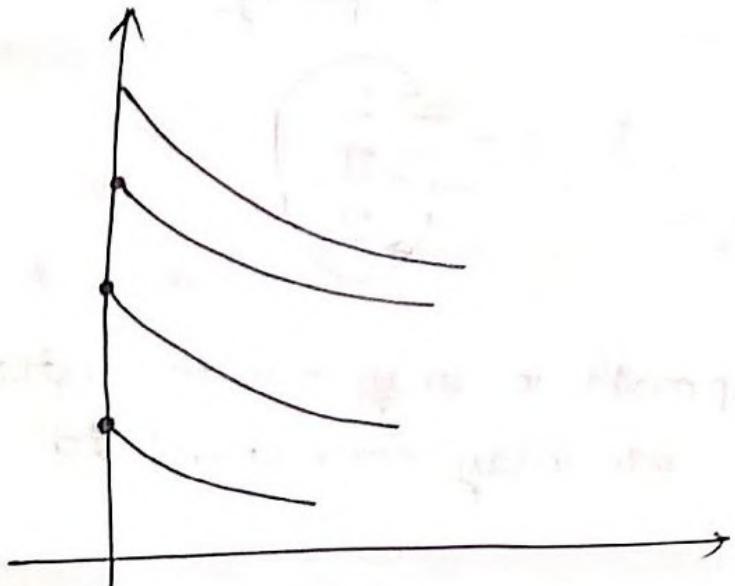
state

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.

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

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

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

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

$$A = U - TS$$

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

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V, n_1, \dots, n_N}^{-S} dT + \left(\frac{\partial A}{\partial V}\right)_{T, n}^{-P} dV$$

$$+ \sum_{i=1}^N \left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_i} dh_i$$

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

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

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

↓
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

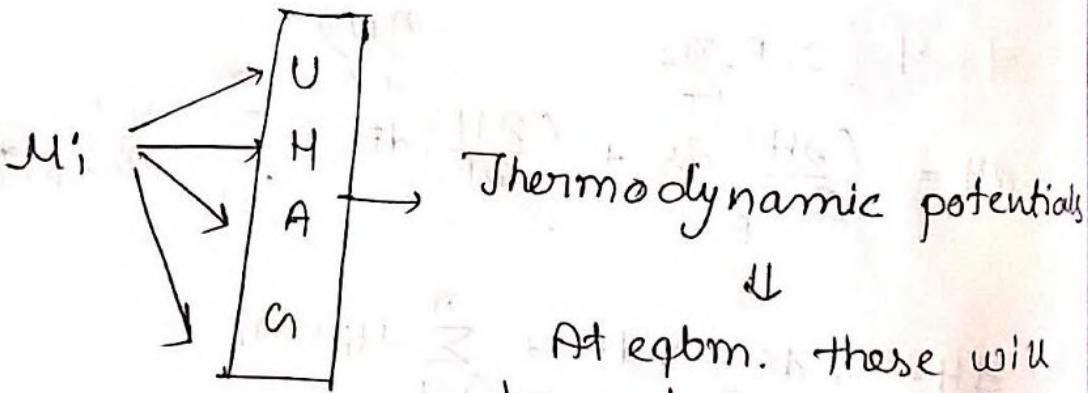
$$\gamma^{(2)} = \gamma^{(0)} - \sum_{i=1}^2 m^{(i)} x^{(i)}$$

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

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

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

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



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 eqⁿ 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/dsT
$\textcircled{2}$ 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

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

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

all three are inconsistent

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

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

Euler Integration

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

$$\longleftrightarrow I \longleftrightarrow$$

$x \rightarrow kx$
 $y \rightarrow ky$ } 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

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

$$H - U = PV$$

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

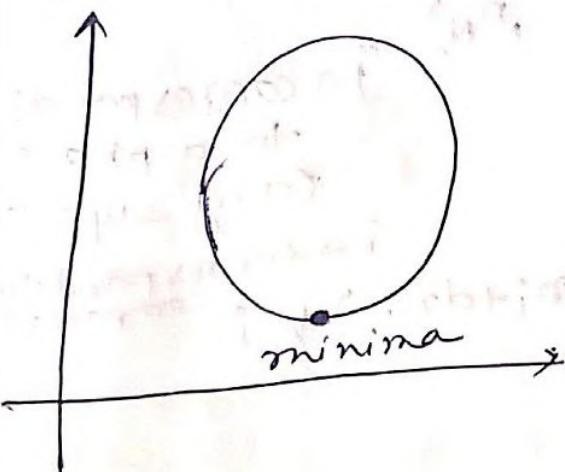
$$G = \sum_{i=1}^N \mu_i n_i \quad T, P \rightarrow \text{both intensive}$$

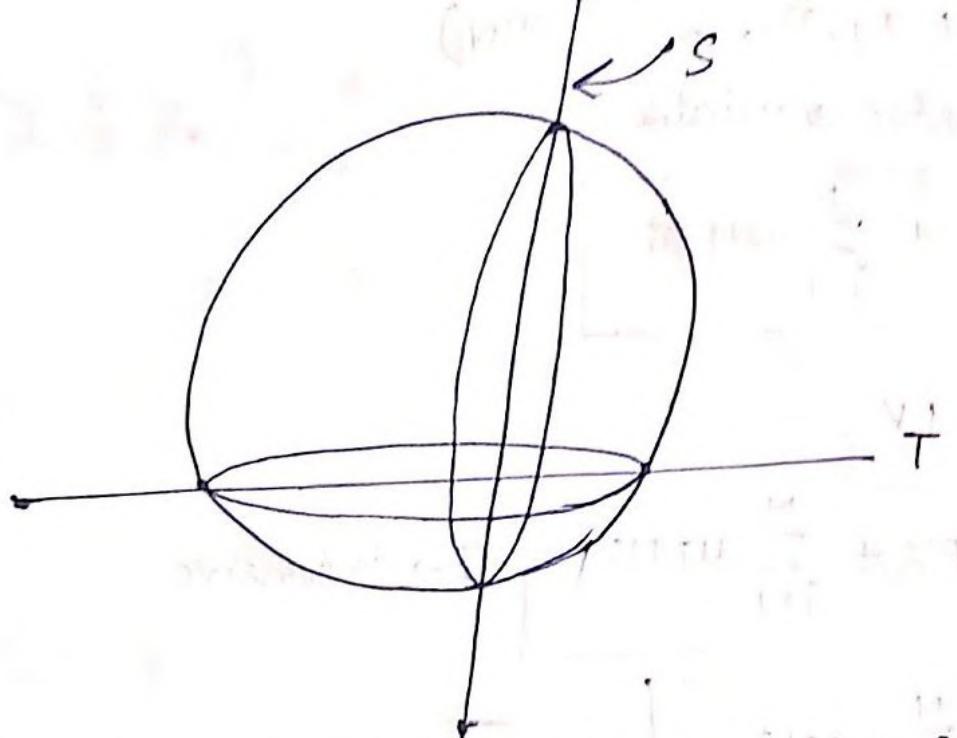
order of dependence for intensive variable
= 0, zero

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

$$S^j = S^j(U, V, n_1, n_2, \dots, n_N) \quad j \rightarrow \text{corresponds to a phase}$$

(any superscript)

$i \rightarrow \text{correspond to component}$

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

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

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

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

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

For a binary system at eqbm.

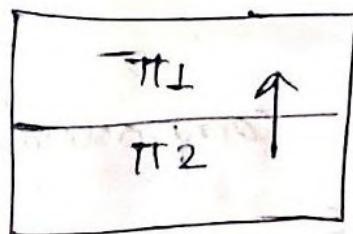
$$\cancel{\frac{1}{T^1} dU^1 + \frac{P^1}{T^1} dV^1}$$

$$\left[\frac{1}{T^1} dU^1 + \frac{1}{T^2} dU^2 \right] + \left[\frac{P^1}{T_1} dV^1 + \frac{P^2}{T^2} dV^2 \right] -$$

$$\sum_{i=1}^N \left[\frac{u_i^1}{T^1} + \frac{u_i^2}{T^2} \right] dN_i^i = 0$$

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

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

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

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

$$T^1 = T^2$$

$$P^1 = P^2$$

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

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

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

$$T_1 = T_2$$

$$P_1 = P_2$$

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

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

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

$$ax + by + cz = 0$$

$$a = b = c = 0$$

if x, y, z are independent

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

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

$$\cancel{\frac{\partial H}{\partial u_i}} \left(\frac{\partial T}{\partial u_i} \right)_{S, P, n_i^*} = - \left(\frac{\partial n_i}{\partial S} \right)_{P, u_1, u_2, \dots, u_N}$$

$$dH = Tds + vdp + \sum_{i=1}^N u_i dn_i$$

$$U = U(S, V, \overset{u_1}{n_1}, \overset{u_2}{n_2}, \dots, \overset{u_N}{n_N})$$

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

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

$$\left(\frac{\partial f_L}{\partial S} \right)_{P, u_i, n_1, n_2, \dots, n_N} = T$$

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

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

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

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

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

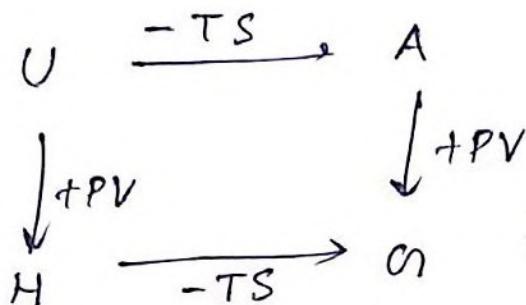
Q.3 Eqⁿ of state

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

$$T = f_2(C) \quad \text{but } T + 273 \text{ K}$$

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

Q.5



Q.4 reverse of ③

Find a fundamental eqⁿ

Q.6

Important

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

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

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

conditions of equilibrium

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

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

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

driving force for mass transfer is difference of chemical potential.

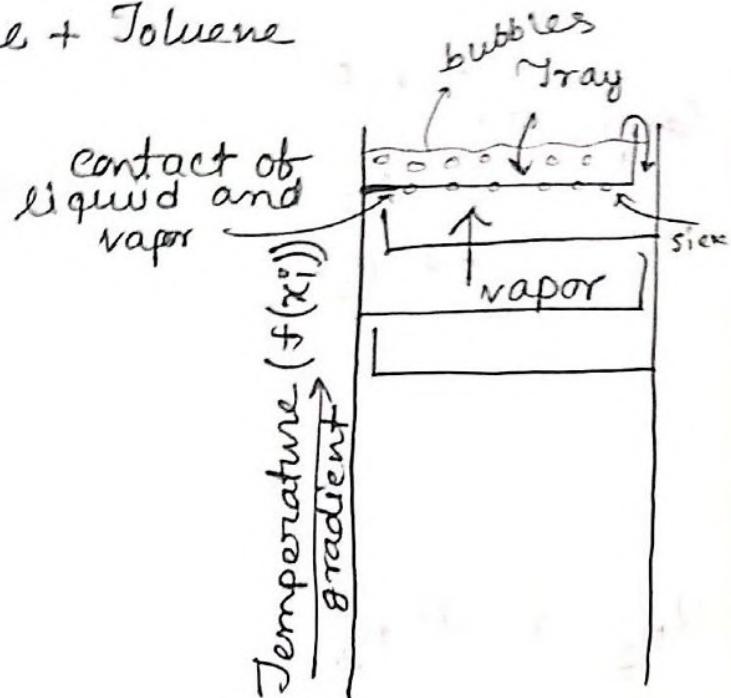
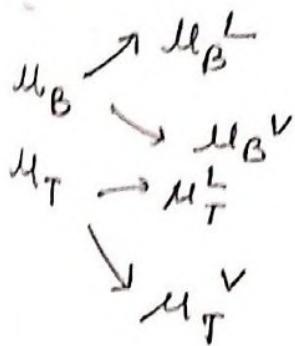
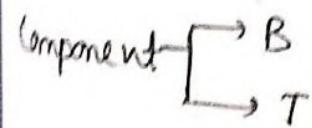
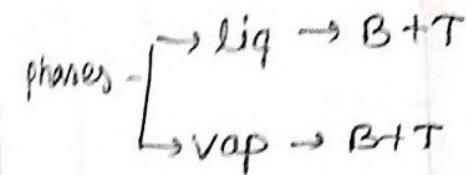
1) Distillation

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

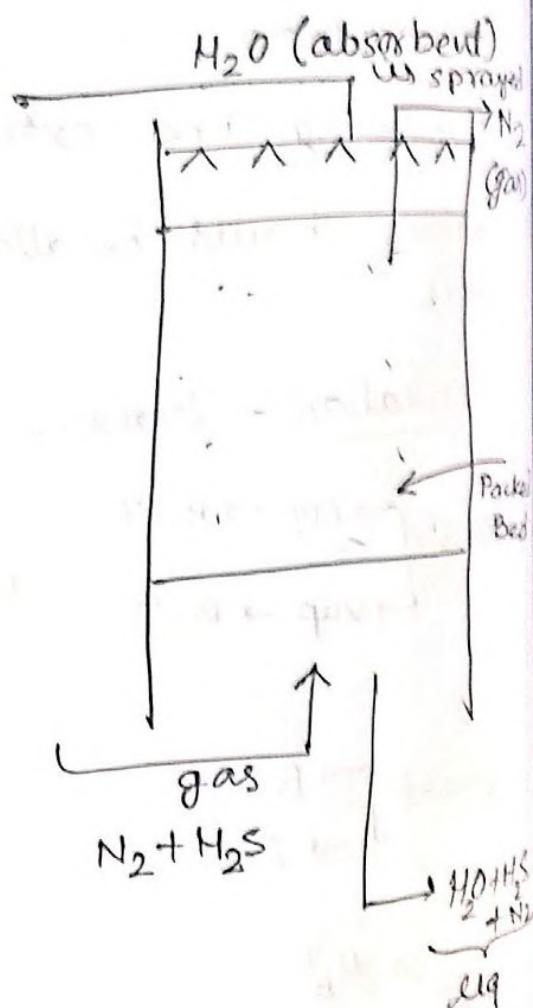
Temp. gradient $\rightarrow f(x_i)$

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

2) Absorption: H_2S

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

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



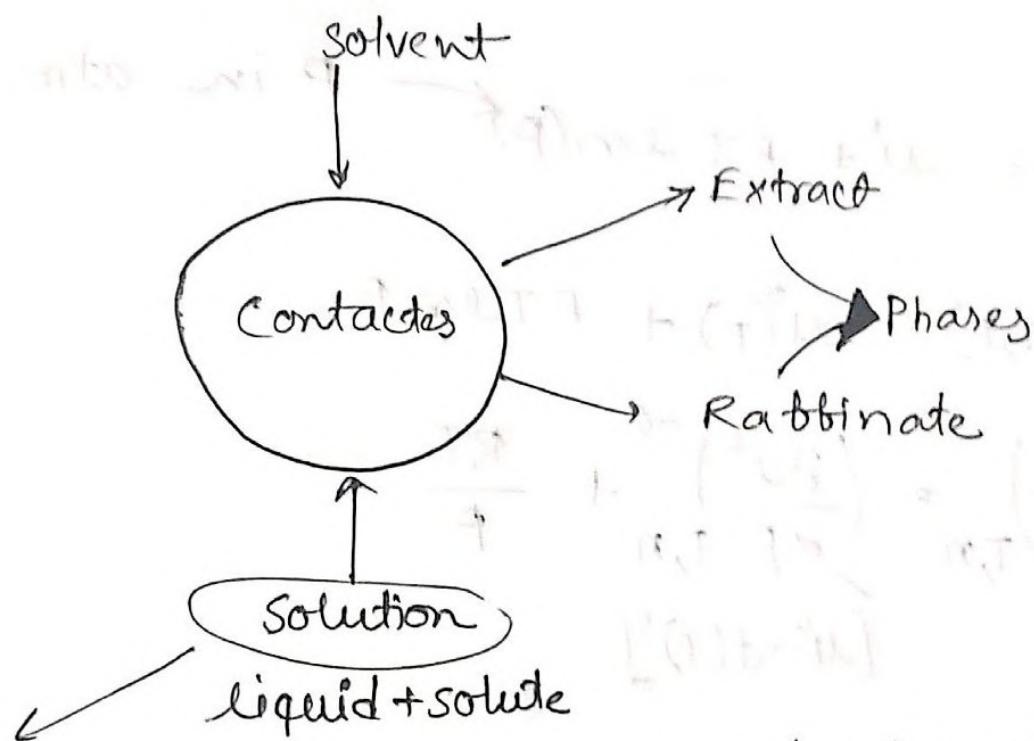
$$\mu_{N_2}^L = \mu_{N_2}^G$$

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

$$\left. \begin{array}{l} \mu_{H_2S}^L = \mu_{H_2S}^V \end{array} \right\}$$

i) Tea

solid \rightarrow Inert + Solute $\xleftarrow{\text{Leaching}}$
liquid \rightarrow liquid + solute $\xleftarrow{\text{Extraction}}$



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

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

$P \rightarrow$ in atm

, $P_0 = 1$ atm

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

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

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

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

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

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

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

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

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

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

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

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

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

$$H = G - TS$$

$$h = \mu + TS$$

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

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

$\downarrow \qquad \qquad \qquad \downarrow$

$f(T) \qquad \qquad f(T)$

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

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

↑
Fugacity

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

↓
fugacity coefficient → indicator of non-idealities 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.

$$PV = nRT$$

$$PV = z nRT$$

02/03/17

Mixture of Gas

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

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

$f/p \rightarrow$ 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.

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

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

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

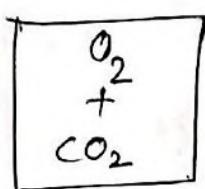
$$RT d[\ln(f/P)] \Big|_{T,n} = \left(\frac{V}{n} - \frac{RT}{P}\right) dP \Big|_{T,n}$$

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

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

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

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



$$a_{O_2} \quad a_{CO_2}$$

$$b_{O_2} \quad b_{CO_2}$$

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.

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

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

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

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, n_2, \dots, n_N}$$

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

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

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

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

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

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

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

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

$$PV_T = n_T RT$$

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

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

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

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

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

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

$$\sigma_i = H_i - TS_i$$

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

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

~~$$\mu_i^{\circ} = \bar{\mu}_i^{\circ}$$~~

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

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

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

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

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

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

$(\Delta H_{\text{mixing}})^{\text{ideal}} = 0$ 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

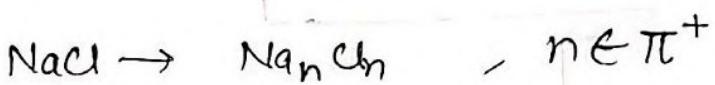
- Particles that constitute the gas, do not interact
- The size of the particle is negligible

when compared to vessel volume.

Ideal liquid mixture

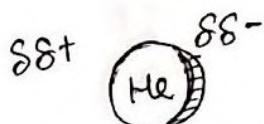
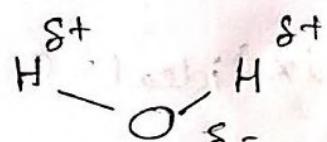
No interactions \rightarrow fundamentally impossible.

Solids + liquids } condensed matter phase

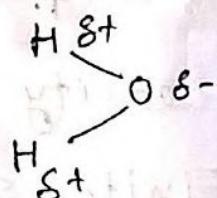


Interactions in a system

1) Electrostatic



Time fluctuating dipole moment

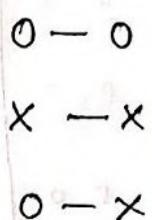
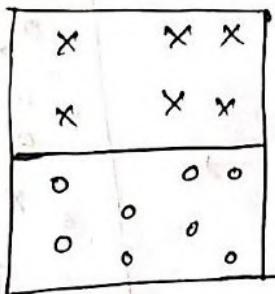
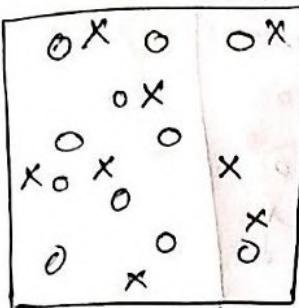


2) gravitational

3) Weak Force

{ in the nucleus

4) Strong Force



Ideality is defined in terms of interactions between molecules.

