MME231: Lecture 16

# Thermodynamics of Solutions

## Partial Molar Properties

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# Today's Topics

- Composition of solutions
- Partial molar properties

# Introduction

- Materials of practical applications are either:
  - **mixtures of metals** (alloys), or
  - **mixture of compounds** (slags, mattes, glasses, ceramics)

- When mixed, materials can exist either as separate **mixtures** of several components, or as **solutions**.

- During mixing, changes in chemical composition can occur in either of the following two ways:

  **1.** **Transfer of atoms** or molecules across the boundary (during the formation of multi-component, homogeneous non-reacting systems, also known as the solutions)

  **2.** Occurrence of **chemical reactions** within the boundary (in the multi-component, reactive systems)

- A solution is a **homogeneous phase** composed of two or more chemical substances, whose concentration may be varied without the precipitation of a new phase.

- Formed as a result of physical mixing involving:
  - **intermolecular interactions** in such a way that the molecules maintain their individual identity.

- Nearly all substances of metallurgical interest are solutions.

- The thermodynamic properties of a component in solution are significantly different from the properties of that component when it is pure.

- Some basic concepts in thermodynamics of solution include:
  - concept of **activity**
  - concept of **free energy of mixing**

# Composition of Solutions

- Number of moles of component k ($n_k$) and mole fraction ($X_k$)

$$X_k = \frac{n_k}{n_T}$$

- Weight percentage of component k (wt.% k)

$$\text{wt.\% k} = \frac{w_k}{w_T} \times 100$$

- Molality of solute k in solution, $m_k$

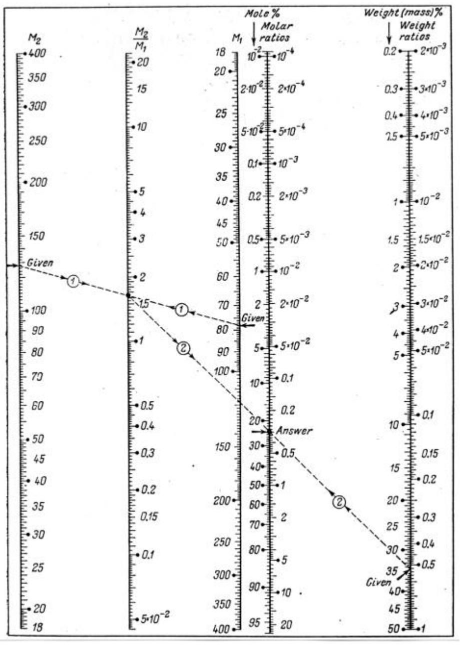
$$m_k = \frac{n_k}{w_0} \times 1000 = \frac{1000\, n_k}{M_0 n_0}$$

*$n_k$ = gram moles of solute k*
*$w_0$ = gram of solvent*
*$n_0$ = gram moles of solvent*
*$M_0$ = molecular weight of solvent*

- Molarity of solute k in solution, $c_k$

$$c_k = \frac{n_k}{V}$$

*V volume of solution in litres*




## Use of Nomogram

### Example 6.2

The solubility of naphthalene ($C_{10}H_8$) in benzene ($C_6H_6$) at 20 C is 34.3 wt.%. Find its mole fraction.

**Answer:**

1. Connect the point corresponds to the molecular weight of naphthalene, $M_2$=128 (the first scale on the left) to the point corresponds to the molecular weight of benzene, $M_1$=78 (the third scale from the left).
2. The line gives the ratio $M_2/M_1$ on the second scale.
3. Now connecting this point to the point 34.3 wt.% on the fifth scale (i.e., the rightmost scale) will give the desired mole fraction 24 mole % (or, $X_2$=0.24) on the fourth scale.

# Partial Molar Properties

- How can we express the molar properties of a component in solution?
- For single component systems, volume occupies by two moles of oxygen at 298 K and 1 atm is exactly twice that occupies by one mole under the same conditions, i.e., **V = V'/ n**.
- What is the molar volume of each of the components **present in solution**?
- We can measure this by adding a very small quantity of a component in solution without significantly changing the overall composition of the solution and then converting the measured change in volume to one mole of the component being added.

