Free Energy of Dissolution

Essential Question

What decides whether a salt dissolves?

Dissolving Has a ΔG° Too

- Dissolving has its own Δ*H*°, Δ*S*°, and Δ*G*°
- Δ*G*° = −*RT* ln K_{sp} still works

$$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

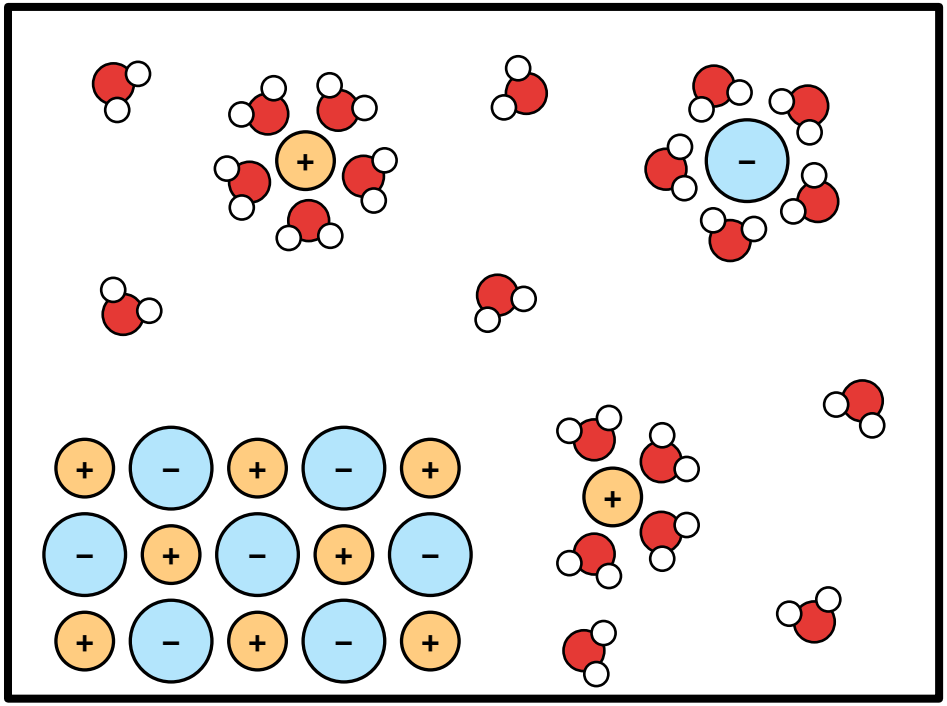
Δ*G*° < 0
K > 1, dissolves well

Δ*G*° > 0
K_{sp} < 1, slightly soluble

The Particle Picture

- Ions leave the solid one at a time
- Water molecules surround each ion

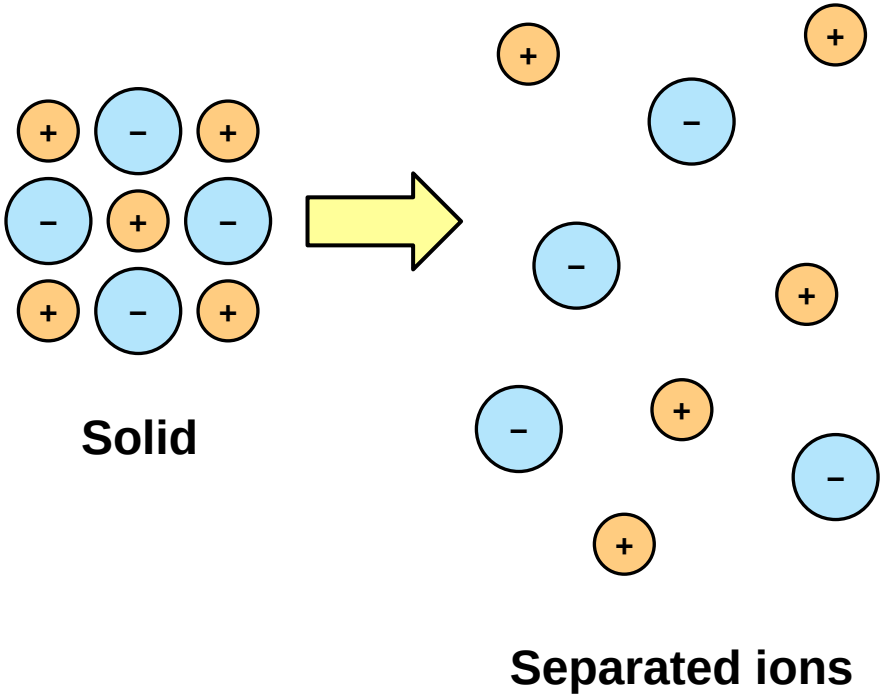
= H_2O (red O, white H)