→ If $O-X$ is similar to $O-O$ and $X-X$, then the solⁿ 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

x x	o o
x x	o o
x x	o o
x x	o o



o x	o x
x o	x o
x o	x o
x o	x o
x o	x o

Mixing of gas

x	o
x	o
10^{23}	10^{23}

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

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

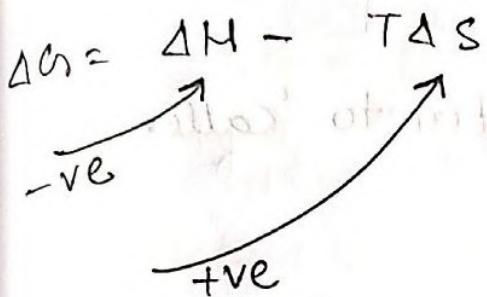
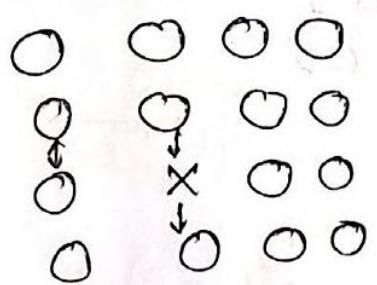
For practical purposes
highly improbable

x, o	o
o	x x o
x x	o
o	x o
o x	x

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

\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)

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

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

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

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

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

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

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

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

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

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

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

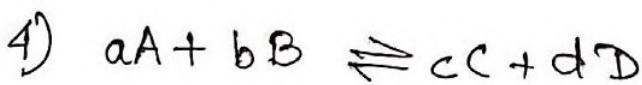
$$= U - TS + PV - \sum_{i=1}^N u_i n_i$$

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

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

$$- \sum_{i=1}^N n_i du_i$$

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



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

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

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

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

For non-reactive system

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

$A dx + B dy + C dz = 0 \Rightarrow$ not applicable
for reactive system

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

For reaction eqbm:

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

⑥ combination of
 ① Gibbs-Duhem eqⁿ
 +

$$② \sum \alpha \gamma_i \mu_i = 0$$

⑦ condition of eq^{bm}

$$P^1 = P^2$$

$$T^1 = T^2$$

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

N ₂	1
O ₂	1
He	1
CO ₂	1
NO _x	1
CO	1

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

7

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

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

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

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

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

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

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

↑
 $f(T)$

↑
 $g(T, P)$

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

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

$$\underbrace{\mu_i^\circ(T) - \mu_i^*(T, P)}_{\text{f' of } T, P} = -RT \ln \left(\frac{f_i}{y_i} \right)$$

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

$$\mu_i = \overline{\mu_i}$$

Gibbs-Duhem eqⁿ

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

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

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

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

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

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

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^{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
 ΔG_{mix} and ΔG^{Ex}
 ΔA_{mix} and ΔA^{Ex} } need
 not equal
 ↓
 Entropy dependent

1. Ideal solution behavior

2. Regular solⁿ behavior

→ ~~if~~ system has difference in interaction between different molecules. Enthalpic contribution dependent

3. Athermal solⁿ behavior

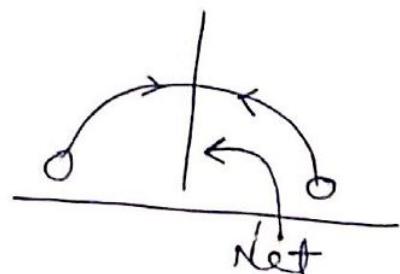
→ Interactions are similar but depends on entropy also. Both ~~enthalpic and~~ Entropic contribution is dependent.

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?

$$b = b(c_1, c_2, c_3, \dots, c_{N+1}, n_T)$$

$$db = \sum_{i=1}^{N+1} \left(\frac{\partial b}{\partial c_i} \right) dc_i + \boxed{\left(\frac{\partial b}{\partial n_T} \right) dn_T} \xrightarrow{c_i \rightarrow 0}, \text{ as } b \rightarrow \text{intensive}$$

$$b = b(c_1, c_2, \dots, c_{N+1})$$

my intensive property can be expressed as $(N+1)$ independent variable intensive properties within a phase.

component, π -phase system
of variables to be specified in π 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

$$\text{Max \# of intensive variable} = N - \pi + 2$$

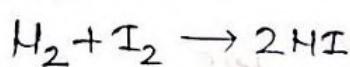
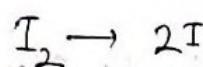
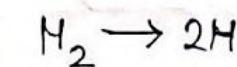
$$\text{total \# variable (Int + extensive)} = \pi(N+2)$$

Non reactive system ($N-\pi$)

$$f = n - \pi + 2$$

Reactive system with "R" number of independent reaction

$$f = n - \pi + 2 - R$$



$$-H_2 + 2H = 0$$

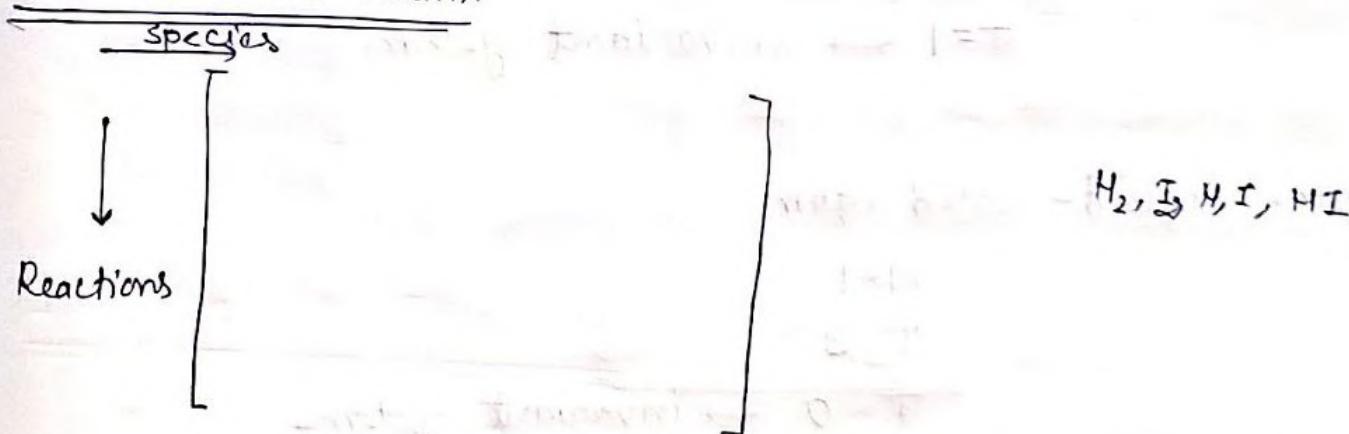
$$-I_2 + 2I = 0$$

$$-H_2 - I_2 + 2HI = 0$$

$$-2H - 2I + 2NI = 0$$

can be obtained from rest three

Stoichiometric Matrix



$$\begin{array}{l} R_1 \\ R_2 \\ R_3 \\ R_4 \end{array} \begin{bmatrix} H_2 & H & I_2 & I & HI \\ -1 & +2 & 0 & 0 & 0 \\ 0 & 0 & -1 & +2 & 0 \\ -1 & 0 & -1 & 0 & +2 \\ 0 & -2 & 0 & -2 & +2 \end{bmatrix} = A$$

Elementary-Row operation

→ Non zero rows

→ Rank of the matrix

4th reaction as a linear combination of other reactions

$$\rho(A) = R$$

↑ 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

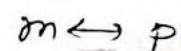
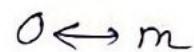
$$\pi = 2$$

$$N = 3$$

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?

Solⁿ $f = 1$

$$f_{NR} = N - \pi + 2$$



$$f_R = N - \pi + 2 - R$$

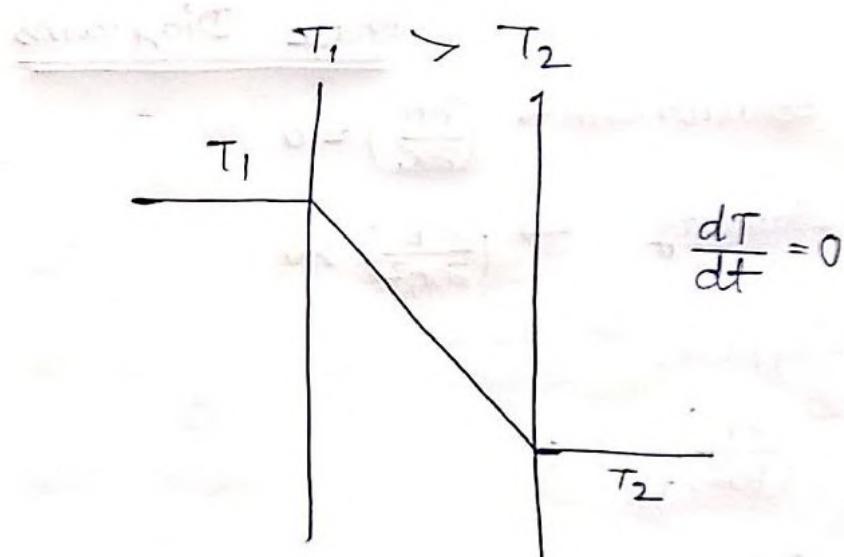
$$f_{NR} = 3 - 2 + 2 = 3$$

$$f_R = 3 - 2 + 2 - 2 = 1$$

Eqbm. & stability

→ at eqbm,

$$\text{net flux} = 0$$

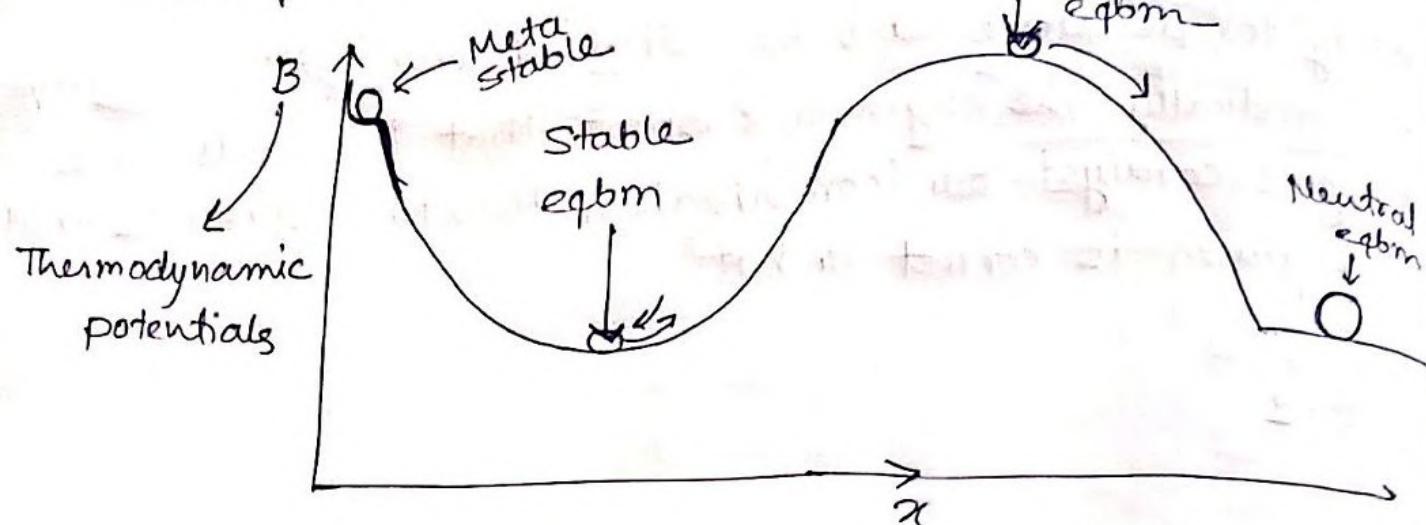


→ Steady state

→ Net flux ≠ 0

→ Not in eqbm.

$\frac{\partial B}{\partial x} = 0$ 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

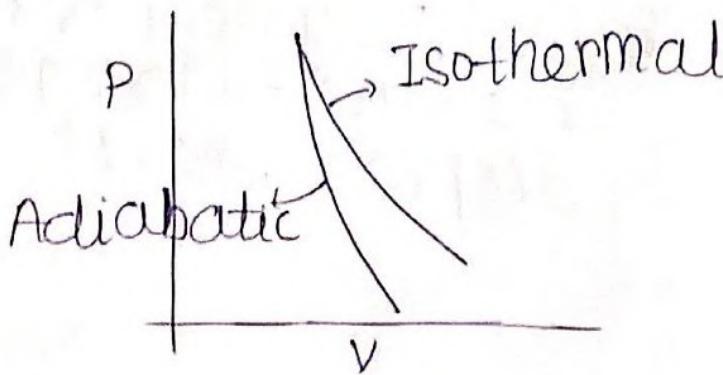
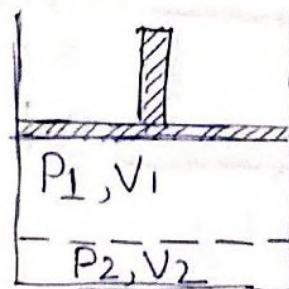
VLE systems

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)



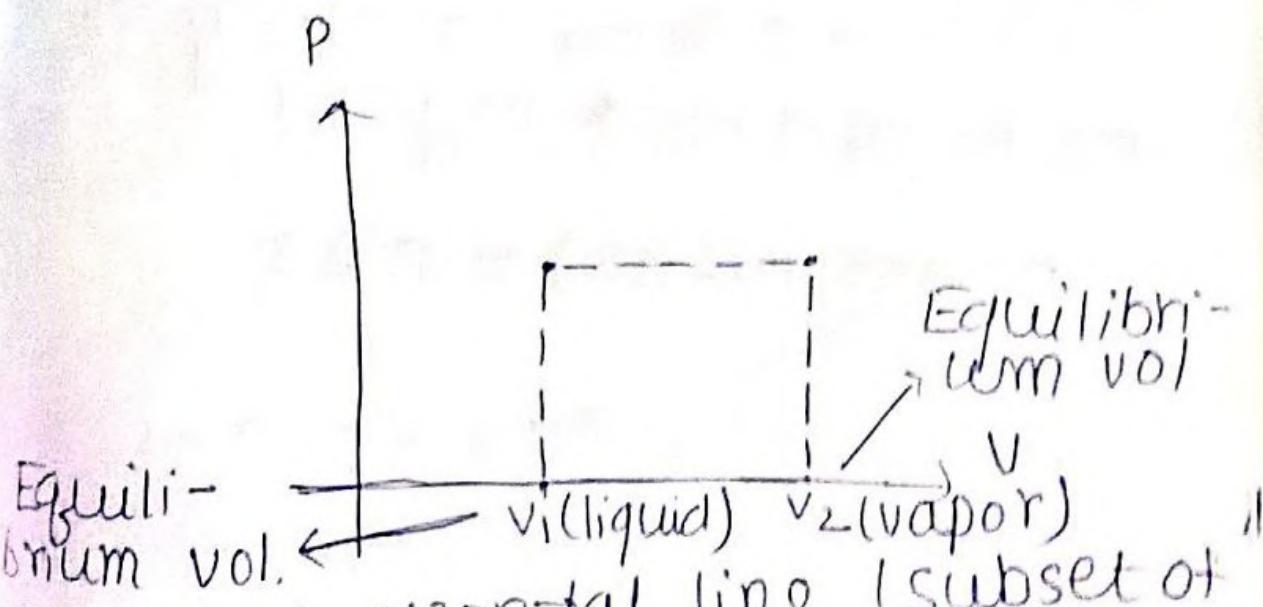
$$\left[\frac{\partial}{\partial V} \left(\frac{\partial A}{\partial V} \right) \right]_{T,n} > 0$$

$$\Rightarrow \boxed{\left(\frac{\partial P}{\partial V} \right)_{T,n} < 0} \rightarrow \text{stability criteria}$$

criterion for mechanical stability of a system

*Importance of stability criterion:

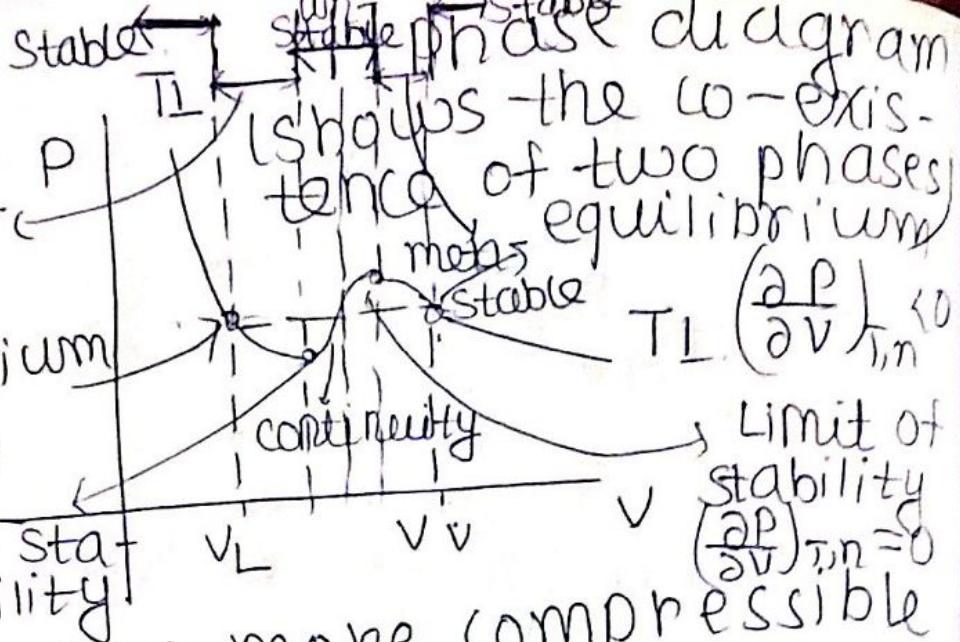
① coordinates of phase diagram



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)

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

$$\alpha V^3 + \beta V^2 + \gamma V + \delta = 0 \rightarrow V_1$$

$$\alpha x^3 + b x^2 + cx + d = 0. \quad V_2$$

↓

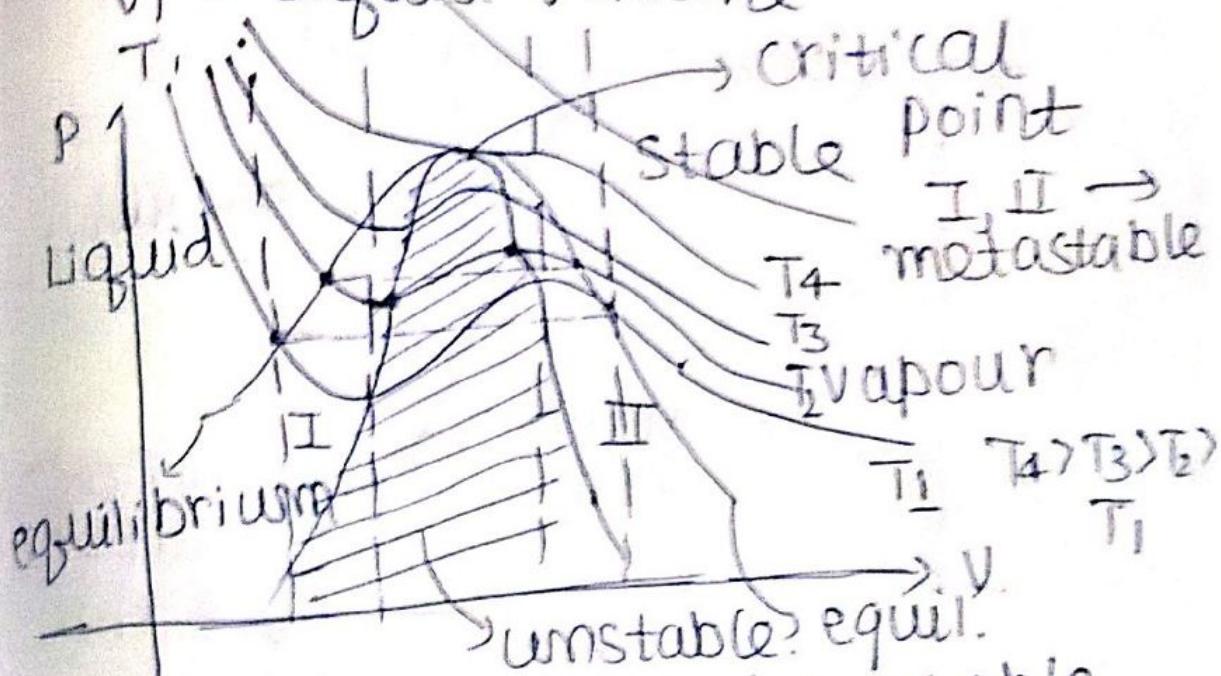
3 solutions

$\left. \begin{matrix} V_1 \\ V_2 \\ V_3 \end{matrix} \right\}$ Let All are real solutions
(positive)

