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Lecture notes with exercises

Thermodynamics of Solutions

Intended for third-year undergraduate students
in Fundamental Chemistry (L3)

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FOREWORD

This course handout is intended for third-year undergraduate (L3) students in Fundamental Chemistry at the Faculty of Matter Sciences, University of Tiaret. It is part of the course ‘‘Thermodynamics of Solutions’’, a discipline essential for understanding physicochemical phenomena occurring in real systems.

The main objective of this document is to provide students with the theoretical foundations and the necessary tools for the analysis and modeling of mixtures, whether ideal or real. Particular emphasis is placed on the physical interpretation of thermodynamic quantities as well as their use in phase equilibrium calculations, which are fundamental in many fields such as chemical engineering, environmental science, and industrial processes.

This handout is organized into three main chapters:

The first chapter is devoted to the characterization of homogeneous mixtures. It introduces fundamental concepts such as partial molar properties, chemical potential, fugacity, and mixing properties. The notions of activity, ideal solutions, as well as excess properties and activity coefficients are also developed, with particular attention given to Henry’s law constant and the conventions used.

The second chapter addresses deviations from ideality in the liquid phase. It presents various thermodynamic models used to describe the behavior of real solutions, ranging from classical empirical models (Margules, Van Laar, Redlich–Kister) to models based on the local composition concept (Wilson, NRTL), as well as group contribution models (UNIQAC, UNIFAC). Other approaches, such as regular, athermal, associated, and ionic solutions, are also discussed.

The third chapter deals with phase equilibria, including vapor–liquid, liquid–liquid, and vapor–liquid–liquid equilibria, as well as solid–liquid equilibria in binary systems. Particular attention is given to the solubility of gases in liquids, a phenomenon of practical and industrial importance.

To reinforce the understanding of theoretical concepts, this handout also includes a set of fully worked exercises provided at the end of each chapter. These exercises aim to develop students’ analytical, reasoning, and calculation skills, while familiarizing them with practical applications of the concepts studied. The detailed solutions allow students to follow a rigorous approach and better understand problem-solving methods.

This document has been designed with a focus on pedagogical clarity and logical progression, in order to facilitate knowledge acquisition and the development of critical thinking skills. It can serve both as a course support and as a training tool for exam preparation.

Table of Contents

Chapter 1: Characterization of Mixtures

I. Partial Molar Quantities in a Homogeneous Phase	1
1. Introduction	1
2. Definition	1
3. Key Characteristics	1
4. Homogeneous Phase Systems	1
5. Examples of Partial Molar Quantities	2
6. Fundamental Relation	2
7. Differential Form	2
8. Physical Interpretation	3
9. Ideal vs Real Solutions	3
10. Gibbs–Duhem Equation	3
11. Applications in Chemistry	4
12. Experimental Determination	4
13. Conclusion	5
II. Chemical Potential (μ)	6
1. Introduction	6
2. Definition	6
3. Physical Meaning	6
4. Differential Form of Gibbs Energy	6
5. Chemical Potential in Different Systems	6
6. Condition of Equilibrium	8
7. Importance of Chemical Potential	8
8. Link with Partial Molar Quantities	8
9. Conclusion	9
III. Fugacity and Fugacity Calculations	10
1. Introduction	10
2. Definition of Fugacity	10
3. Physical Meaning of Fugacity	10
4. Fugacity Coefficient	10
5. Differential Relation for Fugacity	10
6. Calculation of Fugacity	11
7. Fugacity Using Compressibility Factor (Z)	11

8. Special Cases	12
9. Fugacity in Liquids	12
10. Fugacity in Mixtures	13
11. Applications of Fugacity	13
IV. Mixing Properties and Activity	14
1. Introduction	14
2. Thermodynamic Functions of Mixing	14
3. Ideal vs Real Solutions	16
4. Partial Molar Quantities (Reminder)	16
5. Activity and Activity Coefficient	16
6. Activity in Different Standard States	17
7. Activity Coefficient Behavior	18
8. Applications	18
9. Conclusion	18
V. Ideal Solutions	19
1. Definition of an Ideal Solution	19
2. Thermodynamic Conditions	19
3. Raoult's Law	19
4. Chemical Potential in Ideal Solutions	19
5. Entropy of Mixing	20
6. Gibbs Free Energy of Mixing	20
7. Activity in Ideal Solutions	20
8. Examples of Ideal Solutions	20
9. Deviations from Ideal Behavior	20
10. Importance of Ideal Solutions	21
11. Conclusion	21
VI. Excess Properties and Activity Coefficients	22
1. Introduction	22
2. Ideal vs Real Solutions	22
3. Definition of Excess Properties	22
4. Excess Gibbs Energy	23
5. Activity and Activity Coefficients	23
6. Chemical Potential and Activity	23

7. Expressions of Chemical Potential in Condensed Phases	23
8. Applications	25
9. Conclusion	25
VII. Asymmetric Convention and Henry's Law Constant	26
1. Introduction	26
2. The Asymmetric Convention	26
3. Henry's Law	26
4. Activity and Activity Coefficient	27
5. Comparison with Symmetric Convention	27
6. Graphical Interpretation	27
7. Applications	28
8. Important Remarks	28
9. Example	28
10. Conclusion	29

Exercises

Exercise 1	30
Exercise 2	31
Exercise 3	31
Exercise 4	32
Exercise 5	32
Exercise 6	33
Exercise 7	33
Exercise 8	34
Exercise 9	34
Exercise 10	34
Exercise 11	35
Exercise 12	35
Exercise 13	35
Exercise 14	36
Exercise 15	36
Exercise 16	37
Exercise 17	38
Exercise 18	39

Chapter 2 : Deviations from Ideality in Liquid Phase

I- The Concept of Local Composition.....	40
1. Introduction.....	40
2. Why Global Composition is Not Enough.....	40
3. Definition of Local Composition.....	40
4. Physical Meaning.....	40
5. Key Assumption of Local Composition Theory.....	41
6. Relation with Activity Coefficients.....	41
7. Conceptual Interpretation (Microscopic View)	41
8. Importance in Thermodynamics.....	41
9. Applications.....	41
10. Conclusion.....	42
II- Empirical Models for Non-Ideal Liquid Solutions (Margules, Van Laar, Redlich–Kister Models)	43
1. Introduction.....	43
2. Excess Gibbs Energy Concept.....	43
3. Margules Model.....	43
4. Van Laar Model.....	44
5. Redlich–Kister Model.....	44
6. Comparison of Models.....	45
7. Typical Applications.....	45
8. Worked Example.....	45
9. Conclusion.....	45
III- Regular Solutions.....	46
1. Introduction.....	46
2. Key Assumptions of Regular Solutions.....	46
3. Enthalpy of Mixing.....	46
4. Gibbs Free Energy of Mixing.....	46
5. Activity Coefficients.....	46
6. Physical Meaning.....	47
7. Link with Solubility Parameter (Hildebrand Theory)	47
8. Phase Separation.....	47
9. Advantages and Limitations.....	47
10. Comparison with Other Models.....	48

11. Worked Example.....	48
12. Conclusion.....	48
IV- Empirical Models Based on the Local Composition Concept (Wilson, NRTL)	49
1. Introduction.....	49
2. Concept of Local Composition.....	49
3. The Wilson Model.....	49
4. The NRTL Model (Non-Random Two-Liquid Model)	50
5. Comparison : Wilson vs NRTL.....	51
6. Physical Interpretation.....	51
7. Conclusion.....	51
V- Group Contribution Models (UNIQUAC and UNIFAC)	52
1. Introduction.....	52
2. The UNIQUAC Model.....	52
3. The UNIFAC Model.....	53
4. Comparison Between UNIQUAC and UNIFAC.....	54
5. Applications.....	54
6. Conclusion.....	54
VI- Athermal Solution Model.....	55
1. Introduction.....	55
2. Definition of an Athermal Solution.....	55
3. Physical Interpretation.....	55
4. Gibbs Free Energy of Mixing.....	55
5. Entropy of Mixing.....	55
6. Activity Coefficients.....	56
7. Comparison with Ideal and Regular Solutions.....	56
8. Applications.....	56
9. Limitations.....	56
10. Conclusion.....	56
VII- The Associated Solutions Model.....	57
1. Introduction.....	57
2. Basic Concept.....	57
3. Chemical Equilibrium of Association.....	57
4. Composition of the Mixture.....	57
5. Activity Coefficients.....	57

6. Thermodynamic Implications.....	58
7. Comparison with Other Models.....	58
8. Applications.....	58
9. Advantages and Limitations.....	58
10. Example	59
11. Conclusion.....	59
VIII- Ionic Solutions.....	60
1. Introduction.....	60
2. Electrolytes.....	60
3. Degree of Dissociation (α)	60
4. Ionic Strength (I)	60
5. Activity and Activity Coefficients.....	61
6. Debye–Hückel Theory.....	61
7. Conductivity of Ionic Solutions.....	61
8. Kohlrausch’s Law.....	62
9. Acid–Base Ionic Equilibria.....	62
10. Applications of Ionic Solutions.....	62
11. Conclusion	62
Exercises	
Exercise 1	63
Exercise 2	63
Exercise 3	63
Exercise 4	64
Exercise 5	64
Exercise 6	64
Exercise 7	64
Exercise 8	64
Exercise 9	65
Exercise 10	65
Exercise 11	66
Exercise 12	66
Exercise 13	66
Exercise 14	67
Exercise 15	67

Exercise 16	67
Exercise 17	67
Exercise 18	67
Exercise 19	67
Exercise 20	67
Exercise 21	68
Exercise 22	68
Exercise 23	68

Chapter 3 : Phase Equilibria

I- Vapor–Liquid Equilibria (VLE).....	69
1. Introduction.....	69
2. Phase Equilibrium Condition).....	69
3. VLE for Pure Substances).....	69
4. VLE in Binary Mixtures).....	69
5. Non-Ideal Solutions).....	70
6. VLE Diagrams).....	70
7. Bubble Point and Dew Point).....	71
8. Azeotropes).....	71
9. Flash Distillation (Basic Concept)).....	71
10. Applications of VLE).....	72
11. Limitations and Models.....	72
12. Conclusion.....	72
II- Liquid–Liquid and Liquid–Liquid–Vapor Equilibria.....	73
1. Introduction.....	73
2. Liquid–Liquid Equilibrium (LLE)	73
3. Liquid–Liquid–Vapor Equilibrium (LLVE)	74
4. Modeling of LLE and LLVE.....	76
5. Comparison : LLE vs LLVE.....	76
6. Conclusion.....	77
III- Solid–Liquid Equilibria in Binary Systems.....	78
1. Introduction.....	78
2. Basic Concepts.....	78
3. Types of Solid–Liquid Phase Diagrams.....	79
4. Thermodynamic Description.....	79

5. Phase Diagram Interpretation.....	80
6. Applications.....	80
7. conclusion.....	80
IV- Solubility of Gases in Liquids.....	81
1. Introduction.....	81
2. Henry's Law.....	81
3. Physical Interpretation.....	81
4. Effect of Temperature.....	81
5. Effect of Pressure.....	82
6. Nature of Gas and Solvent.....	82
7. Thermodynamic Aspect.....	82
8. Deviations from Henry's Law.....	82
9. Applications.....	83
10. conclusion.....	83
Exercises	
Exercise 1.....	84
Exercise 2.....	84
Exercise 3.....	84
Exercise 4.....	84
Exercise 5	85
Exercise 6.....	85
Exercise 7.....	85
Exercise 8	86
Exercise 9.....	86
Exercise 10.....	87

General Introduction

The thermodynamics of solutions is a fundamental field of physical chemistry that aims to describe, understand, and predict the behavior of real mixtures. It is based on the general principles of thermodynamics in order to establish relationships between measurable macroscopic properties and microscopic interactions between the chemical species present in a system.

Unlike ideal systems, real solutions are characterized by more complex and often non-equivalent molecular interactions between their different components. These interactions directly influence the thermodynamic properties of the mixture as well as its phase equilibrium conditions. Taking these effects into account is therefore essential to obtain a realistic description of chemical systems.

The study of solutions thus plays an important role both from a theoretical and practical point of view. It helps to better understand fundamental physicochemical phenomena and finds numerous applications in industrial processes, particularly in separation operations, distillation, extraction, as well as in the formulation of mixtures used in chemistry, environmental science, and chemical engineering.

This lecture notes, intended for third-year undergraduate (L3) students in fundamental chemistry, aims to provide the theoretical foundations and essential tools of solution thermodynamics. It offers a progressive approach to the key concepts required for the analysis of mixtures and phase equilibria, with emphasis on the fundamental thermodynamic quantities that allow a rigorous description of the behavior of multicomponent systems.

I- Partial Molar Quantities in a Homogeneous Phase

1. Introduction

In materials chemistry and thermodynamics, many systems are mixtures (solutions, alloys, polymers). To understand their behavior, we need to describe how each component contributes to the overall properties.

A partial molar quantity represents the contribution of one component to a total thermodynamic property of a mixture.

It is essential for :

- Solutions (liquid mixtures).
- Alloys (solid mixtures) .
- Gas mixtures.
- Nanomaterials and composites.

2. Definition

A partial molar property is defined as:

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

Where:

- X : extensive property (volume, enthalpy, Gibbs energy, etc.)
- n_i : number of moles of component i
- T, P : constant temperature and pressure

It is the change in a total property when one mole of component i is added to a large mixture.

3. Key Characteristics

- *Intensive nature* : Partial molar quantities are intensive properties, even though they are derived from extensive ones.
- *Dependence on composition* : They depend on temperature (T), pressure (P) and composition of the mixture.
- *Not equal to pure molar properties* : ($\bar{X}_i \neq X_i^{pure}$) because interactions between different species modify the property.

4. Homogeneous Phase Systems

A homogeneous phase is a system in which the composition is uniform throughout and only one phase exists (liquid, gas, or solid).

Examples : salt solution (NaCl in water), liquid alloys (Cu–Ni), polymer blends

In such systems :

- ✓ Properties vary smoothly with composition
- ✓ Partial molar quantities are well-defined

5. Examples of Partial Molar Quantities

➤ *Partial molar volume* : Volume change when adding 1 mole of component i.

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P}$$

- ✓ It is not equal to the molar volume of the pure substance
- ✓ It reflects intermolecular interactions

➤ *Partial molar Gibbs free energy* : This is called the chemical potential.

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

It is the most important partial molar property, as it governs equilibrium, controls diffusion, and determines phase stability.

➤ *Other examples* : Partial molar enthalpy $\bar{H}_i$, Partial molar entropy $\bar{S}_i$.

6. Fundamental Relation

For a mixture : $X = \sum_i n_i \bar{X}_i$

Example (volume) : $V = n_1 \bar{V}_1 + n_2 \bar{V}_2$

This shows that the total property is equal to the sum of the contributions of each component.

7. Differential Form

For a homogeneous system : $dX = \sum_i \bar{X}_i dn_i$

❖ Gibbs energy:

The Gibbs free energy is defined as : $G = H - TS$.

And enthalpy is: $H = U + PV$.

So : $G = U + PV - TS$.

We differentiate: $dG = dU + d(PV) - d(TS)$.

Now expand each term:

a) Product PV : $d(PV) = PdV + VdP$.

b) Product TS : $d(TS) = TdS + SdT$.

So : $dG = dU + PdV + VdP - TdS - SdT$.

Applying the First Law of Thermodynamics to an open system (variable composition) allows

us to write: $dU = T dS - P dV + \sum_i \mu_i dn_i$

The extra term $\sum_i \mu_i dn_i$ accounts for changes in composition.

Substitute dU into the equation:

$$dG = (T dS - P dV + \sum_i \mu_i dn_i) + P dV + V dP - T dS - S dT$$

After simplification, we obtain the following expression:

$$dG = -S dT + V dP + \sum_i \mu_i dn_i$$

At constant temperature and pressure:

$$dG = \sum_i \mu_i dn_i$$

This equation is fundamental in phase equilibrium, chemical reactions, and materials design.

8. Physical Interpretation

Imagine adding 1 mole of A to a large solution :

- The total volume changes slightly.
- The change = partial molar volume $\bar{V}_A$.

Important :

- Interactions (attractive/repulsive forces) affect the result.
- Therefore:
 - Ideal mixtures → simple behavior.
 - Real mixtures → complex behavior.

9. Ideal vs Real Solutions

- Ideal solution: $\bar{X}_i = X_i^{pure}$
- Real solution: $\bar{X}_i \neq X_i^{pure}$

The differences arise due to hydrogen bonding, Van der Waals forces, and electrostatic interactions.

10. Gibbs–Duhem Equation

For a multicomponent system, the fundamental equation is :

$$dG = -S dT + V dP + \sum_i \mu_i dn_i$$

Gibbs energy is an extensive property, so it satisfies:

$$G = \sum_i n_i \mu_i$$

This is a key thermodynamic identity for mixtures. Using total differentiation :

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

Now compare with the fundamental equation, we also have:

$$dG = -S dT + V dP + \sum_i \mu_i dn_i$$

Set both expressions equal:

$$\sum_i \mu_i dn_i + \sum_i n_i d\mu_i = -S dT + V dP + \sum_i \mu_i dn_i$$

Final form of the Gibbs-Duhem equation :

$$\sum_i n_i d\mu_i = -S dT + V dP$$

At constant temperature and pressure (T, P constant) : dT = 0, dP = 0.

So the equation becomes:

$$\sum_i n_i d\mu_i = 0$$

or per mole:

$$\sum_i x_i d\mu_i = 0$$

where $x_i = \frac{n_i}{\sum n_i}$ is the mole fraction.

