

Salt Water

*In recitation last week you had a qualitative discussion about the energetic and entropic effects associated with dissolving salt in water. In this problem you'll have the opportunity to be a bit more quantitative, and to see the essential role that **entropy** plays in the ability of electrolytic ions to remain soluble in an aqueous cellular environment.*

Why electrolytes?

An electrolyte fluid contains ions that are essential to keeping the physiological engine running smoothly. They help to regulate the hydration of the body, the pH of blood, and an organism's nerve and muscle functioning. Every higher life form that we know of requires a subtle balance of electrolyte ions (most notably Na⁺, K⁺, Ca²⁺, Mg²⁺, and Cl⁻) between the intracellular and extracellular environment in order to maintain proper functioning. Sodium is the main electrolyte found in extracellular fluid and is primarily responsible for blood pressure control and fluid balance. For that reason and others, it is essential to our survival that NaCl be soluble in physiological environments. Let's see why it is!

Why does salt dissolve in water?

Dissolving a solute like NaCl in a solvent like H₂O can be thought of as a three step process: (1) the solute must be broken up into its component ions, (2) the solvent molecules must be separated to make room for the solute, and (3) solute-solvent interactions must form. Each step in that process is associated with an enthalpy change ΔH :

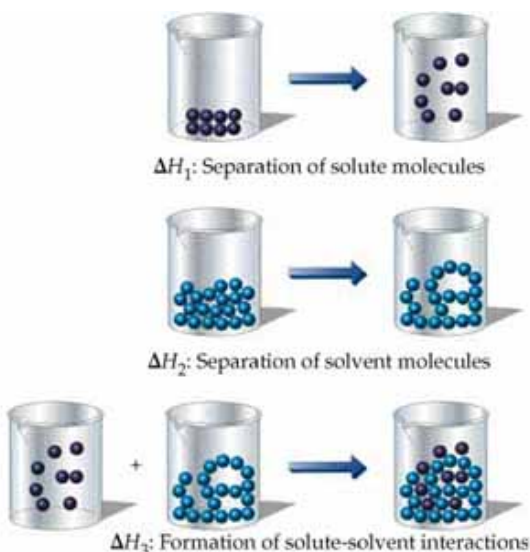


Figure 1. The three-step process by which a solute dissolves in a solvent. The enthalpy change associated with Step 1 is called the **lattice enthalpy**, since it is the enthalpy associated with breaking a solute lattice. The sum of the enthalpies associated with Steps 2 and 3 is called the **hydration enthalpy**, since it's the enthalpy associated with surrounding the solute ions by water molecules.

A molecular depiction of Na^+ and Cl^- ions dissolving in water looks something like this:

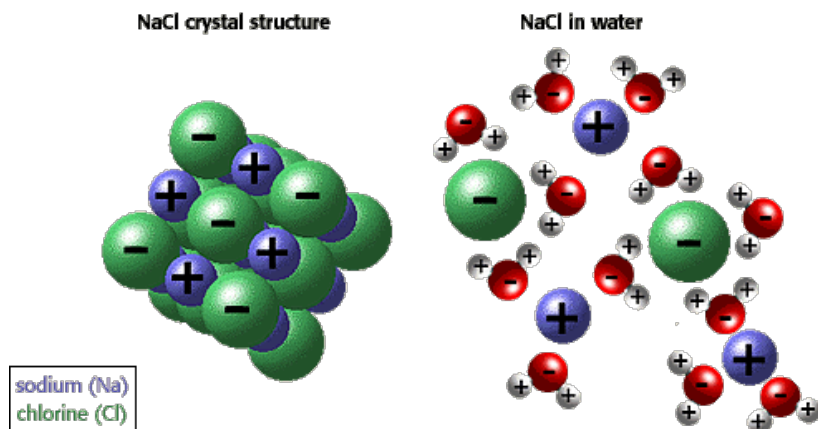


Figure 2. The NaCl ionic lattice is disrupted and the individual ions are surrounded by water molecules.

The lattice enthalpies for some ionic compounds and the hydration enthalpies, as found experimentally, are given in the following Tables:

Ionic Compound	Lattice Enthalpy (kJ/mol)
LiF	1030
NaF	910
NaCl	788
KCl	701
KBr	671
CsCl	657
MgCl ₂	2326
CaO	3414

Cation	Ion Radius (pm)	Hydration Enthalpy (kJ/mol)
Li ⁺	90	-515
Na ⁺	116	-405
K ⁺	152	-321
Rb ⁺	166	-296
Cs ⁺	181	-268
Anion		
Cl ⁻	167	-364

1. Use the pictures in Figure 2 to explain why the lattice enthalpies are positive and the hydration enthalpies are negative.
2. Use the pictures in Figure 2 to explain the correlation between ion radius and hydration enthalpy for cations. Why might the anion Cl^- not fit with that trend?
3. What is the overall enthalpy change for dissolving table salt (NaCl) in water? What does the sign of the overall enthalpy change indicate, if anything, about the solubility of salt in water?
4. As you know, table salt *is* soluble in water at room temperature! What does this tell you about the sign of the overall entropy change ΔS_{tot} upon dissolving salt in water? How do you know?
5. You found the sign of the overall entropy change ΔS_{tot} for dissolving salt in water in Question 4. If we let $\Delta S_{\text{tot}} = \Delta S_{\text{salt}} + \Delta S_{\text{water}}$, what are the signs of the individual ΔS_{salt} and ΔS_{water} values? How do you know?
6. What effect would increasing the temperature have on the solubility of salt in water? How do you know?