1. Introduction

In thermodynamics of mixtures, it is important to understand how **thermodynamic properties change when substances are mixed together**. Real mixtures often deviate from ideal behavior due to **intermolecular interactions** between different species.

Two important tools used to describe mixture behavior are:

- **Gibbs–Duhem Equation**
- **Excess Properties of Mixtures**

These concepts are widely used in **chemical engineering, phase equilibrium calculations, and thermodynamic modeling**.

To here Group A&B & Evening_10/3/2026

2. Partial Molar Properties

Before introducing the Gibbs–Duhem equation, we must understand **partial molar properties**.

For any extensive thermodynamic property M of a mixture:

$$M = \sum_{i=1}^{n} n_i \bar{M}_i$$

Where:

- M= total property of mixture
- n_i = number of moles of component i
- $\bar{M}_i$ = partial molar property of component i

Examples:

- Partial molar volume
- Partial molar enthalpy
- Partial molar Gibbs free energy

The **partial molar Gibbs free energy** is called the **chemical potential**.

$$\mu_i = \bar{G}_i$$

3. Gibbs Free Energy of a Mixture

For a mixture:

$$G = \sum n_i \mu_i$$

Taking the differential:

$$dG = \sum n_i d\mu_i + \sum \mu_i dn_i$$

But from thermodynamics:

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

Comparing the two equations gives an important relationship.

4. Gibbs–Duhem Equation

After simplification:

$$\sum n_i d\mu_i = -SdT + VdP$$

At **constant temperature and pressure**:

$$\sum n_i d\mu_i = 0$$

Dividing by total moles n:

$$\sum x_i d\mu_i = 0$$

Where:

x_i = mole fraction of component *i*

This is the **Gibbs–Duhem Equation**.

5. Binary Mixture Form

For a **binary mixture (components 1 and 2)**:

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

or

$$x_1 d\mu_1 = -x_2 d\mu_2$$

This means:

The chemical potentials of mixture components are not independent.

If one changes, the other must change accordingly.

بالعربي: (لا تُعدّ الكمونات الكيميائية لمكونات الخليط مستقلة. فإذا تغيّر أحدها، فلا بدّ أن يتغيّر الآخر تبعاً لذلك)

Email (Hussein.kadhim@uomus.edu.iq)

6. Application Using Activity Coefficients

In real mixtures:

$$\mu_i = \mu_i^* + RT \ln a_i$$

Where:

a_i = activity

$$a_i = \gamma_i x_i$$

γ_i = activity coefficient

Substituting into Gibbs–Duhem equation gives:

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

This is commonly used to **check consistency of activity coefficient models**.

يُستخدم هذا بشكل شائع للتحقق من اتساق نماذج معامل النشاط.

7. Ideal and Real Solutions

Ideal Solution

For ideal mixtures:

$$\gamma_i = 1$$

So,

$$a_i = x_i$$

Examples:

- Benzene + Toluene mixture (approximately ideal)

Real Solutions

Real solutions deviate due to molecular interactions:

تحيد الحلول الحقيقية بسبب التفاعلات الجزيئية:

- Hydrogen bonding (روابط هيدروجينية)
- Polarity differences (إختلافات قطبية)
- Molecular size differences (إختلافات بحجم الجزيئات)

Examples:

- Water + ethanol
- Water + acetone

8. Excess Properties

To measure deviation from ideal behavior we define **excess properties**.

Excess property = difference between real and ideal mixture property.

$$M^E = M_{real} - M_{ideal}$$

9. Types of Excess Properties

Common excess properties include:

Excess Gibbs Energy

$$G^E = G_{real} - G_{ideal}$$

Email (Hussein.kadhim@uomus.edu.iq)

Most important excess property.

a. Excess Enthalpy:

$h^E = h_{real} - h_{ideal}$ (Represents heat of mixing.)

b. Excess Volume:

$V^E = V_{real} - V_{ideal}$ (Indicates volume change during mixing.)

c. Excess Entropy:

$S^E = S_{real} - S_{ideal}$ (Measures deviation in randomness.)

10. Excess Gibbs Energy and Activity Coefficients

Excess Gibbs energy relates to activity coefficients by:

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

This equation is very important in **phase equilibrium calculations**.

11. Models for Excess Gibbs Energy

Several thermodynamic models use excess properties:

a. Margules Model

$$\ln \gamma_1 = A x_2^2$$

$$\ln \gamma_2 = A x_1^2$$

b. Van Laar Model

$$\ln \gamma_1 = \frac{A_{12}x_2^2}{(A_{12}x_1 + A_{21}x_2)^2}$$

c. Wilson Model

Used for liquid mixtures with strong interactions.

d. NRTL Model

Widely used in distillation and chemical process simulations.

12. Importance in Chemical Engineering

Gibbs–Duhem equation and excess properties are important for:

- Phase equilibrium calculations
- Distillation design
- Absorption processes
- Extraction processes
- Thermodynamic modeling

Used in software such as:

- Aspen Plus
- HYSYS
- PRO/II

Example:

For a binary mixture: $x_1 = 0.4$, $x_2 = 0.6$, d($\ln\gamma_1$) $= 0.2$, Find d($\ln\gamma_2$)?

Solution:

$$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$$

$$0.4(0.2) + 0.6(d\ln\gamma_2) = 0$$

$$0.8 + 0.6(d\ln\gamma_2) = 0$$

$$d\ln\gamma_2 = -0.133 \quad \underline{\text{Ans}}$$