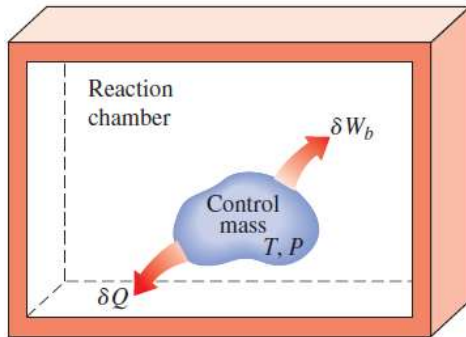# *Phase Rule*

Raj Pala,
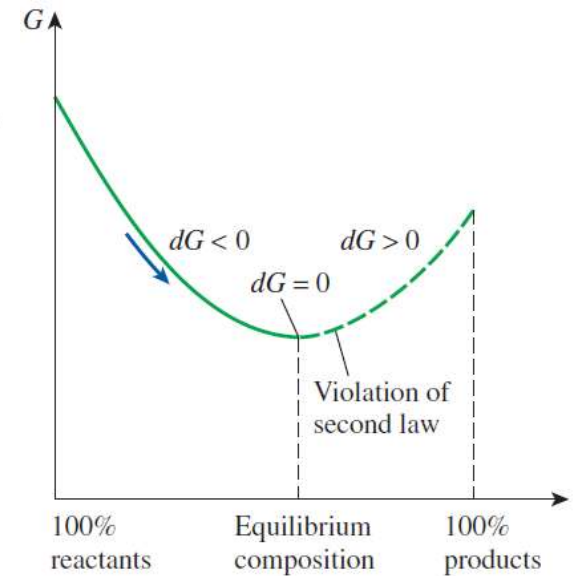rpala@iitk.ac.in
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Previously: Phase Equilibria & Kirchhoff Equation

$$(dG)_{T,P} = dH - T\,dS - S\,dT$$

$$= (dU + P\,dV + V\,dP)^{\nearrow 0} - T\,dS - S\,dT^{\nearrow 0}$$

$$= dU + P\,dV - T\,dS$$

$$(dG)_{T,P} \leq 0$$

$$\nu_C \bar{g}_C + \nu_D \bar{g}_D - \nu_A \bar{g}_A - \nu_B \bar{g}_B = 0$$

Criterion for chemical equilibrium

$$\bar{g}_i(T, P_i) = \bar{g}_i^*(T) + R_u T \ln P_i$$

$$K_P = e^{-\Delta G^*(T)/R_u T}$$

$$\ln \frac{K_{P_2}}{K_{P_1}} \cong \frac{\bar{h}_R}{R_u}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\frac{d\Delta H}{dT} \equiv \frac{d}{dT}(\Sigma \nu_i h_i)$$

$$= \Sigma \nu_i c_{p_i}$$

Figs: TD-Cengel & Boles

Previously: Fundamental equations of TD (Table TD)

Function	Extremum at Equilibrium	Fundamental Equation	Definition
$U(S,V,\mathbf{N})$	Minimum	$dU = T\,dS - p\,dV + \sum_j \mu_j\,dN_j$	
$S(U,V,\mathbf{N})$	Maximum	$dS = \left(\dfrac{1}{T}\right)dU + \left(\dfrac{p}{T}\right)dV - \sum_j \left(\dfrac{\mu_j}{T}\right)dN_j$	
$H(S,p,\mathbf{N})$	Minimum	$dH = T\,dS + V\,dp + \sum_j \mu_j\,dN_j$	$H = U + pV$
$F(T,V,\mathbf{N})$	Minimum	$dF = -S\,dT - p\,dV + \sum_j \mu_j\,dN_j$	$F = U - TS$
$G(T,p,\mathbf{N})$	Minimum	$dG = -S\,dT + V\,dp + \sum_j \mu_j\,dN_j$	$G = H - TS = F + pV$

Molecular Driving Forces by K. Dill & S. Bromberg

The Limits on Constructing Thermodynamic Functions

What are the limits on constructing functions of T, S, p, V, N, U, F, H, and G? You can divide thermodynamic functions into four categories:

FUNDAMENTAL AND USEFUL. Table TD lists the main fundamental thermodynamic functions and their natural variables. The states of equilibrium are identified by extrema in these functions.

