

Molar Gibbs Energy $G_m = G/n$
[Intensive Property] \Rightarrow depends on phase.

$$\Delta G = nG_m(2) - nG_m(1) = n \{ G_m(2) - G_m(1) \}$$

$G_m(1)$ - G_m of Phase 1 $G_m(2)$ - G_m of Phase 2

When ΔG is -ve \Rightarrow Spontaneous change

\rightarrow A substance has a spontaneous tendency to change into the Phase with lower G_m .

$$G = H - TS$$

$$\begin{aligned} G + dG &= H + dH - (T + dT)(S + dS) \\ &= \underline{H} + dH - \underline{TS} - Tds - SdT - dTds \end{aligned}$$

$$dG = dH - Tds - SdT$$

$$\boxed{H = U + PV}$$

$$dH = du + PdV + vdp$$

$$\boxed{U = q + W}$$

$$du = dq + dw$$

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

$$dw = -P_{ex} dv = PdV \text{ [reversible]}$$

$$Tds = dq_{rev}$$

$$du = Tds - PdV$$

$$dH = Tds - PdV + PdV + vdp \quad \boxed{\cancel{Tds} \quad \cancel{SdT}}$$
$$= Tds + vdp$$

$$dG = Tds + vdp - Tds - SdT = \underline{vdp - SdT}$$

$$dG_m = v_m dp \text{ [at constant temp]}$$

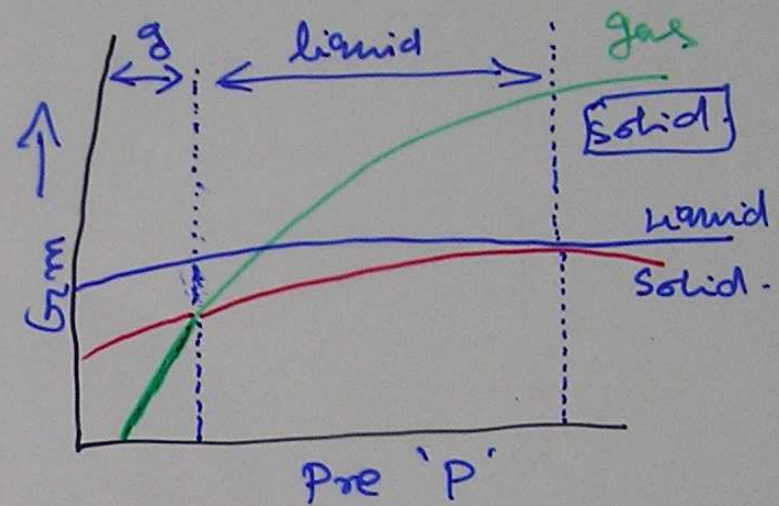
$$\Delta G_m = \underline{\underline{V_m \Delta P}}$$

∴ V_m is +ve $\Delta G > 0$ when $\Delta P > 0$

For liquid and solid effect of "Pre" is less pronounced.

$$V_m(\text{solid}) < V_m(\text{liquid}) < V_m(\text{gas})$$

Low Pressure \Rightarrow gas
medium Pre \Rightarrow liquid
high Pre \Rightarrow solid



for solid and liquid V_m is independent of "Pre"

$$\therefore \Delta G_m = G_m(P_f) - G_m(P_i) ; \underline{\underline{\Delta P = P_f - P_i}}$$

$$G_m(P_f) = \Delta G_m + G_m(P_i)$$

$$= \underline{\underline{V_m(P_f - P_i)}} + G_m(P_i)$$

For solid and liquid G_m is proportional to "Pre"

