

# Selective Precipitation Calculations

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We can use the pH dependence of precipitation reactions to help us control the amount of precipitation of a sparingly soluble salt. We can also sometimes separate two metal ions in solution by varying the pH.

## Zinc and Magnesium Hydroxide Precipitation



*Initial Solution has 1.00 mM Zn<sup>2+</sup> and 1.00 mM Mg<sup>2+</sup>.*

*Can we selectively precipitate Zn(OH)<sub>2</sub> but not Mg(OH)<sub>2</sub>?*

## Zinc vs. Magnesium Hydroxide Precipitation Separation

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Initial Solution has 1.00 mM  $\text{Zn}^{2+}$  and 1.00 mM  $\text{Mg}^{2+}$ .

1) At what pH does Zinc Hydroxide begin to precipitate?

$$[\text{Zn}^{2+}] = 1.00 \times 10^{-3} \text{M}$$

$$K_{sp1} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

\* This effective  $K_{sp}$  value is often used to include zinc hydroxide complexation effects. The true  $K_{sp}$  is  $3 \times 10^{-17}$ .

## Zinc vs. Magnesium Hydroxide Precipitation Separation

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Initial Solution has 1.00 mM  $\text{Zn}^{2+}$  and 1.00 mM  $\text{Mg}^{2+}$ .

1) At what pH does Zinc Hydroxide begin to precipitate?

$$[\text{Zn}^{2+}] = 1.00 \times 10^{-3} \text{M} \quad K_{sp1} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{\frac{K_{sp1}}{[\text{Zn}^{2+}]}} = \sqrt{\frac{3 \times 10^{-16}}{10^{-3}}} = 5.48 \times 10^{-7} \text{M} \quad \begin{array}{l} \text{pOH} = 6.26 \\ \text{pH} = 7.74 \end{array}$$

Zinc Hydroxide begins to precipitate at pH = 7.74

## Zinc vs. Magnesium Hydroxide Precipitation Separation

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Initial Solution has 1.00 mM  $\text{Zn}^{2+}$  and 1.00 mM  $\text{Mg}^{2+}$ .

II) At what pH is 99.9% of the  $\text{Zn}^{2+}$  removed from solution?

$$[\text{Zn}^{2+}] = 1.00 \times 10^{-6} \text{M}$$

$$K_{sp1} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

## Zinc vs. Magnesium Hydroxide Precipitation Separation

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Initial Solution has 1.00 mM  $\text{Zn}^{2+}$  and 1.00 mM  $\text{Mg}^{2+}$ .

II) At what pH is 99.9% of the  $\text{Zn}^{2+}$  removed from solution?

$$[\text{Zn}^{2+}] = 1.00 \times 10^{-6} \text{M} \quad K_{sp1} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

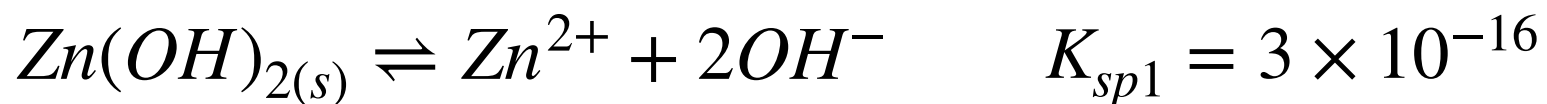
$$[\text{OH}^-] = \sqrt{\frac{K_{sp1}}{[\text{Zn}^{2+}]}} = \sqrt{\frac{3 \times 10^{-16}}{10^{-6}}} = 1.73 \times 10^{-5} \text{M}$$

$$\begin{aligned} \text{pOH} &= 4.76 \\ \text{pH} &= 9.24 \end{aligned}$$

At pH 9.24 we can remove 99.9% of the  $\text{Zn}^{2+}$

## Zinc vs. Magnesium Hydroxide Precipitation Separation

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Initial Solution has 1.00 mM  $\text{Zn}^{2+}$  and 1.00 mM  $\text{Mg}^{2+}$ .

III) At what pH does Magnesium Hydroxide begin to precipitate?

$$[\text{Mg}^{2+}] = 1.00 \times 10^{-3} \text{M}$$

$$K_{sp2} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

## Zinc vs. Magnesium Hydroxide Precipitation Separation

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Initial Solution has 1.00 mM  $\text{Zn}^{2+}$  and 1.00 mM  $\text{Mg}^{2+}$ .

III) At what pH does Magnesium Hydroxide begin to precipitate?

$$[\text{Mg}^{2+}] = 1.00 \times 10^{-3} \text{M}$$

$$K_{sp2} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{\frac{K_{sp2}}{[\text{Mg}^{2+}]}} = \sqrt{\frac{7.1 \times 10^{-12}}{10^{-3}}} = 8.43 \times 10^{-5} \text{M}$$

$$\begin{aligned} \text{pOH} &= 4.07 \\ \text{pH} &= 9.93 \end{aligned}$$

Magnesium Hydroxide begin to precipitate at pH = 9.93



We can separate Zinc and Magnesium!

