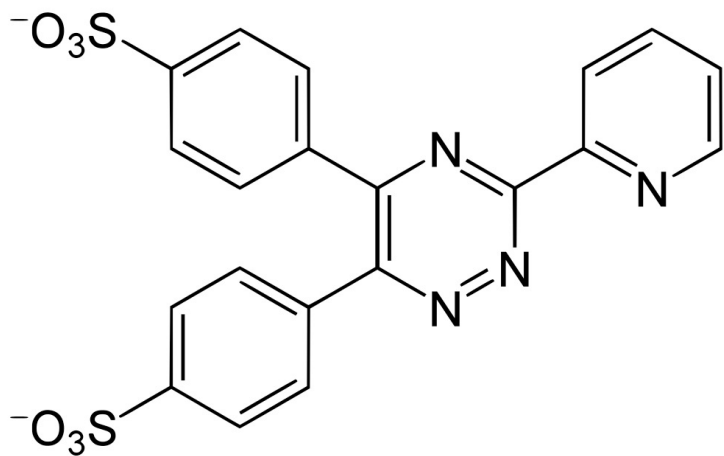
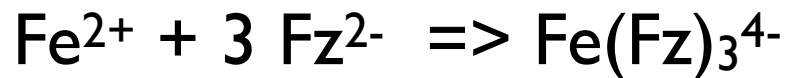
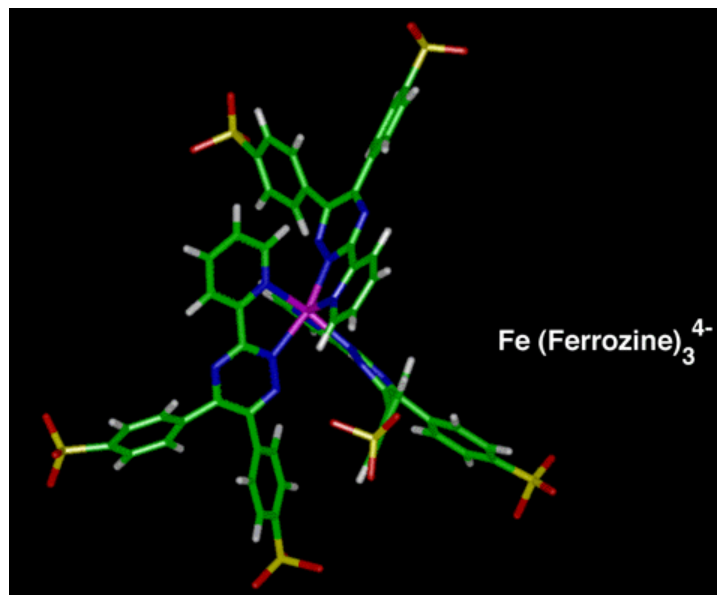


Complexation and EDTA Titrations

We have already used metal complexation in Week 2 to detect Fe^{2+} with Colorimetry:



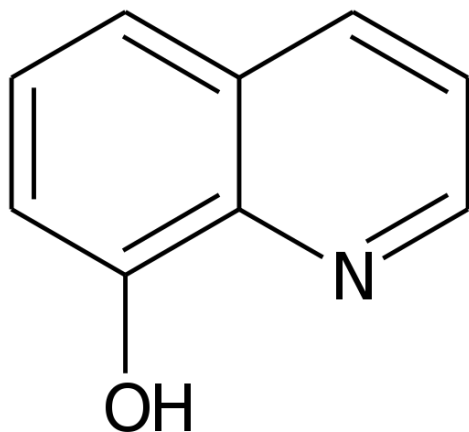
*Ferrozine (Fz^{2-})
is a metal ligand*



*Three Ferrozine will form a
metal-ligand complex with Fe^{2+}*

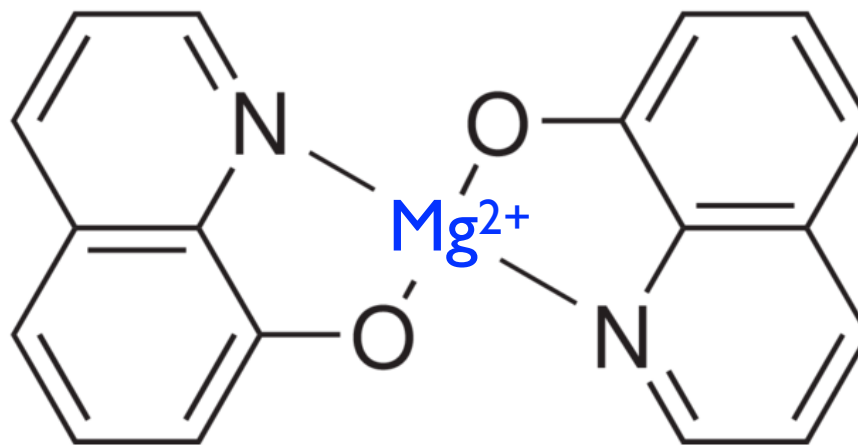
HQS Fluorimetry for Detecting Metal Ions

8-hydroxyquinoline (8-HQ) can be used to detect Mg^{2+} :



8-hydroxyquinoline (8-HQ)

8-HQ is also called oxine

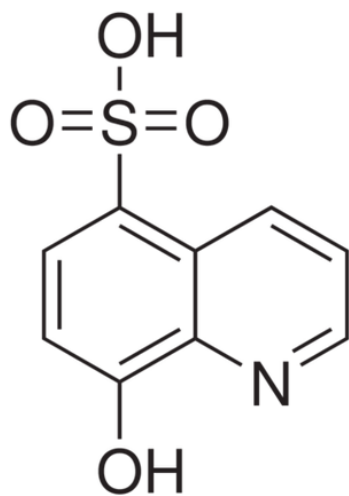


Two 8-HQ form a fluorescent complex with divalent Cations

8-hydroxyquinoline: a metal chelator that fluoresces upon binding!

