

Ksp, precipitation and the common ion effect

AP Chemistry · Lesson

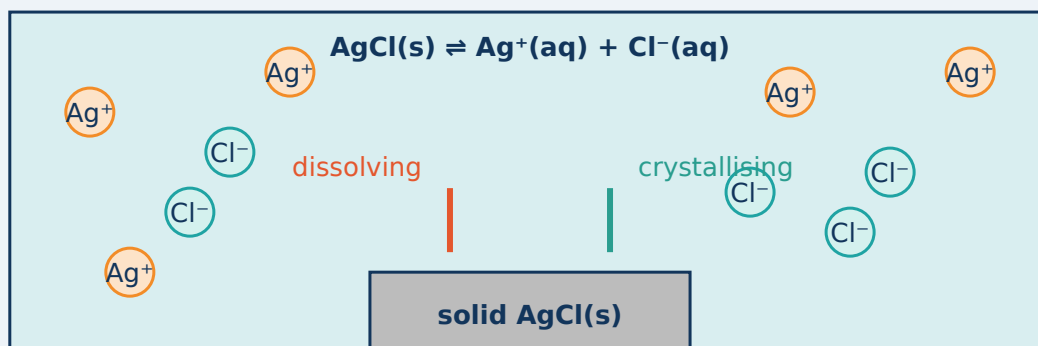
Quick answer: The solubility product K_{sp} is the equilibrium constant for a sparingly soluble ionic solid dissolving, such as $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$, with $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$. It lets you calculate molar solubility, predict precipitation by comparing Q with K_{sp} , and see how common ions and pH change solubility.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 7

What is the solubility product, K_{sp} ?

Definition

For a sparingly soluble ionic solid, **K_{sp}** is the equilibrium constant for dissolving. For $\text{M}_a\text{X}_b(\text{s}) \rightleftharpoons a\text{M}^{(n+)}(\text{aq}) + b\text{X}^{(m-)}(\text{aq})$, $K_{sp} = [\text{M}^{(n+)}]^a[\text{X}^{(m-)}]^b$. The solid does not appear in the expression. **Molar solubility** s is the amount in mol that dissolves per dm^3 of saturated solution.



At saturation the two rates are equal, so the concentrations stay constant.

A saturated solution is a dynamic equilibrium: ions leave the crystal and return at the same rate. A larger K_{sp} , for salts with the same formula type, means a more soluble salt.

Salt	Dissolving equation	K_{sp} expression	K_{sp} in terms of s
AgCl	$\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$	$[\text{Ag}^+][\text{Cl}^-]$	s^2
CaF_2	$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$	$[\text{Ca}^{2+}][\text{F}^-]^2$	$4s^3$
Ag_2CrO_4	$\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$	$[\text{Ag}^+]^2[\text{CrO}_4^{2-}]$	$4s^3$
$\text{Ca}_3(\text{PO}_4)_2$	$\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	$[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$	$108s^5$

How do you find solubility from K_{sp}?

Worked example 1

Find the molar solubility and mass solubility of AgCl ($K_{sp} = 1.8 \times 10^{-10}$, $M = 143.3 \text{ g/mol}$).
 $K_{sp} = s^2$, so $s = \sqrt{(1.8 \times 10^{-10})} = \mathbf{1.34 \times 10^{-5} \text{ mol/dm}^3}$. Mass = $1.34 \times 10^{-5} \times 143.3 = \mathbf{1.92 \text{ mg/dm}^3}$.

