Chapter 9: Polyprotic Acid-Base Equilibria
Section 9.6 Isoelectric and Isoionic pH: غير مطلوب

Introduction   Dr. Abdul-Wahab Rjoob

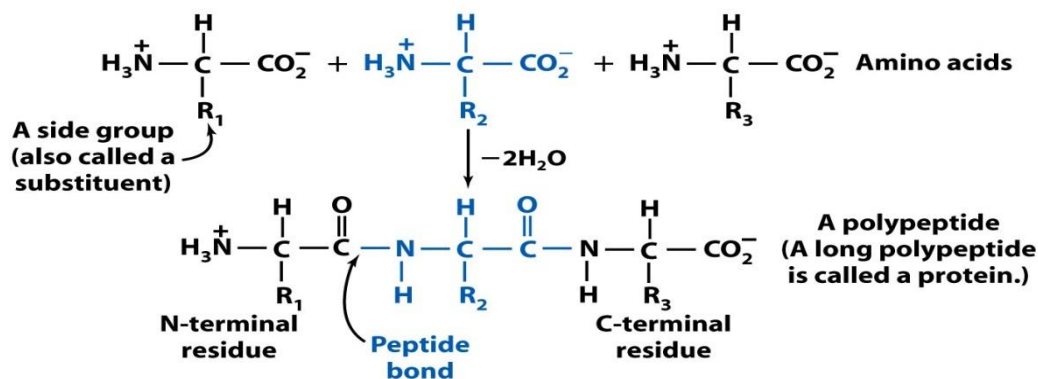### Polyprotic systems

> Acids or bases that can donate or accept more than one proton

Examples of Polyprotic Acids and Bases

Diprotic acids, H_2A vs.   Dibasic species, A^{2-}

   Ex. H_2SO_4, H_2CO_3 Ex. SO_4^{2-}, CO_3^{2-}

Triprotic acids, H_3A vs.   Tribasic species, A^{3-}

   Ex. H_3PO_4, $H_3C_6H_5O_7$ (Citric acid)   Ex. PO_4^{3-}, $C_6H_5O_7^{3-}$
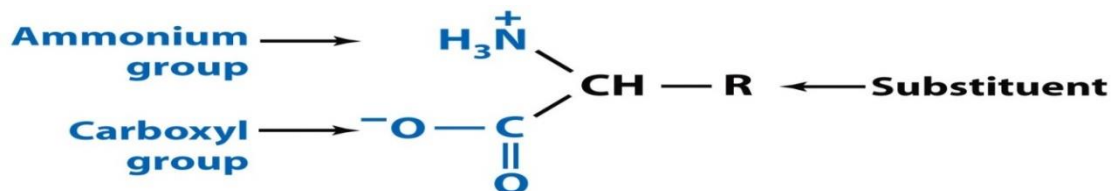
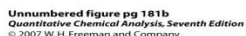• Proteins are a common example of a polyprotic system

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> **Amino acids**
>   - **Some amino acids have acidic or basic substituents**

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- **Carboxyl group (- COOH) is much more acidic (higher K_a; first to dissociate) than the ammonium group ($-NH_3^+$).**
- **R is different group for each amino acid**

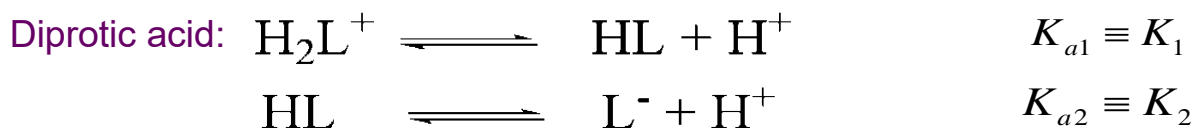

Overall charge is still neutral

Zwitterion

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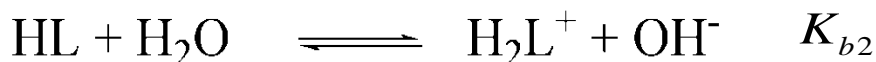© 2007 W.H.Freeman and Company

