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Topic 7.14: Free Energy of Dissolution

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UNIT 7 · EQUILIBRIUM

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What ΔG° of Dissolution Means

Every dissolution has a standard free energy change, ΔG°, which tells you whether the solid wants to dissolve under standard conditions. A negative ΔG° means dissolution is favoured; a positive ΔG° means it is unfavoured, so very little dissolves.

For sparingly soluble salts ΔG° is positive, which is exactly why so little dissolves: AgCl has ΔG° = +55.6 kJ/mol and Ksp = 1.8×10^{-10}, while $Ca(OH)_2$ has ΔG° = +30.0 kJ/mol and Ksp = 5.5×10^{-6}.

This connection is the whole topic: if you know Ksp, you can find ΔG°, and if you know ΔG°, you can find Ksp. If you know how ΔG° changes with temperature, you can predict whether warming raises or lowers the solubility.

Standard conditions. The ° in ΔG° means standard conditions: all dissolved species at 1 mol/L, the solid pure, and the temperature usually 298 K (25 °C). A positive ΔG° does not mean nothing dissolves: the equilibrium lies far to the solid side.

ΔG° = −RT ln Ksp

The link between the free energy and the equilibrium constant is

$$\Delta G^\circ = -RT \ln K_{sp}$$

where R = 8.314 J mol^{-1} K^{-1} and T is the temperature in kelvin. At 298 K,

$$RT = 8.314 \times 298 = 2{,}478 \text{ J/mol}$$

or 2.48 kJ/mol. The natural logarithm, ln, is the logarithm to base e. Ksp values are far below 1 for sparingly soluble salts, so ln Ksp is negative and ΔG° comes out positive.

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For AgCl, Ksp = 1.8×10^{-10}, so ln Ksp = −22.44, and ΔG° = −(2,478)(−22.44) = +55.6 kJ/mol. For $Mg(OH)_2$, Ksp = 5.6×10^{-12}, so ln Ksp = −25.91, and ΔG° = +64.2 kJ/mol. For PbI_2, Ksp = 9.8×10^{-9}, so ln Ksp = −18.44, and ΔG° = +45.7 kJ/mol.

The pattern: the larger the Ksp, the less negative the ln Ksp, and the smaller the ΔG°.

Reading the Pattern: Ksp and ΔG° Side by Side

Lead(II) iodide, with Ksp = 9.8×10^{-9}, has ΔG° = +45.7 kJ/mol, while silver chloride, with Ksp = 1.8×10^{-10}, has ΔG° = +55.6 kJ/mol.

The extreme case is iron(III) hydroxide: Ksp = 2.8×10^{-39} gives ln Ksp = −88.77 and ΔG° = +220 kJ/mol. At the other end, calcium hydroxide has Ksp = 5.5×10^{-6}, ln Ksp = −12.11 and ΔG° = +30.0 kJ/mol.

Barium sulfate sits near silver chloride: Ksp = 1.1×10^{-10}, ln Ksp = −22.93 and ΔG° = +56.8 kJ/mol. Calcium fluoride falls between: Ksp = 3.9×10^{-11}, ln Ksp = −23.97 and ΔG° = +59.4 kJ/mol. Silver chromate is the least favourable of this group: Ksp = 1.1×10^{-12} and ΔG° = +68.2 kJ/mol.

The three landmark values. If Ksp = 1, then ln Ksp = 0 and ΔG° = 0. If Ksp is greater than 1, ln Ksp is positive and ΔG° is negative: dissolution is favoured. If Ksp is less than 1, ln Ksp is negative and ΔG° is positive: dissolution is unfavoured, which is the case for every sparingly soluble salt in this unit.

A useful benchmark: Ksp = 1.0×10^{-3} gives ln Ksp = −6.91 and ΔG° = +17.1 kJ/mol at 298 K.

Finding Ksp from ΔG°

The equation works in reverse:

ln Ksp = −ΔG°/RT

and then Ksp = e^(−ΔG°/RT).

Take calcium fluoride with ΔG° = +59.4 kJ/mol at 298 K: ln Ksp = −59,400/2,478 = −23.97, and Ksp = 3.9×10^{-11}. Take lead(II) iodide with ΔG° = +45.7 kJ/mol: ln Ksp = −18.44, and Ksp = 9.8×10^{-9}. Take silver chloride with ΔG° = +55.6 kJ/mol: ln Ksp = −22.44, and Ksp = 1.8×10^{-10}.

Each calculation returns the Ksp you started from.

Temperature and ΔG° = ΔH° − TΔS°

Free energy also splits into enthalpy and entropy:

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$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Dissolving a salt usually increases disorder, so ΔS° is usually positive. When ΔS° is positive, warming makes the $-T\Delta S^\circ$ term more negative, so ΔG° falls and Ksp rises.

Take a salt with $\Delta H^\circ = +30.0$ kJ/mol and $\Delta S^\circ = +60$ J mol^{-1} K^{-1}. At 298 K, $\Delta G^\circ = 30{,}000 - (298)(60) = +12.1$ kJ/mol, and Ksp = e^(−12,120/2,478) = 0.0075. At 350 K, $\Delta G^\circ = 30{,}000 - (350)(60) = +9.0$ kJ/mol, and Ksp = e^(−9,000/2,910) = 0.045. Warming by 52 K raised Ksp by a factor of six.

