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Topic 7.12: Common-Ion Effect

Revision Notes · AP Chemistry

UNIT 7 · EQUILIBRIUM

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What the Common-Ion Effect Is

The common-ion effect is the drop in solubility of a sparingly soluble salt when the solution already contains one of the salt's ions. Dissolving AgCl in 0.10 M NaCl gives far less dissolved AgCl than dissolving it in pure water, because chloride is already present. The added ion is called the common ion.

This is a direct application of Le Chatelier's principle and of the Qsp versus Ksp comparison.

KNO_3 added to saturated PbI_2 changes nothing, because neither K^+ nor NO_3^- appears in the dissolution equilibrium. Only a shared ion matters.

Why Solubility Falls: Two Views of One Event

The Le Chatelier view. Write the dissolution with the ions as products:

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

Adding NaCl pours extra Cl^-, a product, into the system. The equilibrium shifts left toward the solid, so less AgCl dissolves. The same logic works for any salt: $Mg(OH)_2$ shifts left when NaOH supplies extra OH^-.

The Qsp view. The moment the common ion is added, Qsp jumps above Ksp, and solid precipitates until Qsp falls back to Ksp, at a lower dissolved concentration of the salt's other ion.

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Calculating Solubility with a Common Ion

Let s be the molar solubility of the salt in the common-ion solution, and let C be the given concentration of the common ion. Because s is tiny compared with C, the common ion concentration is treated as fixed at C. Then solve $K_{sp} = s \times C^n$, where n is the exponent on the common ion.

A 1:1 salt. Ksp for AgCl is 1.8×10^{-10} in 0.10 M NaCl. Approximating 0.10 + s as 0.10, s = Ksp ÷ 0.10 = 1.8×10^{-9} M, against 1.3×10^{-5} M in pure water: a factor of about 7,000.

A squared common ion. Ksp for CaF_2 is 4.0×10^{-11} in 0.010 M NaF. Here $K_{sp} = [Ca^{2+}][F^-]^2 = (s)(0.010)^2$, so s = $(4.0 \times 10^{-11}) \div (1.0 \times 10^{-4}) = 4.0 \times 10^{-7}$ M. The fluoride concentration is squared because its coefficient is 2. Forgetting that exponent is the most common calculation error in this topic.

A common cation. Ksp for Ag_2CrO_4 is 1.1×10^{-12} in 0.020 M $AgNO_3$. Then $K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (0.020)^2(s)$, so s = $(1.1 \times 10^{-12}) \div (4.0 \times 10^{-4}) = 2.8 \times 10^{-9}$ M.

A 1:2 hydroxide. Ksp for $Ca(OH)_2$ is 5.5×10^{-6} in 0.10 M NaOH. Then $K_{sp} = (s)(0.10)^2$, giving s = $(5.5 \times 10^{-6}) \div 0.010 = 5.5 \times 10^{-4}$ M.

Checking the Approximation

The shortcut is valid when s is much smaller than C. After solving, glance at the numbers: in the AgCl example s = 1.8×10^{-9} M against C = 0.10 M, so the approximation is excellent. Treating the common-ion concentration as C alone understates it slightly, so the approximate s comes out slightly too large.

When the shortcut breaks. If a question gives a very dilute common-ion solution, such as 1.0×10^{-6} M NaCl with AgCl, s = Ksp ÷ C would give 1.8×10^{-4} M, not much smaller than C, so the full expression $K_{sp} = s(C + s)$ would be needed.

How Much the Common Ion Matters

Solubility falls as the common-ion concentration rises, and the relationship is inverse. AgCl is more soluble in 0.010 M NaCl than in 0.10 M NaCl, because s = Ksp ÷ C. In 0.010 M NaCl, s = 1.8×10^{-8} M; in 0.10 M NaCl, s = 1.8×10^{-9} M. Doubling the common-ion concentration roughly halves the solubility for a 1:1 salt. For salts where the common ion is squared, the effect is stronger: doubling C cuts s by a factor of four. Dilution works the other way: adding pure water lowers C and lets more solid dissolve.

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The power of the common ion decides how hard it bites. PbI_2 in 0.010 M NaI is suppressed through iodide: $s = K_{sp} \div (0.010)^2 = 9.8 \times 10^{-5}$ M. The same salt in 0.010 M $Pb(NO_3)_2$ is suppressed through lead: $K_{sp} = (0.010)(4s^2)$, so $s = \sqrt{(K_{sp} \div (4 \times 0.010))} = 4.9 \times 10^{-4}$ M. The same salt, the same added concentration, but different math because the common ion sits in a different place in the Ksp expression. Always write the full expression first, then decide which terms are negligible.

