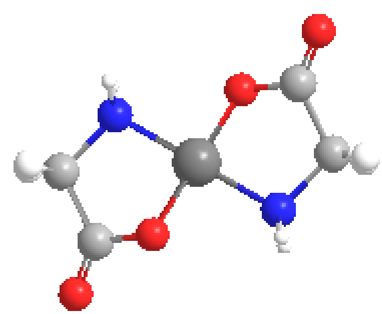
# Inorganic Chemistry Laboratory

## Lab 7

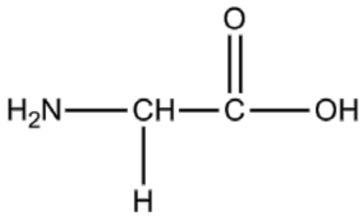
## Experiment 22 (p.219)

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



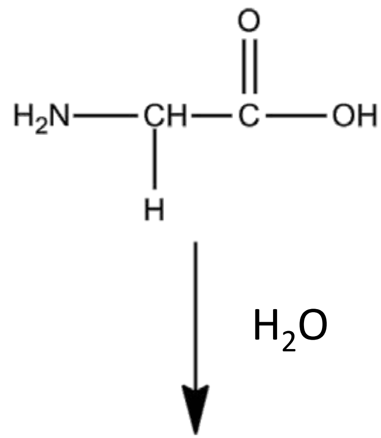
# Acid-Base Chemistry of Glycine

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



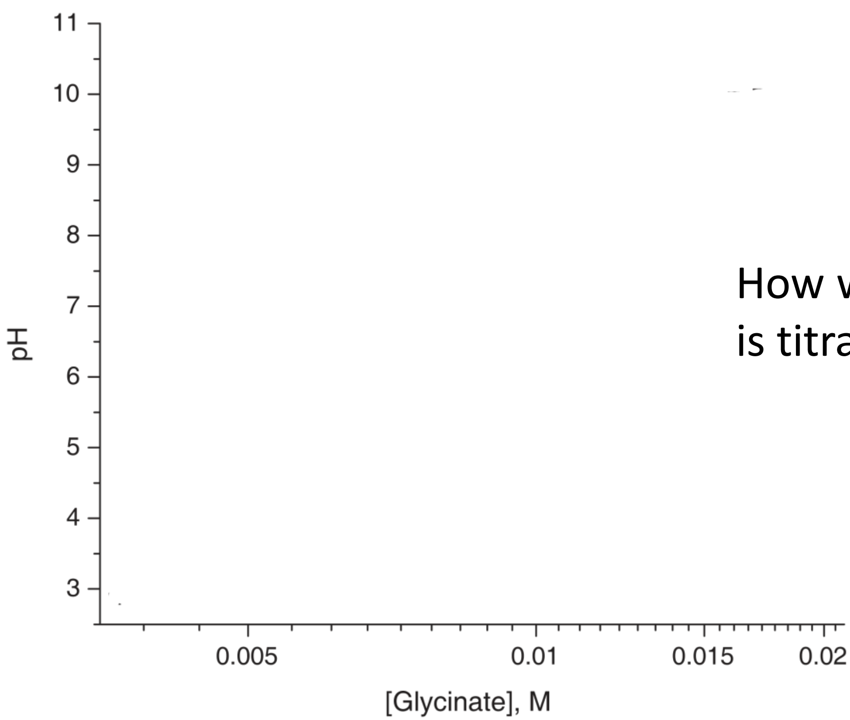
# Glycinate Titration


What is the pH of this solution?

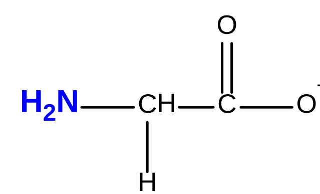
HNO$_3$ is a Strong Acid!

