## POLYPROTIC ACID-BASE TITRATIONS

CHEM 25I SDSU

## POLYPROTIC ACIDS/BASES

- As the polyprotic acids and bases are all weak acids or bases, they can be treated similarly when it comes to pH titrations.
- The key variation is the increase in equivalence points and how the pH is determined at those points.


## SAMPLE PROBLEM

Plot the titration curve for the titration of 12.0 mL of 22.0 mM potassium carbonate with 30.0 mM $\mathrm{HNO}_{3}$.

Determine the pH after the following volumes of titrant have been added:
A) 2.00 mL of titrant B) 5.00 mL of titrant
C) 8.80 mL of titrant
D) 10.00 mL of titrant
E) 13.00 mL of titrant
F) 17.60 mL of titrant

## PH BEFORETHE $V_{E Q}$

- Before any titrant is added the pH is determined by the $\mathrm{K}_{\mathrm{a}}$.
- Before the equivalence point the analyte will be in excess (dominant species).
- As titrant is added the concentration of the conjugate to the analyte is increased.
- This results in a buffer being formed - Henderson-Hasselbach equation.


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## PH AT INTERMEDIATE EQUIVALENCE POINTS

- At the intermediate equivalence points the moles all of the weak polyprotic acid has been converted into a single form, between two equilibria.
- $\mathrm{H}_{3} \mathrm{~A} \rightleftharpoons \mathrm{H}_{2} \mathrm{~A}^{-} \rightleftharpoons \mathrm{HA}^{2-} \rightleftharpoons \mathrm{A}^{3-}$
- We must incorporate the two $K_{a}$ values into the calculation of the pH .

$$
\begin{gathered}
{\left[H^{+}\right]=\sqrt{\frac{K_{a_{1}} K_{a_{2}} F+K_{a_{1}} K_{w}}{K_{a_{1}}+F}} \quad\left[H^{+}\right]=\sqrt{\frac{K_{a_{2}} K_{a_{3}} F+K_{a_{2}} K_{w}}{K_{a_{2}}+F}}} \\
\text { For H2A } \mathrm{A}^{-}
\end{gathered}
$$

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# PH BETWEEN EQUIVALENCE POINTS 

- At this stage the polyprotic acid (or base) begins to act as a buffer once again.
- The Henderson-Hasselbach trick of using volumes can apply, but with a little twist.
- You must account for the volume of titrant that went into getting to the prior equivalence point(s).


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## PH ATTHE FINAL EQUIVALENCE POINT

- At the final equivalence point the weak acid (base) has been fully (de)protonated.
- It can be treated as a simple monoprotic weak acid (base) by using $K_{a l}\left(K_{b}\right)$.
- You must remember to account for the dilution of the acid (find the new formal concentration).


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