Chapter 5.
Simple Mixtures

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Physical Chemistry 1
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Contents

The thermodynamic description of mixtures
  5.1 Partial molar quantities
  5.2 The thermodynamic of Mixing
  5.3 The chemical potentials of liquids

The properties of solutions
  5.4 Liquid mixtures
  5.5 Colligative properties

Phase diagrams of binary systems
  5.6 Vapor pressure diagrams
  5.7 Temperature-composition diagrams
  5.8 Liquid-liquid phase diagrams
  5.9 Liquid-solid phase diagrams

Activities
  5.10 The solvent activity
  5.11 The solute activity
  5.12 The activities of regular solutions
  5.13 The activities of ions in solutions
5.1 Partial molar quantities

Key points

1. The partial molar volume of a substance is the contribution to the volume that a substance makes when it is a part of a mixture.
2. The chemical potential is the partial molar Gibbs energy.
3. The chemical potential shows how the thermodynamic function vary with composition.
4. The Gibbs-Duhem equation.
5.1 Partial molar quantities

(a) Partial molar volume

- When 1 mol H$_2$O is added, the volume of pure water increases by 18 cm$^3$
- When 1 mol H$_2$O is added, the volume of pure ethanol increases by 14 cm$^3$
- The volume occupied by a water molecule depends on the identity of the molecules that surround the water molecule
- There should be a change in the hydrogen bond network
- **The partial molar volume**: the change in volume per mole of A added to a large volume of the mixture
5.1 Partial molar quantities

(a) Partial molar volume

- The partial molar volume, $V_J$ of a substance $J$

$$V_J = \left( \frac{\partial V}{\partial n_J} \right)_{p,T,n'}$$

- $n'$ signifies that the amounts of all other substances present are constant

- The partial molar volume: the slope of the plot of the total volume as the amount of $J$ is changed with $p$, $T$, and $n'$ being held constant

$$\text{d}V = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} \text{d}n_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} \text{d}n_B = V_A \text{d}n_A + V_B \text{d}n_B$$
5.1 Partial molar quantities

(a) Partial molar volume

- Assume that the relative composition is held constant as the amounts of A and B are increased.

\[
dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} \, dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} \, dn_B = V_A \, dn_A + V_B \, dn_B
\]

\[
V = \int_0^{n_A} V_A \, dn_A + \int_0^{n_B} V_B \, dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B
\]

\[
= V_A \, dn_A + V_B \, dn_B
\]

- Because V is a state function the final result of the above equation is valid however the solution is prepared.
- Molar volumes are always positive. But partial molar quantities need not be.
  - The limiting partial molar volume of MgSO₄ in water = -1.4 cm³/mol. The mixture contracts because the salt breaks up the open structure of water.
5.1 Partial molar quantities

(b) Partial molar Gibbs energy

- The concept of a partial molar quantity can be extended to any extensive state function.
- The chemical potential = the partial molar Gibbs energy

\[ \mu_j = \left( \frac{\partial G}{\partial n_j} \right)_{p, T, n', A} \]

\[ G = n_A \mu_A + n_B \mu_B \]

- The chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture.
5.1 Partial molar quantities

(b) Partial molar Gibbs energy

- The chemical potential = the partial molar Gibbs energy
  \[ G = n_A \mu_A + n_B \mu_B \]

- The fundamental equation of chemical thermodynamics
  \[ dG = V dp - S dT + \mu_A dn_A + \mu_B dn_B + \cdots \]

- At constant T and p,
  \[ dG = \mu_A dn_A + \mu_B dn_B + \cdots \]

- Additional (non-expansion) work can arise from the changing composition
  \[ dw_{\text{add, max}} = \mu_A dn_A + \mu_B dn_B + \cdots \]
5.1 Partial molar quantities

(c) The wider significance of the chemical potential

- \( G = U + pV - TS \) and \( U = -pV + TS + G \)

\[
dU = -pdV - Vdp + SdT + TdS + dG = -pdV - Vdp + SdT + TdS + (Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots)
\]

\[
= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \cdots
\]

- At constant \( V \) and \( S \),

\[
dU = \mu_A dn_A + \mu_B dn_B + \cdots
\]

\[
\mu_j = \left( \frac{\partial U}{\partial n_j} \right)_{S,V,n'}
\]

- Similarly,

\[
\mu_j = \left( \frac{\partial H}{\partial n_j} \right)_{S,p,n'} \quad \mu_j = \left( \frac{\partial A}{\partial n_j} \right)_{T,V,n'}
\]
5.1 Partial molar quantities

(d) The Gibbs-Duhem equation

- Because the chemical potential depend on the composition and $G = n_A \mu_A + n_B \mu_B$, when the compositions are changed infinitesimally we might expect $G$ of a binary mixture system to change by

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

- But at constant $T$ and $p$,

$$dG = \mu_A dn_A + \mu_B dn_B$$

- Therefore,

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \sum_j n_j d\mu_j = 0 \quad d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

