ENGINEERING CHEMISTRY

Department of Science and Humanities

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Module 2- Phase equilibria

Class content:

- ***Gibb's Phase rule***
- ***Derivation of Gibb's Phase rule***

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Module 2- Phase equilibria

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Phase rule

- It was given by **Williams Gibbs** in 1874

- **Statement of Gibb's phase rule**

  Provided the equilibrium in a heterogeneous system is not influenced by external forces (gravity, electrical or magnetic forces) , the number of degrees of freedom (F) of the system is related to number of components (C) and number of phases (P) existing at equilibrium to one another by the equation

$$F = C - P + 2$$

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Derivation of the phase rule

- A system at equilibrium satisfies the following conditions:
  - **Thermal equilibrium – Temperature is constant**
  - **Mechanical equilibrium – Pressure is constant**
  - **Chemical or material equilibrium – Chemical potential of a substance is same in all the phases**
- Mathematically, $\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = ...$
- The system considered is: All C components distributed between P phases

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- **Total number of intensive variables that need to be ascertained to describe the system:**

Temperature 1

Pressure 1

Composition mole fraction of each component in every phase

- For each phase, the sum of mole fractions equals unity

$$\chi_1^{\alpha} + \chi_2^{\alpha} + \chi_3^{\alpha} + \ldots\ldots + \chi_c^{\alpha} = 1 \qquad \text{(C-1)}$$

$$\chi_1^{\beta} + \chi_2^{\beta} + \chi_3^{\beta} + \ldots\ldots + \chi_c^{\beta} = 1 \qquad \text{(C-1)}$$

$$\chi_1^{\gamma} + \chi_2^{\gamma} + \chi_3^{\gamma} + \ldots\ldots + \chi_c^{\gamma} = 1 \qquad \text{(C-1)}$$

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$$\chi_1^{P} + \chi_2^{P} + \chi_3^{P} + \ldots\ldots + \chi_c^{P} = 1 \qquad \text{(C-1)}$$

- In each phase (C-1) mole fraction terms need to be defined
- Number of phases : P
- Number of composition variables = P(C-1)
- **Total number of intensive variables = P(C-1) + 2**

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Total number of equations(constraints) :

- At equilibrium the chemical potential of particular component is same in every phase in a system

$$\mu_1^{\alpha} = \mu_1^{\beta} = \mu_1^{\gamma} = \ldots. \quad \text{(P-1)}$$
$$\mu_2^{\alpha} = \mu_2^{\beta} = \mu_2^{\gamma} = \ldots. \quad \text{(P-1)}$$
$$\mu_3^{\alpha} = \mu_3^{\beta} = \mu_3^{\gamma} = \ldots. \quad \text{(P-1)}$$

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$$\mu_c^{\alpha} = \mu_c^{\beta} = \mu_c^{\gamma} = \ldots. \quad \text{(P-1)}$$

- For C components C(P-1)
- **Total number of equations or constraints =C(P-1)**

F = Total number of variables – total number of equations

$$F = P(C-1) + 2 - \{C(P-1)\}$$

F=C-P+2

which is the **Gibb's phase rule**

THANK YOU

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