
VI. Applications of Aqueous Equilibria.

E. Solubility equilibria.

Whether a salt is insoluble or soluble is important in many “real world” phenomena: tooth decay, stalagmite and stalagmite formation, silver tarnish, kidney stones, and photography, to name a few.

1. Solubility product.

The fundamental equilibria for solubility of a salt is the dissolution of the salt in water to form the cation and anion:

Ex. for AgCl; \( \text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \)

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

\( K_{sp} \) (the solubility product) is the equilibrium constant for this equilibrium. Note that the insoluble pure solid does not appear in the \( K_{sp} \) expression. In more general terms:

\( \text{M}_m\text{X}_n(s) \rightleftharpoons m\text{M}^{n+} + n\text{X}^{m-} \)

\( K_{sp} = [\text{M}^{n+}]^m[\text{X}^{m-}]^n \)

To do this correctly, you need to remember the correct formula and charge of all the common ions.

Write the solubility equilibrium and \( K_{sp} \) expressions for:

(a) \( \text{PbI}_2 \) \( \text{PbI}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^- \)

\( K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 \)

(b) \( \text{Ca}_3(\text{PO}_4)_2 \) \( \text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \)

\( K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 \)

Table 4 of Appendix C in M&F has a list of \( K_{sp} \)’s for many salts.

2. Calculations using solubility equilibria. The problem types here follow a similar pattern to the one given in the previous lectures on general equilibria.

Type 1: Given equilibrium conc. of the cation and anion, calculate \( K_{sp} \).

Ex. A saturated solution of \( \text{Ca}_3(\text{PO}_4)_2 \) has \([\text{Ca}^{2+}] = 2.01 \times 10^{-8} \text{ M} \) and \([\text{PO}_4^{3-}] = 1.6 \times 10^{-5} \text{ M} \).

What is \( K_{sp} \) for \( \text{Ca}_3(\text{PO}_4)_2 \)?

Note: a saturated solution contains equilibrium concentrations of the cation and anion. Write the solubility equilibrium and \( K_{sp} \) expression (see above). Plug in the given conc. and solve for \( K_{sp} \):

\[ K_{sp} = (2.01 \times 10^{-8})(1.6 \times 10^{-5})^2 = (8.12 \times 10^{-28})(2.6 \times 10^{-10}) = 2.1 \times 10^{-38} \]

↑ don’t forget the exponents!!

Sometimes the data is the solubility of the salt; see Nakon, ch. 19, pp. 299-302.
Type 2: Given $K_{sp}$, calculate the molar solubility of a salt in pure water.

Ex. What is the molar solubility of AgCl? $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$

Write the solubility equilibrium and $K_{sp}$ expression. Let $x$ = molar solubility of the salt. Express the conc. of each ion in terms of $x$. Plug the expressions of $x$ into the $K_{sp}$ expression and solve for $x$.

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \quad K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$K_{sp} = 1.8 \times 10^{-10} = (x)(x) = x^2; \quad x = (1.8 \times 10^{-10})^{1/2} = 1.3 \times 10^{-5} \text{ M}$$

Ex. What is the solubility of Ag$_2$SO$_4$ in pure water in g/L? What is the molar conc. of each ion? $K_{sp} = 1.2 \times 10^{-5}$.

Calculate the molar solubility first, then convert to g/L.

$$\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2\text{Ag}^+ + \text{SO}_4^{2-} \quad K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] \text{ (don’t forget the exponents!) }$$

$$K_{sp} = 1.2 \times 10^{-5} = (2x)^2(x) = 4x^3; \quad x^3 = (3 \times 10^{-6})^{1/3} = 1.4 \times 10^{-2} \text{ M}$$

$$[\text{Ag}^{2+}] = 2x = 2.9 \times 10^{-2} \text{ M}; \quad [\text{SO}_4^{2-}] = x = 1.4 \times 10^{-2} \text{ M}$$

Since $\text{FW(\text{Ag}_2\text{SO}_4)} = 311.8$, solubility $= (1.4 \times 10^{-2} \text{ mol/L})(311.8 \text{ g/mol}) = 4.4 \text{ g/L}$

3. The common ion effect (yet again!).

Qualitative effects: Addition of any other electrolyte which has a common ion to a solubility equilibrium reduces the solubility of the salt.

