Seawater Analysis Project

Major ionic species in seawater

Ion	Pacific Ocean Water Concentrations / mg L^{-1} CRC values [a]
Na^+	1.05×10^4
K^+	3.80×10^2
Mg^{2+}	1.35×10^3
Ca^{2+}	4.00×10^2
Cl^-	1.90×10^4
SO_4^{2-}	2.65×10^3
Br^-	6.5×10^1

[a] CRC Handbook of Chemistry and Physics, 61st ed.

Concentrations

Cl^- - 536 mM

Na^+ - 457 mM

Mg^{2+} - 56.3 mM

SO_4^{2-} - 27.6 mM

Ca^{2+} - 10.0 mM

K^+ - 9.74 mM

Br^- - 0.823 mM

We will measure six of the top seven ions in sea water!

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R. Corn

Seawater Analysis Project

Concentrations	Relative molar amounts
Cl^- - 536 mM	1000
Na^+ - 457 mM	853
Mg^{2+} - 56.3 mM	105
SO_4^{2-} - 27.6 mM	51.5
Ca^{2+} - 10.0 mM	18.7
K^+ - 9.74 mM	18.2
Br^- - 0.823 mM	1.54

Chemists use molarity!

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SO_4^{2-}	1. Turbidity Measurements for Sulfate
K^+	2. Turbidity Measurements for Potassium
Mg^{2+}	3. Magnesium Complexometric Fluorometry
Mg^{2+} Ca^{2+}	4. EDTA titrations for Magnesium and Calcium
Cl^-	5. AgCl Precipitation titration for Chloride
Br^-	6. Bromide Oxidation and Colorimetric Detection

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Precipitation Reactions:	Detection Methods
$AgCl(s)$	Precipitation Titration
$BaSO_4(s)$	Turbidity
$(C_6H_5)4BK$	Turbidity

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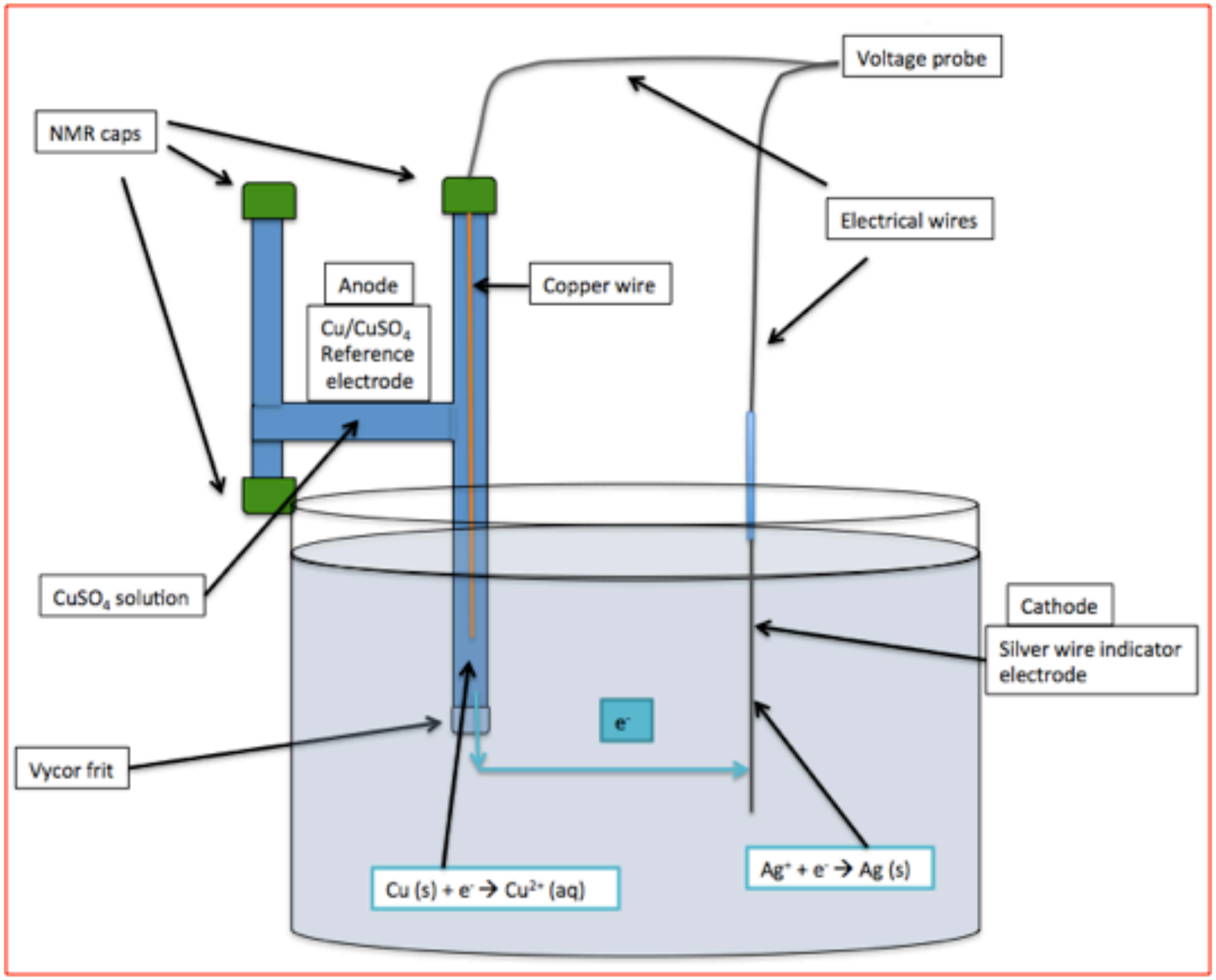
Potentiometric Titration of Chloride



