

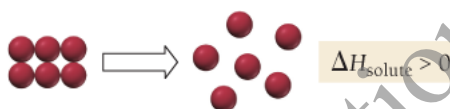
13.3: Energetics of Solution Formation

In [Chapter 9](#), we examined the energy changes associated with chemical reactions. Similar energy changes can occur when a solution forms, depending on the magnitude of the interactions between the solute and solvent particles. For example, when we dissolve sodium hydroxide in water, heat is evolved—the solution process is *exothermic*. In contrast, when we dissolve ammonium nitrate (NH_4NO_3) in water, heat is absorbed—the solution process is *endothermic*. Other solutions, such as sodium chloride in water, barely absorb or evolve heat upon formation. What causes these different behaviors?

Energy Changes in Solution Formation

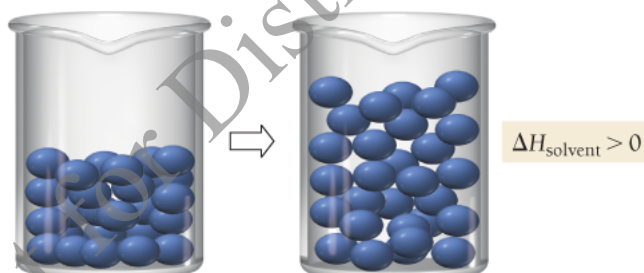
We can understand the energy changes associated with solution formation by envisioning the process as occurring in three steps, each with an associated change in enthalpy:

1. Separating the solute into its constituent particles.



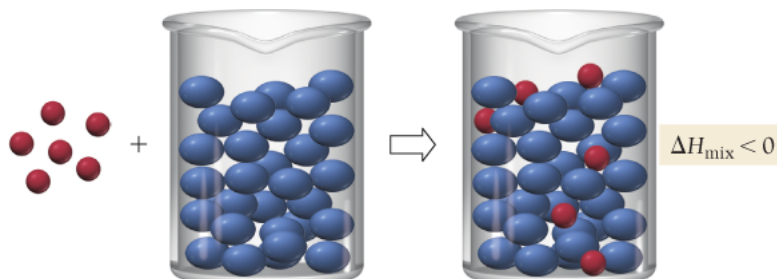
This step is always endothermic (positive ΔH) because energy is required to overcome the forces that hold the solute particles together.

2. Separating the solvent particles from each other to make room for the solute particles.



Like Step 1, this step is also endothermic because energy is required to overcome the intermolecular forces among the solvent particles.

3. Mixing the solute particles with the solvent particles.



This step is exothermic because energy is released as the solute particles interact (through intermolecular forces) with the solvent particles.

According to Hess's law, the overall enthalpy change upon solution formation, called the **enthalpy of solution** (ΔH_{soln}), is the sum of the changes in enthalpy for each step:

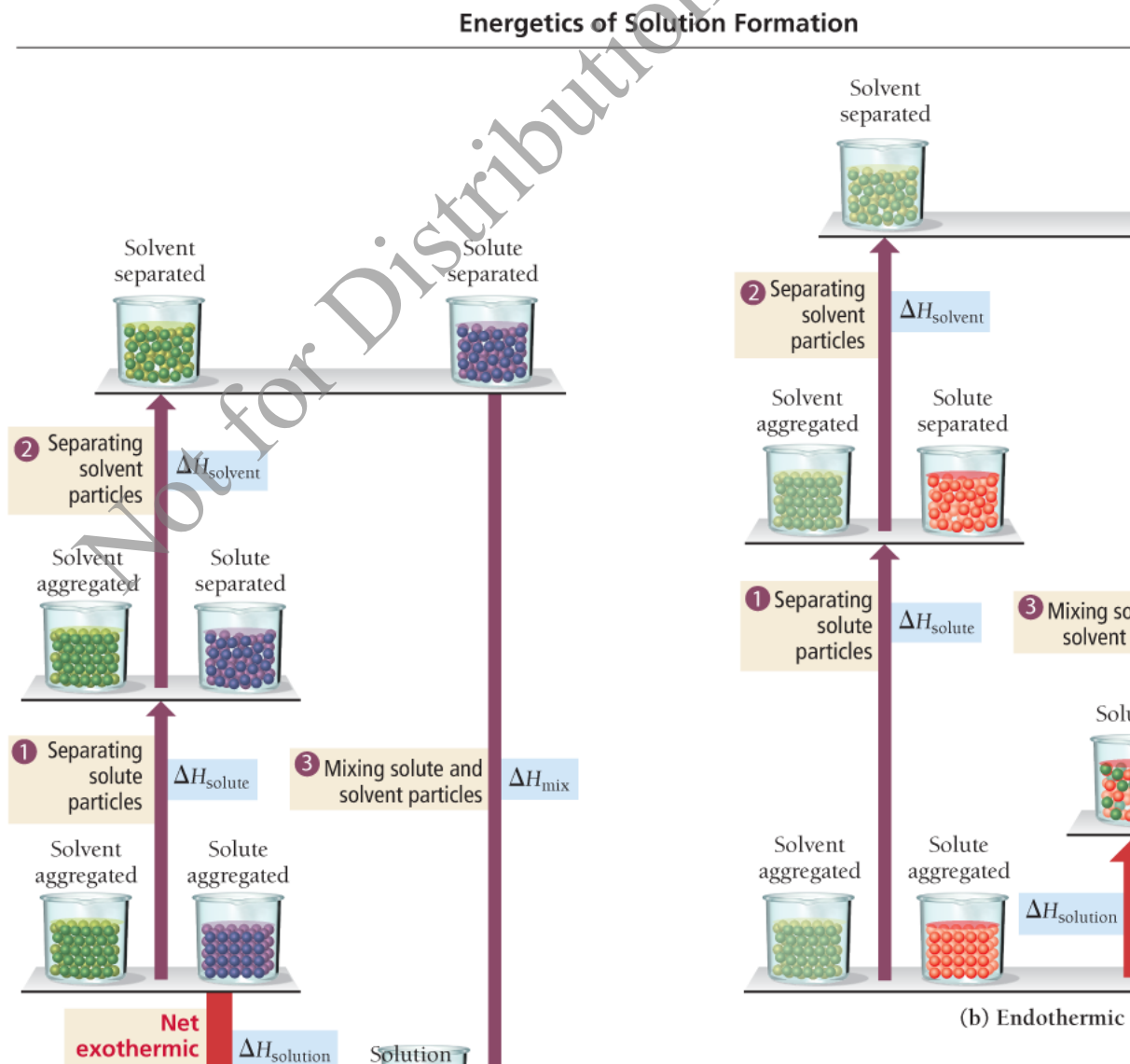
$$\Delta H_{\text{soln}} = \underset{\text{endothermic (+)}}{\Delta H_{\text{solute}}} + \underset{\text{endothermic (+)}}{\Delta H_{\text{solvent}}} + \underset{\text{endothermic (-)}}{\Delta H_{\text{mix}}}$$

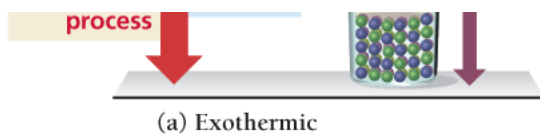
Since the first two terms are endothermic (positive ΔH) and the third term is exothermic (negative ΔH), the overall sign of ΔH_{soln} depends on the magnitudes of the individual terms (Figure 13.5) as outlined here:

1. If the sum of the endothermic terms is approximately equal in magnitude to the exothermic term, then ΔH_{soln} is about zero. The entropy increase upon mixing drives the formation of a solution, while the overall energy of the system remains nearly constant.
2. If the sum of the endothermic terms is smaller in magnitude than the exothermic term, then ΔH_{soln} is negative and the solution process is exothermic. In this case, both the tendency toward lower energy and the tendency toward greater entropy drive the formation of a solution.
3. If the sum of the endothermic terms is greater in magnitude than the exothermic term, then ΔH_{soln} is positive and the solution process is endothermic. In this case, as long as ΔH_{soln} is not too large, the tendency toward greater entropy still drives the formation of a solution. If, on the other hand, ΔH_{soln} is too large, a solution does not form.

