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UNIT-4: CLASSICAL THERMODYNAMICS - STUDY MATERIAL

2025-26

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UNIT-4



NEW SYLLABUS
2025-2026

Classical thermodynamics: Partial molar properties, chemical potential, Gibb's-Duhem equation. Determination of partial molar quantities, Thermodynamics of real gases, fugacity – determination of fugacity by graphical and equation of state methods, dependence of temperature, pressure and composition, Thermodynamics of ideal and non-ideal mixtures. Activity and activity coefficients.

Classical Thermodynamics

Partial molar properties are thermodynamic properties of a mixture that describe the change in a specific property of the mixture when a small amount of one component is added to or removed from the mixture, while keeping the temperature, pressure, and amount of other components constant. These properties are important in the study of solutions and mixtures in chemistry and chemical engineering. Some commonly discussed partial molar properties include:

- 1. Partial Molar Volume (V):** The change in volume of a mixture when a small amount of one component is added to it, keeping temperature and pressure constant. Mathematically, it is represented as:

$$V_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j}$$
 Where V_i is the partial molar volume of component i , V is the total volume of the mixture, and n_i is the amount of component i .
- 2. Partial Molar Enthalpy (H):** The change in enthalpy of a mixture when a small amount of one component is added to it, keeping temperature, pressure, and the amount of other components constant. Mathematically, it is represented as:

$$H_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j}$$
 Where H_i is the partial molar enthalpy of component i , H is the total enthalpy of the mixture, and n_i is the amount of component i .

3. Partial Molar Gibbs Free Energy (G): The change in Gibbs free energy of a mixture when a small amount of one component is added to it, keeping temperature, pressure, and the amount of other components constant. Mathematically, it is represented as:

$$G_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

Partial molar properties are useful in understanding the behavior of solutions and mixtures, particularly in processes such as phase equilibria, chemical reactions, and separations. They provide insights into how the addition or removal of a component affects the overall properties of the mixture.

Determining partial molar quantities involves experimental or theoretical methods to isolate the contribution of a specific component to the overall property of a mixture. Here's how partial molar quantities can be determined:

Experimental Methods:

1. Partial Molar Volume (\bar{V}_iM):

- **Experimental Methods:** Differential scanning calorimetry (DSC), densimetry, or pycnometry can be used to measure changes in volume upon addition of a component while keeping other variables constant.
- **Calculation:** The change in volume upon adding a small amount of a component (ΔV) divided by the amount of substance added (Δn_i) gives the partial molar volume (\bar{V}_iM).

2. Partial Molar Enthalpy (\bar{H}_iM):

- **Experimental Methods:** Calorimetry techniques such as differential scanning calorimetry (DSC) or isothermal titration calorimetry (ITC) can be used to measure the heat exchanged when adding a component.
- **Calculation:** The heat exchanged (q) divided by the amount of substance added (Δn_i) gives the partial molar enthalpy (\bar{H}_iM).

3. Partial Molar Gibbs Free Energy (\bar{G}_iM):

- **Experimental Methods:** For dilute solutions, the Gibbs free energy change can be determined using vapor pressure measurements or osmotic pressure measurements.
- **Calculation:** The change in Gibbs free energy (ΔG) upon adding a small amount of a component, divided by the amount of substance added (Δn_i), gives the partial molar Gibbs free energy (\bar{G}_iM).

Theoretical Methods:

1. Activity Coefficients (γ_i):

- **Experimental Methods:** Experimental data such as vapor-liquid equilibrium (VLE) or activity coefficient measurements can be used to determine activity coefficients.
- **Calculation:** The ratio of the partial molar property to the property of the pure substance ($\rightarrow 1x_i \rightarrow 1$) yields the activity coefficient (γ_i), which is used to calculate the partial molar property.

2. Models:

- **Modeling:** Thermodynamic models such as the Margules, Van Laar, or Wilson models can be employed to predict partial molar properties based on experimental data and molecular interactions.

3. Computer Simulations:

- **Simulation Methods:** Molecular dynamics (MD) simulations or Monte Carlo simulations can be used to calculate partial molar properties by simulating the behavior of individual molecules within a mixture.

4. Derivative Approaches:

- **Mathematical Analysis:** Mathematical derivatives of equations describing the overall properties of the mixture with respect to changes in the amount of a specific component can yield partial molar properties.

In practice, a combination of experimental measurements, theoretical models, and computational simulations is often employed to accurately determine partial molar quantities for various components in a mixture.

