

Systematic Treatment of Equilibrium

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Systematic Treatment of Equilibrium

- Methodology to deal with chemical equilibria systematically: figure out as many **independent** algebraic equations as there are unknown species
- Independent algebraic equations:
 - chemical equilibrium conditions
 - mass balance
 - charge balance

Chemical Equilibrium

Example: dissolve K_3PO_4 into water

- Dissociation reaction



- Other reactions with water



- In aqueous solutions, always self-ionization of water



Charge Balance

- The statement of electroneutrality: The sum of the positive charges in solution equals the sum of the negative charges in solution – to make the electroneutrality of the solution.
 - Creation of one positive charge (ion) must accompany the creation of one negative charge

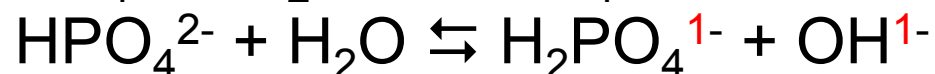
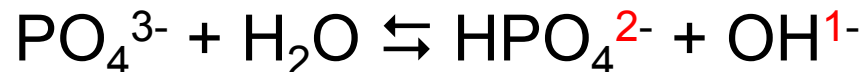
Charge balance

Example: dissolve K_3PO_4 into water

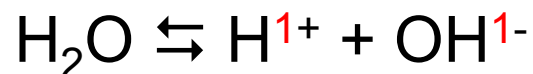
- Dissociation reaction



- Other reactions with water



- In aqueous solutions, always self-ionization of water



Charge balance

- Example: dissolve K_3PO_4
$$K_3PO_4 \rightleftharpoons 3K^{1+} + PO_4^{3-}$$
$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^{1-}$$
$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^{1-} + OH^{1-}$$
$$H_2O \rightleftharpoons H^{1+} + OH^{1-}$$
-

- $\Sigma(\text{positive charge}) = \Sigma(\text{negative charge})$
- Total positive charge = $[K^+] + [H^+]$
Total negative charge = $[OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$
 $[K^+] + [H^+] \equiv [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$

Net charge in the solution = 0

Mass Balance or material balance

- Statement of the conservation of matter: the quantity of all species in a solution containing a particular atom (or group of atoms) must equal to amount of that atom (or group) delivered to the solution
 - Chemical process can not produce new kinds of atom.

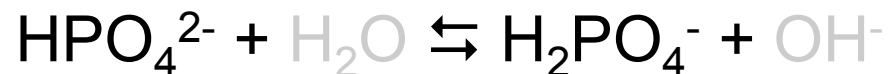
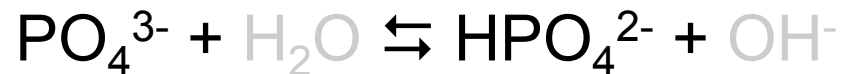
Mass Balance or material balance

Example: dissolve K_3PO_4 into water

- Dissociation reaction



- Other reactions with water



- In aqueous solutions, always self-ionization of water



Mass Balance or material balance

- Example: dissolve K_3PO_4
$$K_3PO_4 \rightleftharpoons 3K^+ + PO_4^{3-}$$
$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$$
$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
-

- The amount that K_3PO_4 puts into the solution:

$$[K_3PO_4] = \underbrace{1/3[K^+]}_{\text{All } K^+ \text{ species}} = \underbrace{[PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-]}_{\text{All } PO_4^{2-} \text{ species}}$$

What about activity?

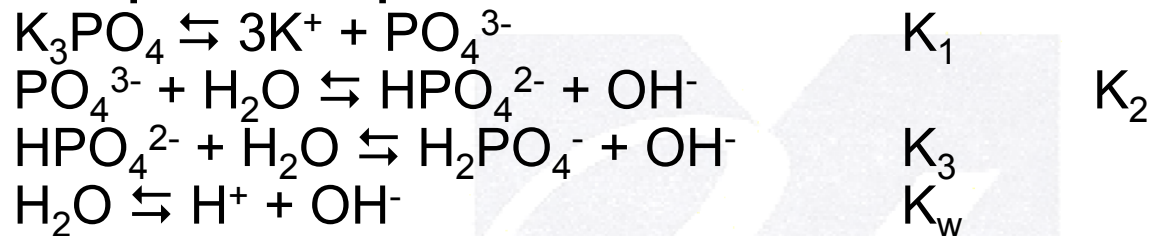
- In concentrated solutions, shouldn't activity replace concentration?
 - Why?
- Concentration rather than activity is used in both mass balance and charge balance.
- Charge Balance:
 - Charge contributed by 0.1M H^+ is *exactly* 0.1M
- Mass Balance:
 - Concentration of each species counts exactly as # of atoms

