Al-Mustaqbal University / College of Technical Engineering
Department (Fuel and Energy) / Class (Second)
Subject (Thermodynamics-2) / Code (UOMU0206042)
Lecturer (Dr. Hussein K. Halwas)
2nd term – Lecture No. & Lecture Name (#7_Phase Equilibria: Criteria for equilibrium between phases in multi component non-reacting systems in terms of chemical potential and fugacity)

1. Introduction

Phase equilibrium is a fundamental concept in thermodynamics that governs systems where multiple phases (e.g., liquid, vapor, solid) coexist.

In multicomponent non-reacting systems, no chemical reactions occur, but mass transfer between phases is allowed. The condition of equilibrium ensures that there is no net transfer of matter or energy between phases.

2. Conditions for Thermodynamic Equilibrium

For a system to be in complete thermodynamic equilibrium, the following must hold:

1. **Thermal equilibrium:**

$$T^{\propto} = T^{\beta}$$

2. **Mechanical equilibrium:**

$$P^{\propto} = P^{\beta}$$

3. **Chemical equilibrium** (most important for phase equilibrium):

$$\mu_i^{\alpha} = \mu_i^{\beta}$$

Where:

- μ_i = chemical potential of component *i*.
- α, β = different phases.

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3. Chemical Potential and Phase Equilibrium

3.1 Definition

The **chemical potential** is defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

It represents the **partial molar Gibbs free energy** of a component.

3.2 Equilibrium Criterion

For a multicomponent system with *k* components and multiple phases:

$$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \cdots \text{ for all components } i$$

Interpretation:

- If $\mu_i^{\alpha} > \mu_i^{\beta}$, component i will transfer from phase α to β
- At equilibrium → no driving force → chemical potentials equal

4. Fugacity and Its Importance

4.1 Definition of Fugacity

Fugacity is an **effective pressure** that accounts for real gas behavior:

$$\mu_i(T, P) = \mu_i^{o}(T) + RT \ln f_i$$

Where:

- f_i = fugacity of component i.
- R = gas constant.
- T = temperature.

4.2 Physical Meaning

- Fugacity replaces pressure in real systems
- For ideal gases:

$$f_i = y_i P$$

5. Phase Equilibrium in Terms of Fugacity

Starting from the equilibrium condition:

$$\mu_i^\alpha = \mu_i^\beta$$

Substitute the fugacity expression:

$$RT \ln f_i^\alpha = RT \ln f_i^\beta \Rightarrow \ln f_i^\alpha = \ln f_i^\beta \Rightarrow$$

$$\boxed{f_i^\alpha = f_i^\beta}$$

Final Criterion (Fugacity Form):

$$\boxed{f_i^\alpha = f_i^\beta = f_i^\gamma} \quad \text{for all components}$$

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6. Application to Vapour–Liquid Equilibrium (VLE)

For component *i* in vapour (v) and liquid (l):

$$f_i^v = f_i^l$$

6.1 Vapour Phase Fugacity

$$f_i^v = y_i \varphi_i P$$

Where:

- y_i = mole fraction in vapour
- φ_i = fugacity coefficient

6.2 Liquid Phase Fugacity

$$f_i^l = x_i \gamma_i f_i^{sat}$$

Where:

- x_i = mole fraction in liquid
- γ_i = activity coefficient
- f_i^{sat} = fugacity at saturation

6.3 Combined VLE Relation

$$\boxed{y_i \varphi_i P = x_i \gamma_i f_i^{sat}}$$

7. Special Cases

7.1 Ideal Gas + Ideal Solution

- $\varphi_i = 1$
- $\gamma_i = 1$

$$\boxed{y_i P = x_i P_i^{sat}}$$

This is **Raoult's Law**.

7.2 Dilute Solutions (Henry's Law)

$$f_i^l = x_i H_i$$

Where H_i is Henry's constant.

8. Concluding Remarks

Understanding phase equilibrium in terms of **chemical potential and fugacity** is essential for:

- Power plant analysis (Rankine cycle condensers & boilers)
- Chemical separation processes (distillation, absorption)
- Petroleum and gas processing

Examples:

1. A binary mixture at equilibrium has total pressure ($P = 100$ kPa), liquid mole fraction ($x_A = 0.4$) and its saturated pressure ($P_A^{sat} = 80$ kPa). Assuming ideal behavior, find vapour mole fraction (y_A)?

Solution:

Using **Raoult's Law**

$$y_A P = x_A P_A^{sat}$$

$$y_A = \frac{x_A P_A^{sat}}{P}$$

$$y_A = \frac{0.4 * 80}{100} = 0.32$$ **Ans**

2. A binary mixture has the following properties:

- $P = 2$ MPa
- $x_i = 0.3$, $y_i = 0.5$
- Fugacity coefficient: $\varphi_i = 0.9$
- Activity coefficient: $\gamma_i = 1.2$
- $f_i^{sat} = 1.5$ MPa

Check if the system is at equilibrium?

Solution:

Equilibrium condition is:

$$f_i^v = f_i^l$$

Vapour phase:

$$f_i^v = y_i \varphi_i P = 0.5 * 0.9 * 2 = 0.9 \text{ MPa}$$

Liquid phase:

$$f_i^l = x_i \gamma_i f_i^{sat} = 0.3 * 1.2 * 1.5 = 0.54 \text{ MPa}$$

Compare: $f_i^v \neq f_i^l$ "**<u>Not at equilibrium</u>**"

3. A vapour- liquid system at equilibrium (VLE) has the following properties:

- $x_i = 0.6$, $y_i = 0.7$
- Fugacity coefficient: $\varphi_i = 0.95$
- Activity coefficient: $\gamma_i = 1.1$
- $f_i^{sat} = 200$ kPa

Find system pressure P?

<u>Solution:</u>

Equilibrium relation is: $y_i \varphi_i P = x_i \gamma_i f_i^{sat}$

Solve for P:

$$P = \frac{x_i \gamma_i f_i^{sat}}{y_i \varphi_i} = \frac{0.6 * 1.1 * 200}{0.7 * 0.95} = \frac{132}{0.665} = 198.5 \text{ kPa}$$

4. At a following condition determine direction of mass transfer:

- $\mu_i^\alpha = 1200$ J/mol
- $\mu_i^\beta = 1150$ J/mol

<u>Solution:</u>

Rule: Mass transfer from **higher chemical potential → lower chemical potential**

Since: $\mu_i^\alpha > \mu_i^\beta$, then component flows from phase $\alpha \rightarrow \beta$

5. A liquid mixture has the following condition:

- $x_A = 0.5$
- $x_B = 0.5$
- $P_A^{sat} = 120\ \text{kPa}$
- $P_B^{sat} = 80\ \text{kPa}$

Find total pressure at bubble point?

<u>Solution:</u>

$$P = x_A P_A^{sat} + x_B P_B^{sat} = 0.56 * 120 + 0.5 * 80 = 60 + 40 = 100\ \text{kPa}$$

Vapour composition:

$$y_A = \frac{x_A P_A^{sat}}{P} = \frac{60}{100} = 0.6$$

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