

Inducing or Preventing Precipitation

Example. A solution at pH 8.1 contains 2 meq/L Alk, 0.2 mmol/L TOTPO₄, and negligible Ca²⁺. The Alk is all from PO₄ and CO₃ species. Lime will be added to remove 95% of TOTPO₄.

(a) Draw a log c – pH diagram showing Ca²⁺ activity in equilibrium with each of two solids: CaCO₃(s) and Ca₅OH(PO₄)₃(s), for the initial TOTCO₃ and TOTPO₄.

(b) Which solid will precipitate first? At what pH?

(c) Add a line showing activity of Ca²⁺ in equilibrium with the solution once the TOTPO₄ target has been reached. How much lime must be added to reach this condition, and what is the solution composition?

(d) What happens as even more lime is added?

A solution at pH 8.1 contains 2 meq/L Alk, 0.2 mmol/L TOTPO₄, and negligible Ca²⁺. Alk is from PO₄ and CO₃ species. Lime will be added to remove 95% of TOTPO₄.

Preliminary step: Determine TOTCO₃

At pH 8.1, almost all PO₄ is present as HPO₄²⁻. At pH 4.5, almost all is present as H₂PO₄⁻. Therefore, TOTPO₄ contributes 1 equiv Alk per mol, or 0.2 meq/L in this solution. Alk due to CO₃ is therefore 1.8 meq/L, and, since TOTCO₃ ≈ [HCO₃⁻], TOTCO₃ is ~1.8x10⁻³ mol/L

For $\text{CaCO}_3(\text{s})$:

$$\{\text{Ca}^{2+}\} = \frac{K_{s0}}{\{\text{CO}_3^{2-}\}}$$

$$\log \{\text{Ca}^{2+}\} = \log K_{s0} - \log \{\text{CO}_3^{2-}\}$$

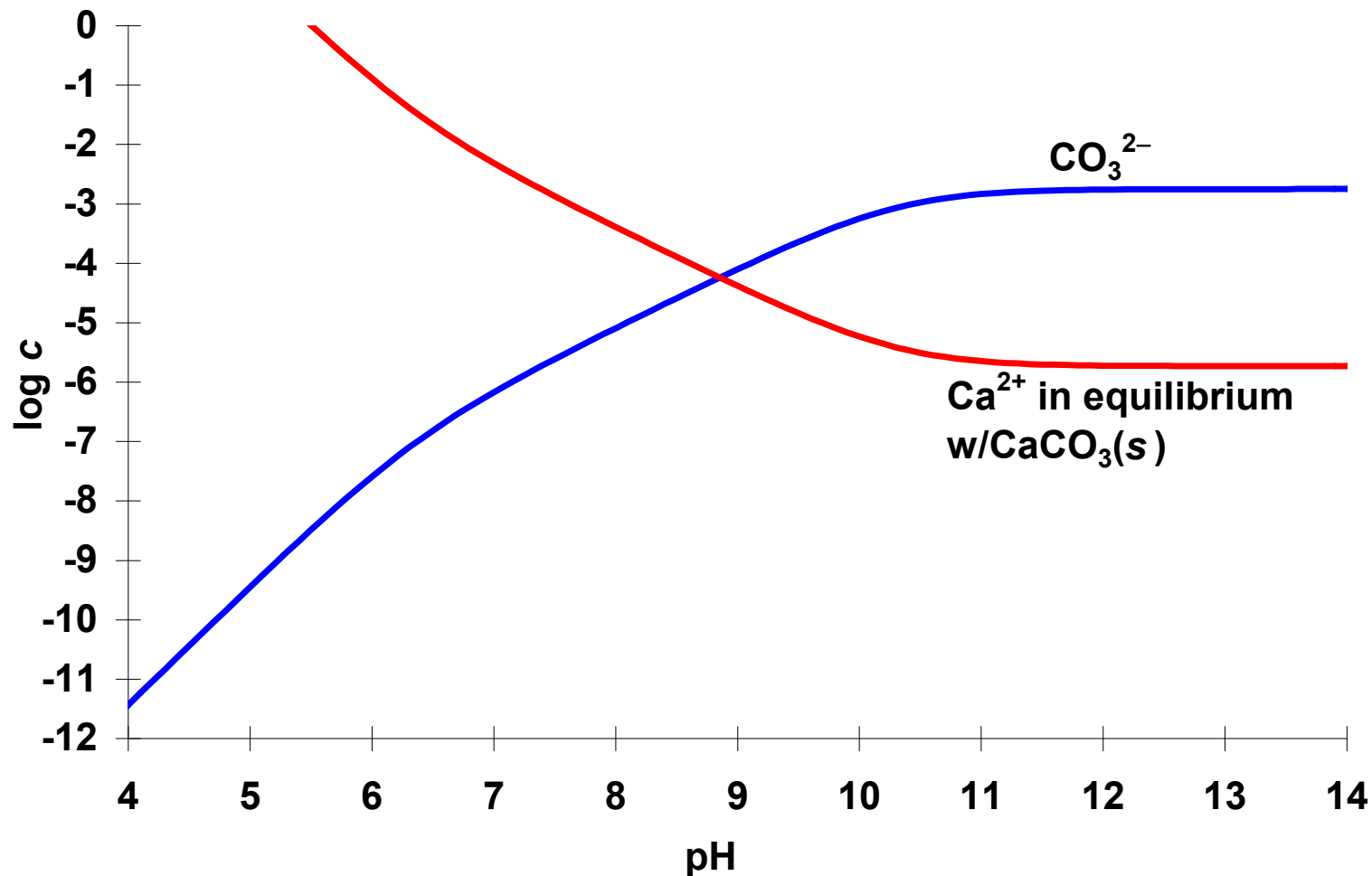
**For
 $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{s})$:**

$$\{\text{Ca}^{2+}\} = \left(\frac{K_{s0}}{\{\text{OH}^-\} \{\text{PO}_4^{3-}\}^3} \right)^{1/5}$$

