Statistical Molecular Thermodynamics

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Video 10.10

Review of Module 10
The free energy of a multicomponent system is the sum of the chemical potentials of the different components.

Partial molar quantities are defined as

$$\bar{Z}_j = \left( \frac{\partial Z}{\partial n_j} \right)_{n_{i \neq j}, P, T}$$

where for a pure substance, the value is that for one mole of that substance, while the value in a mixture will be dependent on the composition.

All extensive thermodynamic quantities have partial molar equivalents.
The Gibbs-Duhem equation establishes a relationship between the chemical potentials of two substances in a mixture as a function of composition:

\[ x_1 d\mu_1 + x_2 d\mu_2 = 0 \]

\[ \text{Gibbs-Duhem Equation} \]

(constant \( T \) and \( P \))

At equilibrium, a given component has the same chemical potential in all phases in which it is present.

For systems having liquid and vapor phases in equilibrium, the chemical potential (1 bar standard state) can be expressed as

\[ \mu_j^{\text{vap}} = \mu_j^{\text{vap},\circ}(T) + RT \ln P_j = \mu_j^{\text{sol}} \]
Critical Concepts from Module 10

• An alternative expression for the chemical potential in the mole fraction standard state is

$$\mu_{j,\text{sol}} = \mu^*_j(l) + RT \ln \frac{P_j}{P_j^*}$$

• For an ideal solution, Raoult’s law holds, which states that for all components $P_j = x_j P_j^*$ where $x_j$ is the mole fraction of component $j$.

• The chemical potential in an ideal solution is then

$$\mu_{j,\text{sol}} = \mu^*_j(l) + RT \ln x_j$$

• Mixing to form an ideal solution is always favorable and is driven entirely by entropy
Critical Concepts from Module 10

• Differing compositions in liquid and vapor phases in equilibrium at a given temperature permit fractional distillation of ideal solutions.

• Non-ideal solutions deviate from Raoult’s Law behavior (either negatively or positively).

• At high dilution, the vapor pressure of the minority component in a non-ideal solution follows Henry’s Law

\[ P_j \to x_j k_{H,j} \text{ as } x_j \to 0 \]

where \( k_{H,j} \) is the Henry’s Law constant for component \( j \).

• At near purity, the vapor pressure of the majority component in a non-ideal solution follows Raoult’s Law (which dictates the Henry’s Law behavior of the minority component).
Critical Concepts from Module 10

• In non-ideal solutions, azeotropes can exist that do not permit purification by distillation of liquid solutions having the azeotropic composition.

• Sufficient positive deviation from Raoult’s Law behavior can lead to phase separation to generate two liquid phases having different compositions.

• The activity $a_j$ takes the place of the mole fraction in non-ideal solutions, and the activity coefficient $\gamma_j$ relates the activity to the mole fraction according to

$$a_j = \frac{P_j}{P_j^*} \quad \gamma_j = \frac{a_j}{x_j}$$
Critical Concepts from Module 10

• The chemical potential in non-ideal solutions can be expressed as

\[ \mu_{j}^{\text{sol}} = \mu_{j}^{*}(l) + RT \ln a_{j} \]

\[ \mu_{j}^{\text{sol}} = \mu_{j}^{*}(l) + RT \ln x_{j} + RT \ln \gamma_{j} \]

• In a regular solution, the excess molar free energy of mixing is entirely associated with enthalpy and is determined as

\[ \frac{G^{E}}{RT} = x_{1} \ln \gamma_{1} + x_{2} \ln \gamma_{2} \]

• Regular solution theory rationalizes activity and phase behavior based on differing intermolecular interaction energies between various liquid phase components.
\[ dU = \delta q + \delta w \]