

Zinc-EDTA Titration

You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Zn^{2+} solution with a 1.00×10^{-4} M EDTA solution.

What is $p\text{Zn}$ at the equivalence point?

Log K_f for the ZnY^{2-} complex is 16.5.

Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

EDTA-Metal ion Complexation.

EDTA is a polyprotic acid - Ethylenediaminetetraacetic Acid. H_4Y .

$pK_1 = 1.99$; $pK_2 = 2.67$; $pK_3 = 6.16$; $pK_4 = 10.26$.

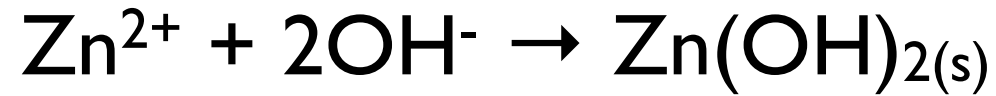
Alpha fraction for Y^{4-} :

$$\alpha_{Y^{4-}} = \frac{K_1 K_2 K_3 K_4}{[H^+]^4 + K_1 [H^+]^3 + K_1 K_2 [H^+]^2 + K_1 K_2 K_3 [H^+] + K_1 K_2 K_3 K_4}$$

$\alpha_{Y^{4-}} = 0.355$ at $pH = 10$.

*We use an ammonia buffer solution
for a reason...*

Zinc Hydroxide

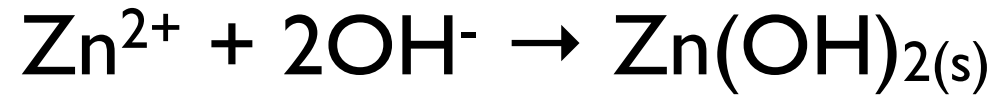


Solubility product $K_{sp} = 3.0 \times 10^{-17}$

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

At pH=10, $[\text{Zn}^{2+}] = ??$

Zinc Hydroxide

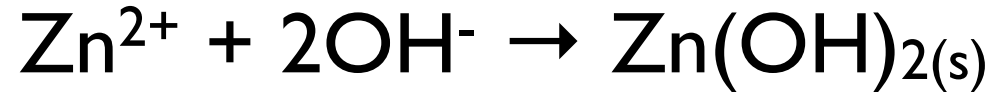


Solubility product $K_{sp} = 3.0 \times 10^{-17}$

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

At pH=10, $[\text{Zn}^{2+}] = K_{sp} / [\text{OH}^-]^2$

Zinc Hydroxide



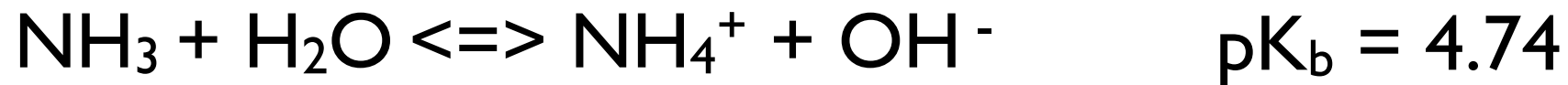
Solubility product $K_{sp} = 3.0 \times 10^{-17}$

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

$$\begin{aligned} \text{At pH}=10, [\text{Zn}^{2+}] &= K_{sp} / [\text{OH}^-]^2 \\ &= (3.0 \times 10^{-17}) / (1.0 \times 10^{-4})^2 \\ &= 3.0 \times 10^{-9} \text{ M} \end{aligned}$$

This is the maximum free Zinc concentration.

Ammonia Buffer Solution



$$[\text{NH}_3]_{\text{total}} = 0.100\text{M}$$

$$\text{At pH}=10, [\text{NH}_3] = ??$$

Ammonia Buffer Solution



$$[\text{NH}_3]_{\text{total}} = 0.100\text{M}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

At pH=10:

$$[\text{NH}_3] = \alpha_{\text{NH}_3} C^{\text{tot}}$$

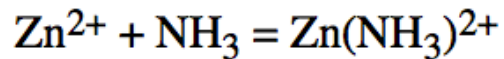
$$[\text{NH}_3] = 0.0846 \text{ M}$$

$$\alpha_{\text{NH}_3} = \left[1 + \frac{K_b}{[\text{OH}^-]} \right]^{-1}$$

Zinc Complexation

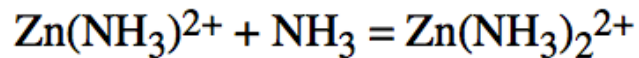
Zinc - Ammonia Complexation

1. Zinc-ammonia complexation



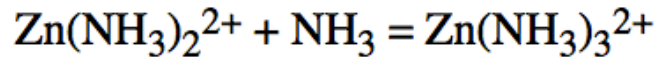
$$K_1 = 180$$

$$\beta_1 = K_1 = 180$$



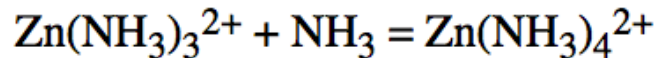
$$K_2 = 220$$

$$\beta_2 = K_1 K_2 = 3.96 \times 10^4$$



$$K_3 = 250$$

$$\beta_3 = K_1 K_2 K_3 = 9.90 \times 10^6$$



$$K_4 = 110$$

$$\beta_4 = K_1 K_2 K_3 K_4 = 1.09 \times 10^9$$

$$\alpha_{\text{Zn}^{2+}} = \frac{1}{1 + K_1[\text{NH}_3] + K_1 K_2[\text{NH}_3]^2 + K_1 K_2 K_3[\text{NH}_3]^3 + K_1 K_2 K_3 K_4[\text{NH}_3]^4}$$

$$\text{At } [\text{NH}_3] = 0.0846\text{M}, \alpha_{\text{Zn}^{2+}} = 1.61 \times 10^{-5}$$

Zinc - Ammonia Complexation

At a TOTAL Zinc concentration of 1.00×10^{-4} M:

$$[\text{Zn}^{2+}] = \alpha_{\text{Zn}^{2+}} [\text{Zn}^{2+}]^{\text{tot}}$$

$$[\text{Zn}^{2+}] = (1.61 \times 10^{-5})(1.00 \times 10^{-4})$$

$$[\text{Zn}^{2+}] = 1.61 \times 10^{-9} \text{ M}$$

Therefore: no precipitation!

Once more, with feeling:

EDTA Titration

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Log K_f for the ZnY^{2-} complex is 16.5.

Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

The alpha fraction for Y^{4-} is 0.355 at a pH of 10.0.

The alpha fraction for Zn^{2+} is 1.61×10^{-5} .

EDTA Titration

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Total moles of Zinc = ??

EDTA Titration

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$$\begin{aligned}\text{Total moles of Zinc} &= (1.00 \times 10^{-4} \text{ M})(0.050\text{L}) \\ &= 5.0 \times 10^{-6} \text{ moles}\end{aligned}$$

EDTA Titration

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Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = ??

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$[\text{ZnY}^{2-}] = ??$

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$[\text{ZnY}^{2-}] = 5.0 \times 10^{-5}$ M

We assume a stoichiometric reaction.

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Total moles of Zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

$[\text{ZnY}^{2-}] = 5.0 \times 10^{-5}$ M

$[\text{Zn}^{2+}] = ??$

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M}$$

We assumed a stoichiometric reaction. But actually, there is a little bit of free (uncomplexed) EDTA and free (uncomplexed) Zinc in solution.

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Free Zn}^{Total}$$

$$[Y^{4-}] = \alpha_{Y^{4-}} C_{Free EDTA}^{Total}$$

$$C_{Free Zn}^{Total} = C_{Free EDTA}^{Total}$$

$$C_{Free Zn}^{Total} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}$$

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M}$$

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$$C_{Free Zn}^{Total} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}$$

$$\text{Log } K_f = 16.5.$$

$$\alpha_{Y^{4-}} = 0.355$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M}$$

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$$[Y^{4-}] = \alpha_{Y^{4-}} C_{Free EDTA}^{Total}$$

$$C_{Free Zn}^{Total} = C_{Free EDTA}^{Total}$$

$$C_{Free Zn}^{Total} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}$$

$$C_{Free Zn}^{Total} = 1.66 \times 10^{-8} \text{ M}$$

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Total moles of zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

$$[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M} \qquad C_{Free Zn}^{Total} = 1.66 \times 10^{-8} \text{ M}$$

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Free Zn}^{Total}$$

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Total moles of zinc = 5.0×10^{-6} moles

Equivalence point volume = 0.100L

$$[\text{ZnY}^{2-}] = 5.0 \times 10^{-5} \text{ M} \quad C_{\text{Free Zn}}^{\text{Total}} = 2.35 \times 10^{-6} \text{ M}$$

$$[\text{Zn}^{2+}] = \alpha_{\text{Zn}^{2+}} C_{\text{Free Zn}}^{\text{Total}} = (1.61 \times 10^{-5}) (1.66 \times 10^{-8} \text{ M})$$

$$[\text{Zn}^{2+}] = 2.59 \times 10^{-13} \text{ M} \quad \text{pZn} = 12.6$$

We are done!