➢ *Amino acids are zwitterion – molecule with both positive and negative charge*

- **At low pH, both ammonium and carboxyl group are protonated**

- **At high pH, neither group is protonated**

- **Stabilized by interaction with solvent**

9-1 Diprotic Acids and Bases   Dr. Abdul-Wahab Rjoob

Multiple Equilibria

➢ Illustration with amino acid leucine (HL)

➢ **Equilibrium reactions**

Diprotic acid: $H_2L^+ \rightleftharpoons HL + H^+$ $K_{a1} \equiv K_1$

$HL \rightleftharpoons L^- + H^+$ $K_{a2} \equiv K_2$

Diprotic base: $\quad L^- + H_2O \rightleftharpoons HL + OH^- \qquad K_{b1}$

$$HL + H_2O \rightleftharpoons H_2L^+ + OH^- \qquad K_{b2}$$

Relationship between $\qquad\qquad K_{a1} \times K_{b2} \equiv K_w$

K_a and K_b : $\qquad\qquad\qquad K_{a2} \times K_{b1} \equiv K_w$

An easy way to remember:

H_2L^+ / HL $\qquad\qquad\qquad\qquad\qquad$ HL / L^-
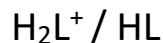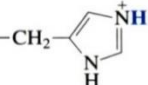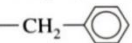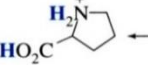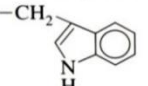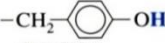
K_{a1} / K_{b2} ($K_{a1} \times K_{b2} = K_w$) $\qquad\qquad$ K_{a2} / K_{b1} ($K_{a2} \times K_{b1} = K_w$)
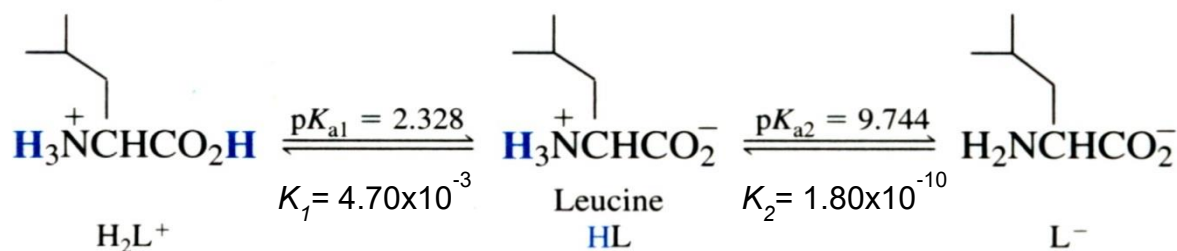
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Table 10-1 Acid dissociation constants of amino acids

Amino acid[a]	Substituent[a]	Carboxylic acid[b] pK_a	Ammonium[b] pK_a	Substituent[b] pK_a	Formula mass
Alanine (A)	—CH₃	2.344	9.868		89.09
Arginine (R)	—CH₂CH₂CH₂NHC(=NH₂⁺)NH₂	1.823	8.991	(12.1[c])	174.20
Asparagine (N)	—CH₂CNH₂ (O)	2.16[c]	8.73[c]		132.12
Aspartic acid (D)	—CH₂CO₂H	1.990	10.002	3.900	133.10
Cysteine (C)	—CH₂SH	(1.7)	10.74	8.36	121.16
Glutamic acid (E)	—CH₂CH₂CO₂H	2.16	9.96	4.30	147.13
Glutamine (Q)	—CH₂CH₂CNH₂ (O)	2.19[c]	9.00[c]		146.15
Glycine (G)	—H	2.350	9.778		75.07
Histidine (H)	—CH₂(imidazole)	(1.6)	9.28	5.97	155.16
Isoleucine (I)	—CH(CH₃)(CH₂CH₃)	2.318	9.758		131.17
Leucine (L)	—CH₂CH(CH₃)₂	2.328	9.744		131.17
Lysine (K)	—CH₂CH₂CH₂CH₂NH₃⁺	(1.77)	9.07	10.82	146.19
Methionine (M)	—CH₂CH₂SCH₃	2.18[c]	9.08[c]		149.21
Phenylalanine (F)	—CH₂—C₆H₅	2.20	9.31		165.19
Proline (P)	(Structure of entire amino acid)	1.952	10.640		115.13
Serine (S)	—CH₂OH	2.187	9.209		105.09
Threonine (T)	—CH(CH₃)(OH)	2.088	9.100		119.12
Tryptophan (W)	—CH₂(indole)	2.37[c]	9.33[c]		204.23
Tyrosine (Y)	—CH₂—C₆H₄—OH	2.41[c]	8.67[c]	11.01[c]	181.19
Valine (V)	—CH(CH₃)₂	2.286	9.719		117.15

pK_a of carboxyl and ammonium group vary depending on substituents

3.)   General Process to Determine pH

> Three components to the process

> Acid Form [H_2L^+]

