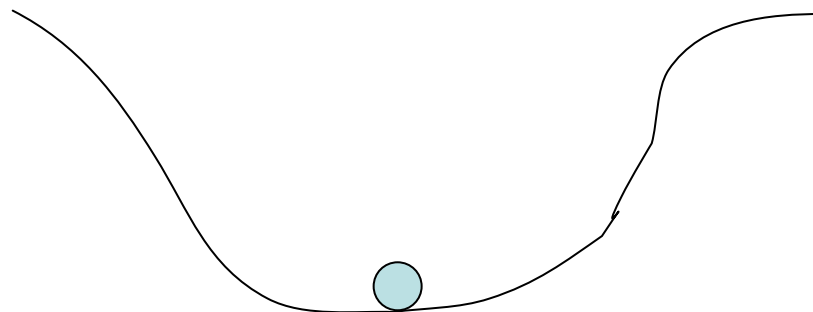
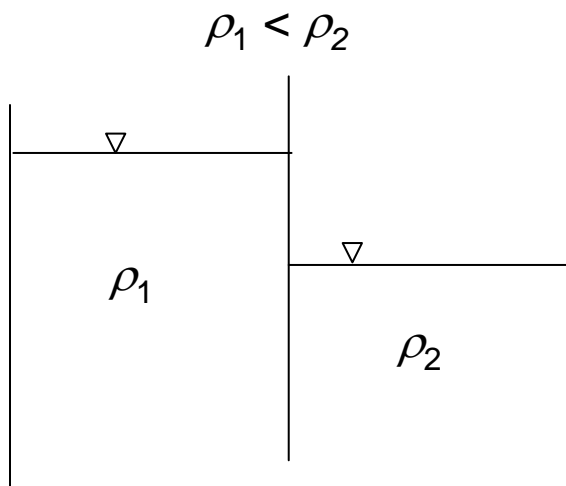


Chemical Equilibrium

A condition in which the system is at its minimum attainable energy level and hence has no tendency to undergo chemical change.

Analogous Physical Equilibria:



The Equilibrium Constant, K_{eq}

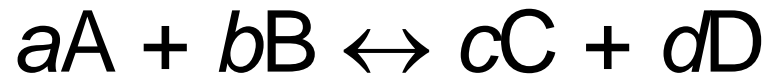
For any reaction with stoichiometry:



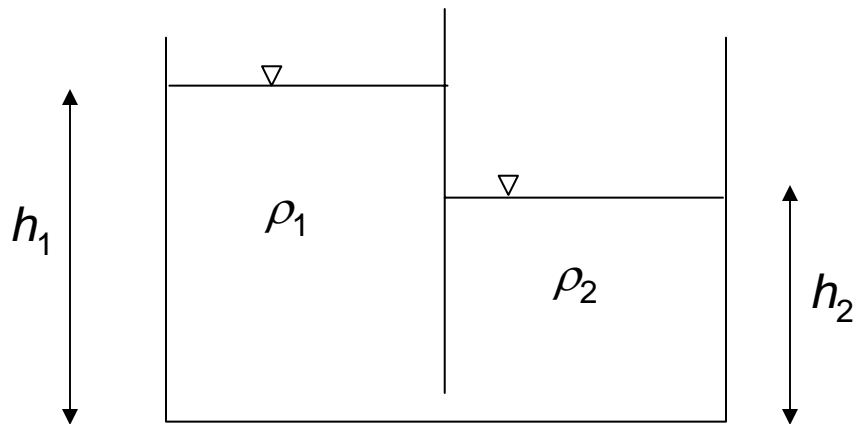
$$K_{eq} = \frac{(C)^c (D)^d}{(A)^a (B)^b}$$

where (i) is a normalized (non-dimensional) concentration of chemical i , and the values are all measured in a system ***at equilibrium***

The Equilibrium Constant, K_{eq}



$$K_{eq} = \frac{(C)^c (D)^d}{(A)^a (B)^b}$$



Analogous to defining an equilibrium constant relating liquids 1 and 2 as the ratio of the liquid column heights (h_2/h_1) for a system that has reached static equilibrium.

Note that one need not know the densities of the fluids (or understand its relation to the heights) if the “ K ” value is given. Also, $h_2/h_1 \neq K$ if the system is not at equilibrium.