The Gibbs–Duhem equation shows that the chemical potentials in a mixture are not independent, so if the chemical potential of one component changes, the others must adjust to maintain thermodynamic consistency.

11. Applications in Chemistry

- Alloys : predict mixing behavior, control phase diagrams.
- Polymers : study miscibility, design blends.
- Nanomaterials : surface effects modify partial molar properties.
- Environmental materials : solubility of pollutants, transport in water/air systems.

12. Experimental Determination

Methods:

- ❖ Density measurements → partial molar volume.
- ❖ Calorimetry → partial molar enthalpy.
- ❖ Electrochemical methods → chemical potential.

Graphical method (binary mixture) :

- ❖ Plot X_m vs composition.
- ❖ Tangent intercept gives partial molar values.

13. Conclusion

- ✧ Partial molar quantities describe individual contributions in mixtures.
- ✧ Defined as derivatives of extensive properties.
- ✧ Crucial for homogeneous phases.
- ✧ Key concept: chemical potential = partial molar Gibbs energy.
- ✧ Used in materials science, thermodynamics, and engineering.

II- Chemical Potential (μ)

1. Introduction

In thermodynamics, the chemical potential is one of the most important quantities for describing matter exchange, phase equilibrium, and chemical reactions.

It answers a fundamental question: *what happens to the energy of a system when we add or remove matter?*

2. Definition

The chemical potential (μ) of a component i is defined as :

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

It is the partial derivative of the Gibbs free energy (G) with respect to the number of moles of component i , at constant temperature and pressure.

☞ Therefore : μ_i = partial molar Gibbs free energy.

3. Physical Meaning

The chemical potential represents:

- The energy change when 1 mole of a substance is added to the system.
- The “escaping tendency” of a species.
- The driving force for mass transfer.

🌈 Matter always moves from : $\mu_{\text{high}} \rightarrow \mu_{\text{low}}$.

4. Differential Form of Gibbs Energy

For a multicomponent system :

$$dG = -S dT + V dP + \sum_i \mu_i dn_i$$

This equation shows that:

- ✓ μ is the conjugate variable of the number of moles n_i .
- ✓ It links energy, composition, temperature, and pressure.

5. Chemical Potential in Different Systems

a) Pure substance : chemical potential equals the molar Gibbs free energy.

$$\mu = G_m$$

b) Ideal gas : Depends on pressure.

$$\mu = \mu^\circ + RT \ln P$$

Demonstration :

From thermodynamics : $dG = V dP - S dT$.

At constant temperature ($T = \text{constant}$) : $dG = V dP$.

Thus : $d\mu = V_m dP$.

For 1 mole of ideal gas : $PV = RT \Rightarrow V_m = \frac{RT}{P}$.

Substitute into the previous equation :

$$d\mu = \frac{RT}{P} dP$$

We integrate between a reference state P° and a pressure P :

$$\int_{\mu^\circ}^{\mu} d\mu = RT \int_{P^\circ}^P \frac{dP}{P}$$

This gives:

$$\mu - \mu^\circ = RT \ln \left(\frac{P}{P^\circ} \right)$$

c) Ideal solution : Depends on composition (mole fraction).

$$\mu_i = \mu_i^\circ + RT \ln x_i$$

Demonstration :

For a multicomponent system :

$$G = \sum_i n_i \mu_i$$

At constant temperature and pressure :

$$dG = \sum_i \mu_i dn_i$$

For an ideal solution, the Gibbs free energy change of mixing is:

$$\Delta G_{\text{mix}} = RT \sum_i n_i \ln x_i$$

This is a fundamental result for ideal mixtures.

The total Gibbs energy becomes:

$$G = \sum_i n_i \mu_i^\circ + RT \sum_i n_i \ln x_i$$

Where : μ_i° = chemical potential of pure component i (standard state).

By definition:

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

We differentiate:

$$\mu_i = \mu_i^\circ + RT \frac{\partial}{\partial n_i} \left(\sum_j n_j \ln x_j \right)$$

For an ideal solution:

$$\frac{\partial}{\partial n_i} \left(\sum_j n_j \ln x_j \right) = \ln x_i$$

This result comes from the relation : $x_i = \frac{n_i}{\sum n_j}$

Final expression :

$$\mu_i = \mu_i^\circ + RT \ln x_i$$

- x_i = mole fraction → describes composition.
- When x_i decreases → μ_i decreases.
- The dependence is logarithmic.

This means:

- A component becomes less stable (lower μ) when diluted.
- Explains diffusion and mixing behavior.

6. Condition of Equilibrium

At equilibrium between phases α and β : $\mu_i^\alpha = \mu_i^\beta$; Same chemical potential in all phases

7. Importance of Chemical Potential

Chemical potential is fundamental because it :

- Determines direction of mass transfer.
- Controls phase stability.
- Governs chemical reactions.
- Is essential for phase diagrams.
- Explains diffusion, osmosis, and equilibrium.

8. Link with Partial Molar Quantities

Chemical potential is a partial molar property : $\mu_i = \bar{G}_i$. It represents the contribution of component i to the total Gibbs energy.

Remark: It is possible to express the chemical potential of the pure gas by using the relation linking total pressure and partial pressure, namely $P_i = x_i P$.

$$\mu_i(T, p) = \mu_i^\circ(T, p^\circ) + RT \ln\left(\frac{p}{p^\circ}\right) + RT \ln(x_i) = \mu_i^*(T, p) + RT \ln(x_i).$$

The chemical potential of a component in a mixture therefore depends on temperature, total pressure, and the composition of the phase.

9. Conclusion

- ✓ Chemical potential = change of G with composition.
- ✓ It is the driving force of matter transfer.
- ✓ At equilibrium $\rightarrow$ chemical potentials are equal.
- ✓ It depends on T , P , and composition.
- ✓ It is a central concept in thermodynamics and materials chemistry.

III- Fugacity and Fugacity Calculations

1. Introduction

In real systems, gases and solutions do not behave ideally. The pressure P is no longer sufficient to describe the thermodynamic state. To correct this, we introduce a new quantity:

∞ Fugacity f :

- Fugacity replaces pressure in real systems.
- It allows us to keep equations similar to ideal ones.
- It is directly linked to the chemical potential.

2. Definition of Fugacity

The fugacity of a substance is defined through the chemical potential:

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

Where:

- ✓ μ : chemical potential.
- ✓ R : gas constant.
- ✓ T : temperature.
- ✓ f : fugacity.
- ✓ f° : standard fugacity.

3. Physical Meaning of Fugacity

Fugacity can be interpreted as :

- Effective pressure of a real gas.
- It measures the escaping tendency of molecules.
- If gas is ideal : $f = P$
- If gas is real : $f \neq P$

4. Fugacity Coefficient

We define the fugacity coefficient : $\phi = \frac{f}{p}$

Interpretation:

- $\phi = 1 \rightarrow$ ideal gas
- $\phi < 1 \rightarrow$ attractive forces dominate
- $\phi > 1 \rightarrow$ repulsive forces dominate

5. Differential Relation for Fugacity

Starting from thermodynamics: $d\mu = V_m dp$.

For real gases: $d\mu = RT d \ln f$.

Thus : $RT \, d \ln f = V_m \, dP$.

6. Calculation of Fugacity

According to the previous formula : $d \ln f = \frac{V_m}{RT} dP$

Subtraction: real – ideal : $d \ln f - d \ln P = \left(\frac{V_m}{RT} - \frac{1}{P} \right) dP$

$$\Rightarrow d \ln \left(\frac{f}{P} \right) = \left(\frac{V_m}{RT} - \frac{1}{P} \right) dP$$

We integrate between 0 and P : $\ln \left(\frac{f}{P} \right) = \int_0^P \left(\frac{V_m}{RT} - \frac{1}{P} \right) dP$

So :

$$\ln \left(\frac{f}{P} \right) = \frac{1}{RT} \int_0^P \left(V_m - \frac{RT}{P} \right) dP$$

Cette formule vient donc de :

- ✓ comparer gaz réel (avec V_m).
- ✓ à un gaz idéal (avec RT/P).

L'intégrale mesure : l'écart au comportement idéal

7. Fugacity Using Compressibility Factor Z

We define: $Z = \frac{PV_m}{RT} \Rightarrow V_m = \frac{ZRT}{P}$

We replace ϕ (the fugacity coefficient = f/P) in the following formula :

$$\ln \left(\frac{f}{P} \right) = \frac{1}{RT} \int_0^P \left(V_m - \frac{RT}{P} \right) dP$$

Then:

$$\ln \phi = \frac{1}{RT} \int_0^P \left(\frac{ZRT}{P} - \frac{RT}{P} \right) dP$$

After Simplification :

$$\ln \phi = \int_0^P \frac{Z - 1}{P} dP$$

Cette forme est beaucoup plus pratique car :

- Z est mesurable expérimentalement.
- Elle évite de manipuler directement V_m .

Et surtout : $Z - 1$ = écart à l'idéalité.

8. Special Cases

➤ Ideal Gas : si $Z = 1 \rightarrow$ gaz idéal $\rightarrow \phi = 1 \Rightarrow f = P$.

➤ Low Pressure Approximation : $\phi \approx 1 \Rightarrow f \approx P$.

➤ Virial Equation : If : $Z = 1 + BP + CP^2 + \dots$

$$\Rightarrow Z - 1 = BP + CP^2 + \dots$$

Substitution in the integral : $\ln \phi = \int_0^P \frac{BP + CP^2 + \dots}{P} dP$

Simplification : $\ln \phi = \int_0^P (B + CP + \dots) dP$

Then :

$$\ln \phi = BP + \frac{C}{2}P^2 + \dots$$

Virial coefficients :

- $B \rightarrow$ two-body interactions.
- $C \rightarrow$ three-body interactions.

Therefore: $\ln \phi \sim$ corrections due to molecular interactions.

9. Fugacity in Liquids

At constant temperature: $d\mu = V_m dP$.

And by definition of Fugacity : $d\mu = RT d\ln f$.

So : $RT d\ln f = V_m dP$.

Integration for a liquid : we integrate between two states:

- $P = P^{sat}$ (reference pressure).
- P (system pressure).

$$\int_{f^{sat}}^f RT d\ln f = \int_{P^{sat}}^P V_m dP$$

$$\Rightarrow RT \ln \left(\frac{f}{f^{sat}} \right) = \int_{P^{sat}}^P V_m dP$$

Liquids are only slightly compressible, therefore : $V_m \approx$ constant.

We can extract V_m from the integral:

$$RT \ln \left(\frac{f}{f^{sat}} \right) = V_m (P - P^{sat})$$

So :

$$f = f^{sat} \exp \left(\frac{V_m (P - P^{sat})}{RT} \right)$$

This relation indicates that the fugacity of a liquid is only weakly dependent on pressure due to the small molar volume V_m .

10. Fugacity in Mixtures

For component i: $\mu_i = \mu_i^\circ + RT \ln f_i$

Define: $f_i = x_i \gamma_i f_i^\circ$

Where :

- x_i : mole fraction
- γ_i : activity coefficient

11. Applications of Fugacity

- Phase equilibrium (Vapor–Liquid Equilibrium VLE, Liquid–Liquid Equilibrium LLE).
- Chemical equilibrium.
- Real gas behavior.
- Petroleum and materials science.

IV- Mixing Properties and Activity

1. Introduction

In real systems, substances are often mixed, and their properties differ from those of pure components. Thermodynamics introduces mixing quantities and activity to describe these deviations. These concepts are essential in :

- Phase equilibria.
- Solutions chemistry.
- Materials science.
- Chemical engineering.

2. Thermodynamic Functions of Mixing

2.1 Definition

A mixing quantity represents the change in a thermodynamic property when pure components are mixed at constant temperature and pressure.

For any extensive property X :

$$\Delta X_{mix} = X_{solution} - \sum_i n_i X_i^{pure}$$

2.2 Gibbs Free Energy of Mixing

$$\Delta G_{mix} = G - \sum_i n_i G_i^{pure}$$

For a binary mixture :

$$\Delta G_{mix} = nRT \sum_i x_i \ln x_i \quad (\text{ideal solution})$$

Always negative for ideal mixtures → spontaneous mixing.

Demonstration :

Now write the total Gibbs energy of the mixture using chemical potentials :

$$G = \sum_i n_i \mu_i$$

and for pure components :

$$G_i^{pure} = \mu_i^{pure}$$

So :

$$\Delta G_{mix} = \sum_i n_i \mu_i - \sum_i n_i \mu_i^{pure}$$

$$\Delta G_{mix} = \sum_i n_i (\mu_i - \mu_i^{pure})$$

For an ideal solution, the chemical potential is :

$$\mu_i = \mu_i^{pure} + RT \ln x_i$$

Substitute into the equation :

$$\Delta G_{mix} = \sum_i n_i (\mu_i^{pure} + RT \ln x_i - \mu_i^{pure})$$

Simplification :

$$\Delta G_{mix} = \sum_i n_i RT \ln x_i$$

So :

$$\Delta G_{mix} = RT \sum_i (n x_i \ln x_i) \quad (\text{because } n_i = x_i n)$$

$$\Delta G_{mix} = nRT \sum_i x_i \ln x_i$$

2.3 Enthalpy of Mixing

$$\Delta H_{mix} = H - \sum_i n_i H_i^{pure}$$

- Ideal solution : $\Delta H_{mix} = 0$
- Real solution : $\Delta H_{mix} \neq 0$

Depends on intermolecular interactions :

- Stronger interactions $\rightarrow$ exothermic.
- Weaker interactions $\rightarrow$ endothermic.

2.4 Entropy of Mixing

$$\Delta S_{mix} = S - \sum_i n_i S_i^{pure}$$

For an ideal solution :

$$\Delta S_{mix} = -nR \sum_i x_i \ln x_i$$

Always positive $\rightarrow$ disorder increases.

Demonstration :

We use the fundamental relation : $G = H - TS$.

So for mixing : $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$

Rearrange to isolate entropy :

$$\Delta S_{mix} = \frac{\Delta H_{mix} - \Delta G_{mix}}{T}$$

For an ideal solution : $\Delta H_{\text{mix}} = 0$.

So : $\Delta S_{\text{mix}} = -\frac{\Delta G_{\text{mix}}}{T}$

Substitute ΔG_{mix} :

$$\Delta S_{\text{mix}} = -\frac{nRT \sum_i x_i \ln x_i}{T}$$

Simplify :

$$\Delta S_{\text{mix}} = -nR \sum_i x_i \ln x_i$$

3. Ideal vs Real Solutions

3.1 Ideal Solution

A solution is ideal if :

- Interactions A–A, B–B, and A–B are identical.
- Follows Raoult's Law : $P_i = x_i P_i^*$.

Properties : $\Delta H_{\text{mix}} = 0$ $\Delta V_{\text{mix}} = 0$.

3.2 Real Solution

Deviations occur when interactions differ.

Positive deviation:

- Weaker A–B interactions
- Higher vapor pressure

Negative deviation:

- Stronger A–B interactions
- Lower vapor pressure

4. Partial Molar Quantities (Brief Reminder)

For any property X:

$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i} \right)_{T,P,n_j}$$

Total property:

$$X = \sum_i n_i \bar{X}_i$$

Important for describing mixtures at the molecular level.

5. Activity and Activity Coefficient

5.1 Why Activity?

Concentration alone is not sufficient in real systems. *Activity* replaces concentration to account for non-ideal behavior.

5.2 Definition of Activity

$$a_i = \gamma_i x_i$$

Where:

- a_i : activity.
- γ_i : activity coefficient.
- x_i : mole fraction.

5.3 Physical Meaning

- $a_i = x_i \rightarrow$ ideal solution.
- $\gamma_i = 1 \rightarrow$ ideal behavior.
- $\gamma_i \neq 1 \rightarrow$ real solution.

5.4 Relation with Chemical Potential

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

This equation shows that activity controls equilibrium.

6. Activity in Different Standard States

6.1 Liquid Solutions

Standard state : pure liquid

$$a_i = \gamma_i x_i$$

6.2 Dilute Solutions

Uses *Henry's Law*:

$$a_i = \gamma_i \frac{c_i}{c^\circ}$$

6.3 Electrolyte Solutions

Activity in electrolyte solutions depends on ionic interactions and is therefore expressed using the mean ionic activity, as described by the Debye-Hückel Theory.

➤ *Debye-Hückel Theory* :

The Debye-Hückel Theory explains how ionic interactions in electrolyte solutions cause deviations from ideal behavior.

Each ion is surrounded by an ionic atmosphere of opposite charge, which reduces its effective chemical potential. As a result, the activity coefficient becomes different from 1.

- *Mean Ionic Activity Coefficient*

For an electrolyte $A_{\nu+}B_{\nu-}$:

$$\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$$

Debye–Hückel Limiting Law (very dilute solutions)

$$\log \gamma_{\pm} = -A z_+ z_- \sqrt{I}$$

Ionic Strength :

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

where:

- c_i : concentration of ion i.
- z_i : charge of ion i.

As ionic strength I increases $\rightarrow$ interactions increase $\rightarrow \gamma_{\pm} < 1$.

The theory is valid mainly for dilute solutions.

7. Activity Coefficient Behavior

7.1 Interpretation

- $\gamma_i > 1$: repulsive interactions
- $\gamma_i < 1$: attractive interactions

7.2 Graphical Representation

Typical plot :

- ✓ γ_i vs x_i
- ✓ Shows deviation from ideality

8. Applications

8.1 Phase Equilibrium

- Vapor-liquid equilibrium (VLE).
- Liquid-liquid equilibrium (LLE).