Figure 13.5 Energetics of the Solution Process

(a) When ΔH_{mix} is greater in magnitude than the sum of ΔH_{solute} and $\Delta H_{\text{solvent}}$, the heat of solution is negative (exothermic). (b) When ΔH_{mix} is smaller in magnitude than the sum of ΔH_{solute} and $\Delta H_{\text{solvent}}$, the heat of solution is positive (endothermic).





Aqueous Solutions and Heats of Hydration

Many common solutions, such as seawater, contain an ionic compound dissolved in water. For these aqueous solutions, we combine $\Delta H_{\text{solvent}}$ and ΔH_{mix} into a single term called the **heat of hydration** ($\Delta H_{\text{hydration}}$) (Figure 13.6). The heat of hydration is the enthalpy change that occurs when 1 mol of the gaseous solute ions is dissolved in water. Because the ion-dipole interactions that occur between a dissolved ion and the surrounding water molecules (Figure 13.7) are much stronger than the hydrogen bonds in water, $\Delta H_{\text{hydration}}$ is always large and negative (exothermic) for ionic compounds.

Figure 13.6 Heat of Hydration and Heat of Solution

The heat of hydration is the heat emitted when 1 mol of gaseous solute ions is dissolved in water. The sum of the negative of the lattice energy and the heat of hydration is the heat of solution. (Recall that the negative of lattice energy is ΔH_{solute} .)

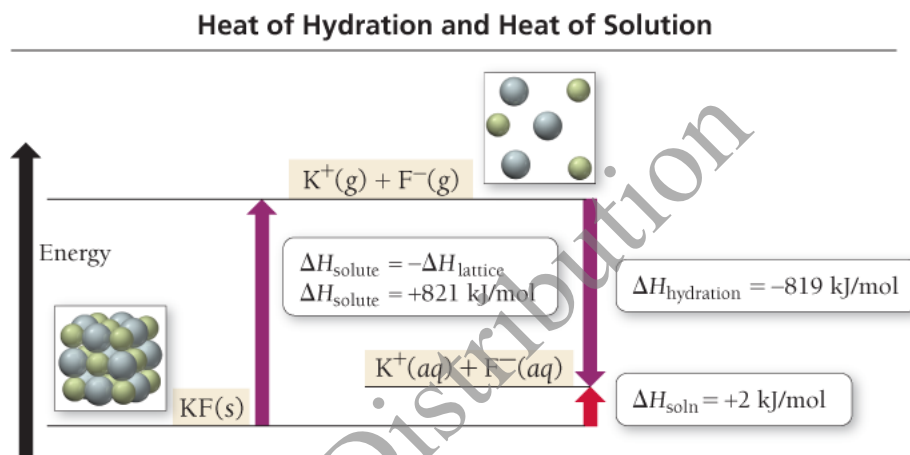
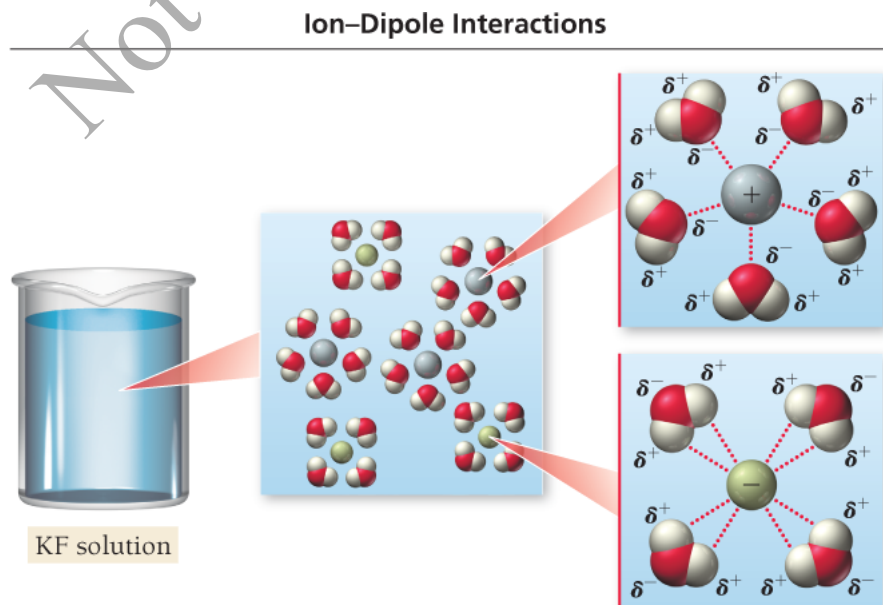


