

## 16.9: Properties of Ideal Solutions

We have found the chemical potential of any component in an ideal solution. Now let us find some other thermodynamic properties of an ideal solution. The value of an extensive thermodynamic property of the solution will be the sum of the values of that property for the separate pure components plus the change that occurs when these components are mixed. (The initial state of the system comprises the pure, separate components at a particular temperature and pressure. The mixed state is a homogeneous liquid solution at the same temperature and pressure.) If the solution contains  $n_A$  moles of component  $A$  and  $n_B$  moles of component  $B$ , the Gibbs free energy is

$$G_{\text{solution}}(n_A, n_B) = n_A \mu_A + n_B \mu_B$$

Dividing through by  $n_A + n_B$  to find the Gibbs free energy of the mixture per mole of solution, we have

$$\begin{aligned}\bar{G}_{\text{solution}}(y_A, y_B) &= y_A \mu_A + y_B \mu_B \\ &= y_A \Delta_f G^\circ(A) + y_A RT \ln y_A + y_B \Delta_f G^\circ(B) + y_B RT \ln y_B\end{aligned}$$

To make this mixture, we need  $y_A$  moles of  $A$  and  $y_B$  moles of  $B$ . The Gibbs free energy of these amounts of unmixed pure  $A$  and  $B$ , each in its standard state, is

$$\bar{G}_{\text{initial}} = y_A \Delta_f G^\circ(A) + y_B \Delta_f G^\circ(B)$$

For the process of mixing pure  $A$  and pure  $B$ , each originally in its standard state, to form one mole of an ideal solution, the Gibbs free energy change is

$$\Delta_{\text{mix}} \bar{G} = \bar{G}_{\text{solution}} - \bar{G}_{\text{initial}} = y_A RT \ln y_A + y_B RT \ln y_B$$

In [Section 13.3](#), we found this same relationship for mixing ideal gases:

$$\Delta_{\text{mix}} \bar{G}(\text{gas}) = x_A RT \ln x_A + x_B RT \ln x_B$$

From  $(\partial \Delta_{\text{mix}} G / \partial T)_P = -\Delta_{\text{mix}} S$ , we find

$$\Delta_{\text{mix}} \bar{S} = -y_A R \ln y_A - y_B R \ln y_B$$

and the entropy of the liquid solution is

$$\bar{S}_{\text{solution}} = y_A S_A^\circ + y_B S_B^\circ - y_A R \ln y_A - y_B R \ln y_B$$

From  $(\partial \Delta_{\text{mix}} G / \partial P)_T = \Delta_{\text{mix}} V$ , we find

$$\Delta_{\text{mix}} \bar{V} = 0$$

and from  $\Delta_{\text{mix}} H = \Delta_{\text{mix}} G + T \Delta_{\text{mix}} S$ , we find

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

Thus,  $\Delta_{\text{mix}} \bar{S}$ ,  $\Delta_{\text{mix}} \bar{V}$ , and  $\Delta_{\text{mix}} \bar{H}$  for forming an ideal solution are identical also to the relationships we found for mixing ideal gases.

These results have an important physical interpretation. That  $\Delta_{\text{mix}} \bar{V} = 0$  implies that the molecules of  $A$  and the molecules of  $B$  occupy the same volume in the mixture as they do in the pure state. From  $\Delta_{\text{mix}} \bar{V} = 0$  and  $\Delta_{\text{mix}} \bar{H} = 0$ , it follows that  $\Delta_{\text{mix}} \bar{E} = 0$  at constant pressure. In turn, this implies that the forces between an  $A$  molecule and a  $B$  molecule are the same as the forces between two  $A$  molecules or between two  $B$  molecules. If the force of attraction between an  $A$  molecule and a  $B$  molecule were stronger than that between two  $A$  molecules or between two  $B$  molecules, molecules in the mixture would be—on average—closer together in the mixture than in the separate components; we would find  $\Delta_{\text{mix}} \bar{V} < 0$ . Moreover, the potential energy of the mixed state would be lower than that of the separate components; the mixing process would evolve heat at constant temperature; we would find  $\Delta_{\text{mix}} \bar{E} < 0$ .

Conversely, if the repulsive force between an  $A$  molecule and a  $B$  molecule were stronger than the repulsive forces between two  $A$  molecules or between two  $B$  molecules, the average separation would be greater in the mixture; we would find  $\Delta_{\text{mix}}\bar{V} > 0$ . The potential energy of the mixed state would be greater than that of the separate components; the mixing process would consume heat at constant temperature; we would find  $\Delta_{\text{mix}}\bar{E} > 0$ .

In an ideal gas, molecules do not interact at all. In an ideal solution, the molecules must interact, because only their mutual attraction can keep them in the liquid state. The ideal solution behaves ideally not because the intermolecular interactions are zero but rather because the intermolecular interactions are the same for all of the kinds of molecules present in the mixture. This interpretation implies that the vapor pressures of the pure components of an ideal solution should be equal. Even for solutions that follow Raoult's law quite closely, this expected equality is often imperfectly realized. Not surprisingly, ideal-solution behavior is best exhibited when the components are isotopically-substituted versions of the same compound.

In an ideal solution, the activities of the components are equal to their mole fractions. The activity of the solvent depends only on the solvent mole fraction. The properties of the solvent in an ideal solution are independent of the specific substance that comprises the solute; they depend only on the concentration of solute particles present. Systems in which this is a useful approximation are sufficiently common that their properties are given a special name: A **colligative property** of a solution is a property that depends only on the concentration of solute particles and not on the specific chemical properties of the solute. We expect this approximation to become better as the solute concentration approaches zero. When a solute obeys Raoult's law or Henry's law, its effects on the thermodynamic properties of the solvent depend only on the concentration of the solute. Consequently, Raoult's law and Henry's law prove to be useful when we seek to model colligative properties.

In Sections 16.10 through 16.14, we evaluate five colligative properties: boiling-point elevation, freezing-point depression, osmotic pressure, solid-solute solubility and gas-solute solubility. We derive the first three of these properties from the perspective that they enable us to determine the molar mass of solutes. However, boiling-point elevation, freezing-point depression, and osmotic pressure are important methods for the measurement of activity coefficients in non-ideal solutions. To illustrate the measurement of activity coefficients, we develop a more detailed analysis of freezing-point depression in Section 16.15.

---

This page titled 16.9: Properties of Ideal Solutions is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Paul Ellgen via source content that was edited to the style and standards of the LibreTexts platform.