Phase Rule :

It was deduced theoretically by J. W. Gibbs.
It is a general rule involving correlation of various conditions of equilibrium between phases like number of phases, components & degrees of freedom.
It is a qualitative treatment of system in equilibrium
It is useful because it acts as a preliminary treatment to the exact treatment & to experimental investigation. It enables us to predict in general terms, conditions that must be satisfied for a given system to be in equilibrium & relations that may be expected among the variables defining its state.
Phase Rule states that for a system in complete internal equilibrium in which phases can exchange material, heat & work, the following relation holds.

$$F = C - P + 2$$

'2' → Temperature & Pressure as intensive variables, which must be specified to describe the state of equilibrium.

Phase is uniform throughout. We are not bothered about molecular level.
For e.g. NaCl → at molecular level has 2 ions, Na^+ & Cl^-.
but phase = 1.

$$F = C - P + 2.$$

Maximum F for maximum C & minimum P.

F = No. of degree of freedom
C = No. of components
P = No. of phases

Derivation of Phase Rule:

It allows phase diagram to be understood.
It is a general rule applicable to all types of reactive & non-reactive system. It involves distribution of various components in different phases without any chemical reaction between components (non-reactive system).

(A) For a non-reactive system:

Assumptions:

- Heterogeneous system.
- 'P' no. of phases at equilibrium containing 'C' components. ~~in each phase~~.
- All the 'C' components are present in all 'P' phases.

System at equilibrium can be described completely if we know the values of the variables.

Total no. of variables:

Variables	Number	
Temperature of the system	1	(Thermal equilibrium)
Pressure of the system	1	(Mechanical equilibrium)

In one phase, 'C' components & hence 'C' no. of variables are there.
In 'P' phases, 'PC' components & hence 'PC' no. of variables are there.
Total no. of variables that need to be specified $= PC + 2$.

No of variables that can be obtained from a set of equations = No. of equations.

If there are as many equations as there are variables, then temperature, pressure & composition of the whole system in equilibrium can be determined. It becomes non-variant system.

If the no. of variables exceeds the no. of equations by 1, then equilibrium of the system cannot be determined until one of variables is chosen arbitrarily. The system becomes monovariant or univariant.

If no. of variables = no. of equations, all variables can be determined from the equations.

F = Degree of freedom, it actually represents excess of variables over equations.

It is also called variance.

F = (Total no. of variables that need to be specified) − (Total no. of equations that are available)

~~F = C + 2~~

No. of equations:

(1) Sum of amount or mole fractions of components in any phase is equal to 1.

Equations — Number

$x_1(1) + x_2(1) + \ldots\ldots x_c(1) = 1$

(1) → In phase 1, sum of mole fraction of components 1, 2 ... c = 1.

$x_1(2) + x_2(2) + \ldots\ldots x_c(2) = 1$

(2) → For phase 2.

$x_1(P) + x_2(P) + \ldots\ldots x_c(P) = 1$ — P

No. of phases = no. of equations of mole fraction.

(2.) Thermodynamic condition of Phase Equilibria

According to this, the species will be distributed in such a manner that value of molar free energy of the system at equilibrium ~~(chemical potential)~~ is minimum.

Since the species distributes itself between various phases, so once equilibrium is attained, there is no movement of any component between different phases. We can say that escaping tendency or chemical potential of a components in all phases becomes equal as there is no movement at equilibrium.

Equations — Number

For 1 component,

$\mu_i(1) = \mu_i(2) = \ldots\ldots = \mu_i(P)$

Chemical potential of component 'i' is same in all phase 'P' at equilibrium. This is

called chemical equilibrium.

for any two phases, one equation for '1' component i.e. $\mu_1(1) = \mu_1(2)$

So for 'P' phases, (P-1) equations of chemical potential for '1' component

$$\mu_1(1) = \mu_1(2) = \cdots = \mu_1(P).$$

Similarly, for component 2, (P-1) equations

$$\mu_2(1) = \mu_2(2) = \cdots = \mu_2(P)$$

$$\mu_C(1) = \mu_C(2) = \cdots = \mu_C(P)$$

So for 'C' components, no. of equations = $\underline{\underline{C(P-1)}}$

Total number of equations (from points (1) & (2))

$$= C(P-1) + P$$

$$f = CP + 2 - (P + C(P-1))$$

$$= CP + 2 - P - CP + C$$

$$\boxed{f = C - P + 2}$$ (Phase Rule)