The dissolution is endothermic, so warming shifts the equilibrium toward the dissolved ions.

When Warming Lowers Solubility

If dissolution is exothermic, ΔH° is negative, and warming can lower the solubility. Take a salt with $\Delta H^\circ = -10.0$ kJ/mol and $\Delta S^\circ = +40$ J mol^{-1} K^{-1}. At 298 K, $\Delta G^\circ = -10{,}000 - (298)(40) = -21.9$ kJ/mol, and Ksp = e^(21,920/2,478) = 7.0×10^3, a very soluble salt.

Warming lowers solubility when dissolution is exothermic, whatever the sign of ΔS°. The general rule: for an endothermic dissolution with positive entropy, solubility rises with temperature.

This is why hot water dissolves more solid than cold water: as T grows, the $-T\Delta S^\circ$ term drags ΔG° down and Ksp up.

Worked Examples

Example 1: ΔG° for AgCl. AgCl has Ksp = 1.8×10^{-10} at 298 K. First find ln Ksp = −22.44. Then $\Delta G^\circ = -RT \ln K_{sp} = -(2{,}478)(-22.44) = +55.6$ kJ/mol. The positive sign is expected: Ksp is far below 1, so ln Ksp is negative.

Example 2: ΔG° for $Mg(OH)_2$, compared with PbI_2. $Mg(OH)_2$ has Ksp = 5.6×10^{-12}, so ln Ksp = −25.91 and $\Delta G^\circ = -(2{,}478)(-25.91) = +64.2$ kJ/mol. PbI_2 has Ksp = 9.8×10^{-9}, ln Ksp = −18.44 and $\Delta G^\circ = +45.7$ kJ/mol. The difference is 64.2 − 45.7 = 18.5 kJ/mol.

Example 3: Ksp from ΔG° for CaF_2. CaF_2 has $\Delta G^\circ = +59.4$ kJ/mol at 298 K. Then ln Ksp = $-\Delta G^\circ/RT = -59{,}400/2{,}478 = -23.97$, and Ksp = e^(−23.97) = 3.9×10^{-11}.

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Example 4: Warming an endothermic dissolution. A salt has ΔH° = +30.0 kJ/mol and ΔS° = +60 J mol^{-1} K^{-1}. At 298 K, ΔG° = 30,000 − (298)(60) = +12.1 kJ/mol, and Ksp = 0.0075. At 350 K, ΔG° = 30,000 − (350)(60) = +9.0 kJ/mol. At 350 K, RT = 8.314 × 350 = 2,910 J/mol, so Ksp = e^(−9,000/2,910) = 0.045. Warming raised Ksp from 0.0075 to 0.045, a factor of six.

Traps That Cost Marks in Topic 7.14

"ΔG° is negative because the salt dissolves a little." A sparingly soluble salt has Ksp below 1, so ln Ksp is negative and ΔG° is positive.

"log$_{10}$ Ksp works in ΔG° = −RT ln Ksp." The equation needs the natural logarithm: for AgCl, log$_{10}$ Ksp is −9.74 while ln Ksp is −22.44, and mixing them up changes ΔG° by a factor of 2.303.

"ΔH° = +30 kJ/mol, so ΔG° = 30,000 − 298 × 60 in kJ." The units must match: convert ΔH° from kJ/mol to J/mol before subtracting TΔS° in J/mol.

"T = 25 °C in ΔG° = −RT ln Ksp." T must be in kelvin: at 25 °C, T = 298 K.

"A larger Ksp means a larger ΔG°." It is the reverse: a larger Ksp means a less negative ln Ksp and a smaller ΔG°.

"Warming always raises solubility." Warming raises solubility when the dissolution is endothermic, and lowers it when the dissolution is exothermic.

Key Relationships to Remember

- ΔG° = −RT ln Ksp, with R = 8.314 J mol^{-1} K^{-1} and T in kelvin; at 298 K, RT = 2,478 J/mol
- Ksp below 1 gives a positive ΔG°; Ksp above 1 gives a negative ΔG°; Ksp = 1 gives ΔG° = 0
- AgCl, Ksp = 1.8 × 10^{-10}: ln Ksp = −22.44, ΔG° = +55.6 kJ/mol
- $Mg(OH)_2$, Ksp = 5.6 × 10^{-12}: ln Ksp = −25.91, ΔG° = +64.2 kJ/mol
- PbI_2, Ksp = 9.8 × 10^{-9}: ln Ksp = −18.44, ΔG° = +45.7 kJ/mol
- $Fe(OH)_3$, Ksp = 2.8 × 10^{-39}: ln Ksp = −88.77, ΔG° = +220 kJ/mol
- $Ca(OH)_2$, Ksp = 5.5 × 10^{-6}: ln Ksp = −12.11, ΔG° = +30.0 kJ/mol
- ln Ksp = −ΔG°/RT, so Ksp = e^(−ΔG°/RT)
- ΔG° = ΔH° − TΔS°; with ΔS° positive, warming lowers ΔG° and raises Ksp
- Use ln, not log$_{10}$; convert kJ to J; use kelvin, not Celsius

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