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

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




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



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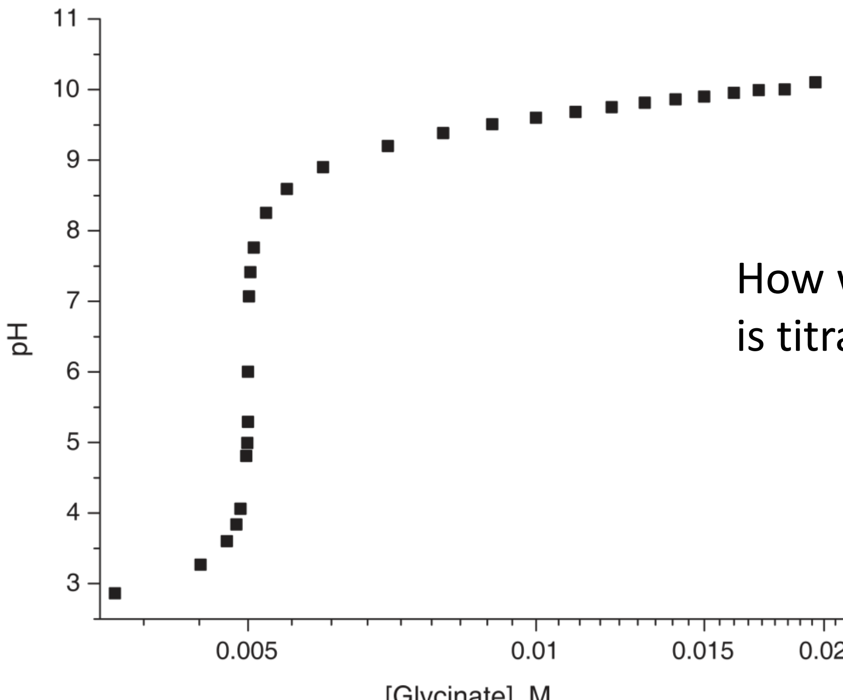


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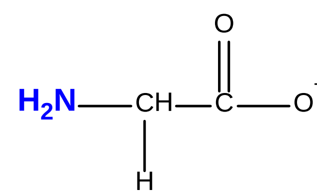
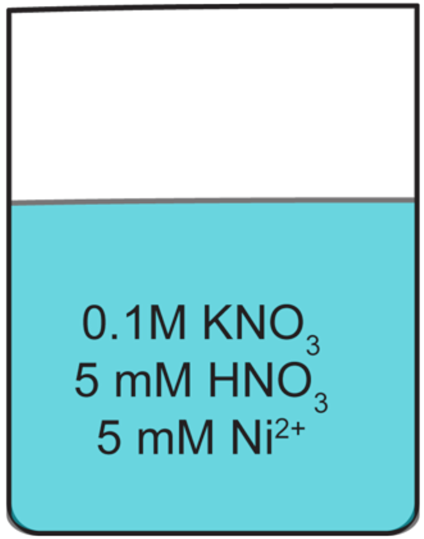


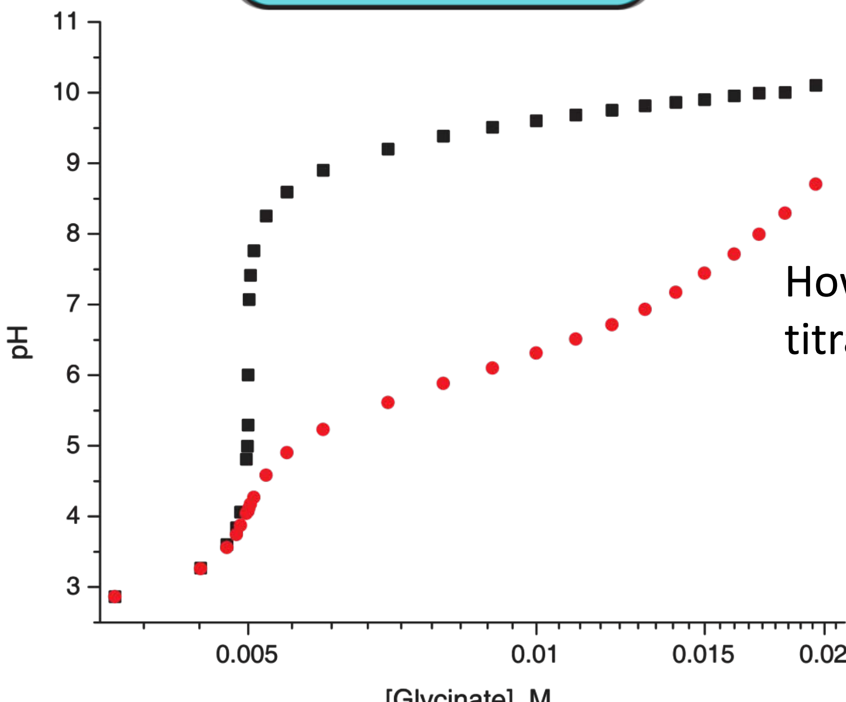
# Glycinate Titration with Nickel



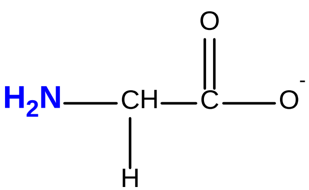

What is the pH of this solution?