Distinguishing Real Common Ions

HCl lowers the solubility of AgCl because it supplies Cl^-, but HNO_3 does not, because it supplies neither Ag^+ nor Cl^-. Na_2SO_4 lowers the solubility of $BaSO_4$ through sulfate, while NaCl leaves $BaSO_4$ alone.

Watch for polyatomic ions that look similar but are not identical. Adding Na_2SO_4 to saturated $BaSO_3$ would do nothing, because sulfite and sulfate are different ions.

Common Ion from Two Sources at Once

Sometimes the common ion comes from more than one added salt: AgCl in a solution 0.050 M in NaCl and 0.050 M in KCl has total $[Cl^-] = 0.10$ M, so $s = K_{sp} \div 0.10 = 1.8 \times 10^{-9}$ M. Always add up every source of the common ion before solving. The same care applies when a common-ion solution is prepared by mixing: a saturated AgCl solution mixed with an equal volume of 0.20 M NaCl ends with $[Cl^-] = 0.10$ M, so $[Ag^+] = 1.8 \times 10^{-9}$ M once equilibrium is reestablished.

Worked Examples

Example 1: AgCl in 0.10 M NaCl. $K_{sp} = [Ag^+][Cl^-] = (s)(0.10) = 1.8 \times 10^{-10}$, so $s = (1.8 \times 10^{-10}) \div 0.10 = 1.8 \times 10^{-9}$ M. In pure water $s = 1.3 \times 10^{-5}$ M, a factor of about 7,000 higher.

Example 2: CaF_2 in 0.010 M NaF. $K_{sp} = [Ca^{2+}][F^-]^2 = (s)(0.010)^2 = 4.0 \times 10^{-11}$, so $s = (4.0 \times 10^{-11}) \div (1.0 \times 10^{-4}) = 4.0 \times 10^{-7}$ M. In pure water $s = 2.2 \times 10^{-4}$ M, a factor of about 550 higher.

Example 3: Ag_2CrO_4 in 0.020 M $AgNO_3$. $K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (0.020)^2(s) = 1.1 \times 10^{-12}$, so $s = (1.1 \times 10^{-12}) \div (4.0 \times 10^{-4}) = 2.8 \times 10^{-9}$ M. In pure water $s = 6.5 \times 10^{-5}$ M, a factor of about 2.3×10^4 higher.

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Example 4: $Ca(OH)_2$ in 0.10 M NaOH. $K_{sp} = [Ca^{2+}][OH^-]^2 = (s)(0.10)^2 = 5.5 \times 10^{-6}$, so $s = (5.5 \times 10^{-6}) \div 0.010 = 5.5 \times 10^{-4}$ M. In pure water $s = 1.1 \times 10^{-2}$ M, a factor of about 20 higher.

Traps That Cost Marks in Topic 7.12

"Adding a common ion lowers Ksp." Ksp is constant at a given temperature; only the solubility changes.

"For CaF_2 in NaF, $K_{sp} = s(C + s)^2$." The fluoride released by the salt is 2s, not s: $K_{sp} = s(C + 2s)^2$.

"The small-s approximation is always safe." It fails whenever C is not far above the dissolved amount. Run the check every time.

"Use the pure-water solubility out of habit." In a common-ion solution the solubility must be solved fresh from $K_{sp} = s(C)^n$.

"Any added salt is a common ion." Only a salt that shares an ion with the dissolving solid counts.

"Adding more solid raises the solubility back toward pure water." A saturated solution cannot dissolve more solid at the same temperature however much is added.

Key Relationships to Remember

- A common ion is an ion shared between the sparingly soluble salt and another solute in the same solution
- Solubility with a common ion present is always lower than in pure water, and falls further as the common-ion concentration rises
- Adding a common ion does not change Ksp; it changes the ion concentrations at which the Ksp product is reached
- With the common ion at concentration C, solve $K_{sp} = s \times C^n$, where n is the exponent on the common ion
- The common ion's equilibrium concentration is C plus its stoichiometric multiple of s
- For a 1:1 salt, doubling C halves s; where the common ion is squared, doubling C cuts s by a factor of four
- If an addition pushes Qsp above Ksp, solid precipitates until Qsp returns to Ksp
- Solubility changes caused by pH belong to Topic 7.13; in this topic only the shared ion changes the solubility

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