11.1 ENERGY CHANGES WHEN SUBSTANCES DISSOLVE

On many college campuses, winter brings sub-freezing temperatures and snow - sometimes a lot of it. To keep walk ways clear on these campuses after plowing or shovelling, pellets of calcium chlouride are often spread to melt packed snow and ice and to prevent new ice from forming (Figure 11.1). Meanwhile, road crews apply mixtures of sand and sodium chloride to keep streets and high ways navigable.

Later in this chapter we will explore why $CaCl_2$ and $NaCl$ are affective in melting ice (Hint: it has to do with there capacity to lower the freezing point of water). For now, the question to be addressed is why $CaCl_2$, which costs much more than ClNa, so widely used to keep sidewalks ice-free. There are several reasons, but we focus here on just one: when $NaCl$ dissolves in melting ice, there is little change in the temperature of the water, but when $CaCl_2$ dissolves, the water heats up, which helps melt more ice. In this section we investigate why the two salts produce such different temperature changes when they dissolve--that is, why dissolving CaCl2 is a decidedly endothermic process, but dissolving $NaCl$ is slightly exothermic (Figure 11.2). To understand why, we need to analyse, step by step, how salts dissolve in water, and to track the changes in entropy that accompany each of these steps.

As we have discussed in prior chapters, ionic compounds are held together by strong colavent bonds that have bond energies of many hundreds of kilojoules per mole. For their part, molecules of H^2O interact with each other principly through hydrogen bonding. When an ionic solid dissolves in water, the ionic bonds that hold it's ions together must be broken. Similarly, many hydrogen bonds must be broken as molecules of H_2O must make space for and cluster

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around the dissolved ions. These endothermic processes require investments of thermal energy, which we can calculate by summing the enthalpy change that accompanies each process:

$$\text{Thermal energy invested} = \Delta H_{\text{ionic bonds}} + \Delta H_{\text{H}_2\text{O}-\text{H}_2\text{O}}$$

When ionic compounds dissolve in water, their ions interact with the temporary dipoles of water molecules that form spheres of hydration around the ions. We assign the change in enthalpy that accompanies this exothermic process the symbol $\Delta H_{\text{ion–dipole}}$. The overall change in enthalpy that accompanies the dissolution process, called the **heat of solution** ($\Delta H_{\text{solution}}$), is the sum of the thermal energies absorbed and released (see Figure 11.2):

$$\Delta H_{\text{sol}} = [\Delta H_{\text{ionic bonds}} - \Delta H_{\text{H}_2\text{O}-\text{H}_2\text{O}}] + \Delta H_{\text{ion–dipole}} \qquad (11.1)$$

Endothemic   Exothermic

Keep in mind that the energy required to break the ionic bonds in one mole of an ionic compound is equal in magnitude but opposite in sign to the lattice energy (U) of the compound:

$$\Delta H_{\text{ion bonds}} = -U \qquad (11.2)$$

We can determine the value of $\Delta H_{\text{solution}}$ experimentaly using calorimetric methods such as the one shown in figure 11.3. The heat of solution can be positive or negative, that is, the dissolution process can be exothermic — as it is for NaCl (Figure 11.2)—or endthermic, as it is for $CaCl_2$. Table 11.1 lists ΔH_{soln} values for several common anionic compounds. The compounds in the

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