Chemical Potential: The partial molar gibbs free energy has been given a specific symbol μ because of its univerversality in dealing with various aspects of thermodynamics studies. Its signifecance is discussed here. For a multicomponent system, free energy is a function of T,P and number of moles (n_i) of various specis.

$$\begin{aligned} \text{Thus, } G &= f(T, P, n_1, n_2, \dots n_i) \text{ And } dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT \\ &+ \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \dots \\ &= \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \dots \text{-----(1)} \end{aligned}$$

Where

$$\bar{G}_1 = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i, \quad j \neq i \text{ -----(2)}$$

It is intensive property and is a measure of escaping tendency. For a closed system $dn_1 =$

$$\begin{aligned} 0, dn_2 = 0 \text{ and equation (1) gives } (dG)_N &= \left(\frac{\partial G}{\partial T}\right)_{P,n} dT \\ &+ \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP \text{-----(3)} \end{aligned}$$

But for a closed system

$$dG = -SdT + VdP \text{ -----(4)}$$

Comparing the coefficient in the equation (3) and (4) we get,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \left(\frac{\partial G}{\partial P}\right)_T = V \text{-----(5)}$$

From the equation (1),(2) and (5) we have $dG = -S dT + V$

$$\begin{aligned} &dP + \mu_1 dn_1 + \mu_2 dn_2 + \dots \\ &= -SdT + Vdp + \sum_i \mu_i dn_i \text{ -----(6)} \\ dG &= \sum_i \mu_i dn_i \end{aligned}$$

$$= \mu_1 dn_1 + \mu_2 dn_2 + \dots \text{-----(7)}$$

$$G = \mu_1 n_1 + \mu_2 n_2 + \dots = \sum_i \mu_i n_i \text{ -----(8)}$$

(Chemical Potential)

The total differential of G is given by

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + n_2 d\mu_2 + \mu_2 dn_2 \text{-----(9)}$$

Comparing eqn. (6) and (9) we get

$$\begin{aligned} -S dT + VdP + \sum_i \mu_i dn_i &= \mu_1 dn_1 + n_1 d\mu_1 + n_2 d\mu_2 + \mu_2 dn_2 \\ &= \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2 \end{aligned}$$

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

$$\text{Terms getting cancel and we get} \quad \text{Or} \quad -S dT + VdP - \sum_i n_i d\mu_i = 0 \text{----- (10)}$$

$$-S dT + VdP = \sum n_i d\mu_i \quad \sum_i n_i d\mu_i = 0$$

Variation of temperature on chemical potential

Chemical potential of i th component of a system is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \text{-----(1)}$$

Differentiating equation(1) wrt T at constant P and composition we get

$$\left(\frac{\partial \mu_i}{\partial T} \right)_{P,n_i} = \frac{\partial}{\partial T} \left[\left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \right]_{P,n_i}$$

$$\text{Since G is a state function} \quad \frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial T}$$

$$\begin{aligned} \therefore \left(\frac{\partial \mu_i}{\partial T} \right)_{P,n_i} &= \frac{\partial}{\partial n_i} \left[\left(\frac{\partial G}{\partial T} \right)_{P,n_i} \right]_{T,P,n_j} \\ &= - \frac{\partial}{\partial n_i} (S)_{T,P,n_j} = -\bar{S}_i \text{----- (2)} \end{aligned}$$

Where $\bar{S}_i = \left(\frac{\partial S}{\partial n_i} \right)_{T,P,n_j}$ = Partial molar entropy. $S^g > S^l > S^s$.

Variation of Pressure on chemical potential ;

Chemical potential of i th component of a system is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)$$

$$\int d\mu_i = \int \bar{V}_i dP$$

Equation (3) can be used to calculate the chemical potential of the gases, liquids and solids , provide we know the pressure dependence of volume.

Gibbs-Duhem equation

The Gibbs-Duhem equation is a fundamental relation in thermodynamics that describes the behavior of extensive properties of a thermodynamic system. It states that for any mixture of chemical substances at equilibrium, there exists a linear relationship between changes in the intensive properties of the system.

Let's start with the expression of the Gibbs free energy G for a system of constant temperature and pressure: $G = H - TS$

For a system containing N moles of substances, we can express G in terms of the chemical potential μ_i for each component:

$$G = \sum_{i=1} \mu_i = (\partial G / \partial n_i)_{T,P}$$

Now, differentiate the Gibbs free energy expression with respect to the number of n_i :

$$dG = \sum_{i=1} (\partial \mu_i / \partial n_i)_{T,P} dn_i + \sum_{i=1} \mu_i dn_i$$

Since the total number of moles is constant, $\sum_{i=1} dn_i = 0$, so we have: $dG = \sum_{i=1} (\partial \mu_i / \partial n_i)_{T,P} dn_i$

$$\partial \mu_i / \partial n_i = (\partial \mu_i / \partial x_i)_{T,P}$$

$$dG = \sum_{i=1} (\partial \mu_i / \partial x_i)_{T,P} dx_i$$

$$G_i = (\partial G / \partial n_i)_{T,P}$$

$$G_i dn_i$$

$$dG = \sum_{i=1} G_i dn_i$$

$$x_i = n_i / \sum_{i=1} n_i$$

$$dn_i = n dx_i + x_i dn$$

$$dG = \sum_{i=1} G_i (n dx_i + x_i dn)$$

$$dG = n \sum_{i=1} G_i dx_i + \sum_{i=1} x_i G_i dn$$

$$dG = n \sum_{i=1} G_i dx_i + \sum_{i=1} x_i \mu_i dn$$

$$\mu_i = G_i + RT \ln x_i$$

$$dG = \sum_{i=1} G_i dx_i + \sum_{i=1} x_i (G_i + RT \ln x_i) dn$$

$$dG = n \sum_{i=1} G_i dx_i + \sum_{i=1} x_i G_i dn + RT \sum_{i=1} x_i \ln x_i dn$$

Since $\sum_{i=1} x_i dn = dn$, we have:

$$dG = n \sum_{i=1} G_i dx_i + \sum_{i=1} x_i G_i dn + RT dn \sum_{i=1} x_i \ln x_i$$

$$dG = n \sum_{i=1} G_i dx_i + \sum_{i=1} x_i \ln x_i$$

$$dG = \sum_{i=1} (G_i + RT \ln x_i) dx_i$$

$$dG = \sum_{i=1} \mu_i dx_i$$

Therefore, the Gibbs-Duhem equation is:

$$\sum_{i=1} \mu_i dx_i = 0$$

This equation states that for any mixture of chemical substances at equilibrium, there exists a linear relationship between changes in the intensive properties of the system.

