1. Introduction

In thermodynamics and chemical engineering, many real systems involve **mixtures** rather than pure substances. Examples include:

- Air (mixture of gases)
- Salt dissolved in water
- Fuel mixtures
- Refrigerant mixtures
- Liquid solutions in power plants and chemical industries

To properly analyze such systems, we must understand:

1. **Thermodynamic properties of solutions**
2. **Partial molar properties**
3. **Ideal vs. non-ideal behavior**

2. Basic Definitions

2.1 Solution

A **solution** is a homogeneous mixture of two or more components.

- **Solvent** → component present in larger amount
- **Solute** → component present in smaller amount

Example: In salt water, water is the solvent and salt is the solute.

2.2 Composition of a Solution

(a) Mole Fraction

For component *i*:

$$x_i = \frac{n_i}{\sum n_i}$$

Where:

- n_i = number of moles of component *i*
- $\sum n_i$ = total moles

For binary solution:

$$x_1 + x_2 = 1$$

(b) Mass Fraction

$$w_i = \frac{m_i}{\sum m_i}$$

3. Thermodynamic Properties of Solutions

For mixtures, properties such as:

- Volume (V)
- Internal Energy (U)
- Enthalpy (H)
- Entropy (S)
- Gibbs Free Energy (G)

depend on

- Temperature (T)
- Pressure (P)
- Composition (x)

Thus:

$$M = f(T, P, x_1, x_2, \ldots)$$

Where M is any extensive property.

4. Partial Molar Properties

4.1 Definition

The **partial molar property** of component ***i*** is defined as:

$$\overline{M_i} = \left(\frac{\partial M}{\partial n_i}\right)_{T,P,n_i}$$

This represents:

The change in total property M when one mole of component i is added to a large amount of solution at constant T and P.

4.2 Physical Meaning

If we add 1 mole of ethanol to water:

- The total volume does NOT increase exactly by the pure ethanol molar volume.
- Intermolecular interactions affect the final volume.

Therefore:

$$V \neq n_1 V_1 + n_2 V_2$$

Instead:

$$V = n_1 \overline{V_1} + n_2 \overline{V_2}$$

Where:

- $\overline{V_1}$ = partial molar volume of component 1
- $\overline{V_2}$ = partial molar volume of component 2

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4.3 Total Property in Terms of Partial Molar Properties

For any extensive property *M*:

$$M = \sum n_i \overline{M_i}$$

For binary mixture:

$$M = n_1 \overline{M_1} + n_2 \overline{M_2}$$

Example (1):

The need arises in a laboratory for 2000 cm^3 of an antifreeze solution consisting of 30 mol-% methanol in water. What volumes of pure methanol and of pure water at 25°C must be mixed to form the 2000 cm^3 of antifreeze, also at 25°C? Partial molar volumes for methanol and water in a 30 mol-% methanol solution and their pure-species molar volumes, both at 25°C, are:

Methanol (1): $\overline{V_1} = 38.632\ cm^3.mol^{-1}$ $\qquad V_1 = 40.727\ cm^3.mol^{-1}$

Water (2): $\overline{V_2} = 17.762\ cm^3.mol^{-1}$ $\qquad V_2 = 18.068\ cm^3.mol^{-1}$

Solution

The summability relation is written for the molar volume of the binary antifreeze solution, and known values are substituted for the mole fractions and partial molar volumes:

$$V = n_1\overline{V_1} + n_2\overline{V_2} = (0.3)(38.632) + (0.7)(17.762) = 24.025\ cm^3.mol^{-1}$$

Because the required total volume is $V^t = 2000\ cm^3.mol^{-1}$, the total number of moles required is:

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$$n = \frac{V^t}{V} = \frac{2000}{24.025} = 83.246\, mol$$

Of this, 30% is methanol, and 70% is water:

$$n_1 = (0.3)(83.246) = 24.974\, mol$$

$$n_2 = (0.7)(83.246) = 58.272\, mol$$

The volume of each pure species is $V^t = n_i V_i$, thus:

$$V_1^t = (24.974)(40.727) = 1017\, cm^3$$

$$V_2^t = (58.272)(18.068) = 1053\, cm^3$$

5. Ideal Solutions

5.1 Definition

An **ideal solution** is one in which:

Intermolecular forces between unlike molecules are equal to those between like molecules

القوى الجزيئية بين الجزيئات المختلفة تكون مساوية لتلك بين الجزيئات المتشابهة

That is:

$$A - A = B - B = A - B$$

5.2 Characteristics of Ideal Solutions

1. Obey **Raoult's Law** over entire composition range
2. No heat of mixing:

$$\Delta H_{mix} = 0$$

3. No volume change on mixing:

$$\Delta V_{mix} = 0$$

5.3 Raoult's Law

For component i:

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

Where:

- P_i = partial pressure
- x_i = mole fraction
- P_i^{sat} = vapor pressure of pure component

Total pressure:

$$P = \sum x_i P_i^{sat}$$

Examples of Nearly Ideal Solutions

- Benzene + Toluene
- Hexane + Heptane

These have similar molecular structures.

6. Non-Ideal Solutions

6.1 Definition

A **non-ideal solution** is one in which:

$$A - A \neq B - B \neq A - B$$

Intermolecular interactions differ.

6.2 Types of Deviations from Raoult's Law

(a) Positive Deviation

When:

$$A - B < A - A \quad and \quad B - B$$

Effects:

- Weaker interactions
- Higher vapor pressure
- Lower boiling point

- $\Delta H_{mix} > 0$

Example:

- Ethanol + Hexane

B) Negative Deviation

When:

$$A - B > A - A \quad and \quad B - B$$

Effects:

- Stronger interactions
- Lower vapor pressure
- Higher boiling point
- $\Delta H_{mix} < 0$

Example:

- Acetone + Chloroform

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Example (2):

A liquid mixture contains 2 kmol of Benzene and 3 kmol of Toluene in a system at 80°C. Vapor pressure of pure Benzene is 101.3 kPa and Vapor pressure of pure Toluene is 38.0 kPa, Assume the solution behaves ideally:

1. Calculate the partial pressure of each component.
2. Calculate the total pressure of the system.
3. Calculate the vapor-phase mole fractions.

Solution

Step 1: Calculate Liquid Mole Fractions

Total moles:

$$n_{total} = 2 + 3 = 5\ kmol$$

Mole fraction of Benzene:

$$x_B = \frac{2}{5} = 0.4$$

Mole fraction of Toluene:

$$x_T = \frac{3}{5} = 0.6$$

Step 2: Apply Raoult's Law

For an ideal solution:

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

Partial Pressure of Benzene

$$P_B = (0.4)(101.3) = 40.52\ kPa \quad (Ans)$$

Partial Pressure of Toluene

$$P_T = (0.6)(38.0) = 22.8\ kPa \quad (Ans)$$

Step 3: Calculate Total Pressure

$$P_{total} = P_B + P_T = 40.52 + 22.8 = 63.32\ kPa \qquad (Ans)$$

Step 4: Calculate Vapor-Phase Mole Fractions

$$y_i = \frac{P_i}{P_{total}}$$

Vapor Mole Fraction of Benzene

$$y_B = \frac{40.52}{63.32} = 0.64 \quad (Ans)$$

Vapor Mole Fraction of Toluene

$$y_T = \frac{22.8}{63.32} = 0.36 \quad (Ans)$$

(Check: 0.64 + 0.36 = 1)