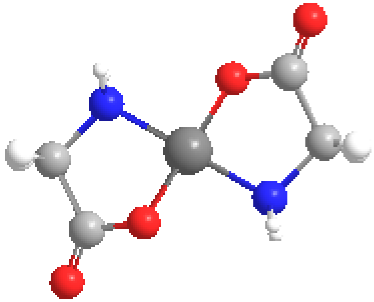
Inorganic Chemistry Laboratory

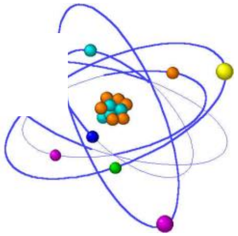
Lab 7

Experiment 22 (p.219)

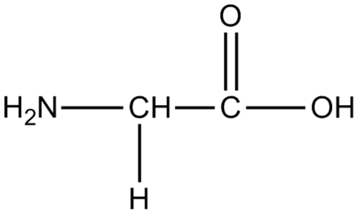
Amino Acid Complexes: Stability constants of Ni(glycinate)$_n^{(2-n)+}$



Acid-Base Chemistry of Glycine



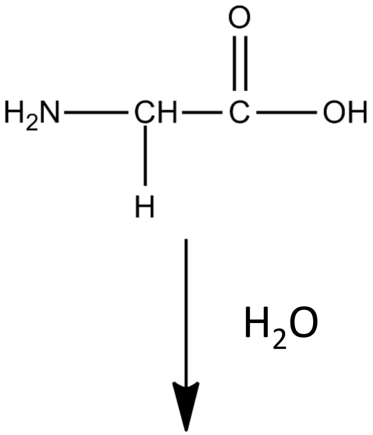
Glycine is an example of a zwitterion.



$$H_2N-\underset{H}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$$

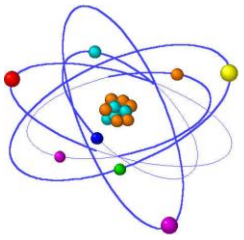
What is a zwitterion?

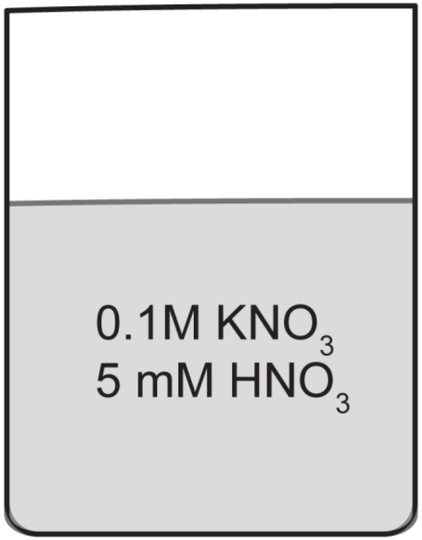
A molecule that contains a (+) and (-) electrical charge at different location within the molecule