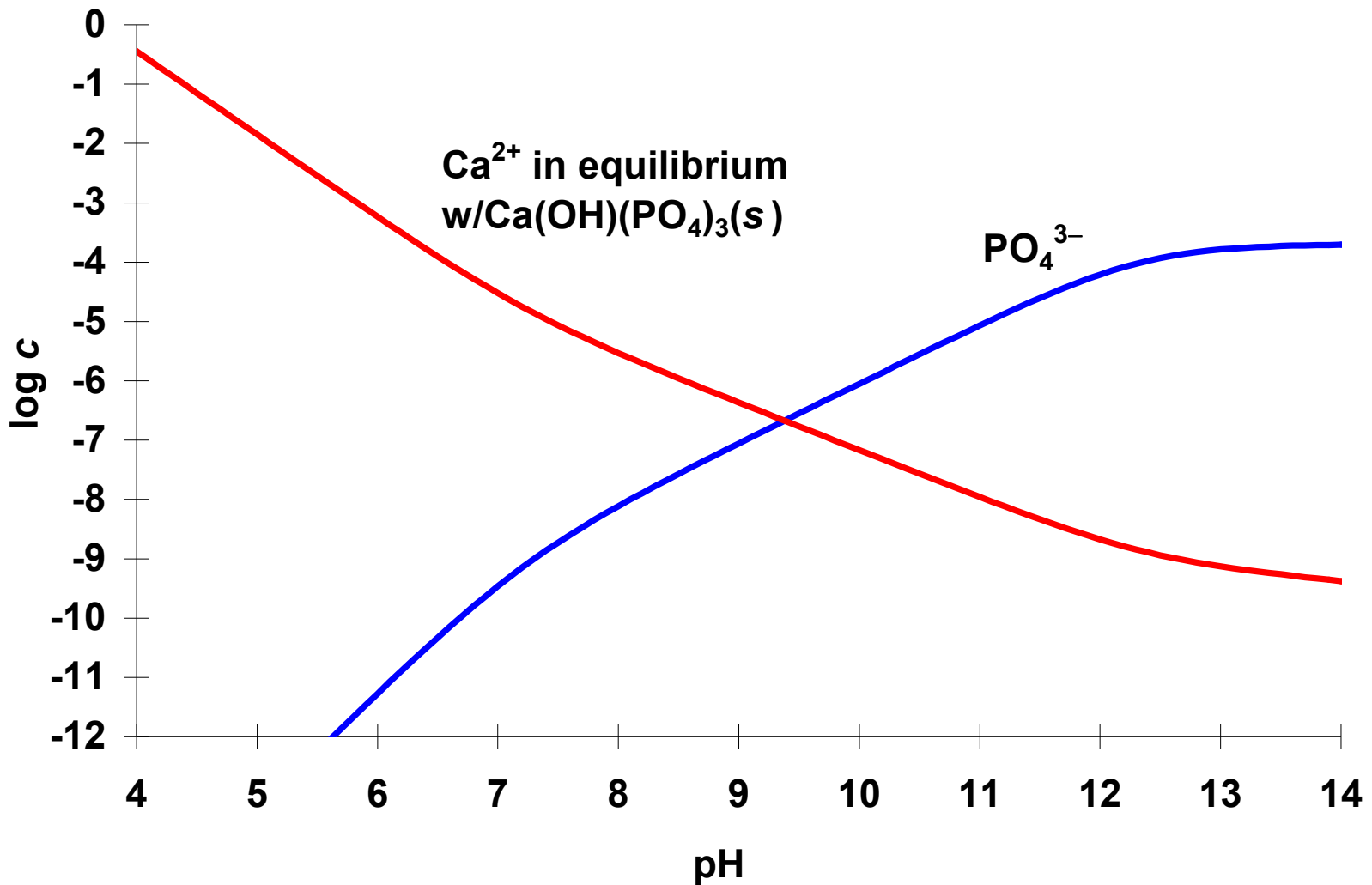
$$\log \{\text{Ca}^{2+}\} = \frac{1}{5} \left(\log K_{s0} - \log \{\text{OH}^-\} - 3 \log \{\text{PO}_4^{3-}\} \right)$$

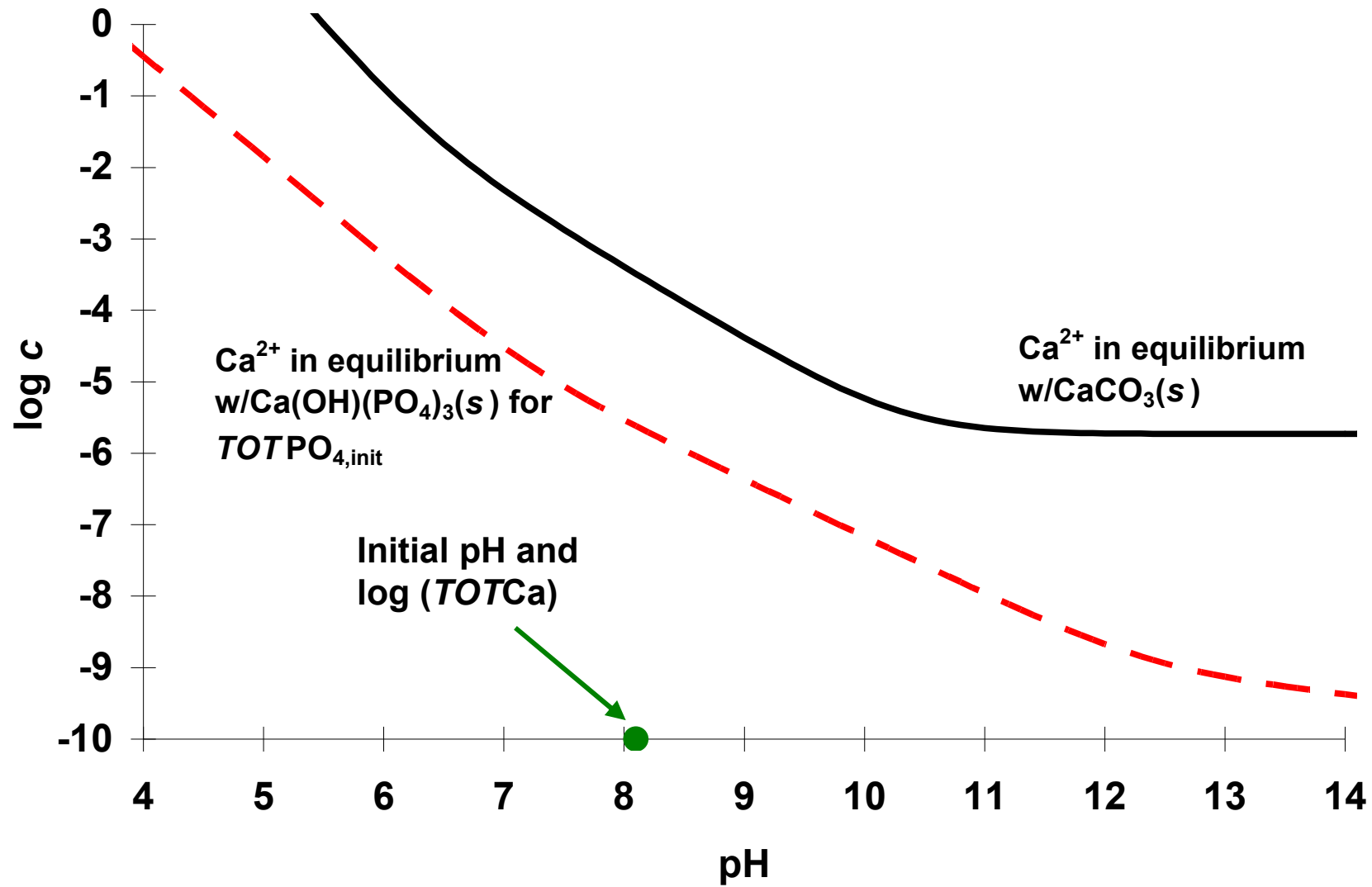
(a) Draw a $\log c - \text{pH}$ diagram showing Ca^{2+} activity in equilibrium with $\text{CaCO}_3(\text{s})$ or $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{s})$, for the initial TOTCO_3 and TOTPO_4 .

