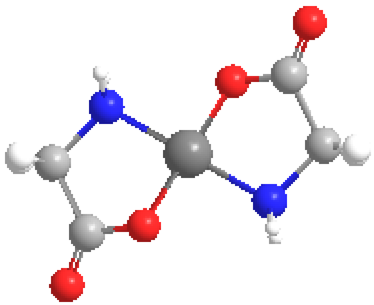
Inorganic Chemistry Laboratory

Lab 7

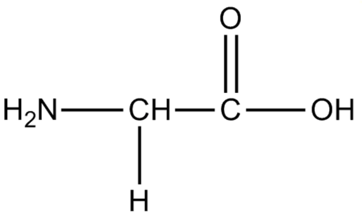
Experiment 22 (p.219)

Amino Acid Complexes: Stability constants of $Ni(glycinate)_n^{(2-n)+}$



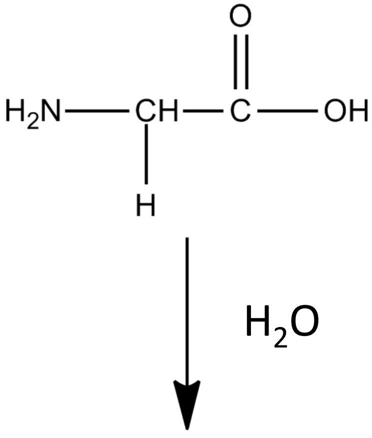
Acid-Base Chemistry of Glycine

Glycine is an example of a zwitterion.



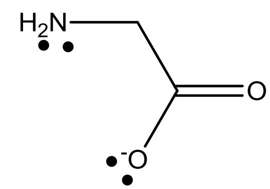
What is a zwitterion?

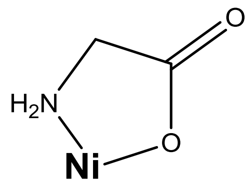
A molecule that contains a (+) and (-) electrical charge at different location within the molecule



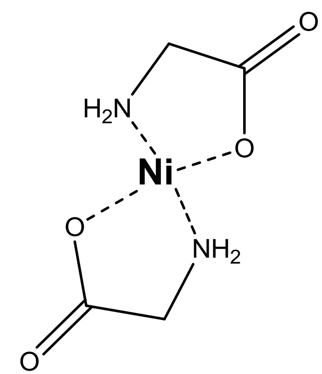
Ni^{2+}-Glycinate Interactions

How will glycinate interact with Ni^{2+}?