$$Ag^+(aq) + Cl^-(aq) \leftrightharpoons AgCl(s)$$

R. Corn
Chem M3LC
Fall 2013

Potentiometric Titration of Chloride

In this experiment, silver ions will be added to a chloride solution. As Ag^+ is added to the Cl^-, AgCl will form as follows:

$$Ag^+ (aq) + Cl^- (aq) \rightleftharpoons AgCl (s)$$

This equation illustrates the solubility equilibrium of silver chloride. Solubility equilibrium exists when a solid compound is in equilibrium with the dissolved ions of that compound. The corresponding solubility constant of AgCl is:

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

The equilibrium constant, K_T, of the titration is:

$$K_T = \frac{1}{[Ag^+][Cl^-]} = \frac{1}{K_{sp}} = \frac{1}{1.8 \times 10^{-10}} \gg 1$$

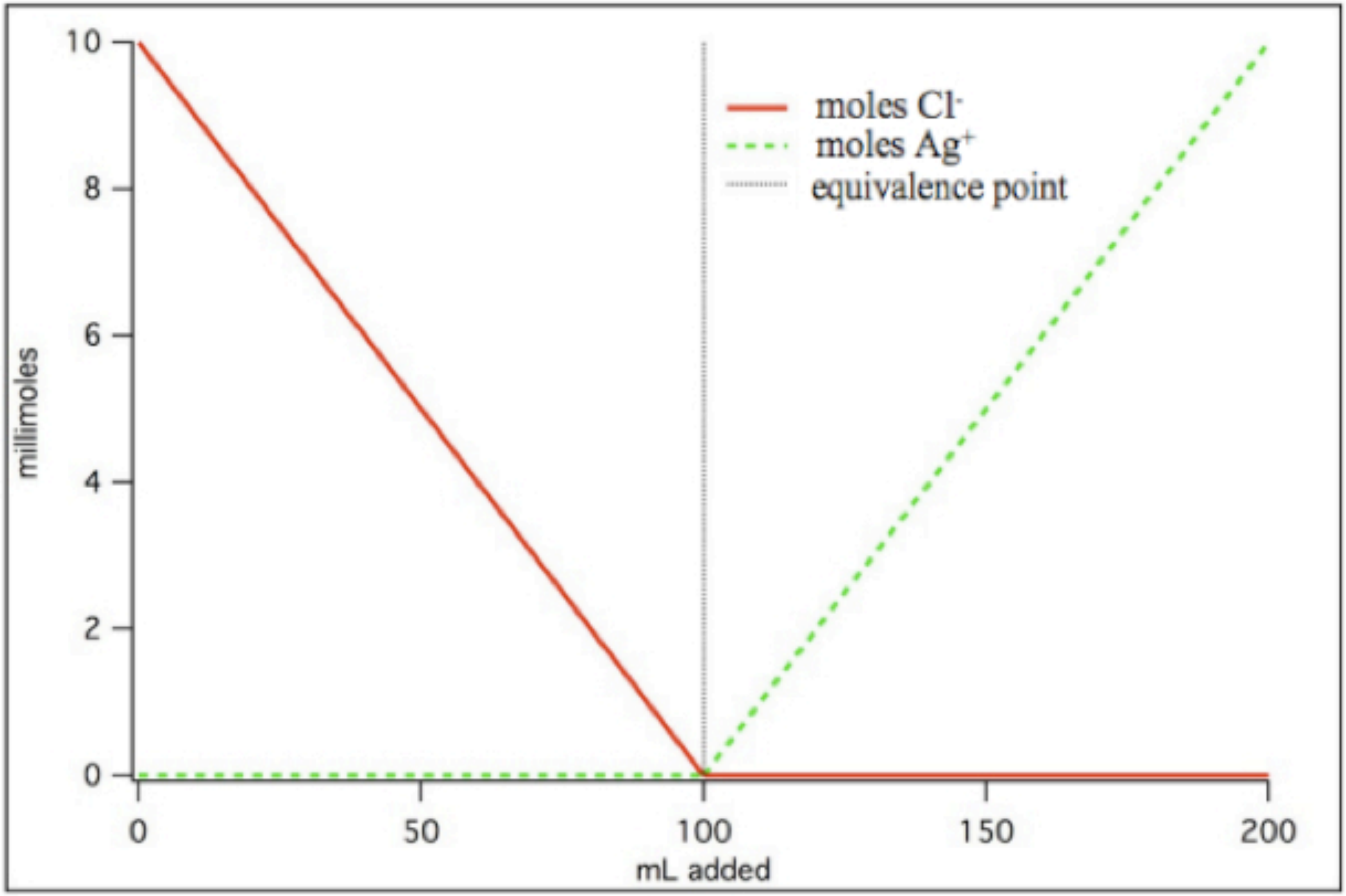
As the titration proceeds, the number of moles of chloride decreases.