$$H_2N-\underset{H}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{H_2O}$$

Glycinate Titration



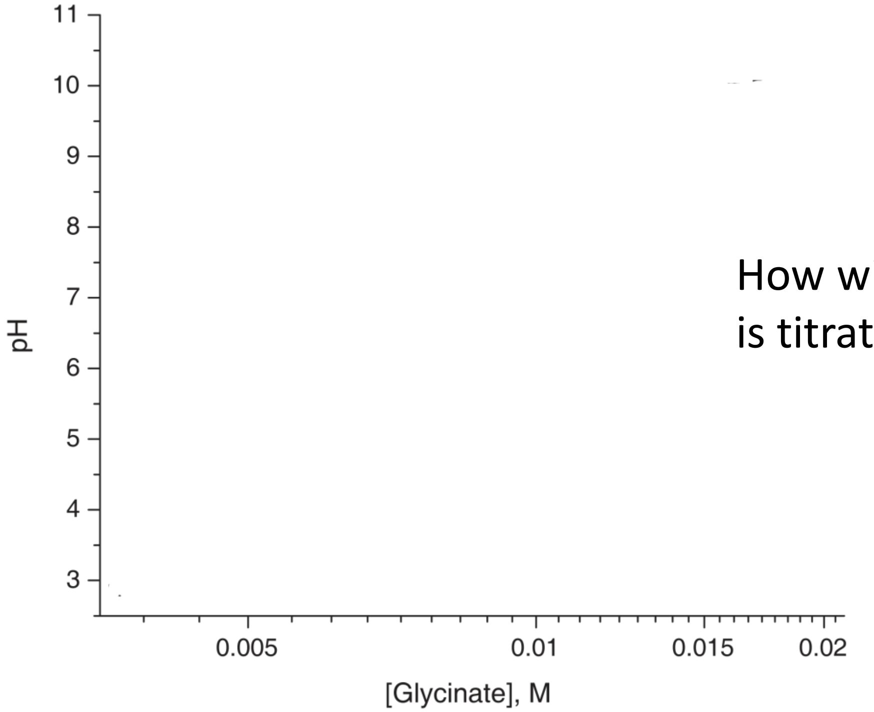


What is the pH of this solution?

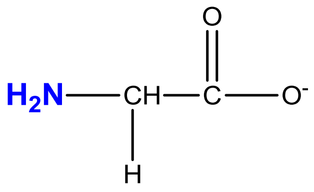
HNO$_3$ is a Strong Acid!

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

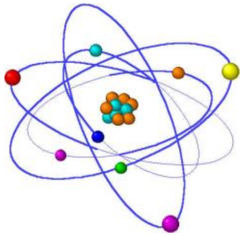
$$[H^+]=[HNO_3]$$
$$pH=-\log(0.005)=2.3$$

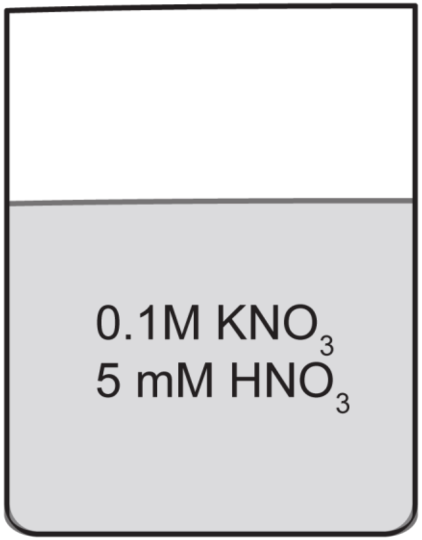


How will the pH respond when glycinate is titrated into the solution?



Glycinate Titration



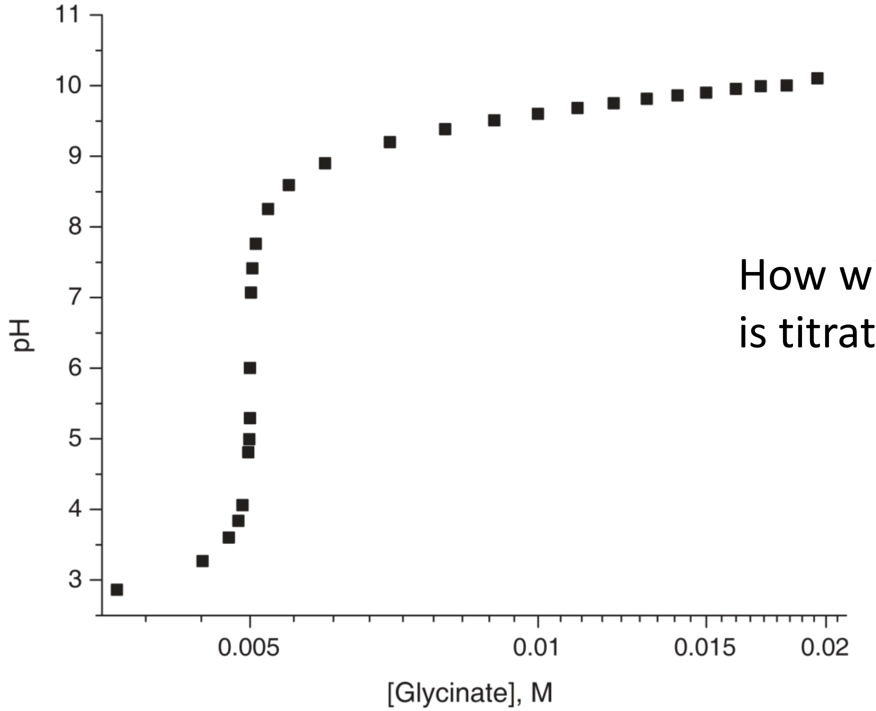


What is the pH of this solution?