8.2 Materials Science

- Alloy formation.
- Polymer mixtures.
- Surface chemistry.

9. Conclusion

- ❖ Mixing properties describe how thermodynamic quantities change upon mixing.
- ❖ Ideal solutions: no interaction change.
- ❖ Real solutions: deviations due to intermolecular forces.
- ❖ Activity corrects concentration for non-ideal systems.
- ❖ Activity coefficient measures deviation from ideality.

V- Ideal Solutions**1. Definition of an Ideal Solution**

An ideal solution is a mixture of two or more components that obeys Raoult's Law over the entire composition range. In an ideal solution :

- Interactions between unlike molecules (A–B) are equal to those between like molecules (A–A and B–B).
- No heat is absorbed or released during mixing.
- The volume of the solution is equal to the sum of the volumes of pure components.

2. Thermodynamic Conditions of Ideal Solutions

For an ideal solution, the following conditions are satisfied :

2.1 Enthalpy of Mixing

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

No heat effect during mixing.

- Indicates identical intermolecular interactions.

2.2 Volume of Mixing

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

- No expansion or contraction occurs.

3. Raoult's Law

For a binary ideal solution (components A and B) :

$$P_A = x_A P_A^0$$

$$P_B = x_B P_B^0$$

Where:

- P_A, P_B : partial vapor pressures.
- x_A, x_B : mole fractions.
- P_A^0, P_B^0 : vapor pressures of pure components.

Total Pressure :

$$P_{total} = P_A + P_B = x_A P_A^0 + x_B P_B^0$$

4. Chemical Potential in Ideal Solutions

The chemical potential of component i in an ideal solution is given by:

$$\mu_i = \mu_i^0 + RT \ln x_i$$

Where:

- μ_i^0 : chemical potential of pure component.
- R: gas constant.

- T: temperature.
- x_i : mole fraction.

This equation shows that the chemical potential depends only on composition.

5. Entropy of Mixing

The entropy change upon mixing is:

$$\Delta S_{mix} = -nR(x_A \ln x_A + x_B \ln x_B)$$

- ✓ Always positive $\rightarrow$ mixing is spontaneous.
- ✓ Reflects increased disorder.

6. Gibbs Free Energy of Mixing

$$\Delta G_{mix} = RT(x_A \ln x_A + x_B \ln x_B)$$

- ✓ Always negative for ideal solutions.
- ✓ Indicates spontaneous mixing.

7. Activity in Ideal Solutions

In an ideal solution :

$$a_i = x_i$$

Where : a_i : activity of component i.

Thus, activity equals mole fraction.

8. Examples of Ideal Solutions

Typical examples include:

- Benzene + Toluene.
- n-Hexane + n-Heptane.

These mixtures have :

- Similar molecular size.
- Similar intermolecular forces.

9. Deviations from Ideal Behavior

Real solutions may deviate from ideality:

☞ Positive Deviation

- Weaker A–B interactions.
- Higher vapor pressure than predicted.

☞ Negative Deviation

- Stronger A–B interactions.
- Lower vapor pressure than predicted.

10. Importance of Ideal Solutions

Ideal solutions are important because :

- They simplify thermodynamic calculations.
- They serve as a reference model for real solutions.
- They are fundamental in phase equilibrium studies VLE (Vapor–Liquid Equilibrium).

11. Conclusion

- ❖ Ideal solutions obey Raoult's Law.
- ❖ No heat or volume change upon mixing.
- ❖ Activity equals mole fraction.
- ❖ Mixing is spontaneous due to entropy increase.
- ❖ Real solutions deviate due to molecular interactions.

VI- Excess Properties and Activity Coefficients

1. Introduction

In real solutions, molecular interactions between different components are not identical to those in pure substances. As a result, mixtures often deviate from ideal behavior.

To quantify these deviations, we introduce:

- Excess properties.
- Activity and activity coefficients.

These concepts are fundamental in chemical thermodynamics, especially for :

- Phase equilibrium (VLE, LLE).
- Electrolyte solutions.
- Industrial separation processes.

2. Ideal vs Real Solutions

Ideal Solution

A solution is ideal if :

- Interactions A–A, B–B, and A–B are identical .
- No heat or volume change upon mixing ($\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$).

Real Solution

A real solution exhibits : $\Delta H_{\text{mix}} \neq 0$ and $\Delta V_{\text{mix}} \neq 0$.

Due to :

- Different intermolecular forces
- Hydrogen bonding, dipole interactions, etc.

3. Definition of Excess Properties

An excess property measures the deviation of a real solution from ideal behavior.

$$X^E = X_{\text{real}} - X_{\text{ideal}}$$

Where:

- X^E : excess property
- X_{real} : actual property
- X_{ideal} : property assuming ideal solution

Common Excess Properties

- Excess Gibbs energy : G^E
- Excess enthalpy: H^E
- Excess volume: V^E
- Excess entropy: S^E

4. Excess Gibbs Energy (G^E)

This is the most important excess function.

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

It is directly related to non-ideality and plays a key role in equilibrium.

Relation to Activity Coefficients

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i$$

Where:

- x_i : mole fraction.
- γ_i : activity coefficient.
- R: gas constant.
- T: temperature.

5. Activity and Activity Coefficients

5.1 Activity

The activity a_i represents the *effective concentration* of a species.

$$a_i = \gamma_i x_i$$

5.2 Activity Coefficient (γ)

The activity coefficient measures deviation from ideality :

- Ideal solution: $\gamma_i = 1$.
- Real solution: $\gamma_i \neq 1$.

6. Chemical Potential and Activity

The chemical potential of component i is :

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

Substituting activity:

$$\mu_i = \mu_i^\circ + RT \ln(x_i \gamma_i)$$

Several models describe non-ideal behavior, including the Margules equation, the Van Laar model, the Wilson model, and the Debye–Hückel theory.

7 – Different Expressions of the Chemical Potential of a Component in a Condensed Phase (Liquid or Solid)

The composition of a phase plays an important role in determining the properties of the chemical species present. So far, this composition has been described using the mole fraction in the phase under study. However, other practical ways exist to specify phase composition, particularly in the case of solutions.

The expression of the chemical potential of a component in a condensed phase depends on two choices:

- ★ the reference state (when the system is highly diluted),
- ★ the way the phase composition is described (concentration scale or molality scale).

Infinitely Dilute Reference State

There are three ways to describe the composition of the phase :

➤ Mole fraction scale

The expression used is of the form :

$$\mu_i^\ell(T, p, \text{comp.}) = \mu_{i,x}^{\circ,\infty,\ell}(T, p^\circ) + RT \ln(\gamma_{i,x}^{\circ,\infty,\ell} x_i^\ell).$$

The activity coefficient $\gamma_{i,x}^{\circ,\infty,\ell}$ satisfies the following asymptotic behavior : $\lim_{x_i^\ell \rightarrow 0} \gamma_{i,x}^{\circ,\infty,\ell} = 1$

However, due to the very low compressibility of condensed phases, the effect of pressure on the activity coefficient is generally neglected. This choice is used in molar mass determination techniques such as ebullioscopy and cryoscopy.

➤ Concentration scale

The expression used is of the form :

$$\mu_i = \mu_{i,c}^{\circ,\infty} + RT \ln \left(\gamma_{i,c}^{\circ,\infty} \frac{c_i}{c_{\text{ref}}} \right)$$

$$\mu_i^\ell(T, p, \text{comp.}) = \mu_{i,c}^{\circ,\infty,\ell}(T, p^\circ) + RT \ln \left(\gamma_{i,c}^{\circ,\infty,\ell} \left(\frac{c_i^\ell}{c_{\text{ref}}} \right) \right).$$

The subscript c indicates that the phase composition is expressed in terms of volumetric concentration, and the superscript ∞ indicates that the physical reference state is the infinitely dilute solution. The reference concentration c_{ref} is taken as $1 \text{ mol} \cdot \text{L}^{-1}$.

➤ Molality scale

The expression used is of the form :

$$\mu_i^\ell(T, p, \text{comp.}) = \mu_{i,M}^{\circ,\infty,\ell}(T, p^\circ) + RT \ln \left(\gamma_{i,M}^{\circ,\infty,\ell} \left(\frac{M_i^\ell}{M_{\text{ref}}} \right) \right).$$

The subscript M indicates that the phase composition is expressed in terms of molality, and the superscript ∞ indicates the infinitely dilute reference state. The reference molality M_{ref} is taken as $1 \text{ mol} \cdot \text{kg}^{-1}$ (per kilogram of solvent). This scale is very commonly used in research.

7. Applications

- Distillation design.
- Phase diagrams.
- Electrolyte chemistry.

- Environmental chemistry.
- Chemical engineering processes.

8. Conclusion

- Excess properties quantify deviation from ideality.
- G^E is the key thermodynamic function.
- Activity replaces concentration in real systems.
- Activity coefficients measure non-ideal interactions.
- Models help predict real solution behavior

VII- Asymmetric Convention and Henry's Law Constant**1. Introduction**

In real (non-ideal) solutions, the behavior of components deviates from ideality. To describe this, we introduce the concept of activity and activity coefficients. However, defining activity requires a reference state, which leads to different conventions :

- Symmetric convention (Raoult's law standard state)
- Asymmetric convention (Henry's law standard state)

This part of the course focuses on the asymmetric convention, which is particularly useful for dilute solutions.

2. The Asymmetric Convention**Definition**

The asymmetric convention defines the standard state of a solute based on infinite dilution, where the solute obeys Henry's law.

- The solvent follows Raoult's law
- The solute follows Henry's law

This creates an asymmetry between solvent and solute → hence the name.

Reference States

- Solvent (component 1) :
 - Standard state : pure solvent.
 - Behavior : Raoult's law.

$$f_1 = x_1 f_1^*$$

- Solute (component i):
 - Standard state : hypothetical state at infinite dilution.
 - Behavior: Henry's law.

$$f_i = x_i H_i$$

3. Henry's Law

At low concentrations, the partial pressure (or fugacity) of a solute is proportional to its mole fraction :

$$f_i = x_i H_i$$

or (in terms of pressure) :

$$P_i = x_i H_i$$

where:

- H_i = Henry's law constant

- x_i = mole fraction of solute

Physical Meaning

- H_i represents the escaping tendency of the solute from the solution.
- It depends on :
 - Nature of solute and solvent
 - Temperature
 - Pressure (weak effect at low pressure)

4. Activity and Activity Coefficient (Asymmetric Convention)

Definition of Activity

For a solute i :

$$a_i = \frac{f_i}{H_i}$$

Using Henry's law:

$$a_i = x_i \gamma_i$$

Activity Coefficient

$$\gamma_i = \frac{f_i}{x_i H_i}$$

Key Property : $\lim_{x_i \rightarrow 0} \gamma_i = 1$

This is the defining feature of the asymmetric convention.

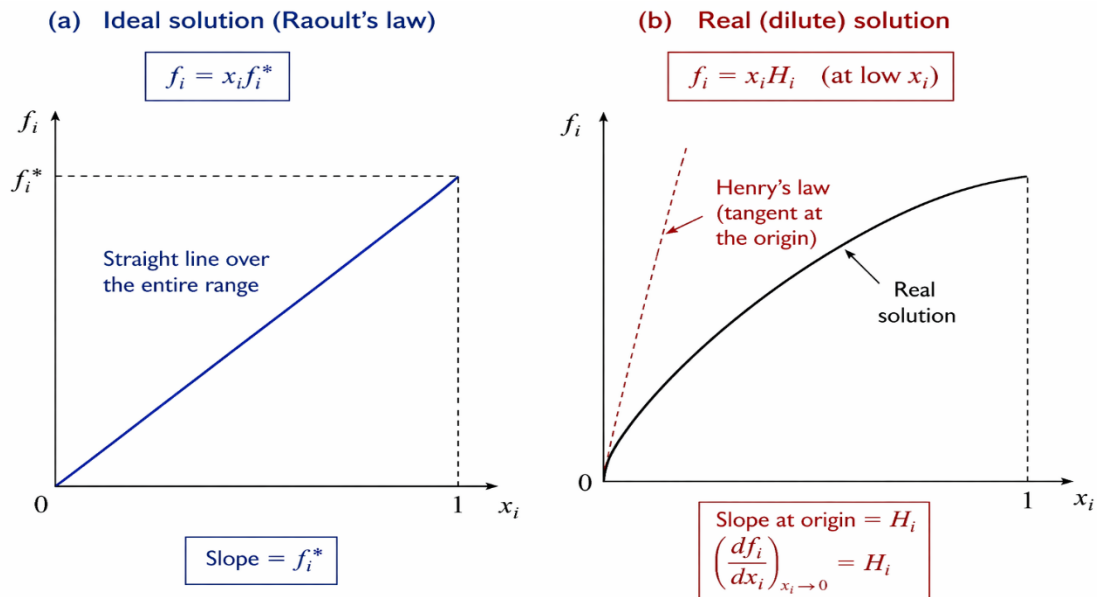
5. Comparison with Symmetric Convention

Feature	Symmetric Convention	Asymmetric Convention
Standard state	Pure component	Infinite dilution (solute)
Law used	Raoult's law	Henry's law
Valid for	Solvent	Dilute solute
Limit of γ	$\gamma \rightarrow 1$ when $x \rightarrow 1$	$\gamma \rightarrow 1$ when $x \rightarrow 0$

6. Graphical Interpretation

- Plot of f_i vs x_i :
 - Ideal solution: straight line (Raoult).
 - Dilute solution: linear at low x_i (Henry region).

The slope at origin = Henry's constant H_i .



7. Applications

- Gas solubility in liquids (e.g., CO₂ in water)
- Environmental chemistry
- Electrolyte solutions (with modifications)
- Phase equilibrium calculations (VLE at low concentration)

8. Important Remarks

- Henry's law is valid only at low concentration.
- Different definitions of H_i exist (based on pressure, concentration, etc.).
- Units of H_i vary :
 - Pa
 - atm
 - mol·L⁻¹·atm⁻¹

9. Example

For a dilute solution :

Given :

- $x_i = 0.01$.
 - $H_i = 500$ atm
- $\Rightarrow P_i = x_i H_i = 0.01 \times 500 = 5$ atm.

10. Conclusion

- The asymmetric convention uses Henry's law as reference for solutes.
- It is adapted to dilute solutions.

- The activity coefficient tends to 1 at infinite dilution.
- Henry's constant measures solute volatility or solubility.

Exercise1 :

1. Define partial molar volume and explain its physical meaning.
2. Show that: $V = n_1 \bar{V}_1 + n_2 \bar{V}_2$
3. Why is : $\bar{V}_i \neq V_i^{pure}$ in real mixtures?
4. Explain the importance of chemical potential in phase equilibrium.

Solution :

1. Definition of Partial Molar Volume

The partial molar volume of component i, denoted $\bar{V}_i$, is defined as:

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

Physical meaning:

It represents the change in the total volume of a mixture when one mole of component i is added, while keeping: temperature, pressure and the amounts of other components constant.

In simple terms: it tells us how much component i contributes to the total volume inside the mixture, not in its pure state.

2. Demonstration of the Relation : $V = n_1 \bar{V}_1 + n_2 \bar{V}_2$

- Consider volume as a function : the total volume depends on : $V = V(T, P, n_1, n_2)$.

- Total differential of V :

$$dV = \left(\frac{\partial V}{\partial T} \right) dT + \left(\frac{\partial V}{\partial P} \right) dP + \bar{V}_1 dn_1 + \bar{V}_2 dn_2$$

- At constant T and P : $dT=0, dP=0$.

So : $dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2$

- Use extensivity (Euler's theorem) : Since V is an extensive property, it is proportional to the amount of matter. Therefore : $V = n_1 \bar{V}_1 + n_2 \bar{V}_2$.

3. Why $\bar{V}_i \neq V_i^{pure}$ in real mixtures ?

In real mixtures, molecules interact with each other due to hydrogen bonding, Van der Waals forces, and electrostatic interactions.

Explanation : When a component is in a mixture :

- Its environment is different from the pure state.
- Intermolecular distances change.
- Packing of molecules changes.

Thus, the volume contribution is modified.

So : $\bar{V}_i \neq V_i^{pure}$

Example : A mixture of water and ethanol exhibits volume contraction due to intermolecular interactions, particularly hydrogen bonding.

4. Importance of Chemical Potential in Phase Equilibrium

The chemical potential is: $\mu_i = \bar{G}_i$, It represents the partial molar Gibbs free energy.

Key role in equilibrium: at phase equilibrium:

$$\mu_i^{(phase\ 1)} = \mu_i^{(phase\ 2)}$$

Explanation :

If $\mu_i^{(1)} > \mu_i^{(2)}$, the substance transfers from phase 1 to phase 2.

If $\mu_i^{(1)} < \mu_i^{(2)}$, the opposite occurs (transfer from phase 2 to phase 1).

At equilibrium, there is no net transfer of the substance between the phases.

Why it is important: Chemical potential:

- Determines direction of mass transfer.
- Controls phase stability.
- Governs chemical reactions.
- Is fundamental in phase diagrams.

Final Summary

- Partial molar volume describes the contribution of each component in a mixture.
- The total volume is the sum of partial contributions.
- In real mixtures, interactions cause deviations from pure values.
- Chemical potential is the key quantity for phase equilibrium.

Exercise 2 :

Calculate the change in chemical potential of an ideal gas when pressure increases from 1 bar to 10 bar at T=298 K.