USEFUL BUT NOT FUNDAMENTAL. $U(T, V, N)$, $S(T, V, N)$, $H(T, p, N)$, and $S(T, p, N)$ are not functions of natural variables. These functions do not have corresponding extremum principles, but they are useful because they are components of $F(T, V, N)$ and $G(T, p, N)$.

COMPLETE BUT NOT USEFUL. Rearrangements of the dependent and independent variables from a fundamental thermodynamic function are possible, but not often useful. For example, $T(F, V, N)$ is a rearrangement of the fundamental Helmholtz free energy function, $F(T, V, N)$. This function is not very useful because you usually cannot constrain F at the system boundary.

INCOMPLETE. Additional functions could be constructed, such as $U(p, V, N)$ or $S(U, \mu, N)$ but because these involve conjugate pairs p and V, or μ and N, and are missing other variables, they do not uniquely specify the state of a system. Such functions cannot be obtained by Legendre transforms of the fundamental equations.

Molecular Driving Forces by K. Dill & S. Bromberg

The GIBBS PHASE RULE-What is it for?

❑ The phase rule connects the Degrees of Freedom, the number of Components in a system and the number of Phases present in a system
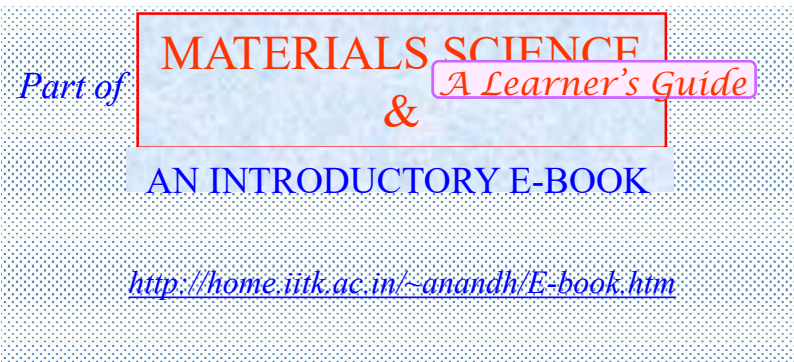
For a system in equilibrium

The phase rule ⟹

$$F = C - P + 2$$

or

$$F - C + P = 2$$

- F – Degrees of Freedom
- C – Number of Components
- P – Number of Phases
- The '2' comes from– Pressure & T