$$\log \left\{ \text{Ca}^{2+} \right\} = \log K_{s0} - \log \left\{ \text{CO}_3^{2-} \right\}$$



$$\log \{ \text{Ca}^{2+} \} = \frac{1}{5} \left(\log K_{s0} - \log \{ \text{OH}^- \} - 3 \log \{ \text{PO}_4^{3-} \} \right)$$





(b) Which solid will precipitate first? At what pH?

At any pH, the Ca^{2+} concentration required for $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{s})$ precipitation is less than that for $\text{CaCO}_3(\text{s})$ precipitation, so $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{s})$ will precipitate first.

To find trajectories of pH and (Ca^{2+}) as a function of lime added, develop a titration curve showing pH vs. lime dose, assuming that no solid precipitates. Then check results against K_{s0} for $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{s})$ to see if the assumption applies. Lowest lime dose where the assumption fails indicates the condition of initial precipitation.

Tableau showing species present at equilibrium ($TOTH_{eq}$), assuming no precipitation

	H_2O	H^+	CO_3^{2-}	PO_4^{3-}	Ca^{2+}
H_2O	1	0	0	0	0
H^+	0	1	0	0	0
CO_3^{2-}	0	0	1	0	0
PO_4^{3-}	0	0	0	1	0
Ca^{2+}	0	0	0	0	1
OH^-	1	-1	0	0	0
HCO_3^-	0	1	1	0	0
H_2CO_3	1	2	1	0	0
HPO_4^{2-}	2	1	0	1	0
$H_2PO_4^-$	3	2	0	1	0
H_3PO_4	4	3	0	1	0

$$\begin{aligned}
 TOTH_{eq} = & \left[H^+ \right]_{eq} - \left[OH^- \right]_{eq} + 2 \left[H_2CO_3 \right]_{eq} + \left[HCO_3^- \right]_{eq} \\
 & + 3 \left[H_3PO_4 \right]_{eq} + 2 \left[H_2PO_4^{2-} \right]_{eq} + \left[HPO_4^{2-} \right]_{eq}
 \end{aligned}$$

All terms contributing to $TOTH_{eq}$ can be expressed as known values or values that depend only on pH_{eq} :

$$TOTH_{eq} = [H^+]_{eq} - [OH^-]_{eq} + 2[H_2CO_3]_{eq} + [HCO_3^-]_{eq} \\ + 3[H_3PO_4]_{eq} + 2[H_2PO_4^{2-}]_{eq} + [HPO_4^{2-}]_{eq}$$

$$TOTH_{eq} = [H^+]_{eq} - \frac{K_w}{[H^+]_{eq}} + (2\alpha_{0,CO_3} + \alpha_{1,CO_3})[TOTCO_3] \\ + (3\alpha_{0,PO_4} + 2\alpha_{1,PO_4} + \alpha_{2,PO_4})[TOTPO_4]$$

TOTH_{in} for a given lime dose equals TOTH of the constituents present initially (before any lime addition, when pH = 8.1), plus TOTH added with the lime. So, the 'input' portion of the tableau is as follows, where all α values are computed at pH 8.1

	H ₂ O	H ⁺	CO ₃ ²⁻	PO ₄ ³⁻	Ca ²⁺	c_{in}
H ⁺	0	1	0	0	0	10 ^{-8.1}
CO ₃ ²⁻	0	0	1	0	0	$\alpha_{2,CO_3}TOTCO_3$
PO ₄ ³⁻	0	0	0	1	0	$\alpha_{3,PO_4}TOTPO_4$
OH ⁻	1	-1	0	0	0	10 ^{-5.9}
HCO ₃ ⁻	0	1	1	0	0	$\alpha_{1,CO_3}TOTCO_3$
H ₂ CO ₃	0	2	1	0	0	$\alpha_{0,CO_3}TOTCO_3$
HPO ₄ ²⁻	0	1	0	1	0	$\alpha_{2,PO_4}TOTPO_4$
H ₂ PO ₄ ⁻	0	2	0	1	0	$\alpha_{1,PO_4}TOTPO_4$
H ₃ PO ₄	0	3	0	1	0	$\alpha_{0,PO_4}TOTPO_4$
Ca(OH) ₂	2	-2	0	0	1	x

$$TOTH_{in} =$$

$$\left\{ \begin{array}{l} [\text{H}^+] - [\text{OH}^-] + 2\alpha_{0,\text{CO}_3} [\text{TOTCO}_3] + \alpha_{2,\text{CO}_3} [\text{TOTCO}_3] \\ + 3\alpha_{0,\text{PO}_4} [\text{TOTPO}_4] + 2\alpha_{1,\text{PO}_4} [\text{TOTPO}_4] + \alpha_{2,\text{PO}_4} [\text{TOTPO}_4] \end{array} \right\}_{\text{pH } 8.1} - 2x$$

$$TOTH_{in} = 10^{-8.1} - 10^{-5.9} + \left(2\alpha_{0,\text{CO}_3} + \alpha_{1,\text{CO}_3} \right)_{\text{pH } 8.1} [\text{TOTCO}_3]$$