- For a multi-component system, V is a function not only of T and P (as in one-component system) but also of the number of moles of each component in the system ($n_1$, $n_2$, ….., $n_C$).

$$V' = V'(T, P, n_1, n_2, \ldots, n_C)$$

- For an arbitrary infinitesimal change in state

$$dV' = \left(\frac{\partial V'}{\partial T}\right)_{P, n_k} dT + \left(\frac{\partial V'}{\partial P}\right)_{T, n_k} dP$$
$$+ \left(\frac{\partial V'}{\partial n_1}\right)_{P, T, n_2, n_3, \ldots, n_C} dn_1 + \left(\frac{\partial V'}{\partial n_2}\right)_{P, T, n_1, n_3, \ldots, n_C} dn_2 + \ldots$$
$$+ \left(\frac{\partial V'}{\partial n_C}\right)_{P, T, n_1, n_2, \ldots, n_{C-1}} dn_C$$

$$dV' = \left(\frac{\partial V'}{\partial T}\right)_{P,\, n_k} dT + \left(\frac{\partial V'}{\partial P}\right)_{T,\, n_k} dP + \sum_{K=1}^{C} \left(\frac{\partial V'}{\partial n_k}\right)_{P,\, T,\, n_j \neq n_k} dn_k$$

- The coefficient of each of the changes in number of moles

$$\overline{V}_k \equiv \left(\frac{\partial V'}{\partial n_k}\right)_{P,\, T,\, n_j \neq n_k} \qquad (k = 1, 2, 3, .... C)$$

- These quantities are defined to be the **partial molar volumes** for each component in the system.

***It represents the rate of change of volume with respect to addition of substance k and is equal to the increase in volume resulting the addition of one mole of k to an infinite amount of all the components in the system without significantly altering the overall composition of the system.***

$$dV' = \left(\frac{\partial V'}{\partial T}\right)_{P,\, n_k} dT + \left(\frac{\partial V'}{\partial P}\right)_{T,\, n_k} dP + \sum_{K=1}^{C} \left(\frac{\partial V'}{\partial n_k}\right)_{P,\, T,\, n_j \neq n_k} dn_k$$

- For any extensive variable Z',

$$dZ' = MdT + NdP + \sum_{K=1}^{C} \overline{Z}_k \, dn_k$$

where the partial molar property of Z of component k

$$\overline{Z}_k \equiv \left(\frac{\partial Z'}{\partial n_k}\right)_{P,\, T,\, n_j \neq n_k} \qquad (k = 1, 2, 3, .... C)$$

**Self-Assessment Question 6.2**
Write an expression for the partial molar Gibbs free energy of component A in the A-B binary solution.

## General Properties of Partial Molar Properties

① $$Z' = n_1\bar{Z}_1 + n_2\bar{Z}_2 + \dots + n_C\bar{Z}_C = \sum_{K=1}^{C} n_k \bar{Z}_k$$

- Dividing both sides with the total number of moles, $n_T$

$$Z = X_1\bar{Z}_1 + X_2\bar{Z}_2 + \dots + X_C\bar{Z}_C = \sum_{K=1}^{C} X_k \bar{Z}_k$$

$Z = Z'/n_T$
$X_k = n_k/n_T$

- Differentiating completely

② $$dZ = \sum_{K=1}^{C} (X_k\, d\bar{Z}_k + \bar{Z}_k\, dX_k)$$

$$dZ' = MdT + NdP + \sum_{K=1}^{C} \bar{Z}_k\, dn_k$$

- At constant T and P

③ $$dZ' = \sum_{K=1}^{C} \bar{Z}_k\, dn_k \quad \text{and} \quad dZ = \sum_{K=1}^{C} \bar{Z}_k\, dX_k$$

- Since $$dZ = \sum_{K=1}^{C} (X_k\, d\bar{Z}_k + \bar{Z}_k\, dX_k)$$

④ $$\sum_{K=1}^{C} X_k\, d\bar{Z}_k = 0$$ (At constant T and P) **Gibbs-Duhem Equation**

- Each of the four categories of relationships developed earlier for the **total properties** of system between the various state functions (the laws, definitions, coefficient relations, and Maxwell relations) are applicable also to the **partial molar properties** of the component of a system.