Ex. AgCl$(s) = \text{Ag}^+ + \text{Cl}^-$

Adding Ag$^+$ (say, from soluble AgNO$_3$) or Cl$^-$ (say, from NaCl or HCl) lowers the solubility of AgCl by Le Chatelier’s Principle. Chemists use this principle to collect ionic products; they add excess counter ion to the solution to force the product to precipitate.

If the anion is OH$^-$ or a weak base, then adding acid increases the solubility of the salt.

Ex. Mg(OH)$_2$ becomes more soluble as the pH is lowered ([H$^+$] is raised) because [OH$^-$] is lowered.

Ex. CaCO$_3(s) = \text{Ca}^{2+} + \text{CO}_3^{2-}$

Adding H$^+$ lowers the CO$_3^{2-}$ conc. via the equilibrium: CO$_3^{2-} + H^+ \rightleftharpoons HCO_3^-$
Consequently, the solubility of CaCO$_3$ increases as acid is added. Cave chemistry: as CO$_2$ dissolves in water, it raises the H$^+$ conc. (CO$_2$ + H$_2$O $\rightleftharpoons$ H$_2$CO$_3$ $\rightleftharpoons$ H$^+$ + HCO$_3^-$), and limestone dissolves. As CO$_2$ escapes from the solution, H$^+$ conc. decreases, and limestone precipitates.

If the metal cation forms a complex, then adding the ligand increases the solubility of the salt.

Ex. Ag$^+$ forms a complex with ammonia; the equilibrium constant is large.

$$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+ \quad K_f \gg 1$$

Adding NH$_3$ to AgCl(s) causes the AgCl to dissolve.

Ex. Amphoterism. Many metal cations form insoluble hydroxides. Some metal cations form soluble complexes with OH$^-$. These ions will first precipitate and then redissolve as OH$^-$ is added.

Ex. Al(OH)$_3$(s) $\rightleftharpoons$ Al$^{3+}$ + 3OH$^-$ (adding OH$^-$ to Al$^{3+}$ precipitates Al(OH)$_3$)

Al(OH)$_3$(s) + OH$^-$ $\rightleftharpoons$ Al(OH)$_4^-$ (adding excess OH$^-$ dissolves the precipitate)

Quantitative effects: Type 3 problem: Given K$_{sp}$, calculate the molar solubility of a salt in the presence of a common ion.

Ex. Calculate the molar solubility of MgF$_2$ in 0.10 M MgCl$_2$. $K_{sp}$(MgF$_2$) = 7.4×10$^{-11}$

The common ion is Mg$^{2+}$. Write the solubility equilibrium and expression, let x = molar solubility, put in initial, change and final conc., and solve for x. Use an assumption to make the calculation simpler.

$$\text{MgF}_2(s) \rightleftharpoons \text{Mg}^{2+} + 2\text{F}^- \quad K_{sp} = [\text{Mg}^{2+}][\text{F}^-]^2$$

$$0.10 + x \quad 0 + 2x \quad (0.10 \text{ M Mg}^{2+} \text{ from MgCl}_2)$$

$$K_{sp} = 7.4\times10^{-11} = (0.10 + x)(2x)^2 \approx (0.10)(2x)^2 = 0.40x^2$$

Assumption: x << 0.10 (generally true)

$$x^2 = 7.4\times10^{-11}/0.40 = 1.8\times10^{-10}, \ x = 1.4\times10^{-5}$$

Use Finklea’s 10% rule: is x < (0.1)(0.1)? Yes! The assumption is OK.

The molar solubility is 1.4×10$^{-5}$ M. For comparison, the molar solubility in pure water is 2.6×10$^{-4}$ M.

Type 3 variation: Calculate the molar solubility of a hydroxide salt in a solution of given pH.

Ex. What is the solubility of Mg(OH)$_2$ in a pH 9.00 solution? $K_{sp}$(Mg(OH)$_2$) = 5.6×10$^{-12}$

The common ion is OH$^-$. [OH$^-$] is fixed by a buffer. Hence, calculate [OH$^-$] from the pH.

pH = 9.00; pOH = 14.00 - pH = 5.00; [OH$^-$] = 10$^{-5.00} = 1.0\times10^{-5}$ M

$$\text{Mg(OH}_2(s) = \text{Mg}^{2+} + 2\text{OH}^- \quad K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$K_{sp} = 5.6\times10^{-12} = [\text{Mg}^{2+}](1.0\times10^{-5})^2; \ [\text{Mg}^{2+}] = 5.6\times10^{-2} \text{ M = molar solubility}$$
4. Selective precipitation.