Solution :

We use : $\mu = \mu^\circ + RT \ln \left(\frac{P}{P^\circ} \right)$

So: $\Delta\mu = RT \ln \left(\frac{P_2}{P_1} \right)$

$$\Rightarrow \Delta\mu = 8.314 \times 298 \times \ln(10).$$

$$\Rightarrow \Delta\mu \approx 8.314 \times 298 \times 2.303 \approx 5697 \text{ J/mol}.$$

Exercise 3:

A binary ideal solution contains: $x_A = 0.2$ and $x_B = 0.8$.

Calculate the chemical potential of A at T = 298 K.

Solution :

$$\begin{aligned}\mu_A &= \mu_A^\circ + RT \ln x_A \\ \mu_A &= \mu_A^\circ + (8.314 \times 298) \ln(0.2) \\ \ln(0.2) &\approx -1.609 \\ \mu_A &= \mu_A^\circ - 8.314 \times 298 \times 1.609 \\ \mu_A &\approx \mu_A^\circ - 3985 \text{ J/mol}\end{aligned}$$

The chemical potential decreases due to dilution.

Exercise 4 :

Show that mixing in an ideal solution is spontaneous.

Solution :

$$\Delta G_{\text{mix}} = RT \sum n_i \ln x_i$$

Since:

- $0 < x_i < 1.$
- $\ln x_i < 0.$

Thus : $\Delta G_{\text{mix}} < 0 \Rightarrow$ Mixing is spontaneous.

Exercise 5 :

Given the compressibility factor expressed as $Z=1+ 0.1P$, determine the fugacity coefficient ϕ .

Solution :

$$\begin{aligned}\ln \phi &= \int_0^P \frac{Z-1}{P} dP = \int_0^P \frac{0.1P}{P} dP \\ \ln \phi &= \int_0^P 0.1 dP = 0.1P \\ \phi &= e^{0.1P} \\ f &= P e^{0.1P}\end{aligned}$$

13. Summary

- Fugacity replaces pressure in real systems.
- $f = P$ for ideal gases.
- Fugacity coefficient : $\phi = f / P$.
- Calculated using :
 - Compressibility factor Z .
 - Virial equation.

➤ Essential for :

- ✓ Phase equilibrium
- ✓ Chemical reactions

Exercise 6 :

A binary ideal solution contains :

- $x_A = 0.40$
- $P_A^0 = 200 \text{ mmHg}$
- $P_B^0 = 100 \text{ mmHg}$

Calculate:

1. Partial pressures P_A and P_B .
2. Total pressure P_{total} .

Solution :

Using Raoult's Law:

$$P_A = x_A P_A^0 = 0.40 \times 200 = 80 \text{ mmHg}$$

$$x_B = 1 - x_A = 0.60$$

$$P_B = x_B P_B^0 = 0.60 \times 100 = 60 \text{ mmHg}$$

$$P_{\text{total}} = P_A + P_B = 80 + 60 = 140 \text{ mmHg}$$

Exercise 7 : Show that $\Delta G_{\text{mix}} < 0$

Question : Show that for an ideal solution : $\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B) < 0$

Solution

For any mole fraction : $0 < x_i < 1$.

Therefore : $\ln x_i < 0$.

Thus: $x_A \ln x_A < 0$ and $x_B \ln x_B < 0$

So : $x_A \ln x_A + x_B \ln x_B < 0$

Since : $n > 0$, $R > 0$, $T > 0$.

We conclude : $\Delta G_{\text{mix}} < 0 \Rightarrow$ Mixing is spontaneous.

Exercise 8 :

Question : Derive the expression of entropy of mixing for an ideal solution.

Solution : From thermodynamics:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

For an ideal solution:

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

So :

$$\Delta G_{mix} = -T\Delta S_{mix}$$

But :

$$\Delta G_{mix} = nRT(x_A \ln x_A + x_B \ln x_B)$$

Thus:

$$-T\Delta S_{mix} = nRT(x_A \ln x_A + x_B \ln x_B)$$

Divide by $-T$:

$$\Delta S_{mix} = -nR(x_A \ln x_A + x_B \ln x_B)$$

Exercise 9 :

At very low concentration, measurements give : $x_i = 0.005$ and $P_i = 2$ atm. Determine H_i .

Solution :

$$H_i = \frac{P_i}{x_i}$$

$$H_i = \frac{2}{0.005} = 400 \text{ atm}$$

So : $H_i = 400 \text{ atm}$

Exercise 10 :

Given: $f_i = 5$ atm, $x_i = 0.01$ and $H_i = 400 \text{ atm}$. Calculate the activity coefficient γ_i .

Solution

$$\gamma_i = \frac{f_i}{x_i H_i}$$

$$\gamma_i = \frac{5}{0.01 \times 400} = \frac{5}{4} = 1.25$$

$\Rightarrow \gamma_i = 1.25 \Rightarrow \gamma_i > 1 \rightarrow$ positive deviation from ideality.

Exercise 11 :

A graph of f_i vs x_i near the origin gives a straight line with slope :

$$\left(\frac{df_i}{dx_i} \right)_{x_i \rightarrow 0} = 600 \text{ atm}$$

Question : What is the value of H_i ?

Solution

By definition:

$$H_i = \left(\frac{df_i}{dx_i} \right)_{x_i \rightarrow 0}$$

$$H_i = 600 \text{ atm}$$

Exercise 12 :

Given : $f_i^* = 200 \text{ atm}$ and $H_i = 500 \text{ atm}$.

Question

Which law dominates :

- at low x_i ?
- near $x_i = 1$?

Solution

- At low x_i : Henry's law dominates.
- Near $x_i=1$: Raoult's law dominates.
- ❖ Dilute $\rightarrow$ Henry.
- ❖ Concentrated $\rightarrow$ Raoult.

Exercise 13 :

Henry's constant follows:

$$\ln H_i = -\frac{\Delta H}{RT} + C$$

Question : If dissolution is endothermic ($\Delta H > 0$), what happens to H_i when temperature increases?

Solution

- When $T \uparrow$, term $-\frac{\Delta H}{RT}$ becomes less negative.
- So $\ln H_i \uparrow$.
- Therefore $H_i \uparrow$.

So : H_i increases with temperature.

Exercise 14 : True or False

Statements

1. H_i is an enthalpy.
2. Henry's law is valid at high concentration.
3. $\gamma_i \rightarrow 1$ when $x_i \rightarrow 0$ (asymmetric convention)

Solution

1. False

2. False
3. True

Exercise 15 :

In the case of a dilute solution, several choices are possible for expressing the chemical potential of a solute i . Among these, we choose either the infinitely dilute solute reference with the mole fraction scale, or the infinitely dilute solute reference with the concentration scale.

1. In the particular case of a very dilute solution, write the two expressions of the chemical potential of a solute resulting from the proposed choice, clearly showing the standard chemical potentials.
2. The solvent having a molar mass M and a density ρ (for the pure solvent), show that there exists a relation between the standard potentials appearing in the expressions of the chemical potentials.
3. Numerical application for water as solvent at $T = 298$ K. Calculate the difference :

$$\mu_{i,x}^{\circ,\infty,\ell}(T, p^{\circ}) - \mu_{i,c}^{\circ,\infty,\ell}(T, p^{\circ})$$

With : $M = 18$ g/mol and $\rho = 998$ Kg/m³.

Solution :

1. In the case of the mole fraction scale:

$$\mu_i^{\ell}(T, p, \text{comp.}) = \mu_{i,x}^{\circ,\infty,\ell}(T, p^{\circ}) + RT \ln(\gamma_{i,x}^{\circ,\infty,\ell} x_i^{\ell}).$$

- In the case of the concentration scale:

$$\mu_i^{\ell}(T, p, \text{comp.}) = \mu_{i,c}^{\circ,\infty,\ell}(T, p^{\circ}) + RT \ln \left(\gamma_{i,c}^{\circ,\infty,\ell} \left(\frac{c_i^{\ell}}{c_{\text{réf}}^{\ell}} \right) \right).$$

By definition :

$$x_i^{\ell} = \frac{n_i}{(n + n_i)} \quad \text{et} \quad c_i^{\ell} = \frac{n_i}{V}.$$

In the case of very dilute solutions (activity coefficients equal to 1), the volume of the solution is determined by the amount of solvent :

$$V \approx \frac{m}{\rho} \quad \text{soit} \quad V \approx \frac{nM}{\rho}.$$

$$c_i^{\ell} = \frac{n_i \rho}{nM} = x_i^{\ell} \frac{\rho}{M}.$$

$$\mu_{i,x}^{\circ,\infty,\ell}(T, p^{\circ}) + RT \ln(x_i^{\ell}) = \mu_{i,c}^{\circ,\infty,\ell}(T, p^{\circ}) + RT \ln \left(x_i^{\ell} \frac{\rho}{M c_{\text{réf}}^{\ell}} \right)$$

$$\mu_{i,x}^{\circ,\infty,\ell}(T, p^{\circ}) - \mu_{i,c}^{\circ,\infty,\ell}(T, p^{\circ}) = RT \ln \left(\frac{\rho}{M c_{\text{réf}}} \right).$$

3. For the numerical application, the reference concentration is in $\text{mol} \cdot \text{m}^{-3}$:

$$RT \ln \left(\frac{\rho}{M c_{\text{réf}}} \right) = 8,314 \times 298 \times \ln \left(\frac{998}{18.10^{-3} \times 10^3} \right) = 9,95 \text{ kJ} \cdot \text{mol}^{-1}.$$

Exercise 16 : Carbon allotropes

At 298 K, $M_c = 12 \text{ g} \cdot \text{mol}^{-1}$, under $P^{\circ} = 1 \text{ bar}$:

	Enthalpy of Combustion ($\text{kJ} \cdot \text{mol}^{-1}$)	Molar Entropy ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	Density ($\text{kg} \cdot \text{m}^{-3}$)
Diamond (C)	-395.3	2.439	3513
Graphite (C)	-393.4	5.694	2270

1. Determine the molar volume of graphite or diamond.
2. Determine the difference in molar enthalpies between graphite and diamond.
3. Determine which form is more stable at 298 K.
4. Comment on the fact that at ambient temperature and pressure, both graphite and diamond exist in nature.
5. Estimate the pressure at which the two crystalline forms are in equilibrium at 298 K. By what method can synthetic diamond be produced?

Solution :

1. The molar volume of the pure solid is given by : $V_m = \rho / M$

We obtain:

$$\text{Graphite: } V_m(g) = 5.286 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$$

$$\text{Diamond: } V_m(d) = 3.416 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$$

2. The combustion reaction at 298 K is written as : $\text{C} + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g})$.

Depending on whether we start from graphite or diamond, different values are obtained for the enthalpy of combustion. Hence:

$$\Delta_{\text{comb}} H_d^{\circ} - \Delta_{\text{comb}} H_g^{\circ} = H_m^{\circ}(g) - H_m^{\circ}(d) = -1.9 \text{ kJ} \cdot \text{mol}^{-1}$$

3. It is sufficient to compare the chemical potentials:

$$\begin{aligned} \mu^{\circ}(T) &= H_m^{\circ}(T) - T S_m^{\circ}(T) \\ \mu_g^{\circ} - \mu_d^{\circ} &= [H_m^{\circ}(g) - H_m^{\circ}(d)] - T [S_m^{\circ}(g) - S_m^{\circ}(d)] \\ &= -1.9 \times 10^3 - T(3.255) \end{aligned}$$

At $T=298\text{K}$, we obtain:

$$\mu_g^\circ - \mu_d^\circ = -2870 \text{ J} \cdot \text{mol}^{-1}$$

The stable form is graphite, which has the lower chemical potential.

4. From a thermodynamic point of view, diamond should spontaneously and completely transform into graphite at 25 °C and 1 bar.

$$(\mu_d^\circ > \mu_g^\circ)$$

If it nevertheless exists, it is because the rate of this reaction is infinitely slow (kinetic metastability).

5. Two-phase equilibrium assumes :

$$\mu^*(T, P)_{(g)} = \mu^*(T, P)_{(d)}, \quad \text{that is:}$$

$$\mu_g^\circ + V_{m(g)}(P - P^\circ) = \mu_d^\circ + V_{m(d)}(P - P^\circ)$$

$$P = P^\circ + \frac{\mu_g^\circ - \mu_d^\circ}{V_{m(d)} - V_{m(g)}}$$

$$P \approx 15\,350 \text{ bar}$$

Remark : Synthetic diamond is produced by compressing graphite at high temperature.

Exercise 17 :

We consider, on the one hand, solid iodine at 25 °C and 1 bar, for which:

$$\mu_{I_2(s)}^0 = 0 \text{ KJ} \cdot \text{mol}^{-1}$$

On the other hand, we consider aqueous iodine at 25 °C and 1 bar, for which:

$$|\mu_{I_2(aq)}^0| = 16,4 \text{ KJ} \cdot \text{mol}^{-1}$$

- Specify the two standard states to be considered.
- Deduce the solubility of iodine at 25 °C.

Solution :

- a) $I_2(s)$: standard state pure solid at $P = P^\circ$ and T .

$I_2(aq)$: standard state solute at concentration $C^\circ = 1 \text{ mol} \cdot \text{L}^{-1}$ behaving as an infinitely dilute solution.

- b) System at equilibrium : $\mu_{I_2(s)}^0 = \mu_{I_2(aq)}^0 + RT \ln \frac{C}{C^\circ}$

$$\Rightarrow C = C^\circ \exp\left[\frac{\mu_s^0 - \mu_{aq}^0}{RT}\right] = 1,3 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}.$$

Exercise 18 :

A water–ethanol mixture is a non-ideal mixture. The volume V of a solution containing n_1 moles of ethanol in 1 kg of water at 25 °C is expressed as:

$$V = a + b n_1 + c n_1^2 \quad a, b, c \text{ constantes.}$$

- a) Determine the partial molar volumes of water and ethanol as a function of n_1 , a , b , and c .
 b) Determine the molar volume of pure water at 25 °C as a function of a .

Solution :

$$\text{a) } V_{m,1} = \left(\frac{\partial V}{\partial n_1} \right)_{T,P,n_2} = b + 2 c n_1.$$

$$\begin{aligned} & \text{de } V = n_1 V_{m,1} + n_2 V_{m,2} \\ \Rightarrow V_{m,2} &= \frac{V - n_1 V_{m,1}}{n_2} \quad \text{avec } n_2 = \frac{1\,000}{18}, \\ \Rightarrow V_{m,2} &= (a - c n_1^2) \frac{18}{1\,000}. \end{aligned}$$

$$\text{b) } n_1 = 0 \Rightarrow V = n_2 V_{m,2}^* \Rightarrow V_{m,2}^* = \frac{18}{1\,000} a.$$

I- The Concept of Local Composition

1. Introduction

In real liquid mixtures, especially non-ideal solutions, the molecular environment around a given molecule is often very different from the overall (bulk) composition of the mixture. To describe this microscopic non-ideality, the concept of local composition is introduced.

The idea is that each molecule “feels” a local environment that can be enriched or depleted in one of the components compared to the global composition.

This concept is fundamental in the development of modern thermodynamic models such as : Wilson model, NRTL (Non-Random Two-Liquid) model, UNIQUAC model.

2. Why Global Composition is Not Enough

In an ideal solution:

- Molecules are randomly distributed.
- Interactions A–A, B–B, and A–B are similar.
- Local composition = bulk composition.

However, in real systems:

- Strong molecular interactions exist (H-bonding, polarity, size effects).
- Molecules tend to cluster selectively.
- The assumption of randomness fails.

Therefore, the bulk mole fraction x_i does not represent the true molecular environment.

3. Definition of Local Composition

The local composition describes the effective mole fraction of component i in the immediate neighborhood of another molecule j.

It is written as : $x_{ij}^{(local)}$

Where: $x_{ij}^{(local)}$ is the fraction of molecules of type i surrounding a central molecule j.

4. Physical Meaning

Consider a binary mixture (A + B) :

- Bulk composition : x_A, x_B .
- Local composition around A : $x_{BA}^{(local)}$.
- Local composition around B : $x_{AB}^{(local)}$.

If:

- A–B interactions are strong → enrichment of unlike molecules.
- A–A interactions are stronger → clustering of same molecules.

Therefore: $x_{ij}^{(local)} \neq x_i$

5. Key Assumption of Local Composition Theory

The central idea is:

The energy of interaction depends on the local environment, not the bulk composition.

Thus, the excess Gibbs energy can be expressed as a function of local compositions :

$$G^E = f(x_{ij}^{(local)}, \Delta u_{ij})$$

Where Δu_{ij} represents the interaction energy between molecules i and j.

6. Relation with Activity Coefficients

Local composition models aim to predict the activity coefficient γ_i :

$$\mu_i = \mu_i^{ideal} + RT \ln \gamma_i$$

The activity coefficient accounts for non-ideality caused by :

- Molecular size differences
- Energetic interactions
- Local composition effects

7. Conceptual Interpretation (Microscopic View)

Imagine a molecule A in a liquid:

- ✓ In an ideal solution → random neighbors
- ✓ In a real solution → selective neighbors

Example:

Ethanol + water : strong H-bonding → water-rich local environment around ethanol. This leads to :

- ✓ Non-random mixing
- ✓ Non-linear thermodynamic behavior

8. Importance in Thermodynamics

The concept of local composition allows us to:

- Explain deviations from Raoult's law.
- Predict vapor–liquid equilibrium (VLE).
- Model strongly non-ideal mixtures.
- Build predictive thermodynamic models.

9. Applications

Local composition theory is used in:

- Chemical engineering (distillation design).
- Solvent selection.

- Pharmaceutical formulation.
- Petrochemical separation processes.