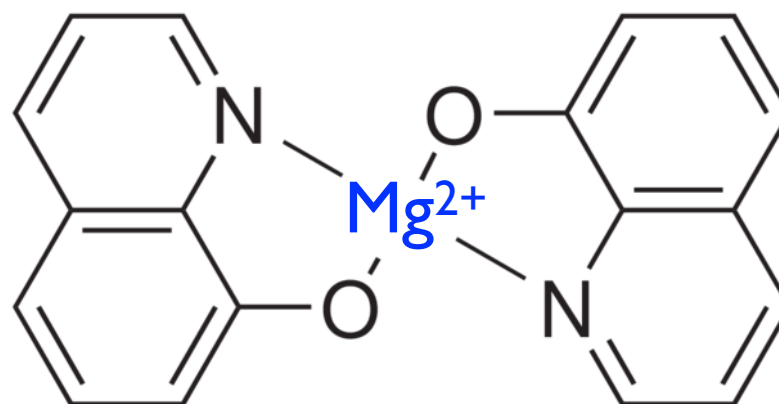
HQS Fluorimetry for Detecting Metal Ions

This week we will use 8-hydroxyquinoline-5-sulfonic Acid (HQS) to detect Mg^{2+} :



8-hydroxyquinoline-5-sulfonic Acid
(HQS)

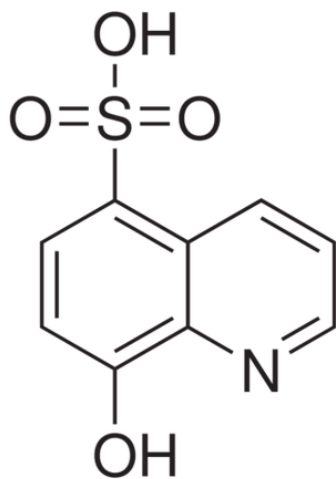
HQS is more water soluble than 8-HQ.



Two HQS will form a fluorescent complex with divalent cations

Three HQS also can form a fluorescent complex with trivalent cations like Al^{3+}

HQS Fluorimetric Detection of Mg^{2+} in Seawater



8-hydroxyquinoline-5-sulfonic Acid
(HQS)

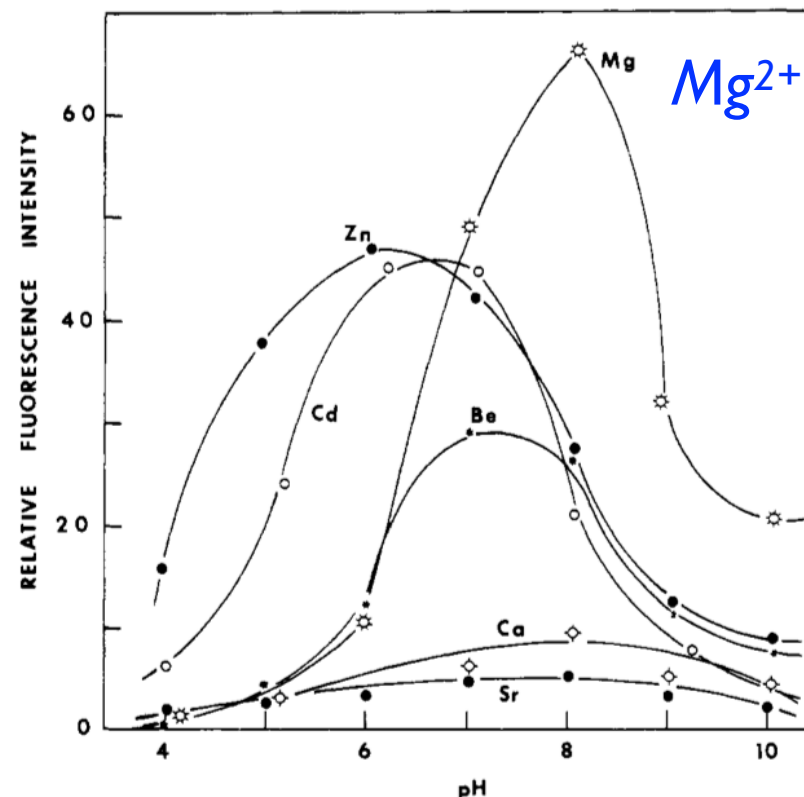


Figure 1. pH dependence of the fluorescence intensities of group II metal-HQS chelates: Cd, 2 μ M; all other metals in this and following figures, 20 μ M; HQS, 1 mM.