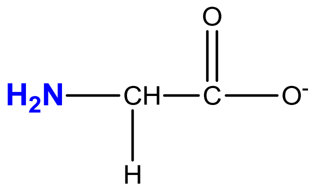
HNO_3 is a Strong Acid!

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

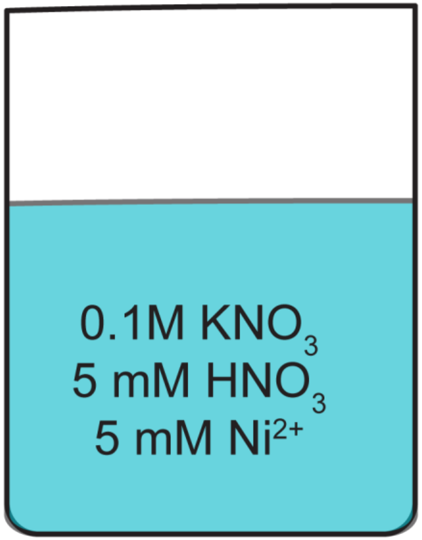
$$[H^+] = [HNO_3]$$
$$pH = -\log(0.005) = 2.3$$



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



Glycinate Titration with Nickel

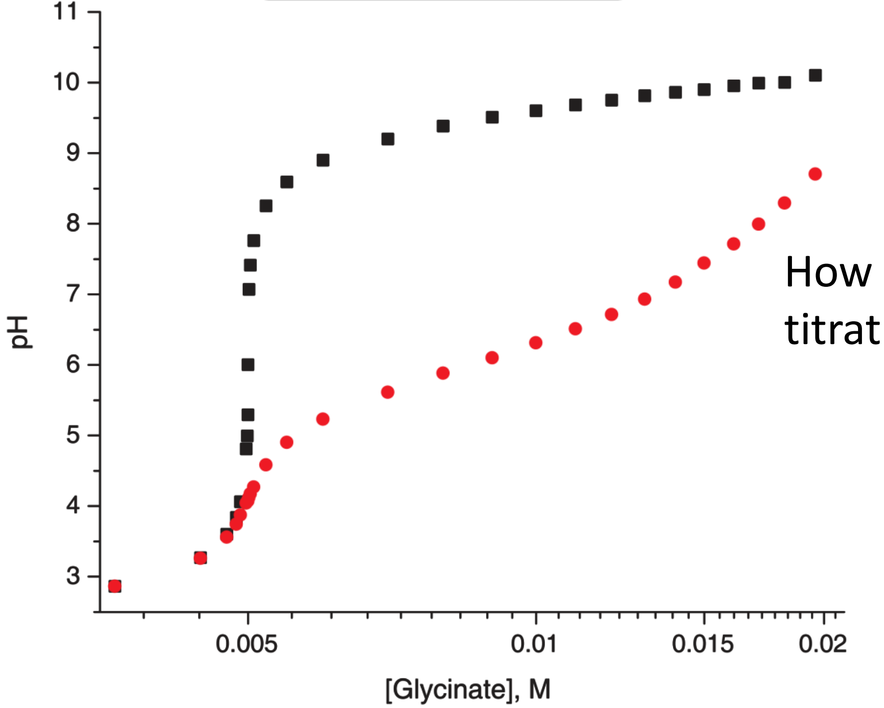


0.1M KNO_3
5 mM HNO_3
5 mM Ni^{2+}

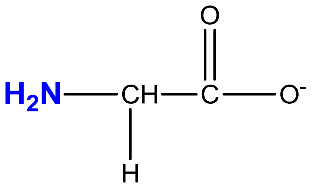
What is the pH of this solution?

HNO_3 is a still a Strong Acid!