Fugacity:

Fugacity is a concept in thermodynamics and statistical mechanics that represents an effective measure of the escaping tendency or escaping tendency per particle of a substance from a non-ideal mixture or solution. It is often denoted by the symbol f or f_i for a specific component i in a mixture. Fugacity is particularly useful in describing non-ideal gases and solutions, where the pressure or concentration does not directly correspond to the escaping tendency of the substance.

Escape Tendency: Fugacity represents the escaping tendency of a substance from a mixture or solution. It accounts for deviations from ideal behavior due to interactions between molecules or particles.

Non-Ideal Systems: In non-ideal systems, the fugacity of a component may differ from its partial pressure or concentration. This is because the activity coefficient, which reflects the deviation from ideal behavior, modifies the fugacity.

Relation to Pressure and Chemical Potential: In an ideal gas or solution, fugacity is equal to pressure or chemical potential. However, in non-ideal systems, the relationship between fugacity, pressure, and chemical potential becomes more complex and is governed by equations such as the Van der Waals equation or activity models.

Fugacity Coefficient: In some contexts, especially in thermodynamics, the fugacity coefficient (ϕ) is used. It relates the fugacity of a substance to its ideal pressure or concentration. For an ideal gas or solution, the fugacity coefficient is equal to 1.

Units: Fugacity has the same units as pressure (e.g., pascals, atmospheres) or concentration (e.g., moles per cubic meter).

Calculation: Fugacity can be calculated using various equations of state or activity models, depending on the nature of the system and the level of approximation required.

Importance of Fugacity:

- Fugacity plays a crucial role in understanding and predicting the behavior of nonideal systems, including phase equilibria, chemical reactions, and separation processes.
 - It is particularly relevant in industries such as chemical engineering, where accurate predictions of thermodynamic properties are essential for process design and optimization.
- Overall, fugacity provides a more accurate description of the escaping tendency of substances in nonideal systems compared to pressure or concentration alone, making it a valuable concept in thermodynamics and statistical mechanics.

Measuring fugacity directly can be challenging because it is a concept used to describe the escaping tendency of a substance from a non-ideal mixture or solution, rather than a directly measurable quantity. However, there are indirect methods and techniques used to estimate or infer fugacity in various experimental settings. Here are some approaches:

1. Equations of State (EOS):

- Fugacity can be calculated using equations of state such as the Van der Waals equation, Redlich-Kwong equation, or Peng-Robinson equation. These equations relate fugacity to pressure, volume, temperature, and the properties of the substance.
- Experimental data, such as pressure-volume-temperature (PVT) measurements, can be used to fit parameters in these equations, allowing for the determination of fugacity.

2. Activity Coefficients:

- In the context of solutions, fugacity can be related to activity coefficients through activity models such as the Van Laar equation, Wilson equation, or NRTL equation. These models describe deviations from ideal behavior in terms of activity coefficients, which affect the fugacity of each component.
- Experimental measurements of vapor-liquid equilibria (VLE) or osmotic pressure can be used to determine activity coefficients, which can then be used to calculate fugacity.

3. Phase Equilibrium Measurements:

- Phase equilibrium experiments, such as vapor-liquid equilibrium (VLE) measurements or liquid-liquid equilibrium (LLE) measurements, provide valuable data for estimating fugacity.
- By measuring the composition of phases in equilibrium and applying phase equilibrium models, fugacity coefficients and fugacities can be estimated.

4. Empirical Correlations:

- Empirical correlations based on experimental data or theoretical models can provide estimates of fugacity in specific systems or conditions.
- These correlations may be based on regression analysis of experimental data or derived from theoretical considerations.

5. Theoretical Models:

- Quantum chemical calculations or molecular simulations can provide insights into intermolecular interactions and their effects on fugacity.

- Computational methods such as density functional theory (DFT) or Monte Carlo simulations can be used to predict fugacity in complex systems.

Ternary Systems

Ternary phase diagrams are graphical representations used to understand the behavior of a system composed of three components. These diagrams are commonly used in materials science, chemistry, and metallurgy to depict the phase relationships between the components at various combinations of temperature, pressure, and composition.