V_m is small for solid @ liquid at normal "Pre". But for gas it is not

$$G_m(P_f) = G_m(P_i) + RT \ln \frac{P_f}{P_i}$$

$$dG_m = V_m dp$$

$$\Delta G_m = \int_{P_i}^{P_f} V_m dp$$

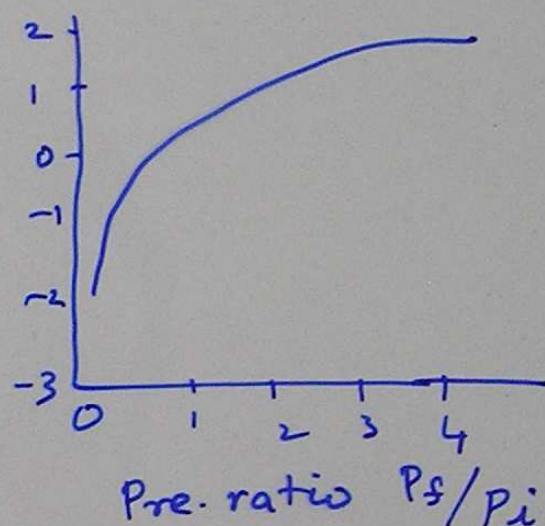
for perfect gas $V_m = RT/P$

$$= \int_{P_i}^{P_f} RT/P dp = RT \int_{P_i}^{P_f} \frac{dp}{P}$$

$$= RT \ln \frac{P_f}{P_i}$$

G_m increases with $\ln P$. At higher P V_m gets small so G_m does not change much.

$$\frac{G_m(P_f) - G_m(P_i)}{RT}$$



Relationship of "G" and "T"

$$\Delta G_m = -S_m \Delta T$$

$$\Delta G_m = G_m(T_f) - G_m(T_i)$$

$$\Delta T = T_f - T_i$$

when $S = +ve$

ΔG_m decrease with increase in temp.

$$S(\text{gas}) > S(\text{liquid}) > S(\text{solid})$$

$$\Delta G_m = V_m \Delta P - S_m \Delta T$$

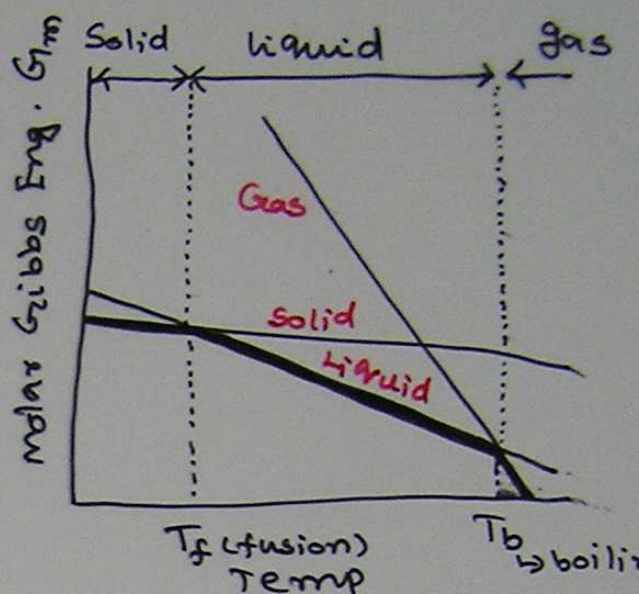
at constant P

$$\Delta G_m = -S_m \Delta T$$

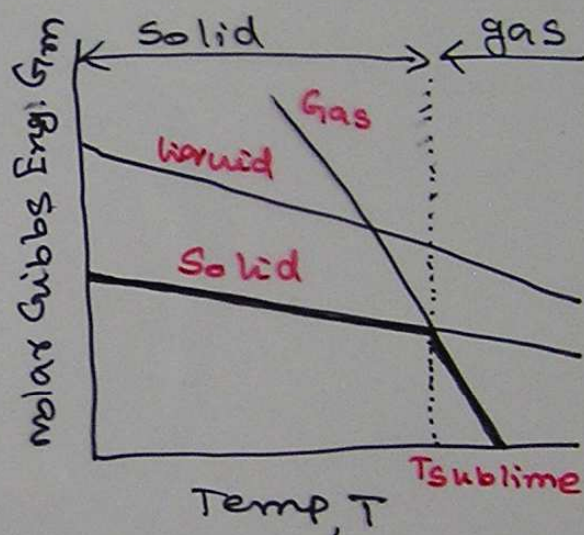
Low temp \Rightarrow low " G " so
Solid phase is stable.

Increase temp \Rightarrow " G " ~~de~~crease
[the substance melts].

