Topic 9.6: Free Energy of Dissolution

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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Dissolving in Three Enthalpy Steps

Step 1: pull the solid apart. Separating an ionic crystal into gaseous ions breaks every ion-ion attraction. Breaking attractions costs energy, so the step is strongly endothermic.

Step 2: make room in the solvent. Solvent molecules must be pushed apart. That breaks solvent-solvent attractions, hydrogen bonds in water, so this step is endothermic too, though much smaller than step 1.

Step 3: let the particles mix in. New solute-solvent attractions form. In water these are ion-dipole attractions, and the step is called hydration. Forming attractions releases energy: the one exothermic step of the three.

The enthalpy of solution is the sum.

ΔH_solution = lattice separation + solvent separation + hydration

Two costs against one payoff, so ΔH_solution can land on either side of zero.

Sodium chloride is the standing example. Its lattice separation is very endothermic, yet it dissolves readily, because hydration of Na^+ and Cl^- releases energy on nearly the same scale.

Hydration Strength: Charge Density Rules

Small, highly charged ions hydrate hardest. Al^{3+} grips water dipoles far more strongly than Na^+: its charge is packed onto a smaller ion, so its hydration enthalpy is far more exothermic.

Comparing two salts starts here. If two salts have similar lattice enthalpies, the one whose ions release more hydration energy finishes with the more exothermic, or less endothermic, ΔH_solution: the lattice cost is shared, so hydration decides.

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The Entropy Contest: Dispersal Against Ordering

Dispersal pushes ΔS up. Ions locked in fixed lattice positions spread through the whole solvent. More positions and arrangements mean more microstates, so this contribution is positive.

Hydration shells push ΔS down. Water molecules locked into shells around ions lose freedom to move and tumble. That ordering contributes a negative term, biggest for small, highly charged ions.

The total can come out negative. For some salts the ordering term outweighs the dispersal gain, and ΔS_solution is negative even though a solid has dissolved: "dissolving always increases entropy" is false.

A gas dissolving is the clearest negative case. Gas particles surrender the volume they roamed for confinement in a liquid, losing most of their microstates.

Free Energy Decides

One equation settles it.

$$\Delta G_{solution} = \Delta H_{solution} - T\Delta S_{solution}$$

Negative means dissolution is thermodynamically favorable; positive means unfavorable. The sign reports favorability only, nothing about speed.

ΔH negative, ΔS positive: favorable at all temperatures. Both terms pull ΔG downward.

ΔH positive, ΔS negative: favorable at no temperature. Both terms push ΔG upward.

ΔH positive, ΔS positive: favorable when hot enough. The TΔS term must outgrow ΔH. Below the crossover temperature ΔG is positive; above it, negative.

$$T = \Delta H / \Delta S$$

ΔH negative, ΔS negative: favorable when cold enough. The enthalpy payoff must dominate before the growing TΔS penalty overtakes it.

Temperature Tips the Balance

Endothermic dissolution and heat. When both are positive, raising T enlarges the favorable TΔS term and ΔG grows more negative, so most solid salts dissolve better hot. Le Chatelier agrees: adding heat shifts an endothermic dissolution forward.

Ammonium nitrate is the cold pack case.

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

It runs with ΔH_solution positive and draws heat from the water, so the pack turns cold. It still dissolves spontaneously at room temperature: dispersing the ions raises entropy enough for TΔS to exceed ΔH.

Dissolved gases run the other way. A gas pays a heavy entropy penalty on entering a liquid, and warming enlarges the TΔS penalty on that negative ΔS, so heating drives dissolved gas out.

Dissolution Is an Equilibrium

A saturated solution is a balance, not a full stop. Solid dissolves and ions deposit at equal rates.

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

The equilibrium constant is the solubility product.

$K_{sp} = [Ag^+][Cl^-]$

Ksp plugs straight into Topic 9.5.

$\Delta G°_{solution} = -RT \ln K_{sp}$

AgCl has $K_{sp} = 1.8 \times 10^{-10}$ at 298 K, so $\ln K_{sp} = -22.44$ and $\Delta G°_{solution} = +55.6$ kJ mol^{-1}. A tiny Ksp and a large positive ΔG° are the same fact in two languages.

A positive ΔG° does not mean "does not dissolve". ΔG° refers to standard conditions. In pure water Q starts at zero, far below Ksp, so solid does dissolve, a little, until Q climbs to Ksp and the solution saturates. There ΔG reaches zero.