10. Conclusion

- Bulk composition describes the whole mixture.
- Local composition describes the microscopic environment.
- Real solutions are governed by local molecular interactions.
- This concept is the foundation of modern activity coefficient models.

In real liquids, molecules do not mix randomly; they organize their surroundings, and this local structure governs thermodynamic behavior.

II- Empirical Models for Non-Ideal Liquid Solutions (Margules, Van Laar, Redlich–Kister Models)

1. Introduction

Real liquid mixtures often deviate from ideal behavior because intermolecular interactions between unlike molecules differ from those between like molecules.

In an ideal solution :

- Raoult's law is valid over the entire composition range.
- Activity coefficients: $\gamma_i = 1$.

In real solution :

- $\gamma_i \neq 1$.
- Excess Gibbs energy $G^E \neq 0$.

Empirical models are used to describe G^E , γ_i , and phase equilibria (VLE, LLE).

2. Excess Gibbs Energy Concept

The key thermodynamic quantity is :

$$G^E = RT \sum x_i \ln \gamma_i$$

For binary systems :

$$G^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

Empirical models provide expressions for G^E , from which activity coefficients are derived.

3. Margules Model

3.1 One-parameter Margules equation

For binary mixtures :

$$\ln \gamma_1 = Ax_2^2$$

$$\ln \gamma_2 = Ax_1^2$$

Where :

- A = empirical interaction parameter.
- symmetric model

Excess Gibbs energy :

$$\frac{G^E}{RT} = Ax_1x_2$$

3.2 Two-parameter Margules model

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

$$\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]$$

Features:

- ♦ Asymmetric mixtures
- ♦ Better fit for real systems

3.3 Advantages / Limitations

- ✓ Simple.
- ✓ Good for moderate non-ideality.
- ✗ Purely empirical.
- ✗ No molecular interpretation.

4. Van Laar Model**4.1 Equations**

$$\ln \gamma_1 = \frac{A_{12}}{\left(1 + \frac{A_{12}x_1}{A_{21}x_2}\right)^2}$$

$$\ln \gamma_2 = \frac{A_{21}}{\left(1 + \frac{A_{21}x_2}{A_{12}x_1}\right)^2}$$

4.2 Excess Gibbs energy:

$$\frac{G^E}{RT} = \frac{A_{12}A_{21}x_1x_2}{A_{12}x_1 + A_{21}x_2}$$

4.3 Features

- Works well for liquid–liquid equilibria.
- Strongly non-ideal systems.
- Captures asymmetry better than Margules.
- Still empirical.
- Less accurate for dilute limits.

5. Redlich–Kister Model**5.1 General expression**

Used widely for binary systems :

$$\frac{G^E}{RT} = x_1x_2 \sum_{k=0}^n A_k (x_1 - x_2)^k$$

Often truncated to 1–3 terms :

$$\frac{G^E}{RT} = x_1x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]$$

5.2 Activity coefficients

$$\ln \gamma_1 = x_2^2 [A_0 + A_1(2x_1 - 1) + A_2(3x_1^2 - 3x_1x_2 + x_2^2)]$$

- similar expression for γ_2

5.3 Features

- Very flexible.
- High accuracy fitting experimental data.
- Widely used in thermodynamic databases.
- No physical meaning of parameters.
- Requires regression fitting.

6. Comparison of Models

Model	Complexity	Accuracy	Asymmetry
Margules	Low	Medium	Limited
Van Laar	Medium	Good	Strong
Redlich–Kister	High	Very high	Very strong

7. Typical Applications

These models are used in :

- ∞ Vapor–liquid equilibrium (VLE)
- ∞ Liquid–liquid equilibrium (LLE)
- ∞ Process simulation (Aspen Plus, etc.)
- ∞ Design of separation processes (distillation, extraction)

8. Worked Example

Given: A binary system with Margules parameter $A=1.8$, $x_1=0.4$

Calculate :

$$\ln \gamma_1 = Ax_2^2$$

$$x_2 = 0.6$$

$$\ln \gamma_1 = 1.8 \times (0.6)^2 = 1.8 \times 0.36 = 0.648$$

$$\gamma_1 = e^{0.648} \approx 1.91$$

9. Conclusion

- All models describe excess Gibbs energy.
- They are empirical fitting tools.
- Accuracy increases from Margules $\rightarrow$ Van Laar $\rightarrow$ Redlich–Kister.
- None provide true molecular-level prediction.

III- Regular Solutions

1. Introduction

In real liquid mixtures, deviations from ideal behavior are often observed. While ideal solutions assume that there is no enthalpy change upon mixing ($\Delta H_{\text{mix}} = 0$) and that intermolecular interactions between unlike molecules are similar to those between like molecules, these conditions are rarely satisfied in practice. In order to better describe such systems, the Regular Solution Model was introduced. A regular solution is defined as a solution in which the enthalpy of mixing is non-zero ($\Delta H_{\text{mix}} \neq 0$), while the entropy of mixing remains ideal.

2. Key Assumptions of Regular Solutions

The model is based on the following hypotheses:

1. Random mixing (no local composition effects).
2. Entropy of mixing is ideal : $\Delta S_{\text{mix}} = -R(x_1 \ln x_1 + x_2 \ln x_2)$
3. Enthalpy of mixing is non-zero due to different interactions : $\Delta H_{\text{mix}} \neq 0$

3. Enthalpy of Mixing

The enthalpy of mixing for a binary solution is given by : $\Delta H_{\text{mix}} = x_1 x_2 \Omega$

Where:

- x_1, x_2 : mole fractions
- Ω : interaction parameter

Interpretation of Ω

∞ $\Omega > 0 \rightarrow$ repulsive interactions :

- Components dislike each other.
- Possible phase separation.

∞ $\Omega < 0 \rightarrow$ attractive interactions :

- Components prefer mixing
- Stronger cohesion

∞ $\Omega = 0 \rightarrow$ ideal solution

4. Gibbs Free Energy of Mixing

The Gibbs free energy is :

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

Substituting expressions :

$$\Delta G_{\text{mix}} = x_1 x_2 \Omega + RT(x_1 \ln x_1 + x_2 \ln x_2)$$

5. Activity Coefficients

The activity coefficients describe deviation from ideality.

For a binary regular solution :

$$\ln \gamma_1 = \frac{\Omega}{RT} x_2^2$$

$$\ln \gamma_2 = \frac{\Omega}{RT} x_1^2$$

Key Insights :

- If $\Omega = 0$, then $\gamma_i = 1 \rightarrow$ ideal behavior.
- Larger $|\Omega| \rightarrow$ stronger deviation.

6. Physical Meaning

Unlike empirical models (Margules, Van Laar), the regular solution model has a semi-physical basis :

- Based on intermolecular interaction energies.
- Uses cohesive energy density.

7. Link with Solubility Parameter (Hildebrand Theory)

The interaction parameter Ω can be expressed using the Hildebrand solubility parameter (δ) :

$$\Omega = V_m(\delta_1 - \delta_2)^2$$

Where:

- V_m : molar volume.
- δ : solubility parameter.

Interpretation :

- ✓ Similar $\delta \rightarrow$ good miscibility.
- ✓ Large difference $\rightarrow$ poor miscibility.

8. Phase Separation

If Ω is sufficiently large and positive :

- ✓ The curve of ΔG_{mix} becomes non-convex.
- ✓ Leads to liquid-liquid phase separation.

This gives rise to Binodal curve and Spinodal decomposition.

9. Advantages and Limitations

Advantages :

- Simple analytical expressions.
- Physical meaning (interaction parameter).
- Useful for non-polar mixtures.

Limitations :

- Assumes random mixing.

- Not valid for :
 - Strongly polar systems.
 - Hydrogen bonding.
 - Associating liquids.

10. Comparison with Other Models

Model	Nature	Physical Meaning	Complexity
Margules	Empirical	No	Low
Van Laar	Empirical	No	Medium
Regular Solution	Semi-physical	Yes	Medium
Wilson/NRTL	Local comp.	Yes	High

11. Worked Example

Given : $x_1 = 0.4$, $x_2 = 0.6$, $\Omega = 2000$ J/mol and $T=298$ K. Calculate $\ln\gamma_1$.

Solution

$$\begin{aligned}
 \ln \gamma_1 &= \frac{\Omega}{RT} x_2^2 \\
 &= \frac{2000}{8.314 \times 298} \times (0.6)^2 \\
 &= \frac{2000}{2477.6} \times 0.36 \\
 &\approx 0.29
 \end{aligned}$$

12. Conclusion

The Regular Solution Model is an important intermediate model :

- More realistic than ideal solutions.
- Simpler than local composition models.

It provides a useful framework for understanding :

- Thermodynamic properties
- Phase behavior
- Miscibility of liquids

IV- Empirical Models Based on the Local Composition Concept (Wilson, NRTL)

1. Introduction

In real liquid mixtures, deviations from ideal behavior are frequently observed due to differences in intermolecular interactions. Classical models such as Raoult's law fail to describe these systems accurately.

To better represent non-ideal mixtures, empirical and semi-theoretical models have been developed. Among them, models based on the local composition concept-introduced by Grant M. Wilson and later expanded by Henri Renon and John M. Prausnitz-are widely used.

These models include : Wilson model and NRTL (Non-Random Two-Liquid) model.

2. Concept of Local Composition

Unlike ideal models that assume uniform composition throughout the mixture, the local composition concept assumes :

- The environment surrounding a molecule is not identical to the bulk composition.
- Molecules tend to be surrounded preferentially by certain types of molecules depending on interaction energies.

The local mole fraction of component i around component j differs from the global mole fraction. This concept accounts for molecular size differences, interaction energy differences and non-random distribution of molecules.

3. The Wilson Model

3.1 Assumptions

The Wilson model assumes :

- ✓ No phase separation (completely miscible liquids).
- ✓ Non-random distribution due to energetic differences.
- ✓ Local composition depends on interaction energies.

3.2 Mathematical Expression

The activity coefficient γ_i is given by:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right)$$

Λ_{ij} is an interaction parameter between molecules i and j .

3.3 Parameters

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left(-\frac{\Delta u_{ij}}{RT} \right)$$

Where:

- V_i, V_j : molar volumes.
- Δu_{ij} : interaction energy difference.
- R : gas constant.
- T : temperature.

3.4 Advantages

- ❖ Simple and relatively accurate for many systems.
- ❖ Requires only two adjustable parameters.

3.5 Limitations

- ◆ Cannot predict liquid-liquid phase separation.
- ◆ Less accurate for highly non-ideal systems.

4. The NRTL Model (Non-Random Two-Liquid Model)

The NRTL (Non-Random Two-Liquid) model, developed by Henri Renon and John M. Prausnitz, is based on the idea that liquid mixtures do not exhibit perfectly random molecular distributions. Instead, it introduces a specific parameter known as the non-randomness parameter, denoted by α , which quantifies the extent to which the system deviates from ideal random mixing. This parameter reflects the degree of local ordering in the mixture, meaning that molecules may preferentially surround themselves with certain types of neighboring molecules due to differences in interaction energies. As a result, the NRTL model provides a more realistic description of highly non-ideal systems by explicitly accounting for this non-random behavior at the molecular level.

4.1 Mathematical Formulation

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

τ_{ij} is a dimensionless energy interaction parameter that represents the difference in energy between molecular interactions.

4.2 Parameters

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT}, \quad G_{ij} = \exp(-\alpha \tau_{ij})$$

Where:

- Δg_{ij} : interaction energy parameter.

- α : non-randomness parameter (typically 0.2 – 0.47)

4.3 Advantages

- Can represent :
 - Strong deviations from ideality.
 - Partial miscibility.
 - Liquid-liquid equilibria (LLE).

4.4 Limitations

- More complex than Wilson.
- Requires more parameters.
- Parameter estimation can be difficult.

5. Comparison : Wilson vs NRTL

Feature	Wilson Model	NRTL Model
Complexity	Simple	More complex
Parameters	2	2–3
Phase separation	No	Yes
Accuracy	Moderate	High
Non-randomness	Implicit	Explicit (α)

6. Physical Interpretation

- ⇒ Both models rely on interaction energy differences between molecules.
- ⇒ Wilson assumes smooth variation of local composition.
- ⇒ NRTL explicitly accounts for molecular clustering and non-random mixing.

7. Conclusion

Empirical models based on the local composition concept, such as the Wilson and NRTL models, play a crucial role in chemical engineering practice. They are extensively used in the design and optimization of separation processes, particularly in distillation and liquid–liquid extraction, where accurate prediction of non-ideal behavior is essential. These models also provide reliable tools for calculating phase equilibria, including vapor–liquid equilibrium (VLE) and liquid–liquid equilibrium (LLE), which are fundamental for process analysis and design. Moreover, they are implemented in industrial simulation software such as Aspen Plus, allowing engineers to model complex systems with greater precision and efficiency.

V- Group Contribution Models (UNIQUAC and UNIFAC)

1. Introduction

In real liquid mixtures, deviations from ideal behavior are common due to differences in molecular size, shape, and intermolecular interactions. To describe such non-ideal systems, activity coefficient models are used.

Among them, group contribution models are particularly useful because they allow the prediction of thermodynamic properties without requiring experimental data for every mixture. These models are based on the idea that:

A molecule can be decomposed into functional groups, and the behavior of the mixture depends on interactions between these groups.

The two most widely used models are :

- ⇒ UNIQUAC (Universal Quasi-Chemical model).
- ⇒ UNIFAC (UNIQUAC Functional-group Activity Coefficients).

2. The UNIQUAC Model

2.1 Basic Concept

The UNIQUAC model separates the activity coefficient into two contributions :

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res}$$

Where:

- $\ln \gamma_i^{comb}$: combinatorial part (size and shape effects).
- $\ln \gamma_i^{res}$: residual part (energy interactions).

2.2 Combinatorial Contribution

This term accounts for differences in molecular size and shape.

$$\ln \gamma_i^{comb} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

Where :

- x_i : mole fraction.
- ϕ_i : volume fraction.
- θ_i : surface fraction.
- l_i, q_i : structural parameters (volume and surface area).
- z : coordination number (usually 10).

2.3 Residual Contribution

This term represents intermolecular interactions :

$$\ln \gamma_i^{res} = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right]$$

Where :

- $\tau_{ij} = \exp(-a_{ij}/RT)$.
- a_{ij} : interaction energy between molecules i and j.

2.4 Characteristics of UNIQUAC

- Semi-empirical model.
- Requires binary interaction parameters.
- Good accuracy for many systems.
- Applicable to :
 - Vapor–liquid equilibrium (VLE).
 - Liquid–liquid equilibrium (LLE).

3. The UNIFAC Model

3.1 Basic Concept

UNIFAC extends UNIQUAC by introducing group contributions. Instead of using molecule – molecule interactions, it uses interactions between functional groups (–CH₃, –OH, –COOH, etc.). The activity coefficient is expressed as :

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res}$$

Same structure as UNIQUAC, but the residual term is calculated differently.

3.2 Combinatorial Part

Similar to UNIQUAC :

- Depends on molecular size and shape.
- Uses group volume and surface parameters.

3.3 Residual Part (Group Contribution)

The residual contribution is calculated in two steps :

1. Group activity coefficients : $\ln \Gamma_k$
2. Molecular activity coefficient :

$$\ln \gamma_i^{res} = \sum_k \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)})$$

Where :

- $\nu_k^{(i)}$: number of groups k in molecule i.
- Γ_k : activity coefficient of group k in the mixture.
- $\Gamma_k^{(i)}$: activity coefficient in a reference state.

3.4 Group Interaction Parameters

Group interactions are described by :

$$\Psi_{mn} = \exp(-a_{mn}/T)$$

Where: Ψ_{mn} : interaction parameter between groups m and n.

3.5 Advantages of UNIFAC

- ✓ Predictive model (no need for experimental data for every mixture).
- ✓ Applicable to a wide range of systems.
- ✓ Widely used in process simulation (e.g., Aspen Plus).

3.6 Limitations

- ✗ Accuracy depends on available group parameters.
- ✗ Less reliable for:
 - Strongly associating systems (e.g., hydrogen bonding).
 - Electrolytes.

4. Comparison Between UNIQUAC and UNIFAC

Feature	UNIQUAC	UNIFAC
Type	Semi-empirical	Predictive
Basis	Molecules	Functional groups
Parameters	Binary interaction	Group interaction
Experimental data	Required	Not always required
Accuracy	High (with data)	Moderate to high

5. Applications

These models are widely used in :

- ✧ Vapor–liquid equilibrium (VLE) calculations.
- ✧ Liquid–liquid equilibrium (LLE).
- ✧ Distillation design.
- ✧ Extraction processes.
- ✧ Chemical process simulation (Aspen Plus, HYSYS).

6. Conclusion

Group contribution models such as UNIQUAC and UNIFAC are essential tools in chemical thermodynamics. UNIQUAC provides accurate results when experimental data are available, while UNIFAC offers predictive capabilities by using functional group interactions. Together, they play a crucial role in the design and optimization of chemical processes.

VI- Athermal Solution Model

1. Introduction

In real liquid mixtures, deviations from ideal behavior are often observed due to differences in intermolecular interactions. Several models have been developed to describe these deviations. The athermal solution model represents a simplified case where no heat is exchanged upon mixing, making it useful for understanding entropy-driven mixing processes.

2. Definition of an Athermal Solution

An athermal solution is defined as a mixture in which :

- The enthalpy of mixing is zero : $\Delta H_{mix} = 0$.
- However, unlike ideal solutions, the molecules may differ in size or structure.