Figure 13.7 Ion-Dipole Interactions

Ion-dipole interactions such as those between potassium ions, fluoride ions, and water molecules cause the heat of hydration to be largely negative (exothermic) for ionic compounds.

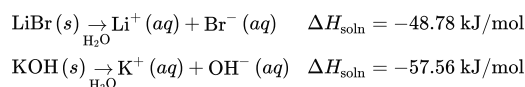


Using the heat of hydration, we can write the enthalpy of solution as a sum of just two terms, one endothermic and one exothermic:

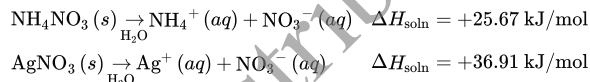
$$\begin{aligned}\Delta H_{\text{soln}} &= \Delta H_{\text{solute}} + \underbrace{\Delta H_{\text{solvent}} + \Delta H_{\text{mix}}}_{\Delta H_{\text{hydration}}} \\ \Delta H_{\text{soln}} &= \underbrace{\Delta H_{\text{solute}}}_{\substack{\text{endothermic} \\ \text{(positive)}}} + \underbrace{\Delta H_{\text{hydration}}}_{\substack{\text{exothermic} \\ \text{(negative)}}}\end{aligned}$$

For ionic compounds, ΔH_{solute} , the energy required to separate the solute into its constituent particles is the negative of the solute's lattice energy ($\Delta H_{\text{solute}} = -\Delta H_{\text{lattice}}$) discussed in [Section 9.11](#). For ionic aqueous solutions, then, the overall enthalpy of solution depends on the relative magnitudes of ΔH_{solute} and $\Delta H_{\text{hydration}}$ with three possible scenarios (in each case we refer to the *magnitude or absolute value* of ΔH):

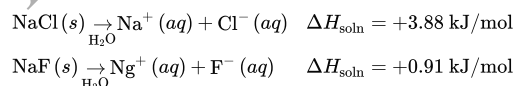
1. $|\Delta H_{\text{solute}}| < |\Delta H_{\text{hydration}}|$ The amount of energy required to separate the solute into its constituent ions is less than the energy given off when the ions are hydrated. ΔH_{soln} is therefore negative, and the solution process is exothermic. Solutes with negative enthalpies of solution include lithium bromide and potassium hydroxide. When these solutes dissolve in water, the resulting solutions feel warm to the touch:



2. $|\Delta H_{\text{solute}}| > |\Delta H_{\text{hydration}}|$ The amount of energy required to separate the solute into its constituent ions is greater than the energy given off when the ions are hydrated. ΔH_{soln} is therefore positive, and the solution process is endothermic (if a solution forms at all). Solutes that form aqueous solutions with positive enthalpies of solution include ammonium nitrate and silver nitrate. When these solutes dissolve in water, the resulting solutions feel cool to the touch:



3. $|\Delta H_{\text{solute}}| \approx |\Delta H_{\text{hydration}}|$ The amount of energy required to separate the solute into its constituent ions is roughly equal to the energy given off when the ions are hydrated. ΔH_{soln} is therefore approximately zero, and the solution process is neither appreciably exothermic nor appreciably endothermic. Solutes with enthalpies of solution near zero include sodium chloride and sodium fluoride. When these solutes dissolve in water, the resulting solutions do not undergo a noticeable change in temperature:



Conceptual Connection 13.2 Energetics of Aqueous Solution Formation

Interactive

Not for Distribution