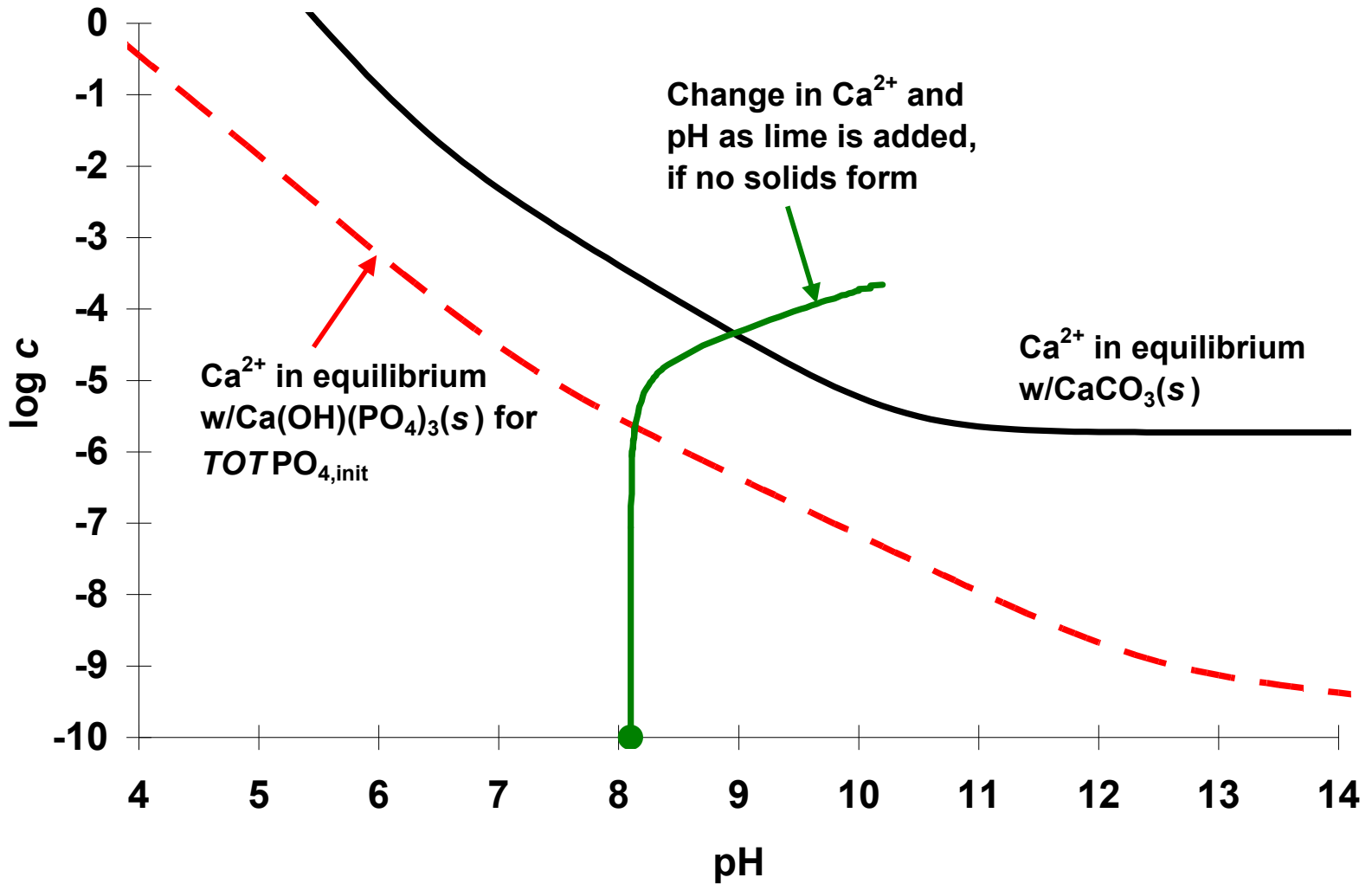
$$+ \left(3\alpha_{0,\text{PO}_4} + 2\alpha_{1,\text{PO}_4} + \alpha_{2,\text{PO}_4} \right)_{\text{pH } 8.1} [\text{TOTPO}_4] - 2x$$

pH of initial precipitation is found by solving TOTH equation ($TOTH_{in} = TOTH_{eq}$) for various lime doses (various values of x) and determining the minimum dose that causes K_{s0} to be exceeded.