The Equilibrium Constant, K_{eq}

- If the actual ratio of normalized concentrations (Q) equals K_{eq} , the reaction is at equilibrium
- If Q does not equal K_{eq} , the reaction will proceed in the direction that causes Q to approach K_{eq}
- Evaluation/use of K_{eq} requires knowledge of:
 - the chemical reaction (stoichiometry)
 - conventions for quantifying and normalizing the concentrations of the reactants and products

The Equilibrium Constant, K_{eq}

- Concentration Conventions
 - For species (e.g., Na^+ , Cl^-) that are dissolved in a large amount of a bulk phase (e.g., water), concentrations are expressed in mol/L, and the normalizing concentration is 1.0 mol/L
 - For constituents that make up the bulk of a *condensed* phase (e.g., water, or a pure solid that has precipitated), concentrations are expressed in terms of the fraction of that phase that the species represents, and the normalizing concentration is a mole fraction of 1.0. This fraction is typically so close to 1.0 that we can use the approximation that the concentration is exactly 1.0.
 - For gases, the concentration are expressed in terms of the pressure that the species exerts, in atmospheres, and the normalizing concentration is 1.0 atm.

The Equilibrium Constant for Water Dissociation, K_w



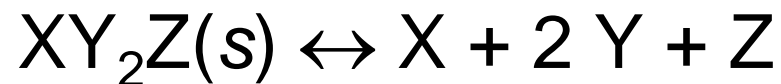
$$K_{eq} = \frac{(\text{H}^+)(\text{OH}^-)}{(\text{H}_2\text{O})} = \frac{(\text{H}^+)(\text{OH}^-)}{1.0} = 10^{-14.0} \equiv K_w$$

$$\text{pH} = -\log_{10}(\text{H}^+)$$

Some Important Equilibria in Water Treatment Involving Solids

- $\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$ Hardness
- $\text{Mg}(\text{OH})_2(\text{s}) \leftrightarrow \text{Mg}^{2+} + 2 \text{OH}^-$ Hardness
- $\text{PbCO}_3(\text{s}) \leftrightarrow \text{Pb}^{2+} + \text{CO}_3^{2-}$ Lead & Copper Rule (LCR)
- $\text{Cu}(\text{OH})_2(\text{s}) \leftrightarrow \text{Cu}^{2+} + 2 \text{OH}^-$ LCR
- $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s}) \leftrightarrow 2\text{Cu}^{2+} + 2 \text{OH}^- + \text{CO}_3^{2-}$ LCR
- $\text{Fe}(\text{OH})_3(\text{s}) \leftrightarrow \text{Fe}^{3+} + 3 \text{OH}^-$ Coagulation
- $\text{Al}(\text{OH})_3(\text{s}) \leftrightarrow \text{Al}^{3+} + 3 \text{OH}^-$ Coagulation
- $\text{SiO}_2(\text{s}) + 2 \text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4$ Membrane fouling, Arsenic treatment

Equilibrium Constants Involving Solids



$$K_{eq} = \frac{(X)(Y)^2(Z)}{(XY_2Z(s))} = \frac{(X)(Y)^2(Z)}{1.0} \equiv K_{sp} \text{ or } K_{so}$$

- “Solubility product” (K_{sp} or K_{so}) is K_{eq} for **dissolution** of the solid into its constituents
- The solid (and sometimes H_2O) are the only chemicals on the left side

Some Solids are Very Soluble or Very Insoluble

- Some solids (e.g., NaCl, CaCl₂, Na₂SO₄) are so **soluble** under normal water treatment conditions that we never consider the possibility that the solid will be present in an equilibrium solution.
- Other solids (e.g., Fe(OH)₃, MnO₂) are so **insoluble** under normal water treatment conditions that we assume 100% of the metal precipitates.
- Some solids (CaCO₃) are “**slightly soluble**” under normal water treatment conditions, so neither assumption applies. Others (PbCO₃, AlPO₄) are very insoluble, but the trace amount that dissolves is still of concern.

Issues that Arise Regarding Slightly Soluble Solids in Water Treatment

- Is Q_{s0} greater than, less than, or equal to K_{s0} initially?
- How much does the concentration of some constituent have to change to cause Q_{s0} to equal or exceed K_{s0} (i.e., for precipitation to begin)?
- How much of some chemical must be added to cause Q_{s0} to equal or exceed K_{s0} ?
- Will a solid precipitate if a specified amount of some chemical is added? If so, how much solid forms?
- If a solution with known composition comes into contact with a solid, how much solid will dissolve?