At the equivalence point, the number of moles of Ag^+ *added* is equal to the number of moles of Cl^- present *initially*.

We will use Electrochemistry to determine the equivalence point.

Potentiometric Titration of Chloride

$$Ag^{+}(aq) + Cl^{-}(aq) \leftrightharpoons AgCl(s)$$



Ag^{+} solution is added to react with Cl^{-}

We will use Electrochemistry to determine the equivalence point.

Potentiometric Titration of Chloride

Electrochemical cell

In this experiment, a $Cu/CuSO_4$ **reference electrode** will be used in conjunction with a silver wire **indicator electrode**. The oxidation of copper takes place at the anode while the reduction of silver takes place at the cathode. See the Figure for an illustration of the electrochemical cell.

The balanced electrochemical reaction is as follows:

$$Cu^{o}(s) + 2Ag^{+}(aq) \rightarrow 2Ag^{o}(s) + Cu^{2+}(aq)$$

The line notation for the cell is:

$$Cu(s)\,|\,Cu^{2+}(0.100\ M)\,||\,Ag^{+}(x\ M)\,|\,Ag(s)$$

The overall standard electrochemical potential, E^{o}_{cell} is:

$$E^{0}_{cell} = E^{0}_{Ag} - E^{0}_{Cu}$$

We use the Nernst Equation to calculate the standard cell potential.

Potentiometric Titration of Chloride

$$Cu(s)\,|\,Cu^{2+}(0.100\ M)\,||\,Ag^{+}(x\ M)\,|\,Ag(s)$$

Silver is being reduced:

$$Ag^{+} + e^{-} \rightarrow Ag(s)$$

$$E_{Ag} = E^{0}_{Ag} - \frac{.0592}{1}\log\left(\frac{1}{[Ag^{+}]}\right)$$

Copper is being oxidized:

$$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$$

*Note: we still use reduction reaction to calculate E_{Cu}

$$E_{Cu} = E^{0}_{Cu} - \frac{.0592}{2}\log\left(\frac{1}{[Cu^{2+}]}\right)$$

$$E_{cell} = E_{Red} - E_{Ox} = E_{Ag} - E_{Cu}$$

E_{Cu} is constant during the titration

Potentiometric Titration of Chloride

We measure pAg during the titration with potentiometry:

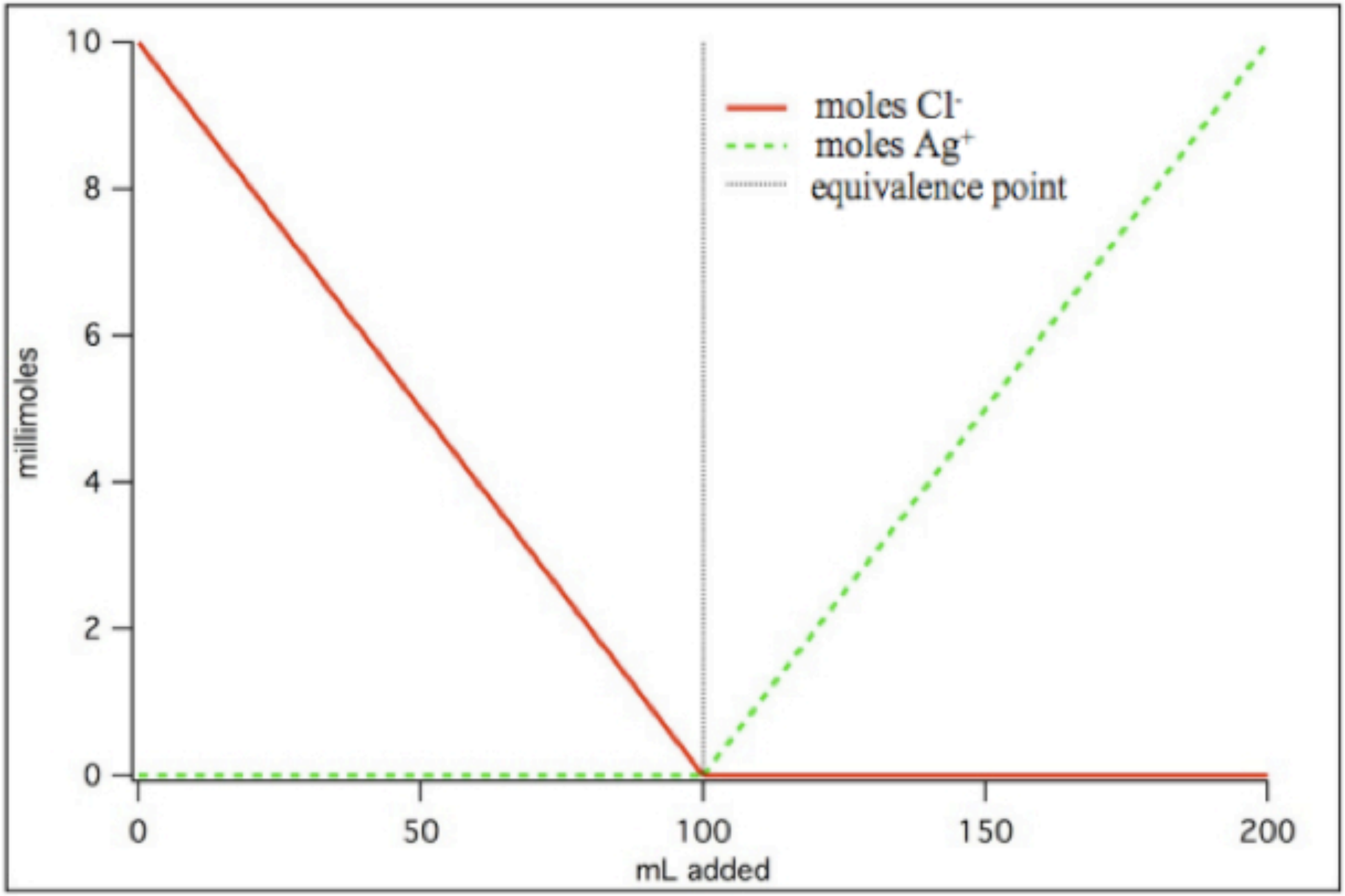
pAg = - log [Ag^+]

$$E_{cell} = E_{Ag} - E_{Cu}$$

$$E_{cell} = A + B \times pAg$$

A and B are constants

Potentiometric Titration of Chloride



Ag^+ solution is added to react with Cl^-

Potentiometric Titration of Chloride

At the equivalence point, $[Ag^+]$ and $[Cl^-]$ are almost zero, but not quite!

At the eq. pt:

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Ag^+] = [Cl^-]$$

$$[Ag^+] = (K_{sp})^{1/2}$$

$pAg = ??$

Potentiometric Titration of Chloride

At the equivalence point, $[Ag^+]$ and $[Cl^-]$ are almost zero, but not quite!

