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:

$$aA + bB \leftrightarrow cC + dD$$

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

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, $K_{eq}$

$$aA + bB \leftrightarrow cC + dD$$

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

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, $K_w$

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

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

\[ \text{pH} = -\log_{10}(\text{H}^+) \]
Some Important Equilibria in Water Treatment Involving Solids

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

\[ XY_2Z(s) \leftrightarrow X + 2Y + Z \]

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

- “Solubility product” \((K_{sp} \text{ or } K_{so})\) is \(K_{eq}\) for dissolution of the solid into its constituents
- The solid (and sometimes H\(_2\)O) are the only chemicals on the left side
Some Solids are Very Soluble or Very Insoluble

- Some solids (e.g., NaCl, CaCl$_2$, Na$_2$SO$_4$) 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)$_3$, MnO$_2$) are so insoluble under normal water treatment conditions that we assume 100% of the metal precipitates.

- Some solids (CaCO$_3$) are “slightly soluble” under normal water treatment conditions, so neither assumption applies. Others (PbCO$_3$, AlPO$_4$) are very insoluble, but the trace amount that dissolves is still of concern.
Issues that Arise Regarding Slightly Soluble Solids in Water Treatment

• Is $Q_{so}$ greater than, less than, or equal to $K_{so}$ initially?

• How much does the concentration of some constituent have to change to cause $Q_{so}$ to equal or exceed $K_{so}$ (i.e., for precipitation to begin)?

• How much of some chemical must be added to cause $Q_{so}$ to equal or exceed $K_{so}$?

• 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 (CaSO$_4$(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 \( \text{CaSO}_4(s) \)

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

\[
\left(\text{Ca}^{2+}\right) = \left(\text{SO}_4^{2-}\right)
\]

\[
10^{-4.6} = \left(\text{Ca}^{2+}\right)^2
\]

\[
\left(\text{Ca}^{2+}\right) = \left(10^{-4.6}\right)^{0.5} = 10^{-2.3} = 5.0 \times 10^{-3} = \left(\text{SO}_4^{2-}\right)
\]
Example: Dissolution of CaSO$_4$(s)

\[
(Ca^{2+}) = \left(10^{-2.3} \, \text{mol/L}\right) \left(40 \, \text{g/mol}\right) = 0.20 \, \text{g/L}
\]

\[
(SO_4^{2-}) = \left(10^{-2.3} \, \text{mol/L}\right) \left(96 \, \text{g/mol}\right) = 0.48 \, \text{g/L}
\]

CaSO$_4$(s) dissolved = 0.68 g/L

CaSO4(s) remaining undissolved = 0.32 g/L (32%)
Dissolution of CaSO$_4$(s) with (SO$_4^{2−}$)$_{\text{init}} > 0$

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

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

\[
x = 4.08 \times 10^{-3}
\]
Dissolution of CaSO$_4$(s) with (SO$_4^{2-}$)$_{\text{init}}>0$

\[
\begin{align*}
(Ca^{2+})_{\text{final}} &= x = 4.08 \times 10^{-3} \text{ mol} \left( \frac{40,000 \text{ mg}}{\text{mol}} \right) = 163 \text{ mg/L} \\
(SO_4^{2-})_{\text{final}} &= (x + 2.08 \times 10^{-3}) \text{ mol} \left( \frac{6.16 \times 10^{-3} \text{ mol}}{\text{L}} \right) \left( \frac{96,000 \text{ mg}}{\text{mol}} \right) = 591 \text{ mg/L}
\end{align*}
\]

CaSO$_4$(s) dissolved = 163 mg/L + (591 – 200)mg/L = 554 mg/L
CaSO$_4$(s) remaining undissolved = 446 mg/L (44.6%)
The Carbonate Chemical Group in Water

- **Dissolved Carbonate-containing species**
  - **Carbonic Acid: H\(_2\)CO\(_3\)**. Can form by combination of a carbon dioxide molecule and water:
    \[
    \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3
    \]
    \[
    K_{eq} = \frac{(\text{H}_2\text{CO}_3)}{(\text{CO}_2(\text{g}))} \frac{1}{(\text{H}_2\text{O})}
    \]
  - **Bicarbonate Ion: HCO\(_3^-\)**. Can form by “dissociation” of carbonic acid:
    \[
    \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+
    \]
    \[
    K_{eq} = \frac{(\text{HCO}_3^-)(\text{H}^+)}{(\text{H}_2\text{CO}_3)} \equiv K_{a1}
    \]
The Carbonate Chemical Group

• Dissolved Carbonate-containing species
  – **Carbonate Ion**: $\text{CO}_3^{2-}$. Can form by dissociation of bicarbonate ion:

  \[ \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]

  \[ K_{eq} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \equiv K_{a2} \]

• Other Commonly Defined Quantities
  – **Total Dissolved Carbonate**: $\text{TOTCO}_3$

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

  – **Alkalinity**: $\text{ALK}$

    \[ \text{ALK} = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+) \]
Units for Expressing Alkalinity

• **Equivalents:** One *equivalent* (equiv) of alkalinity refers to one mole of "H⁺ binding capacity."
  