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

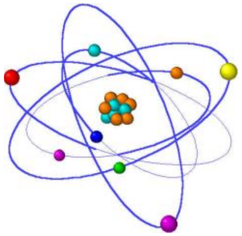


How will the pH response to glycinate titration differ with Ni^{2+} in the solution?

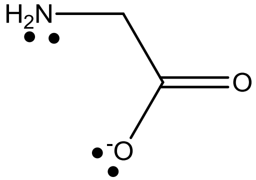


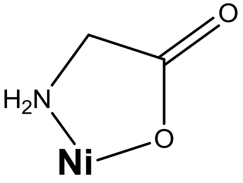
$$H_2N-\underset{\displaystyle H}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$$

Ni^{2+}-Glycinate Interactions

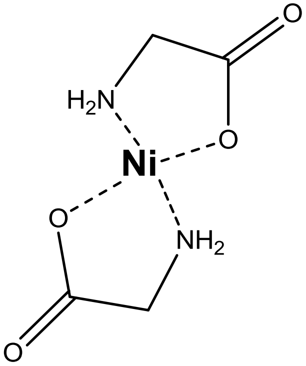


How will glycinate interact with Ni^{2+}?

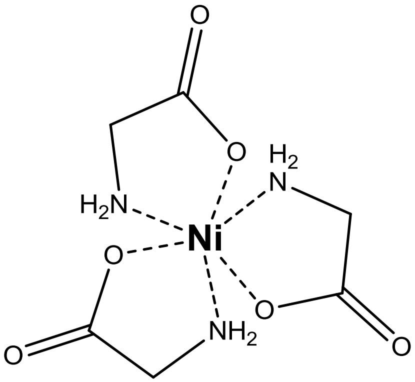




MX$^+$

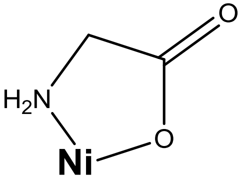


MX_2

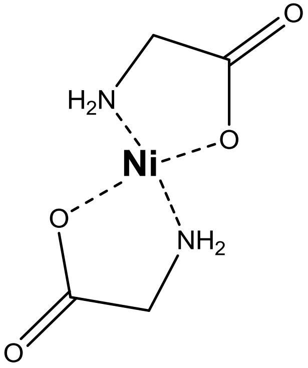


MX_3

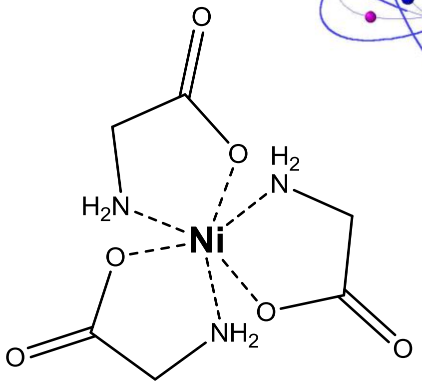
Ni^{2+}-Glycinate Interactions



MX^+

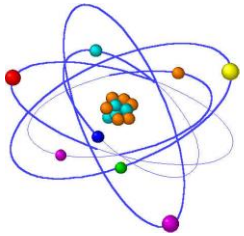


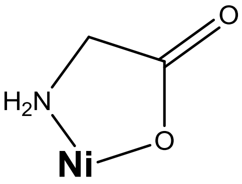
MX_2



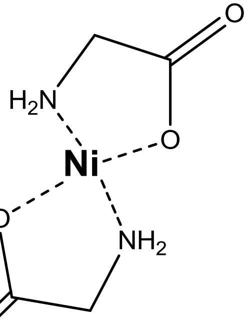
MX_3^-

Ni^{2+}-Glycinate Interactions

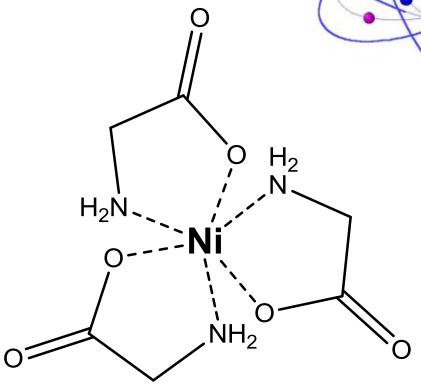




MX^{+}



MX$_2$



MX$_3^-$

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

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

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

The Effect of Ni^{2+} on pH

Consider the simple glycine (HA) dissociation reaction:

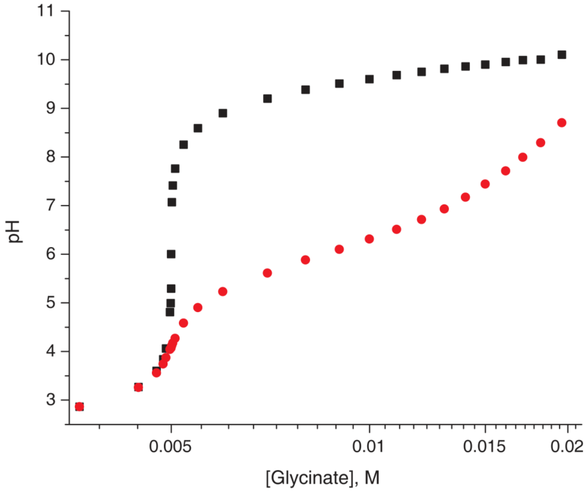
$$HA \rightleftharpoons H^+ + A^-$$

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

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

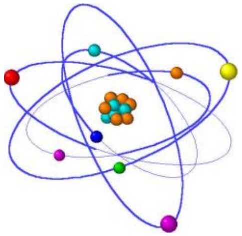
So why does Ni^{2+} influence this reaction?

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

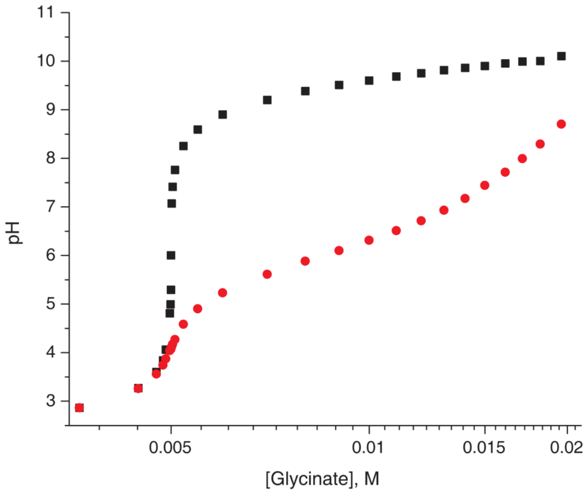
Glycinate is your titrant

$M_1V_1=M_2V_2$

pH at any point in the titration

This is what you measure

A_{tot} = [A-] + [HA] + [MA$^+$] + [MA$_2$] + [MA$_3^-$]

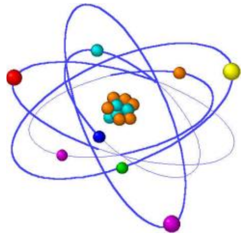


Equilibrium Expressions that describe these concentrations

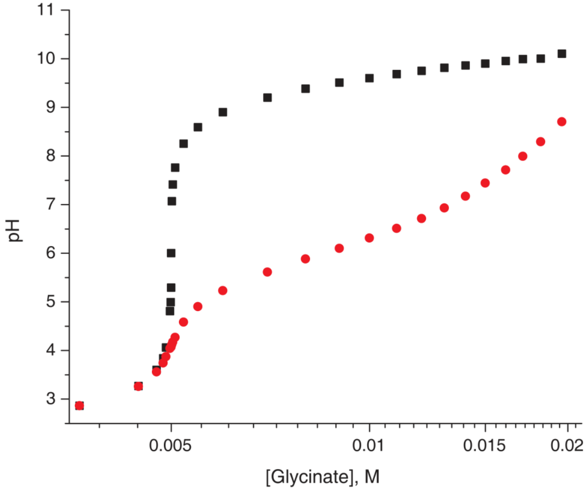
$HA \rightleftharpoons H^+ + A^-$ $\quad$ $A^- + M^{2+} \rightleftharpoons MA^+$ $\quad$ $2A^- + M^{2+} \rightleftharpoons MA_2$ $\quad$ $3A^- + M^{2+} \rightleftharpoons MA_3^-$