At the eq. pt:

$$K_{sp} = [Ag^+][Cl^-]$$

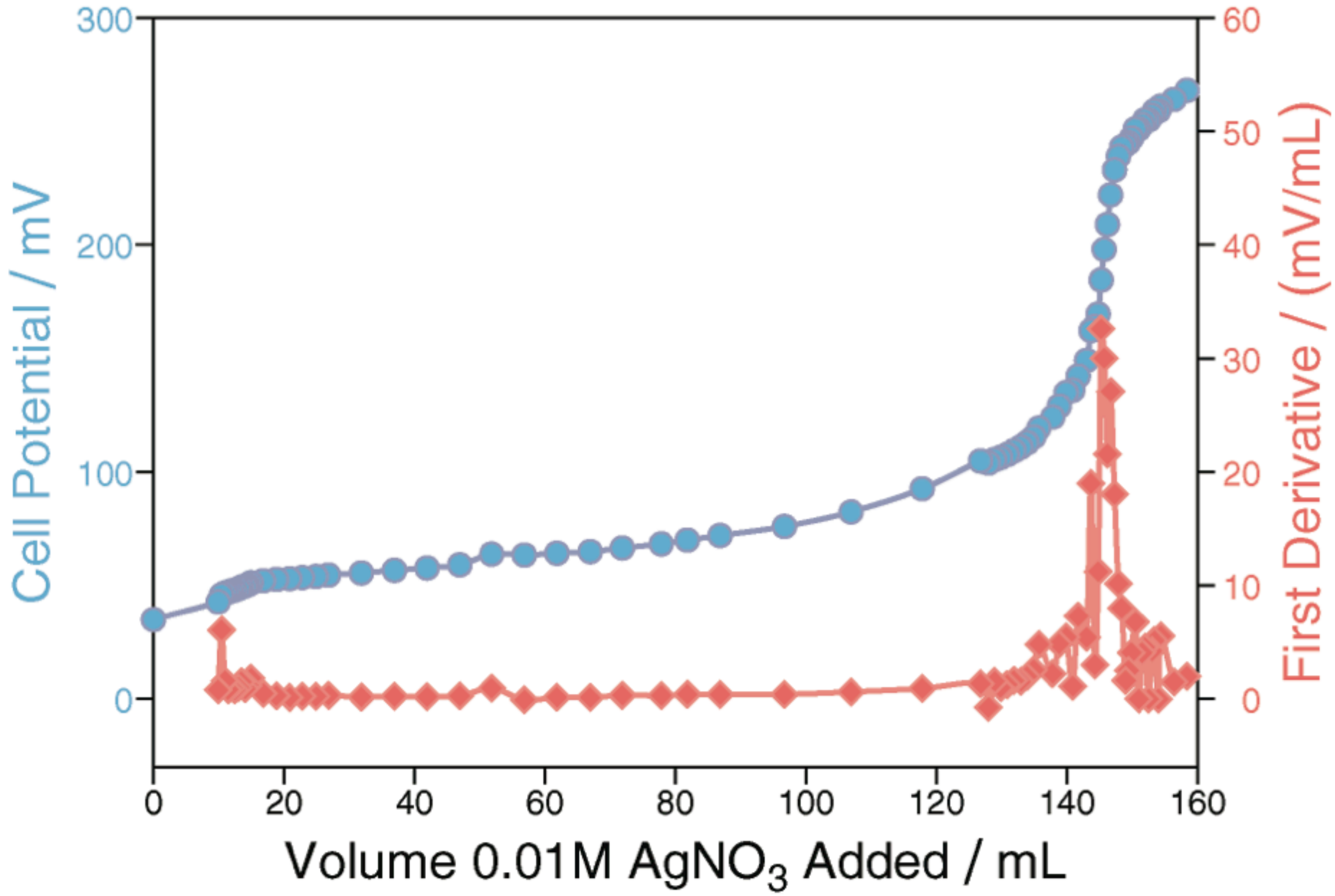
$$[Ag^+] = [Cl^-]$$

$$[Ag^+] = (K_{sp})^{1/2}$$

$$K_{sp} = 1.8 \times 10^{-10}$$

$$pAg = 4.87$$

Potentiometric Titration of Chloride



Example of Potentiometric Titration Data

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

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

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

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

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^{-} \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^{-} \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

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

$$[OH^{-}] = \sqrt{\frac{K_{sp1}}{[Zn^{2+}]}} = \sqrt{\frac{3 \times 10^{-16}}{10^{-3}}} = 5.48 \times 10^{-7} M$$

pOH = 6.26
pH = 7.74

Zinc Hydroxide begins to precipitate at pH = 7.74

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

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

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

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

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

pOH = 4.76
pH = 9.24

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

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

$$[Mg^{2+}] = 1.00 \times 10^{-3} M \qquad K_{sp2} = [Mg^{2+}][OH^-]^2$$

Zinc vs. Magnesium Hydroxide Precipitation Separation

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+} + 2OH^- \qquad K_{sp1} = 3 \times 10^{-16}$$

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp2} = 7.1 \times 10^{-12}$$

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

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

$$[Mg^{2+}] = 1.00 \times 10^{-3} M \qquad K_{sp2} = [Mg^{2+}][OH^-]^2$$

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

pOH = 4.07
pH = 9.93

Magnesium Hydroxide begin to precipitate at pH = 9.93

We can separate Zinc and Magnesium!