Increase temp further \Rightarrow
" G " drops even lower. i.e.
gas phase is stable



For CO_2 . liquid line
does not meet solid.
So CO_2 does not
become liquid from
solid. It does meet
the gas line. In other
words solid \rightarrow gas
transition [sublimation] occurs.



For CO_2 $G_m(\text{liquid}) > G_m(\text{solid})$ [Always]

When G_m of two phases are equal at a
Particular temp. that is called ~~critical~~ transition
Either of the phase can exist.

They may (or) even may not switch
Phases at measurable time (or) speed. In
other words they are not ^{changing} spontaneously.

Exception to " G_m ".

Not always the Phase with lower " G_m " will be most stable. Between Graphite and diamond, Graphite is more stable because its G_m is $(+)$ 3 kJ mol^{-1} lower than diamond.

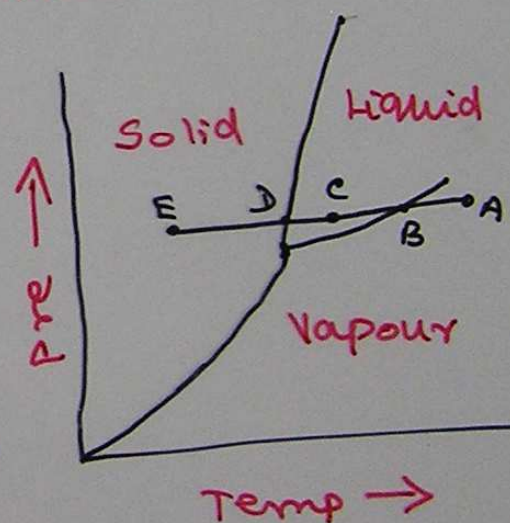
For the "diamond" phase to change to "graphite" phase lot of change needs to occur. For ex. location of atoms, bonds between the atoms needs to change.

\Rightarrow for solids there is exception.



FACE? "PHASE DIAGRAM"
diagram

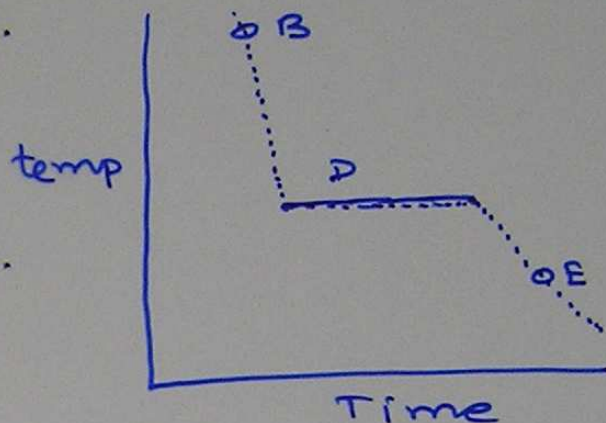
A map showing the conditions of P_{re} and $temp$ at which its various Phases are thermodynamically Stable.



Phase boundary: The values of " P_{re} " and " $temp$ " at which two neighbouring Phases are in equilibrium.

sample of interest is cooled.
 Monitor the temp. During
 transition energy is
 released in the form of heat.

Because of the heat released
 cooling stops. Vary the
 pressure and find out transition temp.



Dynamic equilibrium: Forward and reverse
 process occur at the same rate between two
 adjacent phases.

Location of Phase boundaries.

when two phases are in equilibrium, a
 change in either temp. or pressure shifts the
 boundaries.

Clapeyron eqn: [relationship between pressure
 and temp. of equilibrium].

$$\Delta \beta = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V} \times \Delta T$$

For solid-liquid equilibrium $\Delta_{\text{trs}} H = \Delta_{\text{fus}} H$.

Since fusion is endothermic $\Delta_{\text{fus}} H = +ve$.

Similarly $\Delta_{\text{trs}} V$ is also +ve but small.

Increase in pressure \Rightarrow small increase in melting
 temp.

For H_2 increase in pressure \Rightarrow small decrease in
 melting temp [reason $\Delta_{\text{trs}} V = -ve$, ice lighter than
 liquid]

Vapour Pressure: The "Pre" of the Vapour in equilibrium with its condensed phase.

Vapour Pre. \propto Temp.