Example: Dissolution of Gypsum ($\text{CaSO}_4(\text{s})$)

- K_{so} for gypsum is $10^{-4.6}$
- 1.0 g of gypsum is dispersed in 1.0 L of water containing no Ca^{2+} or SO_4^{2-} . How much solid (if any) remains after the system reaches equilibrium?
- Repeat the analysis if the solution initially contains 200 mg/L SO_4^{2-} .

Example: Dissolution of $\text{CaSO}_4(s)$

$$K_{sp} = 10^{-4.6} = \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{(\text{CaSO}_4(s))} = \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{1.0} = (\text{Ca}^{2+})(\text{SO}_4^{2-})$$

$$(\text{Ca}^{2+}) = (\text{SO}_4^{2-})$$

$$10^{-4.6} = (\text{Ca}^{2+})^2$$

$$(\text{Ca}^{2+}) = (10^{-4.6})^{0.5} = 10^{-2.3} = 5.0 \times 10^{-3} = (\text{SO}_4^{2-})$$

Example: Dissolution of $\text{CaSO}_4(\text{s})$

$$(\text{Ca}^{2+}) = \left(10^{-2.3} \frac{\text{mol}}{\text{L}} \right) \left(40 \frac{\text{g}}{\text{mol}} \right) = 0.20 \frac{\text{g}}{\text{L}}$$

$$(\text{SO}_4^{2-}) = \left(10^{-2.3} \frac{\text{mol}}{\text{L}} \right) \left(96 \frac{\text{g}}{\text{mol}} \right) = 0.48 \frac{\text{g}}{\text{L}}$$

$\text{CaSO}_4(\text{s})$ dissolved = 0.68 g/L

$\text{CaSO}_4(\text{s})$ remaining undissolved = 0.32 g/L (32%)

Dissolution of $\text{CaSO}_4(\text{s})$ with $(\text{SO}_4^{2-})_{\text{init}} > 0$

$$(\text{SO}_4^{2-})_{\text{init}} = \left(200 \frac{\text{mg}}{\text{L}} \right) \left(\frac{1 \text{ mol}}{96,000 \text{ mg}} \right) = 2.08 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$K_{sp} = 10^{-4.6} = (\text{Ca}^{2+})_{\text{final}} (\text{SO}_4^{2-})_{\text{final}} = (x) (2.08 \times 10^{-3} + x)$$

$$x = 4.08 \times 10^{-3}$$

Dissolution of $\text{CaSO}_4(\text{s})$ with $(\text{SO}_4^{2-})_{\text{init}} > 0$

$$(\text{Ca}^{2+})_{\text{final}} = x = 4.08 \times 10^{-3} \frac{\text{mol}}{\text{L}} \left(40,000 \frac{\text{mg}}{\text{mol}} \right) = 163 \frac{\text{mg}}{\text{L}}$$

$$(\text{SO}_4^{2-})_{\text{final}} = \left(x + 2.08 \times 10^{-3} \right) \frac{\text{mol}}{\text{L}} = \left(6.16 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) \left(96,000 \frac{\text{mg}}{\text{mol}} \right) = 591 \frac{\text{mg}}{\text{L}}$$

$\text{CaSO}_4(\text{s})$ dissolved = $163 \text{ mg/L} + (591 - 200) \text{ mg/L} = 554 \text{ mg/L}$

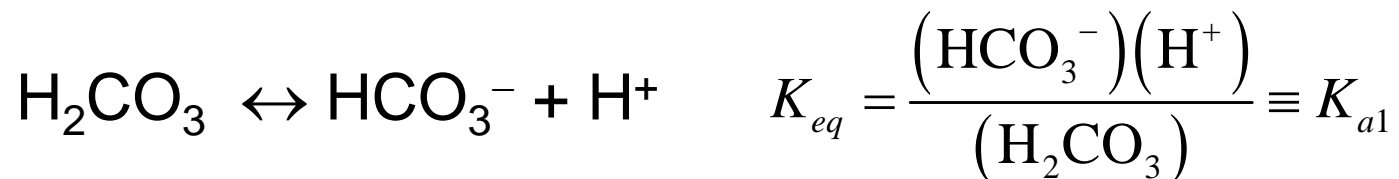
$\text{CaSO}_4(\text{s})$ remaining undissolved = 446 mg/L (44.6%)