Diprotic Weak Acids: Sulfuric Acid and Hydrogen Sulfide

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad K_1 = \infty$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad pK_2 = 1.99$$

$$\boxed{BaSO_4(s) \quad K_{sp} = 1.1 \times 10^{-10}}$$

$$H_2S \rightleftharpoons H^+ + HS^- \qquad pK_1 = 7.02$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad pK_2 = 13.89$$

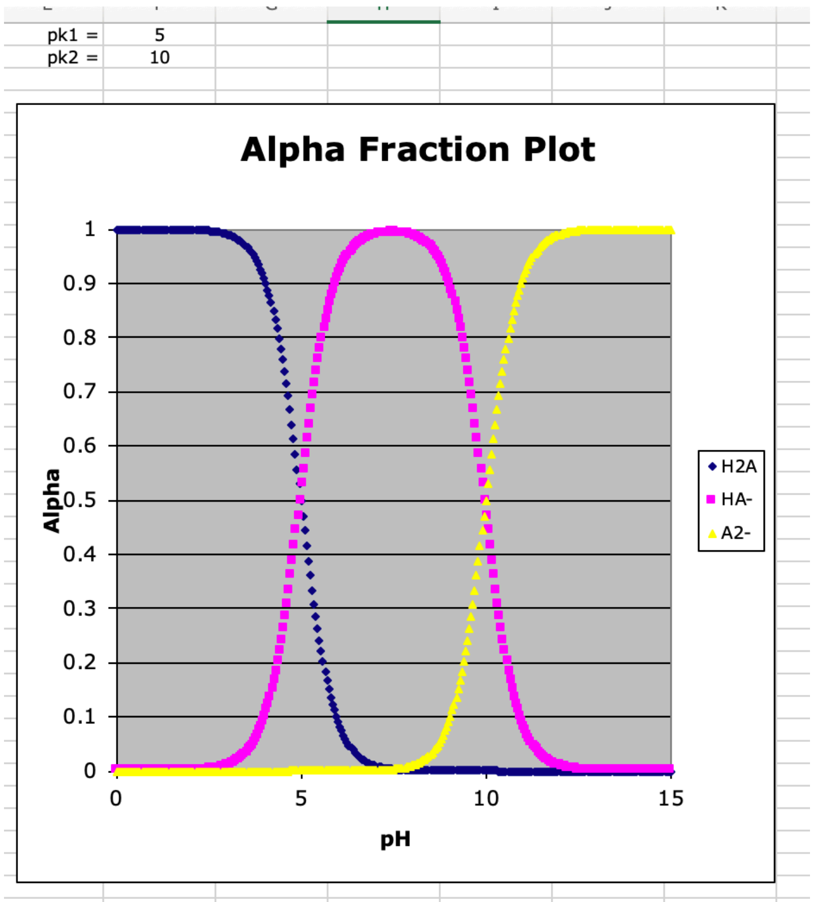
$$\boxed{CdS(s) \quad K_{sp} = 1.0 \times 10^{-27}}$$

Diprotic Weak Acids: Alpha Fractions

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_1$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_2$$

$$K_1 \gg K_2$$



Diprotic Weak Acid

Constants: K1, K2, Kw, Ctot

Five species: [H2A], [HA-], [A2-], [H+], [OH-]

K1 = [H+][HA-]/[H2A]	acid dissociation 1
K2 = [H+][A2-]/[HA-]	acid dissociation 2
Kw = [H+][OH-]	water dissociation
[H+] = [HA-]+ 2[A2-] + [OH-]	charge balance
Ctot = [H2A] + [HA-] + [A2-]	mass balance