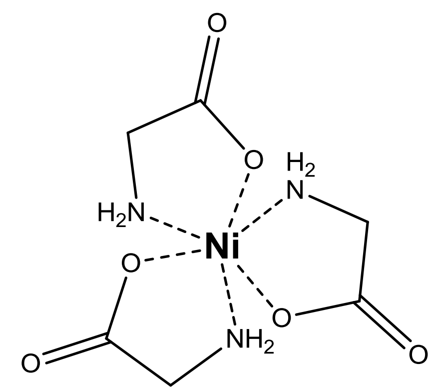




MX^{+}

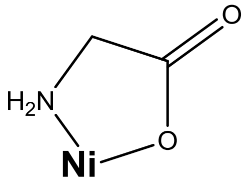


MX_2

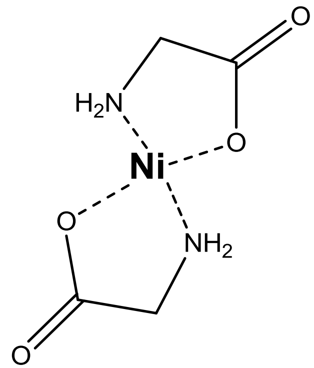


MX_3

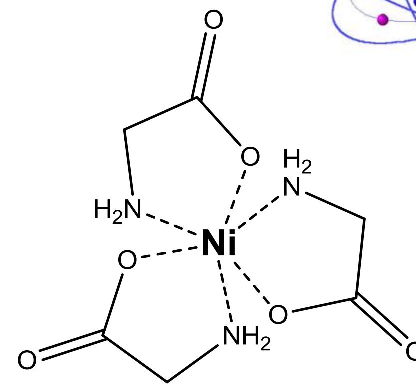
Ni^{2+}-Glycinate Interactions



MX^+

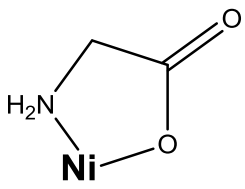


MX_2

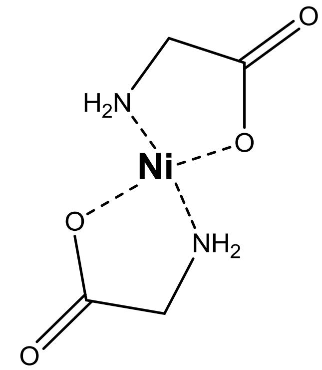


MX_3^-

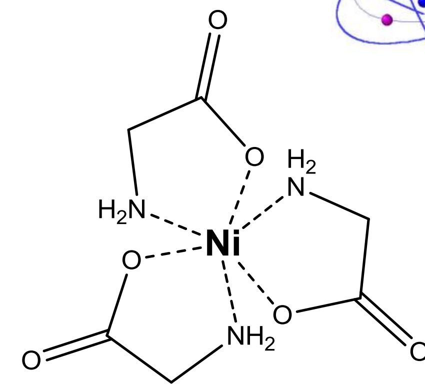
Ni^{2+}-Glycinate Interactions



MX^{+}



MX_2



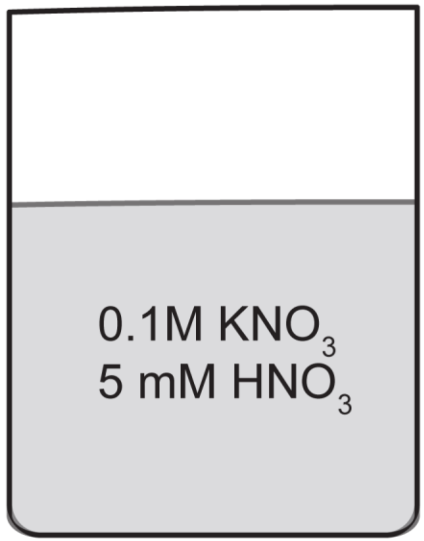
MX_3^-

$$\beta_1 = \frac{\left[MA^-\right]}{\left[M^{2+}\right]\left[A^-\right]}$$

$$\beta_2 = \frac{\left[MA_2\right]}{\left[M^{2+}\right]\left[A^-\right]^2}$$

$$\beta_3 = \frac{\left[MA_3^-\right]}{\left[M^{2+}\right]\left[A^-\right]^3}$$

Glycinate Titration

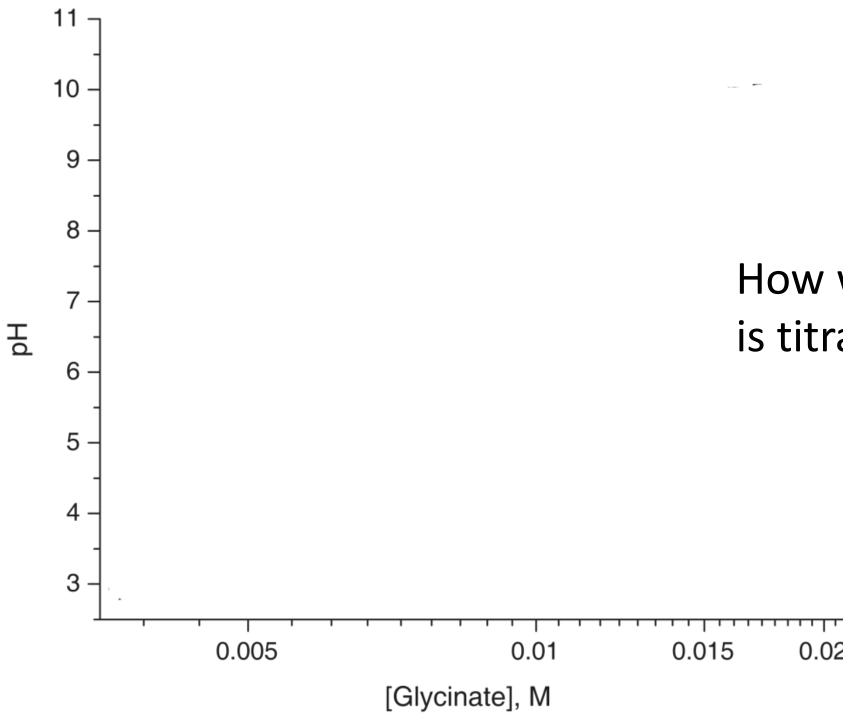


What is the pH of this solution?