The Carbonate Chemical Group in Water

- Dissolved Carbonate-containing species
 - **Carbonic Acid: H_2CO_3** . Can form by combination of a carbon dioxide molecule and water:



- **Bicarbonate Ion: HCO_3^-** . Can form by “dissociation” of carbonic acid:



The Carbonate Chemical Group

- Dissolved Carbonate-containing species
 - **Carbonate Ion: CO_3^{2-}** . Can form by dissociation of bicarbonate ion:



- Other Commonly Defined Quantities

- **Total Dissolved Carbonate: $TOT\text{CO}_3$**

$$TOT\text{CO}_3 = (\text{H}_2\text{CO}_3) + (\text{HCO}_3^-) + (\text{CO}_3^{2-}) + [\text{others?}]$$

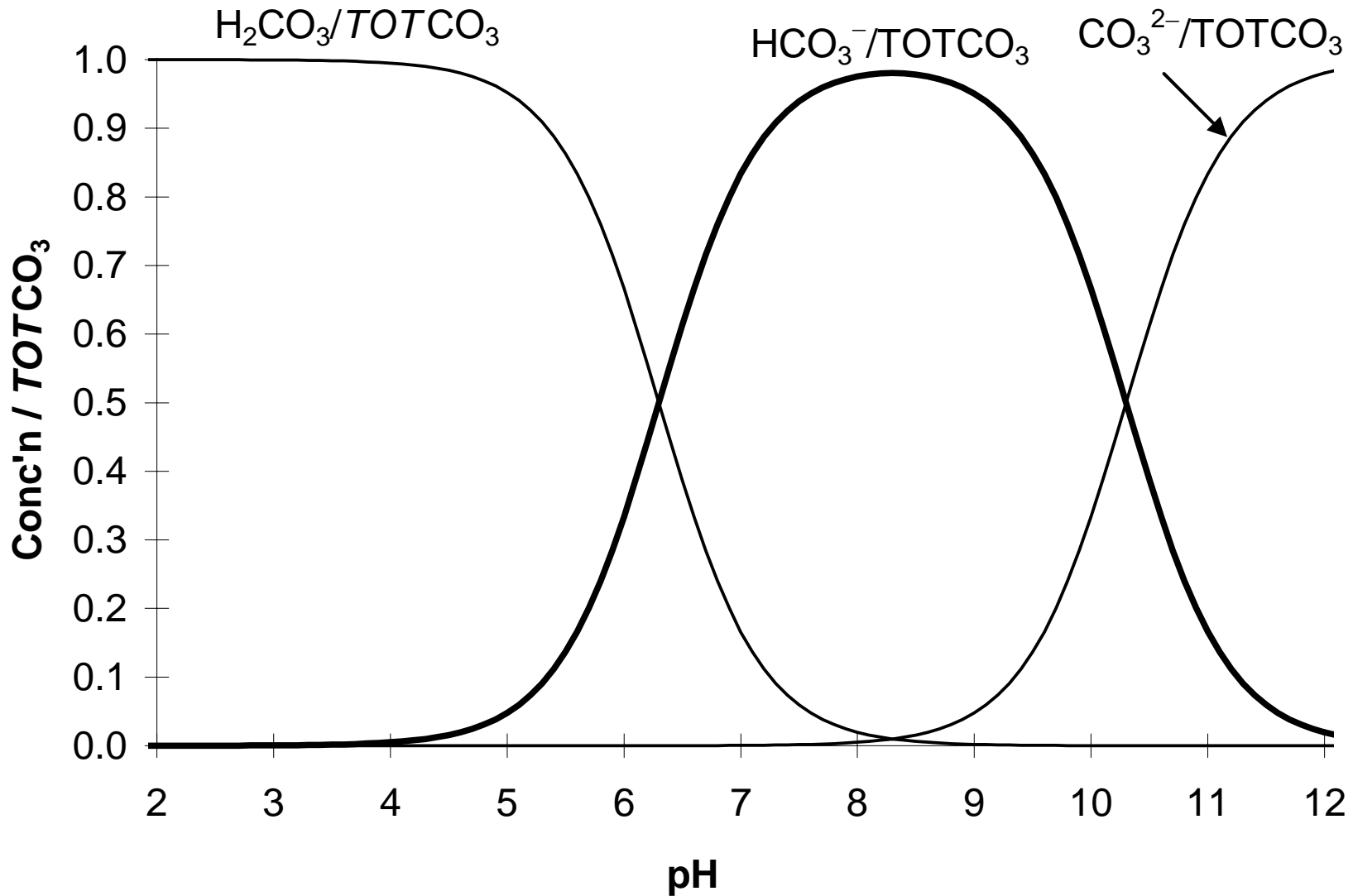
- **Alkalinity: ALK**

$$ALK = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+)$$

Units for Expressing Alkalinity

- **Equivalents: One *equivalent* (equiv) of alkalinity refers to one mole of "H⁺ binding capacity."**
 - one mole of HCO_3^- has the capacity to combine with one mole of H^+ , so one mole of HCO_3^- is one equivalent of alkalinity
 - one mole of CO_3^{2-} has the capacity to combine with two moles of H^+ , so one mole of CO_3^{2-} is two equivalents of alkalinity
- **mg/L as CaCO_3 : The number of mg/L of CaCO_3 that would have to be dissolved into pure water for that water to have the same alkalinity as the water of interest**
 - one mole of CaCO_3 can combine with two moles of H^+ , so one mole of CaCO_3 is two equivalents of alkalinity
 - the MW of CaCO_3 is 100, so 50 g of CaCO_3 is one equivalent. An alkalinity of 75 mg/L as CaCO_3 is therefore identical to 1.5 meq/L

Equilibrium Among Dissolved Carbonate Species



Other Types of Precipitation & Dissolution Problems

- In preceding example (precipitation of $\text{CaSO}_4(\text{s})$), $TOT\text{Ca}$ & $TOT\text{SO}_4$ varied due to solid precipitation, but under all conditions, $TOT\text{Ca}=(\text{Ca}^{2+})$ and $TOT\text{SO}_4=(\text{SO}_4^{2-})$.