We can use either a linear calibration curve or standard addition methods to quantitate the HQS fluorimetry.

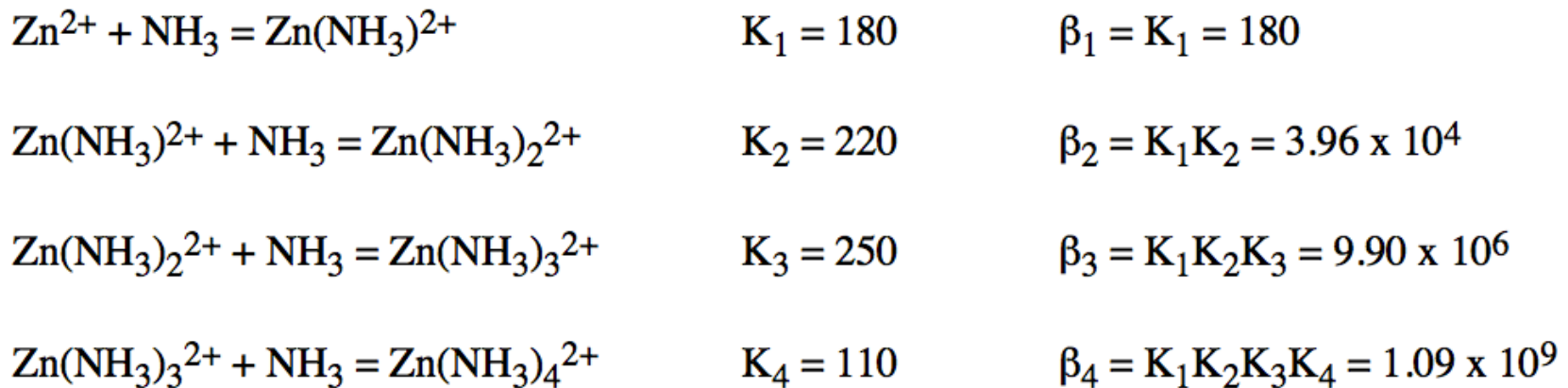
In sea water, there may be some background due to Ca^{2+} .

Ammonia: A Weak Metal Complexation Agent

Four different Zn^{2+} -ammonia species co-exist in solution!

Zinc Complexation

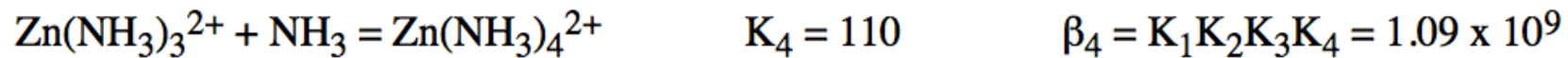
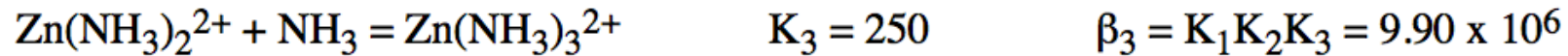
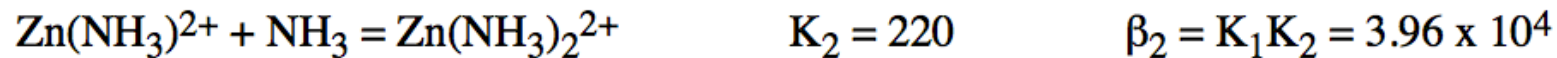
1. Zinc-ammonia complexation



Weak Metal Complex Formation Constants have similar values of K_1 to K_n

Ammonia: A Weak Metal Complexation Agent

1. Zinc-ammonia complexation



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

We can use the alpha fraction for Zn^{2+} to calculate the amount of free Zn^{2+} in solution.

Ammonia Buffer Control of Zinc Hydroxide Precipitation



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

1) At pH 10.0, what is the Zn^{2+} concentration at which zinc hydroxide just begins to precipitate?

* The true K_{sp} for $\text{Zn}(\text{OH})_{2(s)}$ is 3×10^{-17} . An effective K_{sp} value of 3×10^{-16} is often used to include zinc hydroxide complexation effects; we will ignore hydroxide complexation in this calculation.

Ammonia Buffer Control of Zinc Hydroxide Precipitation



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

1) At pH=10.0, what is the Zn^{2+} concentration at which zinc hydroxide just begins to precipitate?

$$[\text{OH}^-] = 1 \times 10^{-4} \text{M}$$

$$[\text{Zn}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{3 \times 10^{-17}}{10^{-8}} = 3 \times 10^{-9} \text{M}$$

$$[\text{Zn}^{2+}] = 3 \times 10^{-9} \text{M}$$

This is the maximum free Zn^{2+} concentration at pH = 10.0.

Ammonia Buffer Control of Zinc Hydroxide Precipitation

Consider a solution with a TOTAL Zinc concentration of $1.00 \times 10^{-4} M$.

This solution would definitely form a zinc hydroxide precipitate at a solution pH of 10.0.

