

6.4: Gibbs Energy and Solubility

Try adding NaCl to water, you can do this at the dinner table. You will see that the NaCl dissolves and the temperature of the solution goes down. Is this the case with all salts? No, it is not. If you dissolve calcium chloride (CaCl_2) or magnesium chloride (MgCl_2), the solution gets warmer, not colder. Dissolving CaCl_2 or MgCl_2 in water clearly involves some kind of energy release (recall that if the temperature increases, the average kinetic energy of the molecules in the solution also increases).

How do we explain why dissolving NaCl causes the temperature of the solution to decrease, whereas dissolving CaCl_2 or MgCl_2 makes the temperature increase? Because both processes (that is the dissolving of NaCl and $\text{CaCl}_2/\text{MgCl}_2$ into water) occur, they must be thermodynamically favorable. In fact, all of these compounds are highly soluble in water, the ΔG for the formation of all three solutions is negative, but the process results in different temperature changes. Let us look at the example of calcium chloride: as a crystal of CaCl_2 dissolves in water, interactions between ions are broken and new interactions between water molecules and ions are formed. The table below lists the types of interactions forming in the crystal and the solvent.

Within the crystal, there are ion–ion interaction while in the solvent there are H-bonding, dipole–dipole, and LDF interactions. As the crystal dissolves, new ion–dipole interactions form between calcium ions and water molecules, as well as between chloride ions and molecules. At the same time, the majority of the interactions between water molecules are preserved.

Interactions Present Before Solution	Interactions Present After Solution
ion-ion (interactions between Ca^{2+} and Cl^-)	ion-dipole interactions between Ca^{2+} and H_2O and Cl^- and H_2O)
Interactions Between Water Molecules H-bonding, dipole–dipole, and LDFs	Interactions Between Water Molecules H-bonding, dipole–dipole, and LDFs

In order to connect our observation that the temperature increases with thermodynamic data, we have to be explicit about what we mean by the system and what we mean by the surroundings. In calcium chloride, the system is CaCl_2 and the water molecules it interacts with. The surroundings are the rest of the water molecules (the solution). So when we measure the temperature change, we are actually measuring the temperature change of the surroundings (not the system). If the temperature rises, that means thermal energy is transferred from the $\text{CaCl}_2\text{—H}_2\text{O}$ system to the water. Therefore, the interactions after the solution is formed are stronger and more stable than those for the solid CaCl_2 and water separately. If we look up the enthalpy change for the solution of calcium chloride, it is around -80 kJ/mol : dissolving is exothermic and heat is transferred from the system to the surroundings.

So what is going on with NaCl? Solution temperatures decrease when NaCl is dissolved, so the solution (surroundings) loses energy to the ion–solvent interactions (system). Energy from the surroundings breaks up the NaCl lattice and allows ions to move into the solution. That would imply that ion–ion and $\text{H}_2\text{O—H}_2\text{O}$ interactions are stronger than the ion–water interactions for the NaCl— H_2O system. But why does NaCl dissolve at all? The answer is that enthalpy is not the critical factor determining whether solution happens. If we factor in the entropy change for the solution, which in this case is positive, then ΔG is negative. The dissolving of salt is an entropy-driven process!

To recap: for a solution to form, the Gibbs energy change must be negative. When calcium chloride dissolves in water, ΔH is negative and as it turns out ΔS is slightly negative (although this cannot be determined from observations). This results in a large negative ΔG and a very high solubility (595 g/L). By contrast, when sodium chloride dissolves, ΔH is positive, but ΔS is positive enough to overcome the effect of ΔH . This means that the Gibbs free energy change is also negative for this process. In fact, many solutes dissolve in water with a decrease in temperature. Ethanol—which is infinitely soluble in water—has an unfavorable enthalpy of solution. Thus, the entropy of mixing is the important factor.

Questions

Questions to Answer

- When ammonium chloride dissolves in water, the temperature of the solution drops. Predict the signs of ΔH , ΔS , and ΔG and explain your reasoning by drawing molecular level pictures
- Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_3$) is insoluble in water. The ΔH for solution is about zero. Predict the signs of ΔS and ΔG and explain your reasoning by drawing molecular-level pictures.

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