Worked example 2

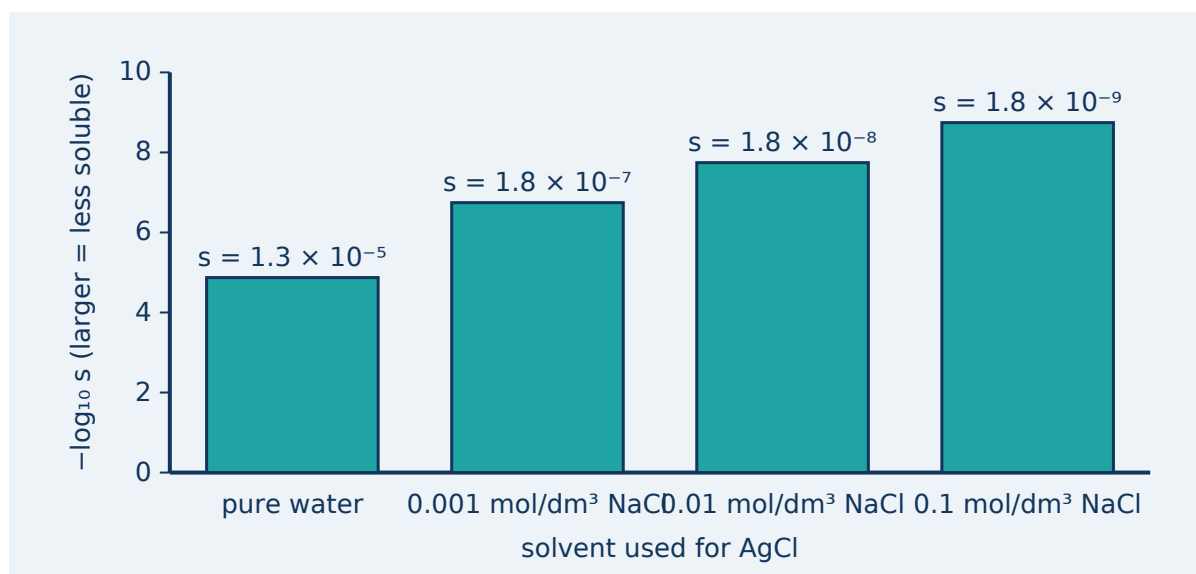
Find s for CaF_2 , $K_{sp} = 3.5 \times 10^{-11}$. Each unit gives one Ca^{2+} and two F^- , so $[\text{Ca}^{2+}] = s$ and $[\text{F}^-] = 2s$. $K_{sp} = s(2s)^2 = 4s^3$, so $s = \sqrt[3]{(3.5 \times 10^{-11} / 4)} = \sqrt[3]{(8.75 \times 10^{-12})} = \mathbf{2.06 \times 10^{-4} \text{ mol/dm}^3}$.

Key rule

To compare Q with K_{sp} : if $Q < K_{sp}$ the solution is unsaturated, if $Q = K_{sp}$ it is saturated, and if $Q > K_{sp}$ a precipitate forms. Q has the same form as K_{sp} but uses the concentrations present right now, after mixing.

How does the common ion effect change solubility?

Adding a solution that contains one of the salt's ions pushes the equilibrium to the left, in line with Le Chatelier's principle. The salt becomes less soluble. When the added ion concentration is large, it is almost equal to the total concentration of that ion, so the other ion's concentration equals s .



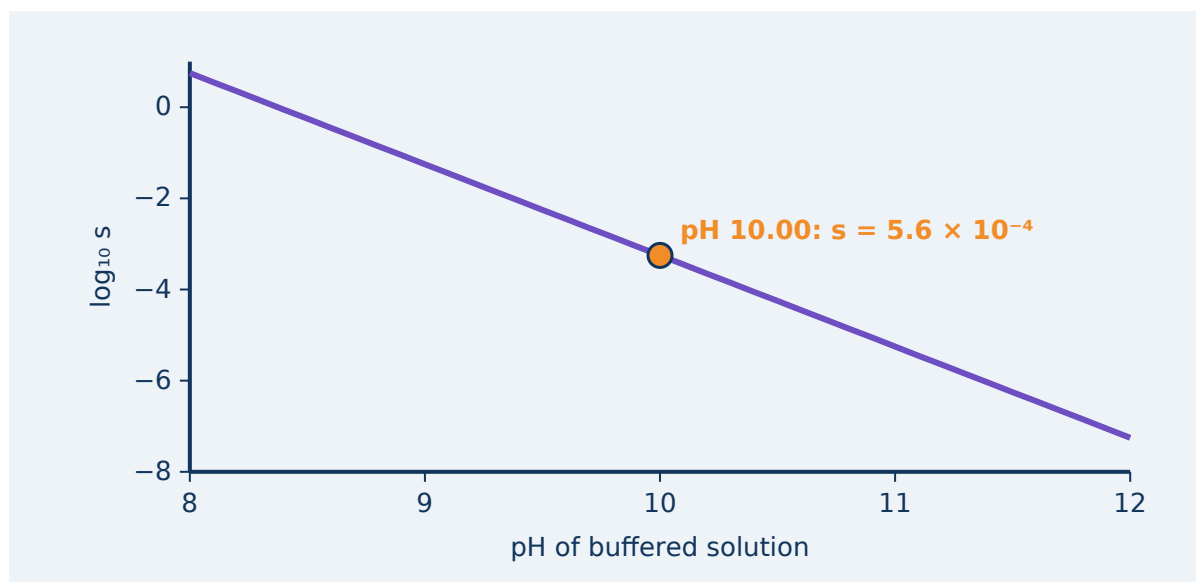
The common ion Cl^- lowers the molar solubility of AgCl ($K_{sp} = 1.8 \times 10^{-10}$).