- In other commonly encountered systems, the concentration of one or both precipitating ions depends not only on the amount of solid formed, but also other variables (especially pH).

Example: Precipitation & Dissolution of a Hydroxide Solid

- Industrial waste solution, flow rate 150 L/min, pH 2.0, 10^{-2} M Zn^{2+}
- Treatment goal: Reduce conc'n of Zn^{2+} to 0.1 mg/L by precipitating $\text{Zn}(\text{OH})_2(\text{s})$, $K_{s0} = 10^{-13.5}$
- Questions
 - pH to achieve treatment goal?
 - Dose of NaOH required, if the only reactions involving OH^- are formation of water and solids?
 - Production rate (kg/d) of solid?

$$\left(\text{Zn}^{2+}\right)_{fin} = \frac{0.1 \text{ mg/L}}{65,400 \text{ mg/mol}} = 1.53 \times 10^{-6} \frac{\text{mol}}{\text{L}}$$

$$K_{s0} = \frac{\left(\text{Zn}^{2+}\right)_{fin} \left(\text{OH}^{-}\right)_{fin}^2}{\left(\text{Zn}(\text{OH})_2(s)\right)} = \left(\text{Zn}^{2+}\right)_{fin} \left(\text{OH}^{-}\right)_{fin}^2$$

$$\left(\text{OH}^{-}\right)_{fin} = \sqrt{\frac{K_{s0}}{\left(\text{Zn}^{2+}\right)_{fin}}} = \sqrt{\frac{10^{-13.5}}{1.53 \times 10^{-6}}} = 1.44 \times 10^{-4}$$

$$\left(\text{H}^{+}\right)_{fin} = \frac{K_w}{\left(\text{OH}^{-}\right)_{fin}} = \frac{10^{-14.0}}{1.44 \times 10^{-4}} = 6.95 \times 10^{-11}$$

$$\text{pH} = 10.16$$

Dose of NaOH Required

- Reactions
 - $\text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O}$
 - $\text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{Zn}(\text{OH})_2(\text{s})$
- Conc'n changes during treatment
 - (H^+) decreases from 10^{-2} to $10^{-10.16}$; requires 10^{-2} mol/L OH^-
 - (OH^-) increases from 10^{-12} to $10^{-3.84}$; requires $10^{-3.84}$ mol/L OH^-
 - $\text{Zn}(\text{OH})_2(\text{s})$ formation consumes two OH^- per Zn^{2+} ion precipitated; requires 2×10^{-2} mol/L OH^-
- **Total OH^- Req't = 3.01×10^{-2} mol/L OH^-**