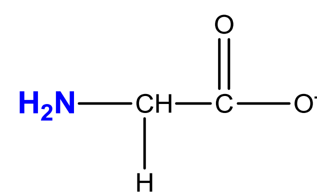
HNO_3 is a Strong Acid!

$HNO_3 \rightarrow H^+ + NO_3^-$

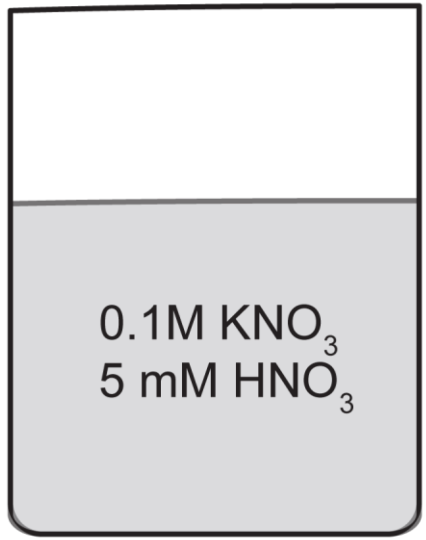
$$[H^+] = [HNO_3]$$
$$pH = -\log(0.005) = 2.3$$



How will the pH respond when glycinate is titrated into the solution?



Glycinate Titration

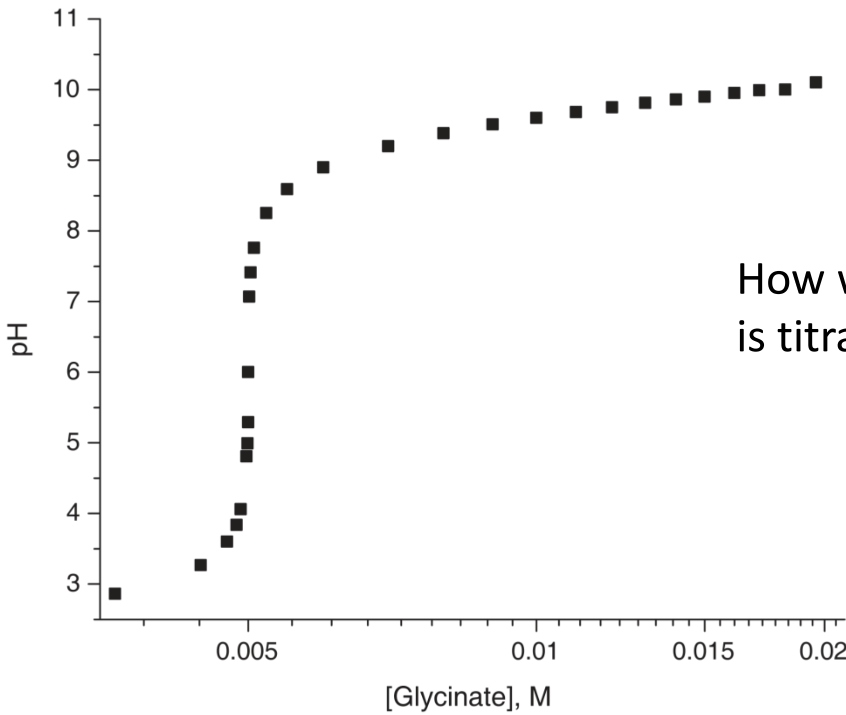


What is the pH of this solution?

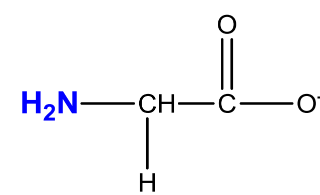
HNO$_3$ is a Strong Acid!