Steps to treat the equilibrium

- **Step 1:** write all possible reactions
- **Step 2:** write charge balance equations
- **Step 3:** write mass balance equations
- **Step 4:** write the equilibrium constant for each chemical reaction – only time activity MAY be used.
- **Step 5:** count the numbers of equation and unknowns (concentration of species)
- **Step 6:** solve the equation to find out unknowns

Example: dissolve K_3PO_4

- Step 1: All possible reactions



- Step 2: Charge balance

$$[K^+] + [H^+] \equiv [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

- Step 3: Mass balance

$$[K_3PO_4] = 1/3[K^+]$$

$$[K_3PO_4] = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-]$$

Example: dissolve K_3PO_4

- Write the equilibrium constant for each chemical reaction – only here is when activity MAY be used.

$$K_1 = \{[K^+]^3 \gamma_{K^+}^3 \times [PO_4^{3-}] \gamma_{PO_4^{3-}}\} / [K_3PO_4]$$

$$K_2 = \{[HPO_4^{2-}] \gamma_{HPO_4^{2-}} \times [OH^-] \gamma_{OH^-}\} / [PO_4^{3-}] \gamma_{PO_4^{3-}}$$

$$K_3 = \{[H_2PO_4^-] \gamma_{H_2PO_4^-} \times [OH^-] \gamma_{OH^-}\} / [HPO_4^{2-}] \gamma_{HPO_4^{2-}}$$

$$K_w = [H^+] \gamma_{H^+} [OH^-] \gamma_{OH^-}$$

In dilute solutions, γ can be omitted ($\gamma \cong 1$)

- Count the numbers of equation and unknowns (concentration of species)

7 unknown: $[K^+], [H^+], [OH^-], [H_2PO_4^-], [HPO_4^{2-}], [PO_4^{3-}], [K_3PO_4]$

7 equations: K_1, K_2, K_3, K_w , one charge balance and 2 mass balances

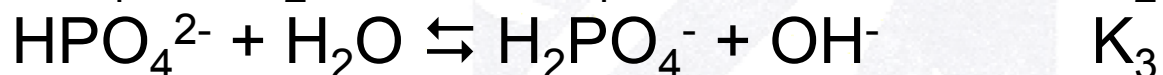
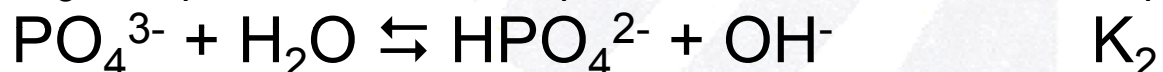
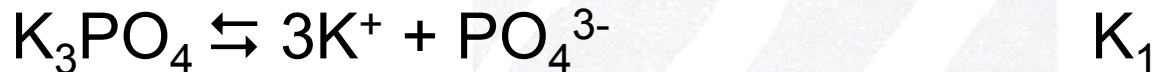
- Solve the equation to find out unknowns

In general, the solubility of MA is high, if A is from a weak acid

Coupled Equilibria

- The product of one reaction is the reactant of another or others

Example 1:



Example 2:



Acids and Bases

Weak Acid/Base Equilibria

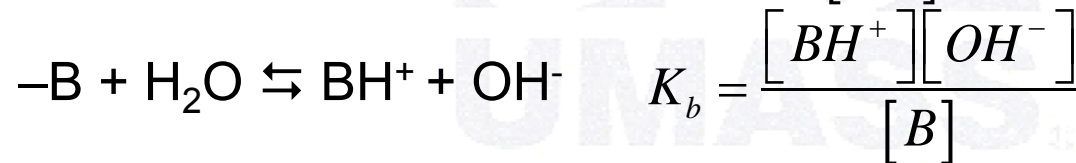
pH Revisited: Acids and Bases

- Remember $\text{pH} = -\log[\text{H}^+]$?

$$\text{pH is } -\log A_{\text{H}^+} = -\log[\text{H}^+] \odot_{\text{H}}$$

$$K_w = [\text{H}^+] \odot_{\text{H}} [\text{OH}^-] \odot_{\text{OH}}$$

- Strong acids or bases \rightarrow complete dissociation
- Weak acids or bases \rightarrow exist in equilibrium



- Formal concentration (F): the total number of moles of a compound dissolved in a liter.

