# Statistical Molecular Thermodynamics

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Video 10.10

Review of Module 10

# CRITICAL CONCEPTS FROM 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.

# CRITICAL CONCEPTS FROM MODULE 10

- The Gibbs-Duhem equation establishes a relationship between the chemical potentials of two substances in a mixture as a function of composition:

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

*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

$$\mu_j^{vap} = \mu_j^{vap,\circ}(T) + RT \ln P_j = \mu_j^{sol}$$

# CRITICAL CONCEPTS FROM MODULE 10

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

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln \frac{P_j}{P_j^*}$$

- 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

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j$$

- 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

$$P_j \rightarrow x_j k_{H,j} \ \text{ as } x_j \rightarrow 0$$

  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

$$a_j = \frac{P_j}{P_j^*} \qquad\qquad \gamma_j = \frac{a_j}{x_j}$$

# CRITICAL CONCEPTS FROM MODULE 10

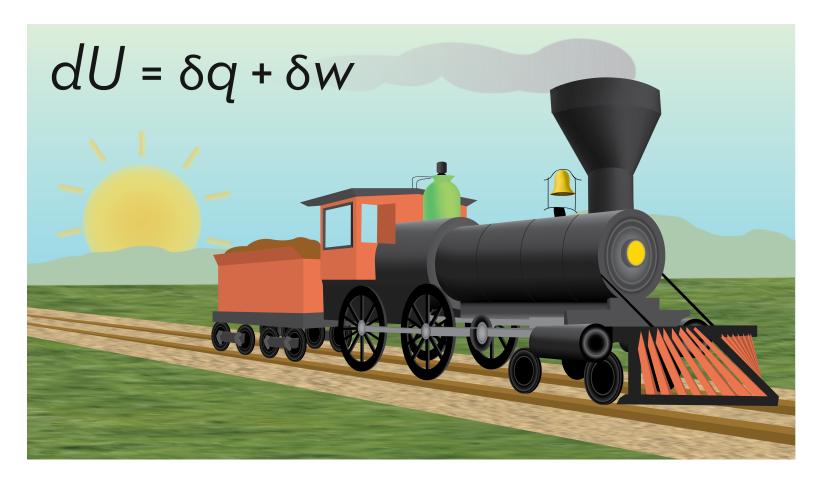- The chemical potential in non-ideal solutions can be expressed as

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln a_j$$

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j + RT \ln \gamma_j$$

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

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

- Regular solution theory rationalizes activity and phase behavior based on differing intermolecular interaction energies between various liquid phase components.

$$dU = \delta q + \delta w$$

*Next:  Module 11*