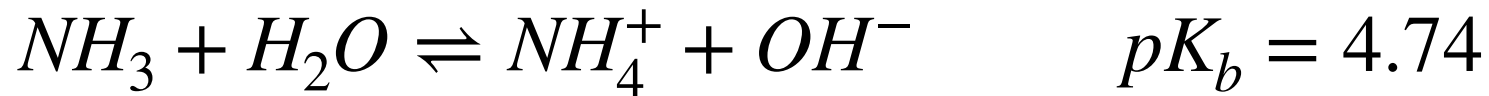
However, we can use an ammonia buffer to reduce the amount of free Zn^{2+} in solution.

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Zn}^{tot} \quad C_{Zn}^{tot} = 1.00 \times 10^{-4} M$$

$$\alpha_{Zn^{2+}} = \frac{1}{1 + K_1[NH_3] + K_1K_2[NH_3]^2 + K_1K_2K_3[NH_3]^3 + K_1K_2K_3K_4[NH_3]^4}$$

Ammonia Buffer Control of Zinc Hydroxide Precipitation

We can use a 0.100M ammonia buffer to reduce the amount of free Zn^{2+} in solution.



$$C_{NH_3}^{tot} = 0.100M$$

At pH = 10.0:

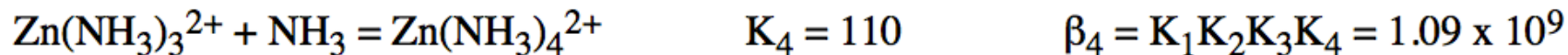
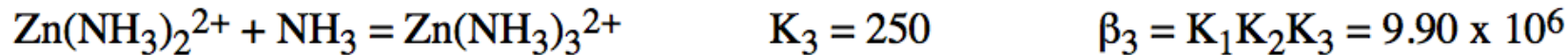
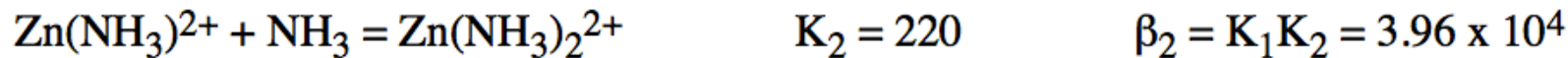
$$[NH_3] = \alpha_{NH_3} C_{NH_3}^{tot} = \left(1 + \frac{K_b}{[OH^-]} \right)^{-1} C_{NH_3}^{tot}$$

$$[NH_3] = \left(1 + \frac{10^{-4.74}}{10^{-4}} \right)^{-1} \times 0.100 = 0.0846M$$

Note that α_{NH_3} is an acid-base alpha fraction!

Ammonia Buffer Control of Zinc Hydroxide Precipitation

1. Zinc-ammonia complexation



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

At $\text{pH} = 10$,
 $[\text{NH}_3] = 0.0846\text{M}$
and we can calculate:

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

Note that $\alpha_{\text{Zn}^{2+}}$ is a complexation alpha fraction!

Zinc - Ammonia Complexation

Consider a solution with a TOTAL Zinc concentration of $1.00 \times 10^{-4} M$ in a $0.100M$ Ammonia buffer at $pH=10.0$:

$$[NH_3] = 0.0846M$$

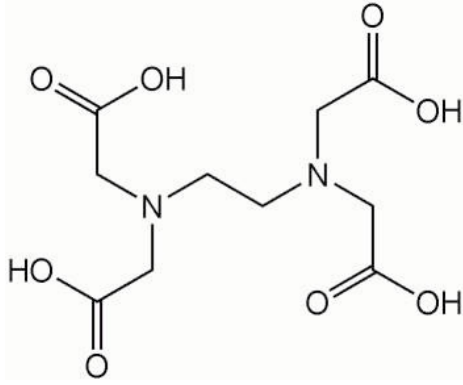
$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$

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

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

This is less than $3 \times 10^{-9}M$, so there is no precipitation!

EDTA Metal Ion Complexation Equilibria



Ethylenediamine Tetra-acetic Acid (H₄Y)

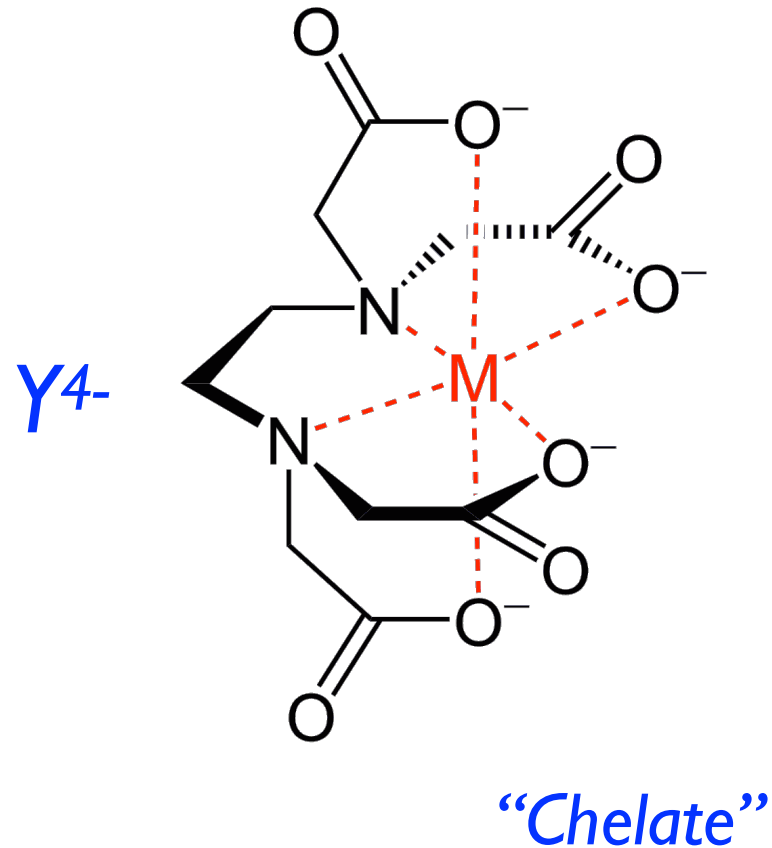
EDTA - the world's best metal ion chelator