Here's a general explanation of how ternary phase diagrams work and what they depict:

1. **Components:** A ternary phase diagram represents a system composed of three components. These components could be elements, compounds, or mixtures.
2. **Axes:** Ternary phase diagrams typically have three axes. Each axis represents the composition of one of the components. These compositions are usually expressed as fractions or percentages of the total.
3. **Phases:** The different phases of the system, such as solid, liquid, and gas, are represented within the diagram. Boundaries between these phases are shown as lines or curves.
4. **Phase Regions:** Each area within the diagram represents a different phase or combination of phases that exist under specific conditions of temperature, pressure, and composition.
5. **Phase Boundaries:** Phase boundaries indicate the conditions under which two phases coexist in equilibrium. These boundaries can include solid-solid, liquid-liquid, solid-liquid, etc.
6. **Tie Lines:** Tie lines are lines drawn between two points within a phase region. They indicate the compositions of the coexisting phases at equilibrium.
7. **Invariant Reactions:** Points where three phase boundaries intersect are known as invariant points. At these points, three phases coexist in equilibrium.
8. **Solid Solutions:** Ternary phase diagrams can also depict solid solutions, where different components are dissolved in each other in the solid state.
9. **Eutectic Points:** In some ternary phase diagrams, eutectic points may exist. These are points where a mixture of three components melts at the lowest possible temperature.

When interpreting a ternary phase diagram, it's essential to understand the behavior of the system under different conditions and how changes in temperature, pressure, or composition affect the phase relationships. Additionally, experimental data and theoretical models are often used to construct and interpret ternary phase diagrams accurately.

- Each apex represents one component of the system (A, B, and C).
- The sides connecting the apexes represent binary phase boundaries between pairs of components.
- The central region represents the ternary phase space, where all three components coexist.
- The lines and curves within the diagram represent phase boundaries and tie lines, indicating regions of phase equilibrium and phase compositions.
- The symbols inside the phase regions indicate the phases present in those regions (e.g., liquid, solid, gas).

Please note that the actual appearance and details of a ternary phase diagram can vary significantly based on the specific properties and interactions of the components involved. Real-world ternary phase diagrams are often more complex and may require professional software or experimental data to construct accurately.

Thermodynamics of ideal and non-ideal binary systems

Ideal Binary Systems:
An ideal binary system is a theoretical concept that simplifies the analysis of mixtures. In an ideal binary system:

1. **No Interactions Between Molecules:** Molecules of different components do not interact with each other, meaning there are no attractive or repulsive forces between them.
2. **Mixing is Energetically Neutral:** Mixing of the components does not result in any energy changes.
3. **Raoult's Law Applies:** Raoult's law states that the partial vapor pressure of each component in the

mixture is directly proportional to its mole fraction in the liquid phase and the vapor pressure of the pure component. Mathematically, for an ideal binary mixture:

$$P_i = x_i P_i^*$$

4. **Ideal Behavior is Observed at All Compositions and Temperatures:** This means that the behavior of the mixture is predicted perfectly by Raoult's law.

Non-Ideal Binary Systems:

Non-ideal binary systems exhibit deviations from ideal behavior due to molecular interactions between different components. There are two types of deviations:

1. **Positive Deviation:** In a positive deviation from Raoult's law, the observed vapor pressure of the mixture is higher than predicted by Raoult's law. This typically occurs when molecules in the mixture have stronger attractions for each other than for themselves. It often happens in mixtures containing dissimilar molecules.

2. **Negative Deviation:** In a negative deviation, the observed vapor pressure of the mixture is lower than predicted by Raoult's law. This occurs when the intermolecular attractions between different molecules are weaker than those within individual pure components. This often occurs in mixtures where components are similar in nature.

Thermodynamics of Non-Ideal Binary Systems:

1. **Gibbs Free Energy:** For non-ideal mixtures, the Gibbs free energy (G) of mixing differs from ideal behavior. The excess Gibbs free energy (G^E) is introduced to account for this difference. For a binary mixture:

$$G = G_{\text{ideal}} + G^E$$

2. **Activity Coefficients:** Activity coefficients (γ_i) are introduced to quantify deviations from ideal behavior. They are defined as:

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

3. **Phase Equilibria:** Non-ideal mixtures may exhibit different phase behaviors compared to ideal mixtures. Phase diagrams for non-ideal mixtures may show azeotropes or immiscibility regions, which are not observed in ideal mixtures.

4. **Activity Models:** Various activity models, such as Margules, Van Laar, and Wilson models, are used to correlate and predict activity coefficients for non-ideal mixtures based on experimental data. Henry's Law describes the solubility of a gas in a liquid at a constant temperature, under conditions where the gas does not react chemically with the solvent. It states that the concentration of a gas dissolved in a liquid is directly proportional to the partial pressure of that gas above the liquid. This law is typically expressed mathematically as:

$$C = k_H \cdot P$$

For an ideal binary system, Henry's Law can be applied to each component separately. Let's consider a binary system consisting of components A and B, where A is the gas being dissolved in the liquid solvent:

$$C_A = k_{HA} \cdot P_A$$

$$C_B = k_{HB} \cdot P_B$$

In an ideal binary system, the behavior of the components is independent of each other, so each component follows Henry's Law independently. This implies that the solubility of each gas in the liquid is directly proportional to its own partial pressure and governed by its respective Henry's law constant.

It's important to note that Henry's Law is an approximation that holds well for dilute solutions and low to moderate pressures. For highly concentrated solutions or high pressures, deviations from Henry's Law behavior may occur, especially in non-ideal systems.