The direction test for any sample. Compare Q with Ksp, as in Topic 9.5. Q < Ksp: unsaturated, more can dissolve. Q > Ksp: precipitation runs until Q falls back to Ksp. Q = Ksp: saturated, at equilibrium.

Like Dissolves Like

Step 3 must repay steps 1 and 2, and only between matching forces. Ethanol and water mix freely: both hydrogen bond, keeping attractions as strong as those given up. Oil and water fail because water's hydrogen bonds would be broken for only weak dispersion attractions in return, and an ionic solid in hexane fails the same way.

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Worked Examples

Example 1: Adding the three steps. An ionic solid has lattice separation +788 kJ mol^{-1}, solvent separation +120 kJ mol^{-1} and hydration −900 kJ mol^{-1}. Sum: ΔH_solution = 788 + 120 − 900 = +8 kJ mol^{-1}. The breaking steps cost 908 kJ mol^{-1} and hydration returns 900, so dissolving is slightly endothermic and leaves the verdict to the entropy term.

Example 2: A salt that needs warmth. A salt has ΔH_solution = +25 kJ mol^{-1} and ΔS_solution = +110 J mol^{-1} K^{-1}. At 298 K, TΔS = 298 × 0.110 = 32.8 kJ mol^{-1}, so ΔG = 25 − 32.8 = −7.8 kJ mol^{-1}: favorable. At 200 K, TΔS = 22.0 kJ mol^{-1}, so ΔG = +3.0 kJ mol^{-1}: unfavorable. The crossover sits at T = ΔH / ΔS = 25,000 / 110 = 227 K.

Example 3: ΔG° from Ksp for AgCl. AgCl has Ksp = 1.8 × 10^{-10} at 298 K, so ln Ksp = −22.44. Then ΔG°_solution = −RT ln Ksp = −(2477.6)(−22.44) = +55,600 J mol^{-1} = +55.6 kJ mol^{-1}.

Example 4: Ksp from ΔG° for PbI_2. PbI_2 has ΔG°_solution = +45.7 kJ mol^{-1} at 298 K, or +45,700 J mol^{-1}. Then ln Ksp = −ΔG° / RT = −45,700 / 2477.6 = −18.45, so Ksp = $e^{-18.45}$ = 9.8 × 10^{-9}.

Traps That Cost Marks in Topic 9.6

Letting the lattice energy decide alone. ΔH_solution is a three-step sum, with TΔS still to come in ΔG. A huge lattice enthalpy says nothing alone: NaCl has one and dissolves readily.

Reading "hydration is exothermic" as "dissolution is exothermic". Hydration is one step of three. The worked example above finishes at +8 kJ mol^{-1} overall, not at hydration's −900.

Claiming ΔS_solution is always positive. Hydration shells order the solvent, and for strongly hydrating ions that term can win outright. A gas dissolving is negative every time.

Confusing fast with favorable. Stirring and crushing speed up dissolving by improving contact; neither changes ΔG, Ksp or the saturated concentration.

Reading a positive ΔG° as "insoluble, full stop". Every salt dissolves until Q reaches Ksp. "Insoluble" means the saturated concentration is very small, not zero.

Blaming temperature effects on the lattice. Heating does not shrink lattice energy: temperature acts through TΔS, never through step 1.

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Key Relationships to Remember

- ΔH_solution = lattice separation (+) + solvent separation (+) + hydration (−): breaking attractions is always endothermic, forming them always exothermic
- Hydration grows more exothermic as ion charge rises and size falls, and those ions order the solvent most
- ΔS_solution = dispersal gain (+) plus hydration shell ordering (−): often positive for solids, sometimes negative, sharply negative for a dissolving gas
- ΔG_solution = ΔH_solution − TΔS_solution: its sign decides favorability, never the sign of ΔH alone and never the rate
- ΔH < 0 with ΔS > 0: favorable at all temperatures; ΔH > 0 with ΔS < 0: favorable at none; matching signs put the crossover at T = ΔH / ΔS
- Endothermic dissolution with positive ΔS grows more favorable as T rises; dissolved gases are driven out by warming
- Dissolution is an equilibrium: Ksp is its constant, and ΔG°_solution = −RT ln Ksp, so a smaller Ksp means a larger positive ΔG°
- Q < Ksp means more can dissolve; Q > Ksp means precipitation until Q = Ksp; even a salt with positive ΔG° dissolves up to saturation

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