Part of

MATERIALS SCIENCE
A Learner's Guide
&
AN INTRODUCTORY E-BOOK

http://home.iitk.ac.in/~anandh/E-book.htm

- F – Degrees of Freedom
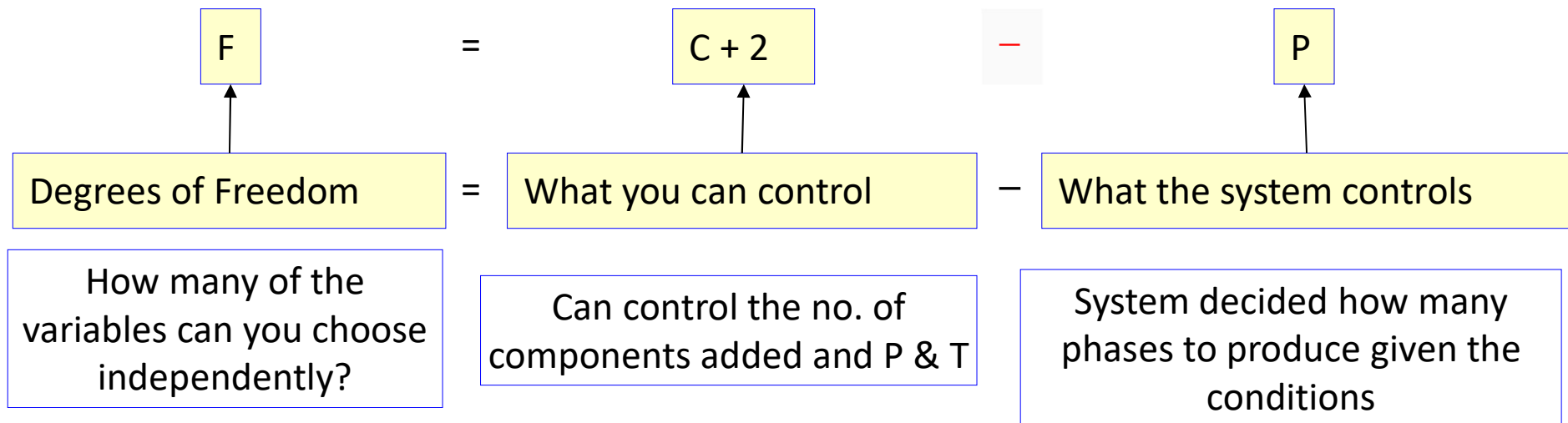- C – Number of Components
- P – Number of Phases

- Variables in the system =

  Composition variables + Thermodynamic variables

- Composition of a phase specified by (C – 1) variables

  No. of variables required to specify the composition of all Phases: P(C – 1)

  Thermodynamic variables = P + T *(usually considered) = 2*

  Total no. of variables in the system = P(C – 1) + 2.

- The degrees of freedom (F) has be less than (or equal to) the number of variables in the system.

  I.e.: F $\leq$ no. of variables $\Rightarrow$ F $\leq$ P(C – 1) + 2.

- For a system in equilibrium the chemical potential of each species is same in all the phases.

  ➢ If α, β, γ,... are phases, then: $\mu_A(\alpha) = \mu_A(\beta) = \mu_A(\gamma)$....

- F = (Total number of variables) − (number of relations between variables)

  $= [P(C - 1) + 2] - [C(P - 1)] = C - P + 2$

$$F = C - P + 2$$

F	=	C + 2	−	P

Degrees of Freedom	=	What you can control	−	What the system controls

How many of the variables can you choose independently?	Can control the no. of components added and P & T	System decided how many phases to produce given the conditions

Phase rule in practice

C = 2

2 components

No. of phases	Total variables $P(C-1)+2$	Degrees of Freedom $C-P+2$	Degrees of Freedom $C-P+1$
1	3	3	2
2	4	2	1
3	5	1	0
4	6	0	*Not possible*

C = 3

3 components

No. of phases	Total variables $P(C-1)+2$	Degrees of Freedom $C-P+2$	Degrees of Freedom $C-P+1$
1	4	4	3
2	6	3	2
3	8	2	1
4	10	1	0