$HNO_3 \rightarrow H^+ + NO_3^-$

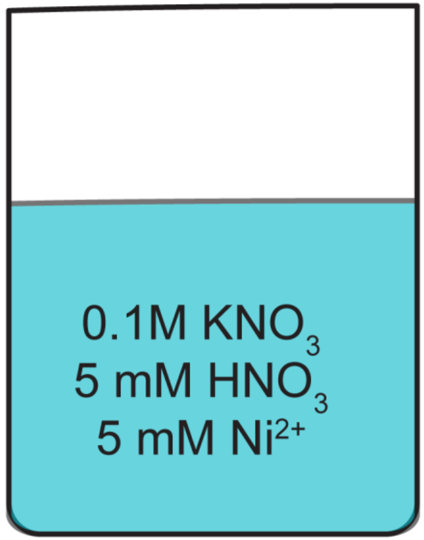
$$[H^+] = [HNO_3]$$
$$pH = -\log(0.005) = 2.3$$



How will the pH respond when glycinate is titrated into the solution?



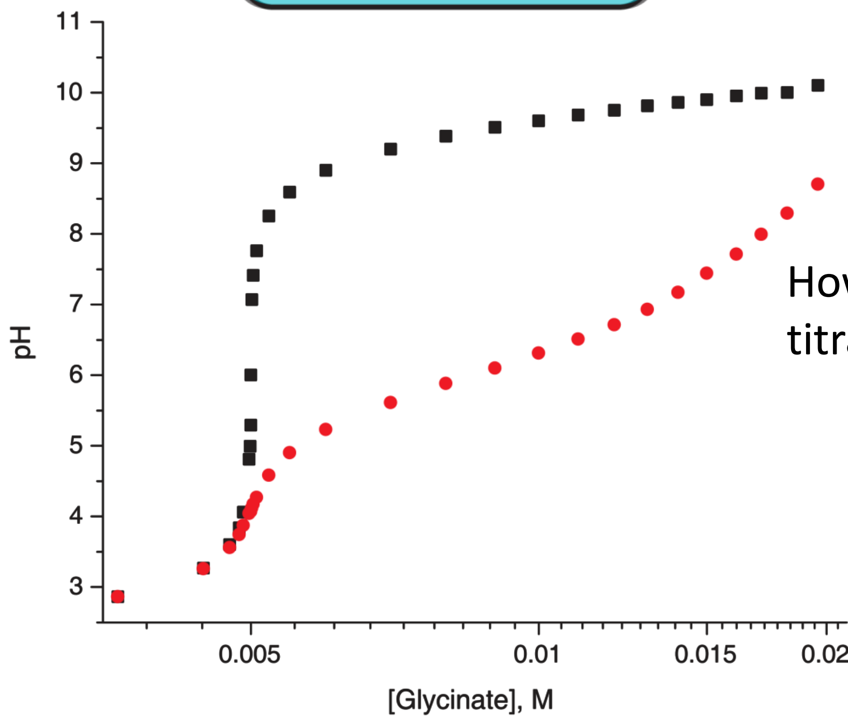
Glycinate Titration with Nickel



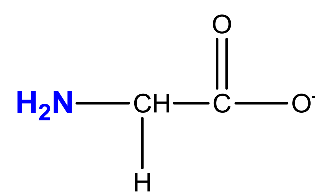
What is the pH of this solution?

HNO$_3$ is a still a Strong Acid!

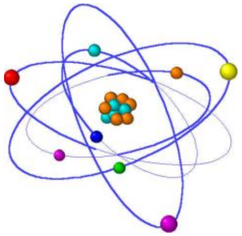
$$[H^+] = [HNO_3]$$
$$pH = -\log(0.005) = 2.3$$



How will the pH response to glycinate titration differ with Ni^{2+} in the solution?



The Effect of Ni^{2+} on pH



Consider the simple glycine (HA) dissociation reaction:

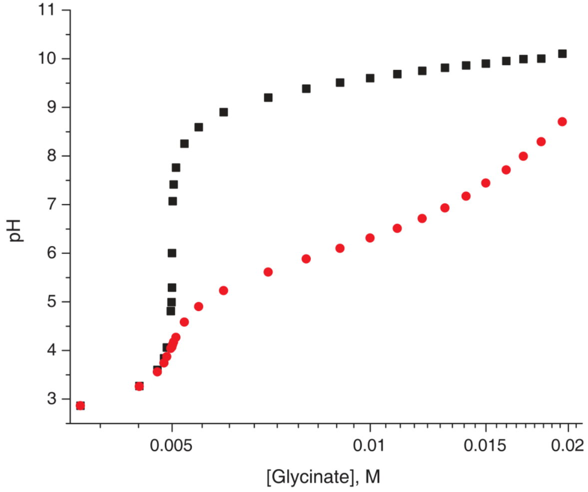
$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

A_{tot} = [A-] + [HA]

So why does Ni^{2+} influence this reaction?