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

Equilibrium Theory Approach



Fractional Saturation (ñ or θ)



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

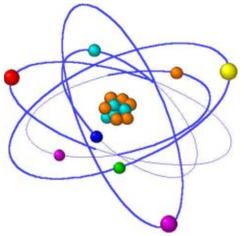
A_{tot} = [A-] + [HA] + [MA$^+$] + [MA$_2$] + [MA$_3^-$]

[Bound] =

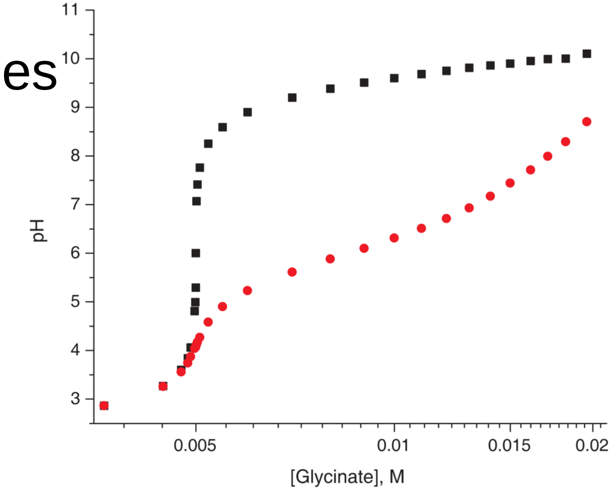
[Metal] =

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

Equilibrium Theory Approach



Our goal is to cast θ in terms of known values



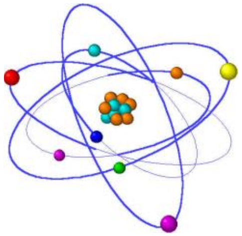
$$\theta = \frac{\beta_1[A^-] + 2\beta_2[A^-]^2 + 3\beta_3[A^-]^3}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3}$$

