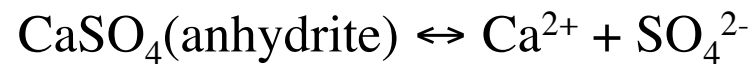


Solubility Product

The solubility of a mineral is governed by the solubility product, the equilibrium constant for a reaction such as:



The solubility product is given by:

$$K_{SP} = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}{a_{\text{CaSO}_4}}$$

If anhydrite is a pure solid, then $a_{\text{CaSO}_4} = 1$.

and in dilute solutions: $a_{\text{Ca}^{2+}} \approx (\text{Ca}^{2+})$ and $a_{\text{SO}_4^{2-}} \approx (\text{SO}_4^{2-})$.

$$K_{SP} = \frac{a_{Ca^{2+}} a_{SO_4^{2-}}}{a_{CaSO_4}}$$

$$K_{SP} \approx [Ca^{2+}][SO_4^{2-}] = 10^{-4.5}$$

What is the solubility of anhydrite in pure water?

If anhydrite dissolution is the only source of both Ca^{2+} and SO_4^{2-} , then:

$$[Ca^{2+}] = [SO_4^{2-}] = x$$

$$x^2 = 10^{-4.5}$$

$$x = 10^{-2.25} = 5.62 \times 10^{-3} \text{ mol/L}$$

$$MW_{\text{anhydrite}} = 136.14 \text{ g/mol}$$

$$\text{Solubility} = (5.62 \times 10^{-3} \text{ mol/L})(136.14 \text{ g/mol}) = 0.765 \text{ g/L}$$

Saturation index

In a natural solution, it is not likely that $[Ca^{2+}] = [SO_4^{2-}]$, for example, because there will be more than one source of each of these ions. In this case we use saturation indices to determine if the water is saturated with respect to anhydrite.

$$K_{SP} = 10^{-4.5} \approx [Ca^{2+}]_{eq}[SO_4^{2-}]_{eq}$$

$$IAP = [Ca^{2+}]_{act}[SO_4^{2-}]_{act}$$

Saturation index

$$\Omega = \frac{[Ca^{2+}]_{act}[SO_4^{2-}]_{act}}{K_{SP}} = \frac{IAP}{K_{SP}}$$

Suppose a groundwater is analyzed to contain 5×10^{-2} mol/L Ca^{2+} and 7×10^{-3} mol/L SO_4^{2-} . Is this water saturated with respect to anhydrite ($\text{CaSO}_4(\text{s})$)?



$$K_{\text{SP}} = 10^{-4.5}$$

$$\text{IAP} = (5 \times 10^{-2})(7 \times 10^{-3}) = 3.5 \times 10^{-4} = 10^{-3.45}$$

$$\Omega = 10^{-3.45} / 10^{-4.5} = 10^{1.05} = 11.22$$

$\Omega > 1$, i.e., $\text{IAP} > K_{\text{SP}}$, so the solution is supersaturated and anhydrite should precipitate

If $\Omega = 1$, i.e., $\text{IAP} = K_{\text{SP}}$, the solution would be saturated (equilibrium conditions)

If $\Omega < 1$, i.e., $\text{IAP} < K_{\text{SP}}$, the solution would be undersaturated; the mineral should dissolve

How much salt should precipitate?

Returning to the previous example, i.e., the groundwater with 5×10^{-2} mol/L Ca^{2+} and 7×10^{-3} mol/L SO_4^{2-} , how much anhydrite should precipitate at equilibrium?

If x mol/L of anhydrite precipitate, then at equilibrium:

$$[\text{Ca}^{2+}] = 5 \times 10^{-2} - x; [\text{SO}_4^{2-}] = 7 \times 10^{-3} - x$$

$$\text{and } [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.5}$$

$$(5 \times 10^{-2} - x)(7 \times 10^{-3} - x) = 10^{-4.5}$$

$$x^2 - (5.7 \times 10^{-2})x + (3.18 \times 10^{-4}) = 0$$

After solving for the quadratic equation:

$$x_1 = 5.07 \times 10^{-2} \text{ mol/L}; x_2 = 6.26 \times 10^{-3} \text{ mol/L}$$

We choose $x_2 (=6.26 \times 10^{-3})$ because the first root
($x_1 = 5.07 \times 10^{-2}$) causes $[\text{SO}_4]$ to be negative.