Ni^{2+} preferentially binds to the base form (A^-) which alters the *apparent* K_a according to mass action (LeChatlier's Principle)



A_{tot} = [A-] + [HA] + [MA^+] + [MA_2] + [MA_3^-]

Equilibrium Theory Approach

What we know…..

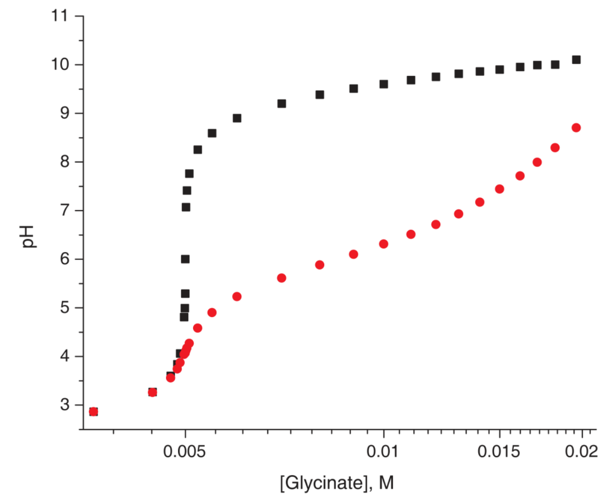
M_{tot}, H_{tot} and A_{tot} at any point in the titration

Glycinate is your titrant

$M_1V_1=M_2V_2$

pH at any point in the titration

This is what you measure



A_{tot} = [A-] + [HA] + [MA^+] + [MA_2] + [MA_3^-]

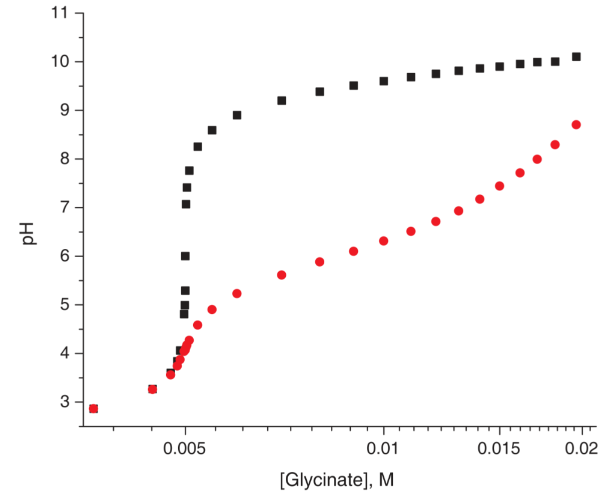
Equilibrium Expressions that describe these concentrations

$HA \rightleftharpoons H^+ + A^-$ $\quad$ $A^- + M^{2+} \rightleftharpoons MA^+$ $\quad$ $2A^- + M^{2+} \rightleftharpoons MA_2$ $\quad$ $3A^- + M^{2+} \rightleftharpoons MA_3^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} = 2.5x10^{-10} \qquad \beta_1 = \frac{[MA^-]}{[M^{2+}][A^-]} \qquad \beta_2 = \frac{[MA_2]}{[M^{2+}][A^-]^2} \qquad \beta_3 = \frac{[MA_3^-]}{[M^{2+}][A^-]^3}$$

Equilibrium Theory Approach

Fractional Saturation (ñ or θ)



The total number of ligands **bound** per metal ion

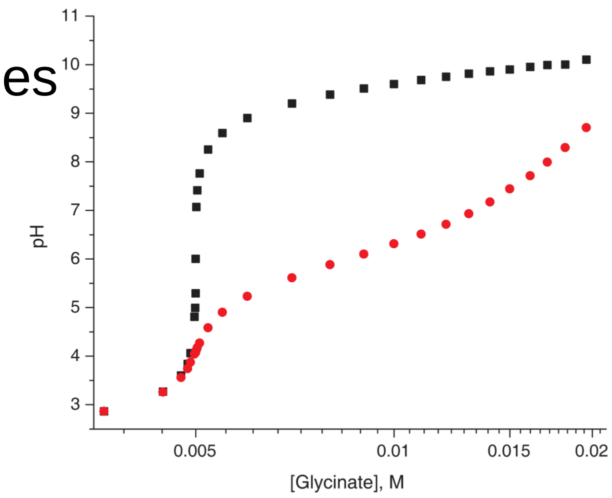
A_{tot} = [A-] + [HA] + [MA^+] + [MA_2] + [MA_3^-]

