Topic 7.13: pH and Solubility

Revision Notes · AP Chemistry

UNIT 7 · EQUILIBRIUM

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Why pH Controls Solubility

Some salts dissolve more as the pH changes, while others are completely unaffected by pH. The difference is whether an ion in the dissolution equilibrium reacts with H^+ or OH^-.

Hydroxides are the clearest case:

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

Hydroxide ion is a product of this equilibrium, so anything that changes $[OH^-]$ changes the solubility. Adding acid lowers $[OH^-]$ by neutralizing it to water, so the equilibrium shifts right and more solid dissolves. Adding base raises $[OH^-]$ and pushes it left.

Salts of weak acids behave the same way through their anions:

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

Fluoride is the conjugate base of the weak acid HF, so in acid it is protonated:

$F^-(aq) + H^+(aq) \rightleftharpoons HF(aq)$

Removing fluoride pulls the dissolution equilibrium to the right.

Hydroxide Solubility at a Fixed pH

For a hydroxide salt the solubility at a fixed pH follows directly from the Ksp expression: the pH fixes $[OH^-]$ through $pOH = 14 - pH$, and then

$s = Ksp/[OH^-]^n$

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where n is the number of hydroxide ions in the formula.

Take $Mg(OH)_2$ with $K_{sp} = 5.6 \times 10^{-12}$:

$K_{sp} = [Mg^{2+}][OH^-]^2$

so $s = K_{sp}/[OH^-]^2$. At pH 9, $[OH^-] = 1.0 \times 10^{-5}$ M and $s = 5.6 \times 10^{-2}$ M. At pH 10, $s = 5.6 \times 10^{-4}$ M. At pH 11, $s = 5.6 \times 10^{-6}$ M. Each unit of pH cuts the solubility by a factor of one hundred, because $[OH^-]$ is squared.

In pure water $Mg(OH)_2$ dissolves to $s = 1.1 \times 10^{-4}$ M. A saturated solution in pure water has $[OH^-] = 2s = 2.2 \times 10^{-4}$ M, giving pOH = 3.65 and pH = 10.35, the dividing line: below it the salt dissolves more than in pure water, above it less.

The Exponent Rule

For $Mg(OH)_2$ and $Ca(OH)_2$ the exponent on $[OH^-]$ is 2, so a tenfold change in $[OH^-]$ changes the solubility by a factor of one hundred. For $Fe(OH)_3$ the exponent is 3, so the factor is one thousand.

Iron(III) hydroxide, with $K_{sp} = 2.8 \times 10^{-39}$, shows this. At pH 7, $s = 2.8 \times 10^{-18}$ M, essentially nothing. At pH 4, $s = 2.8 \times 10^{-9}$ M. At pH 3, $s = 2.8 \times 10^{-6}$ M. Three pH units of acid raise the solubility by a factor of a billion.

Calcium hydroxide, with $K_{sp} = 5.5 \times 10^{-6}$, is much more soluble: at pH 12, $s = 5.5 \times 10^{-2}$ M, and at pH 13, $s = 5.5 \times 10^{-4}$ M.

When a Hydroxide First Precipitates

The same K_{sp} expression predicts the pH at which a hydroxide first precipitates: precipitation begins when Q_{sp} reaches K_{sp}, so the threshold hydroxide concentration is

$[OH^-] = (K_{sp}/[M^{n+}])^{(1/n)}$

and the threshold pH follows from $pOH = -\log[OH^-]$.

For 0.010 M Mg^{2+}, the threshold is $[OH^-] = \sqrt{(5.6 \times 10^{-12})/0.010} = 2.4 \times 10^{-5}$ M, giving pOH = 4.63 and pH = 9.37. Below pH 9.37 no solid forms; above it, $Mg(OH)_2$ precipitates.

For 1.0×10^{-4} M Fe^{3+}, the threshold is $[OH^-] = ((2.8 \times 10^{-39})/(1.0 \times 10^{-4}))^{(1/3)} = 3.0 \times 10^{-12}$ M, giving pOH = 11.52 and pH = 2.48. For 0.10 M Ca^{2+}, the threshold is $[OH^-] = \sqrt{(5.5 \times 10^{-6})/0.10} = 7.4 \times 10^{-3}$ M, giving pOH = 2.13 and pH = 11.87.

The threshold pH rises as the metal ion concentration falls.

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Salts of Weak Acids

Acid increases the solubility of any salt whose anion is the conjugate base of a weak acid: the acid protonates the anion and removes it from the equilibrium. Calcium carbonate dissolves as

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

and in acid the carbonate is protonated:

$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$

With enough acid the bicarbonate is protonated again to carbonic acid, which breaks down to CO_2 and water: this is why limestone fizzes in acid.

The same reasoning applies to calcium fluoride through HF formation, to sulfides through H_2S formation, and to phosphates through HPO_4^{2-} and $H_2PO_4^-$ formation.

The reverse case: salts of weak bases. Salts containing the ammonium ion, NH_4^+, become more soluble in base: ammonium is the conjugate acid of the weak base NH_3, so hydroxide removes a proton:

$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

Removing NH_4^+ pulls the dissolution equilibrium to the right.