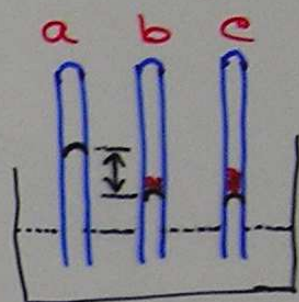
Vapour Pre. is independent of "vol./mass"

Phase boundary in a phase-diagram is the plot of equilibrium points between the phases with respect to temp and Pre.

a - Hg only

b & c - H₂O vapour + Hg

we need to allow liquid-gas equilibrium for measurement.



In a two phase system [vapour, liquid] if one phase is either removed [vapour by applying Pre] (or) converted [removal of Pre] only one phase will exist.

Sublimation Vapour Pressure: The pressure of the vapour in equilibrium with a solid at a particular temp. [lower than vap. Pre.]

For finding solid-solid phase boundaries "thermal analysis" is used. This is based on "heat released during transition."

Clausius-Clapeyron equation:

$$\Delta(\ln P) = \frac{\Delta_{\text{vap}} H}{RT^2} \times \Delta T$$

For liquid-vapour equilibrium, P_{re} has marked effect on " $\Delta_{\text{trs}} V$ ". But if we assume perfect gas behaviour for the vapour " v " can be replaced by " RT ".

$$\ln P' = \ln P + \frac{\Delta_{\text{vap}} H}{R} \left[\frac{1}{T} - \frac{1}{T'} \right]$$

① For liquid-vapour boundary "vapourisation" is the transition. [$\Delta_{\text{trs}} H = \Delta_{\text{vap}} H$]

Clausius-Clapeyron equation is

$$\frac{\Delta \beta}{\Delta T} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V}$$

② For gas $V_{m(g)} \gg V_{m(l)}$
 \therefore $\Delta_{\text{trs}} V = \Delta_{\text{vap}} V = V_{m(g)}$

$$\frac{d\beta}{dT} = \frac{\Delta_{\text{vap}} H}{T V_{m(g)}}$$

③ For perfect gas

$$\underline{V_{m(g)} = \underline{RT/P}}$$

$$\therefore \frac{dp}{dT} = \frac{\Delta_{\text{vap}} H}{T \times RT/P} = \frac{P \Delta_{\text{vap}} H}{RT^2}$$

(4) divide both side by 'p'.

$$\text{use } dp/p = d \ln P$$

$$\Rightarrow \frac{d \ln P}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

$$d \ln P = \frac{\Delta_{\text{vap}} H}{RT^2} dT. \text{ --- c-c-eam.}$$

\Rightarrow Integrate c c eam.

$$\int_P^{P'} d \ln P = \int_T^{T'} \frac{\Delta_{\text{vap}} H}{RT^2} dT$$

$$\ln \left[\frac{P'}{P} \right] = \frac{\Delta_{\text{vap}} H}{R} \int_T^{T'} \frac{1}{T^2} dT = \frac{\Delta_{\text{vap}} H}{R} \left[\frac{1}{T} - \frac{1}{T'} \right]$$

$$\left[\int \frac{1}{T^2} dT = -\frac{1}{T} + \text{constant} \right]$$

$$\Rightarrow \ln P' - \ln P = \frac{\Delta_{\text{vap}} H}{R} \left[\frac{1}{T} - \frac{1}{T'} \right]$$

$$\ln P' = \ln P + \frac{\Delta_{\text{vap}} H}{R} \left[\frac{1}{T} - \frac{1}{T'} \right]$$

when ΔT increases, vapour pre. also inc
ase

$$\Rightarrow \log p = A - B/T$$

Characteristic Points

Boiling Point: The temp at which vapour Pre. of a liquid is equal to external pressure.

Normal B.P \Rightarrow external Pre = 1 atm.

when Heat is supplied
Liquid \Rightarrow Vapour.