[Bound] =

$[\text{Metal}]_{\text{total}}$ =

$$\theta = \frac{[MA^-] + 2[MA_2] + 3[MA_3]}{[M^{2+}] + [MA^-] + [MA_2] + [MA_3]} \longrightarrow \theta = \frac{\beta_1[A^-] + 2\beta_2[A^-]^2 + 3\beta_3[A^-]^3}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3}$$

Equilibrium Theory Approach



Our goal is to cast θ in terms of known values

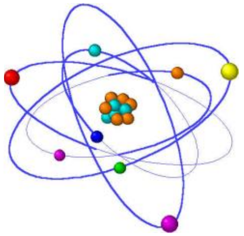
$$\theta = \frac{\beta_1[A^-] + 2\beta_2[A^-]^2 + 3\beta_3[A^-]^3}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3}$$

$$[A^-] = \frac{K_a}{[H^+]}\left(C_H + [OH^-] - [H^+]\right)$$

$C_H \rightarrow [H^+]$ from original HNO_3 solution

$$\theta = \frac{A_{tot} - \left(1 + \frac{K_a}{[H^+]}\right)\left(C_H + [OH^-] - [H^+]\right)}{M_{tot}}$$

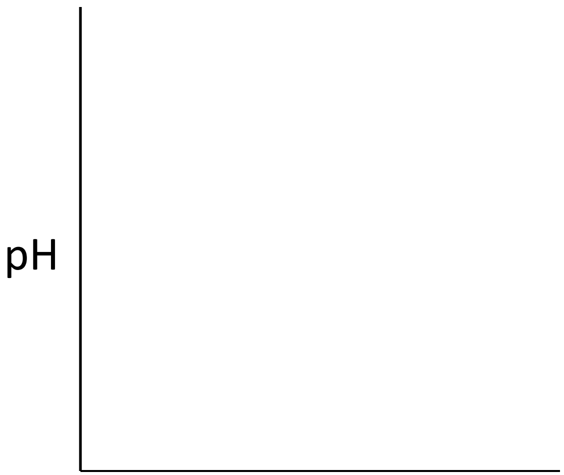
Graphical Approximation of K_n



How are pKa values approximated from a pH titration?