Production Rate of $\text{Zn}(\text{OH})_2(s)$

- Conc'n of $\text{Zn}(\text{OH})_2(s)$ precipitated $\approx 10^{-2}$ mol/L
- MW of $\text{Zn}(\text{OH})_2(s)$: $65.4 + 17 \cdot 2 = 99.4$

$$\begin{aligned} &\text{Zn}(\text{OH})_2(s) \text{ formed} \\ &= \left(654 \frac{\text{mg Zn removed}}{\text{L}} \right) \left(\frac{99.4 \text{ mg Zn}(\text{OH})_2(s)}{65.4 \text{ mg Zn}} \right) = 994 \frac{\text{mg Zn}(\text{OH})_2(s)}{\text{L of water}} \end{aligned}$$

Rate of $\text{Zn}(\text{OH})_2(s)$ production

$$\begin{aligned} &= \left(994 \frac{\text{mg Zn}(\text{OH})_2(s)}{\text{L of water}} \right) \left(150 \frac{\text{L}}{\text{min}} \right) \left(1440 \frac{\text{min}}{\text{d}} \right) \left(\frac{1 \text{ kg}}{10^6 \text{ mg}} \right) \\ &= 215 \frac{\text{kg Zn}(\text{OH})_2(s)}{\text{d}} \end{aligned}$$

Example: Precipitation & Dissolution of a Phosphate Solid

- Drinking water at pH 8.0 contains 3.22×10^{-6} mol/L $TOTPO_4$ (0.1 mg/L $TOTPO_4$ -P); Corrosion of galvanized pipe releases Zn^{2+}
- $TOTPO_4$ distributed among four $H_xPO_4^{x-3}$ species:
 - $H_3PO_4 \leftrightarrow H_2PO_4^- + H^+ \quad K_{a1}=10^{-2.2}$
 - $H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+ \quad K_{a2}=10^{-7.2}$
 - $HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+ \quad K_{a3}=10^{-12.4}$
- Question: What is the maximum concentration of Zn^{2+} that can be dissolved in solution, considering possible precipitation of $Zn_3(PO_4)_2(s)$ ($K_{s0}=10^{-36.7}$)

$$K_{a1} = \frac{(\text{H}_2\text{PO}_4^-)(\text{H}^+)}{(\text{H}_3\text{PO}_4)} = 10^{-2.2}$$

$$K_{a2} = \frac{(\text{HPO}_4^{2-})(\text{H}^+)}{(\text{H}_2\text{PO}_4^-)} = 10^{-7.2}$$

$$K_{a3} = \frac{(\text{PO}_4^{3-})(\text{H}^+)}{(\text{HPO}_4^{2-})} = 10^{-12.4}$$

$$K_{a2}K_{a3} = \frac{(\text{PO}_4^{3-})(\text{H}^+)^2}{(\text{H}_2\text{PO}_4^-)} = 10^{-19.6}$$

$$K_{a1}K_{a2}K_{a3} = \frac{(\text{PO}_4^{3-})(\text{H}^+)^3}{(\text{H}_3\text{PO}_4)} = 10^{-21.8}$$

$$\begin{aligned}(\text{HPO}_4^{2-}) &= 10^{12.4} (\text{PO}_4^{3-})(\text{H}^+) \\ &= 10^{4.4} (\text{PO}_4^{3-})\end{aligned}$$

$$\begin{aligned}(\text{H}_2\text{PO}_4^-) &= 10^{19.6} (\text{PO}_4^{3-})(\text{H}^+)^2 \\ &= 10^{3.6} (\text{PO}_4^{3-})\end{aligned}$$

$$\begin{aligned}(\text{H}_3\text{PO}_4) &= 10^{21.8} (\text{PO}_4^{3-})(\text{H}^+)^3 \\ &= 10^{-2.2} (\text{PO}_4^{3-})\end{aligned}$$