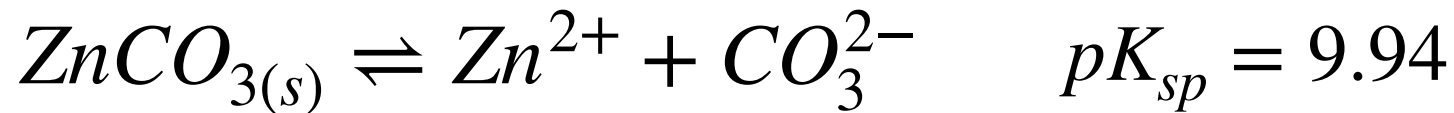


## Alpha Fractions in Selective Precipitation Calculations

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We can use alpha fractions to help calculate the correct pH for selective precipitation reactions. For example:

Zinc Carbonate,  $ZnCO_{3(s)}$ , is a sparingly soluble solid in aqueous solution:



$$\alpha_{CO_3^{2-}} = \frac{[CO_3^{2-}]}{C^{tot}} = \left( 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2} \right)^{-1}$$

*Diprotic Acid*  
 $pK_1 = 6.35$   
 $pK_2 = 10.33$

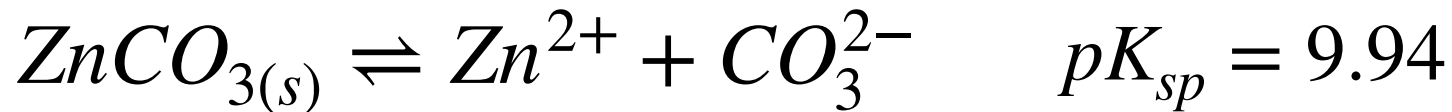
The fraction of carbonic acid in the  $CO_3^{2-}$  form is a function of pH.



## Alpha Fractions in Selective Precipitation Calculations

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Consider a solution with a total  $H_2CO_3$  concentration of 10.0 mM, and a  $Zn^{2+}$  concentration of 1.0 mM. At what pH will  $ZnCO_{3(s)}$  begin to precipitate in this solution?



$$K_{sp} = [Zn^{2+}][CO_3^{2-}] = [Zn^{2+}]\alpha_{CO_3^{2-}}C^{tot}$$

$$\frac{K_{sp}}{[Zn^{2+}]C^{tot}} = \alpha_{CO_3^{2-}} = \left( 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2} \right)^{-1}$$

$$\frac{[Zn^{2+}]C^{tot}}{K_{sp}} = 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}$$

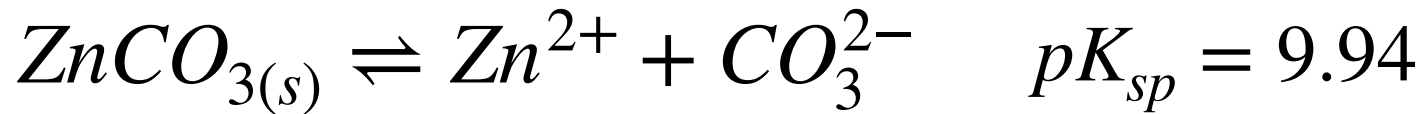
$$pK_1 = 6.35$$

$$pK_2 = 10.33$$

## Alpha Fractions in Selective Precipitation Calculations

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Consider a solution with a total  $H_2CO_3$  concentration of 10.0 mM, and a  $Zn^{2+}$  concentration of 1.0 mM. At what pH will  $ZnCO_{3(s)}$  begin to precipitate in this solution?



$$K_{sp} = [Zn^{2+}][CO_3^{2-}]$$

$$pK_1 = 6.35$$

$$pK_2 = 10.33$$

$$\frac{[Zn^{2+}]C^{tot}}{K_{sp}} = \frac{(10^{-3}M)(10^{-2}M)}{10^{-9.94}}$$

Solve Quadratic:

$$[H^+] = 1.14 \times 10^{-6}M$$

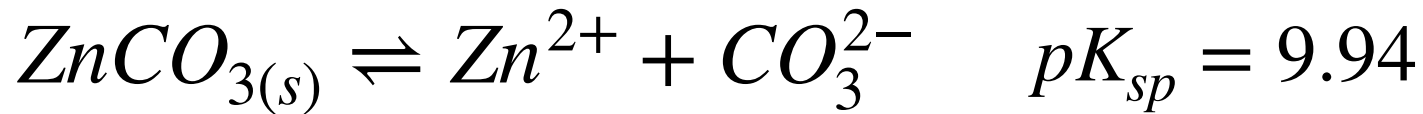
$$10^{4.94} = 1 + \frac{[H^+]}{10^{-10.33}} + \frac{[H^+]^2}{10^{-16.68}}$$

$$pH = 5.94$$

## Alpha Fractions in Selective Precipitation Calculations

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Consider a solution with a total  $H_2CO_3$  concentration of 10.0 mM, and a  $Zn^{2+}$  concentration of 1.0 mM. At what pH will 99.9% of the  $Zn^{2+}$  be removed from this solution?



$$K_{sp} = [Zn^{2+}][CO_3^{2-}]$$

$$pK_1 = 6.35$$

$$pK_2 = 10.33$$

$$\frac{[Zn^{2+}]C^{tot}}{K_{sp}} = \frac{(10^{-6}M)(10^{-2}M)}{10^{-9.94}}$$

Solve Quadratic:

$$[H^+] = 4.0 \times 10^{-9}M$$

$$10^{1.94} = 1 + \frac{[H^+]}{10^{-10.33}} + \frac{[H^+]^2}{10^{-16.68}}$$

$$pH = 8.40$$

## EDTA Titrations of Sea water: $Mg^{2+}$ and $Ca^{2+}$

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EDTA Titrations are used in the analysis of sea water for  $Mg^{2+}$  and  $Ca^{2+}$

In the ocean:  $[Mg^{2+}] = 60 \text{ mM}$   
 $[Ca^{2+}] = 10 \text{ mM}$

We can use selective precipitation to separate  $Mg^{2+}$  and  $Ca^{2+}$



- i) At what pH will Magnesium Hydroxide start to precipitate? (9.20)
- ii) At what pH will Calcium Hydroxide start to precipitate? (12.37)
- iii) How much of the  $Mg^{2+}$  in the seawater sample will be removed (precipitated) from solution at a pH of 11.0? (99.75%)