- The chemical potential of one component of a mixture cannot change independently of that of other components

- This reasoning also applies to the partial molar volume (See Figure 5.1)
5.2 The thermodynamics of mixing

Key points

1. The Gibbs energy of mixing is calculated
2. The entropy of mixing and the enthalpy of mixing for perfect gases
5.2 The thermodynamics of mixing

(a) The Gibbs energy of mixing of perfect gases

- The chemical potential of a perfect gas $A$
  \[ \mu = \mu^\Theta + RT \ln \frac{p}{p^\Theta} \]
  \[ \mu = \mu^\Theta + RT \ln p \]

- The Gibbs energy ($G_i$) before mixing
  \[ G_i = n_A \mu_A + n_B \mu_B = n_A \left( \mu_A^\Theta + RT \ln p \right) + n_B \left( \mu_B^\Theta + RT \ln p \right) \]

- After mixing, $p = p_A + p_B$.
- The Gibbs energy ($G_f$) after mixing
  \[ G_f = n_A \left( \mu_A^\Theta + RT \ln p_A \right) + n_B \left( \mu_B^\Theta + RT \ln p_B \right) \]

- The Gibbs energy of mixing = the Gibbs energy difference, $\Delta_{mix}G = G_f - G_i$
  \[ \Delta_{mix}G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p} \]
5.2 The thermodynamics of mixing

(a) The Gibbs energy of mixing of perfect gases

- Because $p_j/p = x_j$,

\[ \Delta_{\text{mix}} G = nRT \left( x_A \ln x_A + x_B RT \ln x_B \right) \]

- Because $\ln(x) < 0$ for $0 < x < 1$, $\Delta_{\text{mix}} G < 0$

- The negative $\Delta_{\text{mix}} G$ confirms that the perfect gas mix spontaneously for all possible compositions
5.2 The thermodynamics of mixing

(b) Other thermodynamic mixing functions

- The entropy of mixing, $\Delta_{mix}S$

$$\Delta_{mix}S = \left( \frac{\partial \Delta_{mix}G}{\partial T} \right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

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

$$\Delta_{mix}H = 0$$

- The whole of the driving force for mixing comes from the increase in entropy of the system because the entropy of the surroundings is unchanged
5.2 The thermodynamics of mixing

(b) Other thermodynamic mixing functions

• The entropy of mixing, $\Delta_{\text{mix}}S$

$$\Delta_{\text{mix}}S = \left( \frac{\partial \Delta_{\text{mix}} G}{\partial T} \right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

• $\Delta G = \Delta H - T\Delta S$ or $\Delta H = \Delta G + T\Delta S$

$$\Delta_{\text{mix}} H = 0$$

• The whole of the driving force for mixing comes from the increase in entropy of the system because the the entropy of the surroundings is unchanged
5.3 The chemical potentials of liquids

Key points

1. Raoult’s law provides a relation between the vapor pressure of a substance and its mole fraction

2. Henry’s law provides a relation between the vapor pressure of a solute and its mole fraction
5.3 The chemical potentials of liquids

(a) Ideal Solutions

- \( \mu^* \): a quantity related to pure substances
  
  \( (\mu_A^*(l) : \text{the chemical potential of pure A in liquid phase}) \)

- Pure substance A

\[
\mu_A^* = \mu_A^\Theta + RT \ln p_A^*
\]

- When another substance exists,

\[
\mu_A = \mu_A^\Theta + RT \ln p_A
\]

- When we combine the above two equations,

\[
\mu_A = \mu_A^* - RT \ln p_A^* + RT \ln p_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}
\]
5.3 The chemical potentials of liquids

(a) Ideal Solutions

- When we combine the above two equations,

\[ \mu_A = \mu_A^* - RT \ln p_A^* + RT \ln p_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} \]

- F. Raoult found that the ratio of the partial vapor pressure of each component to its vapor pressure as a pure liquid is approximately equal to the mole fraction in the liquid mixture

\[ p_A = x_A p_A^* : \text{Raoult's law} \]

- Then,

\[ \mu_A = \mu_A^* + RT \ln x_A \]

- Ideal solutions: the mixtures that obey the above equation
5.3 The chemical potentials of liquids

(a) Ideal Solutions

- Two similar liquids may behave almost ideally!
- The law is a good approximation for the properties of the solvent if the solution is dilute

![Graphs showing pressure vs mole fraction for benzene, methylbenzene, carbon disulfide, and acetone.](image)
(a) Ideal-dilute Solutions

- For real solutions at low concentrations, although the vapor pressure of the solute is proportional to its mole fraction, the constant of proportionality is not the vapor pressure of the pure substance.

\[ p_B = x_B K_B : \text{Henry's law} \]

- \( K_B \) is the empirical constant.
- Ideal-dilute solution: Mixtures for which the solute obeys Henry’s law and the solvent obeys Raoult’s law.
- Important for respiration.