

# Solubility & Complex-Ion Equilibria

K<sub>sp</sub>, molar solubility, the common-ion effect, Q vs K<sub>sp</sub>, selective precipitation, and coupled equilibria.

## 01 K<sub>sp</sub> expression

CORE RULE

K<sub>sp</sub> = product of ion concentrations, each to its coefficient, in a saturated solution. The pure solid is excluded.  $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ :

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

## 02 K<sub>sp</sub> in terms of solubility s

REFERENCE

| Salt type                           | K <sub>sp</sub> |
|-------------------------------------|-----------------|
| MX                                  | $s^2$           |
| MX <sub>2</sub> or M <sub>2</sub> X | $4s^3$          |
| MX <sub>3</sub> or M <sub>3</sub> X | $27s^4$         |
| M <sub>2</sub> X <sub>3</sub>       | $108s^5$        |

## 03 Molar solubility from K<sub>sp</sub>

METHOD

ICE with x for the reference ion, write the K<sub>sp</sub> polynomial, solve for x. If solubility is given in g/L, convert to mol/L (÷ molar mass) before using K<sub>sp</sub>.

## 04 Insoluble hydroxides & pH

CORE RULE

For  $\text{M}(\text{OH})_n$ ,  $[\text{OH}^-] = n \cdot s$ , so  $\text{pOH} = -\log[\text{OH}^-]$ ,  $\text{pH} = 14 - \text{pOH}$ .  
Given pH instead:  $[\text{OH}^-] = 10^{-(14-\text{pH})}$ , then solve K<sub>sp</sub> for the metal-ion concentration.

## 05 Common-ion effect

CORE RULE

A shared ion already in solution goes into the ICE initial row, lowering molar solubility vs pure water. The x-small approximation ( $x \ll$  common-ion concentration) is usually valid; check  $x < 5\%$ .

## 06 Q vs K<sub>sp</sub> (will it precipitate?)

CORE RULE

Compute Q from initial ion concentrations (apply dilution when mixing:  $[\text{ion}] \times V_{\text{part}}/V_{\text{total}}$ ).  $Q < K_{sp} \rightarrow$  no precipitate;  $Q > K_{sp} \rightarrow$  precipitates until  $Q = K_{sp}$ ;  $Q = K_{sp} \rightarrow$  just saturated.

## 07 Selective precipitation

CORE RULE

Find the counter-ion concentration each salt needs to hit  $Q = K_{sp}$ ; the lowest threshold precipitates first. Comparing K<sub>sp</sub> values directly is valid only for the same salt stoichiometry.

## 08 Complex-ion / coupled equilibria

CORE RULE

Coupling dissolution to complex formation raises solubility:  
 $K_{\text{overall}} = K_{sp} \times K_f$ . E.g.  $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^-$ . With excess ligand ( $[\text{L}] \approx [\text{L}]_0$ ), a 1:1 salt gives  $s = \sqrt{(K_{\text{overall}} \cdot [\text{L}])}$ .  
Acid-coupled  $\text{M}(\text{OH})_n$ :  $K = K_{sp}/K_w^n$ .