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

C_H → $[H^+]$ from original HNO_3 solution

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

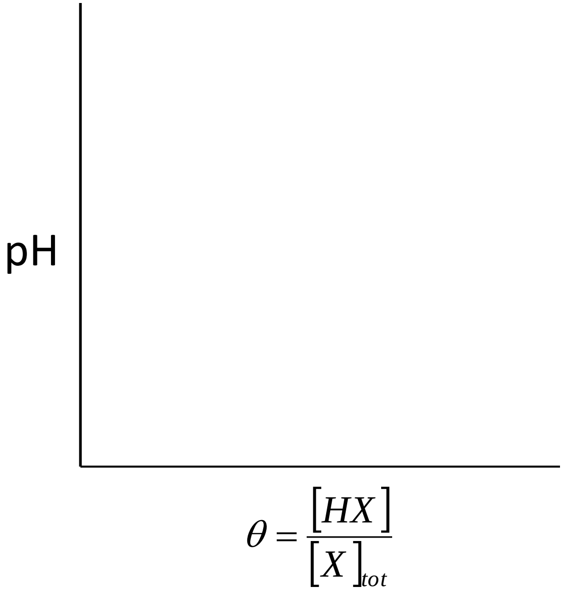
Graphical Approximation of K_n



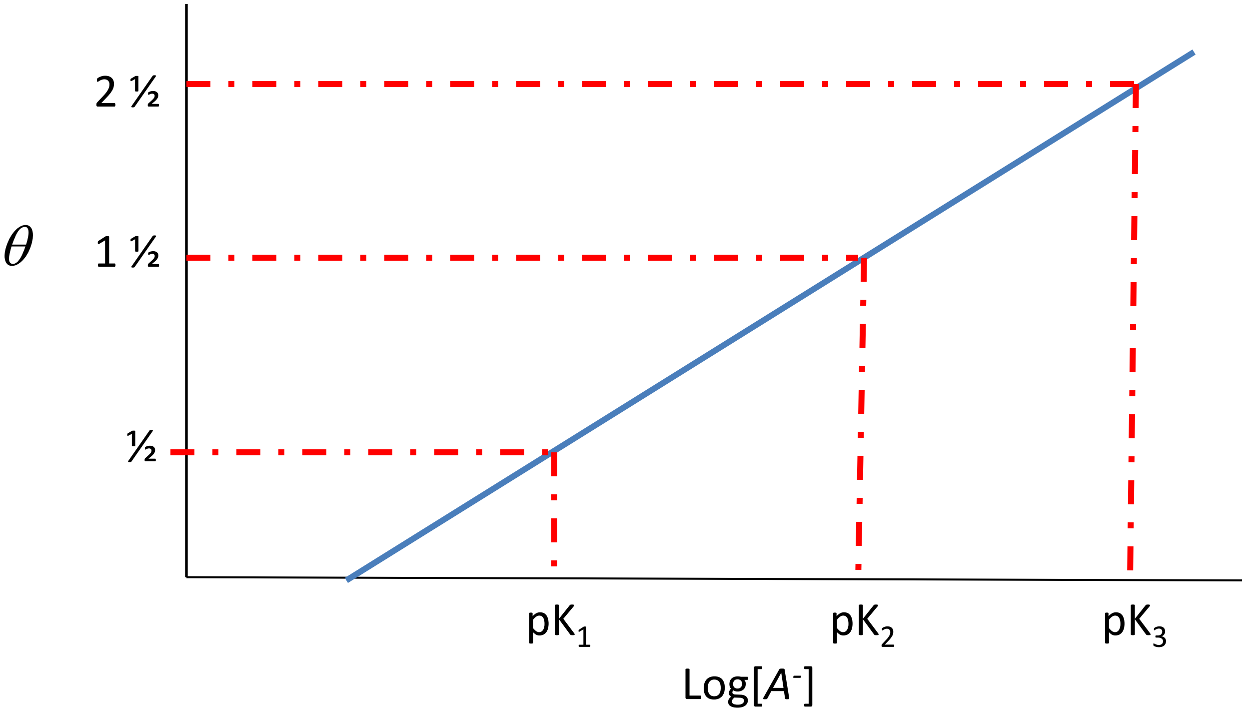
How are pKa values approximated from a pH titration?

pH @ ½ Equivalence Point

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

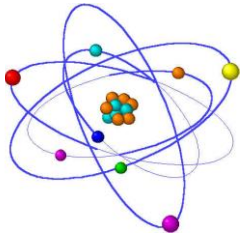


Graphical Approximation of K_n

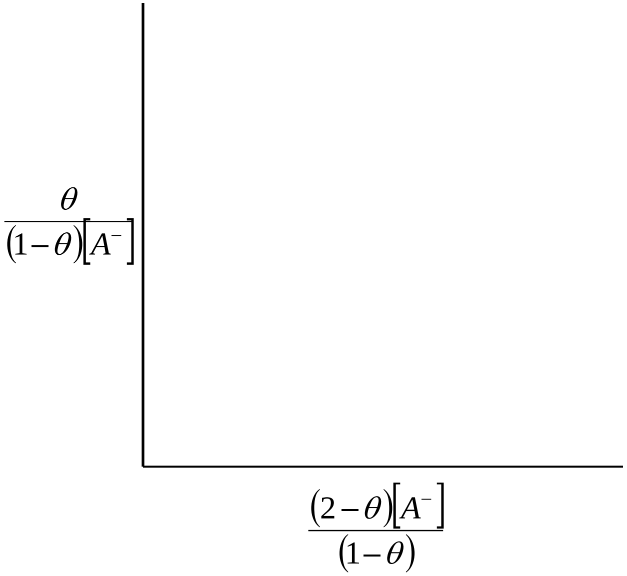


$$pK_1 = -\log K_1$$
$$pK_2 = -\log K_2$$
$$pK_3 = -\log K_3$$

Graphical Determination of β_n



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



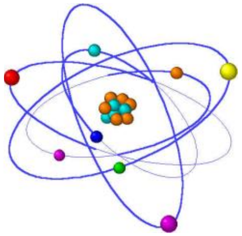
This expression can be rearranged to generate a less complex polynomial:

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

What happens at very low [A$^-$]?