Metal complexation reactions with Y⁴⁻:

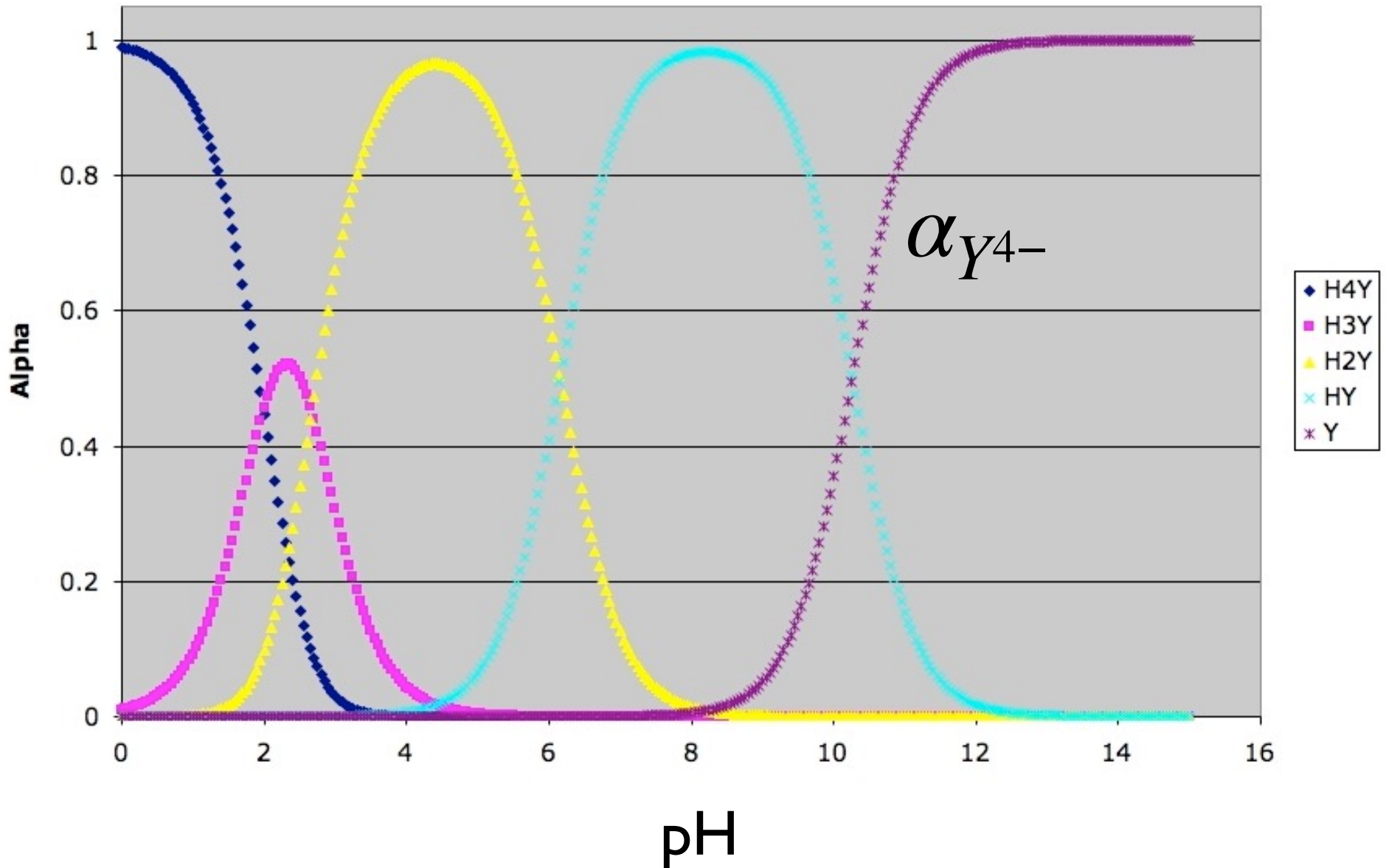


Metal Ion	log K _f
Ag ⁺	7.32
Mg ²⁺	8.69
Ca ²⁺	10.70
Co ²⁺	16.31
Cd ²⁺	16.46
Al ³⁺	15.89
Fe ³⁺	25.10
V ³⁺	25.90

Conditional formation constant: $K'_f = \alpha_{Y^{4-}} K_f$



EDTA Alpha Fractions



Most EDTA titrations are performed at pH \geq 10.