This means that:

- There are no energetic interactions favoring or opposing mixing.
- Non-ideality arises only from entropy effects, not from enthalpy.

3. Physical Interpretation

In an athermal solution :

- Interactions between molecules are energetically equivalent: $u_{AA} \approx u_{BB} \approx u_{AB}$.
- The system does not release or absorb heat during mixing.
- Deviations from ideality come from :
 - Differences in molecular size.
 - Differences in molecular shape.

4. Gibbs Free Energy of Mixing

The Gibbs free energy of mixing is given by : $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$.

Since : $\Delta H_{mix} = 0$.

We obtain : $\Delta G_{mix} = -T\Delta S_{mix}$.

Therefore :

- ♦ Mixing is driven entirely by entropy.
- ♦ The process is spontaneous if : $\Delta S_{mix} > 0$.

5. Entropy of Mixing

For simple cases (similar to ideal solutions), the entropy of mixing can be approximated by :

$$\Delta S_{mix} = -R(x_1 \ln x_1 + x_2 \ln x_2)$$

However, in athermal solutions this expression may be modified to account for :

- Molecular size differences.
- Segment-based models (e.g., polymers).

6. Activity Coefficients

Even though : $\Delta H_{\text{mix}} = 0$, the solution is not necessarily ideal, meaning : $\gamma_i \neq 1$.

☞ Why ?

Because :

- ☞ Non-ideality arises from combinatorial entropy effects.
- ☞ Larger molecules occupy more space, affecting local composition.

7. Comparison with Ideal and Regular Solutions

Property	Ideal Solution	Regular Solution	Athermal Solution
ΔH_{mix}	0	$\neq 0$	0
ΔS_{mix}	Ideal	Ideal	Non-ideal possible
Molecular size effects	No	No	Yes
Activity coefficients	$= 1$	$\neq 1$	$\neq 1$
Origin of non-ideality	None	Enthalpy	Entropy

8. Applications

The athermal solution model is particularly useful in :

- Polymer solutions.
- Mixtures with large size differences.
- Flory–Huggins theory (special case when interaction parameter $\chi = 0$).
- Understanding entropy-driven mixing.

9. Limitations

- ✎ Assumes no enthalpic contribution, which is rarely true in real systems.
- ✎ Not suitable for :
 - Strongly interacting systems (hydrogen bonding, polarity).
 - Highly non-ideal mixtures.

10. Conclusion

The athermal solution model is a simplified thermodynamic model where :

- ✎ Mixing occurs without heat exchange.
- ✎ Non-ideal behavior arises only from entropy effects.
- ✎ It is especially relevant for systems with large molecular size differences, such as polymers.

Although limited, it provides important insight into the role of entropy in solution thermodynamics.

VII- The Associated Solutions Model

1. Introduction

In real liquid mixtures, especially those involving strong specific interactions such as hydrogen bonding, the behavior often deviates significantly from ideal or regular solution models. The Associated Solutions Model is introduced to describe systems where molecules interact to form temporary complexes (associates) in the liquid phase.

Typical examples : alcohol + water mixtures, carboxylic acids (dimer formation) and systems with hydrogen bonding.

2. Basic Concept

Unlike ideal or regular solutions, this model assumes that :

- Molecules can associate (combine) to form new species.
- These species coexist in chemical equilibrium with free molecules.

General representation : $A + B \rightleftharpoons AB$

Where:

- A and B: original molecules.
- AB: associated complex.

3. Chemical Equilibrium of Association

The formation of associated species is governed by an equilibrium constant :

$$K = \frac{[AB]}{[A][B]}$$

Where:

- [A],[B],[AB] are concentrations (or mole fractions).
- K depends on temperature.

4. Composition of the Mixture

In this model, the mixture contains:

- Free species : A, B.
- Associated species : AB.

Material balance (example for binary system) :

$$x_A^{total} = x_A + x_{AB}$$

$$x_B^{total} = x_B + x_{AB}$$

The total composition differs from the effective composition due to association.

5. Activity Coefficients

The presence of associated species modifies thermodynamic behavior.

The activity coefficient (γ_i) is calculated based on :

- The fraction of free molecules.
- The equilibrium of association.

General idea : $\gamma_i \neq 1$

Because :

- Interactions are no longer random.
- The mixture structure is altered.

6. Thermodynamic Implications

6.1 Enthalpy of Mixing (ΔH_{mix})

- ⇒ Often negative (exothermic).
- ⇒ Due to formation of stable complexes (e.g., hydrogen bonds).

6.2 Entropy of Mixing (ΔS_{mix})

- ⇒ Can be lower than ideal.
- ⇒ Association reduces disorder.

7. Comparison with Other Models

Model	Key Assumption	Limitation
Ideal Solution	No interaction difference	Not realistic
Regular Solution	Energy difference only	No association
Local Composition (Wilson, NRTL)	Local interactions	No explicit complexes
Associated Solution	Formation of complexes	More complex mathematically

8. Applications

The associated solutions model is widely used in:

- ↻ Systems with hydrogen bonding.
- ↻ Polymer solutions.
- ↻ Biochemical systems.
- ↻ Liquid-liquid equilibria (LLE).
- ↻ Highly non-ideal mixtures.

9. Advantages and Limitations

Advantages :

- ✓ Physically meaningful (accounts for real interactions).
- ✓ Explains strong deviations from ideality.

Limitations :

- ✗ Requires identification of association reactions.
- ✗ Needs equilibrium constants (experimental data).
- ✗ Becomes complex for multiple associations.

10. Example : Acetic Acid in Benzene

Acetic acid forms dimers : $2A \rightleftharpoons A_2$

- Strong hydrogen bonding.
- Significant deviation from ideal behavior.
- Vapor phase composition strongly affected.

11. Conclusion

The Associated Solutions Model provides a more realistic description of liquid mixtures where specific interactions lead to the formation of molecular complexes. It bridges the gap between simple thermodynamic models and the actual microscopic structure of solutions.

VIII- Ionic Solutions

1. Introduction

An ionic solution is a solution in which the solute dissociates into ions when dissolved in a solvent, typically water. These solutions are essential in chemistry because they conduct electricity and are involved in many chemical and biological processes.

Examples :

- $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$
- $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
- $\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-$

2. Electrolytes

2.1 Definition

An electrolyte is a substance that produces ions in solution and therefore conducts electricity.

2.2 Types of Electrolytes

Strong Electrolytes :

- Completely dissociate in solution.
- High electrical conductivity.
- Examples : NaCl , HNO_3 , KOH .

Weak Electrolytes :

- Partially dissociate in solution.
- Establish equilibrium between ions and undissociated molecules.
- Examples: CH_3COOH , NH_3 .

3. Degree of Dissociation (α)

The degree of dissociation (α) represents the fraction of solute that dissociates into ions.

$$\alpha = \frac{\text{number of dissociated molecules}}{\text{total number of dissolved molecules}}$$

- $\alpha = 1 \rightarrow$ complete dissociation (strong electrolyte).
- $0 < \alpha < 1 \rightarrow$ partial dissociation (weak electrolyte).

4. Ionic Strength (I)

4.1 Definition

The ionic strength of a solution measures the total concentration of ions, taking into account their charges.

$$I = \frac{1}{2} \sum c_i z_i^2$$

Where:

- c_i : concentration of ion i.
- z_i : charge of ion i.

4.2 Importance

- ❖ Influences activity coefficients.
- ❖ Affects equilibrium constants.
- ❖ Important in electrochemistry and thermodynamics.

5. Activity and Activity Coefficients

5.1 Activity (a)

In ionic solutions, concentration alone is not sufficient. We use activity : $a_i = \gamma_i c_i$.

Where:

- a_i : activity.
- γ_i : activity coefficient.
- c_i : concentration.

5.2 Activity Coefficient (γ)

- Accounts for interactions between ions.
- Depends on ionic strength.

6. Debye–Hückel Theory

Describes how ionic interactions affect activity coefficients in dilute solutions.

Debye–Hückel Limiting Law :

$$\log \gamma_i = -Az_i^2\sqrt{I}$$

Where :

- A: constant (depends on solvent and temperature).
- z_i : ionic charge.
- I: ionic strength.

Validity : Applicable for dilute solutions ($I < 0.01 \text{ mol}\cdot\text{L}^{-1}$).

7. Conductivity of Ionic Solutions

7.1 Electrical Conductivity (κ)

Measures the ability of a solution to conduct electricity.

$$\kappa = \sum \lambda_i c_i$$

Where: λ_i molar conductivity of ion i.

7.2 Molar Conductivity (Λ_m)

$$\Lambda_m = \frac{\kappa}{c}$$

- For strong electrolytes: decreases with concentration.
- For weak electrolytes: increases with dilution.

8. Kohlrausch's Law

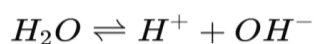
At infinite dilution :

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0$$

Each ion contributes independently to conductivity.

9. Acid–Base Ionic Equilibria

Water Ionization :



$$K_w = [H^+][OH^-]$$

pH Definition :

$$pH = -\log[H^+]$$

10. Applications of Ionic Solutions

- ↗ Electrochemistry (batteries, fuel cells).
- ↗ Biological systems (blood electrolytes).
- ↗ Industrial processes (electrolysis).
- ↗ Environmental chemistry (water treatment).

11. Conclusion

- ↗ Ionic solutions contain mobile charged species.
- ↗ Their behavior deviates from ideality due to electrostatic interactions.
- ↗ Concepts like ionic strength and activity coefficients are essential.
- ↗ The Debye–Hückel theory explains non-ideal behavior in dilute solutions.

Exercise 1 :

Which of the following systems is more likely to show strong local composition effects?

- A) Benzene + Toluene.
- B) Water + Ethanol.
- C) Hexane + Heptane.

Justify your answer.

Solution :

A) Benzene + Toluene $\rightarrow$ nearly ideal (similar size, similar interactions).

B) Water + Ethanol $\rightarrow$ strongly non-ideal :

- hydrogen bonding
- strong A–B interactions
- local enrichment effects

C) Hexane + Heptane $\rightarrow$ almost ideal (similar nonpolar molecules).

Correct answer : B

Strong hydrogen bonding leads to non-random local composition.

Exercise 2 :

In a mixture A + B, it is observed that : $x_{BA}^{(local)} > x_B$. Interpret this result physically.

Solution :

$x_{BA}^{(local)}$: fraction of B molecules around A.

x_B : bulk mole fraction of B.

Since: $x_{BA}^{(local)} > x_B$

Interpretation:

- B molecules are preferentially attracted to A.
- Local environment around A is enriched in B.

This implies:

- ✓ Strong A–B interactions.
- ✓ Non-random molecular distribution.
- ✓ Likely negative deviation from Raoult's law.

Exercise 3 :

A mixture shows $\gamma_A > 1$. What can be inferred about molecular interactions and local composition ?

Solution :

- $\gamma_A > 1$ means positive deviation from Raoult's law.

- Molecules A prefer the vapor phase → weaker interactions in liquid.

Interpretation:

- ✓ A–B interactions are weaker than A–A interactions.
- ✓ Molecules of A are not stabilized in mixture.

Local composition effect :

- ✓ around A, fewer favorable B neighbors.
- ✓ possible self-association or clustering of A.

Exercise 4 : True / False (with justification)

Statements :

1. Local composition is always equal to bulk composition.
2. Hydrogen bonding increases non-ideality.
3. Local composition depends on molecular interactions.

Solutions :

1. False : Only true for ideal solutions.
2. True : Hydrogen bonding creates strong directional interactions.
3. True : Local structure is governed by interaction energies.

Exercise 5 :

For a Margules model with $A=2$, compute γ_2 at $x_2=0.3$.

Answer:

$$x_1 = 0.7$$

$$\ln \gamma_2 = 2(0.7)^2 = 0.98$$

$$\gamma_2 = 2.66$$

Exercise 6 :

Explain why Redlich–Kister is more flexible than Margules.

Answer:

Because it includes polynomial expansion in $(x_1 - x_2)$, allowing higher-order corrections and better fitting of asymmetric experimental data.

Exercise 7 :

State one limitation of Van Laar model.

Answer :

It fails in very dilute regions and lacks molecular interpretation.

Exercise 8 :

Show that when $\Omega=0$, the regular solution reduces to an ideal solution.

Solution

The Gibbs free energy of mixing for a regular solution is :

$$\Delta G_{mix} = x_1 x_2 \Omega + RT(x_1 \ln x_1 + x_2 \ln x_2)$$

If $\Omega=0$, the enthalpy term disappears:

$$\Delta G_{mix} = RT(x_1 \ln x_1 + x_2 \ln x_2)$$

This is exactly the expression for an ideal solution. Also, for activity coefficients :

$$\ln \gamma_1 = \frac{\Omega}{RT} x_2^2 = 0 \Rightarrow \gamma_1 = 1$$

$$\ln \gamma_2 = \frac{\Omega}{RT} x_1^2 = 0 \Rightarrow \gamma_2 = 1$$

Therefore :

- No enthalpy effect.
- Activity coefficients equal to 1.
- Fully ideal behavior.

Conclusion : When $\Omega = 0$, the regular solution becomes an ideal solution.

Exercise 9 :

For a binary system $\Omega = -1500$ J/mol, discuss nature of interactions and deviation from ideality.

Solution

Since : $\Omega < 0 \Rightarrow$ This indicates attractive interactions between unlike molecules (A–B interactions are stronger than A–A and B–B).

Implications

1. Enthalpy of mixing : $\Delta H_{mix} = x_1 x_2 \Omega < 0 \rightarrow$ Exothermic mixing (heat is released).
2. Deviation from ideality:

From :

$$\ln \gamma_1 = \frac{\Omega}{RT} x_2^2$$

Since $\Omega < 0$:

$$\ln \gamma_i < 0 \Rightarrow \gamma_i < 1$$

This corresponds to a negative deviation from Raoult's law.

3. Physical meaning :

- Strong affinity between components.
- Enhanced mixing.
- No phase separation expected.

Conclusion : The system shows attractive interactions, exothermic mixing, and negative deviation from ideality.

Exercise 10 :

Explain why the regular solution model fails for water–alcohol mixtures.

Solution

The regular solution model is based on two key assumptions :

- Random mixing
- No specific interactions (only dispersion forces)

However, in water–alcohol mixtures, these assumptions are violated.

Reasons :

1. Hydrogen bonding :
 - Water and alcohol molecules form strong hydrogen bonds.
 - These are specific, directional interactions.
 - Not accounted for in the model.
2. Association effects : Molecules form structured clusters (not random distribution).
3. Non-ideal entropy :
 - The entropy of mixing is not ideal.
 - Due to structural organization of molecules.
4. Polarity differences :
 - Water is highly polar.
 - Alcohols have both polar (OH) and non-polar parts.

This creates complex interactions beyond the simple parameter Ω .

Exercise 11 :

Explain why the Wilson model cannot predict phase separation.

Solution:

The Wilson model assumes complete miscibility and does not include a mechanism to describe strong repulsive interactions leading to phase splitting. Therefore, it cannot represent liquid-liquid equilibria.

Exercise 12 :

What is the role of the parameter α in the NRTL model?

Solution:

The parameter α controls the degree of non-randomness in the mixture. A higher value indicates stronger deviation from random mixing, improving the model's ability to describe highly non-ideal systems.

Exercise 13 :

Compare the physical meaning of Λ_{ij} (Wilson) and τ_{ij} (NRTL).

Solution:

- Λ_{ij} : incorporates both size and energy effects.

- τ_{ij} : represents normalized interaction energy difference.

Exercise 14 :

Explain the difference between combinatorial and residual contributions.

Answer:

- Combinatorial: accounts for molecular size and shape
- Residual: accounts for intermolecular energy interactions

Exercise 15 :

Why is UNIFAC considered predictive?

Answer:

Because it uses group interaction parameters instead of experimental data for each mixture.

Exercise 16 :

Give two limitations of UNIFAC.

Answer:

- Depends on parameter availability.
- Less accurate for strongly interacting systems.

Exercise 17

Show that mixing is spontaneous in an athermal solution.

Solution :

$$\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}.$$

If : $\Delta S_{\text{mix}} > 0$, then $\Delta G_{\text{mix}} < 0 \rightarrow$ spontaneous mixing.

Exercise 18 :

Why can an athermal solution still be non-ideal?

Solution:

Because molecules may differ in size and shape, leading to non-random mixing and entropy deviations $\rightarrow \gamma_i \neq 1$.

Exercise 19 :

Compare athermal and regular solutions in terms of driving forces.

Solution :

- Athermal : driven by entropy only.
- Regular : driven by enthalpy + entropy.

Exercise 20 :

Explain why ΔH_{mix} is often negative in associated solutions.

Answer:

Because formation of complexes (e.g., hydrogen bonds) releases energy $\rightarrow$ exothermic process.

Exercise 21 :

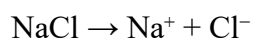
Give two systems where the associated solution model is necessary.

Answer :

- Water–ethanol.
- Acetic acid–benzene.

Exercise 22 :

Calculate the ionic strength of a 0.1 M NaCl solution.

Solution :

$$I = \frac{1}{2}[(0.1)(1)^2 + (0.1)(1)^2] = 0.1$$

Exercise 23 :

Explain why strong electrolytes do not follow ideal solution behavior.

Answer:

Because ions interact through electrostatic forces, which affects their activity. These interactions are not considered in ideal solution models.

I- Vapor–Liquid Equilibria (VLE)

1. Introduction

Vapor–Liquid Equilibrium (VLE) describes the state in which a liquid and its vapor coexist at equilibrium. At this condition, there is no net transfer of mass between phases, even though molecules continuously evaporate and condense. VLE is essential in many chemical engineering processes such as : distillation, absorption, extraction and drying.