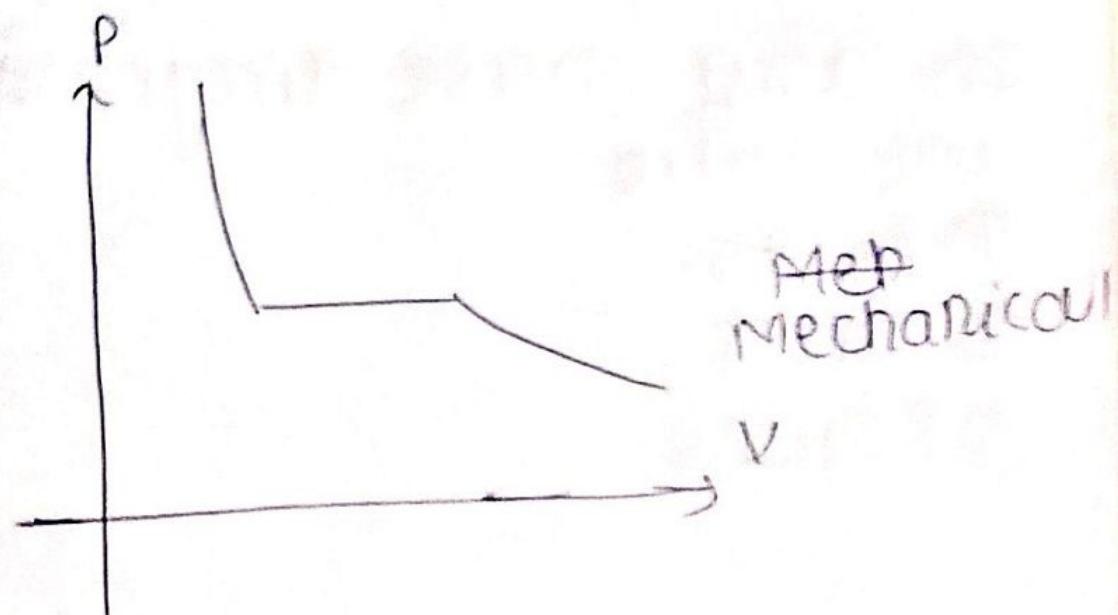
Let $V_3 > V_2 > V_1$

V_3 = Vapor volume

V_1 = Liquid volume

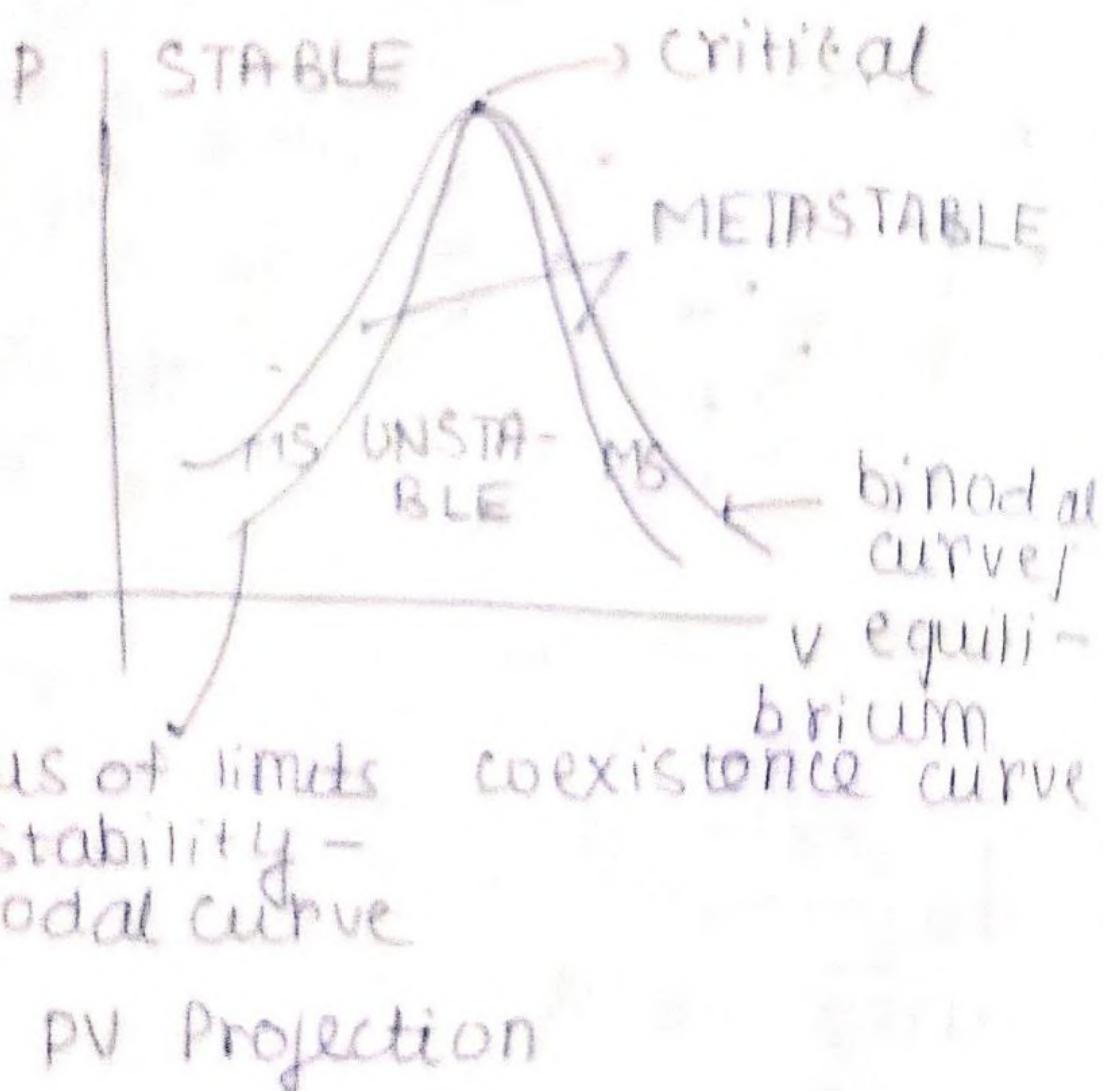


The system will be stable in the region which is on the convex side of the curve (bell shaped)



Above the critical point, we can approximate gas as the ideal one, and we can use the ideal gas equation

$$PV = NRT$$



Locus of limits of stability - spinodal curve

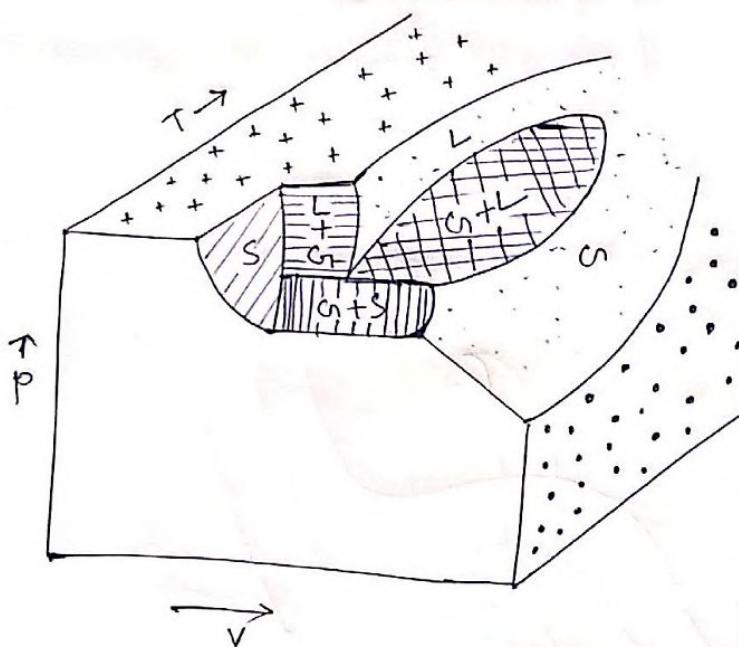
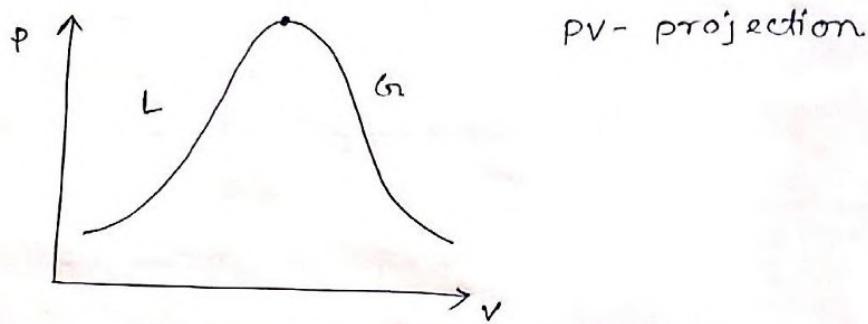
PV Projection

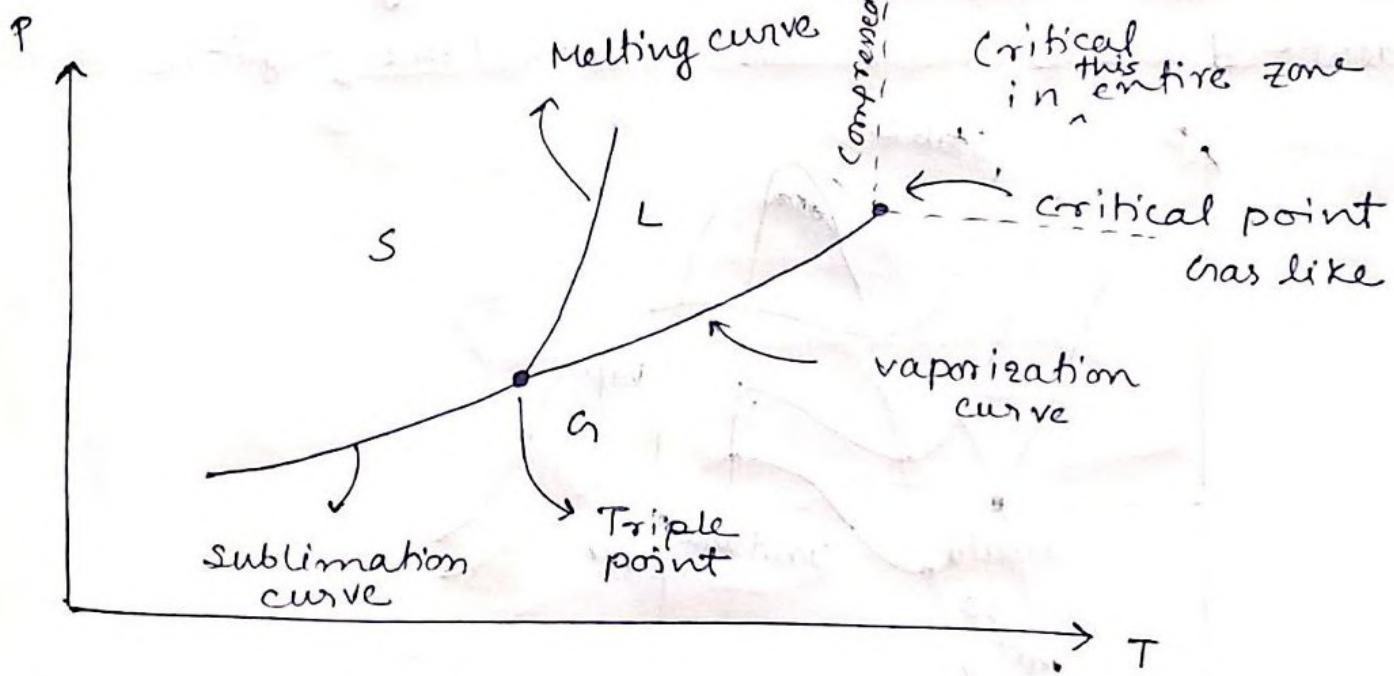
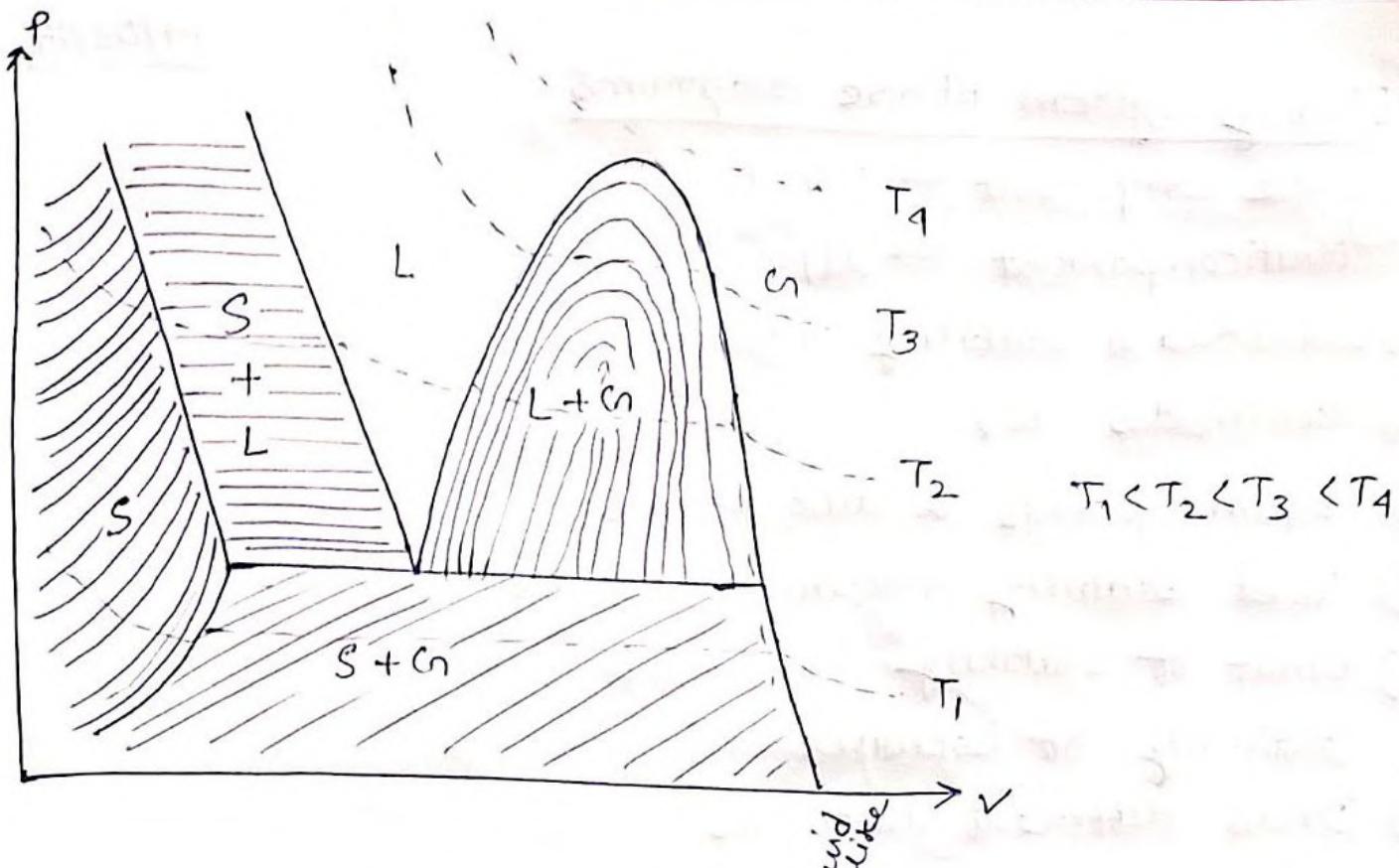
In any phase diagram, we have

- 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

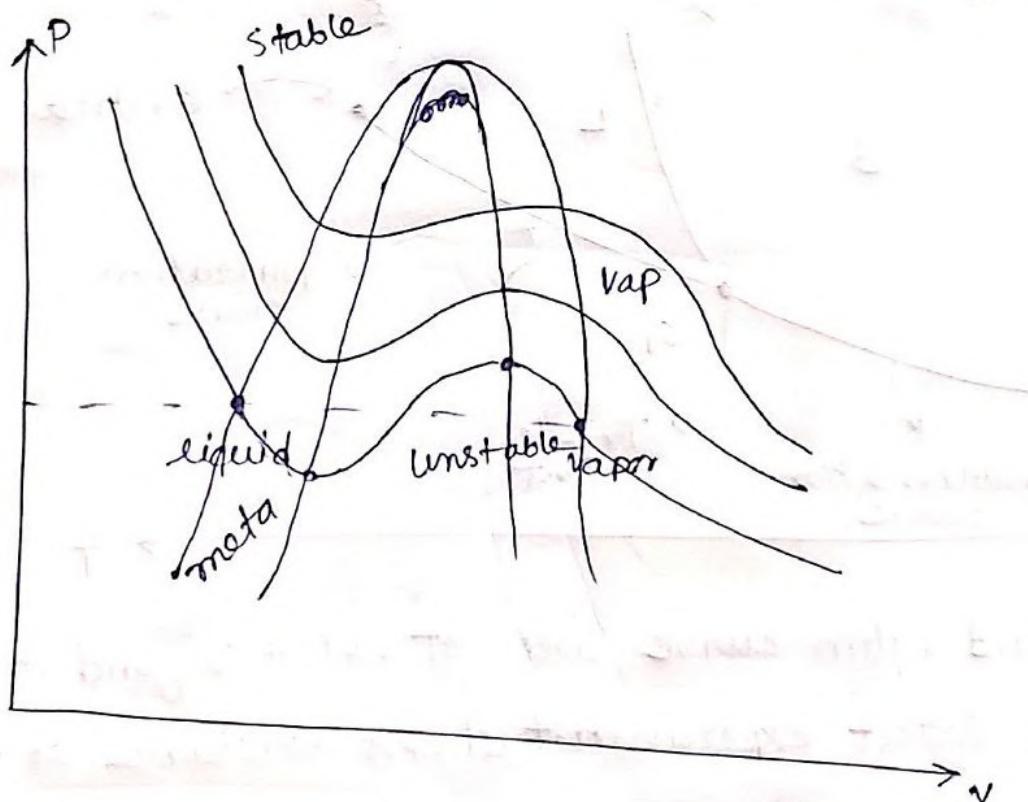
17/03/17

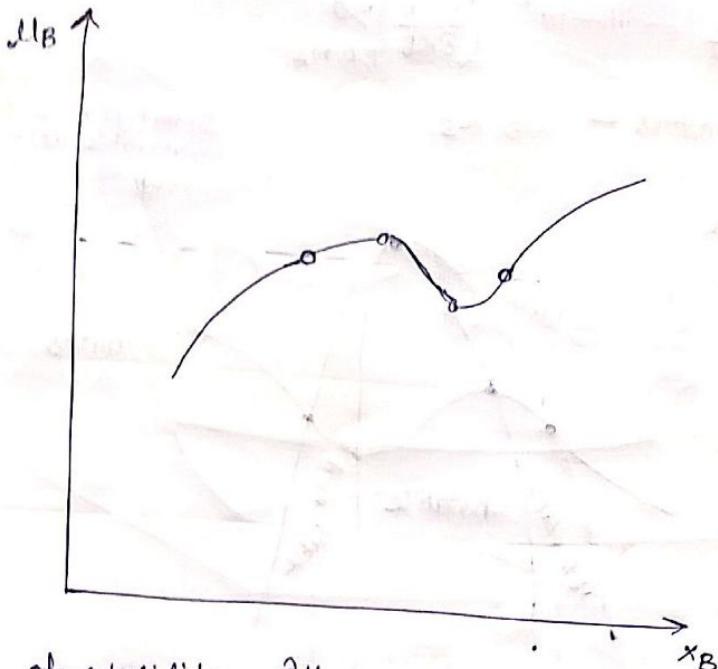
Binary system phase diagrams

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 μ_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

$$\Rightarrow \text{limit of stability} \rightarrow \left(\frac{\partial \mu_B}{\partial x_B} \right) = 0$$

$$\mu_B = \left(\frac{\partial G_B}{\partial n_B} \right)_{T, P, n_A}$$

$$\left(\frac{\partial \mu_B}{\partial x_B} \right)_{T, P, n_A} = \frac{\partial}{\partial x_B} \left[\left(\frac{\partial G}{\partial n_B} \right)_{T, P, n_A} \right]_{T, P, n_A} > 0$$

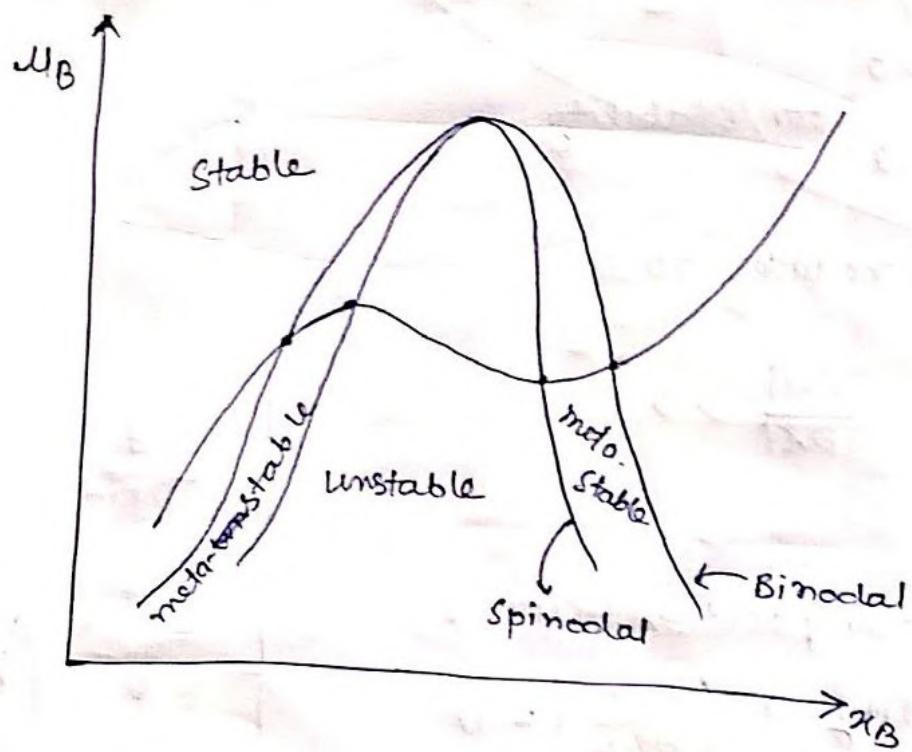
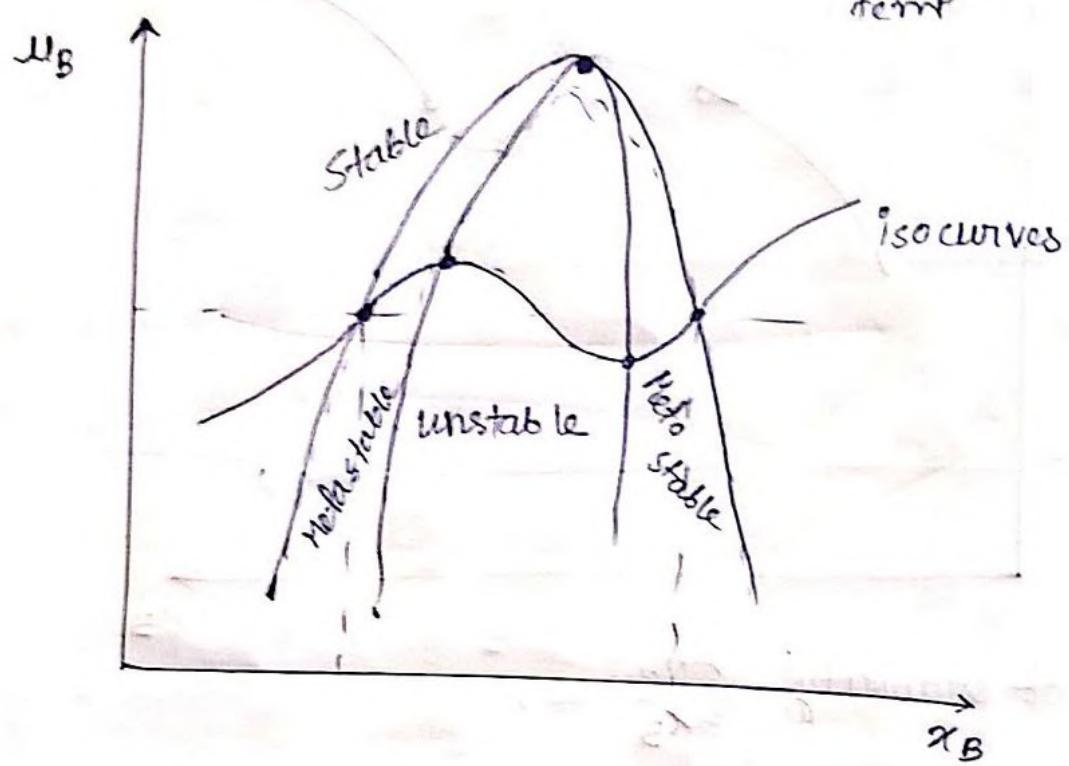
$\frac{\partial^2 f}{\partial x^2}$
 $\frac{\partial^2 f}{\partial y^2}$
 $\frac{\partial^2 f}{\partial x \partial y}$