HNO$_3$ is a still a Strong Acid!

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

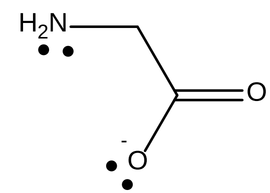


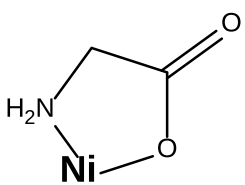

How will the pH response to glycinate titration differ with $Ni^{2+}$ in the solution?



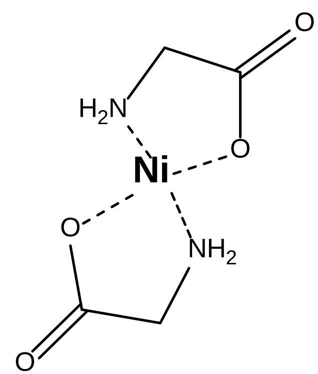
# $Ni^{2+}$-Glycinate Interactions

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

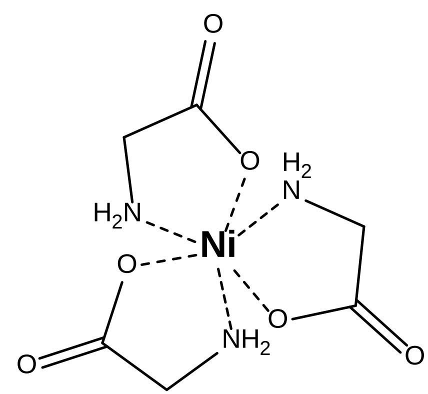



MX+

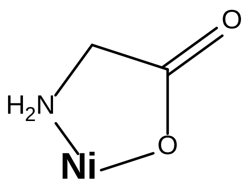



$MX_2$

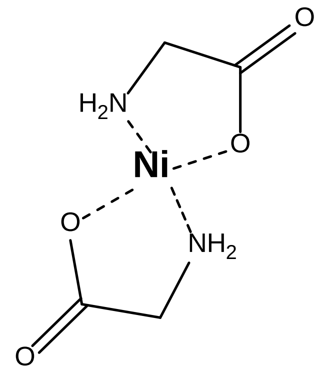



$MX_3$

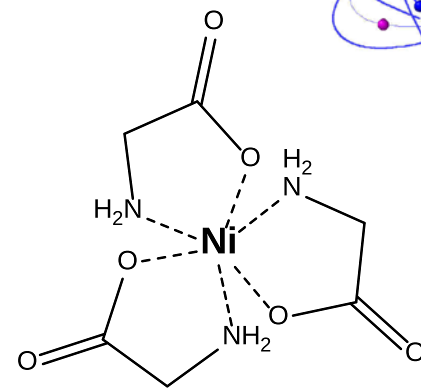
# $Ni^{2+}$-Glycinate Interactions




$MX^+$

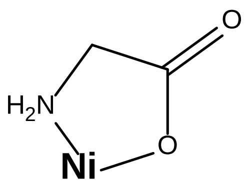



$MX_2$

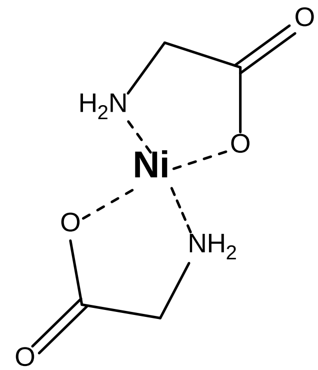



$MX_3^-$

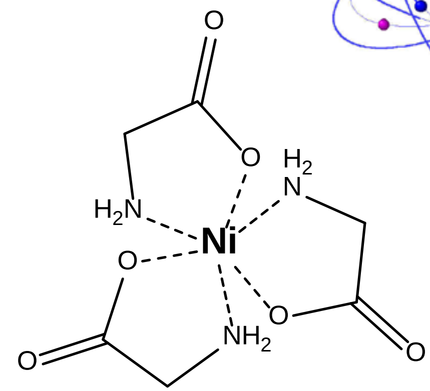
# $Ni^{2+}$-Glycinate Interactions




$MX^{+}$




$MX_2$




$MX_3^{-}$

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

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