So, 6.26×10^{-3} mol/L of anhydrite precipitates, or:

$$(6.26 \times 10^{-3} \text{ mol/L})(136.1 \text{ g/mol}) = 0.852 \text{ g/L}$$

and

$$[\text{Ca}^{2+}] = (5 \times 10^{-2}) - (6.26 \times 10^{-3}) = 4.37 \times 10^{-2} \text{ mol/L}$$

$$[\text{SO}_4^{2-}] = (7 \times 10^{-3}) - (6.26 \times 10^{-3}) = 7.4 \times 10^{-4} \text{ mol/L}$$

$[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ increases with precipitation of anhydrite

Before precipitation:

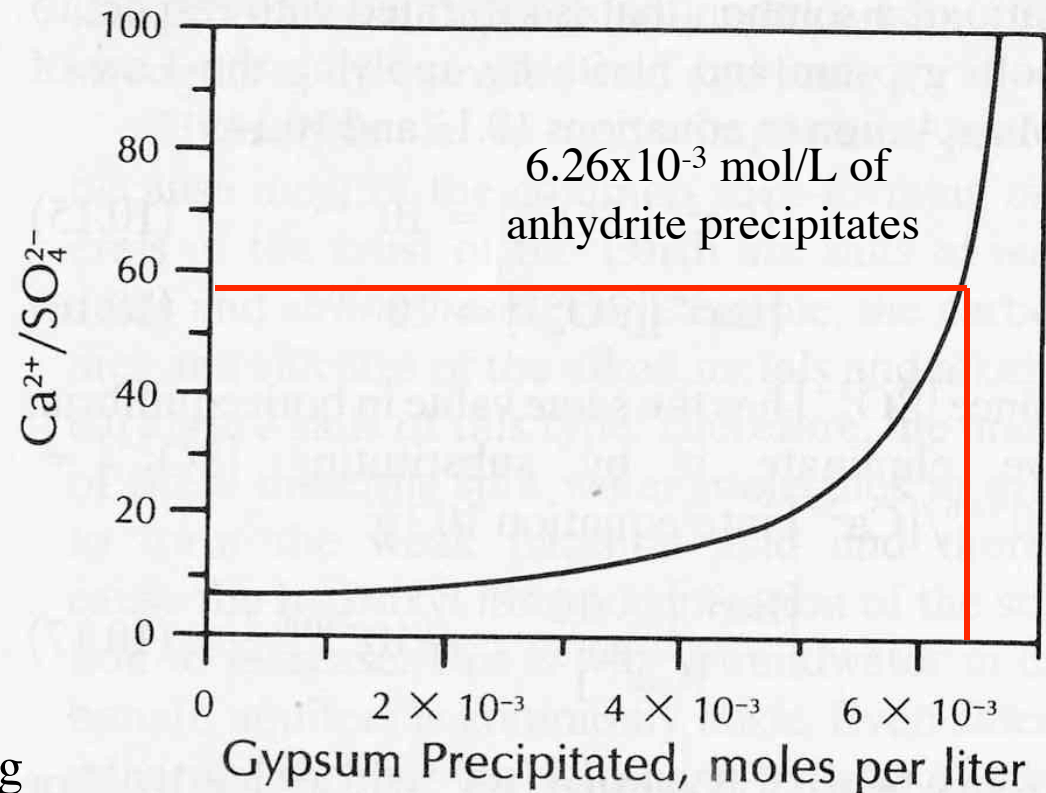
$$5 \times 10^{-2} / 7 \times 10^{-3} = 7.1$$

After precipitation:

$$4.37 \times 10^{-2} / 7.4 \times 10^{-4} = 59$$

Precipitation not only reduces the concentrations of ions and actually changes the chemical composition if the remaining solution...

Because the initial $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}] > 1$, the remaining solution is enriched in Ca^{2+} ; if $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]_i < 1$, the solution would be enriched in SO_4^{2-}



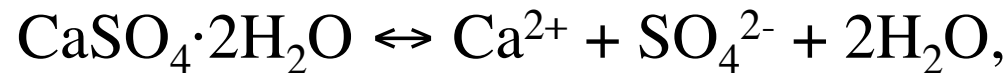
This process occurs when salts precipitate when water undergoes evaporative concentration such as in a desert lake

The common-ion effect

Natural waters are very complex and we may have saturation with respect to several phases simultaneously.

Example: What are the concentrations of all species in a solution in equilibrium with both barite and gypsum?