In a closed
vessel when

the vapour cannot

escape, the density increases. The
density increases so high that the

vapour Pre. is same as that of

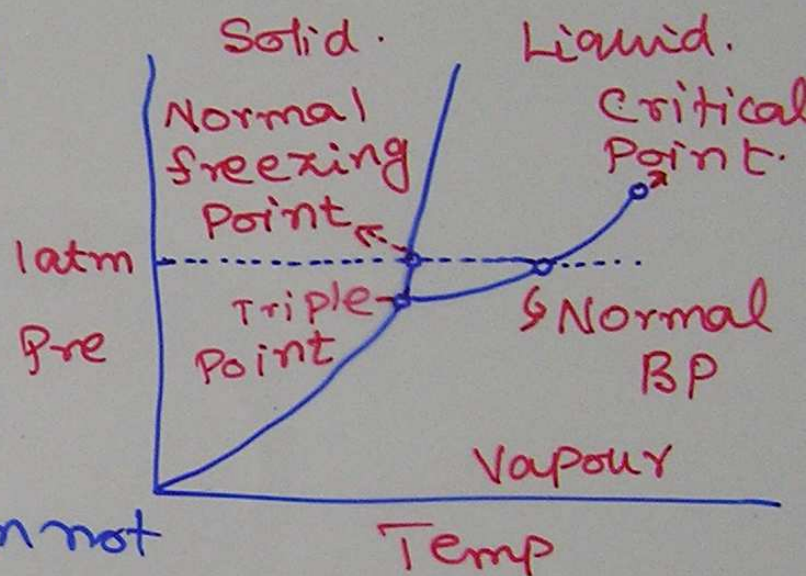
liquid. Phase difference

disappears. This temp is T_c (or)

critical temp. The Pre is called

critical Pre. The temp & Pre is

called critical point.



melting (or) freezing temp: The temp at which solid and liquid phase co-exist in equilibrium at a specific

Pre.

Normal m.p / F.p \Rightarrow $P_{re} = 1 \text{ atm}$.

Triple point: Three phase boundaries meet.

For $H_2O \Rightarrow 273.16 \text{ K}$, 611 Pa .

Triple point \Rightarrow the lowest temp. liquid exists.

Critical point \Rightarrow the highest temp liquid exists.

A substance remains liquid between triple point and critical point.

when P_{re} drops below triple point, a substance becomes solid. [ie. no liquid].

Phase Rule:

$$F = C - P + 2$$

F - degrees of freedom

C - number of components.

P - number of phases.

Four Phase cannot co-exist for any substance according to Phase rule.

Degrees of freedom: Number of intensive variable that can be changed without affecting Phase equilibrium.

Ex.

For water (pure) $c = 1$.

$$\therefore F = 1 - P + 2 = 3 - P.$$

if $P = 1$ [only one phase either solid/liquid/gas]

$$\therefore F = 3 - 1 = 2.$$

Single phase has two degrees of freedom.

(or) else we have two independent intensive properties. i.e. Pressure & temp.

if $P = 2$ [two phase in equilibrium]

$$F = 1 - 2 + 2 = 1.$$

\therefore only one degree of freedom exist.