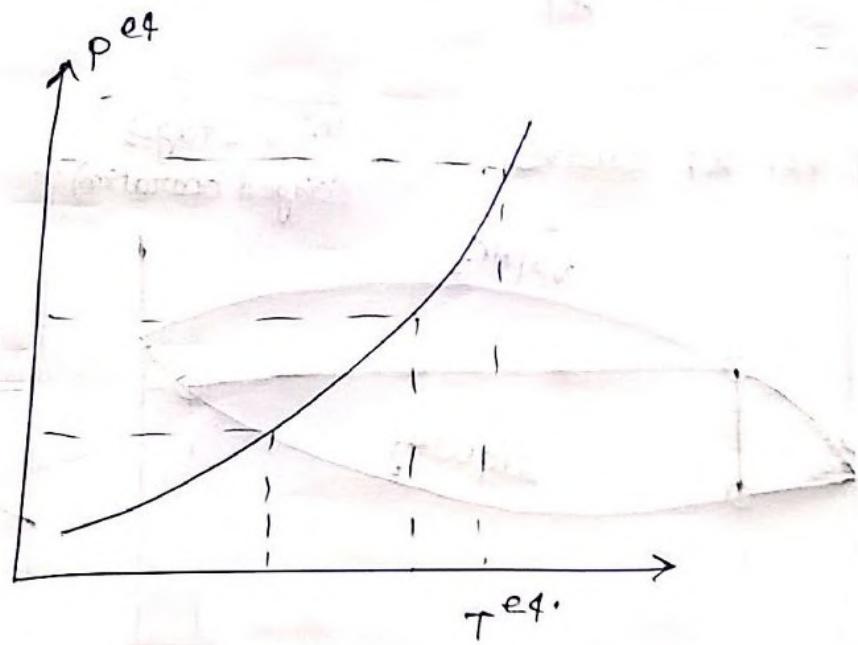
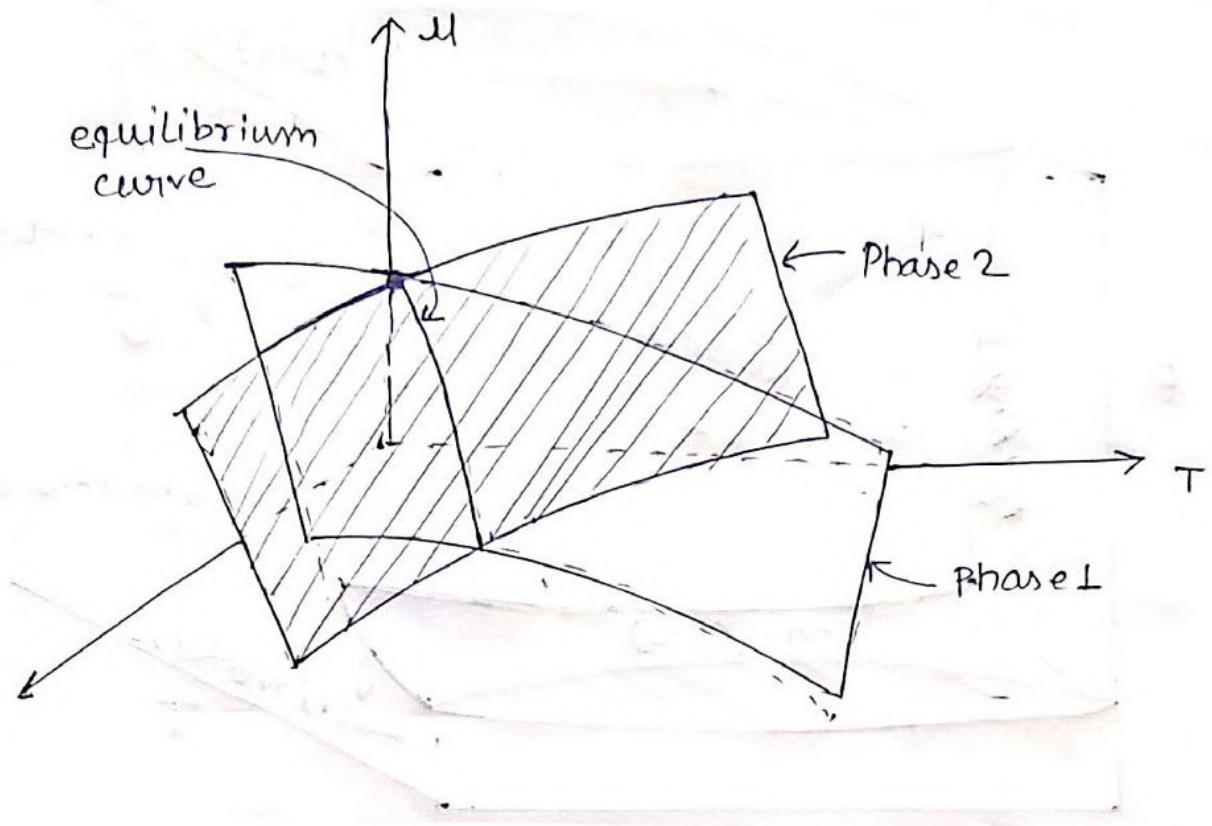
} all can
be used
as stability
criterion

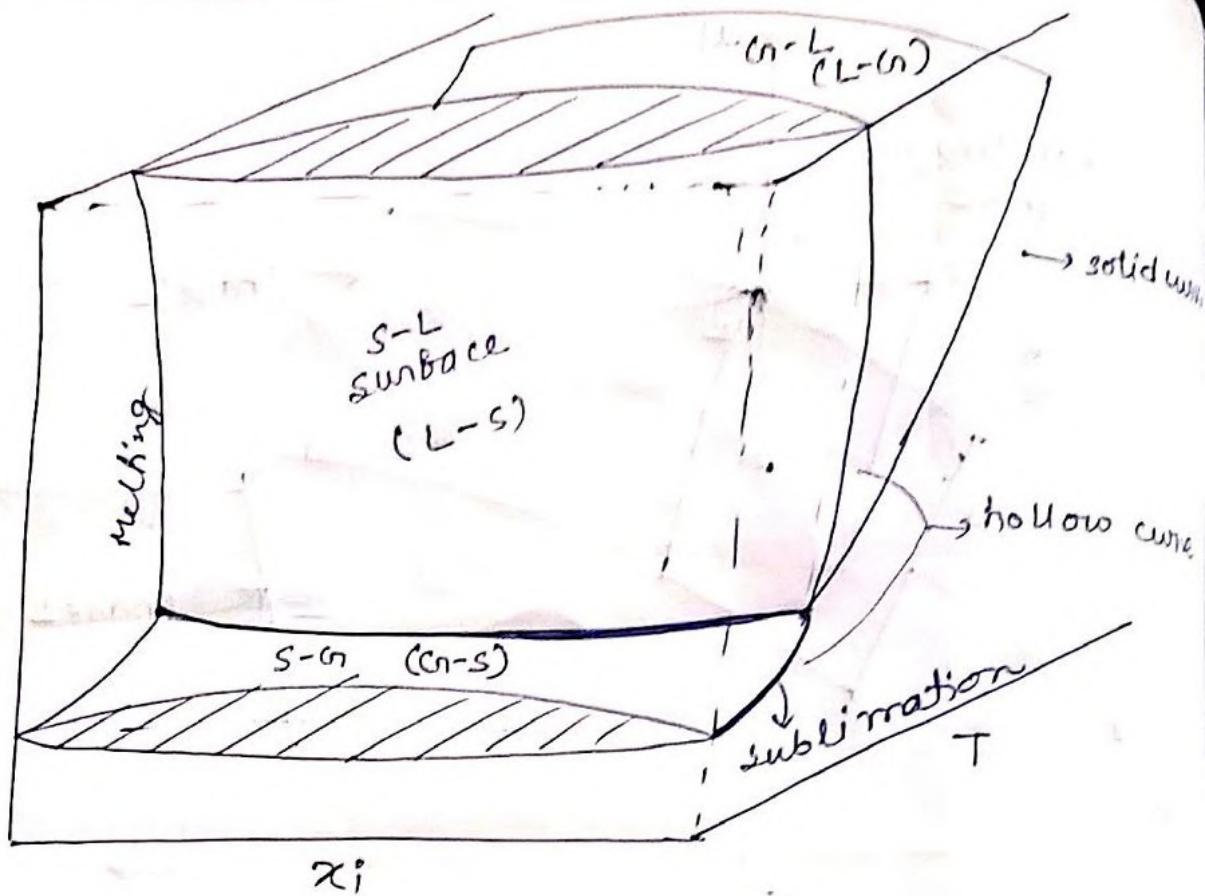
$$\textcircled{1} \text{ Stability criteria: } \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T, P, n_A} > 0$$

\textcircled{2} Co-ordinates $\rightarrow \mu_B, x_B$

Difference in independent variable decreases with temp

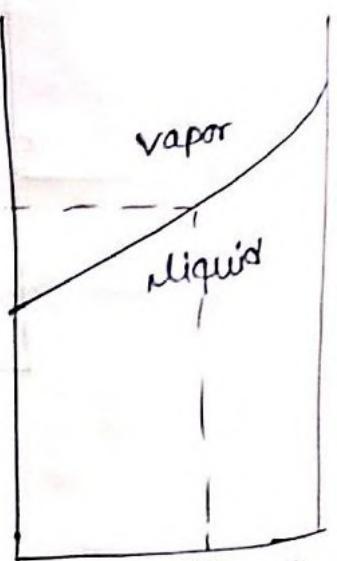
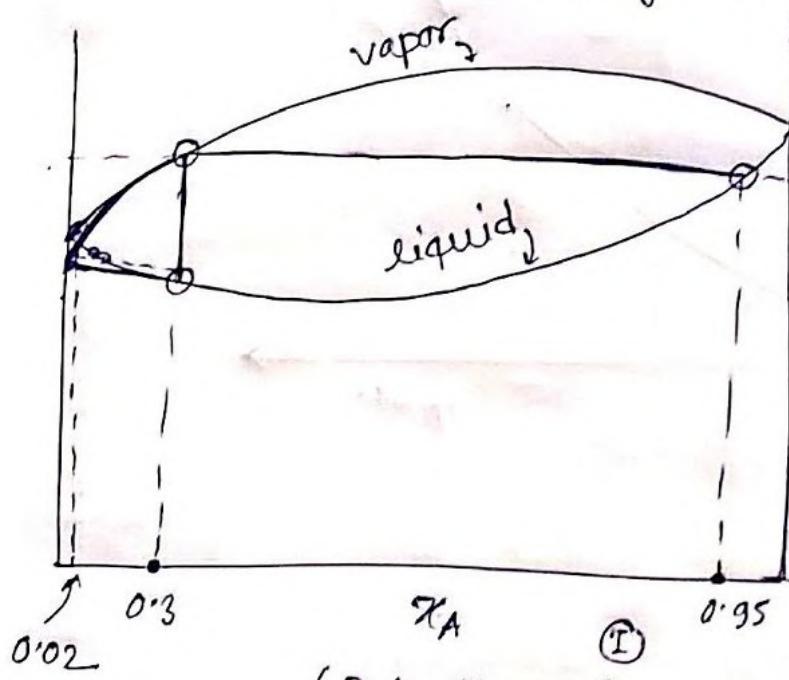






cal T vs. x_i curve

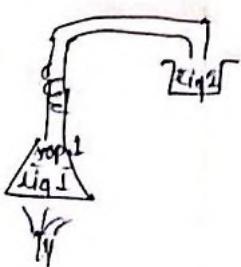
Two stages
(staged operation) T



(Projection of
binary phase
diagram)

(lets assume)
this happen

distillation

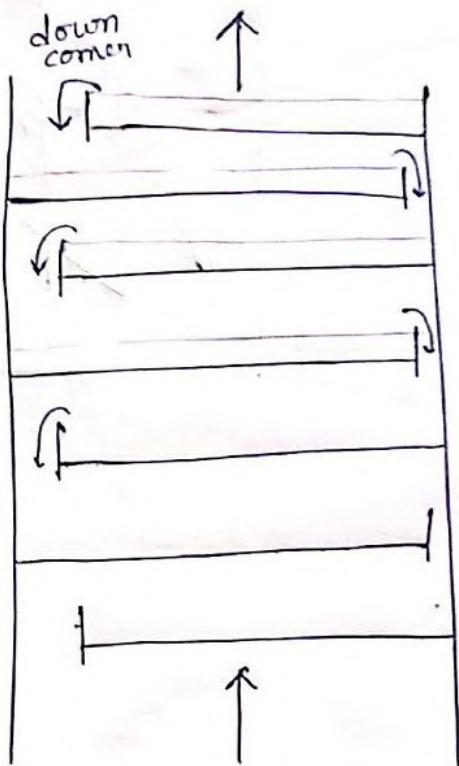


composition of liquid 2

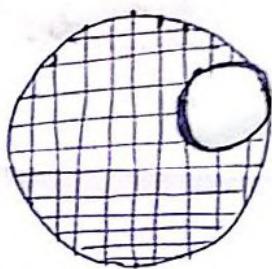
= composition of vapor 1

for case ① distillation simply fails as

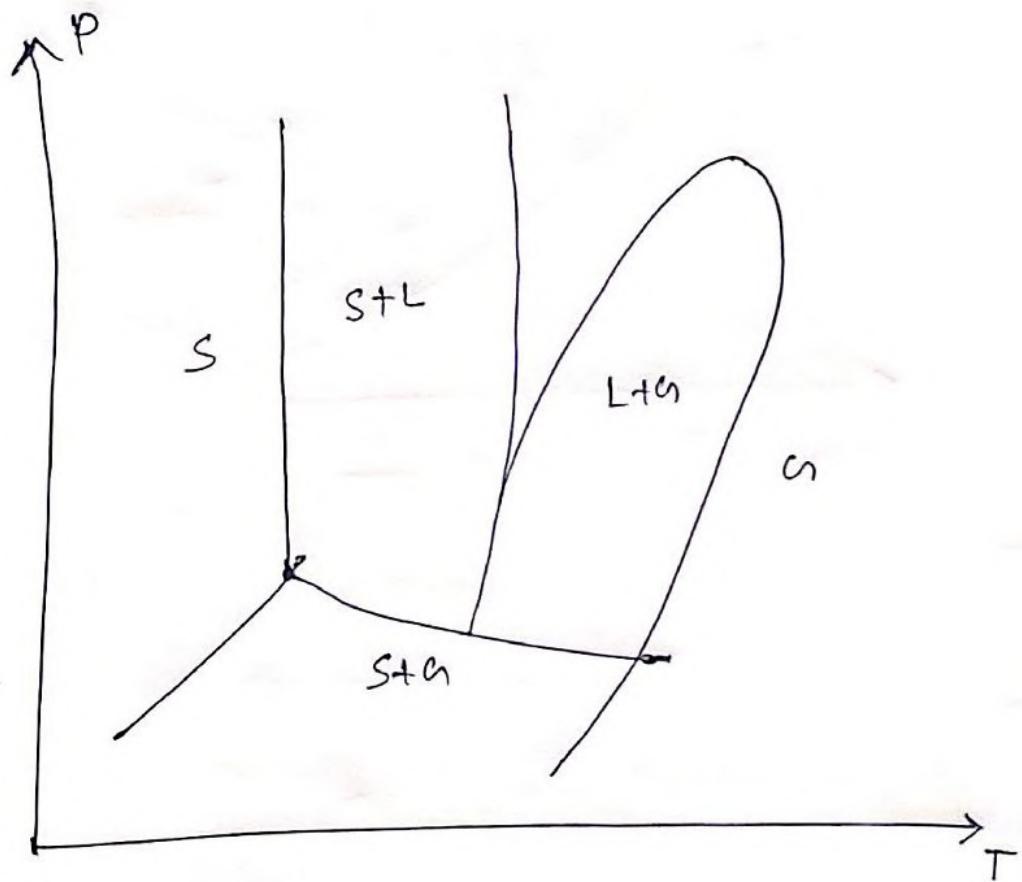
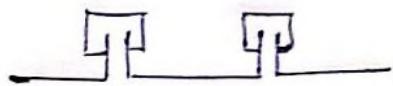
composition of liquid 1 = composition of liquid 2

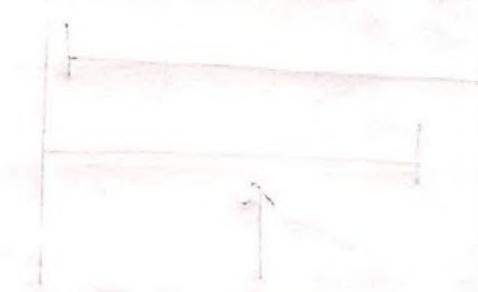
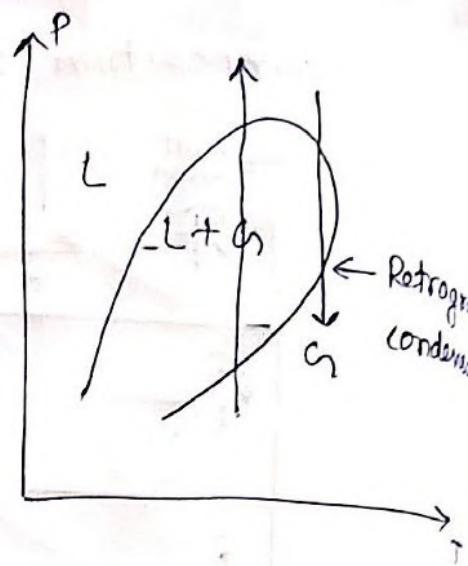
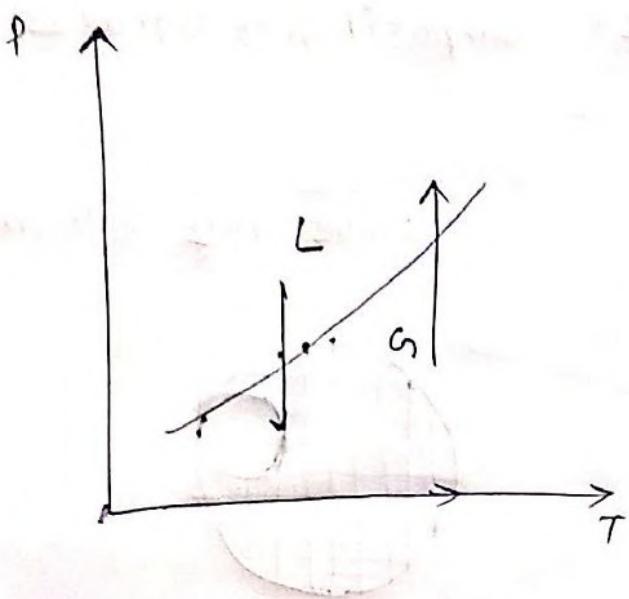


sieve-tray column



Bubble capped column





Critical Phenomenon

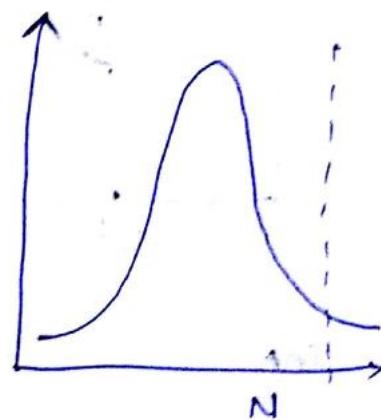
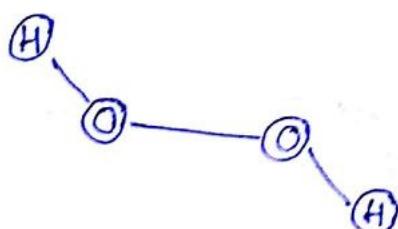
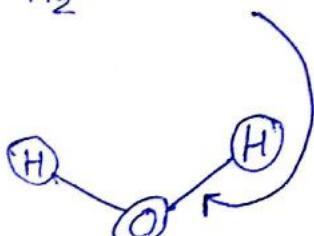
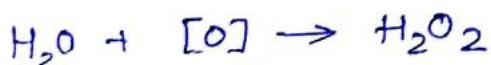
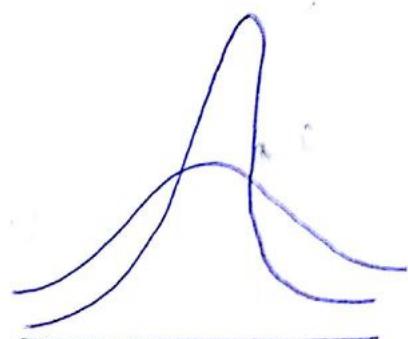
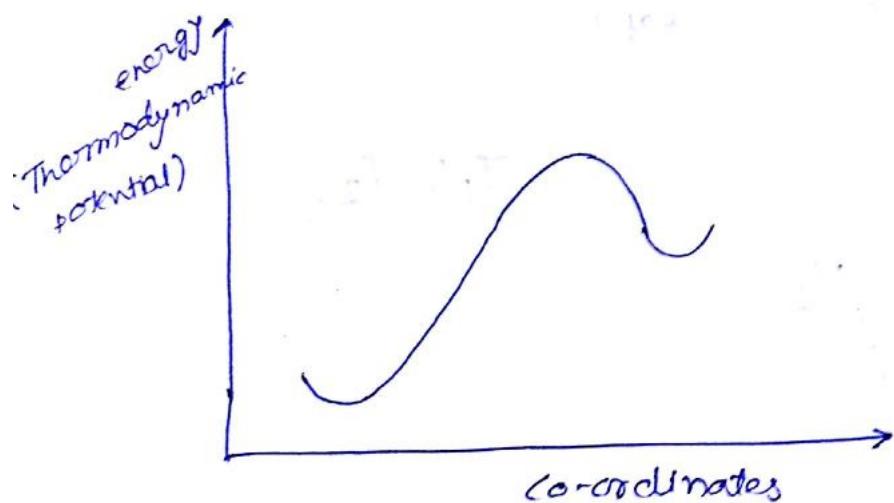
Landau theory ← Lev Landau