Solubility properties are used in qualitative analysis of ions - determination of which ions are present in solution. Solution conditions are adjusted so that certain ions will form a precipitate and others will not. A systematic scheme for this (called the qual. scheme) will be covered later.

Type 4: Determine whether a precipitate will form when two solutions are mixed together. The information will include initial concentrations and volumes and a $K_{sp}$. This is the old trick of comparing the reaction quotient $Q$ to the $K$ value. For a solubility equilibrium, the reaction quotient is called the ion product or IP.

Ex. Will a precipitate form when equal volumes of $3.0 \times 10^{-3}$ M $\text{BaCl}_2$ and $2.0 \times 10^{-3}$ M $\text{Na}_2\text{CO}_3$ are mixed? $K_{sp}(\text{BaCO}_3) = 2.6 \times 10^{-9}$

Step 1: Find the conc. of ions after mixing but before any reaction happens.
Volumes are not given here, so choose a volume. Mix 1.0 L of $\text{BaCl}_2$ with 1.0 L of $\text{Na}_2\text{CO}_3$.

$[\text{Ba}^{2+}] = (3.0 \times 10^{-3} \text{ M})(1.0 \text{ L})/(2.0 \text{ L}) = 1.5 \times 10^{-3} \text{ M}$

$[\text{CO}_3^{2-}] = (2.0 \times 10^{-3} \text{ M})(1.0 \text{ L})/(2.0 \text{ L}) = 1.0 \times 10^{-3} \text{ M}$

Step 2: Calculate the IP. The IP is the same expression as $K_{sp}$.

$\text{BaCO}_3(s) = \text{Ba}^{2+} + \text{CO}_3^{2-}$

$\text{IP} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = (1.5 \times 10^{-3})(1.0 \times 10^{-3}) = 1.5 \times 10^{-6}$

Step 3: Compare IP to $K_{sp}$. If IP $\leq K_{sp}$, no precipitate forms. If IP $> K_{sp}$, the salt precipitates.

Since $1.5 \times 10^{-6} > 2.6 \times 10^{-9}$, $\text{BaCO}_3$ will precipitate.

Many metal cations form insoluble salts with sulfide ($S^{2-}$). The solubility is dependent on pH. By adjusting the pH, it is possible to precipitate certain metal cations selectively. We will use a special equilibrium reaction ($M$ is the metal):

$$\text{MS}(s) + 2\text{H}^{+} = M^{2+} + \text{H}_2\text{S}$$

$K_{spa}$ is the solubility product in acid. Values of $K_{spa}$ are given in Table 5, Appendix C. In water saturated with $\text{H}_2\text{S}$, $[\text{H}_2\text{S}]$ is about 0.1 M.

Type 5. Given the metal ion conc. and $K_{spa}$ and $[\text{H}^+]$ (or pH), predict whether the metal ion will precipitate in the presence of saturated $\text{H}_2\text{S}$ solution. Calculate the reaction quotient and compare it to $K_{spa}$. If $Q > K_{spa}$, the sulfide salt will precipitate.

Ex. Give $[\text{Cd}^{2+}] = 0.005$ M, will CdS precipitate in 0.3 M HCl saturated with $\text{H}_2\text{S}$? $K_{spa}(\text{CdS}) = 8 \times 10^{-7}$.

$$\text{CdS}(s) + 2\text{H}^{+} = \text{Cd}^{2+} + \text{H}_2\text{S}$$

$Q = ([\text{Cd}^{2+}][\text{H}_2\text{S}])/[\text{H}^+]^2$

Since $[\text{H}^+] = 0.3$ M and $[\text{H}_2\text{S}] = 0.1$ M, $Q = ((0.005)(0.1))/(0.3)^2 = (0.0005)/(0.09) = 0.006$.

Since $Q > K_{spa}$ ($6 \times 10^{-3} > 8 \times 10^{-7}$), CdS will precipitate.