Worked example 3

Find s for AgCl in 0.10 mol/dm³ NaCl. Here $[\text{Cl}^-] \approx 0.10 \text{ mol/dm}^3$, so $[\text{Ag}^+] = s = K_{sp}/[\text{Cl}^-] = 1.8 \times 10^{-10} / 0.10 = \mathbf{1.8 \times 10^{-9} \text{ mol/dm}^3}$. That is 7454 times smaller than in pure water.

Why does pH change the solubility?

If the anion is basic, H_3O^+ removes it from solution and pulls the equilibrium to the right. Hydroxides, carbonates, phosphates and fluorides therefore dissolve better in acid, while chlorides, bromides and iodides of silver do not. For a hydroxide, a lower pH means a lower $[\text{OH}^-]$ and a higher s .



Mg(OH)₂ dissolves far better as pH falls: $s = K_{sp} / [\text{OH}^-]^2$.

Worked example 4

$\text{Mg}(\text{OH})_2$ has $K_{sp} = 5.6 \times 10^{-12}$. In pure water $s = \sqrt[3]{(K_{sp}/4)} = 1.12 \times 10^{-4} \text{ mol/dm}^3$, so $[\text{OH}^-] = 2.24 \times 10^{-4} \text{ mol/dm}^3$ and $\text{pH} = 10.35$. In a buffer at $\text{pH} 10.00$, $[\text{OH}^-] = 1.0 \times 10^{-4} \text{ mol/dm}^3$, so $s = K_{sp}/[\text{OH}^-]^2 = \mathbf{5.6 \times 10^{-4} \text{ mol/dm}^3}$, five times larger.

Common mistake

Students write $s = \sqrt{K_{sp}}$ for every salt. That works only for salts with a 1:1 ratio such as AgCl or BaSO_4 . For CaF_2 or Ag_2CrO_4 use $4s^3$, and always write the K_{sp} expression first. Also do not compare K_{sp} values of salts with different formulas to rank solubility.

Lina's tip

Use a three-line ICE table for every K_{sp} problem: write the dissolving equation, put s (or $2s$, $3s$) under each ion and substitute into the K_{sp} expression. Check at the end by multiplying the ion concentrations again.

Key points to remember

- K_{sp} = product of ion concentrations (each raised to its coefficient) at saturation; the solid is omitted.
- Molar solubility: AB gives $s = \sqrt{K_{sp}}$; AB_2 and A_2B give $s = \sqrt[3]{(K_{sp}/4)}$.
- Precipitation: $Q > K_{sp}$ precipitate forms; $Q = K_{sp}$ saturated; $Q < K_{sp}$ unsaturated.
- A common ion lowers solubility, as in $s = K_{sp}/[\text{Cl}^-]$ for AgCl in NaCl .

- Salts of basic anions (OH^- , CO_3^{2-} , F^- , PO_4^{3-}) dissolve better in acid.

Ksp, precipitation and the common ion effect: frequently asked questions

What is the difference between solubility and Ksp?

Solubility is the amount that dissolves in a given volume, often written as molar solubility s in mol/dm^3 . Ksp is the equilibrium constant that links the ion concentrations at saturation. You can convert between them with the dissolving equation.

Why is the solid left out of the Ksp expression?

The concentration of a pure solid is constant, so it is absorbed into the constant. Only dissolved ions appear in Ksp.

How do you know whether a precipitate forms?

Calculate Q from the concentrations after mixing, remembering that volumes add. If Q is greater than Ksp, a precipitate forms until Q falls to Ksp.

Why does a common ion reduce solubility?

The extra ion shifts the dissolving equilibrium to the left, so more solid stays undissolved. The shift is a direct Le Chatelier effect and Ksp itself does not change.

Why does CaCO_3 dissolve in acid?

The carbonate ion reacts with H_3O^+ to form CO_2 and water, which removes CO_3^{2-} from the equilibrium. The solid then dissolves to replace it.