2. Phase Equilibrium Condition

At equilibrium, the chemical potential of each component must be equal in both phases :

$$\mu_i^{(liquid)} = \mu_i^{(vapor)}$$

This leads to the fundamental relation :

$$f_i^{(liquid)} = f_i^{(vapor)}$$

where f_i is the fugacity of component i.

3. VLE for Pure Substances

For a pure substance at equilibrium :

$$P = P^{sat}(T)$$

Where :

- P^{sat} = saturation pressure.
- Depends only on temperature.

Clausius–Clapeyron Equation

$$\frac{d \ln P^{sat}}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

This equation describes how vapor pressure changes with temperature.

4. VLE in Binary Mixtures

4.1 Raoult's Law (Ideal Solutions)

For ideal solutions :

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

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

where:

- x_i : mole fraction in liquid.
- P_i^{sat} : vapor pressure of pure component.

Dalton's Law

$$y_i = \frac{P_i}{P}$$

where y_i is the mole fraction in the vapor phase.

5. Non-Ideal Solutions

Real mixtures often deviate from ideal behavior.

Modified Raoult's Law

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

Where :

- γ_i : activity coefficient.
- Accounts for molecular interactions.

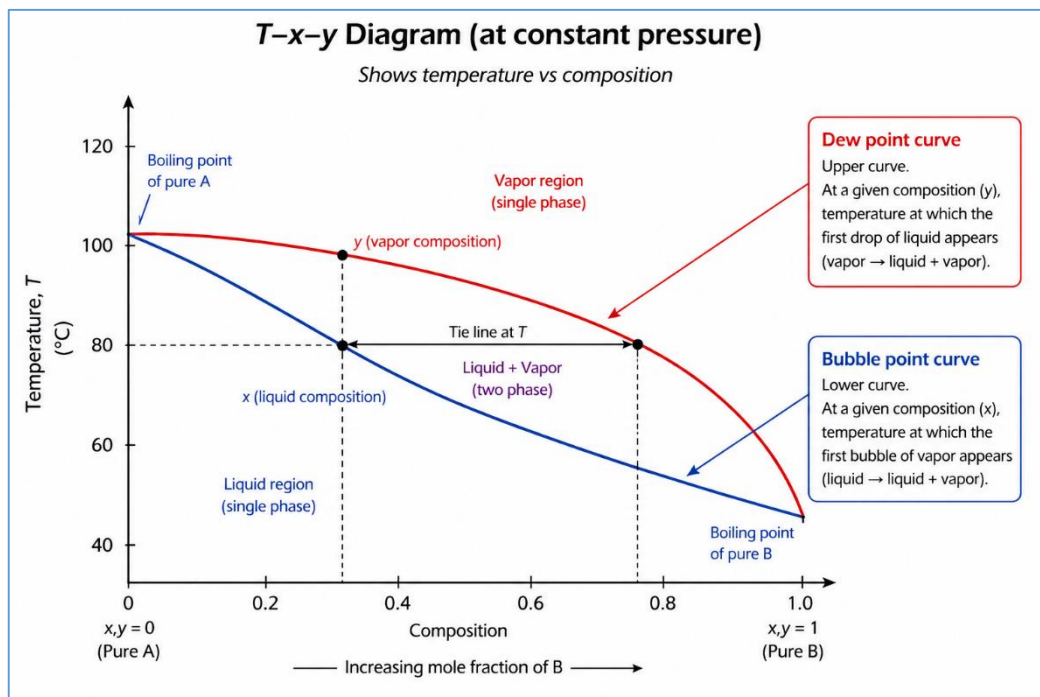
Interpretation :

- $\gamma_i > 1$: positive deviation.
- $\gamma_i < 1$: negative deviation.

6. VLE Diagrams

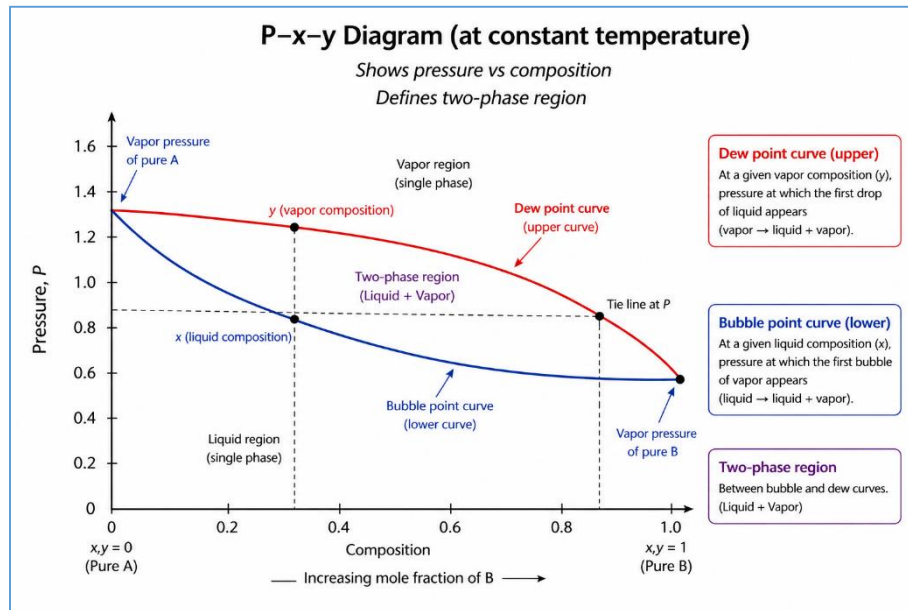
6.1 T–x–y Diagram (at constant pressure)

- Shows temperature vs composition.
- Two important curves : bubble point curve and dew point curve.



6.2 P–x–y Diagram (at constant temperature)

- Shows pressure vs composition
- Defines two-phase region



7. Bubble Point and Dew Point

Bubble Point : Temperature (or pressure) at which the first bubble of vapor appears.

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

Dew Point : Condition where the first drop of liquid forms.

$$\sum \frac{y_i P}{P_i^{sat}} = 1$$

8. Azeotropes

An azeotrope is a mixture that behaves like a pure substance during phase change.

Types :

- Minimum boiling azeotrope (positive deviation).
- Maximum boiling azeotrope (negative deviation).

At azeotropic composition : $x_i = y_i$.

9. Flash Distillation (Basic Concept)

A liquid mixture is partially vaporized, producing :

- Vapor phase enriched in more volatile components.
- Liquid phase enriched in less volatile components.

Mass balances :

$$F = V + L \text{ (total mass balance)}$$

$$Fz_i = Vy_i + Lx_i \text{ (component i mass balance)}$$

F : Feed flow rate (total amount of mixture entering the system).

V : Vapor flow rate (amount of vapor produced after flashing).

L : Liquid flow rate (amount of remaining liquid after flashing).

z_i : Mole fraction of component i in the feed.

y_i : Mole fraction of component i in the vapor phase.

x_i : Mole fraction of component i in the liquid phase.

10. Applications of VLE

VLE data are used in :

- ⇒ Distillation column design.
- ⇒ Petrochemical industry.
- ⇒ Separation of air (cryogenic distillation).
- ⇒ Environmental engineering.

11. Limitations and Models

For accurate predictions, models are used : Margules, Van Laar, Wilson, NRTL and UNIQUAC. These models estimate activity coefficients γ_i .

12. Conclusion

Vapor–Liquid Equilibria are fundamental for understanding phase behavior and designing separation processes. While ideal models provide a first approximation, real systems require activity coefficient models for accurate predictions.

II- Liquid–Liquid and Liquid–Liquid–Vapor Equilibria

1. Introduction

In multicomponent systems, different phases may coexist depending on temperature, pressure, and composition. While vapor–liquid equilibrium (VLE) is widely studied, many industrial and natural processes involve :

- Liquid–Liquid Equilibrium (LLE) : coexistence of two immiscible or partially miscible liquid phases.
- Liquid–Liquid–Vapor Equilibrium (LLVE) : coexistence of two liquid phases and one vapor phase.

These equilibria are essential in separation processes such as extraction, distillation, and purification.

2. Liquid–Liquid Equilibrium (LLE)

2.1 Definition

LLE occurs when a liquid mixture separates into two distinct liquid phases :

- Phase α (rich in component A).
- Phase β (rich in component B).

This happens when components are partially miscible or immiscible.

2.2 Thermodynamic Condition of Equilibrium

At equilibrium, the chemical potential of each component must be equal in both phases :

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

Using activity coefficients :

$$x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta$$

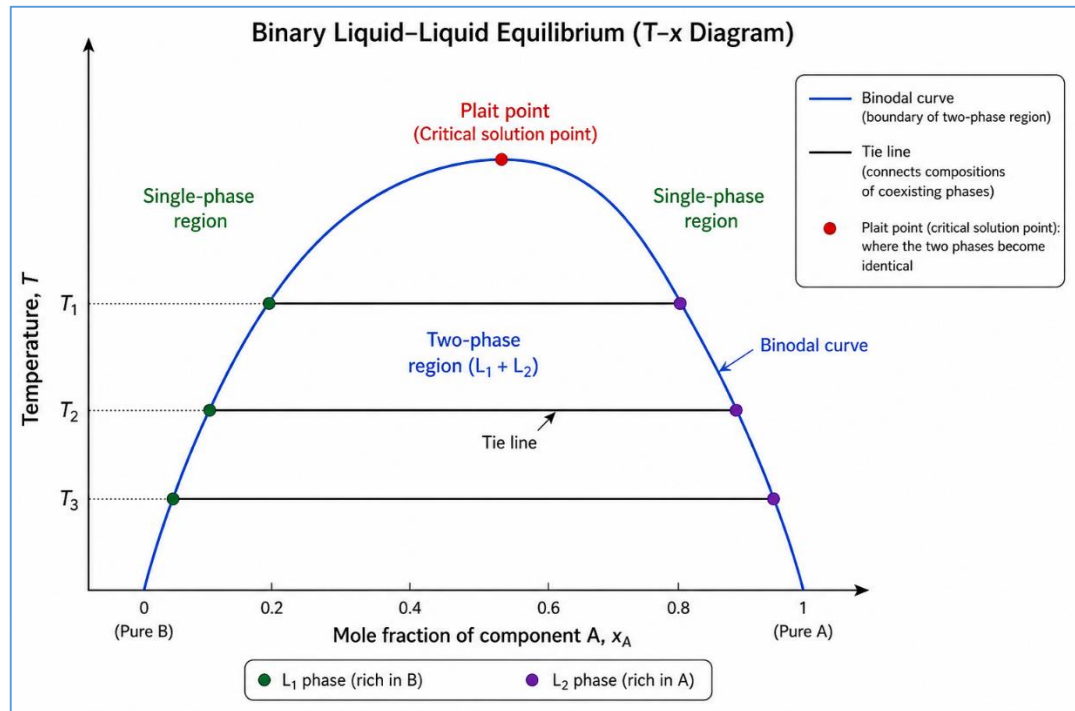
Where :

- x_i : mole fraction
- γ_i : activity coefficient

2.3 Phase Diagram (T–x or x–x diagram)

A typical binary LLE diagram shows :

- Binodal curve : boundary of the two-phase region.
- Tie lines : connect compositions of coexisting phases.
- Plait point (critical solution point) : point where phases become identical.



2.4 Types of Miscibility

↻ *Partial miscibility* : Two phases form at certain compositions.

Example: water + organic solvent.

↻ *Complete miscibility* : Only one liquid phase.

↻ *Immiscibility* : Always two phases.

2.5 Critical Solution Temperature

✓ *UCST (Upper Critical Solution Temperature)*: above this temperature → single phase.

✓ *LCST (Lower Critical Solution Temperature)*: below this temperature → single phase.

2.6 Lever Rule in LLE

Used to determine phase proportions :

$$\frac{n_\alpha}{n_\beta} = \frac{x^\beta - z}{z - x^\alpha}$$

Where : z overall composition.

2.7 Applications of LLE

- ⊗ Liquid-liquid extraction.
- ⊗ Separation of organic compounds.
- ⊗ Pharmaceutical purification.
- ⊗ Environmental remediation.

3. Liquid-Liquid-Vapor Equilibrium (LLVE)

3.1 Definition

LLVE occurs when three phases coexist simultaneously : liquid phase α , liquid phase β and vapor phase V.

3.2 Equilibrium Conditions

For each component i :

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

This leads to :

$$x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta = y_i \phi_i$$

Where :

- y_i : vapor mole fraction.
- ϕ_i : fugacity coefficient.

3.3 Gibbs Phase Rule

$$F = C - P + 2$$

For LLVE : C=2, P=3.

$$F=2-3+2=1$$

→ Only one degree of freedom.

→ If temperature is fixed, pressure is determined (or vice versa).

3.4 Azeotropes and Heterogeneous Azeotropes

LLVE is often associated with heterogeneous azeotropes, where :

- Vapor is in equilibrium with two immiscible liquid phases.
- Common in systems like water + organic solvent.

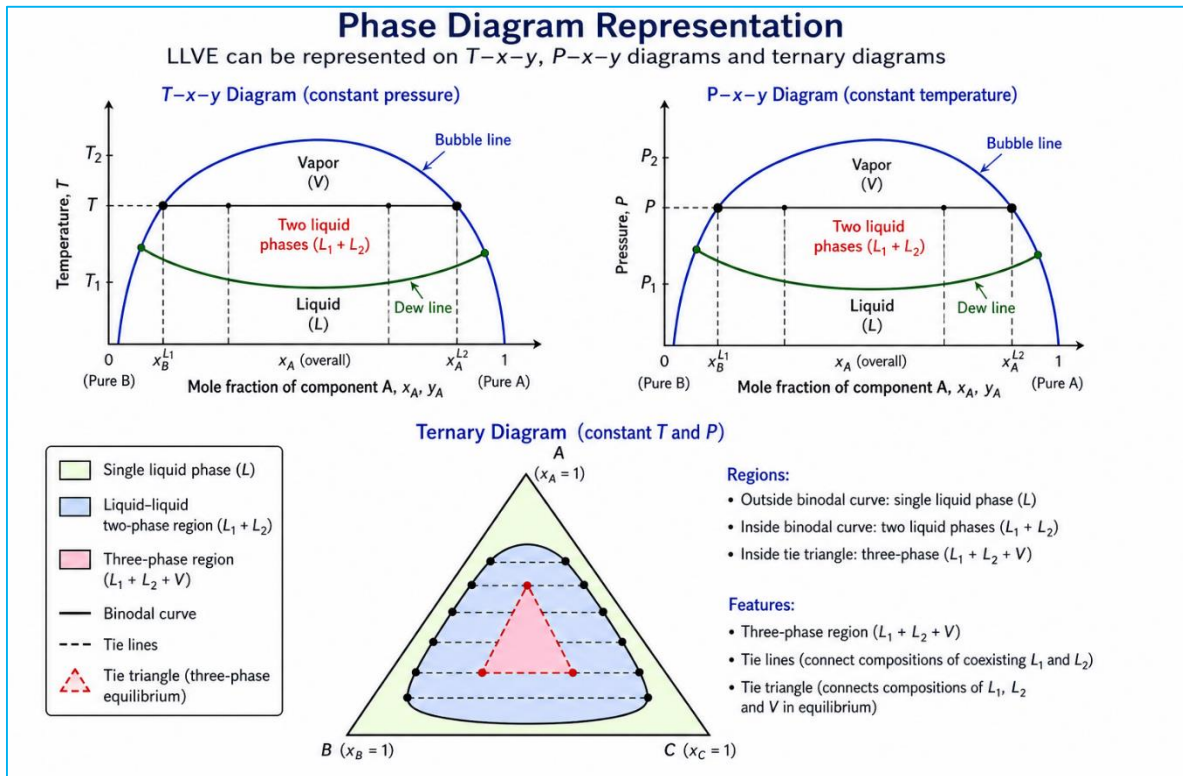
3.5 Phase Diagram Representation

LLVE can be represented on :

- **T-x-y diagrams**
- **P-x-y diagrams**
- **Ternary diagrams** (for three-component systems)

Features include :

- Three-phase region
- Tie triangles (in ternary systems)



3.6 Industrial Applications

- Azeotropic distillation.
- Heterogeneous distillation.
- Separation of water-organic mixtures.
- Petrochemical processes.

4. Modeling of LLE and LLVE

To describe non-ideal behavior, activity coefficient models are used : Margules, Van Laar, NRTL (Non-Random Two-Liquid), UNIQUAC, UNIFAC.

These models predict :

- Phase compositions.
- Tie lines.
- Phase boundaries.

5. Comparison : LLE vs LLVE

Feature	LLE	LLVE
Number of phases	2 liquids	2 liquids + 1 vapor
Equilibrium condition	$\mu_i^\alpha = \mu_i^\beta$	$\mu_i^\alpha = \mu_i^\beta = \mu_i^V$
Complexity	Moderate	Higher
Applications	Extraction	Distillation + extraction

6. Conclusion

Liquid–liquid and liquid–liquid–vapor equilibria play a crucial role in chemical engineering and separation processes. Unlike ideal systems, these equilibria require the use of activity coefficient models to describe non-ideal interactions. Understanding phase diagrams, equilibrium conditions, and thermodynamic models allows engineers and chemists to design efficient separation techniques.

III- Solid–Liquid Equilibria in Binary Systems

1. Introduction

Solid–liquid equilibrium (SLE) describes the coexistence between solid and liquid phases in a mixture at equilibrium. In binary systems (two components), SLE is essential for understanding:

- ✓ Crystallization processes.
- ✓ Purification of substances.
- ✓ Alloy formation.
- ✓ Pharmaceutical formulations.