① $P - V - T$, $\mu - P - T$

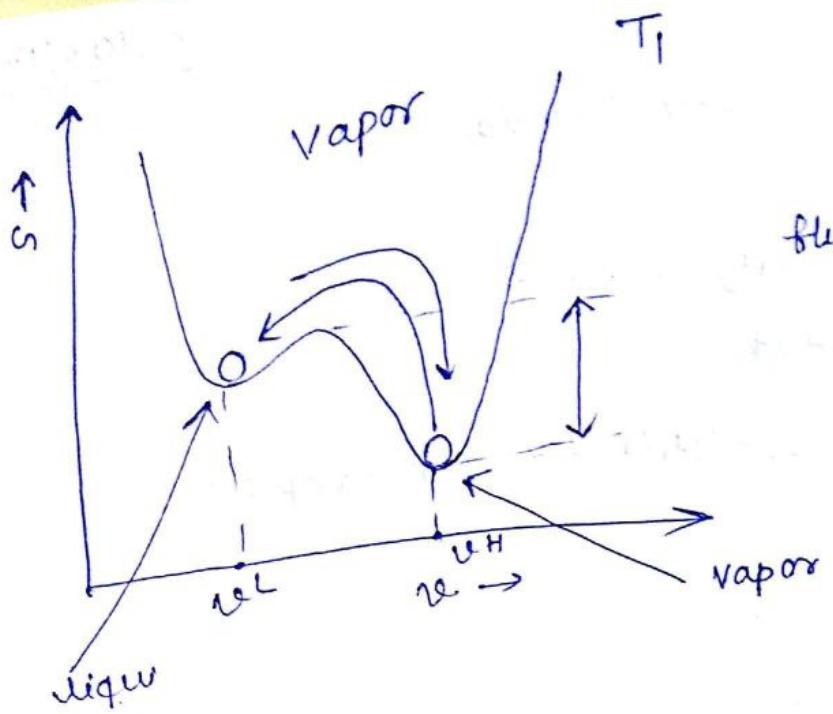
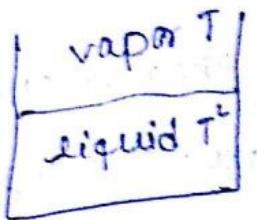
② Projections - stability criteria

③ Super critical state

Energy landscape & distribution of properties

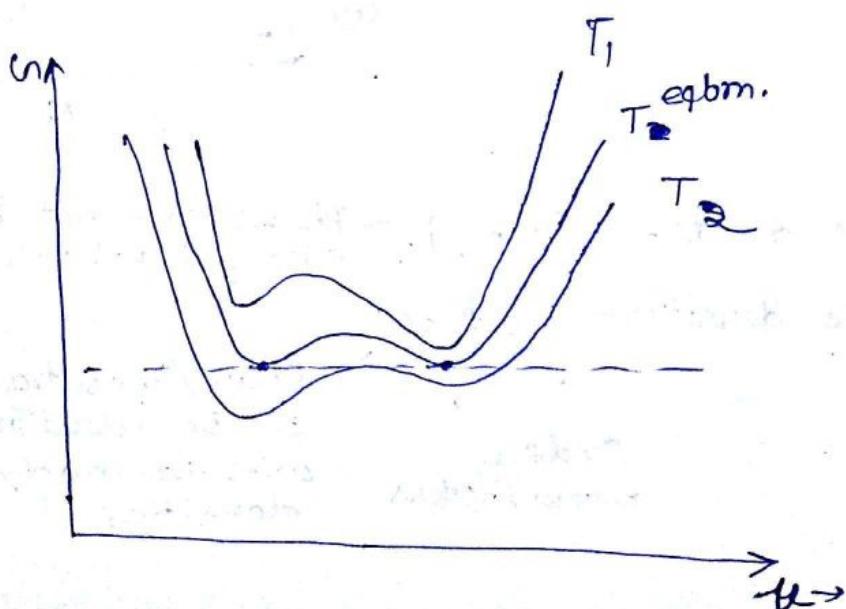
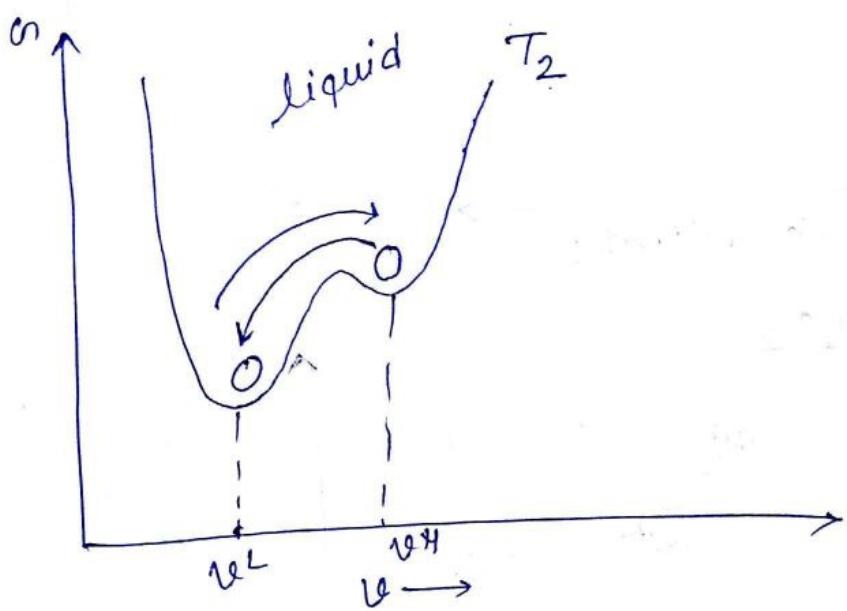


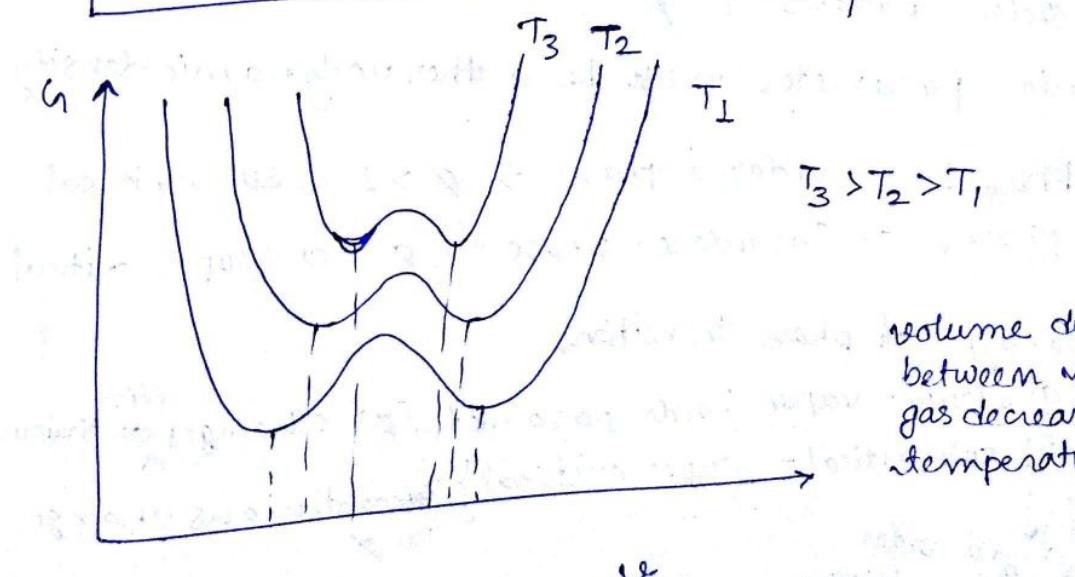
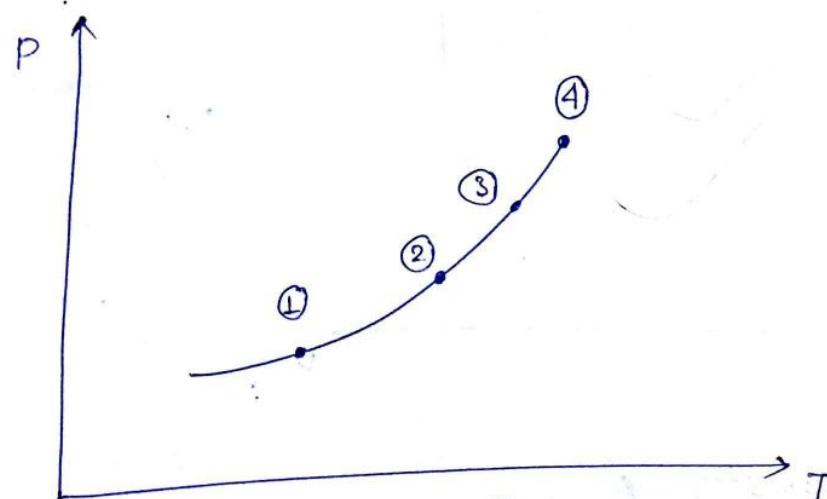
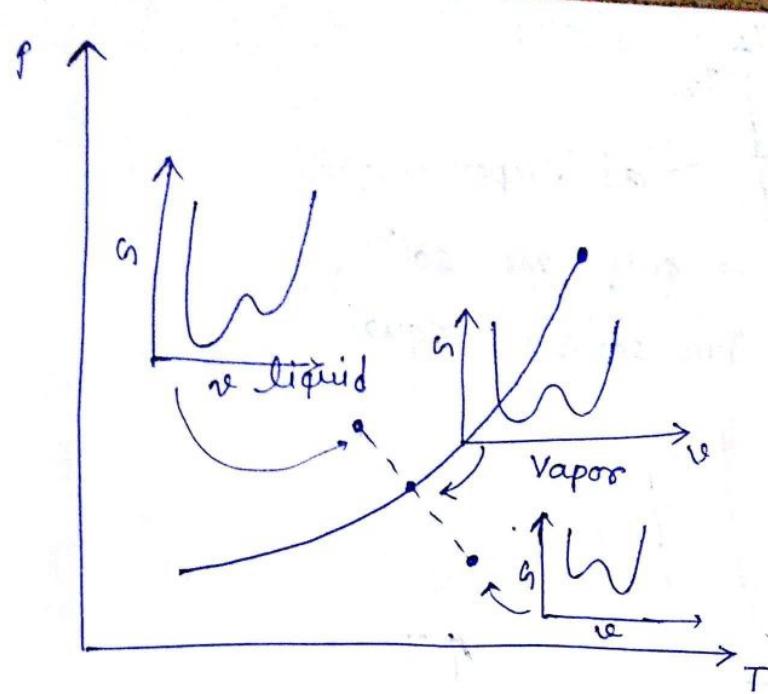
- Thermodynamic fields - (T, P, μ) → phases can not be distinguished with Th. fields
- Thermodynamic densities - (ρ, h, v) → Phase/Phase transition can be identified with thermodynamic densities
Order parameters

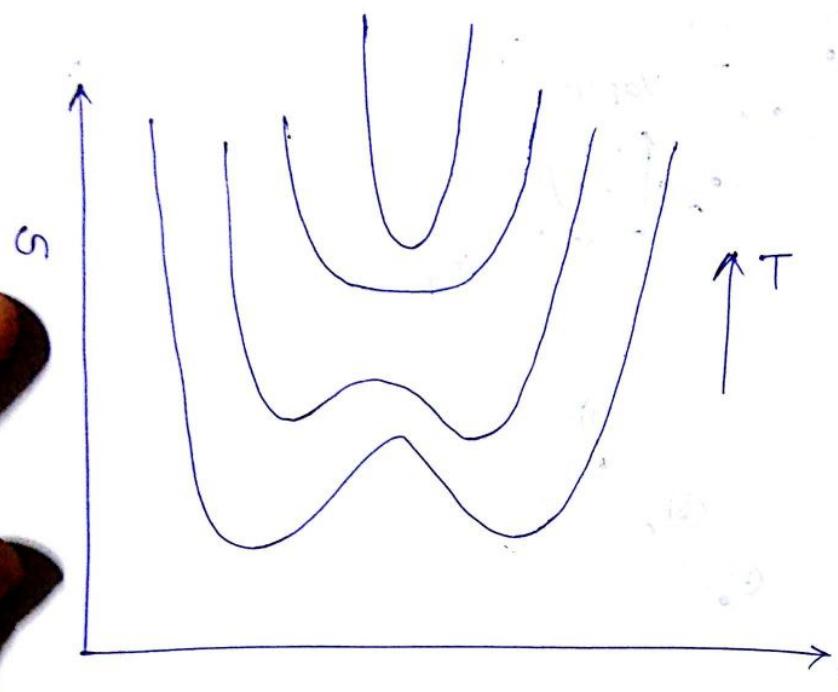
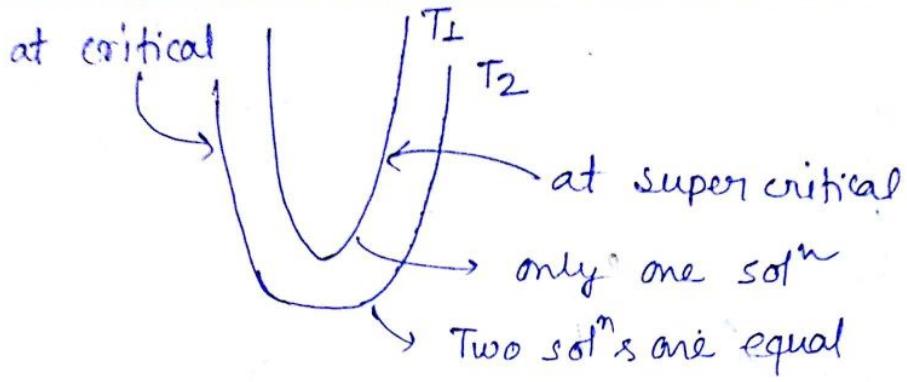


fluctuation - non-systematic disturbance

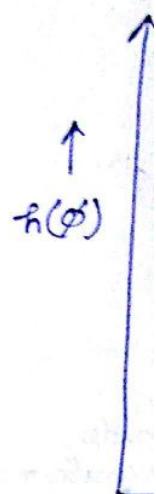
$$T_1 > T_2$$







5) Landau



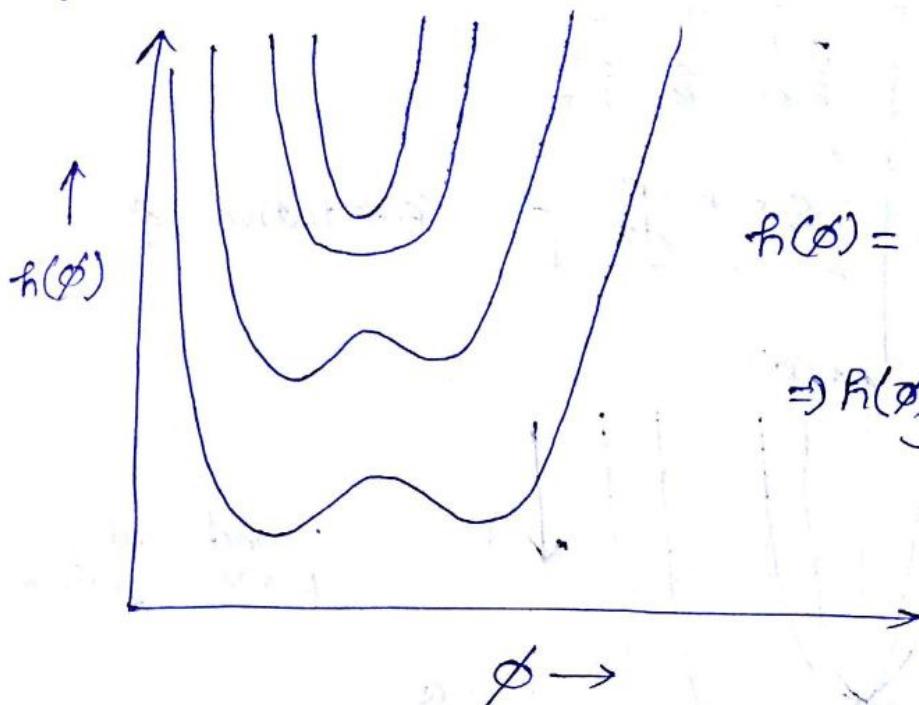
Thermodynamics

- 1) order parameter ϕ
- 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 (ϕ) changes continuously}
 - b) subcritical - supercritical } discontinuous change in ϕ
- 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

The temperature is introduced

With increasing temperature
the probability of occupying
lower energy levels decreases
and the system occupies higher
energy levels.

At low temperatures the system
occupies lower energy states
with maximum probability
at the minimum energy level.

As the temperature increases
the probability of occupying higher
energy states increases.

At high temperatures the system
occupies higher energy states
with maximum probability at
the minimum energy level.