Salts That Ignore pH

A salt does not respond to pH when both of its ions come from a strong acid and a strong base. AgCl is unaffected by pH, since Cl^- is the conjugate base of the strong acid HCl. $BaSO_4$ and PbI_2 are likewise unaffected.

The exam uses these salts as distractors: if a question asks which of several salts becomes more soluble when acid is added, look for the anion that can be protonated.

Acid dissolves salts of weak acids and hydroxides, base dissolves salts of weak bases, and salts of strong acids and strong bases ignore pH entirely.

Worked Examples

> **Example 1: $Mg(OH)_2$ solubility at pH 10. $Mg(OH)_2$ has Ksp = 5.6×10^{-12}. At pH 10, pOH = 4, so $[OH^-] = 1.0 \times 10^{-4}$ M. Then $s = Ksp/[OH^-]^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-4})^2 = 5.6 \times 10^{-4}$ M. That is about five times the pure-water solubility of 1.1×10^{-4} M.**

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Example 2: $Fe(OH)_3$ solubility at pH 4. $Fe(OH)_3$ has Ksp = 2.8×10^{-39}. At pH 4, pOH = 10, so $[OH^-] = 1.0 \times 10^{-10}$ M. Then $s = Ksp/[OH^-]^3 = (2.8 \times 10^{-39})/(1.0 \times 10^{-10})^3 = 2.8 \times 10^{-9}$ M. Forgetting the cube would give 2.8×10^{-29} M, wrong by twenty orders of magnitude.

Example 3: The precipitation threshold for Mg^{2+}. A solution is 0.010 M in Mg^{2+}. Precipitation begins when $[OH^-] = \text{sqrt}(Ksp/[Mg^{2+}]) = \text{sqrt}((5.6 \times 10^{-12})/0.010) = 2.4 \times 10^{-5}$ M. Then $pOH = -\log(2.4 \times 10^{-5}) = 4.63$, and $pH = 14 - 4.63 = 9.37$.

Example 4: $Ca(OH)_2$ at pH 12 and pH 13. $Ca(OH)_2$ has Ksp = 5.5×10^{-6}. At pH 12, $[OH^-] = 1.0 \times 10^{-2}$ M, so $s = (5.5 \times 10^{-6})/(1.0 \times 10^{-2})^2 = 5.5 \times 10^{-2}$ M. At pH 13, $[OH^-] = 0.10$ M, so $s = (5.5 \times 10^{-6})/(0.10)^2 = 5.5 \times 10^{-4}$ M. One pH unit cut the solubility by a factor of one hundred.

Traps That Cost Marks in Topic 7.13

"Ksp changes when the pH changes." Ksp is fixed at a given temperature. Only the solubility changes, because $[OH^-]$ is imposed by the solution.

"s = Ksp/$[OH^-]$ for every hydroxide." The exponent is the number of hydroxide ions in the formula: $Mg(OH)_2$ and $Ca(OH)_2$ need $[OH^-]^2$, $Fe(OH)_3$ needs $[OH^-]^3$.

"pH 9 means $[OH^-] = 1.0 \times 10^{-9}$ M." pH 9 means pOH 5 and $[OH^-] = 1.0 \times 10^{-5}$ M. Always convert through pOH = 14 − pH first.

"AgCl dissolves more in acid." Neither Ag^+ nor Cl^- reacts with H^+ or OH^-. AgCl, $BaSO_4$ and PbI_2 ignore pH entirely.

"$Fe(OH)_3$ is the most soluble because its Ksp is the smallest." A smaller Ksp means a less soluble salt. $Fe(OH)_3$, with Ksp = 2.8×10^{-39}, is the least soluble salt in this unit by an enormous margin.

"The precipitate forms as soon as any OH^- is added." Precipitation starts only when Qsp reaches Ksp. Below the threshold pH the metal ion stays dissolved.

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Key Relationships to Remember

- pH + pOH = 14 at 25 °C; $[OH^-] = 10^{\wedge}(-pOH)$
- For a hydroxide salt, $s = Ksp/[OH^-]^n$, where n is the number of hydroxide ions in the formula
- $Mg(OH)_2$, $Ksp = 5.6 \times 10^{-12}$: $s = 5.6 \times 10^{-2}$ M at pH 9, 5.6×10^{-4} M at pH 10, 5.6×10^{-6} M at pH 11
- $Fe(OH)_3$, $Ksp = 2.8 \times 10^{-39}$: $s = 2.8 \times 10^{-6}$ M at pH 3, 2.8×10^{-9} M at pH 4, 2.8×10^{-18} M at pH 7
- $Ca(OH)_2$, $Ksp = 5.5 \times 10^{-6}$: $s = 5.5 \times 10^{-2}$ M at pH 12, 5.5×10^{-4} M at pH 13
- Precipitation begins when Qsp = Ksp; threshold $[OH^-] = (Ksp/[M^{n+}])^{\wedge}(1/n)$
- Acid dissolves salts of weak acids and hydroxides; base dissolves salts of weak bases
- Salts of strong acids and strong bases (AgCl, $BaSO_4$, PbI_2) ignore pH
- Ksp is fixed at a given temperature; only solubility changes with pH

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