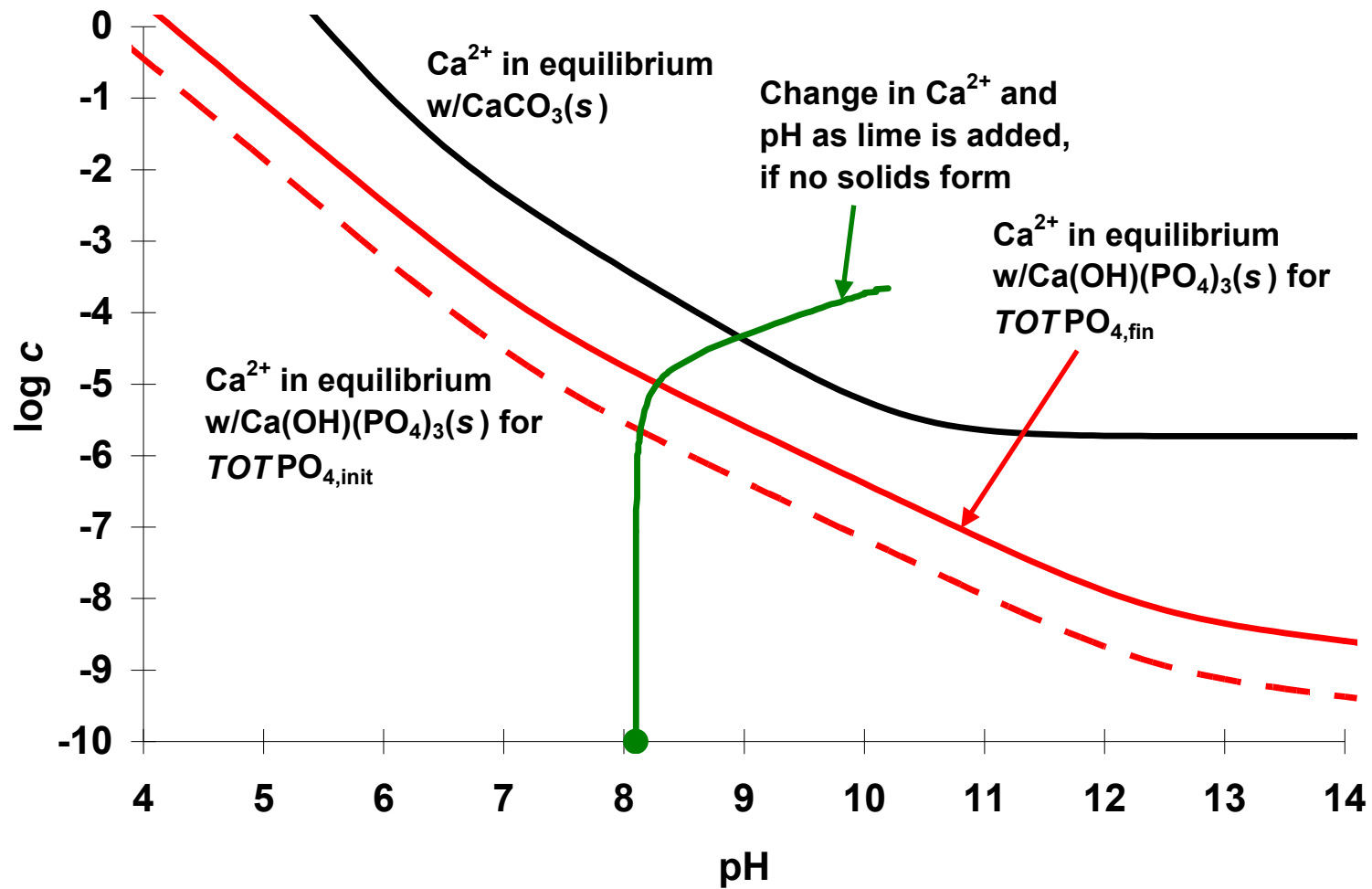
$$TOTH_{in} = TOTH_{eq}$$

$$\begin{aligned}
 & 10^{-8.1} - 10^{-5.9} + \left(2\alpha_{0,CO_3} + \alpha_{1,CO_3} \right)_{pH\ 8.1} [TOTCO_3] \\
 & \quad + \left(3\alpha_{0,PO_4} + 2\alpha_{1,PO_4} + \alpha_{2,PO_4} \right)_{pH\ 8.1} [TOTPO_4] - 2x \\
 = & \left[H^+ \right] - \left[OH^- \right] + 2 \left[H_2CO_3 \right] + \left[HCO_3^- \right] + 3 \left[H_3PO_4 \right] \\
 & \quad + 2 \left[H_2PO_4^{2-} \right] + \left[HPO_4^{2-} \right]
 \end{aligned}$$

Result: Saturation with respect to $\text{Ca}_5\text{OH}(\text{PO}_4)_3$ is reached with a minimal addition of lime (2.5×10^{-6} mol/L, pH 8.13)



(c) Add a line showing activity of Ca^{2+} in equilibrium with the solution once the TOTPO_4 target has been reached.



(c) How much lime must be added to reach the target condition, and what is the solution composition?

The $TOTPO_4$ target will be reached before $CaCO_3(s)$ becomes saturated.

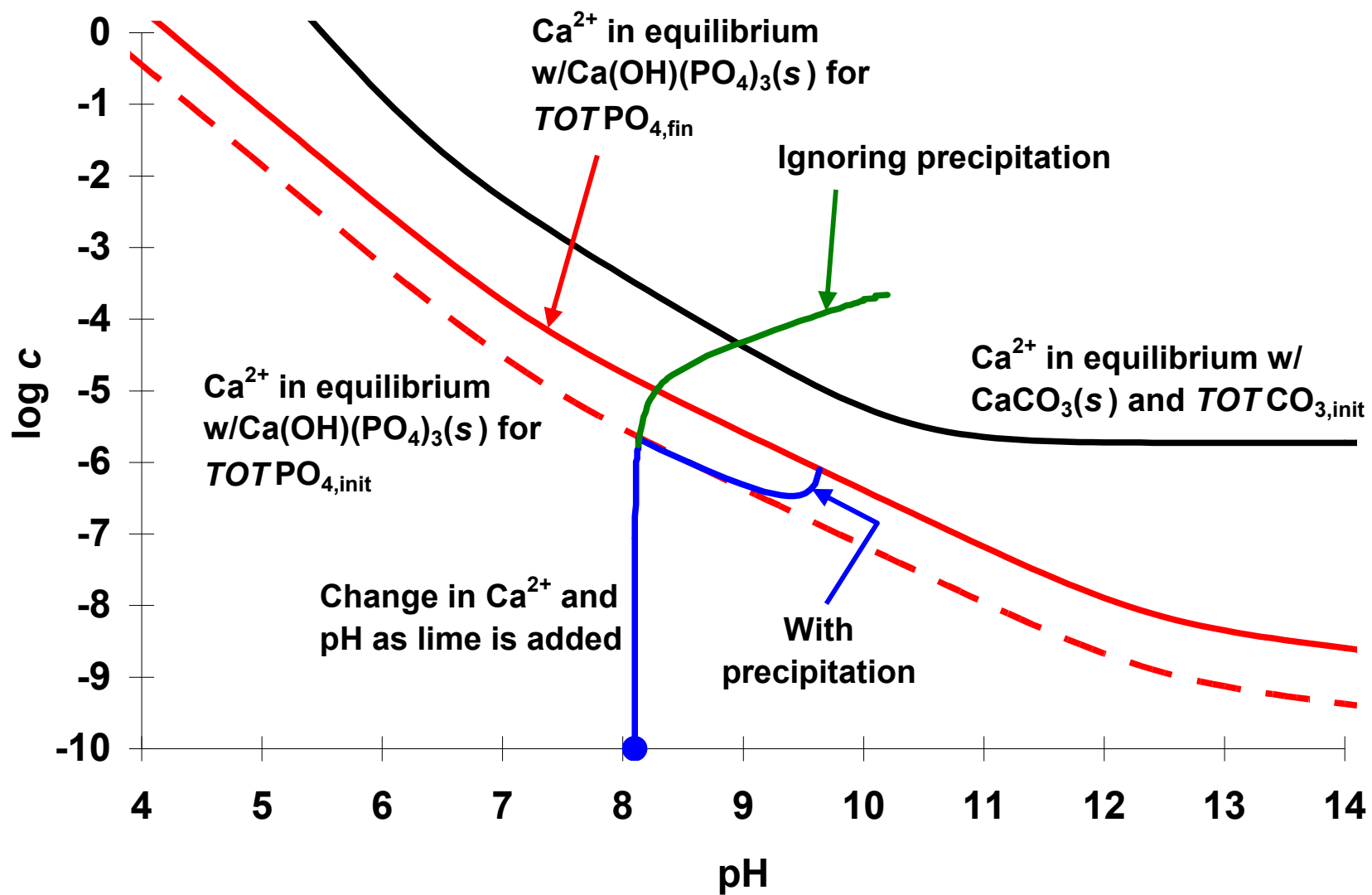
The lime dose and pH when the target is reached can be determined from another TOTH equation that includes the contribution of the solid to $TOTH_{eq}$. For the given choice of components, the TOTH coefficient for the solid is -1 :