Super critical state

24/03/17

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

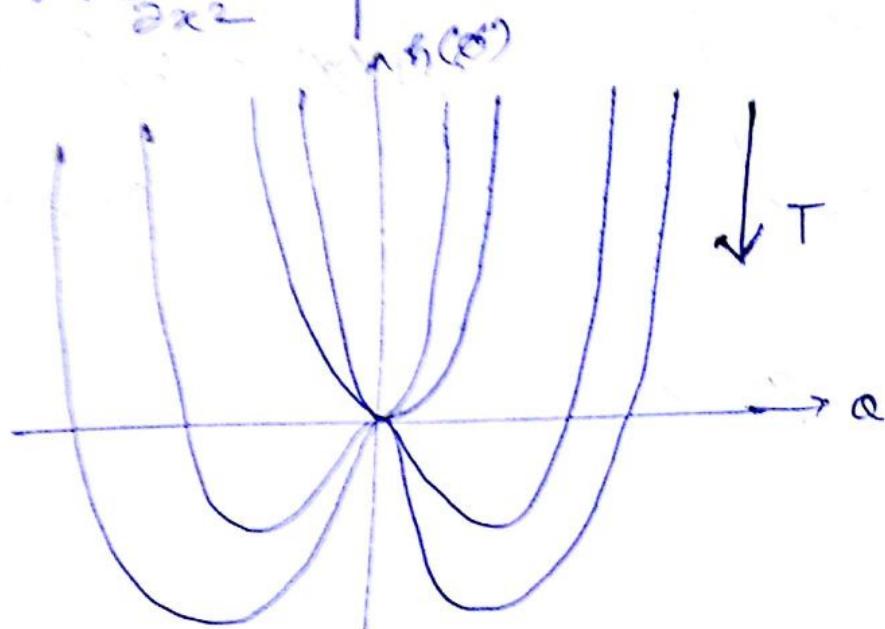
$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial \rho}{\partial t} = \gamma \frac{\partial^2 \rho}{\partial x^2}$$

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t}$$

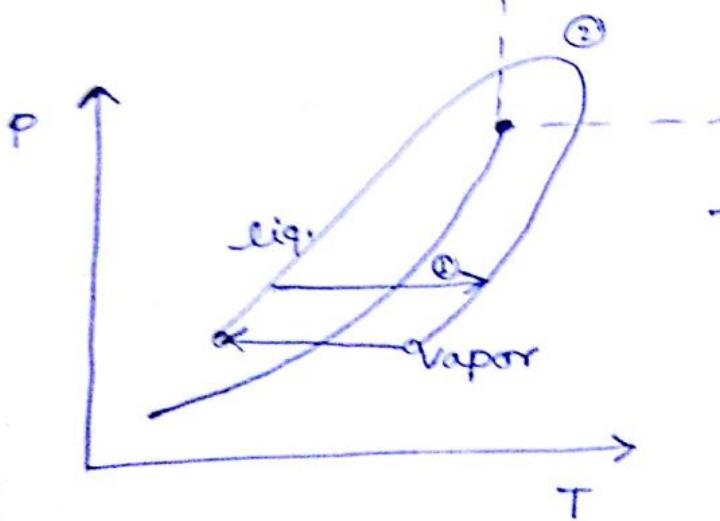
$$\sigma = K \frac{dT}{dx}$$

← constitutive eqn



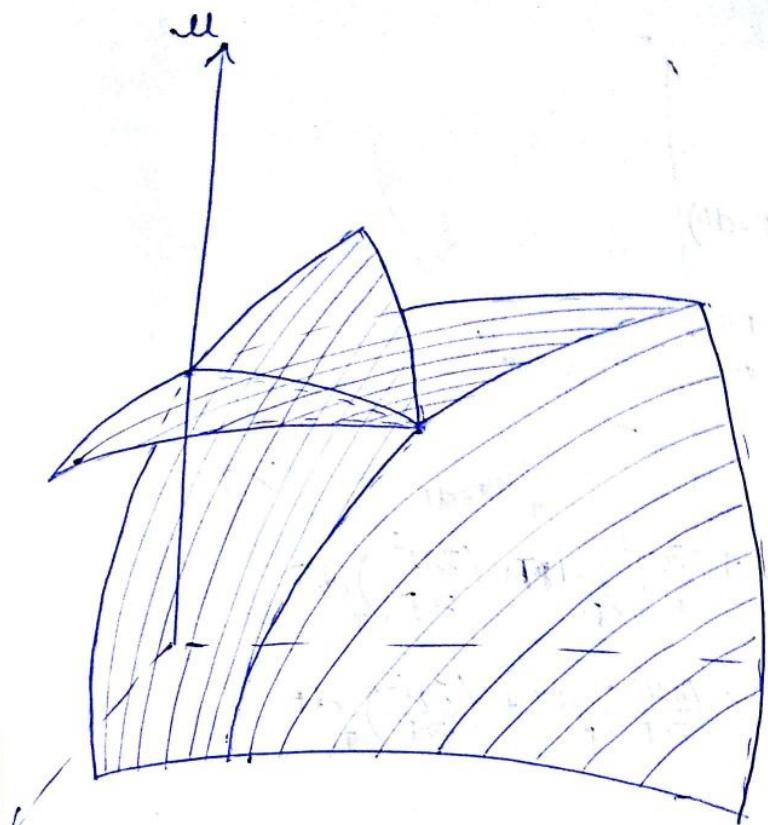
second order
phase transform

← direction of phase transformation

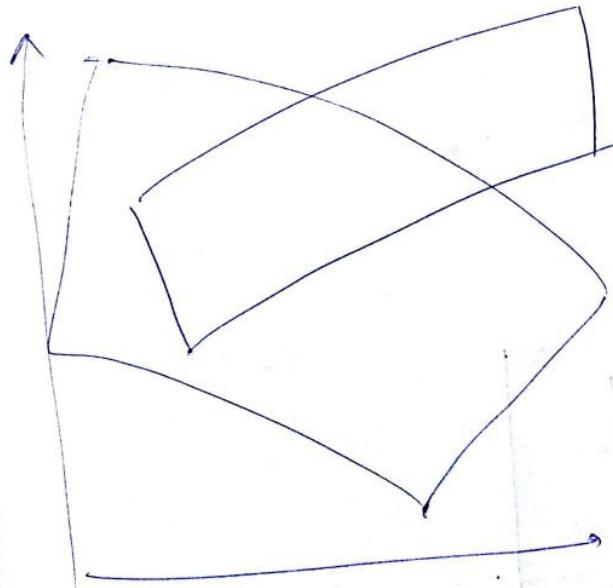


→ When we go from liquid to vapor via path ① there is abrupt change in specific volume.

→ 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

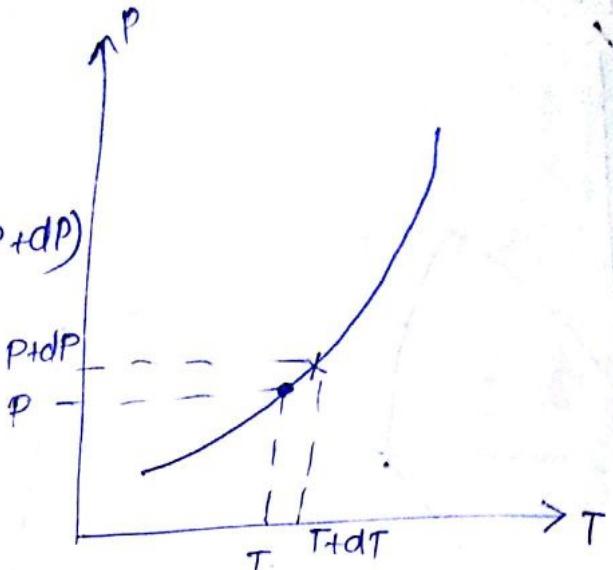


phase diagram normally (not under super critical state)

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 - α and β

Components - A and B

$$T^\alpha = T^\beta \quad \left| \begin{array}{l} \mu_A^\alpha = \cancel{\mu_B^\alpha} \mu_A^\beta \\ \mu_B^\alpha = \mu_B^\beta \end{array} \right. \quad \left| \begin{array}{l} \ln f_A^\alpha = \ln f_A^\beta \rightarrow f = f(T, P, x_A) \\ \ln f_B^\alpha = \ln f_B^\beta \end{array} \right.$$

$$d(\ln f_A^\alpha) = \left(\frac{\partial}{\partial T} \ln f_A^\alpha \right)_{P, x_A} dT + \left(\frac{\partial}{\partial P} \ln f_A^\alpha \right)_{T, x_A} dP + \left(\frac{\partial}{\partial x_A} \ln f_A^\alpha \right)_{T, P} dx_A^\alpha$$

$$d(\ln f_A^\alpha) = \left(\frac{\bar{H}_A^\alpha - H_A'}{RT^2} \right) dT + \left(\frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP + \left(\frac{\partial \ln f_A^\alpha}{\partial x_A} \right)_{T, P} dx_A^\alpha$$

H_A' = partial molar enthalpy of first component when system acts ideally

\bar{H}_A = partial molar enthalpy

$$= \left(\frac{\bar{H}_A^\alpha - \bar{H}_A^\beta}{RT^2} \right) dT + \left(\frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP + \frac{\partial}{\partial x_A^\alpha} (\ln f_A^\alpha)_{T, P} dx_A^\alpha = 0$$

$$-\frac{\partial}{\partial x_A^\beta} (\ln f_A^\beta)_{T, P} dx_A^\beta = 0$$

$$-\left(\frac{\bar{H}_A^\alpha - \bar{H}_A^\beta}{RT^2} \right) dT + \left(\frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP - \frac{\partial}{\partial x_A^\alpha} (\ln f_A^\alpha)_{T, P} dx_A^\alpha = 0 \quad ①$$

$$-\left(\frac{\bar{H}_A^\alpha - \bar{H}_A^\beta}{RT^2} \right) dT + \left(\frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT} \right) dP - \frac{\partial}{\partial x_A^\beta} (\ln f_A^\beta)_{T, P} dx_A^\beta = 0$$

$$+\frac{\partial}{\partial x_A^\alpha} (\ln f_A^\alpha)_{T, P} dx_A^\alpha - \frac{\partial}{\partial x_A^\beta} (\ln f_A^\beta)_{T, P} dx_A^\beta = 0 \quad ②$$

$$x_A^\alpha \left(\frac{\partial \ln f_A^\alpha}{\partial x_A^\alpha} \right) + x_B^\alpha \left(\frac{\partial \ln f_B^\alpha}{\partial x_B^\alpha} \right) = 0$$

$$\left(\frac{\partial P}{\partial T} \right)_{x_A^\beta} = \frac{1}{T} \left\{ \frac{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^\beta) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^\beta)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)} \right\}$$

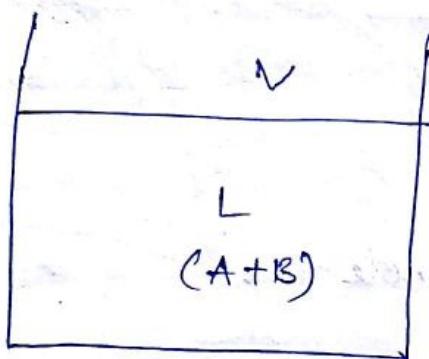
$$\left(\frac{\partial P}{\partial x_A^\beta} \right)_T = RT \left\{ \frac{(x_A^\alpha - x_A^\beta x_B^\alpha / x_B^\beta) (\partial \ln f_A^\beta / \partial \ln x_A^\beta)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)} \right\}$$

$$\left(\frac{\partial T}{\partial x_A^\beta} \right)_P = -RT^2 \left\{ \frac{(x_A^\alpha - x_A^\beta x_B^\alpha / x_B^\beta) (\partial \ln f_A^\beta / \partial x_A^\beta)}{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^\beta) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^\beta)} \right\}$$

29/03/17

Binary Vapor - Liquid eqbm. systems

liquid \rightarrow A + B

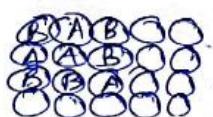
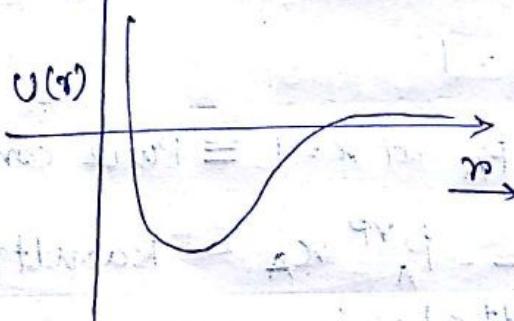
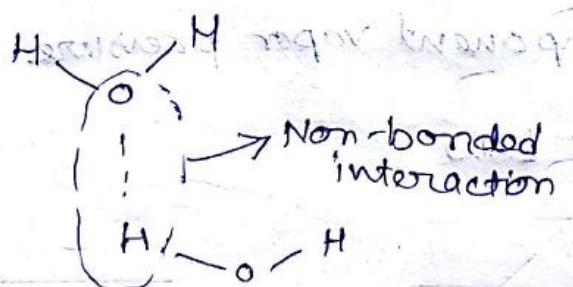
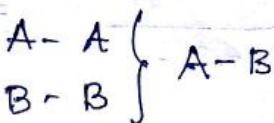


Spatial distribution of molecules of A & B?

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

$$p_A = k x_A$$

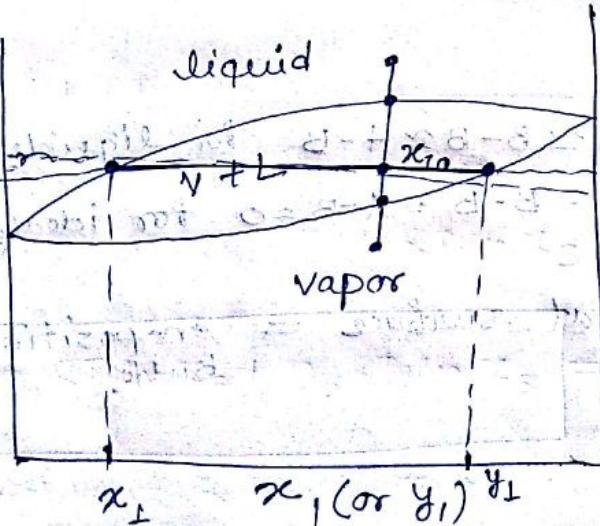
$$x_A = 1$$

$k = p_A^{\circ}$ 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

$$x_{1a} = \frac{n_1^L + n_1^V}{n_T^L + n_T^V} \quad \text{--- } ③$$

$$x_{1a}(n_T^L + n_T^V) = x_1 n_T^L + y_1 n_T^V$$

$$x_{1a} n_T^L + x_{1a} n_T^V = x_1 n_T^L + y_1 n_T^V$$

$$(x_{1a} - x_1) n_T^L = (y_1 - x_{1a}) n_T^V$$

$$\left[\frac{n_T^L}{n_T^V} = \frac{y_1 - x_{1a}}{x_{1a} - x_1} \right] \rightarrow \text{Lever Rule}$$

$$P_{\text{ambient}} = \underbrace{P_1^{VP} x_1}_{\bar{P}_1} + \underbrace{\bar{P}_2^{VP} x_2}_{\bar{P}_2} \quad \sum \bar{P}_i$$

$$P_{\text{amb}} = P_1^{VP} x_1 + P_2^{VP} (1-x_1)$$

$$\Rightarrow P_{\text{amb}} - P_2^{VP} = (P_1^{VP} - P_2^{VP}) x_1$$

$$\Rightarrow x_1 = \frac{P_2^{VP} - P_{\text{amb}}}{P_1^{VP} - P_2^{VP}}$$

$$\text{Composition} = f(P, P_i^{\text{NP}}) \quad i$$

$$P_i^{\text{VP}} = g(T)$$

$$\log(P_i^{\text{NP}}) = A - \frac{B}{T+C} \quad \leftarrow \text{Empirical Correlation}$$

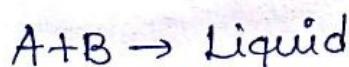
Relation vs. Correlation

$$S = ut + \frac{1}{2} at^2 \quad \text{— Relation}$$

$$S = f(u, a, t)$$

30/03/17

Ideal Solutions



$$\Delta G = G_A^{\text{soln}} + G_B^{\text{soln}} - G_A^{\text{pure}} - G_B^{\text{pure}}$$

$$G_A^{\text{pure}} = n_A \mu_A^{\text{pure}}$$

$$G_B^{\text{pure}} = n_B \mu_B^{\text{pure}}$$

$$G_A^{\text{soln}} = n_A \mu_A^{\text{soln}}$$

$$G_B^{\text{soln}} = n_B \mu_B^{\text{soln}}$$

$$\Delta G = n_A \mu_A^{\text{soln}} + n_B \mu_B^{\text{soln}} - n_A \mu_A^{\text{pure}} - n_B \mu_B^{\text{pure}}$$

$$\mu_i = \mu_i^* + RT \ln x_i$$

~~$$\mu_A^{\text{pure}} = \mu_A^{\text{soln}} + RT \ln x_A$$~~

$$\mu_B^{\text{soln}} = \mu_B^{\text{pure}} + RT \ln x_B$$

$$\Delta G = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Rightarrow \Delta G < 0$$

$$n_i \rightarrow +\text{ve}, \quad R \rightarrow +\text{ve}, \quad T \rightarrow +\text{ve}, \quad x_i \rightarrow +\text{ve} < 1$$