In other words, when temp. (or) Pressure change

the other intensive property gets fixed

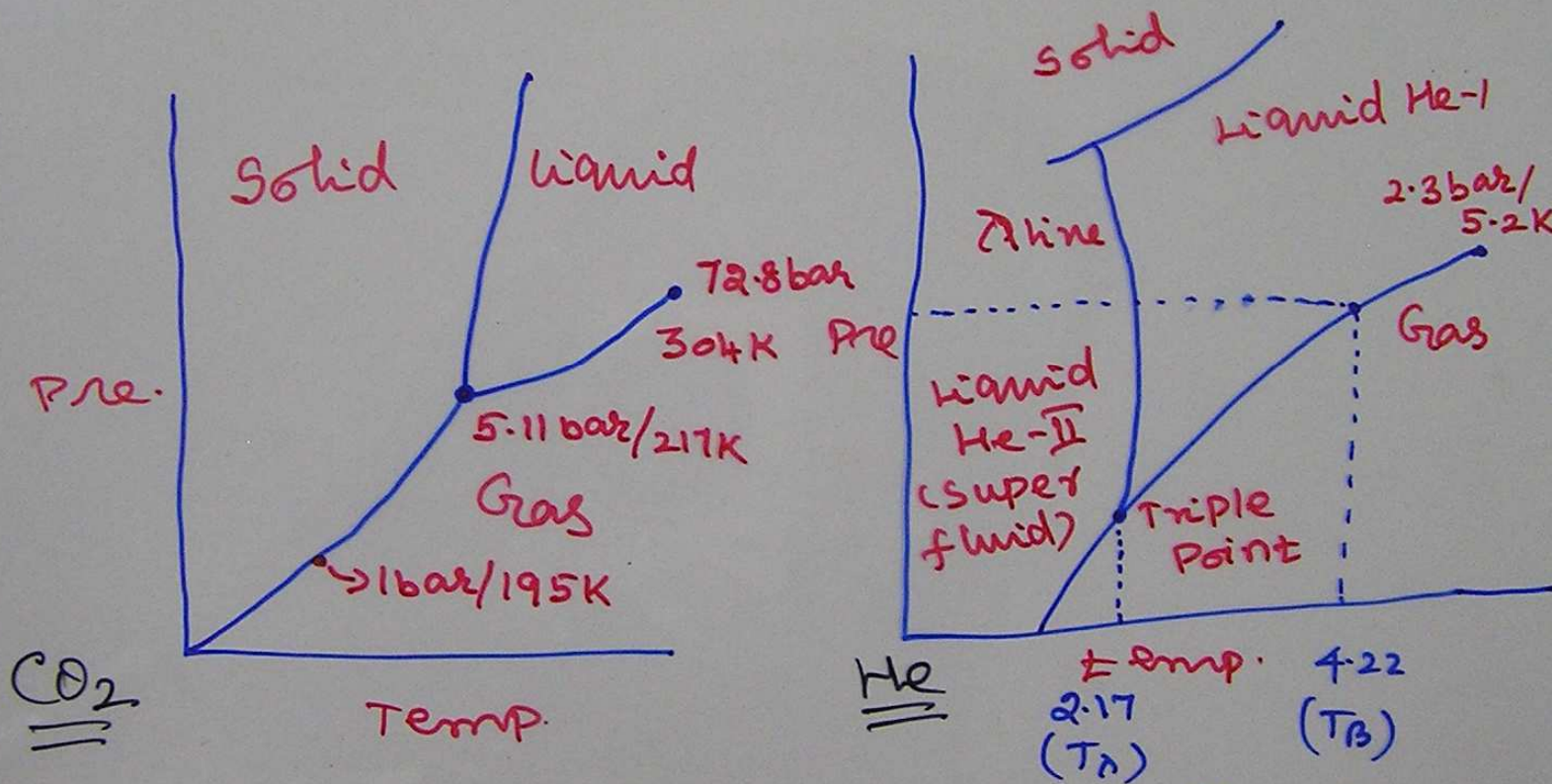
automatically. It is no longer independent

if $P = 3$ [triple point]

$$F = 1 - 3 + 2 = 0.$$

It has no degrees of freedom. That means neither P or $temp.$ is variable.

Polymorphism: Ability of a solid material to exist in more than one form. Each form is called a polymorph.



Superfluid: A substance that flows without viscosity. [viscosity - measure of resistance (or internal friction) to flow].

PHASE - uniform part of a system in equilibrium.

- Ex.
- 1 - a - pure substance [solid, liquid (or) gas]
 - 1 - b - mixture of gases
 - 1 - c - miscible liquids
 - 2 - d - non-miscible liquid
 - n - e - mixture of solids
 - 1 - f - Aqueous solution
 - 2 - g - saturated solution
 - n - h - mixture of substances

COMPONENT: The least number of independent chemical substances required to define a phase completely.

one component \Rightarrow ice, water, water vapour (3 phase)

