1. Introduction

In classical thermodynamics, ideal gases provide a simple and powerful model. However, **real gases deviate from ideal behavior**, especially at:

- High pressures
- Low temperatures
- Near phase boundaries

To properly describe real gases while preserving the mathematical structure used for ideal gases, we introduce the concept of **fugacity**.

2. Why Do We Need Fugacity?

For an ideal gas, the chemical potential depends on pressure as:

$$\mu(T,P) = \mu^o(T) + RT \ln\left(\frac{P}{P^o}\right)$$

Where:

- $\mu^o(T)$ is the chemical potential at a standard state,
- P^o is the pressure at the standard state,
- R is the universal gas constant,
- T is the temperature,
- P is partial pressure,

But for real gases, this equation no longer accurately represents behavior because intermolecular forces and molecular volume effects become significant.

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To maintain the same mathematical form, we define a new "effective pressure" called **fugacity (*f*)**:

$$\mu(T,P) = \mu^o(T) + RT\ln\left(\frac{f}{P^o}\right)$$

Thus:

Fugacity replaces pressure in real-gas thermodynamics.

3. Definition of Fugacity

Fugacity (*f*) is defined as the quantity that replaces pressure in the ideal gas expression for chemical potential such that the equation remains valid for real gases.

Key Properties:

- Units: same as pressure (Pa, bar, atm)
- For ideal gas:

$$f = P$$

- For real gas:

$$f \neq P$$

At low pressure:

$$\lim_{P\to 0} f = P$$

This ensures consistency with ideal-gas behavior.

4. Fugacity Coefficient (φ)

To quantify deviation from ideality, we define the **fugacity coefficient**:

$$\varphi = \frac{f}{P}$$

Interpretation:

- **φ = 1** → Ideal gas behavior
- **φ < 1** → Attractive forces dominate
- **φ > 1** → Repulsive forces dominate

Thus:

$$f = \varphi P$$

Substituting into the chemical potential expression:

$$\mu(T,P) = \mu^o(T) + RT \ln\left(\frac{\varphi P}{P^o}\right)$$

5. Physical Meaning of Fugacity

The word *fugacity* comes from the Latin *fugere* (to flee).

It represents the **escaping tendency** of a gas.

- Higher fugacity → greater tendency to escape
- In phase equilibrium:

$$f^{vapour} = f^{liquid}$$

This replaces the simple equality of pressures used in ideal systems.

6. Fugacity in Liquid and Vapour Phases

a. Fugacity in the Vapour Phase

For a component *i* in the vapour phase, the fugacity is related to the partial pressure (P_i) and the fugacity coefficient (φ_i):

$$f_i^v = \varphi_i P_i$$

b. Fugacity in the Liquid Phase

For a component *i* in the liquid phase, the fugacity is related to the mole fraction (*xi*), the activity coefficient (γi), and the pressure at the standard state P^o:

$$f_i^L = x_i \gamma_i P_i^o$$

Where:

- x_i is the mole fraction of component *i* in the liquid phase,
- γ_i is the activity coefficient, which accounts for deviations from ideal solution behavior,
- P_i^o is the pressure of pure component *i* at the system temperature and pressure (at the standard state).

7. Phase Equilibrium in Multi-Component Systems

7.1. Vapor-Liquid Equilibrium (VLE)

For a multi-component system in vapour-liquid equilibrium, the equilibrium condition for each component *i* is:

$$f_i^v = f_i^L$$

Substituting the expressions for fugacity in the vapour and liquid phases:

$$y_i \varphi_i P_i = x_i \gamma_i P_i^o$$

Where:

y_i is the mole fraction of component *i* in the vapour phase,

P is the total pressure.

This equation is the basis for calculating the composition of phases in equilibrium.

7.2. Raoult's Law and Modified Raoult's Law

For ideal solutions, the activity coefficient γ_i = 1, and the equilibrium condition simplifies to Raoult's Law:

$$y_i P_i = x_i P_i^{sat}$$

Where:

• P_i^{sat} sat is the saturation pressure of pure component *i* at the system temperature.

For non-ideal solutions, Modified Raoult's Law is used:

$$y_i P_i = x_i \gamma_i P_i^{sat}$$

Example Problem: Vapor-Liquid Equilibrium

Example:

A binary mixture of components A and B is in vapour-liquid equilibrium at 80°C. The saturation pressures of A and B at 80°C are 100 kPa and 50 kPa, respectively. The activity coefficients for A and B in the liquid phase are γ_A =1.2 and γ_B=1.5. The total pressure is 80 kPa. Calculate the mole fractions of A and B in the liquid and vapour phases.

Solution

Given Data:

- P_A^{sat} = 100 kPa
- P_B^{sat} = 50 kPa
- γ_A=1.2
- γ_B=1.5
- P=80 kPa

Equilibrium Equations:

For component A:

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

For component B:

$$y_B P = x_B \gamma_B P_B^{sat}$$

Mole Fraction Constraints:

$$x_A + x_B = 1 \qquad 1$$

$$y_A + y_B = 1 \qquad 2$$

Substitute Known Values:

For component A:

$$y_A 80 = x_A (1.2)(100)$$

$$80\, y_A = 120\, x_A$$

$$y_A = 1.5\, x_A \qquad 3$$

For component B:

$$y_B 80 = x_B (1.5)(50)$$

$$80\, y_B = 75\, x_B$$

$$y_B = 0.9375\, x_B \qquad 4$$

Solve the System of Equations using: $x_A + x_B = 1$ and $y_A + y_B = 1$

$$y_A + y_B = 1.5\, x_A + 0.9375\, x_B = 1$$

Substitute $x_B = 1 - x_A$, yields:

$$1.5\, x_A + 0.9375\, (1 - x_A) = 1$$

$$1.5\, x_A + 0.9375 - 0.9375\, x_A = 1$$

$$x_A = 0.1111$$
$$x_B = 1 - x_A = 0.8889$$

Now, calculate y_A and y_B:

$$y_A = 1.5\, x_A = 1.5 * 0.1111 = 0.1667$$

$$y_B = 0.9375\, x_B = 0.9375 * 0.8889 = 0.8333$$

Then: Liquid phase mole fractions are: $x_A = 0.1111, x_B = 0.8889$ Ans1

Then: Vapour phase mole fractions are: $y_A = 0.1667, y_B = 0.833$ Ans2