$$\Delta G = \Delta H - T \Delta S \quad +ve$$

↑ ↑
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. $\Delta H = 0$

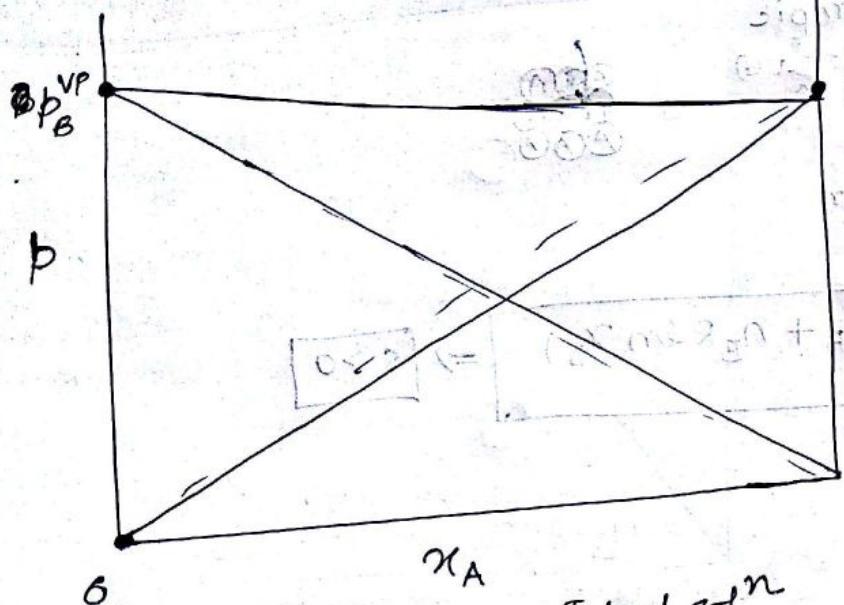
6. $\Delta S > 0$

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 - $S = C_2H_5$

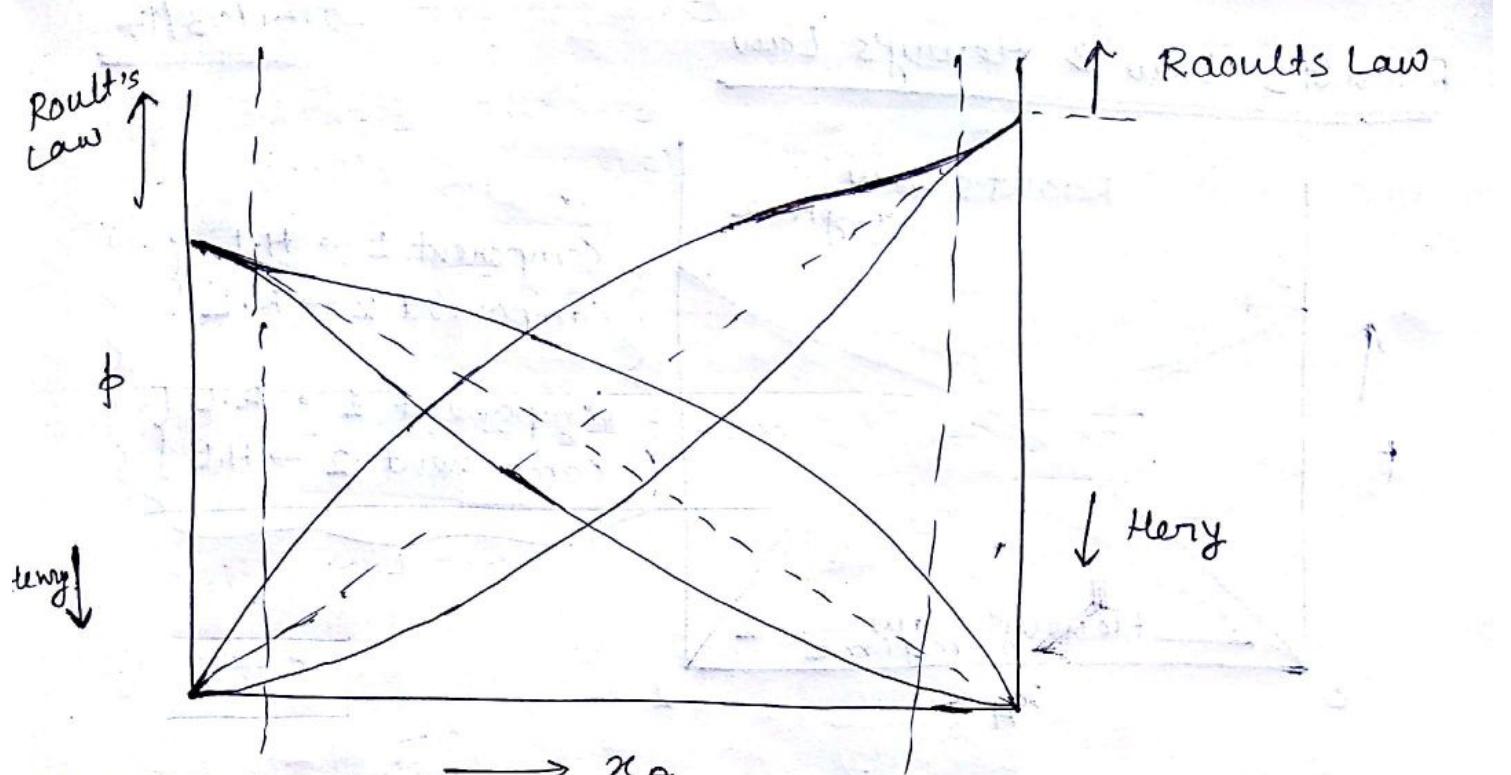
$A+B \rightarrow A-A + B-B$

$A-B < A-A$

$p_A + p_B = p_L$

1

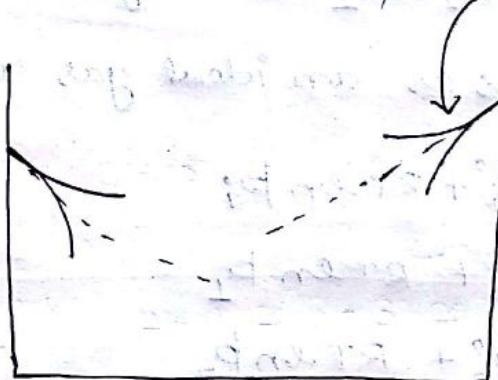
$p_A + p_B = p_L$



A-B interaction



A-A interaction

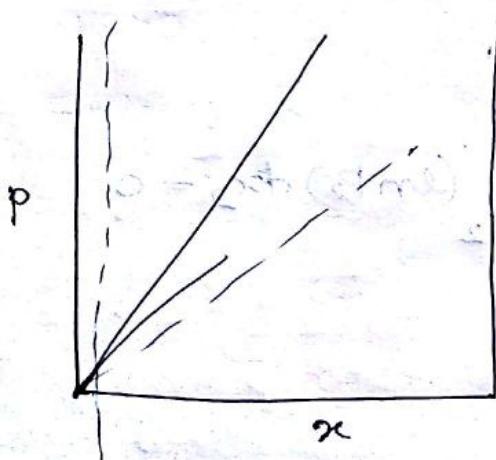


Asymptotically reaches
Raoult's Law behavior



System behaves
like this at ∞ -dilution

A-A' interaction



Sparingly soluble

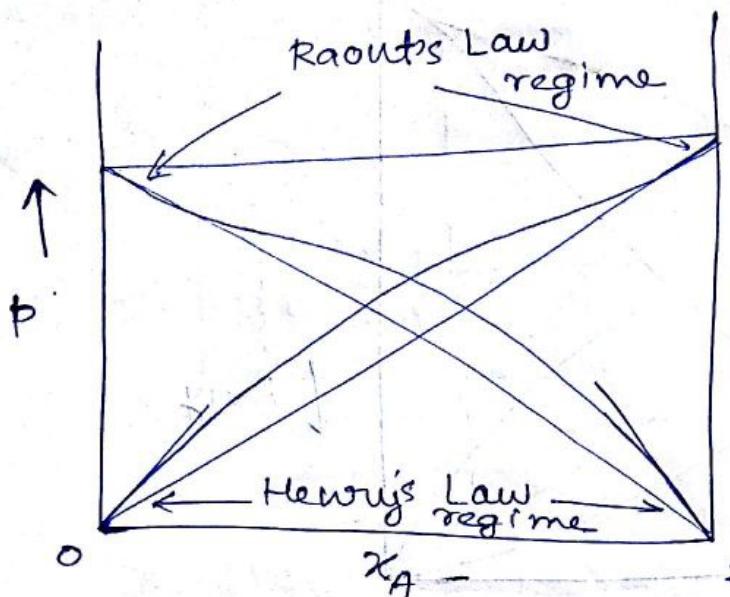
$$P = K_H x$$

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

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

$$\mu_1 = \mu_1^\circ + RT \ln p_1$$

$$\mu_2 = \mu_2^\circ + RT \ln p_2$$

$$d\mu_1(T, P) = RT \frac{\partial}{\partial x_1} (\ln p_1) dx_1$$

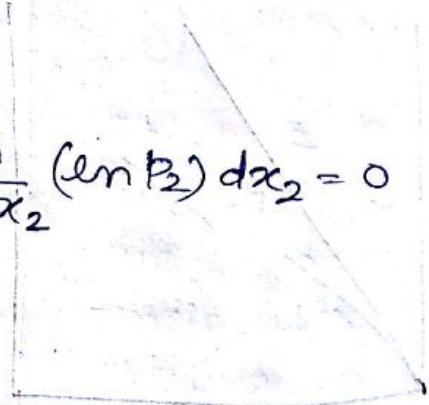
$$d\mu_2(T, P) = RT \frac{\partial}{\partial x_2} (\ln p_2) dx_2$$

$$x_1 \cancel{RT} \frac{\partial}{\partial x_1} (\ln p_1) dx_1 + x_2 \cancel{RT} \frac{\partial}{\partial x_2} (\ln p_2) dx_2 = 0$$

$$x_1 + x_2 = 1$$

$$dx_1 = -dx_2$$

$$x_1 \frac{\partial (\ln p_1)}{\partial x_1} = x_2 \frac{\partial (\ln p_2)}{\partial x_2}$$



If, component 1 follows Raoult's Law

$$p_1 = x_1 p_1^{\text{VP}}$$

$$\cancel{x_1} \frac{p_1^{\text{VP}}}{x_1} = x_2 \frac{\partial(\ln p_2)}{\partial x_2}$$

$$\frac{x_1}{x_2} p_1^{\text{VP}} = \frac{\partial(\ln p_2)}{\partial x_2}$$

$$\cancel{x_1} p_1^{\text{VP}} \ln x_2 = \ln p_2$$

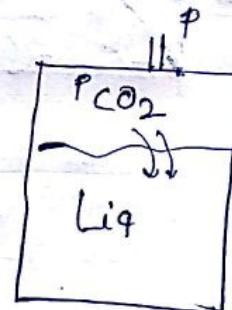
$$x_2 e^{\cancel{x_1} p_1^{\text{VP}}} = \cancel{\ln} p_2$$

$$p_2 = k_H x_2$$

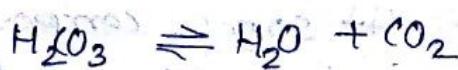
⇒ In cold drinks CO_2 is dissolved. Mole fraction of CO_2 in that ~ 0 as CO_2 is sparingly soluble

$$p_2 = k_H x_2$$

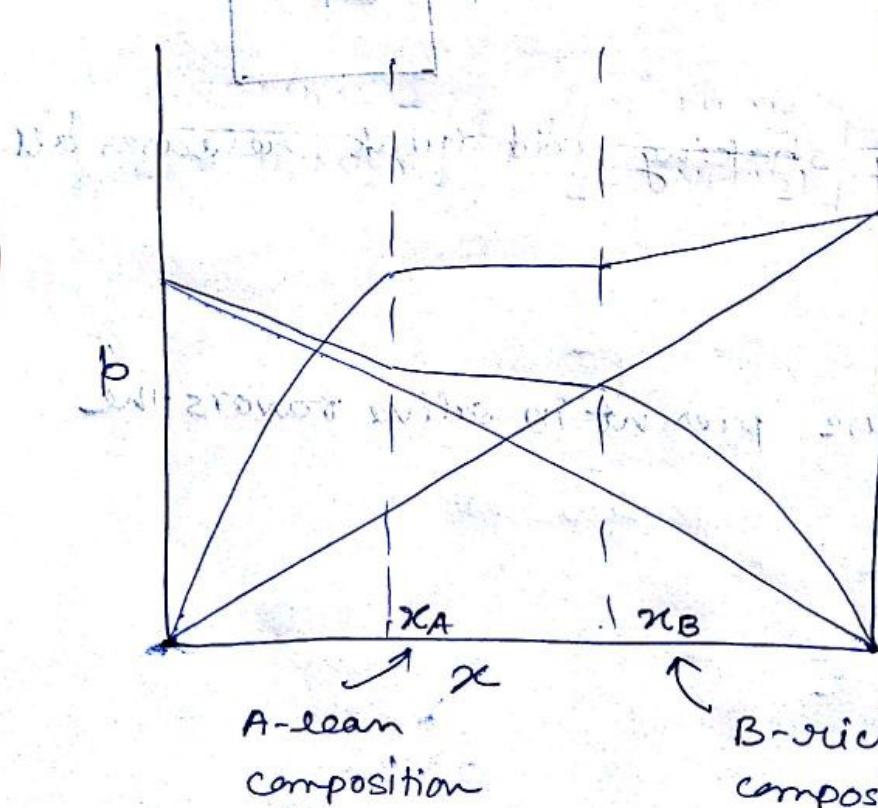
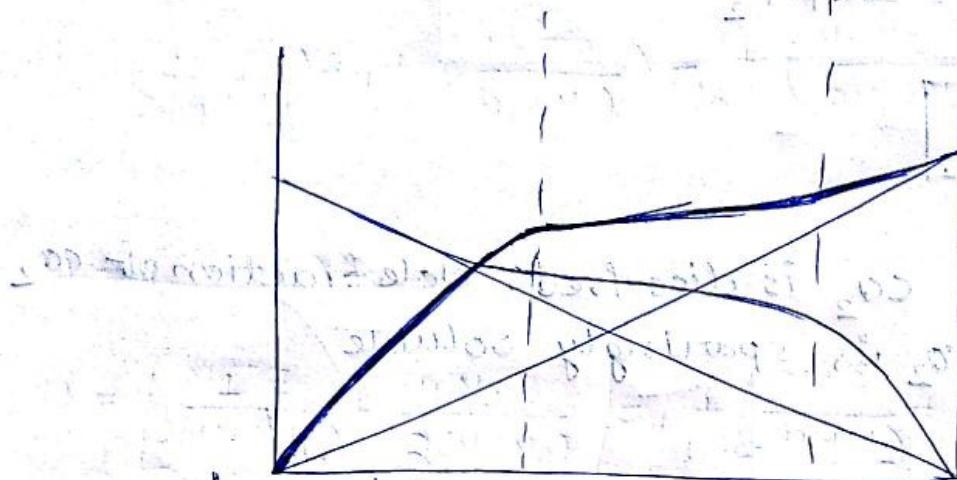
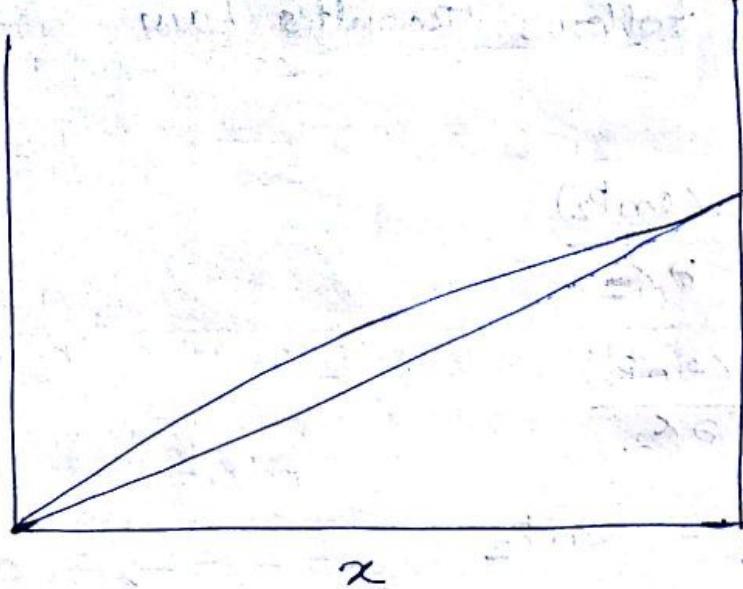
↑
Henry's Law



Why mechanically shaking cold drink, releases all CO_2 ?



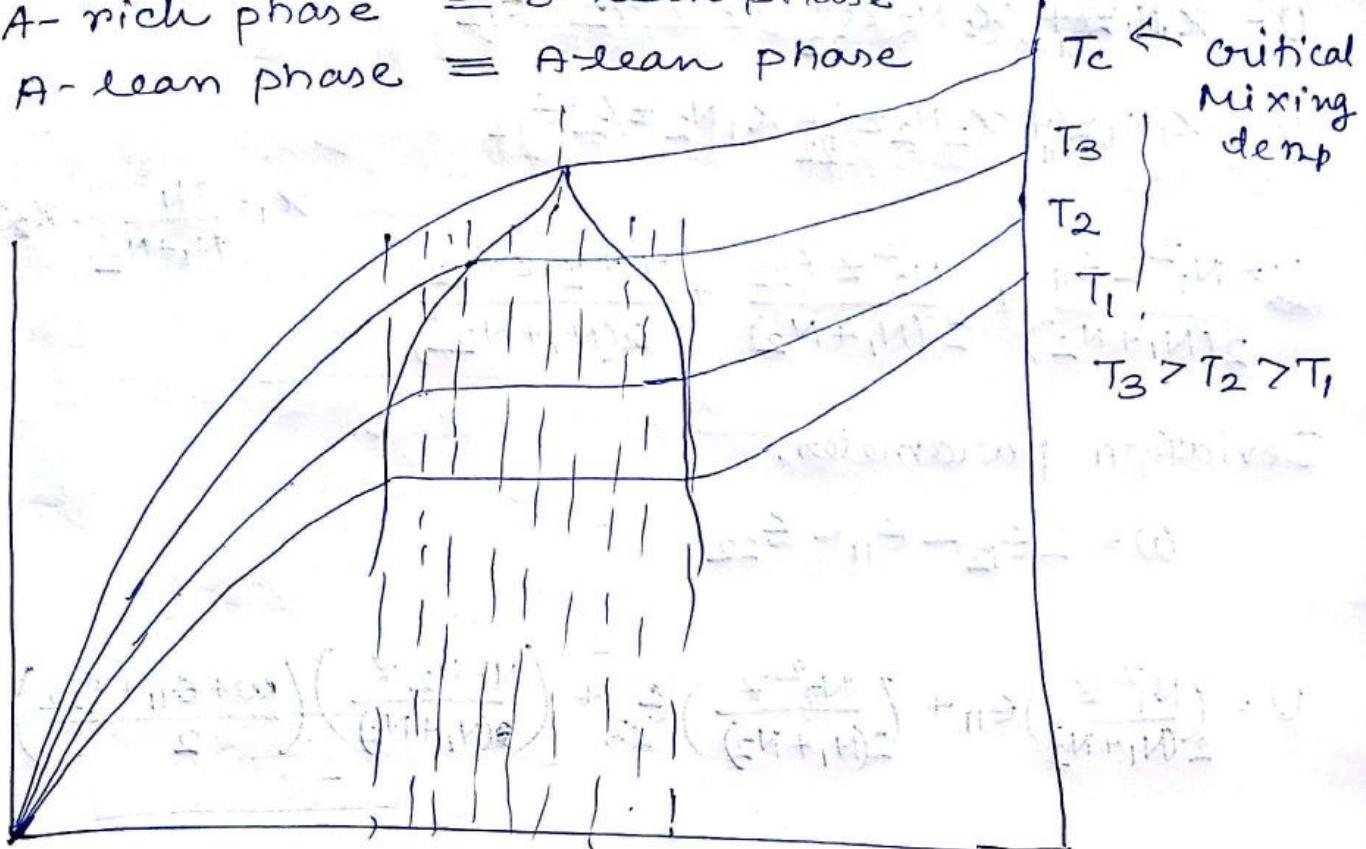
Carbonic anhydrase present in saliva favors the dissociation.



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 - $\frac{\partial \ln \left(\frac{x_1}{x_1^*} \right)}{\partial x^3} = \frac{NAZ\omega}{2RT} x^2 + \frac{NAZ\omega}{2RT} x^3 + \dots$

for both $\frac{\partial \ln \left(\frac{x_1}{x_1^*} \right)}{\partial x^2} = \frac{NAZ\omega}{2RT}$

for both $\frac{\partial \ln \left(\frac{x_1}{x_1^*} \right)}{\partial x^3} = \frac{NAZ\omega}{2RT} x^2$

$$\mu_i = \mu_i^{\circ, \text{Id}} + RT \left[x_1 \exp \left(\frac{NA^2 \omega x^2}{2RT} \right) \right]$$

non ideal

$$\mu_i = \mu_i^* + RT \ln x_1$$

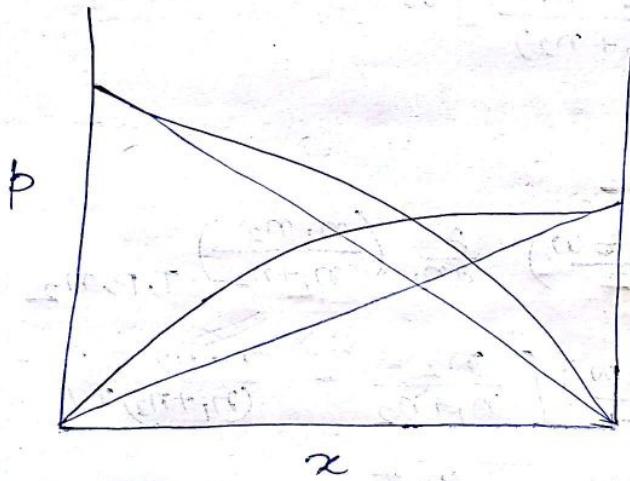
ideal

$$\mu_i = \mu_i^* + RT \ln x_1 - \text{non ideal}$$

determined experimentally

$$a_1 = x_1 \exp \left(\frac{NA^2 \omega}{2RT} x^2 \right) = x_1 e^{\alpha x_2^2 + \beta x_2^3 + \gamma x_2^4 + \dots}$$

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

$$\mu_1 = \mu_1^* + RT \ln x_1$$

$$\mu_1^* = \mu_1^* + RT \ln a_1^*$$

$$x_1 d(\ln a_1) + x_2 d(\ln a_2) = 0$$

$$x_1 d(\ln x_1) + x_2 d(\ln x_2) = 0$$

It, $a_2 = x_2$ (to be proved)

then component 2 also follows Raoult's law.

$$d \ln(a_2) = -\frac{x_1}{x_2} d(\ln x_1)$$

~~$$d \ln(a_2) = -\frac{x_1}{x_2} d(\ln(1-x_1))$$~~

~~$$d \ln(a_2) = -\frac{x_1}{x_2} \left(\frac{1}{x_1}\right) (-dx_1)$$~~

$$d \ln(a_2) = -\frac{x_1}{x_2} d\left(\frac{1}{x_1} dx_1\right)$$

$$d \ln(a_2) = \frac{dx_2}{x_2} = d(\ln x_2)$$

~~$$\ln a_2 = \ln x_2$$~~

$$d(\ln a_2) = d(\ln x_2)$$

~~$$a_2 = x_2$$~~

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

$$a_i = \gamma_i x_i$$

$$a_1 = \gamma_1 x_1 e^{\alpha x_2^2}$$

$$a_2 = \gamma_2 x_2 e^{\alpha x_1^2}$$

$$\frac{\Delta G_{\text{Molar}}}{RT} = x_1 \ln a_1 + x_2 \ln a_2$$

$$= x_1 \ln \gamma_1 + x_1 \ln x_1 + \alpha x_2^2 x_1 + x_2 \ln \gamma_2 + x_2 \ln x_2 + \alpha x_1^2 x_2$$

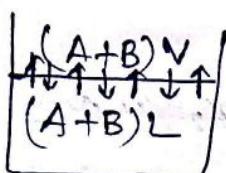
$$\frac{\Delta G_i}{RT}^{\text{Molar}} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2$$

$$\frac{\Delta G_i}{RT}^{\text{Molar excess}} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + \alpha x_1 x_2$$

07/04/17

Solid- liq Equilibrium

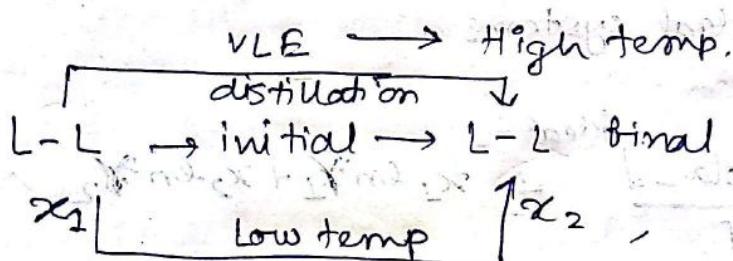
VLE \rightarrow 2 phases \rightarrow V + L



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 $\sim 100^\circ\text{C}$

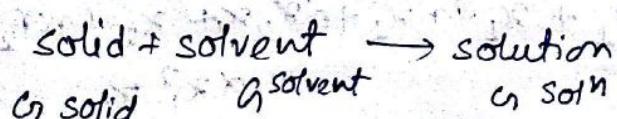
liquid \rightarrow possible to obtain solid

1) Why do solids dissolve in liquids?

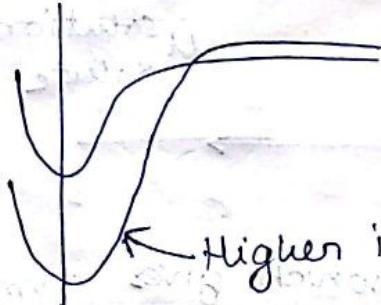
2) Under what condition will a solid dissolve in a liquid?

$$\Delta G = \Delta H - T \Delta S \quad \text{at const. } T, P$$

↑ maintained
 ↓
 -ve Enthalpic Entropic



- solution results in minimization of free energy of system.
- Entropy increases in solⁿ \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 SiO_2 in water

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

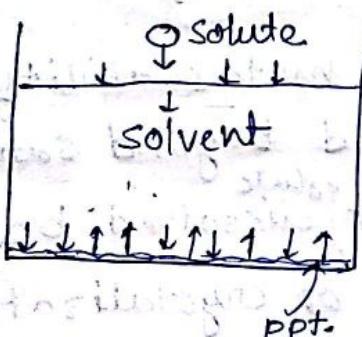
↑ ↑
inhibits Favors

3. How much solid can be dissolved in a given amount of a liquid?

→ saturation is not the cause, it is the result

→ ΔH

→ μ



μ_{solute}	$=$	$\mu_{\text{solute}}^{\text{pure solid}}$
		at const. T, P

Phase 1 \rightarrow solⁿ (liquid)

Phase 2 \rightarrow solute (solid)

$$\mu \rightarrow f(T, P)$$

pure solid
 μ_{solute}

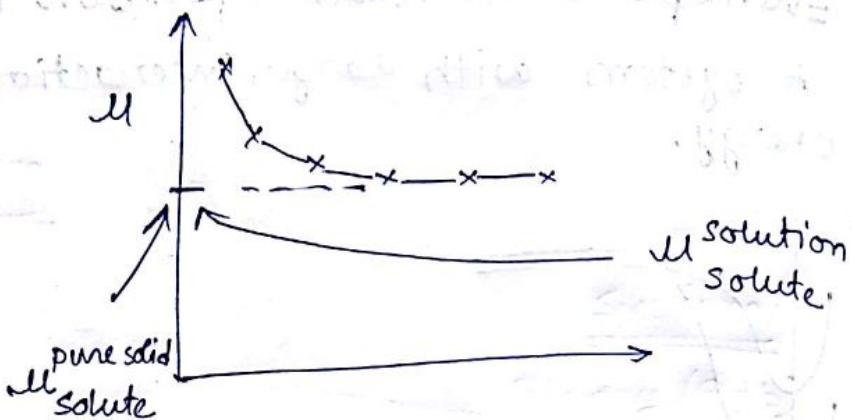
??

