Topic 7.11: Introduction to Solubility Equilibria

Revision Notes · AP Chemistry

UNIT 7 · EQUILIBRIUM

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What a Solubility Equilibrium Is

When a sparingly soluble salt sits in water, a dynamic equilibrium exists between the undissolved solid and its ions.

For silver chloride it is

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

The equilibrium constant for this process is called the solubility product, Ksp. Ksp is fixed at a given temperature and does not depend on how much solid is present.

Ksp is small for sparingly soluble salts, often between 10^{-5} and 10^{-40}, so very little solid dissolves before the solution saturates. The exam only asks about these slightly soluble salts. A saturated solution holds the maximum dissolved amount at equilibrium, with solid still there.

Writing Ksp Expressions

The rules match every other equilibrium expression: pure solids are omitted, so only the aqueous ions appear, each raised to the power of its stoichiometric coefficient.

For AgCl, the expression is

$Ksp = [Ag^{+}][Cl^{-}]$

For CaF_2, the expression is

$Ksp = [Ca^{2+}][F^{-}]^2$

with the fluoride squared. For Ag_2CrO_4, the expression is

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$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

with the silver squared. For $PbCl_2$, the expression is

$K_{sp} = [Pb^{2+}][Cl^-]^2$

The most common writing error is putting the coefficient inside the brackets, as in $[2F^-]$, or forgetting the exponent.

Molar Solubility

Molar solubility, symbol s, is the moles of solid that dissolve per liter of saturated solution, in mol/L. It is not the same number as Ksp, and confusing the two is a classic error.

Dissolving s mol/L gives: AgCl, $[Ag^+] = [Cl^-] = s$; CaF_2, $[Ca^{2+}] = s$ and $[F^-] = 2s$; Ag_2CrO_4, $[Ag^+] = 2s$ and $[CrO_4^{2-}] = s$; $Fe(OH)_3$, $[Fe^{3+}] = s$ and $[OH^-] = 3s$.

The general patterns are worth memorizing. 1:1 salt: $K_{sp} = s^2$. 1:2 or 2:1 salt: $K_{sp} = 4s^3$. 1:3 salt: $K_{sp} = 27s^4$.

Ksp and Molar Solubility in Both Directions

Substitute the s expressions into the Ksp expression. For AgCl with $s = 1.3 \times 10^{-5}$ M, $K_{sp} = s^2 = (1.3 \times 10^{-5})^2 = 1.7 \times 10^{-10}$. For CaF_2 with $s = 2.1 \times 10^{-4}$ M, $K_{sp} = 4s^3 = 4(2.1 \times 10^{-4})^3 = 3.7 \times 10^{-11}$.

A rounding note on CaF_2. Tables quote $K_{sp} = 3.9 \times 10^{-11}$ for CaF_2, while the calculation from $s = 2.1 \times 10^{-4}$ M gives 3.7×10^{-11}. The two agree once s is rounded to two significant figures.

Work backward by solving for s. For $Mg(OH)_2$ with $K_{sp} = 5.6 \times 10^{-12}$, $K_{sp} = 4s^3$, so s is the cube root of Ksp ÷ 4, which gives $s = 1.1 \times 10^{-4}$ M. For $Fe(OH)_3$ with $K_{sp} = 2.8 \times 10^{-39}$, $K_{sp} = 27s^4$, so s is the fourth root of Ksp ÷ 27, about 1.0×10^{-10} M. The skill being tested is setting up the correct power relationship, not arithmetic.

Qsp versus Ksp: Predicting Precipitation

Qsp is the ion product computed from current concentrations, exactly as Q relates to K. If Qsp is less than Ksp, the solution is unsaturated and more solid can dissolve. If Qsp equals Ksp, the solution is saturated and sits at equilibrium. If Qsp is greater than Ksp, the solution cannot hold that many ions, so solid precipitates until Qsp falls back to Ksp.

Mixing dilutes the ions. When two solutions are mixed, each ion is diluted, and you must use the diluted concentrations in Qsp. Equal volumes halve every concentration; for unequal volumes, use

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moles divided by total volume. Forgetting the dilution is the most common precipitation error. Mixing to $[Pb^{2+}] = 0.0010$ M and $[I^-] = 0.0020$ M gives $Q_{sp} = (0.0010)(0.0020)^2 = 4.0 \times 10^{-9}$, below $K_{sp} = 9.8 \times 10^{-9}$ for PbI_2, so no precipitate forms.

Comparing Solubilities

You may only rank solubilities directly from K_{sp} values when the salts have the same stoichiometry. For 1:1 salts, a larger K_{sp} means a larger molar solubility, since $s = \sqrt{K_{sp}}$.

The exam loves this trap. AgCl has $K_{sp} = 1.8 \times 10^{-10}$ while CaF_2 has $K_{sp} = 3.9 \times 10^{-11}$, yet CaF_2 is more soluble: its molar solubility is about 2.1×10^{-4} M versus 1.3×10^{-5} M for AgCl. Always convert to molar solubility before comparing salts with different formulas. Within one stoichiometry the ranking is safe: AgCl is more soluble than $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$) because both are 1:1, with molar solubilities 1.3×10^{-5} M and 1.0×10^{-5} M.