Activity and Activity Coefficients:

1. **Activity:** In thermodynamics, activity (a) is a measure of the "effective concentration" of a species in a mixture, accounting for deviations from ideal behavior due to interactions between molecules. It is defined as the ratio of the chemical potential of a component in a mixture to its chemical potential in a reference state.

$$a_i = \mu_i / \mu_i^0$$

2. **Activity Coefficient:** The activity coefficient (γ_i) quantifies the deviation from ideal behavior in a solution. It is defined as the ratio of the activity of a species to its concentration in a solution at a given condition.

$$\gamma_i = a_i / C_i$$

Standard States:

In thermodynamics, a standard state is a defined reference state used for specifying properties such as pressure, temperature, concentration, etc., which allows for consistency and comparability of measurements. Commonly used standard states include:

- For gases: 1 atm pressure and a specified temperature (e.g., 25°C or 298 K).
- For liquids and solids: Pure substance at a specified pressure and temperature.
- For solutions: An infinitely diluted solution (infinite dilution) under specified conditions.

Determination of Activity and Activity Coefficients:

1. **Vapor Pressure Method:** In this method, the activity coefficients of components in a liquid mixture are determined by comparing the vapor pressures of the components in the mixture to those in their pure states using Raoult's law or other vapor pressure equations.
2. **Electromotive Force (EMF) Method:** Also known as the electromotive force measurement method or cell method, this technique measures the potential difference between electrodes in an electrochemical cell containing the solution of interest. It is used primarily for determining activity coefficients of ions in electrolyte solutions.
3. **Freezing Point Depression Method:** This method involves measuring the depression in the freezing point of a solvent when a solute is dissolved in it. By comparing the observed freezing point depression to the theoretical value predicted by the ideal behavior, activity coefficients of the solute can be determined.

Significance:

- **Process Design:** Understanding activity and activity coefficients is crucial for the design and optimization of chemical processes involving mixtures, such as distillation, extraction, and crystallization.
- **Equilibrium Calculations:** Activity coefficients are essential for accurate predictions of phase equilibria, chemical reactions, and other thermodynamic properties in nonideal systems.
- **Correlation and Prediction:** Experimental data on activity coefficients are often used to develop thermodynamic models that can correlate and predict the behavior of complex mixtures under various conditions.

Vapour pressure method

The vapour pressure method is a common experimental technique used to determine the activity coefficients of components in a liquid mixture. This method involves measuring the vapor pressures of the components in the mixture and comparing them to the vapor pressures of the pure components at the same temperature. From these measurements, activity coefficients can be calculated using Raoult's law or other vapor pressure equations.

Here's a general outline of the experimental procedure for the vapor pressure method:

Equipment and Materials:

1. **Refrigerated Circulator:** To maintain a constant temperature.
2. **Pressure Transducer or Manometer:** To measure vapor pressures.
3. **Temperature Probe or Thermometer:** To monitor temperature.
4. **Glass Apparatus:** Such as a vapor pressure apparatus or a vapor-liquid equilibrium (VLE) setup.
5. **Pure Samples of Components:** Needed for comparison.
6. **Analytical Balance:** To measure sample quantities accurately.
7. **Vacuum Pump:** To evacuate the system and create a vacuum.

Procedure:

1. Preparation of Apparatus:

- Clean all glassware thoroughly to avoid contamination.
- Assemble the vapor pressure apparatus or VLE setup according to the manufacturer's instructions.
- Connect the pressure transducer or manometer to the system to measure vapor pressures.

2. Calibration:

- Calibrate the pressure transducer or manometer using known reference pressures.
- Ensure that the temperature probe or thermometer is accurate and calibrated.

3. Sample Preparation:

- Weigh accurately measured quantities of each component of the liquid mixture.
- Place the samples in separate containers or compartments within the vapor pressure apparatus.

4. Evacuation:

- Evacuate the system using the vacuum pump to remove any air or impurities.
- Ensure that the system is sealed to prevent leaks.

5. Temperature Control:

- Start the refrigerated circulator and set it to the desired temperature.
- Monitor and maintain a constant temperature throughout the experiment.

6. Measurement:

- Once the system reaches the desired temperature, record the vapor pressures of the components in the mixture using the pressure transducer or manometer.
- Repeat the measurements for different compositions of the mixture by varying the proportions of the components.

7. Comparison:

- Compare the vapor pressures of the components in the mixture to the vapor pressures of the pure components at the same temperature.
- Calculate the activity coefficients using appropriate equations, such as Raoult's law or other vapor pressure equations.

8. Analysis:

- Analyze the data and plot graphs of vapor pressure versus composition.

- Use the experimental data to determine the activity coefficients of the components in the mixture.

9. Cleanup:

- Clean and dismantle the apparatus after the experiment.
- Dispose of any waste materials properly.

Data Analysis:

- Calculate the activity coefficients using the measured vapor pressures and known vapor pressures of the pure components.
- Use appropriate equations or models, such as Raoult's law, to determine the activity coefficients.
- Plot graphs of vapor pressure versus composition and analyze the data to verify the behavior of the mixture.