Phase rule in materials science

$$F = C - P + 2$$
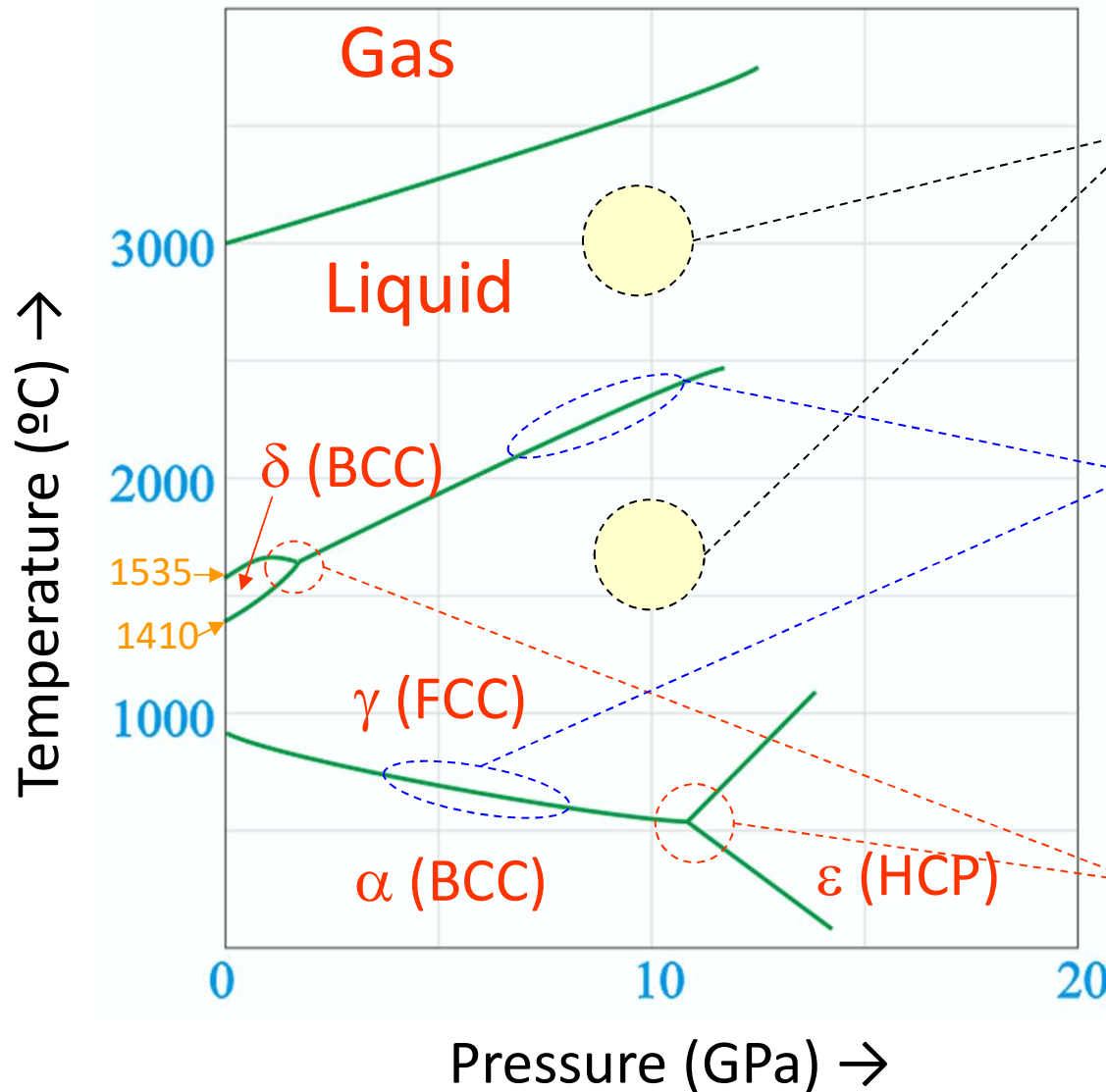
Single phase *regions*
$F = 1 - 1 + 2 = 2$
$\Rightarrow T$ and P can both be varied while still being in the single phase region

Two phase coexistence *lines*
$F = 1 - 2 + 2 = 1$
$\Rightarrow$ we have only one independent variable (we can chose one of the two variables (T or P) and the other is 'automatically' fixed by the phase diagram)

Triple *points*:
3 phase coexistence
$F = 1 - 3 + 2 = 0$
$\Rightarrow$ triple points are fixed points of a phase diagram (we cannot chose T or P)

Gas

Liquid

δ (BCC)

3000

2000

1535

1410

1000

γ (FCC)

α (BCC)

ε (HCP)

Temperature (ºC) $\rightarrow$

0

10

20

Pressure (GPa) $\rightarrow$

"Very High pressures are required for things to happen in the solid state"

The maximum number of phases which can coexist in a unary P-T phase diagram is 3

9

What's next?

- **Gas-Power cycle**