Determining pH: Weak acids

- Systematic treatment: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
 - Charge balance: $[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$
 - Mass balance: $F = [\text{A}^-] + [\text{HA}]$
 - Equilibria:
 - $K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$
 - $K_w = [\text{H}^+][\text{OH}^-]$
 - 4 unknowns $[\text{A}^-]$, $[\text{HA}]$, $[\text{H}^+]$, $[\text{OH}^-]$ and 4 equations

Determining pH: Weak bases

- Systematic treatment: $B + H_2O \rightleftharpoons BH^+ + OH^-$
 - Charge balance: $[BH^+] = [OH^-]$
 - Mass balance: $F = [BH^+] + [B]$
 - Equilibria:
 - $K_b = [BH^+][OH^-]/[B]$
 - ~~$K_w = [H^+][OH^-]$~~ (all OH^- comes from B)
 - 3 unknowns $[B]$, $[BH^+]$, $[OH^-]$ and 3 equations

Weak acid/base problems

- Weak acid problem: $HA \rightleftharpoons H^+ + A^-$

$$\frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F - x} = K_a$$

- Weak base problem: $B + H_2O \rightleftharpoons BH^+ + OH^-$

$$\frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{F - x} = K_b$$

The dependence of solubility on pH

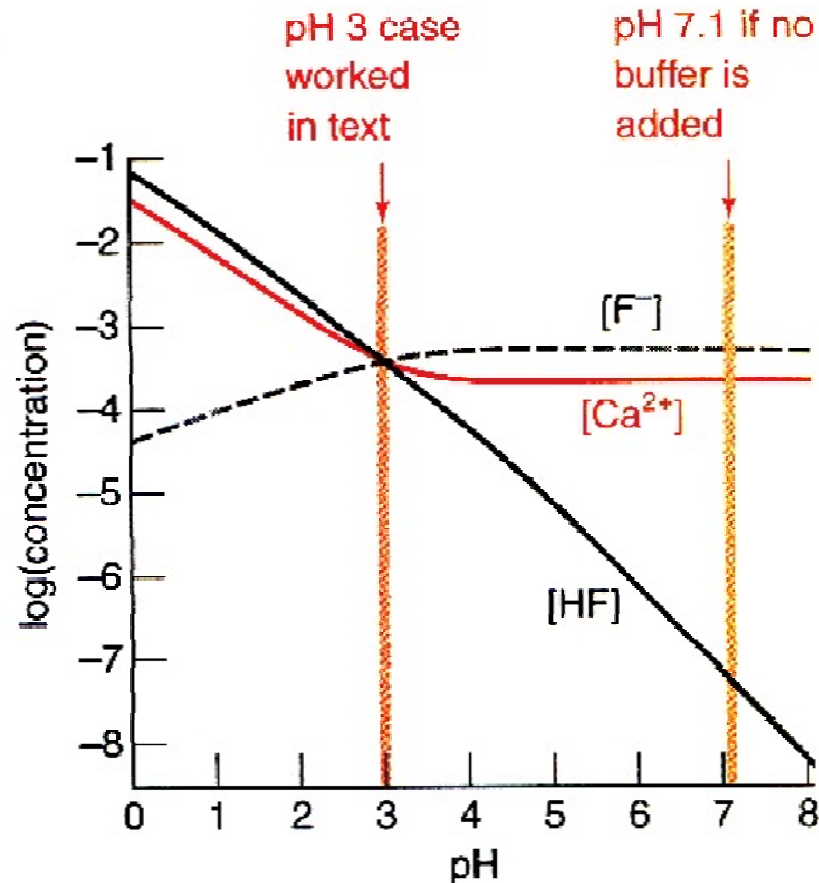


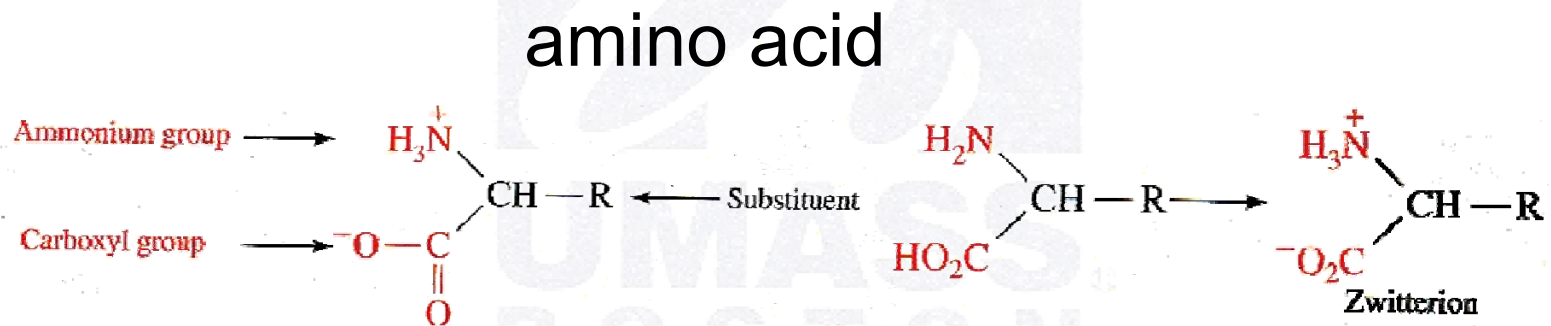
Figure 9-3 pH dependence of the concentration of Ca^{2+} , F^- , and HF in a saturated solution of CaF_2 . As the pH is lowered, H^+ reacts with F^- to make HF , and the concentration of Ca^{2+} increases. Note the logarithmic ordinate.

Polyprotic Acid-Base Equilibria

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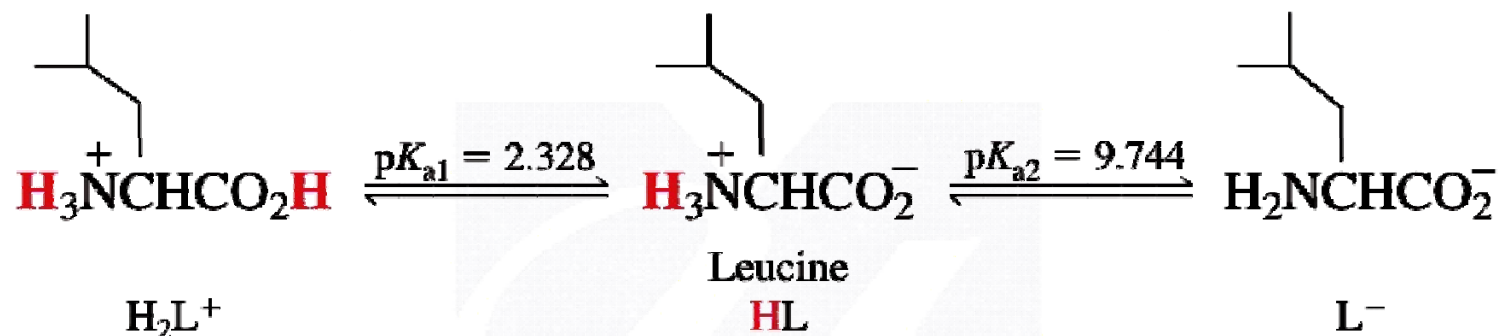
Polyprotic Acids and Bases

- Can donate (acid) or accept (base) more than one proton.
- Diprotic (2), triprotic (3),...