Precautions:

- Ensure that the system is properly sealed to prevent leaks.
- Handle chemicals with care and follow safety procedures.
- Maintain a constant temperature throughout the experiment.
- Calibrate all instruments and equipment accurately.

By following these steps and precautions, the vapor pressure method can provide valuable data for determining the activity coefficients of components in a liquid mixture

Freezing point method

The determination of activity and activity coefficients using the freezing point depression method involves measuring the depression in the freezing point of a solvent caused by the presence of a solute. This method is particularly useful for dilute solutions and relies on the relationship between the concentration of the solute and the freezing point depression, as described by the equation:

$$\Delta T_f = K_f m$$

- ΔT_f is the freezing point depression,
- K_f is the cryoscopic constant of the solvent,
- m is the molality of the solute.

Procedure:

1. Preparation of Solutions:

- Prepare a series of solutions with known concentrations of the solute. These solutions should cover a range of concentrations, typically spanning from very dilute to moderately concentrated.
- Accurately measure the masses of solute and solvent needed to prepare each solution.

2. Determination of Freezing Points:

- Use a suitable apparatus, such as a Beckmann or freezing point depression apparatus, to measure the freezing points of the prepared solutions.
- Calibrate the apparatus according to the manufacturer's instructions.
- Record the freezing points of each solution.

3. Calculation of Freezing Point Depression:

- Calculate the freezing point depression (ΔT_f) for each solution by subtracting the freezing point of the pure solvent from the freezing point of the solution.
- Ensure that the measurements are accurate and consistent.

4. Plotting the Depression vs. Molality:

- Plot a graph of freezing point depression (ΔT_f) versus molality (m) for the solutions.
- The resulting curve should be linear for dilute solutions according to the equation $\Delta T_f = K_f \cdot m$.
- Note any deviations from linearity, which may indicate non-ideal behavior.

5. Determination of Activity Coefficients:

- The cryoscopic constant (K_f) of the solvent is known. By plotting ΔT_f versus m , you can determine the slope of the line, which corresponds to K_f .
- From the slope and known concentration of the solute, calculate the activity coefficients using the equation: $\gamma = 1 - K_f \cdot m \Delta T_f$

Analysis and Interpretation:

- Ideal Behavior:** In ideal solutions, the freezing point depression is directly proportional to the molality of the solute, and the plot of ΔT_f versus m yields a straight line passing through the origin.
- Non-Ideal Behavior:** Deviations from linearity indicate non-ideal behavior. These deviations can be attributed to interactions between solute and solvent molecules and are quantified by activity coefficients.
- Activity Coefficients:** Activity coefficients can be determined from the slopes of the curves and are crucial for understanding the extent of non-ideality in the solution.

Considerations and Precautions:

- Ensure accurate measurements of masses, temperatures, and freezing points.
- Use a suitable solvent with a well-known cryoscopic constant.
- Consider the limitations of the freezing point depression method for concentrated solutions and systems exhibiting phase separation.
- Verify the linearity of the depression vs. molality plot for dilute solutions.

By following these steps and considerations, the freezing point depression method provides a valuable means of determining activity and activity coefficients in solution systems.

Derivation of Duhem-Margules equation

The Duhem-Margules equation is a relation used to describe the excess Gibbs free energy of mixing for non-ideal liquid solutions. It is an empirical equation derived from the concept of activity coefficients in binary liquid mixtures. The equation is given by:

$$\Delta G_{\text{mix}} / RT = x_1 x_2 (A_{21} + A_{12})$$

Derivation:

Starting with the Gibbs-Duhem equation for a binary system:

From thermodynamic principles, the chemical potential μ_i can be expressed as: $x_1 d\mu_1 + x_2 d\mu_2 = 0$

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

$$x_1 d(\mu_1^{\text{ideal}} + RT \ln \gamma_1) + x_2 d(\mu_2^{\text{ideal}} + RT \ln \gamma_2) = 0$$

$$x_1 d\mu_1^{\text{ideal}} + x_1 RT d \ln \gamma_1 + x_2 d\mu_2^{\text{ideal}} + x_2 RT d \ln \gamma_2 = 0$$

$$d \ln \gamma_1 = 1/x_1 (\partial \ln \gamma_1 / \partial x_1)_{T,P} dx_1$$

$$d \ln \gamma_2 = 1/x_2 (\partial \ln \gamma_2 / \partial x_2)_{T,P} dx_2$$

$$x_1 d\mu_1^{\text{ideal}} + x_1 RT 1/x_1 (\partial \ln \gamma_1 / \partial x_1)_{T,P} dx_1 + x_2 d\mu_2^{\text{ideal}} + x_2 RT 1/x_2 (\partial \ln \gamma_2 / \partial x_2)_{T,P} dx_2 = 0$$

$$\mu_i^{\text{ideal}} = (\partial G / \partial n_i)_{T,P} = G^i$$

$$x_1 dG_1 / RT + (\partial \ln \gamma_1 / \partial x_1)_{T,P} dx_1 + x_2 dG_2 / RT + (\partial \ln \gamma_2 / \partial x_2)_{T,P} dx_2 = 0$$

$$A_{12} = -1/RT (\partial \ln \gamma_1 / \partial x_1)_{T,P}$$

$$A_{21} = -1/RT (\partial \ln \gamma_2 / \partial x_2)_{T,P}$$

$$x_1 dG_1 / RT + x_1 A_{12} dx_1 + x_2 dG_2 / RT + x_2 A_{21} dx_2 = 0$$

$$\text{Now, } dG^i / RT = d(\Delta G_i^E / RT) / RT = d\Delta G_i^E / RT^2$$

where ΔG_i^E is the excess Gibbs free energy of component i .