Unsaturated, Saturated, and Supersaturated

An unsaturated solution has Q_{sp} below K_{sp}: it can still dissolve more solid. A saturated solution has Q_{sp} equal to K_{sp}: it is at equilibrium, and added solid just sits there. A supersaturated solution has Q_{sp} above K_{sp}: it holds more ions than equilibrium allows, so precipitation occurs until Q_{sp} drops back to K_{sp}.

Supersaturated solutions are usually made by cooling a hot saturated solution or by mixing concentrated solutions quickly, and a tiny seed crystal can trigger sudden crystallization. Like all equilibrium constants, K_{sp} changes with temperature: for most salts dissolution is endothermic, so warming the solution increases K_{sp} and raises the solubility.

Worked Examples

Example 1: K_{sp} from molar solubility. The molar solubility of CaF_2 is 2.1×10^{-4} M. In the saturated solution $[Ca^{2+}] = s = 2.1 \times 10^{-4}$ M and $[F^-] = 2s = 4.2 \times 10^{-4}$ M. Then $K_{sp} = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = (2.1 \times 10^{-4})(1.76 \times 10^{-7}) = 3.7 \times 10^{-11}$.

Example 2: Molar solubility from K_{sp}. For $Mg(OH)_2$, $K_{sp} = 5.6 \times 10^{-12}$ and $K_{sp} = 4s^3$. Then s = cube root of $(5.6 \times 10^{-12} \div 4)$ = cube root of $1.4 \times 10^{-12} = 1.1 \times 10^{-4}$ M, giving $[Mg^{2+}] = 1.1 \times 10^{-4}$ M and $[OH^-] = 2s = 2.2 \times 10^{-4}$ M.

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Example 3: A fourth-root solubility. For $Fe(OH)_3$, Ksp = 2.8×10^{-39} and Ksp = $27s^4$. Then s = fourth root of ($2.8 \times 10^{-39} \div 27$) = fourth root of 1.04×10^{-40} = 1.0×10^{-10} M. The ion concentrations are $[Fe^{3+}] = 1.0 \times 10^{-10}$ M and $[OH^-] = 3s = 3.0 \times 10^{-10}$ M.

Example 4: Will it precipitate? 50.0 mL of 2.0×10^{-4} M $Ba(NO_3)_2$ is mixed with 50.0 mL of 2.0×10^{-4} M Na_2SO_4, halving each concentration to $[Ba^{2+}] = 1.0 \times 10^{-4}$ M and $[SO_4^{2-}] = 1.0 \times 10^{-4}$ M. Then Qsp = $(1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8}$. Ksp for $BaSO_4$ is 1.1×10^{-10}. Since Qsp exceeds Ksp, $BaSO_4$ precipitates.

Traps That Cost Marks in Topic 7.11

"Ksp includes the solid." The solid never appears in the expression. Ksp for AgCl is $[Ag^+][Cl^-]$.

"For CaF_2, Ksp = s^3." The fluoride concentration is 2s, and it is squared: Ksp = $(s)(2s)^2 = 4s^3$. Dropping the multiplier or the power understates Ksp by a factor of 4.

"Ksp and molar solubility are the same number." s is a concentration in mol/L. Ksp is built from concentrations raised to powers. For AgCl: s = 1.3×10^{-5} M, Ksp = 1.8×10^{-10}.

"The salt with the smaller Ksp is always less soluble." True only within one stoichiometry. CaF_2 (Ksp = 3.9×10^{-11}) is more soluble than AgCl (Ksp = 1.8×10^{-10}) once both are converted to s.

"Use the concentrations printed on the bottles for Qsp." Mixing dilutes them. Equal volumes halve each concentration, and Qsp must use the concentrations in the mixture.

"Adding more solid to a saturated solution raises $[Ag^+]$." In a saturated solution Qsp already equals Ksp, so extra solid cannot dissolve and $[Ag^+]$ stays at 1.3×10^{-5} M at 25 °C.

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Key Relationships to Remember

- Ksp is the equilibrium constant for a solid dissolving into its ions, with the solid itself omitted from the expression
- Each ion concentration is raised to its coefficient; coefficients become exponents, never multipliers
- Molar solubility s is in mol/L; ion concentrations are s times the ion's coefficient in the equation
- 1:1 salts: Ksp = s^2; 1:2 and 2:1 salts: Ksp = $4s^3$; 1:3 salts: Ksp = $27s^4$
- Ksp ranks solubility directly only between salts of the same stoichiometry; otherwise compare molar solubilities
- Qsp below Ksp is unsaturated, Qsp equal to Ksp is saturated, Qsp above Ksp precipitates until Qsp falls back to Ksp
- Mixing dilutes: equal volumes halve each ion concentration before Qsp is computed
- Ksp changes with temperature

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