$$\begin{aligned}
TOTPO_4 &= (H_3PO_4) + (H_2PO_4^-) + (HPO_4^{2-}) + (PO_4^{3-}) \\
&= 10^{-2.2} (PO_4^{3-}) + 10^{3.6} (PO_4^{3-}) + 10^{4.4} (PO_4^{3-}) + (PO_4^{3-}) \\
&= 2.91 \times 10^4 (PO_4^{3-})
\end{aligned}$$

$$(PO_4^{3-}) = \frac{3.22 \times 10^{-6}}{2.91 \times 10^4} = 1.11 \times 10^{-10}$$

$$(Zn^{2+}) = \left[\frac{K_{s0}}{(PO_4^{3-})^2} \right]^{1/3} = \left[\frac{10^{-36.7}}{(1.11 \times 10^{-10})^2} \right]^{1/3} = 2.56 \times 10^{-6}$$

Example: Water Softening

- Drinking water at pH 7.0 contains 3×10^{-3} mol/L Ca^{2+} (120 mg/L), and 1.0×10^{-3} Alk; K_{s0} for $\text{CaCO}_3(\text{s})$ is $10^{-8.3}$
- Questions
 - Is the solution supersaturated, undersaturated, or at equilibrium with respect to $\text{CaCO}_3(\text{s})$?
 - What is the stoichiometric dose of lime ($\text{Ca}(\text{OH})_2$) required to convert H_2CO_3 and HCO_3^- to CO_3^{2-} ?
 - If TOTCO_3 is essentially all converted to CO_3^{2-} , will $\text{CaCO}_3(\text{s})$ precipitate? If so, how much, and what will the final concentration of Ca^{2+} be?

Determine $TOTCO_3$ and Distribution of Carbonate Species

$$ALK = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+)$$

$$1.0 \times 10^{-3} = (\text{HCO}_3^-) + 2 \frac{(\text{HCO}_3^-) K_{a2}}{(\text{H}^+)} + \frac{K_w}{(\text{H}^+)} - (\text{H}^+)$$

$$1.0 \times 10^{-3} = (\text{HCO}_3^-) + 2 \frac{(\text{HCO}_3^-) 10^{-10.3}}{10^{-7.0}} + \frac{10^{-14.0}}{10^{-7.0}} - 10^{-7.0}$$

$$1.0 \times 10^{-3} = 1.001 (\text{HCO}_3^-)$$

$$(\text{HCO}_3^-) = \frac{1.0 \times 10^{-3}}{1.001} \approx 1.0 \times 10^{-3}$$

Determine $TOTCO_3$ and Distribution of Carbonate Species

$$(\text{CO}_3^{2-}) = \frac{(\text{HCO}_3^-)K_{a2}}{(\text{H}^+)} = \frac{10^{-3.0}10^{-10.3}}{10^{-7.0}} = 10^{-6.3}$$

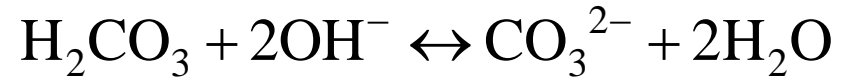
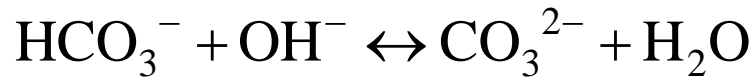
$$(\text{H}_2\text{CO}_3) = \frac{(\text{HCO}_3^-)(\text{H}^+)}{K_{a1}} = \frac{10^{-3.0}10^{-7.0}}{10^{-6.3}} = 10^{-3.7} = 2 \times 10^{-4}$$

$$\begin{aligned}TOTCO_3 &= (\text{H}_2\text{CO}_3) + (\text{HCO}_3^-) + (\text{CO}_3^{2-}) \\ &= 2.0 \times 10^{-4} + 1.0 \times 10^{-3} + 5 \times 10^{-7} = 1.2 \times 10^{-3}\end{aligned}$$

$$(\text{Ca}^{2+})(\text{CO}_3^{2-}) = (3 \times 10^{-3})(10^{-6.3}) = 10^{-8.8} < K_{s0}$$