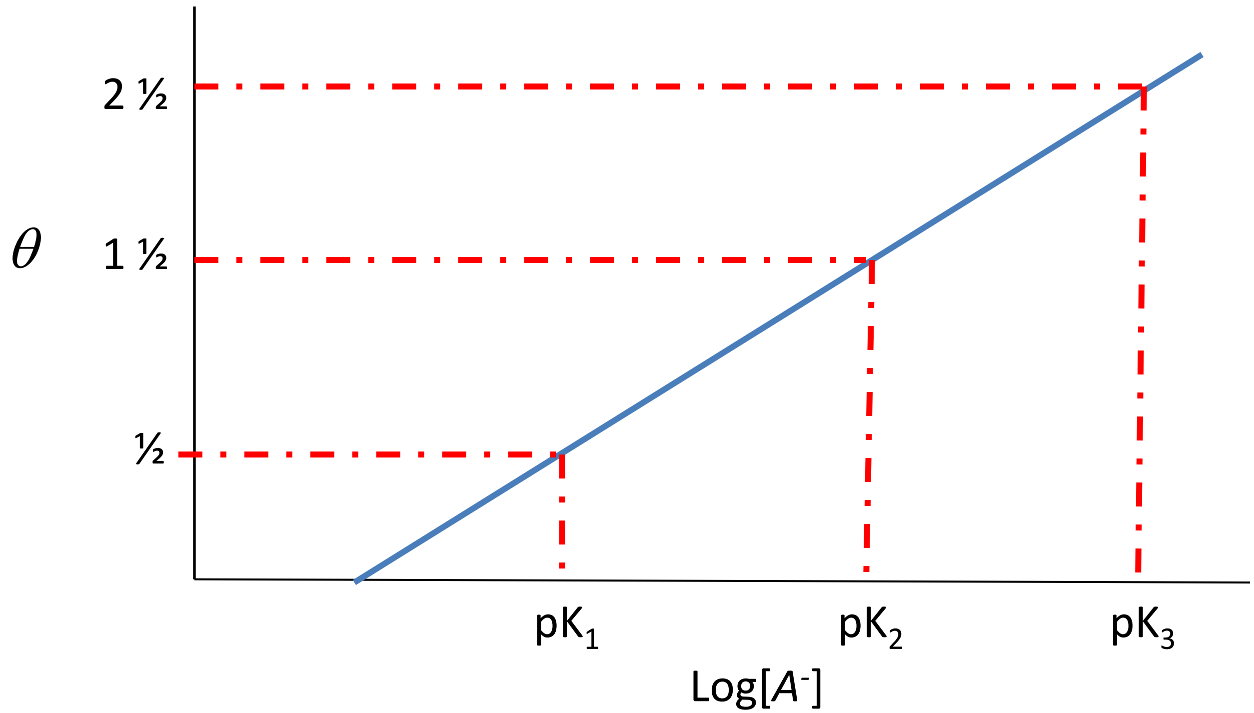
pH @ ½ Equivalence Point

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$



$$\theta = \frac{[HX]}{[X]_{tot}}$$

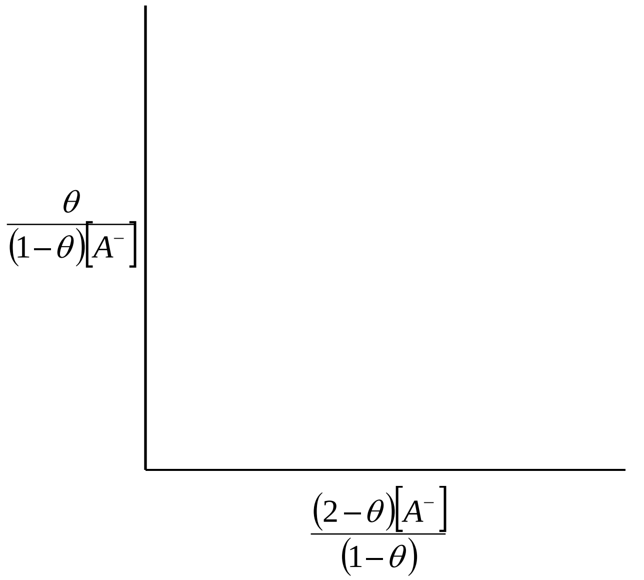
Graphical Approximation of K_n



$$pK_1 = -\log K_1$$
$$pK_2 = -\log K_2$$
$$pK_3 = -\log K_3$$

Graphical Determination of β_n

$$\theta = \frac{\beta_1[A^-] + 2\beta_2[A^-]^2 + 3\beta_3[A^-]^3}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3}$$



This expression can be rearranged to generate a less complex polynomial:

$$\frac{\theta}{(1-\theta)[A^-]} = \frac{(3-\theta)[A^-]^2}{(1-\theta)}\beta_3 + \frac{(2-\theta)[A^-]}{(1-\theta)}\beta_2 + \beta_1$$

What happens at very low [A⁻]?

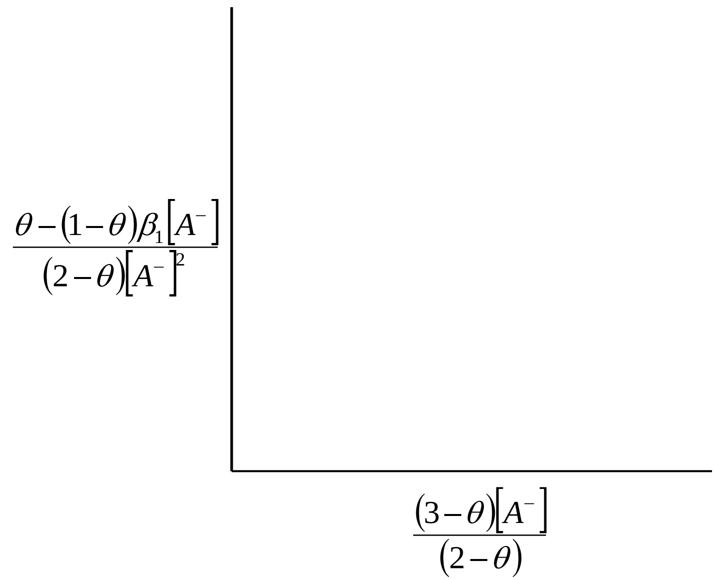
$$\frac{\theta}{(1-\theta)[A^-]} = \frac{(2-\theta)[A^-]}{(1-\theta)}\beta_2 + \beta_1$$