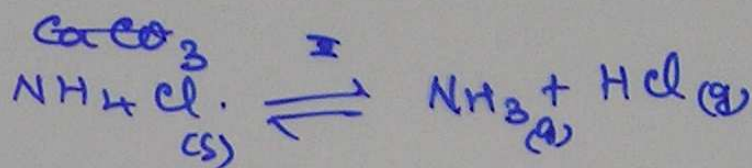
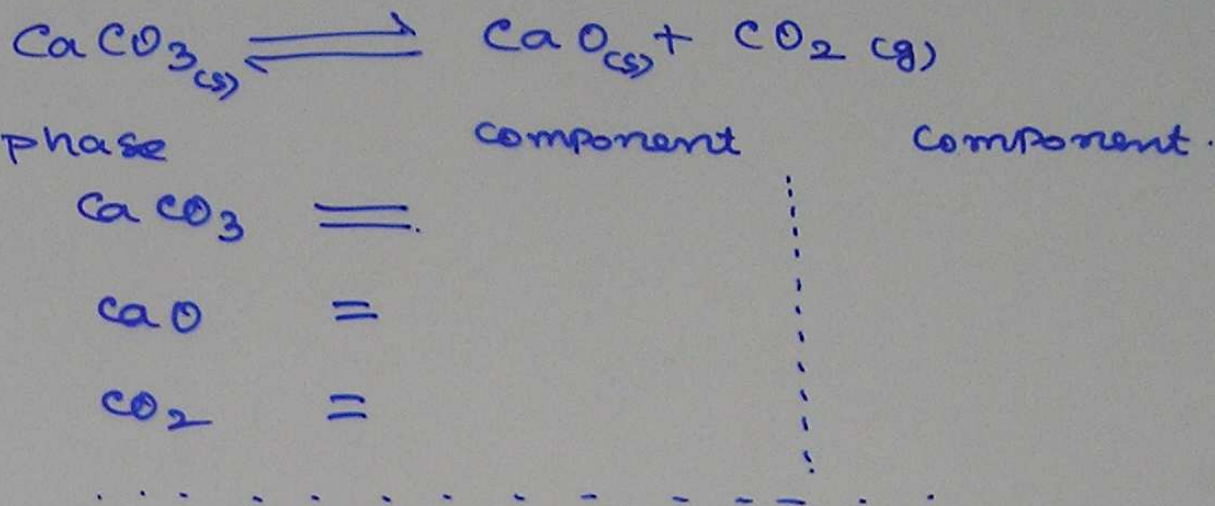
one component \Rightarrow rhombic, monoclinic }
liquid & vapour - S }

(4 phase)

multi component \Rightarrow mixture of gases

two component \Rightarrow aqueous solution

two component \Rightarrow saturated solution



DEGREES OF FREEDOM: The least number of variable factors [concentration, Pressure, Temp] needed to be specified so that remaining variables are fixed automatically and the system is completely defined.

Pure gas $F = 2$ [$PV = RT$]

mixture of gas $F = 3$ [composition, Pressure, Temp]

water \rightleftharpoons water vapour $F = 1$ [Pressure, Temp]

Saturated NaCl solution $F = 1$.

$\text{NaCl}(s) \rightleftharpoons \text{NaCl-solution} \rightleftharpoons \text{water vapour}$.

$\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{water vapour}$. $F = 0$.

$$\Delta H = \Delta E + \Delta n RT$$

$$\Delta C_p = C_p \text{ of product} - C_p \text{ of reactant}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\Delta H_{\text{reaction}} = \Delta H_p - \Delta H_{\text{reactant}}$$

$$\Delta H = \Delta E + P\Delta V$$

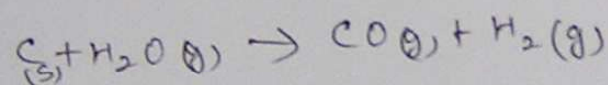
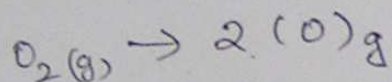
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 0 \text{ for reversible process}$$

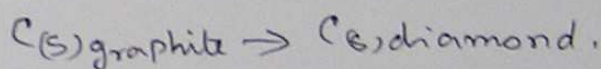
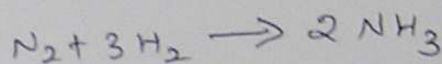
Ex. melting of ice at 0°C

vapourisation of water at 100°C

$$\Delta S \quad +ve$$



-ve



$$\Delta G^\circ = \Delta E^\circ + (\Delta n)RT - T\Delta S^\circ$$

$$\Delta S^\circ_f = \frac{\Delta H^\circ_f - \Delta G^\circ_f}{T}$$