> Basic Form [L^-]

> Intermediate Form [HL]

> **The Acidic Form, (H_2L^+)**

> Illustration with amino acid leucine

$$\underset{\underset{H_2L^+}{}}{\overset{+}{H_3}NCHCO_2H} \quad \underset{K_1= 4.70\times10^{-3}}{\overset{pK_{a1} = 2.328}{\rightleftharpoons}} \quad \underset{\underset{HL}{Leucine}}{\overset{+}{H_3}NCHCO_2^-} \quad \underset{K_2= 1.80\times10^{-10}}{\overset{pK_{a2} = 9.744}{\rightleftharpoons}} \quad \underset{L^-}{H_2NCHCO_2^-}$$

> H_2L^+ is a <u>weak</u> acid and HL is a <u>very weak</u> acid

$$K_1 \gg K_2$$

Assume H_2L^+ behaves as a monoprotic acid
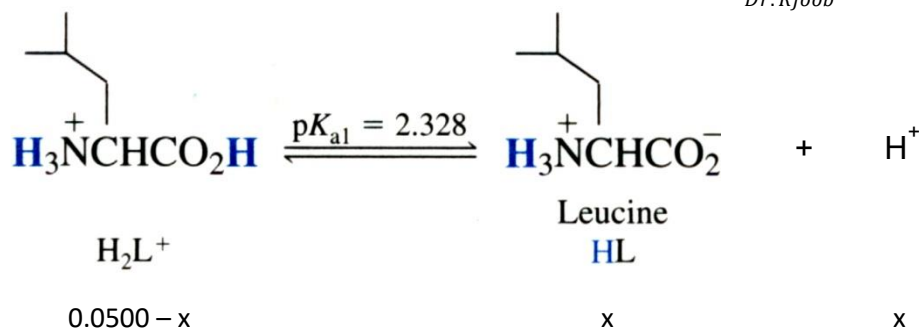
$$K_a = K_1$$

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> Find the pH of 0.050 M leucine hydrochloride(**H_2L^+**)

$H_2L^+, \quad K_{a1} = 4.70 \times 10^{-3} \; (weak\; acid)$

$HL, \quad K_{a2} = 1.80 \times 10^{-10} \; (very\; weak\; acid)$

Since K_{a2} is very small, dissociated HL (that produced from K_{a1} reaction) only dissociates very little to L⁻

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$$H_3\overset{+}{N}CHCO_2H \xrightarrow{\;pK_{a1}\;=\;2.328\;} H_3\overset{+}{N}CHCO_2^- \quad + \quad H^+$$

Leucine

H_2L^+ HL

$0.0500 - x$ x x

Determine $[H^+]$ from K_{a1}:

$$K_{a1} = 4.70 \times 10^{-3} = \frac{[HL][H^+]}{[H_2L^+]} = \frac{x^2}{0.0500 - x}$$

Solve quadratic equation because $\%\alpha = \dfrac{1.53 \times 10^{-2}}{0.0500} \times 100 = 30.7\% \; (> 5\%)$

$$x = 1.32 \times 10^{-2} M = [HL] = [H^+]$$

$$pH = -log[H^+] = -log\, 1.32 \times 10^{-2} = 1.88$$

$$[H_2L^+] = F - x = 0.0500 - 1.32 \times 10^{-2} = 3.68 \times 10^{-2} M$$

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What is the concentration of L⁻ in the solution?