At equilibrium, the chemical potential of each component is the same in both phases.

2. Basic Concepts

- *Binary System* : A binary system contains two components, usually denoted as A and B.
- *Phase* : A phase is a homogeneous, physically and chemically uniform part of a system.
- *Degrees of Freedom (Gibbs Phase Rule)* : $F = C - P + 2$.

For binary systems ($C = 2$) : $F = 4 - P$.

At constant pressure : $F = 3 - P$.

3. Types of Solid–Liquid Phase Diagrams

3.1 Simple Eutectic System

This is the most common type of binary SLE diagram.

Characteristics :

- Complete miscibility in the liquid phase.
- No solid solubility (solids are pure A or pure B).
- Presence of a eutectic point.

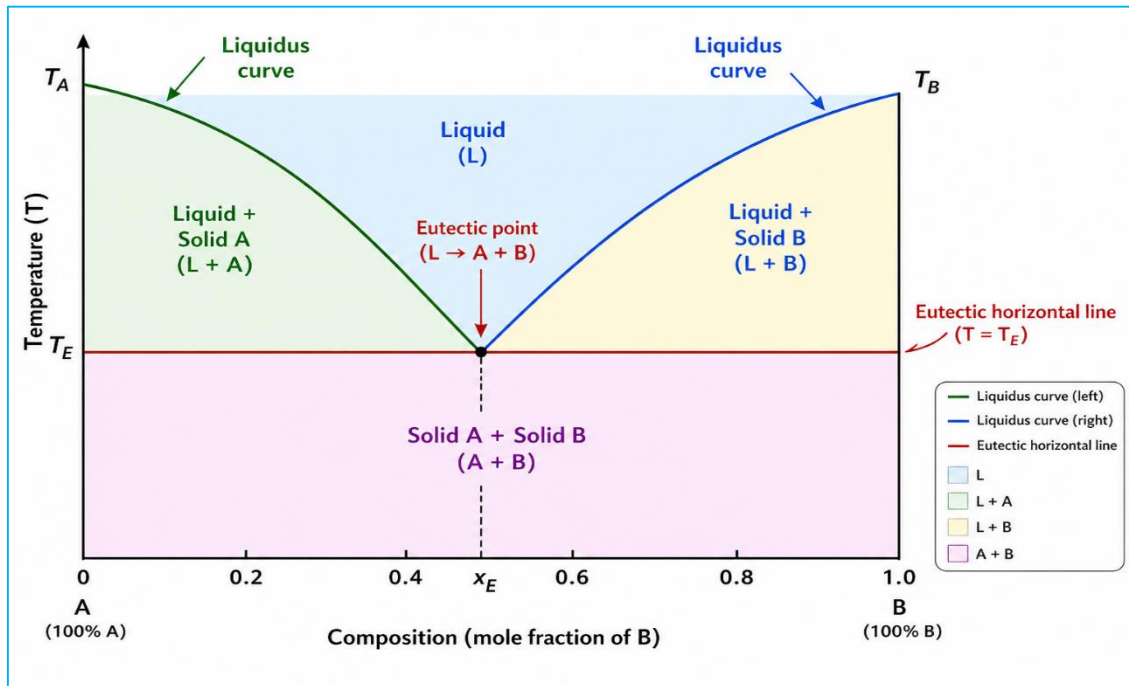
Eutectic Point :

- Lowest temperature at which the liquid phase can exist.
- At this point :
 - Liquid transforms into two solid phases simultaneously
 - Reaction : $L \rightarrow A(s) + B(s)$.

Diagram Features :

- Two liquidus curves.
- One eutectic horizontal line.
- Three regions :
 - Liquid (L).
 - Liquid + solid A (L + A).

- Liquid + solid B (L + B).
- Solid A + solid B below eutectic.



3.2 Lever Rule

Used to determine phase proportions in two-phase regions. For a mixture :

$$\text{Fraction of phase} = \frac{\text{opposite segment length}}{\text{total tie line length}}$$

3.3 Systems with Solid Solubility

Partial Solid Solubility :

- * Components dissolve partially in each other in solid state.
- * Formation of solid solutions (α , β phases).

Complete Solid Solubility :

- * Single solid phase forms (like alloys).
- * Example : isomorphous systems.

3.4 Peritectic System

Peritectic Reaction : $L + A(s) \rightarrow B(s)$

Occurs at a specific temperature and composition.

4. Thermodynamic Description

At equilibrium :

$$\mu_i^{\text{solid}} = \mu_i^{\text{liquid}}$$

The melting behavior depends on : enthalpy of fusion, temperature and composition.

For ideal solutions, the liquidus line can be approximated by :

$$\ln x_i = -\frac{\Delta H_{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)$$

Where :

- x_i : mole fraction.
- T_m : melting temperature of pure component.
- ΔH_{fus} : enthalpy of fusion.

5. Phase Diagram Interpretation

- *Liquidus curve* : boundary above which the system is fully liquid.
- *Solidus curve* : boundary below which the system is fully solid.
- *Eutectic point* : invariant point ($F = 0$).
- *Tie lines* : horizontal lines connecting coexisting phases.

6. Applications

Solid–liquid equilibrium is widely used in :

- ∞ Crystallization processes (purification of chemicals).
- ∞ Metallurgy (alloy design).
- ∞ Pharmaceutical industry (drug stability and formulation).
- ∞ Food industry (fat crystallization, chocolate production).

7. conclusion

Solid–liquid equilibria in binary systems describe how mixtures behave during cooling and solidification. The most important features include eutectic points, phase boundaries, and phase compositions. Understanding these diagrams is essential for many industrial and scientific applications.

IV- Solubility of Gases in Liquids

1. Introduction

The solubility of gases in liquids is a fundamental topic in physical chemistry and chemical engineering. It describes how a gas dissolves in a liquid to form a homogeneous solution.

This phenomenon is essential in many natural and industrial processes such as :

- ∞ Carbonation of beverages.
- ∞ Gas exchange in biological systems (O₂ and CO₂ in blood).
- ∞ Water treatment and environmental chemistry.
- ∞ Industrial gas absorption processes.

Gas solubility depends mainly on pressure, temperature, and the nature of the gas and solvent.

2. Henry's Law

At constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

$$C = k_H P$$

Where:

- C: concentration of dissolved gas (mol·L⁻¹).
- P: partial pressure of the gas (atm or Pa).
- k_H : Henry's constant (depends on gas, solvent, temperature).

Alternative forms :

$$P = k'_H x$$

Where:

- x : mole fraction of gas in liquid.
- k'_H : Henry constant in pressure form.

3. Physical Interpretation

- * A higher pressure increases gas solubility.
- * A higher Henry's constant means lower solubility (gas is less soluble).
- * Each gas has its own specific solubility behavior in a given solvent.

4. Effect of Temperature

Gas solubility in liquids generally decreases with increasing temperature.

Explanation:

- Dissolution of gases is usually exothermic.
- Increasing temperature shifts equilibrium to release gas (Le Chatelier's principle).

Practical consequence:

- Warm water contains less dissolved oxygen than cold water.
- Carbonated drinks lose CO₂ faster at higher temperatures.

5. Effect of Pressure

According to Henry's law:

- Increasing pressure → increases gas solubility.
- Decreasing pressure → gas escapes from solution.

Example :

- Deep-sea conditions : high pressure → more dissolved gases in seawater.
- Opening a soda bottle reduces pressure → CO₂ escapes as bubbles.

6. Nature of Gas and Solvent

Gas solubility depends on intermolecular interactions :

6.1 Nonpolar gases

- O₂, N₂, CH₄.
- Weak interactions → low solubility in water.

6.2 Polar or reactive gases

- NH₃, HCl, CO₂.
- Higher solubility due to :
 - Hydrogen bonding
 - Chemical reactions with water (e.g., CO₂ → H₂CO₃).

7. Thermodynamic Aspect

Gas dissolution can be described by Gibbs free energy :

$$\Delta G = \Delta H - T\Delta S$$

- If $\Delta G < 0$ → spontaneous dissolution.
- Temperature influences entropy and enthalpy contributions.

8. Deviations from Henry's Law

Henry's law is valid for :

- ✓ Dilute solutions.
- ✓ Low gas pressure.
- ✓ No chemical reaction between gas and solvent.

Deviations occur when :

- ❖ Gas reacts with solvent (CO₂ in water).
- ❖ High pressure conditions.
- ❖ Strong solute–solvent interactions.

9. Applications

9.1 Environmental Chemistry

- ↻ Oxygen solubility in rivers and oceans.
- ↻ CO₂ absorption in seawater (climate regulation).

9.2 Biology

- ↻ Oxygen transport in blood (hemoglobin enhances solubility).
- ↻ Carbon dioxide removal via respiration.

9.3 Industrial Processes

- ↻ Gas absorption towers (removal of pollutants).
- ↻ Ammonia production processes.
- ↻ Carbonation of beverages.

9.4 Medical Applications

- ↻ Gas embolism in divers (decompression sickness).
- ↻ Oxygen therapy systems.

10. conclusion

- ☞ Gas solubility follows Henry's law at low concentrations.
- ☞ Solubility increases with pressure.
- ☞ Solubility decreases with temperature.
- ☞ Chemical interactions strongly affect solubility.
- ☞ Many real systems deviate from ideal behavior.

Exercise 1 :

A binary mixture contains :

- $x_A = 0.4, x_B = 0.6.$
- $P_A^{sat} = 80 \text{ kPa}, P_B^{sat} = 40 \text{ kPa}$

Question : Calculate total pressure and vapor composition.

Solution :

$$P = (0.4)(80) + (0.6)(40) = 32 + 24 = 56 \text{ kPa}$$

$$y_A = \frac{0.4 \times 80}{56} = 0.571$$

$$y_B = 1 - 0.571 = 0.429$$

Exercise 2

Explain the difference between bubble point and dew point.

Solution :

- Bubble point : first vapor forms from liquid.
- Dew point : first liquid forms from vapor.

Exercise 3

What does $\gamma_i > 1$ indicate ?

Solution :

It indicates positive deviation from Raoult's law, meaning weaker interactions between unlike molecules.

Exercise 4 :

At equilibrium, a binary system satisfies :

- $x_A^\alpha = 0.7, \gamma_A^\alpha = 1.5$
- $x_A^\beta = 0.3, \gamma_A^\beta = ?$

Question: Find γ_A^β

Solution :

Equilibrium condition : $x_A^\alpha \gamma_A^\alpha = x_A^\beta \gamma_A^\beta$

Substitute :

$$0.7 \times 1.5 = 0.3 \times \gamma_A^\beta$$

$$1.05 = 0.3 \gamma_A^\beta$$

$$\gamma_A^\beta = \frac{1.05}{0.3} = 3.5$$

Exercise 4:

A binary system exhibits liquid–liquid–vapor equilibrium (LLVE).

Question : Determine the number of degrees of freedom.

Solution :

Gibbs phase rule : $F = C - P + 2$.

Where :

- $C = 2$ (components).
- $P = 3$ (phases: $L\alpha$, $L\beta$, V)

$$\Rightarrow F = 2 - 3 + 2 = 1$$

Exercise 5 :

A mixture lies inside the binodal curve of an LLE diagram.

Question:

- How many phases are present?
- What happens to the system?

Solution :

- Inside the binodal curve $\rightarrow$ two-phase region
- The mixture splits into :
 - Phase α (A-rich)
 - Phase β (B-rich)

Compositions are given by tie-line endpoints.

Exercise 6 :

A binary mixture is cooled from the liquid state. What happens when it reaches the eutectic temperature?

Answer:

At the eutectic temperature, the remaining liquid transforms simultaneously into two solid phases (A and B). The system becomes fully solid below this temperature.

Exercise 7:

A binary system A–B exhibits a simple eutectic behavior. The eutectic point is at :

- Composition : $x_B = 0.40$
- Temperature : $T_E = 500$ K

Questions :

1. Identify the phases present at :

(a) $x_B = 0.20$, $T = 550$ K.

(b) $x_B = 0.20$, $T=480$ K.

(c) $x_B = 0.40$, $T=500$ K.

What happens when a liquid of composition $x_B = 0.40$ is cooled slowly ?

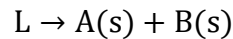
Solution :

1. (a) Above the liquidus $\rightarrow$ Liquid (L).

(b) Below eutectic temperature $\rightarrow$ Solid A + Solid B (A + B).

(c) At eutectic point $\rightarrow$ L + A + B (invariant equilibrium).

2. At $x_B = 0.40$, the system is exactly at the eutectic composition. On cooling :



The liquid solidifies completely at constant temperature into a mixture of two solids.

Exercise 8:

At $T = 520$ K, a mixture with $x_B = 0.30$ lies in the region (L + A).

From the phase diagram :

- Composition of liquid: $x_B^L = 0.45$.
- Composition of solid A: $x_B^A = 0.05$.

Questions :

1. Calculate the fraction of liquid.
2. Calculate the fraction of solid A.

Solution :

Using the lever rule :

$$f_L = \frac{x_B - x_B^A}{x_B^L - x_B^A}$$

$$f_L = \frac{0.30 - 0.05}{0.45 - 0.05} = \frac{0.25}{0.40} = 0.625$$

$$f_A = 1 - f_L = 0.375$$

★ Liquid fraction = 0.625 (62.5%).

★ Solid A fraction = 0.375 (37.5%).

Exercise 9 :

For a component A :

- $\Delta H_{fus} = 10\,000$ J/mol.
- $T_m = 600$ K.

Calculate the liquidus temperature at $x_A = 0.80$.

Solution :

From :

$$\ln x_i = -\frac{\Delta H_{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)$$

we will have :

$$\ln(0.80) = -0.223$$

$$-0.223 = -\frac{10000}{8.314} \left(\frac{1}{T} - \frac{1}{600} \right)$$

$$-0.223 = -1202 \left(\frac{1}{T} - 0.001667 \right)$$

$$0.223 = 1202 \left(\frac{1}{T} - 0.001667 \right)$$

$$\frac{1}{T} - 0.001667 = \frac{0.223}{1202} = 1.85 \times 10^{-4}$$

$$\frac{1}{T} = 0.001667 + 0.000185 = 0.001852$$

$$T = 540 \text{ K}$$

Exercise 10 :

A gas has a Henry constant $k_H = 1.2 \times 10^{-3} \text{ mol.L}^{-1} \cdot \text{atm}^{-1}$.

Calculate the concentration when the gas pressure is 5 atm.

Solution :

$$C = k_H \times P$$

$$C = (1.2 \times 10^{-3}) \times 5$$

$$C = 6 \times 10^{-3} \text{ mol L}^{-1}.$$

Bibliography

1. Atkins, P. and de Paula, J., 2014. *Physical Chemistry*. 10th ed. Oxford: Oxford University Press.
2. Callen, H.B., 1985. *Thermodynamics and an Introduction to Thermostatistics*. 2nd ed. New York: Wiley.
3. Prausnitz, J.M., Lichtenthaler, R.N. and Azevedo, E.G., 1999. *Molecular Thermodynamics of Fluid-Phase Equilibria*. 3rd ed. Upper Saddle River: Prentice Hall.
4. Smith, J.M., Van Ness, H.C. and Abbott, M.M., 2005. *Introduction to Chemical Engineering Thermodynamics*. 7th ed. New York: McGraw-Hill.
5. Çengel, Y.A. and Boles, M.A., 2015. *Thermodynamics: An Engineering Approach*. 8th ed. New York: McGraw-Hill.
6. Koretsky, M.D., 2012. *Engineering and Chemical Thermodynamics*. 2nd ed. Hoboken: Wiley.
7. McQuarrie, D.A., 1973. *Statistical Thermodynamics*. New York: Harper & Row.
8. Gaskell, D.R., 2008. *Introduction to the Thermodynamics of Materials*. 5th ed. New York: Taylor & Francis.
9. Robinson, R.A. and Stokes, R.H., 1959. *Electrolyte Solutions*. 2nd ed. London: Butterworths.
10. Sandler, S.I., 2006. *Chemical and Engineering Thermodynamics*. 4th ed. Hoboken: Wiley.
11. Denbigh, K., 1981. *The Principles of Chemical Equilibrium*. 4th ed. Cambridge: Cambridge University Press.
12. Rock, P.A., 1983. *Chemical Thermodynamics*. Mill Valley: University Science Books.
13. Dill, K.A. and Bromberg, S., 2010. *Molecular Driving Forces: Statistical Thermodynamics in Chemistry and Biology*. 2nd ed. New York: Garland Science.
14. Reif, F., 1965. *Fundamentals of Statistical and Thermal Physics*. New York: McGraw-Hill.
15. Matsoukas, T., 2013. *Fundamentals of Chemical Engineering Thermodynamics*. Upper Saddle River: Prentice Hall.
16. Wilson, G.M., 1964. Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing. *Journal of the American Chemical Society*, 86(2), pp.127–130.
17. Renon, H. and Prausnitz, J.M., 1968. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE Journal*, 14(1), pp.135–144.
18. Abrams, D.S. and Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy. *AIChE Journal*, 21(1), pp.116–128.

19. Fredenslund, A., Jones, R.L. and Prausnitz, J.M., 1975. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE Journal*, 21(6), pp.1086–1099.
20. Debye, P. and Hückel, E., 1923. The theory of electrolytes. I. Lowering of freezing point and related phenomena. *Physikalische Zeitschrift*, 24, pp.185–206.