$$TOTH_{in} = TOTH_{eq, w/ pptn}$$

$$\begin{aligned}
 & 10^{-8.1} - 10^{-5.9} + \left(\alpha_{0,CO_3} - \alpha_{2,CO_3} \right)_{pH\ 8.1} [TOTCO_3] \\
 & \quad + \left(2\alpha_{0,PO_4} + \alpha_{1,PO_4} - \alpha_{3,PO_4} \right)_{pH\ 8.1} [TOTPO_4] - 2x \\
 = & [H^+] - [OH^-] + 2[H_2CO_3] + [HCO_3^-] + 3[H_3PO_4] \\
 & \quad + 2[H_2PO_4^{2-}] + [HPO_4^{2-}] - [Ca_5OH(PO_4)_3(s)]
 \end{aligned}$$

The concentration of solid can be replaced by $TOTPO_{4,in} - TOTPO_{4,eq}$, leaving an equation in which all terms except x are known or depend only on pH. pH and solid concentration can then be determined for any lime dose, and the lime dose required to meet the treatment goal (95% $TOTPO_4$ removal) and the corresponding pH can be determined.



(c) How much lime must be added to reach the target condition, and what is the solution composition?

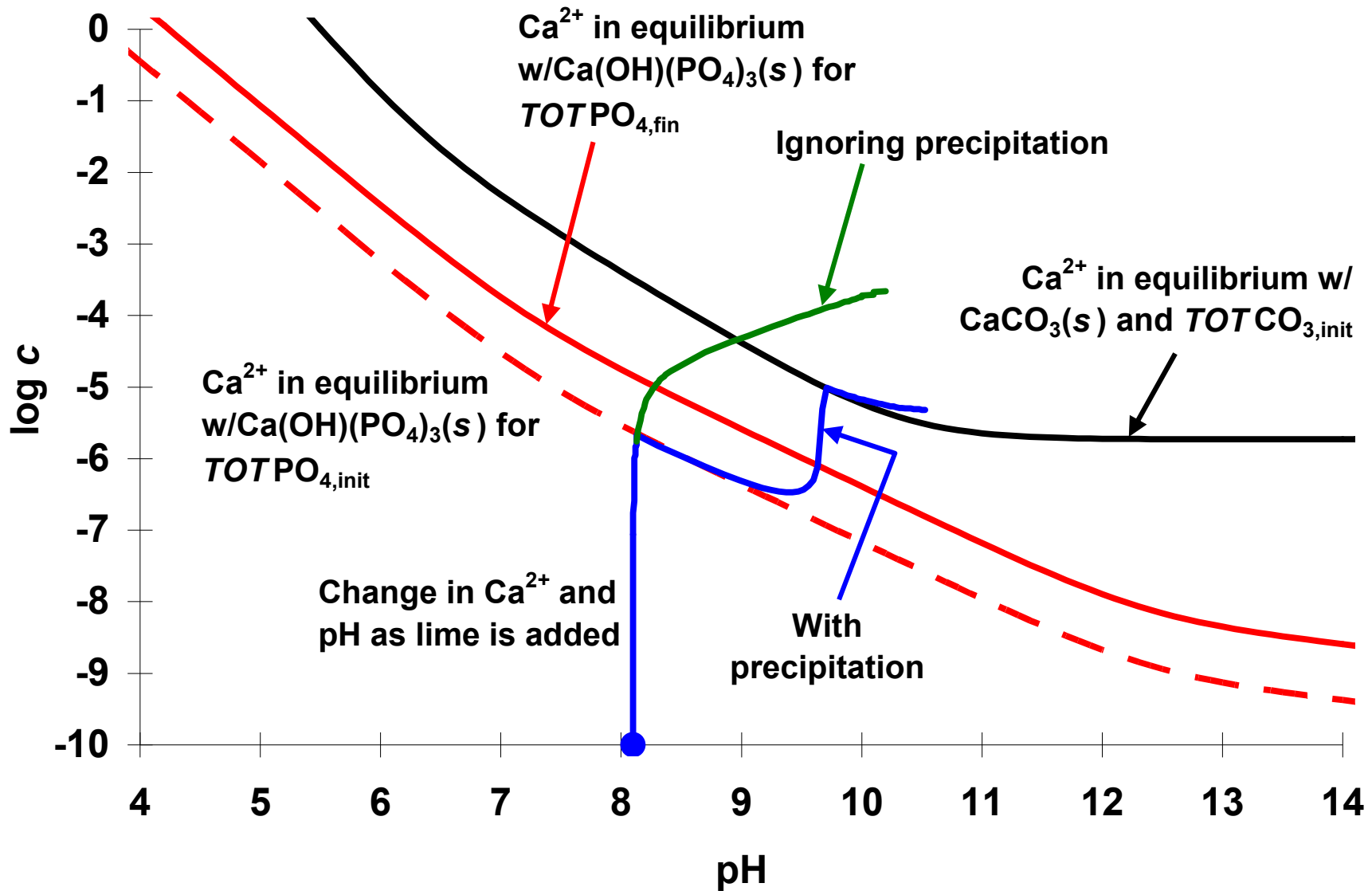
Result: The target $TOTPO_4$ is reached after addition of 3.2×10^{-4} mol/L lime, when the pH is 9.63