Alpha Fractions

$$\alpha_{H_2A} = \frac{1}{1 + \frac{K_1}{[H+]} + \frac{K_1K_2}{[H+]^2}}$$

$$\alpha_{HA^-} = \frac{1}{\frac{[H+]}{K_1} + 1 + \frac{K_2}{[H+]}}$$

$$\alpha_{A^{2-}} = \frac{1}{1 + \frac{[H+]}{K_2} + \frac{[H+]^2}{K_1K_2}}$$

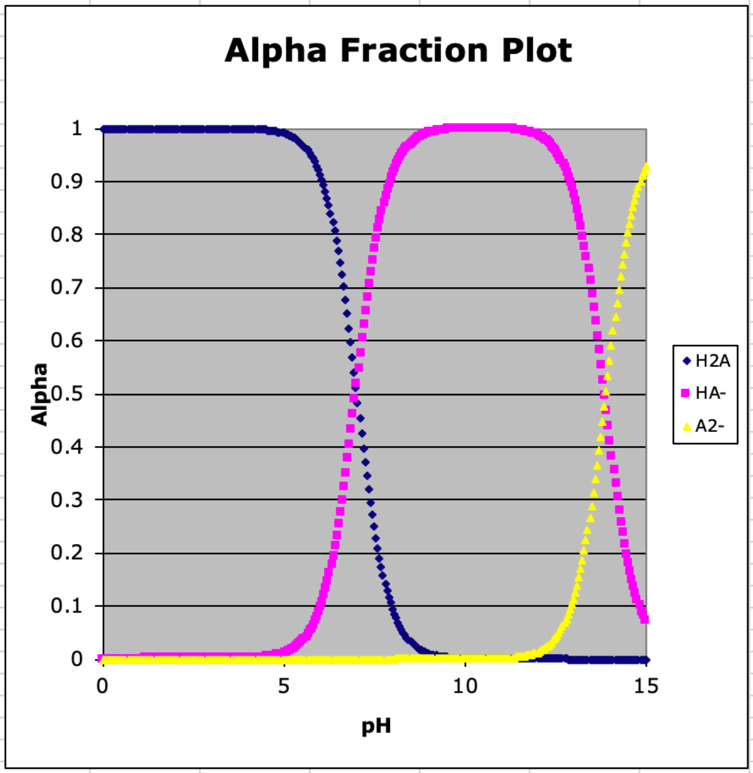
Diprotic Weak Acids: Alpha Fractions and Exact Solutions

$$H_2S \rightleftharpoons H^+ + HS^- \qquad K_1$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_2$$

$$pK_1 = 7.02 \qquad pK_2 = 13.89$$

	pk1 =	7.02
	pk2 =	13.89



Alpha Fractions

$$\alpha_{H_2S} = \frac{1}{1 + \frac{K_1}{[H+]} + \frac{K_1K_2}{[H+]^2}}$$

$$\alpha_{SH^-} = \frac{1}{\frac{[H+]}{K_1} + 1 + \frac{K_2}{[H+]}}$$

$$\alpha_{S^{2-}} = \frac{1}{1 + \frac{[H+]}{K_2} + \frac{[H+]^2}{K_1K_2}}$$

$$pH = 13.89 \qquad \alpha_{S^{2-}} = 0.5$$

$$pH = 7.02 \qquad \alpha_{S^{2-}} = 1.28 \times 10^{-4}$$

Diprotic Weak Acid: Sulfuric Acid

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad K_1 = \infty$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad pK_2 = 1.99$$

Can be considered a monoprotic acid

What is the equilibrium concentration of sulfate in a solution with a total sulfuric acid concentration of 0.200 M and a pH of 1?

$$\alpha_{SO_4^{2-}} = \frac{1}{1 + \frac{[H+]}{K_2}} = \frac{1}{1 + \frac{10^{-1}}{10^{-1.99}}} = 9.28 \times 10^{-2}$$

$$[SO_4^{2-}] = C_{sulfate}^{tot} \alpha_{SO_4^{2-}} = (0.1)(9.28 \times 10^{-2}) = 9.28 \times 10^{-3}\ M$$

Diprotic Weak Acids: Sulfuric Acid and Hydrogen Sulfide

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad K_1 = \infty$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad pK_2 = 1.99$$

$$\boxed{BaSO_4(s) \quad K_{sp} = 1.1 \times 10^{-10}}$$

$$H_2S \rightleftharpoons H^+ + HS^- \qquad pK_1 = 7.02$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad pK_2 = 13.89$$