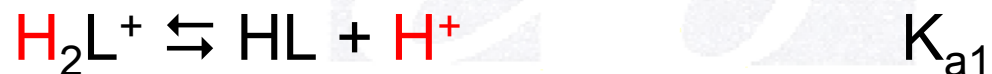


- A molecule that can both donate and accept a proton is call *"amphiprotic"*

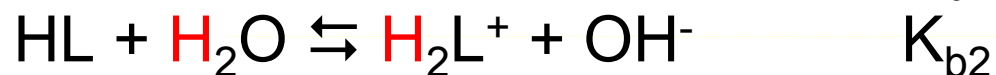
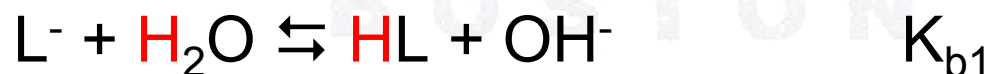
Diprotic acid and base (amino acid)



- Diprotic acid:

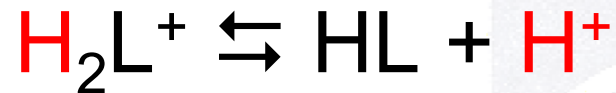


- Diprotic base

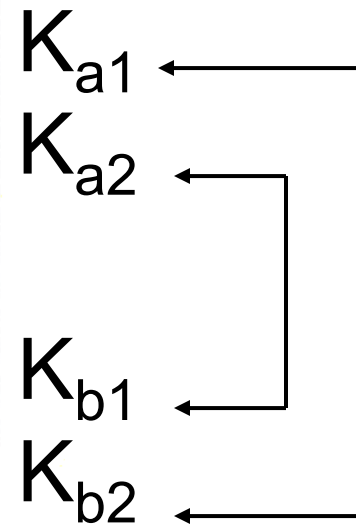
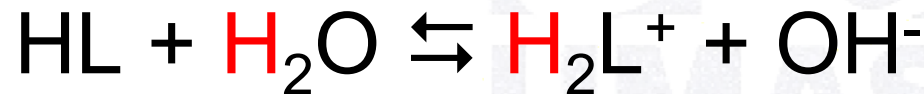
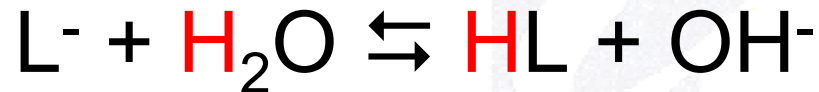


Diprotic acid and base (amino acid)

- Diprotic acid:



- Diprotic base



$$K_{a1} \cdot K_{b2} = K_w$$

$$K_{a2} \cdot K_{b1} = K_w$$

Dissociation of diprotic acid

- For the solution of H_2L^+



$$K_{a1} = 4.69 \times 10^{-3}$$



$$K_{a2} = 1.79 \times 10^{-10}$$

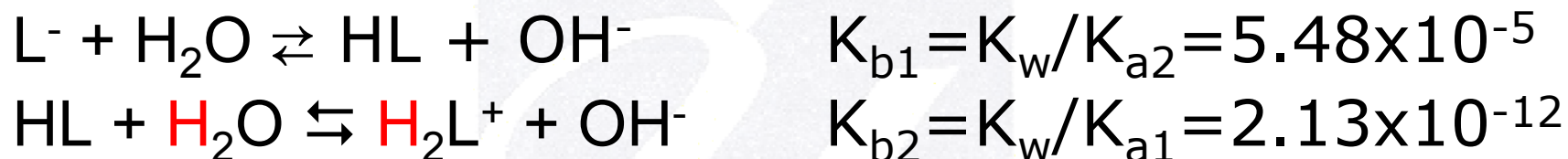
Assumption:

since $K_{a1} \gg K_{a2}$ the dissociation of HL is insignificant compared to the dissociation of H_2L^+ .

$\therefore H_2L^+$ can be treated as a monoprotic acid: only need K_{a1}

Dissociation of diprotic base

- For the solution of L^-



Assumption:

since $K_{b1} \gg K_{b2}$ the reaction of HL with H_2O (hydrolysis) is insignificant compared to the reaction of L^- with H_2O .