Is it const. at given T, P?

$$G_1 = n\mu$$

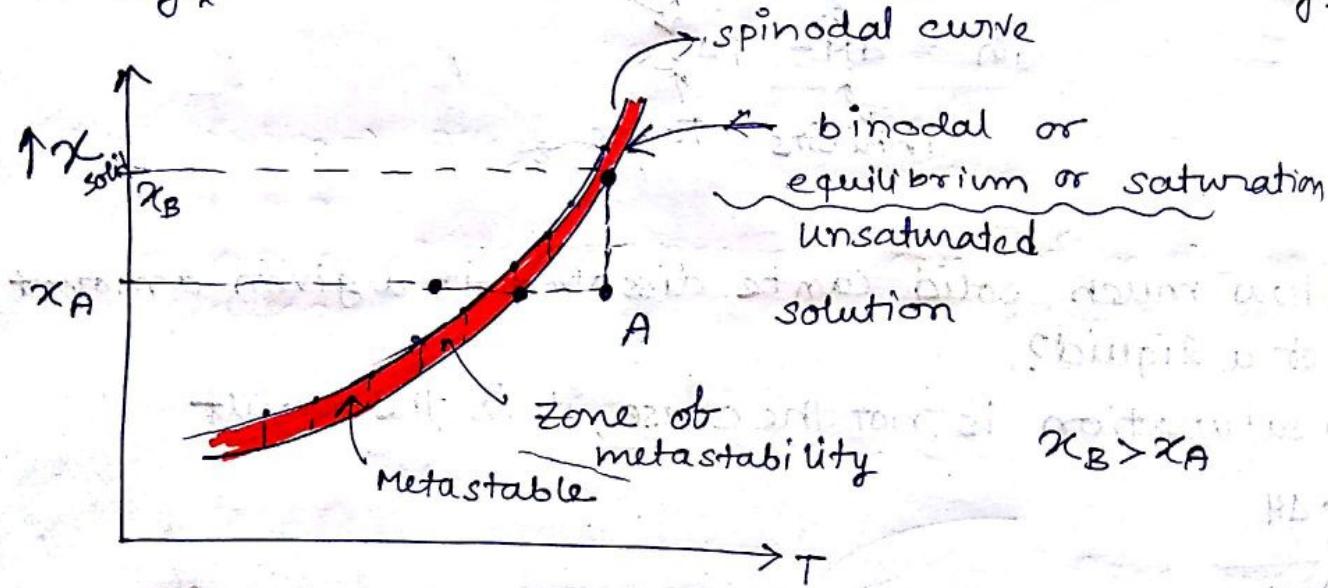
$$\mu = G_1/n$$

Molar quantity

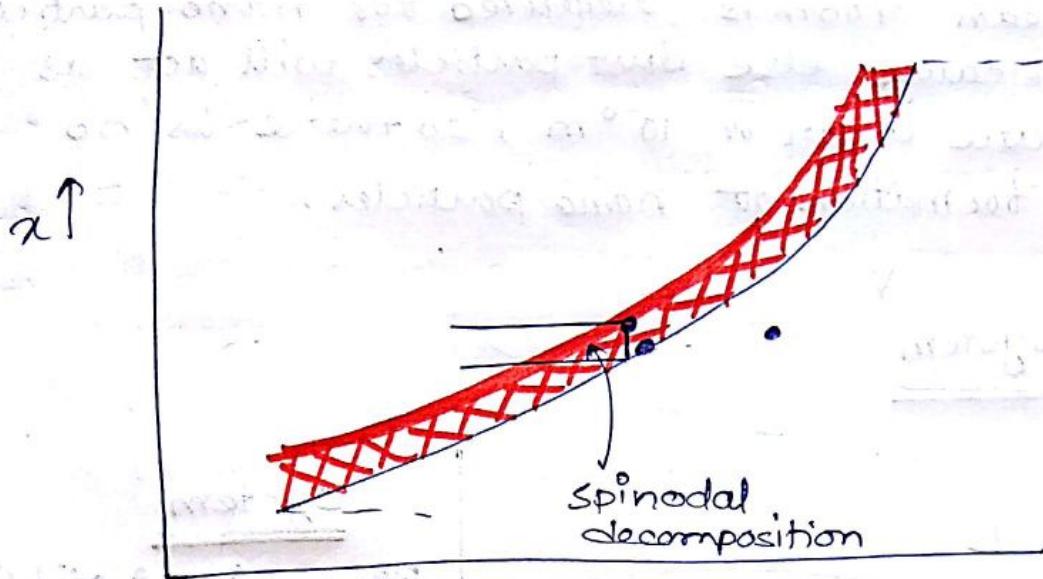


→ The amount of solid in solution which gives same molar gibbs energy of solute can be dissolve in soln at max.

* Why in different solvents, solute has different solubility?



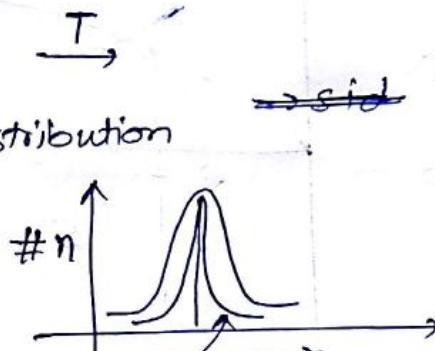
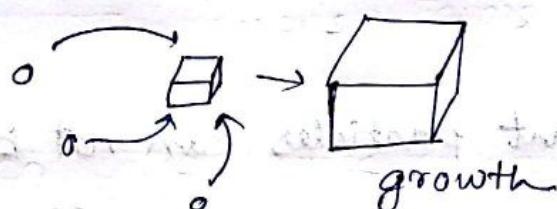
→ Thickness of zone of metastability gives the amount of extra solid dissolved beyond saturation. Thus, more the amount of dissolved beyond saturation more the amount of crystallization



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.

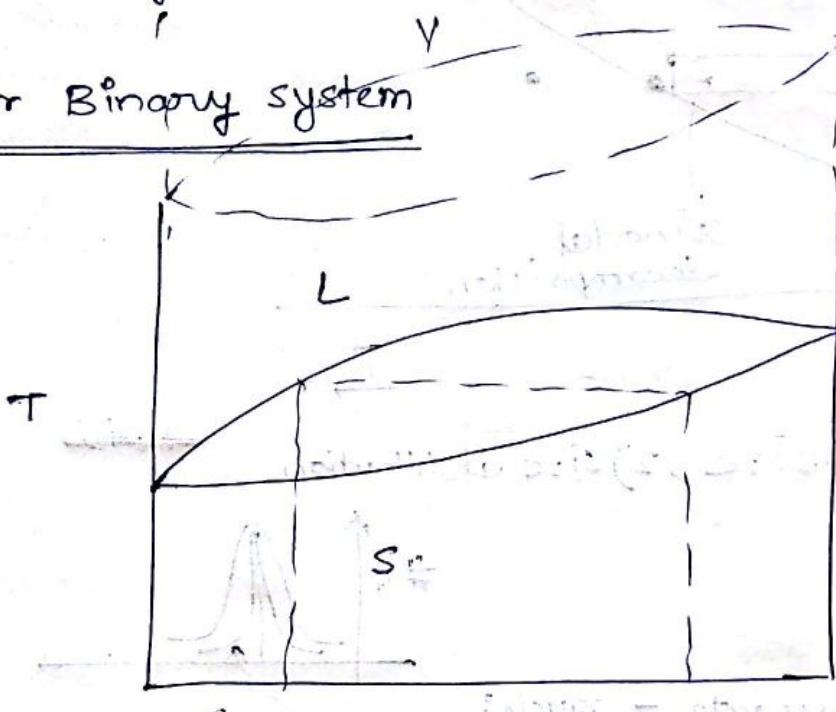
$$\sum (m_i \times n_i) = m_T = \text{const} \quad \leftarrow \text{total mass of mother liquor}$$

$$\sum m_i = m_T \quad \leftarrow \text{No. of particles}$$

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

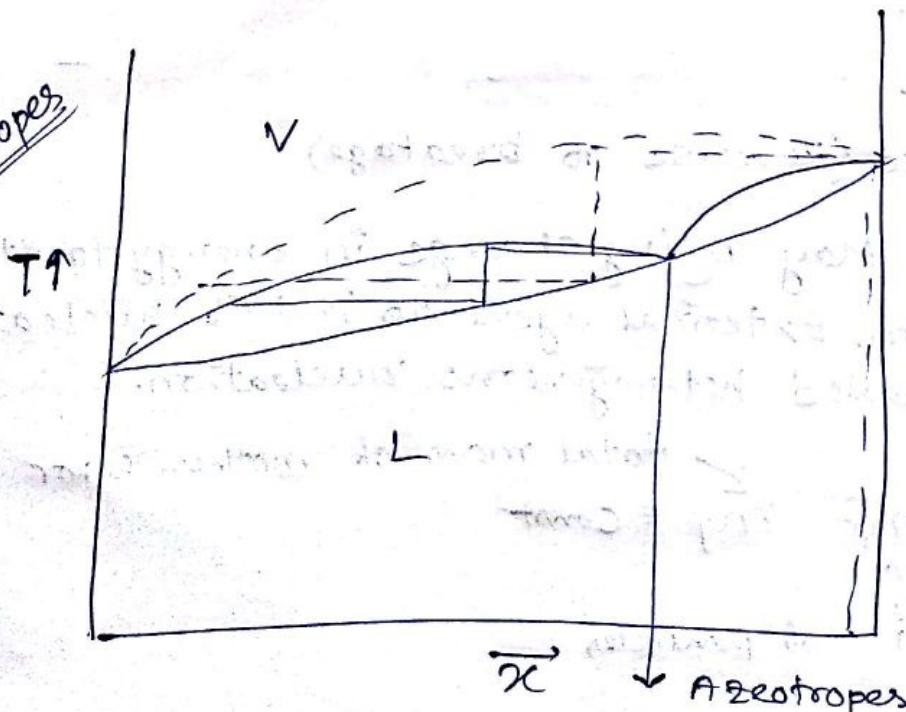
Binary (A+B) solidly soluble in "all" proportions in liquid phase

Solid solution \rightarrow Alloys

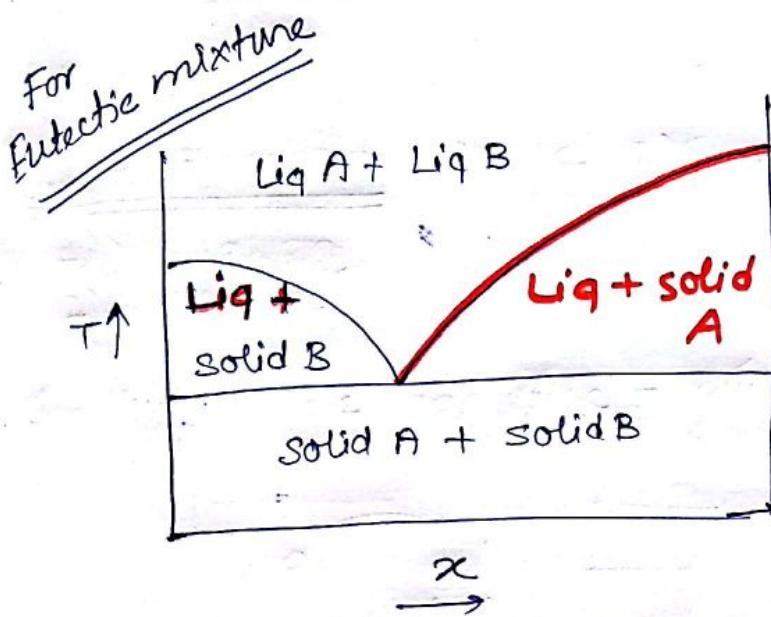
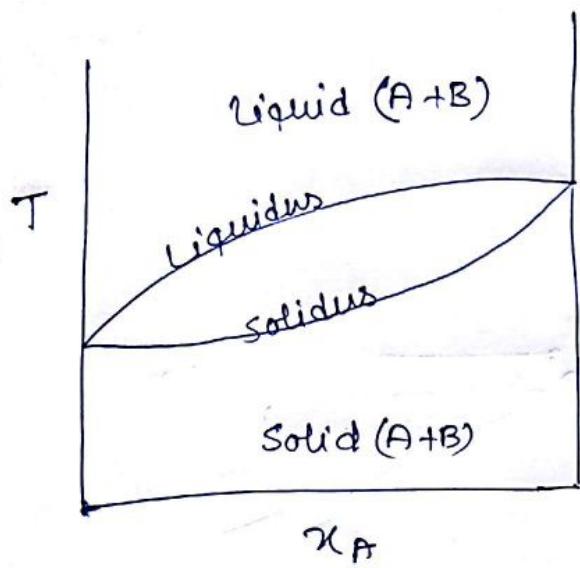
$\begin{matrix} \textcircled{o} & \textcircled{o} & \textcircled{o} \\ \textcircled{o} & \times & \textcircled{o} \\ \textcircled{o} & \textcircled{o} & \textcircled{x} \end{matrix}$

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



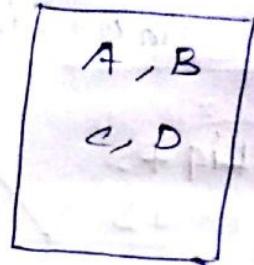
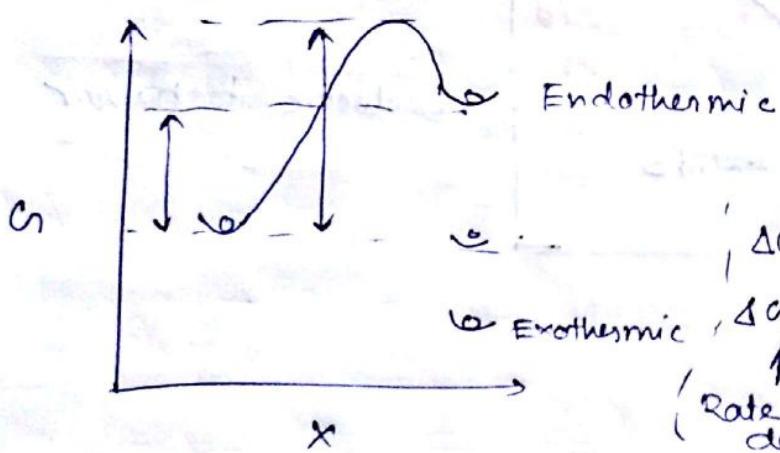
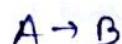
governs

time

size of
the vessel

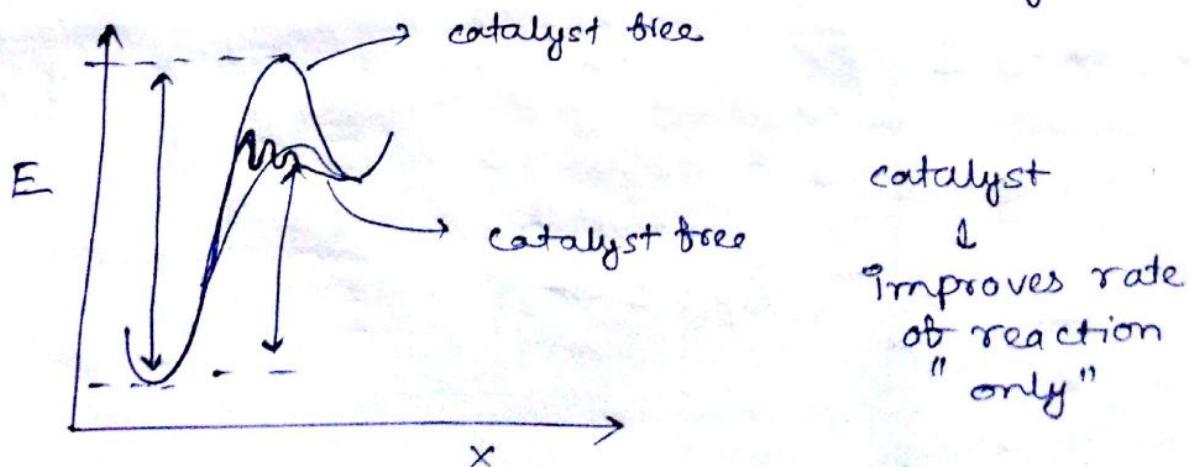
→ Chemical Reaction Engineering

→ Eqbm. conversion can be attained at max.



ΔG^R
 ΔG^{act}
 Rate of reaction
 depends

catalyst \rightarrow rate of reaction improves due to decrease in activation energy



$$\sum \gamma_i u_i = 0$$

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 ΔG°

$$\boxed{-RT \ln K_p = \Delta G^\circ} \quad \rightarrow \text{For ideal } \underline{\text{gas}}$$

$$K_p = \frac{p_c^c \cdot p_d^d \cdots}{p_A^a \cdot p_B^b \cdots}$$

$$\Delta G^\circ = \sum \gamma_i u_i^\circ \leftarrow f(T)$$

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

$$k = A_0 e^{-E_a/RT}$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

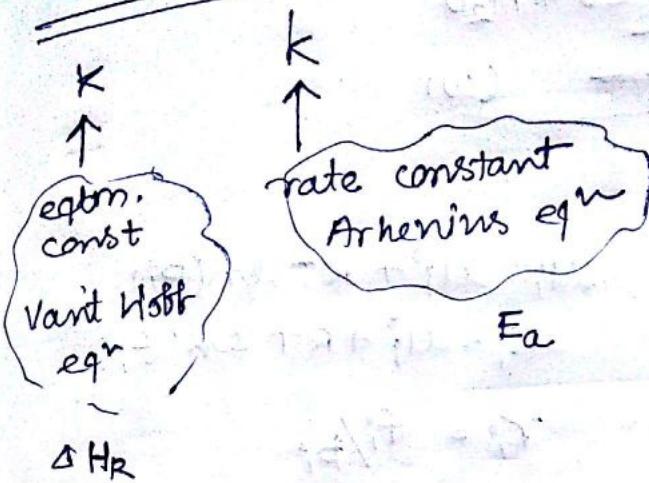
Rate const.

Van't Hoff eqn \rightarrow used to know the eqbm conversion

Arrhenius eqn \rightarrow in $\ln v \propto \ln k$ rate const.

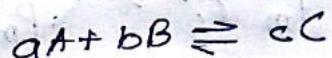
Calculation of Eqbm. Composition

13/04/17



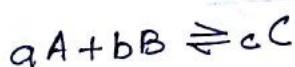
$k \rightarrow$ no fixed units (hence unit)

$$r = -k_1 C_A^\alpha C_B^\beta + k_2 C_C^\gamma$$

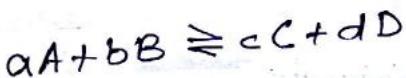


$$\frac{dc}{dt} = \text{mol/L.s}$$

$$\alpha = \beta = \gamma = 1 \Rightarrow r = -k_1 C_A C_B + k_2 C_C$$



$$k_{P_1} = \frac{P_C^c}{P_A^a P_B^b}$$



$$k_{P_2} = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

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

$$\mu_i^\circ = \mu_i^\circ + RT \ln(P_i^\circ/P) \rightarrow \text{gases}$$

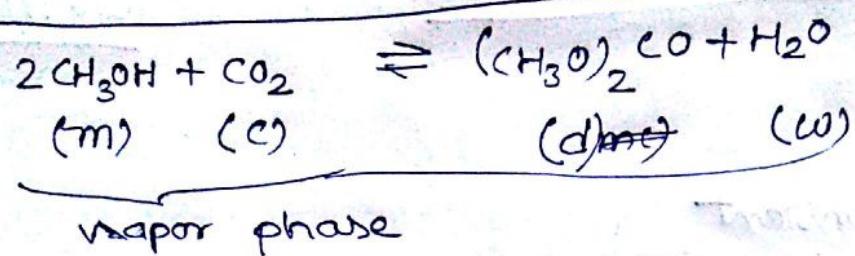
$$\mu_i = \mu_i^\circ + RT \ln x_{ii} \rightarrow \text{liq}$$

* Industrial and Engineering chemistry Research 2015,

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Calculation of eqbm. composition



$$K_f = \frac{f_d f_w}{f_m^2 f_c}$$

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

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

$$\gamma_i^\circ = f_i^\circ / p_i^\circ$$

$$K_f = \left(\frac{\gamma_d \gamma_w}{\gamma_m^2 \gamma_c^\circ} \right) \left(\frac{p_d p_w}{p_m^2 p_c} \right)$$

$$K_f = [\quad] \cdot \left(\frac{p_d \cdot p_w}{p_m^2 \cdot p_c} \right)$$

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 —