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-} :

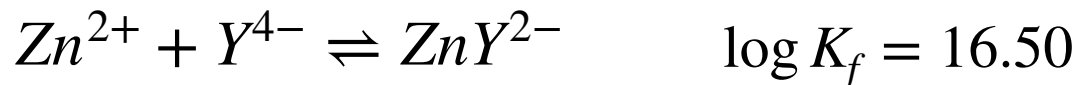
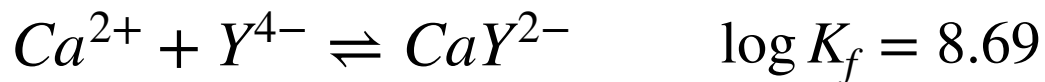
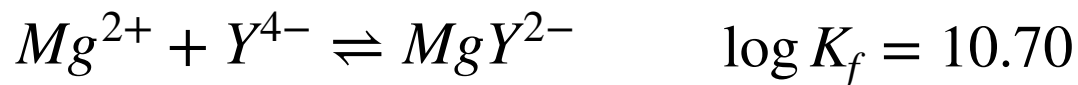
$$\alpha_{Y^{4-}} = \frac{K_1 K_2 K_3 K_4}{[H^+]^4 + K_1 [H^+]^3 + K_1 K_2 [H^+]^2 + K_1 K_2 K_3 [H^+] + K_1 K_2 K_3 K_4}$$

$$\alpha_{Y^{4-}} = 0.355 \text{ at } pH = 10.0$$

EDTA titrations are always run in basic solutions to insure that there is enough Y^{4-} species

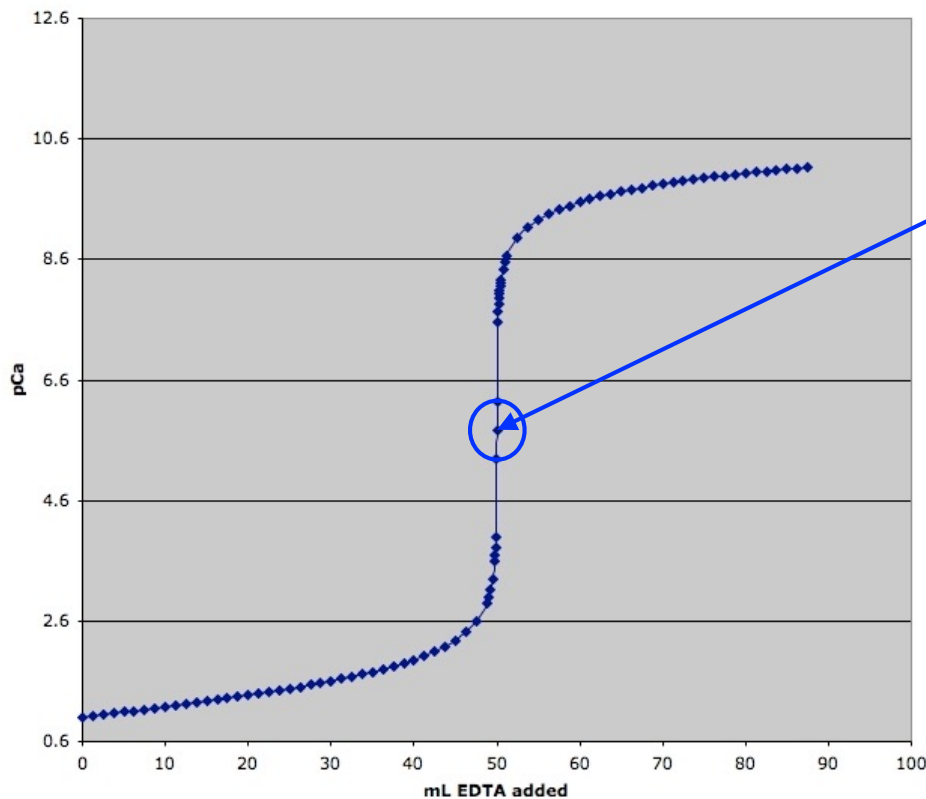
Note that $\alpha_{Y^{4-}}$ is an acid-base alpha fraction!