  – one mole of HCO₃⁻ has the capacity to combine with one mole of H⁺, so one mole of HCO₃⁻ is one equivalent of alkalinity
  – one mole of CO₃²⁻ has the capacity to combine with two moles of H⁺, so one mole of CO₃²⁻ is two equivalents of alkalinity

• **mg/L as CaCO₃:** The number of mg/L of CaCO₃ 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 CaCO₃ can combine with two moles of H⁺, so one mole of CaCO₃ is two equivalents of alkalinity
  – the MW of CaCO₃ is 100, so 50 g of CaCO₃ is one equivalent. An alkalinity of 75 mg/L as CaCO₃ is therefore identical to 1.5 meq/L
Equilibrium Among Dissolved Carbonate Species

The graph shows the distribution of carbonate species with pH. The x-axis represents pH ranging from 2 to 12, and the y-axis represents the concentration of each species relative to the total carbonate concentration (Conc'n / TOTCO₃).

Key species concentrations are:
- $\text{H}_2\text{CO}_3 / \text{TOTCO}_3$
- $\text{HCO}_3^- / \text{TOTCO}_3$
- $\text{CO}_3^{2-} / \text{TOTCO}_3$

The graph indicates that $\text{H}_2\text{CO}_3$ and $\text{CO}_3^{2-}$ peaks at low pH values, while $\text{HCO}_3^-$ dominates at pH around 8.
Other Types of Precipitation & Dissolution Problems

• In preceding example (precipitation of CaSO$_4$(s)), $\text{TOTCa} \& \text{TOTS}\text{SO}_4$ varied due to solid precipitation, but under all conditions, $\text{TOTCa}=(\text{Ca}^{2+})$ and $\text{TOTS}\text{SO}_4=(\text{SO}_4^{2-}).$

• 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 Zn(OH)$_2$(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?
\[
(Zn^{2+})_{\text{fin}} = \frac{0.1 \text{ mg/L}}{65,400 \text{ mg/mol}} = 1.53 \times 10^{-6} \text{ mol/L}
\]

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

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

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

\[\text{pH} = 10.16\]
Dose of NaOH Required

- **Reactions**
  - \[ \text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O} \]
  - \[ \text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{Zn(OH)}_2(\text{s}) \]

- **Conc’n changes during treatment**
  - \( (\text{H}^+) \) decreases from \( 10^{-2} \) to \( 10^{-10.16} \); requires \( 10^{-2} \) mol/L OH\(^-\)
  - \( (\text{OH}^-) \) increases from \( 10^{-12} \) to \( 10^{-3.84} \); requires \( 10^{-3.84} \) mol/L OH\(^-\)
  - \( \text{Zn(OH)}_2(\text{s}) \) formation consumes two OH\(^-\) per \( \text{Zn}^{2+} \) ion precipitated; requires \( 2 \times 10^{-2} \) mol/L OH\(^-\)

- **Total OH\(^-\) Req’t = 3.01 \times 10^{-2} \) mol/L OH\(^-\)**
Production Rate of Zn(OH)$_2$(s)

- Conc’n of Zn(OH)$_2$(s) precipitated $\approx 10^{-2}$ mol/L
- MW of Zn(OH)$_2$(s): $65.4 + 17\times2 = 99.4$

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

Rate of Zn(OH)$_2$(s) production

\[
= \left(994 \frac{\text{mg Zn(OH)$_2$(s)}}{\text{L of water}}\right) \left(150 \frac{\text{L}}{\text{min}}\right) \left(1440 \frac{\text{min}}{\text{d}}\right) \left(\frac{1 \text{ kg}}{10^6 \text{ mg}}\right) = 215 \frac{\text{kg Zn(OH)$_2$(s)}}{\text{d}}
\]
Example: Precipitation & Dissolution of a Phosphate Solid