$$\boxed{CdS(s) \quad K_{sp} = 1.0 \times 10^{-27}}$$

Cadmium Sulfide Precipitation Reaction - pH Dependence

$$CdS(s) \rightarrow Cd^{2+} + S^{2-}$$

$$K_{sp} = 1.0 \times 10^{-27}$$

$$[Cd^{2+}] = C_{sulfide}^{tot} = \frac{[S^{2-}]}{\alpha_{S^{2-}}}$$

total Cd = total S

$$[S^{2-}] = \alpha_{S^{2-}}[Cd^{2+}]$$

$$K_{sp} = [Cd^{2+}][S^{2-}]$$

$$\boxed{[Cd^{2+}] = \sqrt{\frac{K_{sp}}{\alpha_{S^{2-}}}}}$$

$$\alpha_{S^{2-}} = \frac{1}{1 + \frac{[H+]}{K_2} + \frac{[H+]^2}{K_1 K_2}}$$

$$pK_1 = 7.02$$

$$pK_2 = 13.89$$

Cadmium Sulfide Precipitation Reaction - pH Dependence

$$CdS(s) \rightarrow Cd^{2+} + S^{2-} \qquad K_{sp} = 1.0 \times 10^{-27}$$

$$[Cd^{2+}] = \sqrt{\frac{K_{sp}}{\alpha_{S^{2-}}}} \qquad \alpha_{S^{2-}} = \frac{1}{1 + \frac{[H+]}{K_2} + \frac{[H+]^2}{K_1K_2}}$$

$$pK_1 = 7.02$$

$$pK_2 = 13.89$$

$pH = 3$ $\qquad \alpha_{S^{2-}} = 1.42 \times 10^{-15}$ $\qquad [Cd^{2+}] = 8.39 \times 10^{-7}\ M$

$pH = 7.0$ $\qquad \alpha_{S^{2-}} = 1.28 \times 10^{-4}$ $\qquad [Cd^{2+}] = 1.26 \times 10^{-10}\ M$

$pH = 10.0$ $\qquad \alpha_{S^{2-}} = 6.30 \times 10^{-8}$ $\qquad [Cd^{2+}] = 2.80 \times 10^{-12}\ M$

Barium Sulfate Precipitation Reaction - pH Dependence

$$BaSO_4(s) \rightarrow Ba^{2+} + SO_4^{2-} \qquad K_{sp} = 1.1 \times 10^{-10}$$

$$[Ba^{2+}] = C_{sulfate}^{tot} = \frac{[SO_4^{2-}]}{\alpha_{SO_4^{2-}}}$$

total Ba^{2+} = total sulfate

$$[SO_4^{2-}] = \alpha_{SO_4^{2-}}[Ba^{2+}]$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$\boxed{[Ba^{2+}] = \sqrt{\frac{K_{sp}}{\alpha_{SO_4^{2-}}}}}$$

$$\alpha_{SO_4^{2-}} = \frac{1}{1 + \frac{[H+]}{K_2} + \frac{[H+]^2}{K_1 K_2}} \approx \frac{1}{1 + \frac{[H+]}{K_2}}$$

$$K_1 = \infty$$

$$pK_2 = 1.99$$

Barium Sulfate Precipitation Reaction - pH Dependence

$$BaSO_4(s) \rightarrow Ba^{2+} + SO_4^{2-} \qquad K_{sp} = 1.1 \times 10^{-10}$$

$$[Ba^{2+}] = \sqrt{\frac{K_{sp}}{\alpha_{SO_4^{2-}}}} \qquad \alpha_{SO_4^{2-}} \approx \frac{1}{1 + \frac{[H+]}{K_2}} \qquad pK_2 = 1.99$$

$$@\, pH = 1 \qquad \alpha_{SO_4^{2-}} = 9.28 \times 10^{-2}$$

$$[Ba^{2+}] = 3.44 \times 10^{-5}\ M$$

Diprotic Weak Acids: Alpha Fractions and Exact Solutions

Exact Solution:

Iterative eqns for [H+]

[H+][HA-] = K1[H2A]

[H+]([H+] - [OH-] – 2[A2-]) = K1[H2A]

[H+]^2 -2[H+][A2-] - Kw = K1[H2A]

[H+]^2 = K1[H2A] + 2K2[HA-] + Kw

Initial Guess: [H+] = sqrt (K1*Ctot + Kw)

Calculate [H2A], [HA-], [A2-]

[H+] = sqrt(K1[H2A] + 2K2[HA-] + Kw)

Approximate Solutions:

H_2A solution

$$[H^+] = \sqrt{K_1 C^{tot}}$$

(Ignore K_2)

HA^- solution

$$pH = \frac{pK_1 + pK_2}{2}$$

(Ampholyte)

A^{2-} solution

$$[OH^-] = \sqrt{K_{b2} C^{tot}}$$

(Ignore K_1)