EDTA Titrations for Divalent Metal Ions



EDTA works with many metal ions

EDTA/Ca²⁺ Titration

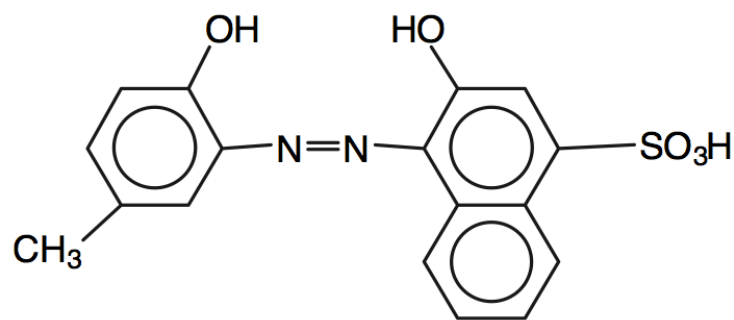


pCa

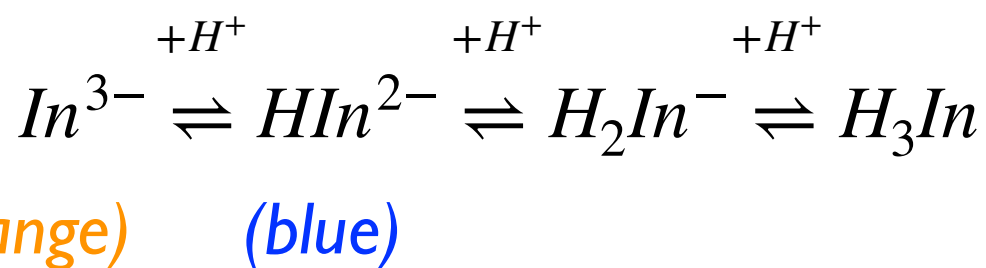
pCa can be measured at the equivalence point.

Sadly, we cannot measure pCa or pMg directly in our M3LC lab. 😞

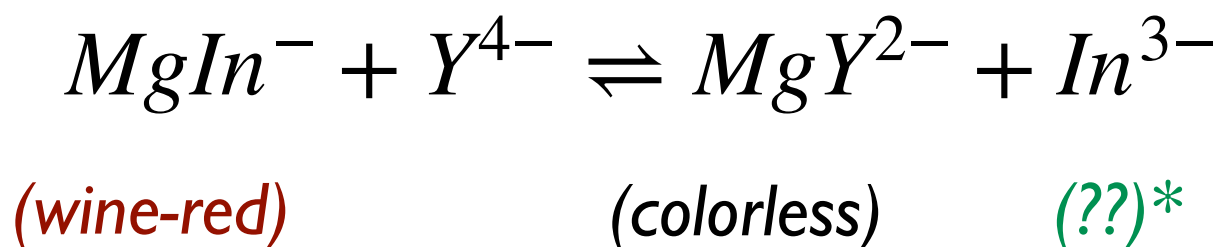
We must use an indicator to detect the endpoint of the EDTA titration



Calmagite (H_3In)



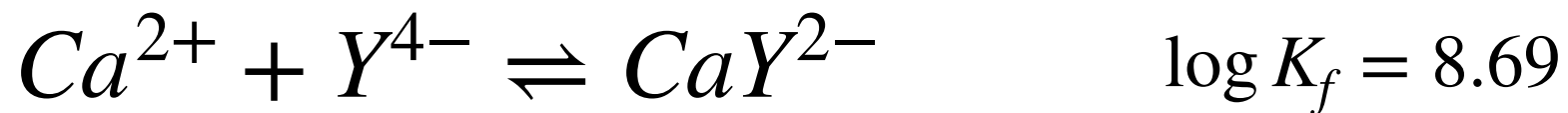
EDTA will displace weaker ligands – you will use this process with calmagite to determine the endpoint of an EDTA titration for Mg^{2+}



*what you see will depend on pH

Ca-EDTA Titration - Equivalence Point Calculation

Ca-EDTA Titration: You would like to perform a titration of 50.00 mL of a 1.00×10^{-4} M Ca^{2+} solution with a 1.00×10^{-4} M EDTA solution. Both solutions are buffered to a pH of 10.0. The alpha fraction for Y^{4-} is 0.355 at a pH of 10.0.



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

Ca-EDTA Titration - Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4} \text{ M}$ Ca^{2+} solution with a $1.00 \times 10^{-4} \text{ M}$ EDTA solution.



Total moles of $\text{Ca}^{2+} = (10^{-4}\text{M})(0.050\text{L}) = 5 \times 10^{-6}$ moles

Equivalence point volume = 0.100L

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

We first assume a stoichiometric reaction.

Ca-EDTA Titration - Equivalence Point Calculation

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



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

We then assume that a little bit of free Ca^{2+} is formed as required by K_f .

$$K_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$$

Ca-EDTA Titration - Equivalence Point Calculation

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



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

We then assume that a little bit of free Ca^{2+} is formed as required by K_f .

$$K_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$$

For every free Ca^{2+} , there is a free EDTA species

$$[\text{Ca}^{2+}] = C_{\text{EDTA}}^{\text{tot}}$$

Ca-EDTA Titration - Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4} \text{ M}$ Ca^{2+} solution with a $1.00 \times 10^{-4} \text{ M}$ EDTA solution.



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

We then assume that a little bit of free Ca^{2+} is formed as required by K_f .

$$K_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$$

For every free Ca^{2+} , there is a free EDTA species

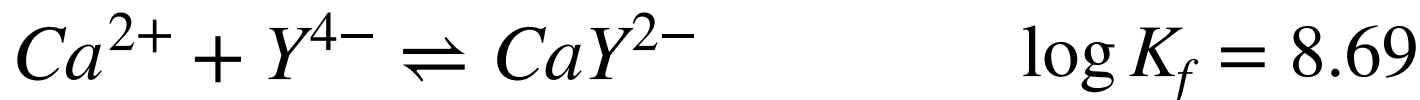
$$[\text{Ca}^{2+}] = C_{\text{EDTA}}^{\text{tot}}$$

$[\text{Y}^{4-}]$ is obtained using the alpha fraction.

$$[\text{Y}^{4-}] = \alpha_{\text{Y}^{4-}} C_{\text{EDTA}}^{\text{tot}} = \alpha_{\text{Y}^{4-}} [\text{Ca}^{2+}]$$

Ca-EDTA Titration - Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4} \text{ M}$ Ca^{2+} solution with a $1.00 \times 10^{-4} \text{ M}$ EDTA solution.