- Drinking water at pH 8.0 contains $3.22 \times 10^{-6}$ 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:
  - $H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$, $K_{a1}=10^{-2.2}$
  - $H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$, $K_{a2}=10^{-7.2}$
  - $HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$, $K_{a3}=10^{-12.4}$

- Question: What is the maximum concentration of Zn$^{2+}$ that can be dissolved in solution, considering possible precipitation of $Zn_3(PO_4)_2(s)$ ($K_{s0}=10^{-36.7}$)
\[ K_{a1} = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} = 10^{-2.2} \]

\[ K_{a2} = \frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]} = 10^{-7.2} \]

\[ K_{a3} = \frac{[PO_4^{3-}][H^+]}{[HPO_4^{2-}]} = 10^{-12.4} \]

\[ K_{a2}K_{a3} = \frac{[PO_4^{3-}][H^+]^2}{[H_2PO_4^-]} = 10^{-19.6} \]

\[ K_{a1}K_{a2}K_{a3} = \frac{[PO_4^{3-}][H^+]^3}{[H_3PO_4]} = 10^{-21.8} \]

\[ [HPO_4^{2-}] = 10^{12.4} [PO_4^{3-}][H^+] = 10^{4.4} [PO_4^{3-}] \]

\[ [H_2PO_4^-] = 10^{19.6} [PO_4^{3-}][H^+]^2 = 10^{3.6} [PO_4^{3-}] \]

\[ [H_3PO_4] = 10^{21.8} [PO_4^{3-}][H^+]^3 = 10^{-2.2} [PO_4^{3-}] \]
\[ TO \text{TPO}_4 = (H_3\text{PO}_4) + (H_2\text{PO}_4^-) + (\text{HPO}_4^{2-}) + (\text{PO}_4^{3-}) \]
\[ = 10^{-2.2} (\text{PO}_4^{3-}) + 10^{3.6} (\text{PO}_4^{3-}) + 10^{4.4} (\text{PO}_4^{3-}) + (\text{PO}_4^{3-}) \]
\[ = 2.91 \times 10^4 (\text{PO}_4^{3-}) \]

\[ (\text{PO}_4^{3-}) = \frac{3.22 \times 10^{-6}}{2.91 \times 10^4} = 1.11 \times 10^{-10} \]

\[ (\text{Zn}^{2+}) = \left[ \frac{K_{s0}}{\left(\text{PO}_4^{3-}\right)^2} \right]^{1/3} = \left[ \frac{10^{-36.7}}{(1.11 \times 10^{-10})^2} \right]^{1/3} = 2.56 \times 10^{-6} \]
Example: Water Softening

• Drinking water at pH 7.0 contains $3 \times 10^{-3}$ mol/L Ca$^{2+}$ (120 mg/L), and $1.0 \times 10^{-3}$ Alk; $K_{s0}$ for CaCO$_3$(s) is $10^{-8.3}$

• Questions
  – Is the solution supersaturated, undersaturated, or at equilibrium with respect to CaCO$_3$(s)?
  – What is the stoichiometric dose of lime (Ca(OH)$_2$) required to convert H$_2$CO$_3$ and HCO$_3^-$ to CO$_3^{2-}$?
  – If TOTCO$_3$ is essentially all converted to CO$_3^{2-}$, will CaCO$_3$(s) precipitate? If so, how much, and what will the final concentration of Ca$^{2+}$ be?
Determine $TOTCO_3$ and Distribution of Carbonate Species

\[
ALK = \left( HCO_3^- \right) + 2 \left( CO_3^{2-} \right) + \left( OH^- \right) - \left( H^+ \right)
\]

\[
1.0 \times 10^{-3} = \left( HCO_3^- \right) + 2 \frac{\left( HCO_3^- \right) K_{a2}}{\left( H^+ \right)} + \frac{K_w}{\left( H^+ \right)} - \left( H^+ \right)
\]

\[
1.0 \times 10^{-3} = \left( HCO_3^- \right) + 2 \frac{\left( HCO_3^- \right) 10^{-10.3}}{10^{-7.0}} + \frac{10^{-14.0}}{10^{-7.0}} - 10^{-7.0}
\]

\[
1.0 \times 10^{-3} = 1.001 \left( HCO_3^- \right)
\]

\[
\left( HCO_3^- \right) = \frac{1.0 \times 10^{-3}}{1.001} \approx 1.0 \times 10^{-3}
\]
Determine $\text{TOTCO}_3$ and Distribution of Carbonate Species

\[
\left(\text{CO}_3^-\right) = \frac{\left(\text{HCO}_3^-\right) K_{a2}}{\left(\text{H}^+\right)} = \frac{10^{-3.0} \times 10^{-10.3}}{10^{-7.0}} = 10^{-6.3}
\]