$$x_1 d\Delta G_1^E / RT^2 + x_2 d\Delta G_2^E / RT^2 + x_1 A_{12} dx_1 + x_2 A_{21} dx_2 = 0$$

Rearranging terms, we obtain: $x_1 dx_1 + x_2 dx_2 + (A_{12} + A_{21}) x_1 x_2 dx_1 = 0$

$$(1 + (A_{12} + A_{21}) x_2) dx_1 + (1 + (A_{12} + A_{21}) x_1) dx_2 = 0$$

$$\int (1 + (A_{12} + A_{21}) x_2) dx_1 + \int (1 + (A_{12} + A_{21}) x_1) dx_2 = 0$$

$$x_1 + (A_{12} + A_{21}) x_1 x_2 = C_1$$

$$x_2 + (A_{12} + A_{21}) x_1 x_2 = C_2$$

$$\Delta G_{\text{mix}} = G - G_{\text{ideal}} = RT \ln \gamma_1 + RT \ln \gamma_2$$

$$\Delta G_{\text{mix}} = RT \ln \gamma_1 + RT \ln \gamma_2 = RT \ln (\gamma_1 \gamma_2)$$

$$\Delta G_{\text{mix}} = RT \ln (\gamma_1 \gamma_2) = RT \ln (1 + (A_{12} + A_{21}) x_1 x_2)$$

$$\Delta G_{\text{mix}} / RT = \ln (1 + (A_{12} + A_{21}) x_1 x_2)$$

$$\Delta G_{\text{mix}} / RT \approx (A_{12} + A_{21}) x_1 x_2$$

$$\Delta G_{\text{mix}} / RT = (A_{12} + A_{21}) x_1 x_2$$

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Statistical Thermodynamics

Statistical thermodynamics: Concepts of statistical thermodynamics, distinguishable and non-distinguishable particles. Assemblies, ensembles, canonical particles. Boltzmann distribution, Bose-Einstein, Fermi-Dirac statistics, comparison and application; kinetic theory of gases, partition function and their relation to thermodynamic quantities, calculation for model systems.

Statistical thermodynamics is a branch of thermodynamics that deals with the statistical behavior of a large number of particles in a system. It aims to bridge the gap between the microscopic properties of individual particles and the macroscopic properties of the system as a whole, such as temperature, pressure, and entropy.

Statistical thermodynamics is based on the principles of probability theory and statistical analysis, and it plays a fundamental role in explaining phenomena observed in classical and quantum mechanical systems.

Statistical thermodynamics provides a microscopic foundation for classical thermodynamics and helps explain the macroscopic behavior of systems.

It is used to study a wide range of physical phenomena, including phase transitions, equilibrium properties of gases, liquids, and solids, chemical reactions, and the behavior of complex materials.

Statistical mechanics is essential for understanding the behavior of systems at the molecular and atomic level and has applications in various fields such as chemistry, physics, materials science, and biology.

Here are some basic terminologies commonly used in statistical thermodynamics:

1. **Ensemble:** A collection of multiple copies of a system, each in different states but sharing the same macroscopic properties like temperature, pressure, and volume.
2. **Microstate:** A specific configuration of the individual particles (atoms or molecules) in a system that fully specifies its state. For example, in a gas, the positions and velocities of all the particles at a particular instant define a microstate.
3. **Macrostate:** A set of macroscopic parameters that describe the overall properties of a system, such as temperature, pressure, volume, and energy.
4. **Probability Distribution:** The distribution of probabilities of finding the system in different microstates, which depends on the macroscopic conditions of the system.
5. **Partition Function (Z):** A fundamental quantity in statistical mechanics that encapsulates all the information about the system's microscopic states. It is defined as the sum or integral over all possible states of the Boltzmann factor $e^{-\beta E_i}$, where E_i is the energy of state i and $\beta = kT^{-1}$ (where k is the Boltzmann constant and T is the temperature).
6. **Boltzmann Distribution:** Describes the distribution of particles over different energy levels in a system at thermal equilibrium. It states that the probability P_i of finding a particle in a particular energy state E_i is proportional to $e^{-\beta E_i}$, where β is the inverse temperature.
7. **Entropy (S):** A measure of the disorder or randomness of a system. In statistical thermodynamics,

entropy is related to the number of microstates associated with a given macrostate.

8. **Free Energy:** A thermodynamic potential that measures the maximum amount of reversible work that can be extracted from a system at constant temperature and volume. In statistical mechanics, free energy is often expressed in terms of the partition function.

In statistical thermodynamics, an ensemble is a collection of multiple copies of a system, each in different states but sharing the same macroscopic properties like temperature, pressure, and volume. Ensembles provide a framework for understanding the statistical behavior of systems with a large number of particles. There are several types of ensembles, each corresponding to different conditions under which the system is studied. Below are the main types of ensembles along with explanations and diagrams:

Canonical Ensemble: An ensemble in statistical mechanics that describes a system in thermal equilibrium with a heat reservoir at constant temperature and volume.

