

Lecture 20

Thermodynamics of Solutions

The Mixing Process



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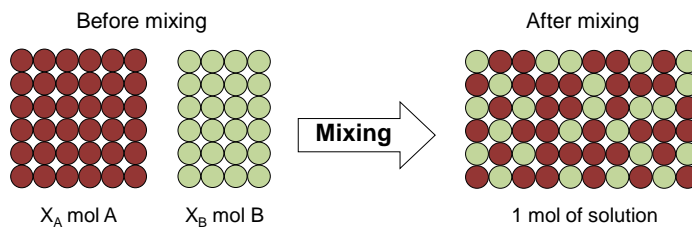
Today's Topics

- Thermodynamics of the mixing process
- The mixing functions for ideal, real and regular solutions

Thermodynamics of the Mixing Process

- When components A and B are mixed together to form a binary A-B solution, thermodynamic properties (free energy, enthalpy, entropy, etc.) are changed.
- For a solution to form, the free energy change during mixing of components must be negative – a sign of spontaneous process.

- Let us calculate the Gibbs free energy change of mixing during the formation of a binary A-B solid solution.
- Consider that the solution is formed by two imaginary steps:
 1. bringing together X_A moles of pure A and X_B moles of pure B
 2. allowing them to mix together to form 1 mol of A-B solution



- The total free energy change of the system after step 1:

$$\Delta G_1 = X_A G_A^0 + X_B G_B^0 \quad (6.66)$$

where G_A^0 and G_B^0 be the molar free energies of pure A and pure B

- During mixing, free energy of the system will change while making the solution and, after step 2, the free energy of the solid solution

$$\Delta G_2 = \Delta G_1 + \Delta G^M \quad (6.67)$$

where ΔG^M is the molar Gibbs free energy change of mixing.

- For a solution to form spontaneously, ΔG^M must be negative.

- The molar Gibbs free energy of solution, ΔG_2 , can be expressed as:

$$\Delta G_2 = X_A \hat{G}_A + X_B \hat{G}_B \quad (6.68)$$

where \hat{G}_A and \hat{G}_B are partial molar Gibbs free energies of A and B.

- The Gibbs free energy of mixing for the solution

$$\begin{aligned} \Delta G^M &= \Delta G_2 - \Delta G_1 \\ \Delta G^M &= X_A (\hat{G}_A - G_A^0) + X_B (\hat{G}_B - G_B^0) \\ \Delta G^M &= X_A \Delta \hat{G}_A^M + X_B \Delta \hat{G}_B^M \end{aligned} \quad (6.69)$$

Please note that \hat{G}_A instead of \bar{G}_A is written for typing convenience only

- Since $\Delta \hat{G}_k = RT \ln a_k$, we have

$$\begin{aligned} \Delta G^M &= RT (X_A \ln a_A + X_B \ln a_B) \\ \Delta G^M &= \sum RT X_k \ln a_k \end{aligned} \quad (6.70a)$$

$$\Delta \hat{G}_k^M = RT \ln a_k \quad (6.70b)$$

Mixing Functions for Ideal Solutions

- Conditions for making ideal solutions:
 1. A-A, A-B and B-B interactions are similar
 2. The mixing between A and B atoms is at random
 3. No energy is released/required due to bond formation

- These three conditions ensures that the Raoult's law is obeyed so that $a_k = X_k$.

$$\Delta G^M = \sum RT X_k \ln a_k \quad (6.70a)$$

- Then, the Gibbs free energy of mixing for ideal solution:

$$\Delta G^{M, id} = RT (X_A \ln X_A + X_B \ln X_B) = \sum RT X_k \ln X_k \quad (6.71a)$$

$$\Delta \hat{G}_k^{M, id} = RT \ln X_k \quad (6.71b)$$

- The entropy of mixing for ideal solution:

$$\Delta \hat{S}_k^{M, id} = - \left[\partial (\Delta \hat{G}_k^{M, id}) / \partial T \right]_{P, n_k}$$

$$\Delta \hat{S}_k^{M, id} = - R \ln X_k \quad (6.72)$$

$$\Delta S^{M, id} = - R (X_A \ln X_A + X_B \ln X_B) = - \sum R X_k \ln X_k \quad (6.73)$$

$$dG = -SdT + VdP + \mu dn$$

$$S = (\partial G / \partial T)_{P, n}$$

- The enthalpy change of mixing for ideal solution:

$$\Delta \hat{H}_k^{M, id} = 0$$

$$G = H - TS$$

Mixing Functions for Real Solutions

- Real solutions do not obey Raoult's law (so that $a_k = \gamma_k \cdot X_k$) because:

- A-A, A-B and B-B interactions are not similar
- Preferential mixing between A and B atoms
- There will be energy released/required due to bond formation

- The partial Gibbs free energy of mixing for real solution:

$$\Delta \hat{G}_k^{M,r} = RT \ln a_k = RT \ln \gamma_k + RT \ln X_k \quad (6.76)$$

$$\Delta \hat{G}_k^{M,r} = \hat{G}_k^{ex} + \Delta \hat{G}_k^{M,id}$$

$$\Delta G^{M,r} = G^{ex} + \Delta G^{M,id} \quad (6.77)$$

where G^{ex} is the excess free energy of mixing.

Mixing Functions for Regular Solutions

- For regular solutions, the deviation from ideal behaviour is minimal, so that the mixing is still considered to be at random/ideal, but there will be some bond formation ($\Delta H^M \neq 0$).

- The entropy of mixing for regular solution

$$\Delta \hat{S}_k^{M,reg} = \Delta \hat{S}_k^{M,id} = -R \ln X_k$$

- The partial Gibbs free energy of mixing for regular solution (which is the same as for the real solution):

$$\Delta \hat{G}_k^{M,reg} = RT \ln a_k$$

- The excess partial Gibbs free energy of mixing for regular solution (which is also the same as for the real solution):

$$\hat{G}_k^{ex,reg} = RT \ln \gamma_k$$

TABLE 6.2: Thermodynamic properties of solutions

Ref: Rashid, Materials Thermodynamics, 2014, pp.116-117.

Next Class

Lecture 21

**Thermodynamics
of Solutions**

Problem Solving