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

# The Effect of $Ni^{2+}$ on pH

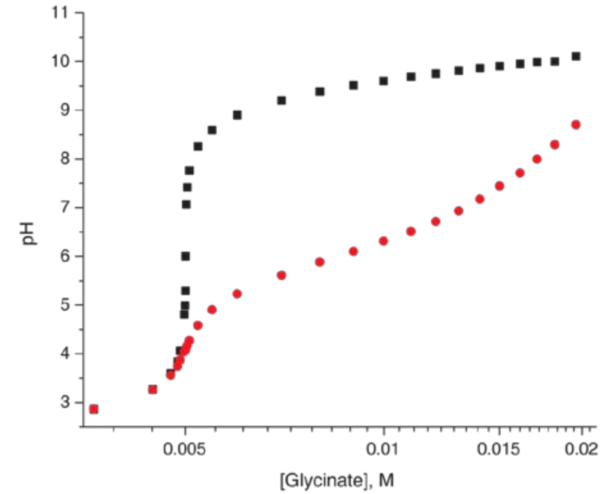
Consider the simple glycine (HA) dissociation reaction:

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

$A_{tot}$ = [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

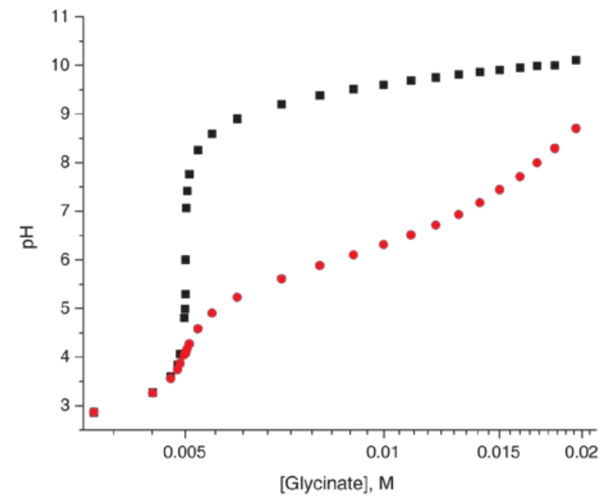
Glycinate is your titrant

$M_1V_1=M_2V_2$

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

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

$A^- + M^{2+} \rightleftharpoons MA^+$

$2A^- + M^{2+} \rightleftharpoons MA_2$

$3A^- + M^{2+} \rightleftharpoons MA_3^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} = 2.5x10^{-10}$$

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

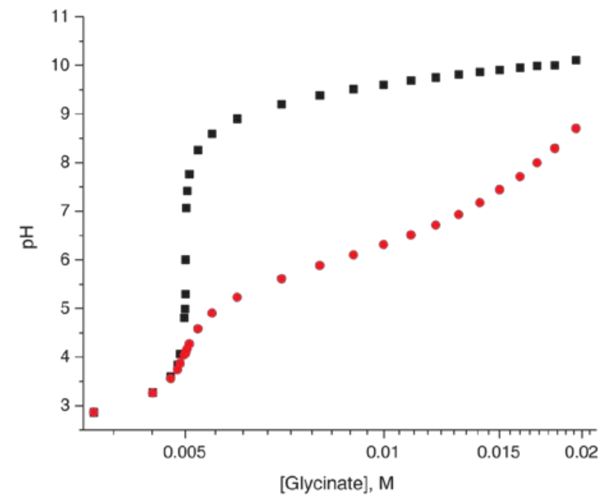
$$\beta_2 = \frac{[MA_2]}{[M^{2+}][A^-]^2}$$

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

# Equilibrium Theory Approach

Fractional Saturation (ñ or θ)