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

We then assume that a little bit of free Ca^{2+} is formed as required by K_f .

$$K_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$$

For every free Ca^{2+} , there is a free EDTA species

$$[\text{Ca}^{2+}] = C_{\text{EDTA}}^{\text{tot}}$$

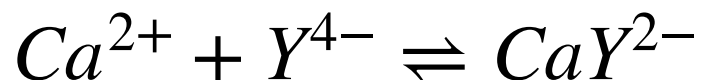
$[\text{Y}^{4-}]$ is obtained using the alpha fraction.

$$[\text{Y}^{4-}] = \alpha_{\text{Y}^{4-}} C_{\text{EDTA}}^{\text{tot}} = \alpha_{\text{Y}^{4-}} [\text{Ca}^{2+}]$$

insert and then solve for $[\text{Ca}^{2+}]$

Ca-EDTA Titration - Equivalence Point Calculation

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



$$\log K_f = 8.69$$

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

$$\text{@ pH} = 10$$

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

At the equivalence point:

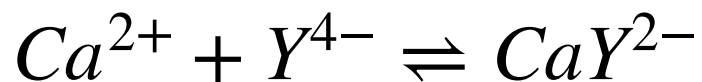
$$[\text{Ca}^{2+}] = \sqrt{\frac{[\text{CaY}^{2-}]}{\alpha_{\text{Y}^{4-}} K_f}}$$

$$\alpha_{\text{Y}^{4-}} K_f = K'_f$$

“conditional formation constant”
depends on pH

Ca-EDTA Titration - Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4} \text{ M}$ Ca^{2+} solution with a $1.00 \times 10^{-4} \text{ M}$ EDTA solution.



$$\log K_f = 8.69$$

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

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

At the equivalence point:

$$[\text{Ca}^{2+}] = \sqrt{\frac{[\text{CaY}^{2-}]}{\alpha_{\text{Y}^{4-}} K_f}} = 5.36 \times 10^{-7} \text{ M}$$

Diagram annotations for the equation above:
- An arrow points from 5.0×10^{-5} to the numerator $[\text{CaY}^{2-}]$.
- An arrow points from 0.355 to the denominator $\alpha_{\text{Y}^{4-}}$.
- An arrow points from $10^{8.69}$ to the denominator K_f .

$$p\text{Ca} = 6.27$$

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

At the Equivalence Point:

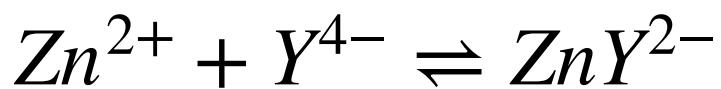
- a) How much total free* Zn is left in solution?
- b) What is the Zn^{2+} concentration?

* “total free Zn” means all Zn^{2+} not in the ZnY^{2-} complex

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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



$$\log K_f = 16.5$$

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

At pH=10:

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

At $[NH_3] = 0.0846M$:

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

Note that $\alpha_{Zn^{2+}}$ is a complexation alpha fraction!

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

We first assume a stoichiometric reaction:

$$\text{Total moles of Zinc} = 5.0 \times 10^{-6} \text{ moles}$$

$$\text{Equivalence point volume} = 0.100\text{L}$$

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

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

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

a) How much total free* Zn is left in solution at the eq. pt.?

* “total free Zn” means all Zn^{2+} not in the ZnY^{2-} complex, C_{Zn}^{tot}

$$C_{Zn}^{tot} = [Zn^{2+}] + [ZnNH_3^{2+}] + [Zn(NH_3)_2^{2+}] + [Zn(NH_3)_3^{2+}] + [Zn(NH_3)_4^{2+}]$$

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

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

a) How much total free Zn is left in solution at the eq. pt.?

@ eq. pt: $C_{Zn}^{tot} = C_{EDTA}^{tot}$

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

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

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

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

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

a) How much total free Zn is left in solution at the eq. pt.?

@ eq. pt: $C_{Zn}^{tot} = C_{EDTA}^{tot}$

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

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

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

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

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

a) How much total free Zn is left in solution?

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

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

or 0.0166%

$\alpha_{Zn^{2+}}\alpha_{Y^{4-}}K_f = K_f''$ “double conditional formation constant”

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

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

b) What is the Zn^{2+} concentration?

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

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

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

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

b) What is the Zn^{2+} concentration?

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

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

1.61×10^{-5}

$1.66 \times 10^{-8} \text{ M}$

Zinc-EDTA Titration Equivalence Point Calculation (with ammonia buffer)

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.

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

$$\log K_f = 16.5$$

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

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

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

b) What is the Zn^{2+} concentration?

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

$$[Zn^{2+}] = 2.67 \times 10^{-13} \text{ M}$$

$$pZn = 12.6$$