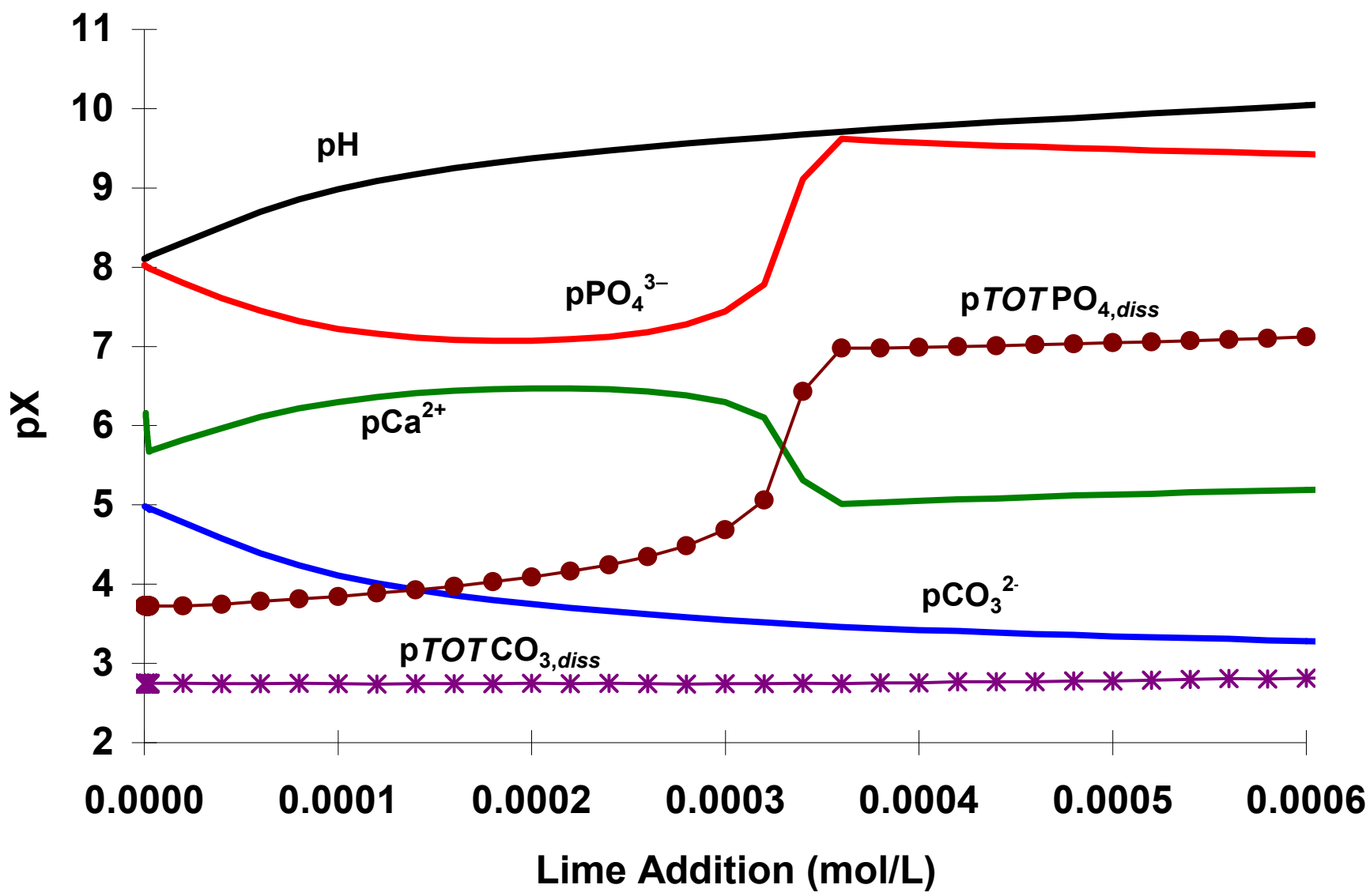
Interpretation: As more lime is added, the pH increases. The deprotonation of H_xPO_4 species increases $\{PO_4^{3-}\}$ and decreases the amount of Ca^{2+} that can remain in solution. As a result, the Ca^{2+} concentration and activity decrease, even though lime is being added. As $TOTPO_4$ in solution decreases, the curve for Ca^{2+} in equilibrium with the solid moves upward, and the data points representing $(pH, \{Ca^{2+}\})$ stay on that (upward moving) curve.

(d) What happens as even more lime is added?