⑤

$$\overline{H}_k = \overline{U}_k + P\overline{V}_k$$

$$\overline{G}_k = \overline{H}_k - T\overline{S}_k$$

$$\left(\frac{\partial \overline{G}_k}{\partial P}\right)_{T,\,n_k} = \overline{V}_k$$

$$d\overline{G}_k = -\overline{S}_k dT + \overline{V}_k dP$$

$$\left(\frac{\partial \overline{G}_k}{\partial T}\right)_{P,\,n_k} = -\,\overline{S}_k$$

## Evaluation of Partial Molar Properties

**Two methods:**

**1.** Measurements of the partial molar properties from the total properties of the solution.

$$\mathbf{Z \Rightarrow \overline{Z}_k}$$

**2.** Measurements of the partial molar properties of one component knowing the partial molar properties of another.

$$\mathbf{\overline{Z}_1 \Rightarrow \overline{Z}_2}$$

## Partial molar properties from the total molar properties

$$Z = \sum_{K=1}^{C} \bar{Z}_k X_k = \bar{Z}_1 X_1 + \bar{Z}_2 X_2$$

$$Z = \bar{Z}_1 X_1 + X_2 \left( \bar{Z}_1 + \frac{dZ}{dX_2} \right)$$

$$Z = \bar{Z}_1 \left( X_1 + X_2 \right) + X_2 \left( \frac{dZ}{dX_2} \right)$$

$$Z = \bar{Z}_1 + X_2 \left( \frac{dZ}{dX_2} \right)$$

$$dZ = \bar{Z}_1 \, dX_1 + \bar{Z}_2 \, dX_2$$

$$X_1 + X_2 = 1$$

$$dX_1 = - dX_2$$

$$dZ = ( \bar{Z}_2 - \bar{Z}_1 ) \, dX_2$$

$$\bar{Z}_2 = \bar{Z}_1 + \frac{dZ}{dX_2}$$

$$\bar{Z}_1 = Z - X_2 \left( \frac{dZ}{dX_2} \right) = Z + (1 - X_1) \left( \frac{dZ}{dX_1} \right)$$

$$\bar{Z}_2 = Z - X_1 \left( \frac{dZ}{dX_1} \right) = Z + (1 - X_2) \left( \frac{dZ}{dX_2} \right)$$

- $\bar{Z}_1$ and $\bar{Z}_2$ can be found from knowledge of Z either analytically or graphically

### Analytical Solution

**Example 6.3**

Derive expressions for the partial molar volumes of each components as functions of composition if the volume change in a binary solution obeys the relation $V = 2.7 \, X_1 X_2^2$ cc/mol.

$$dV/dX_1 = 2.7 \, ( X_2^2 + X_1 \, . \, 2X_2 \, . \, dX_2/dX_1 ) = 2.7 \, (X_2^2 - 2X_1X_2)$$

$$dV/dX_2 = - dV/dX_1 = -2.7 \, (X_2^2 - 2X_1X_2)$$

$$\bar{V}_1 = V - X_2 \, (dV/dX_2) = 2.7 \, X_1 X_2^2 - X_2 \left[ -2.7 \, (X_2^2 - 2X_1X_2) \right]$$

$$\bar{V}_1 = 2.7 \, ( X_2^3 - X_1 X_2^2 )$$

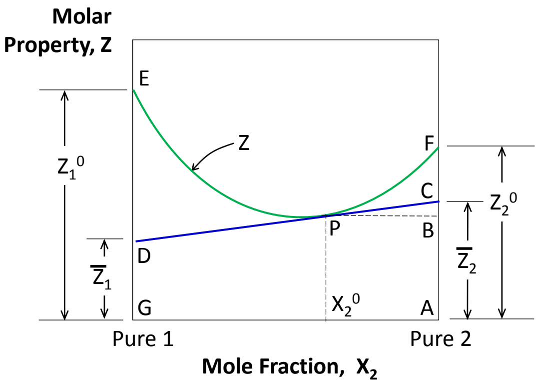
$$\bar{V}_2 = V - X_1 \, (dV/dX_1) = 2.7 \, X_1 X_2^2 - X_1 \left[ 2.7 \, (X_2^2 - 2X_1X_2) \right]$$

$$\bar{V}_2 = 5.4 \, X_1^2 X_2$$

## Graphical Solution

$$\bar{Z}_2 = Z - X_1\,(dZ/dX_1)$$

$$\bar{Z}_2 = Z + (1 - X_2)\,(dZ/dX_2)$$




***Schematic representation of molar property, Z, versus composition, $X_2$, diagram of a binary solution at constant temperature and pressure***

Slope of curve at point P

$$dZ / dX_2 = BC / PB$$

$$\begin{aligned} \bar{Z}_2 &= Z + (1 - X_2)\,(dZ/dX_2) \\ &= AB + PB\,(BC/PB) \\ &= AC \end{aligned}$$

$$\bar{Z}_1 = GD$$

To determine partial molar properties for a solution of a given composition, construct a tangent to the Z curve at that composition and read the intercepts on the two sides of the graph.