An ionic solid dissolving in water

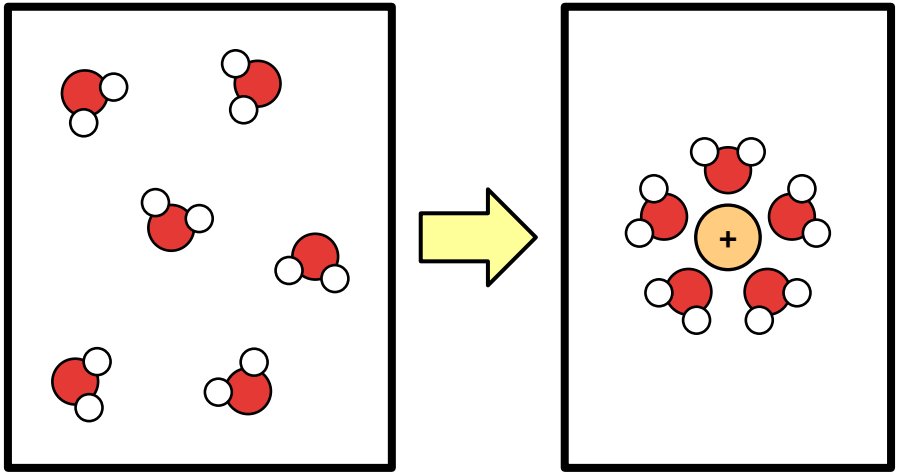
Factor 1: Break Up the Solid

- Ion-ion attractions break: $\Delta H > 0$
- Ions become free to spread out: $\Delta S > 0$



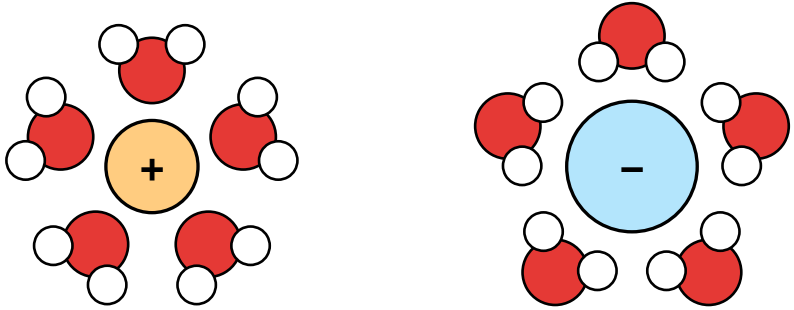
Factor 2: Reorganize the Water

- Some water-water H bonds break: $\Delta H > 0$
- Water lines up around ions: $\Delta S < 0$



Factor 3: Ion-Water Attractions

- Ion-dipole attractions form:
  $\Delta H < 0$
- Water is held tightly in place:
  $\Delta S < 0$



O end (δ−)

faces cation

H end (δ+)

faces anion

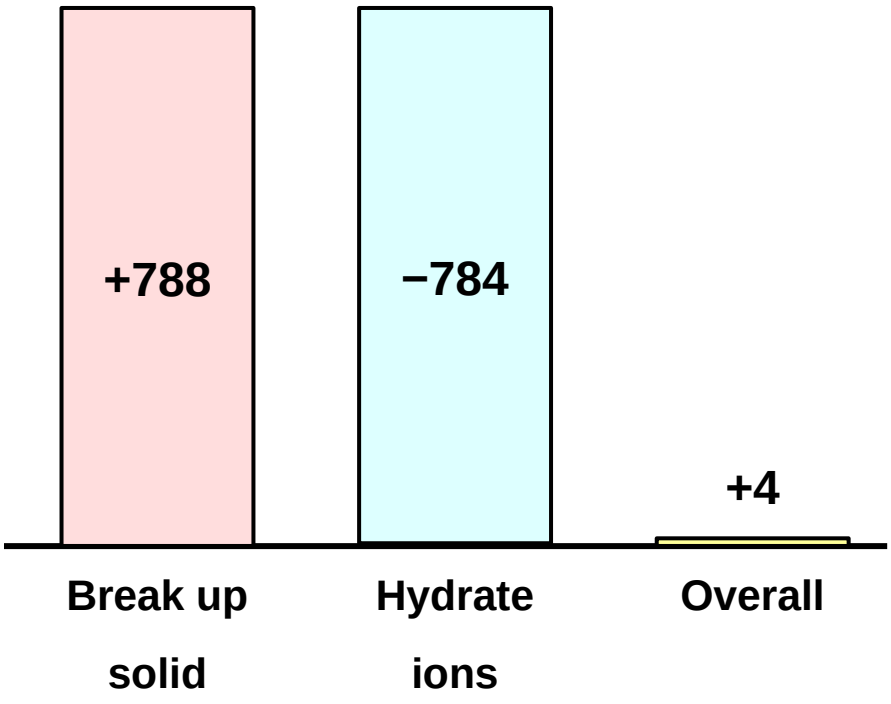
Adding Up the Three Factors

Factor	ΔH	ΔS
1. Break up the solid	+	+
2. Reorganize the water	+	–
3. Ion-water attractions	–	–