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




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

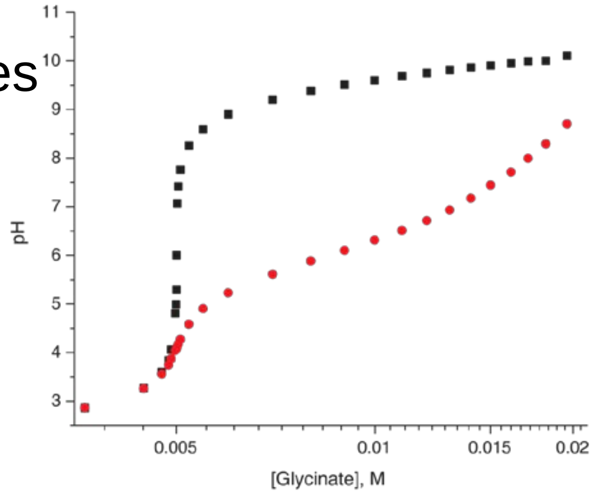
[Bound] =

[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




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

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

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

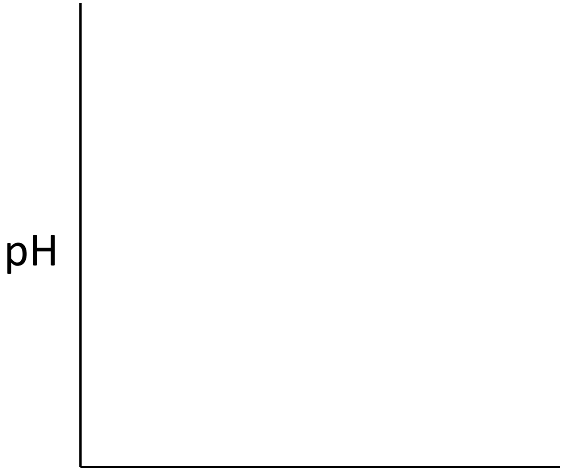
$$\theta = \frac{A_{tot} - \left(1 + \frac{K_a}{[H^+]}\right)\left(C_H + [OH^-] - [H^+]\right)}{M_{tot}}$$

# Graphical Approximation of $K_n$

How are pKa values approximated from a pH titration?