Grand Canonical Ensemble: An ensemble in statistical mechanics that describes a system in thermal and diffusive equilibrium with a heat reservoir and a particle reservoir at constant temperature, volume, and chemical potential.

These are just a few basic terminologies in statistical thermodynamics, and the field involves many more concepts and terms as one delves deeper into the subject.

1. Microcanonical Ensemble:

In the microcanonical ensemble, the system is isolated, meaning it does not exchange energy or particles with its surroundings. The system is described by a fixed total energy E , volume V , and number of particles N .

2. Canonical Ensemble:

In the canonical ensemble, the system is in contact with a heat reservoir at constant temperature T , but it cannot exchange energy or particles with the surroundings. The system is described by its energy E , volume V , and number of particles N , with the total energy allowed to fluctuate.

3. Grand Canonical Ensemble:

In the grand canonical ensemble, the system is in contact with a heat reservoir and a particle reservoir, allowing both energy and particles to exchange with the surroundings. The system is described by its chemical potential μ , temperature T , and volume V , with both energy and number of particles allowed to fluctuate.

Explanation:

- Each ensemble represents a different set of constraints on the system, such as fixed energy, temperature, or chemical potential.
- Ensembles allow us to compute thermodynamic properties by averaging over all possible states of the system consistent with the constraints of the ensemble.
- The choice of ensemble depends on the experimental conditions and the properties of interest.

Ensembles play a crucial role in statistical thermodynamics, providing a framework for understanding the behavior of systems with many particles. By considering different ensembles, we can analyze systems under various conditions and compute thermodynamic properties relevant to different experimental setups.

The derivation of the Maxwell-Boltzmann distribution involves considering the statistical mechanics of a gas of non-interacting particles in thermal equilibrium. Here's a simplified derivation:

Mathematical probability and thermodynamic probability, while sharing some common concepts, operate within different frameworks and contexts. Let's explore each of them along with examples.

Mathematical Probability:

Definition: Mathematical probability deals with the likelihood of an event occurring in a well-defined, non-physical setting. It is expressed as a number between 0 and 1, where 0 indicates impossibility and 1 indicates certainty.

Concepts:

1. **Sample Space (Ω):** The set of all possible outcomes of an experiment.
2. **Event (E):** A subset of the sample space, representing a collection of outcomes.
3. **Probability (P):** A function that assigns a numerical value to each event, representing the likelihood of that event occurring.

Example: Consider rolling a fair six-sided die. The sample space consists of six possible outcomes: {1, 2, 3, 4, 5, 6}. The probability of rolling a 3 is $P(3) = \frac{1}{6}$, assuming the die is fair.

Thermodynamic Probability:

Definition: Thermodynamic probability, also known as statistical mechanics, deals with the likelihood of different microscopic states of a physical system given its macroscopic properties. It is used to describe the behavior of systems consisting of a large number of particles, such as gases, liquids, and solids.

Concepts:

1. **Microstate:** A complete specification of the positions and momenta of all particles in a system at a given instant.
2. **Macrostate:** A description of the system in terms of its macroscopic properties, such as temperature, pressure, volume, and energy.
3. **Boltzmann Distribution:** Describes the probability distribution of particles among different energy states in a system at thermal equilibrium.

Example: Consider a system of gas molecules in a box. The macrostate of the system may be described by its temperature, volume, and pressure. The thermodynamic probability gives the likelihood of finding the system in a particular macrostate given its energy distribution among the molecules.

Comparison:

- **Scope:** Mathematical probability applies to abstract, well-defined scenarios, while thermodynamic probability applies to physical systems governed by statistical mechanics.
- **Nature of Events:** In mathematical probability, events are discrete and clearly defined, while in thermodynamic probability, events correspond to the distribution of energy states among particles in a system.
- **Applications:** Mathematical probability is widely used in fields such as gambling, statistics, and decision-making. Thermodynamic probability is essential for understanding the behavior of physical systems in statistical mechanics, such as gas laws, phase transitions, and chemical kinetics.

Distribution of particles

The distribution of particles, whether distinguishable or non-distinguishable, plays a significant role in various fields such as statistical mechanics, quantum mechanics, and combinatorics. Let's explore the distribution of both types of particles:

Distinguishable Particles:

Distinguishable particles are those that can be uniquely identified from one another.

Each particle has its own distinct properties, such as position, momentum, or energy.

1. Classical Particles:

- In classical statistical mechanics, distinguishable particles are treated as separate entities.
- The distribution of distinguishable particles follows classical statistics, where each particle can occupy its own distinct state without restriction.
- For example, consider a box containing distinguishable classical particles. Each particle can occupy a unique position and momentum within the box.

2. Quantum Particles:

- In quantum mechanics, distinguishable particles are also treated as separate entities with unique quantum states.
- The distribution of distinguishable quantum particles follows quantum statistics, such as Maxwell-Boltzmann statistics for non-interacting particles or Fermi-Dirac/Bose-Einstein statistics for interacting particles with integer/half-integer spin.

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