$\therefore L^-$ can be treated as monobasic: only need K_{b1}

What happens to HL – intermediate form

- Say, dissolve 0.050 M of HL into water

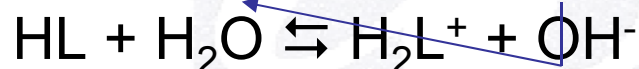
Dissociation (acid):



$$K_a = K_{a2} = 1.79 \times 10^{-10}$$

Hydrolysis (base):

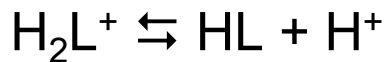
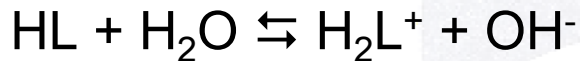
$$K_b = K_{b2} = 2.13 \times 10^{-12}$$



- The two reactions are related and proceed to nearly equal extent, so even though $K_a > K_b$, the hydrolysis reaction cannot be ignored.
- Resort to systematic treatment of equilibrium

Treatment of the intermediates

- Systematic treatment:


 K_{a2}
 K_{b2}

Charge balance $[H^+] + [H_2L^+] = [L^-] + [OH^-] \Rightarrow [H_2L^+] - [L^-] + [H^+] - [OH^-] = 0$

$$K_{a2} = \frac{[H^+][L^-]}{[HL]} \Rightarrow [L^-] = \frac{[HL]K_{a2}}{[H^+]}$$

$$K_{b2} = \frac{[H_2L^+][OH^-]}{[HL]} \Rightarrow [H_2L^+] = \frac{[HL]K_{b2}}{[OH^-]} = [HL][H^+] \frac{K_{b2}}{K_w}$$

$$K_{a1}K_{b2} = K_w \Rightarrow K_{a1} = \frac{K_w}{K_{b2}} \quad [OH^-] = \frac{K_w}{[H^+]}$$

$$[H_2L^+] = [HL][H^+] \frac{K_{b2}}{K_w} \Rightarrow [H_2L^+] = \frac{[HL][H^+]}{K_{a1}}$$

Treatment of the intermediates

$$\frac{[HL][H^+]}{K_{a1}} - \frac{[HL]K_{a2}}{[H^+]} + [H^+] - \frac{K_w}{[H^+]} = 0$$

$$\frac{[HL][H^+]^2}{K_{a1}} - [HL]K_{a2} + [H^+]^2 - K_w = 0$$

$$[H^+]^2 \left(\frac{[HL]}{K_{a1}} + 1 \right) = K_{a2}[HL] + K_w$$

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HL] + K_{a1}K_w}{K_{a1} + [HL]}}$$

No assumption was made (two unknowns)

- Mass Balance:

$$F = [FL] + [L^-] + [H_2L^+]$$

$$= [HL] + \frac{[HL]k_{a2}}{[H^+]} + \frac{[HL][H^+]}{k_{a1}}$$

$$[HL] = \frac{Fk_{a2}[H^+]}{k_{a1}[H^+] + k_{a1}k_{a2} + [H^+]^2}$$

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HL] + K_{a1}K_w}{K_{a1} + [HL]}}$$

$$k_{a1}[H^+]^4 + (k_{a1}^2 + Fk_{a2})[H^+]^3 + (k_{a1}^2k_w - k_{a1}k_w)[H^+]^2 - (k_{a1}k_{a2}^2 + k_{a1}^2k_w)[H^+] + k_{a1}^2k_{a2}k_w = 0$$

Approximations

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HL] + K_{a1}K_w}{K_{a1} + [HL]}}$$

- Since HL is weak acid/base, the $[HL] \approx F$ (added) then

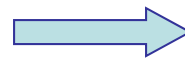
$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

- Assume, $K_{a2}[HL] \gg K_w$, then

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F}{K_{a1} + F}}$$

- Assume, $F \gg K_{a1}$

$$[H^+] = \sqrt{K_{a1}K_{a2}}$$



$$\text{pH} = 1/2(\text{p}K_{a1} + \text{p}K_{a2})$$

Summary for diprotic acid

- Starting material (Page 211)
 - H_2A
 - Treat as monoprotic acid, $K_a = K_{a1}$, ignore K_{a2}
 - Use K_{a2} to solve for $[A^{2-}]$.
 - HA^-
 - Use approximation $[HA^-] \approx F$
 - Use K_{a1} and K_{a2} for $[H_2A]$ and $[A^{2-}]$
 - A^{2-}
 - Treat as monobasic, $K_b = K_{b1} = K_w / K_{a2}$, ignore k_{b2}
 - Use K_{b2} to solve for $[H_2A]$.