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

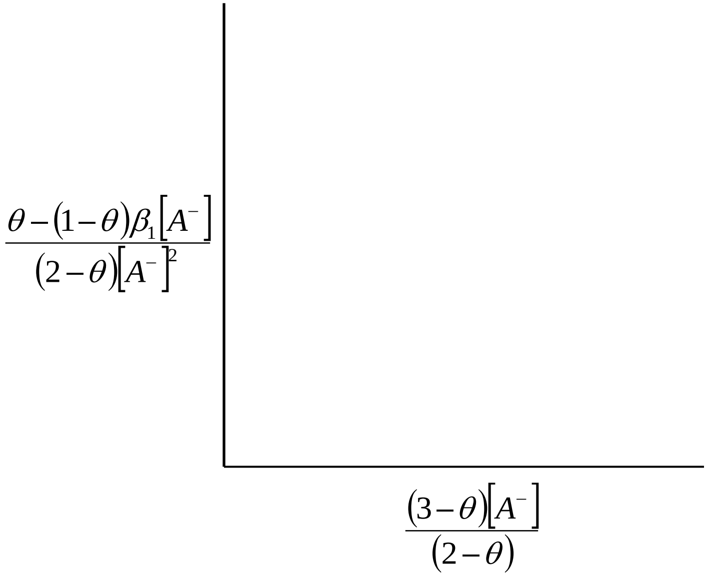
Graphical Determination of β_n



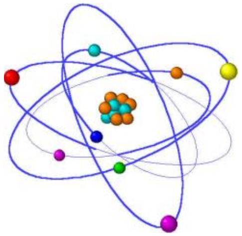
$$\frac{\theta}{(1-\theta)[A^-]} = \frac{(3-\theta)[A^-]^2}{(1-\theta)}\beta_3 + \frac{(2-\theta)[A^-]}{(1-\theta)}\beta_2 + \beta_1$$

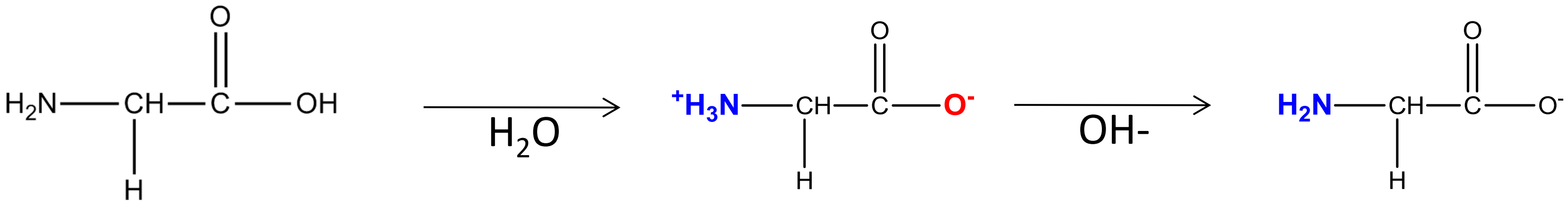
This expression can be further rearranged to generate a less complex polynomial:

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



Experimental Considerations

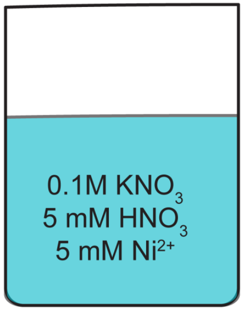




Solid

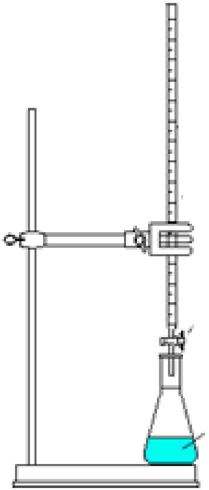
pH ~ 7

Glycinate
0.4 M



Prepare 200 mL of this solution

***Nickel is a carcinogen! ***

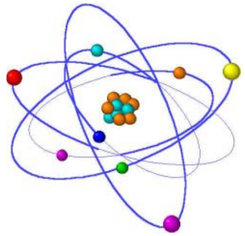


Titrate glycinate into Ni solution in 0.2 mL increments.

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?

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

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

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