Graphical Determination of β_n

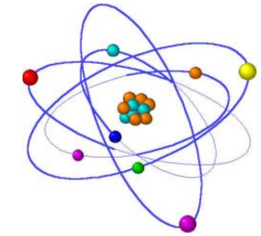
$$\frac{\theta}{(1-\theta)\left[A^-\right]} = \frac{(3-\theta)\left[A^-\right]^2}{(1-\theta)}\beta_3 + \frac{(2-\theta)\left[A^-\right]}{(1-\theta)}\beta_2 + \beta_1$$

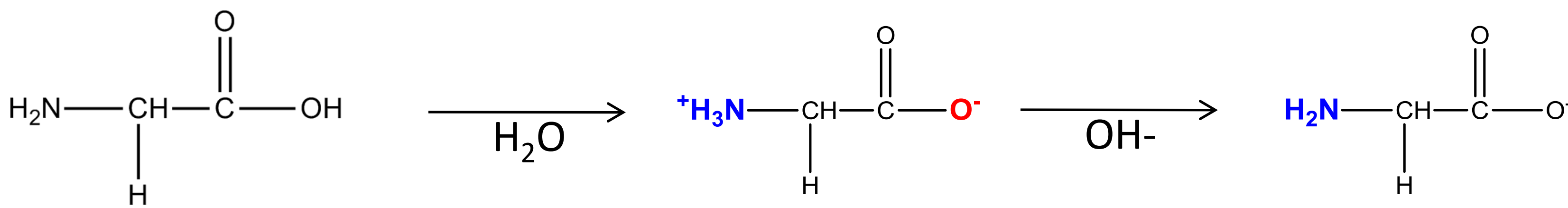
This expression can be further rearranged to generate a less complex polynomial:

$$\frac{\theta-(1-\theta)\beta_1\left[A^-\right]}{(2-\theta)\left[A^-\right]^2} = \frac{(3-\theta)\left[A^-\right]}{(2-\theta)}\beta_3 + \beta_2$$



Experimental Considerations

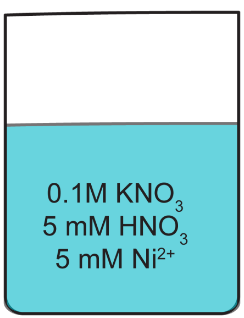




Solid

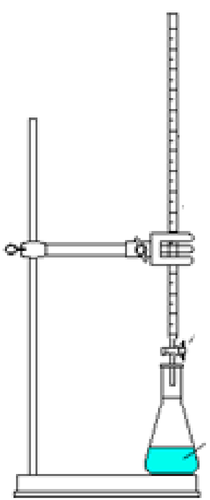
pH ~ 7

Glycinate
0.4 M



Prepare 200 mL of this solution

Nickel is a carcinogen! Ni salt will be massed in the fume hood

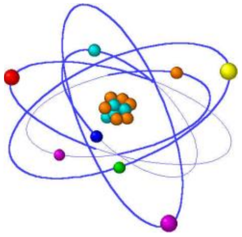


Titrate glycinate into Ni solution in 0.2 mL increments.

Record pH for every aliquot.

……Hope you liked Chemometrics…..

How to start your spreadsheet



$$\frac{\theta}{(1-\theta)[A^-]} = \frac{(3-\theta)[A^-]^2}{(1-\theta)}\beta_3 + \frac{(2-\theta)[A^-]}{(1-\theta)}\beta_2 + \beta_1$$

What do you need to solve for β_n?

$$[A^-] = \frac{K_a}{[H^+]}\left(C_H + [OH^-] - [H^+]\right) \qquad \theta = \frac{A_{tot} - \left(1 + \frac{K_a}{[H^+]}\right)\left(C_H + [OH^-] - [H^+]\right)}{M_{tot}}$$

Injection #	Volume	A_{tot}	pH	$[H^+]$	$[OH^-]$	[A-]	θ