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

\[
\text{TOTCO}_3 = \left(\text{H}_2\text{CO}_3\right) + \left(\text{HCO}_3^-\right) + \left(\text{CO}_3^{2-}\right)
\]

\[
= 2.0 \times 10^{-4} + 1.0 \times 10^{-3} + 5 \times 10^{-7} = 1.2 \times 10^{-3}
\]

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

Thus, CaCO$_3$(s) is undersaturated in the initial solution.
Determine Stoichiometric Dose of Lime

\[
\text{HCO}_3^- + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad \text{H}_2\text{CO}_3 + 2\text{OH}^- \leftrightarrow \text{CO}_3^{2-} + 2\text{H}_2\text{O}
\]

\[
\left(\text{Moles of OH}^- \text{ required to cause } \left(\text{CO}_3^{2-}\right) \approx \text{TOTCO}_3\right) = 2\left(\text{H}_2\text{CO}_3\right) + \left(\text{HCO}_3^-\right)
\]

\[
\left(\text{Moles of lime required to cause } \left(\text{CO}_3^{2-}\right) \approx \text{TOTCO}_3\right) = \frac{1}{2} \left(\text{Moles of OH}^- \text{ required to cause } \left(\text{CO}_3^{2-}\right) \approx \text{TOTCO}_3\right)
\]

\[
\left(\text{Lime required to cause } \left(\text{CO}_3^{2-}\right) \approx \text{TOTCO}_3\right) = \left(\text{H}_2\text{CO}_3\right) + \frac{1}{2} \left(\text{HCO}_3^-\right) = 2.0 \times 10^{-4} + \frac{1}{2} \left(1.0 \times 10^{-3}\right) = 7.0 \times 10^{-4}
\]
After Dosing with Lime, the Solution is Supersaturated

\[ TOT \text{CO}_3 = 1.2 \times 10^{-3} \approx \left( \text{CO}_3^{2-} \right) \]

\[
\left( \text{Ca}^{2+} \right) = \left( \text{Ca}^{2+} \right)_{\text{init}} + \left( \text{Ca}^{2+} \right)_{\text{lime}} = 3.0 \times 10^{-3} + 7.0 \times 10^{-4} = 3.7 \times 10^{-3}
\]

\[
\left( \text{Ca}^{2+} \right) \left( \text{CO}_3^{2-} \right) = \left(3.7 \times 10^{-3}\right) \left(1.2 \times 10^{-3}\right) = 4.44 \times 10^{-6} = 10^{-5.35} > K_{s0}
\]
Determine How Much Solid Will Precipitate

If \( x \) is the amount (moles/L) of \( \text{CaCO}_3(s) \) that precipitates, the concentrations of \( \text{TOTCa} \) and \( \text{TOTCO}_3 \) in solution will each decrease by \( x \). If \( (\text{CO}_3^{2-}) \approx \text{TOTCO}_3 \) after precipitation (i.e., if the pH is \( >\approx10.8 \)), then \( x \) is also the decrease in \( (\text{CO}_3^{2-}) \). In such a case, we can write:

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

\[
10^{-8.3} = \left( 3.7 \times 10^{-3} - x \right) \left( 1.2 \times 10^{-3} - x \right)
\]

\[
x = 1.198 \times 10^{-3}
\]

Precipitation removes 99.8% of \( \text{TOTCO}_3 \) but only 17% of \( \text{TOTCa} \).
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$_2$CO$_3$ to make $TOTCa=TOTCO_3$. If that is done:

\[
(\text{Na}_2\text{CO}_3)_{dose} = TOTCa - TOTCO_3,\text{init} = \\
= 3.7 \times 10^{-3} - 1.2 \times 10^{-3} = 2.5 \times 10^{-3}
\]

Then, when the solution equilibrates with the solid:

\[
\left(\text{Ca}^{2+}\right)\left(\text{CO}_3^{2-}\right) = \left(\text{Ca}^{2+}\right)^2 = 10^{-8.3}
\]

\[
\left(\text{Ca}^{2+}\right) = \sqrt{10^{-8.3}} = 10^{-4.15} = 7.1 \times 10^{-5} = 2.8 \text{ mg/L}
\]

This Ca$^{2+}$ concentration is very low. Since Na$_2$CO$_3$ 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 CaCO₃ 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 CaCO₃ layer can get so thick that it impedes flow.

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