## Partial molar properties of one component from partial molar properties of another

- Using Gibbs-Duhem equation for a binary solution

$$X_1\,d\bar{Z}_1 + X_2\,d\bar{Z}_2 = 0$$

$$d\bar{Z}_1 = -\left(\frac{X_2}{X_1}\right) d\bar{Z}_2$$

- Integrating this equation from $X_1=1$ to $X_1=X_1$

$$\bar{Z}_1\Big|_{X_1 = X_1} - \bar{Z}_1\Big|_{X_1 = 1} = -\int_{X_1 = 1}^{X_1 = X_1} \left(\frac{X_2}{X_1}\right) d\bar{Z}_2$$

$$\bar{Z}_1\Big|_{X_1 = X_1} - \bar{Z}_1\Big|_{X_1 = 1} = -\int_{X_1 = 1}^{X_1 = X_1} \left(\frac{X_2}{X_1}\right) d\bar{Z}_2$$

- For pure component, partial molar property does not exist.

  So at $X_1$=1, $\bar{Z}_1 = 0$

$$\mathbf{\bar{Z}_1 = -\int_{X_1 = 1}^{X_1 = X_1} \left(\frac{X_2}{X_1}\right) d\bar{Z}_2}$$

- Thus, knowing the value of $\bar{Z}_2$, the partial molar properties of one component, and a reference state, the partial molar property of the other component can easily be calculated.

$$d\bar{Z}_1 = -\int_{X_1 = 1}^{X_1 = X_1} \left(\frac{X_2}{X_1}\right) d\bar{Z}_2$$

- If a relationship between $\bar{Z}_2$ and $X_2$ is given, the above relation can be modified as

$$d\bar{Z}_2 = \frac{d\bar{Z}_2}{dX_2}\, dX_2$$

$$\bar{Z}_1 = -\int_{X_1 = 1}^{X_1 = X_1} \left(\frac{X_2}{X_1}\right) \frac{d\bar{Z}_2}{dX_2}\, dX_2$$

- If, on the other hand, the input relationship is between $\bar{Z}_2$ and $X_{1,}$ then

$$\bar{Z}_1 = -\int_{X_1 = 1}^{X_1 = X_1} \left(\frac{X_2}{X_1}\right) \frac{d\bar{Z}_2}{dX_1}\, dX_1$$

**Example 6.4**

The partial molar enthalpy of component 2 in a binary solution is given by the equation $\Delta\bar{H}_2 = aX_1^2$. Compute the partial molar enthalpy for component 1 and the molar enthalpy for the solution.

$$\Delta\bar{H}_1 = -\int_{X_1=1}^{X_1=X_1} \left(\frac{X_2}{X_1}\right) \frac{d(\Delta\bar{H}_2)}{dX_1}\, dX_1 \qquad \frac{d(\Delta\bar{H}_2)}{dX_1} = 2aX_1$$

$$\Delta\bar{H}_1 = -\int_{X_1=1}^{X_1=X_1} \left(\frac{X_2}{X_1}\right) . 2aX_1 . dX_1 = -2a \int_{X_1=1}^{X_1=X_1} X_2\, dX_1$$

$$\Delta\bar{H}_1 = +2a \int_{X_2=0}^{X_2=X_2} X_2\, dX_2 = aX_2^2$$

$$\Delta H = X_1\Delta\bar{H}_1 + X_2\Delta\bar{H}_2 = X_1 . aX_2^2 + X_2 . aX_1^2$$

$$\Delta H = aX_1 X_2 (X_1 + X_2) = aX_1 X_2$$

## Next Class

### Lecture 17

# Thermodynamics of Solutions

The Ideal and Nonideal Solutions