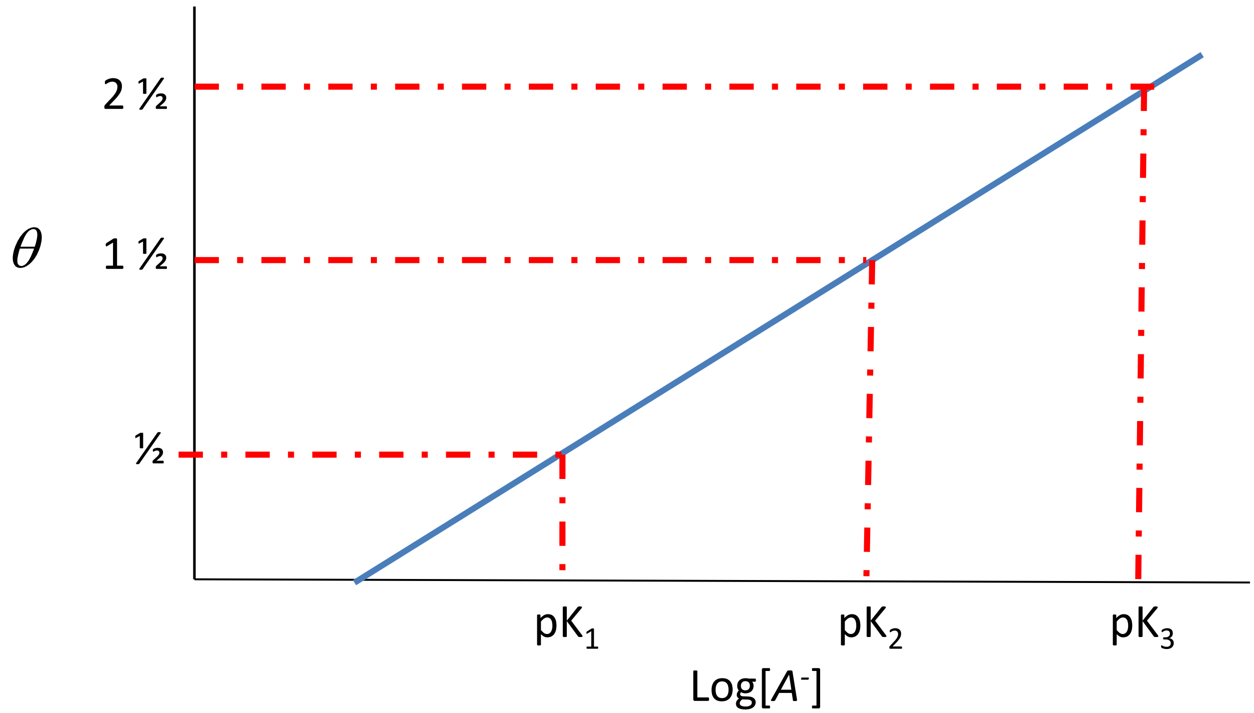
pH @ ½ Equivalence Point

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




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

# Graphical Approximation of $K_n$

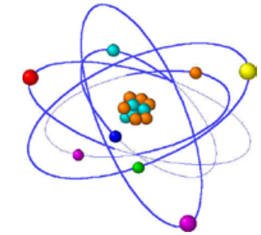



$$pK_1 = -\log K_1$$

$$pK_2 = -\log K_2$$

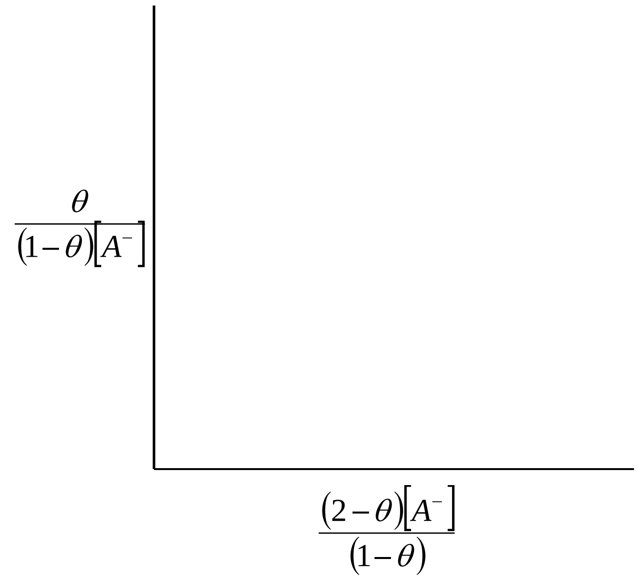
$$pK_3 = -\log K_3$$

# Graphical Determination of $\beta_n$



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

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




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

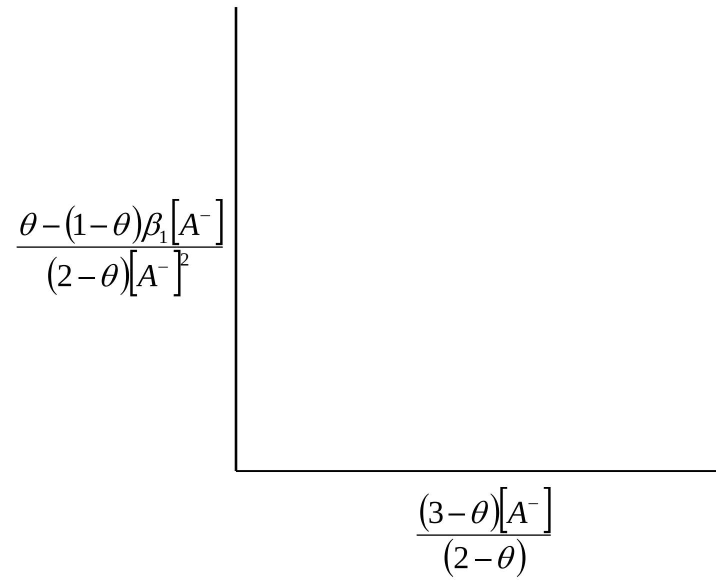
What happens at very low [A$^-$]?

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

# Graphical Determination of $\beta_n$

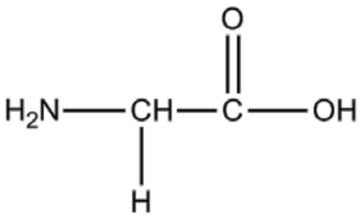
$$\frac{\theta}{(1-\theta)[A^-]} = \frac{(3-\theta)[A^-]^2}{(1-\theta)}\beta_3 + \frac{(2-\theta)[A^-]}{(1-\theta)}\beta_2 + \beta_1$$

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



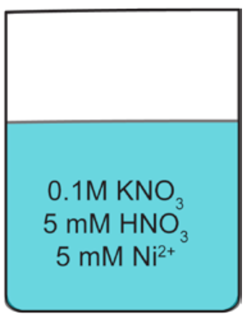

$$\frac{\theta-(1-\theta)\beta_1[A^-]}{(2-\theta)[A^-]^2} = \frac{(3-\theta)[A^-]}{(2-\theta)}\beta_3 + \beta_2$$

# Experimental Considerations



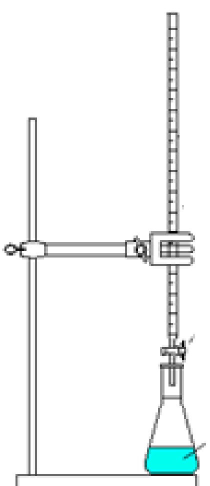
$\xrightarrow{H_2O}$ $\xrightarrow{OH^-}$

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 $\beta_n$?

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

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

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