Thus, $\text{CaCO}_3(\text{s})$ is undersaturated in the initial solution

Determine Stoichiometric Dose of Lime



$$\left(\begin{array}{l} \text{Moles of OH}^- \text{ required to} \\ \text{cause } (\text{CO}_3^{2-}) \approx \text{TOTCO}_3 \end{array} \right) = 2(\text{H}_2\text{CO}_3) + (\text{HCO}_3^-)$$

$$\left(\begin{array}{l} \text{Moles of lime required to} \\ \text{cause } (\text{CO}_3^{2-}) \approx \text{TOTCO}_3 \end{array} \right) = \frac{1}{2} \left(\begin{array}{l} \text{Moles of OH}^- \text{ required to} \\ \text{cause } (\text{CO}_3^{2-}) \approx \text{TOTCO}_3 \end{array} \right)$$

$$\left(\begin{array}{l} \text{Lime required to cause} \\ (\text{CO}_3^{2-}) \approx \text{TOTCO}_3 \end{array} \right) = (\text{H}_2\text{CO}_3) + \frac{1}{2}(\text{HCO}_3^-) = 2.0 \times 10^{-4} + \frac{1}{2}(1.0 \times 10^{-3}) = 7.0 \times 10^{-4}$$

After Dosing with Lime, the Solution is Supersaturated

$$TOTCO_3 = 1.2 \times 10^{-3} \approx (CO_3^{2-})$$

$$(Ca^{2+}) = (Ca^{2+})_{init} + (Ca^{2+})_{lime} = 3.0 \times 10^{-3} + 7.0 \times 10^{-4} = 3.7 \times 10^{-3}$$

$$(Ca^{2+})(CO_3^{2-}) = (3.7 \times 10^{-3})(1.2 \times 10^{-3}) = 4.44 \times 10^{-6} = 10^{-5.35} > K_{s0}$$

Determine How Much Solid Will Precipitate

If x is the amount (moles/L) of $\text{CaCO}_3(\text{s})$ that precipitates, the concentrations of TOTCa and TOTCO_3 in solution will each decrease by x . If $(\text{CO}_3^{2-}) \approx \text{TOTCO}_3$ after precipitation (i.e., if the pH is $>\approx 10.8$), then x is also the decrease in (CO_3^{2-}) . In such a case, we can write:

$$K_{s0} = (\text{Ca}^{2+})_{\text{equil}} (\text{CO}_3^{2-})_{\text{equil}} = [(\text{Ca}^{2+})_{\text{init}} - x][(\text{CO}_3^{2-})_{\text{init}} - x]$$

$$10^{-8.3} = (3.7 \times 10^{-3} - x)(1.2 \times 10^{-3} - x)$$

$$x = 1.198 \times 10^{-3}$$

Precipitation removes 99.8% of TOTCO_3 but only 17% of TOTCa .

Determine How Much Soda Ash to Add

To remove more Ca^{2+} , we must add more TOTCO_3 . A frequently cited, but somewhat outdated rule of thumb is to add Na_2CO_3 to make $\text{TOTCa} = \text{TOTCO}_3$. If that is done:

$$\begin{aligned}(\text{Na}_2\text{CO}_3)_{\text{dose}} &= \text{TOTCa} - \text{TOTCO}_{3,\text{init}} = \\ &= 3.7 \times 10^{-3} - 1.2 \times 10^{-3} = 2.5 \times 10^{-3}\end{aligned}$$

Then, when the solution equilibrates with the solid:

$$\begin{aligned}(\text{Ca}^{2+})(\text{CO}_3^{2-}) &= (\text{Ca}^{2+})^2 = 10^{-8.3} \\ (\text{Ca}^{2+}) &= \sqrt{10^{-8.3}} = 10^{-4.15} = 7.1 \times 10^{-5} = 2.8 \text{ mg/L}\end{aligned}$$

This Ca^{2+} concentration is very low. Since Na_2CO_3 is expensive, the actual dose is usually less than the dose based on the rule of thumb.

Calcium Carbonate Precipitation as a Corrosion Inhibitor

Water quality is sometimes adjusted so that CaCO_3 is slightly supersaturated in the water leaving the WTP. Ideally, a thin layer of the solid forms and coats the pipes, limiting access of the corrosive water to the pipe surface. However, if this process is not controlled carefully, the CaCO_3 layer can get so thick that it impedes flow.

(See picture from Opflow 2003-09 corrosion scales headloss.pdf)