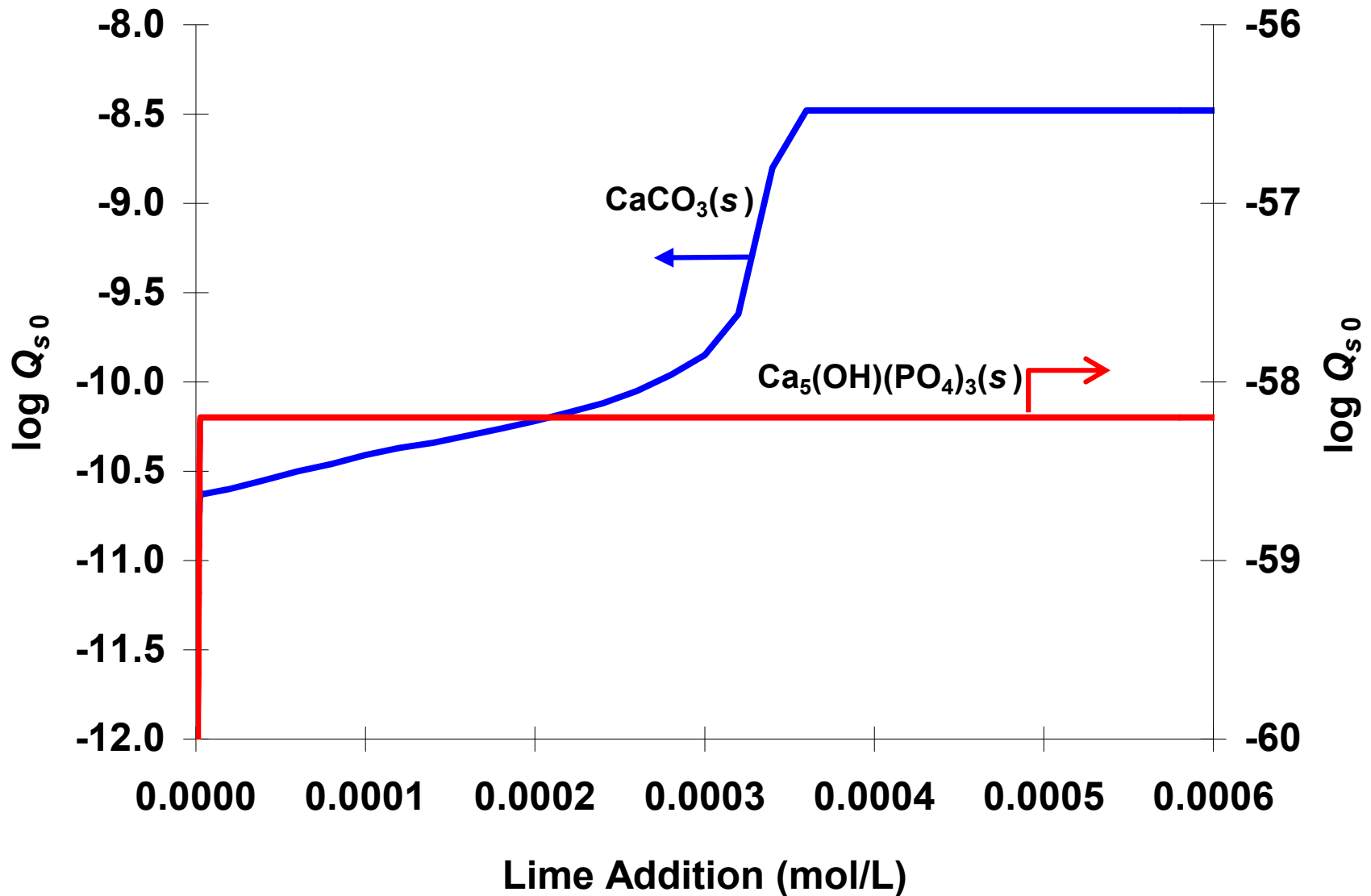
As more lime is added, $TOTPO_4$ in solution continues to decrease, so the curve for $\{Ca^{2+}\}$ in equilibrium with the solid continues to move upward. Also, pH increases steadily.

Eventually, the curve for $\{Ca^{2+}\}$ in equilibrium with $Ca_5OH(PO_4)_3(s)$ intersects the curve for equilibrium with $CaCO_3(s)$, at which point the solution is saturated with respect to both solids. From that point on, lime addition will increase the pH. Solution composition and the identity of any solid(s) that remain depends on the details relating to the TOTH equation, the K_{s0} 's, and mass balances.





In this system, both solids remain equilibrated with solution for additions up to at least 0.006 mol/L lime.



Modeling Solid/Liquid Equilibrium in Visual Minteq

Stoichiometry and log K values for inputting solids

Specifying whether the solution is forced to be in equilibrium with the solid, or whether the solution can be undersaturated

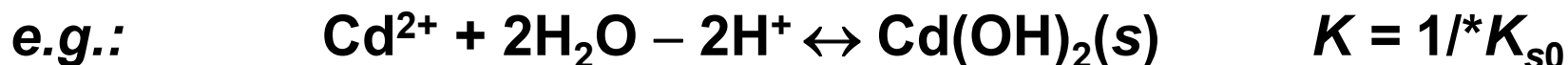
Determining how much solid precipitates, if the inputs cause the solution to be supersaturated

Modeling Solid/Liquid Equilibrium in Visual Minteq

Stoichiometry and log K values for inputting solids

In Visual Minteq, the stoichiometry for forming solids follows the same convention as for forming other species, i.e., based on a reaction in which the solid is a product and all other reactants and products are components:

Σ Components \leftrightarrow 1 Species



However, (for no apparent reason,) the input log K value is for the reverse of this reaction; e.g., for the above example reaction, the input equilibrium constant would be

$$K_{VM} = 1/K = ^*K_{s0}; \quad \log K_{VM} = \log (^*K_{s0})$$

Specifying whether the solution is forced to be in equilibrium with the solid, or whether the solution can be undersaturated

- The input option to specify the presence of an infinite amount of the solid assures that the solution will be in equilibrium with the solid; the program adds or removes the components of the solid to the solution in the appropriate stoichiometric ratio until the solution is saturated with the solid***
- Alternatively, specifying the presence of a fixed amount of solid (including zero, if appropriate) in the initial system allows the solid to be present at equilibrium, but only if the inputs support that outcome (i.e., if the solution would be supersaturated in the absence of the solid)***

Determining how much solid precipitates, if the inputs cause the solution to be supersaturated

As for other, similar situations, the concentration of solids formed (mol/L) can be computed based on the difference between the total input of metal and the total dissolved metal in the equilibrated solution.

$$\mathbf{TOTMe_{solid} = TOTMe_{input} - TOTMe_{diss,eq}}$$

The discussion of the calculations in the preceding example explained how the problem could be answered using a manual approach, but the use of Visual Minteq greatly simplifies all the calculations. The graphs shown were all generated using Visual Minteq simulations.

- 1. Compute TOTH needed for initial pH (Result: $2.042e-3$)*
- 2. Titrate to change TOTCa and TOTH in ratio of 1:-2 (best to carry out titration in two steps, one for small lime doses, one for larger doses)*
- 3. Find minimum TOTCa where a solid forms*