$\Delta G° = \Delta H° - T\Delta S°$ for the whole process

Why Predictions Are Hard

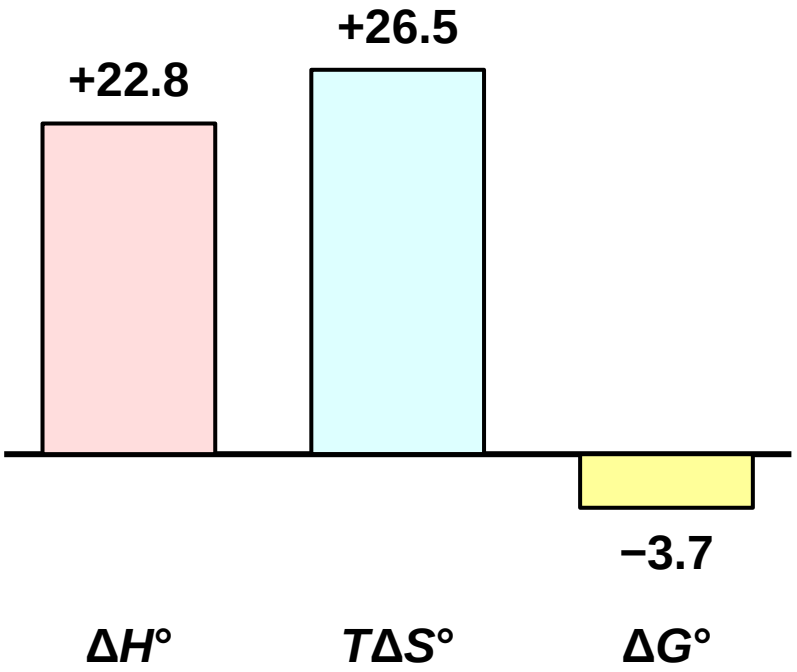
- Big + and − terms partly cancel
- Overall value is a small difference of big numbers



ΔH for dissolving NaCl, kJ/mol

Entropy-Driven Dissolving

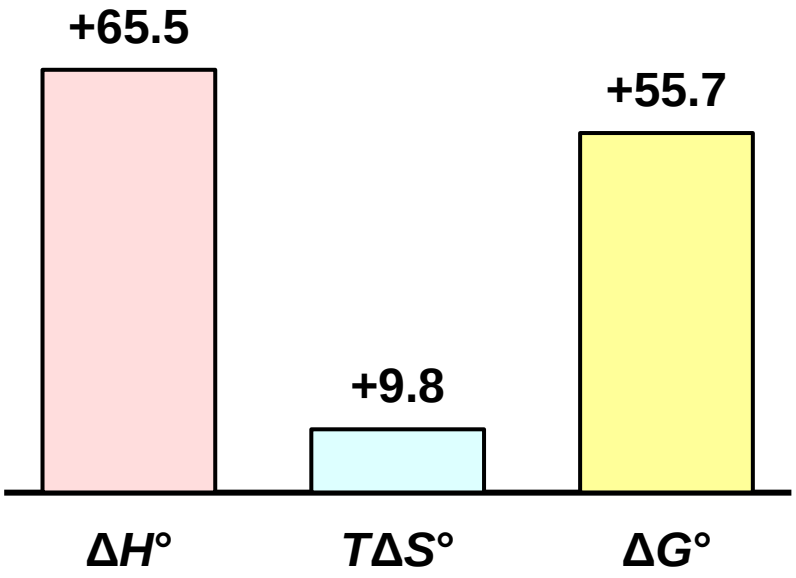
- $NaNO_3$ dissolving is endothermic, yet favored
- $T\Delta S°$ is bigger than $\Delta H°$



$NaNO_3$ at 298 K, kJ/mol

A Sparingly Soluble Salt

- AgCl: $\Delta H°$ is large and positive
- Small $T\Delta S°$ can't overcome it, so $\Delta G° > 0$



AgCl at 298 K, kJ/mol

Example: A Cold Pack

When NH_4NO_3 dissolves in water, the solution gets cold. Is dissolving NH_4NO_3 thermodynamically favored at 298 K? Justify your answer using the data.

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

$\Delta H° = +28.1$ kJ/mol

$\Delta S° = +108.7$ J/(mol·K)

Example: Exothermic but Barely Soluble

Dissolving $CaCO_3$ is exothermic, but $CaCO_3$ is only slightly soluble.

Use the data and the interactions between the ions and water to explain why.

$$CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$\Delta H° = -13.0$ kJ/mol

$\Delta S° = -202.9$ J/(mol·K)

Example: Warming Things Up

Does dissolving KCl become more or less thermodynamically favored as the temperature increases? Justify your answer using the data.

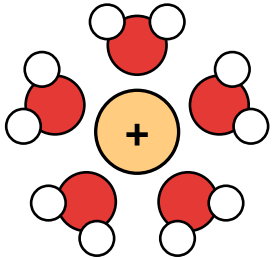
$$KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$$

$\Delta H° = +17.1$ kJ/mol

$\Delta S° = +76.4$ J/(mol·K)

Big Ideas

- Three factors: break up the solid, reorganize the water, ion-water attractions
- Each factor has its own ΔH and ΔS
- The terms partly cancel, so $\Delta G°$ is hard to predict
- $\Delta G° < 0 \rightarrow K > 1$, dissolves well



Hydrated ion