1) Law of mass action expressions:



$$K_{\text{SP}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.6}$$



$$K_{\text{SP}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 10^{-10.0}$$

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.6}$$

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 10^{-10.0}$$

Eliminate $[\text{SO}_4^{2-}]$ by substituting $10^{-4.6}/[\text{Ca}^{2+}]$:

$$[\text{Ba}^{2+}] \cdot 10^{-4.6}/[\text{Ca}^{2+}] = 10^{-10.0}$$

2) Species: Ca^{2+} , Ba^{2+} , SO_4^{2-} , H^+ , OH^-



$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

3) Mass-balance: $[\text{Ba}^{2+}] + [\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$

4) Charge-balance:

$$2[\text{Ba}^{2+}] + 2[\text{Ca}^{2+}] + [\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{OH}^-]$$

$$[Ca^{2+}] = 10^{-4.6} / [SO_4^{2-}], \quad [Ba^{2+}] = 10^{-10.0} / [SO_4^{2-}]$$

$$\left(10^{-4.6} / [SO_4^{2-}] \right) + \left(10^{-10.0} / [SO_4^{2-}] \right) = [SO_4^{2-}]$$

$$10^{-4.6} + 10^{-10.0} = [SO_4^{2-}]^2$$

$$[SO_4^{2-}] = (10^{-4.6} + 10^{-10.0})^{1/2} = 10^{-2.3} \text{ mol/L}$$

$$[Ca^{2+}] = 10^{-4.6} / 10^{-2.3} = 10^{-2.3} \text{ mol/L}$$

$$[Ba^{2+}] = 10^{-10.0} / 10^{-2.3} = 10^{-7.7} \text{ mol/L}$$

The least soluble salt (barite, $K_{SP}=10^{-10}$), contributes a negligible amount of sulfate to the solution. The more soluble salt (gypsum, $K_{SP}=10^{-4.6}$) suppresses the solubility of the less soluble salt (the common-ion effect). Barite can replace gypsum because barite is less soluble than gypsum.

The solubility of gypsum is hardly affected by the presence of barite:

Solubility of barite alone:

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 10^{-10.0}$$

$$[\text{Ba}^{2+}]^2 = 10^{-10.0}$$

$$[\text{Ba}^{2+}] = 10^{-5.0} \text{ mol/L}$$

Solubility of gypsum alone:

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.6}$$

$$[\text{Ca}^{2+}]^2 = 10^{-2.3}$$

$$[\text{Ca}^{2+}] = 10^{-2.3} \text{ mol/L}$$

Replacement reactions

We can also calculate $[Ba^{2+}]/[Ca^{2+}]$ in equilibrium with both barite and gypsum.

$$[Ca^{2+}] = 10^{-4.6} / [SO_4^{2-}] \quad [Ba^{2+}] = 10^{-10.0} / [SO_4^{2-}]$$

$$\frac{[Ba^{2+}]}{[Ca^{2+}]} = \frac{10^{-10}}{10^{-4.6}} = 10^{-5.4}, \text{ or } [Ca^{2+}] = 250,000[Ba^{2+}]$$

What would happen if a solution with $[Ba^{2+}]/[Ca^{2+}] = 10^{-3}$ ($[Ca^{2+}] = 1,000[Ba^{2+}]$) came into contact with a gypsum-bearing rock?

Barite will precipitate (taking Ba^{2+} out of the solution) and gypsum will dissolve until $[Ba^{2+}]/[Ca^{2+}] = 10^{-5.4}$.

Hydrolysis

The interaction between water and one or both ions of a salt that results in the formation of the parental acid or base, or both.

We classify salts by the strength of the acid and base from which they form:

1. Strong acid + strong base \longrightarrow do not hydrolyze
2. Strong acid + weak base \longrightarrow cations + OH^- = acidic soln
3. Weak acid + strong base \longrightarrow anions + H^+ = basic soln
4. Weak acid + weak base \longrightarrow release both cation & anions

Most common rock-forming minerals of the crust are salts of weak acids and strong bases, e.g., carbonates and silicates of alkali metals (Group 1) and alkaline earths (Group 2) form these salts...this is why groundwater in carbonate aquifers is commonly basic

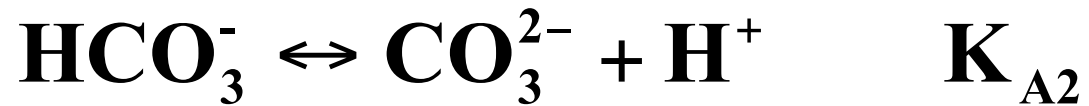
Hydrolysis



$$\mathbf{K_{H1} = ?}$$

$$\mathbf{K_{H2} = ?}$$

Dissociation



What is the pH of a solution prepared by dissolving 0.1 mol of K_2CO_3 in 1 L of water?