$[L^-]$ is very small, but non-zero. Calculate from K_{a2}

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

$$[L^-] = \frac{(1.80 \times 10^{-10})(1.32 \times 10^{-2})}{(1.32 \times 10^{-2})} = 1.80 \times 10^{-10} (= K_{a2})$$

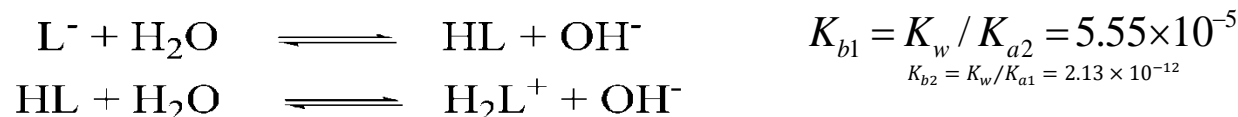***Approximation $[H^+] \approx [HL]$, reduces K_{a2} equation to $[L^-] = K_{a2}$***

$$[L^-] = 1.80 \times 10^{-10} << 1.32 \times 10^{-2} = [HL] \qquad \underline{\textbf{Validates assumption}}$$

> For most diprotic acids, $K_1 \gg K_2$

 - Assumption that diprotic acid behaves as monoprotic is valid

- $K_a \approx K_{a1}$

 > Even if K_{a1} is just 10 times larger than K_{a2}

 - **Error in pH is only 4% or 0.01 pH units**

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The Basic Form (L⁻)

$$L^- + H_2O \rightleftharpoons HL + OH^-$$
$$HL + H_2O \rightleftharpoons H_2L^+ + OH^-$$

$$K_{b1} = K_w / K_{a2} = 5.55 \times 10^{-5}$$
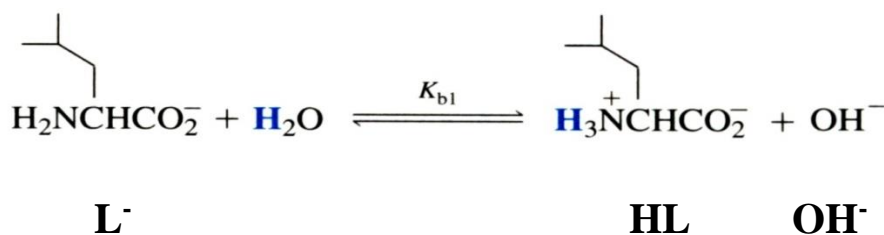$$K_{b2} = K_w / K_{a1} = 2.13 \times 10^{-12}$$

> L⁻ is a <u>weak</u> base and HL is an <u>extremely weak</u> base

$$K_{b1} \gg K_{b2}$$

Assume L⁻ behaves as a monoprotic base

$$K_b = K_{b1}$$

> **Find the pH of 0.050 M leucine salt (*sodium leucinate, NaL*)**

$$H_2NCHCO_2^- + H_2O \xrightarrow{K_{b1}} H_3\overset{+}{N}CHCO_2^- + OH^-$$

L⁻   **HL**   **OH⁻**

0.0500 - x   **x**   **x**

Determine [OH⁻] from K_b: ⬇

$$K_b = 5.55 \times 10^{-5} = \frac{[HL][OH^-]}{[L^-]} = \frac{x^2}{F - x} \Rightarrow x = 1.64 \times 10^{-3} M = [HL] = [OH^-]$$

Determine pH and [H⁺] from K_w: ⬇

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1.64 \times 10^{-3}} = 6.10 \times 10^{-12} M \Rightarrow pH = 11.21$$

<div align="center">Determine [L⁻]: ↓</div>

$$[L^-] = F - x = 0.0500 - 1.64 \times 10^{-3} = 4.84 \times 10^{-2} M$$

What is the concentration of H_2L^+ in the solution?

$[H_2L^+]$ is very small, but non-zero. Calculate from K_{b2}

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

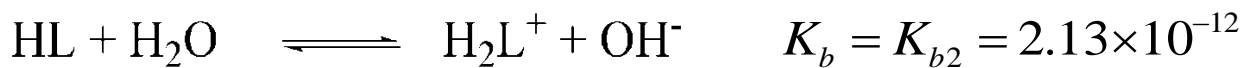$$[H_2L^+] = 2.13 \times 10^{-12} << 1.64 \times 10^{-3} = [HL]$$

Validates assumption [OH⁻] ≈ [HL],

Fully basic form of a diprotic acid can be treated as a monobasic, $K_b = K_{b1}$

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➢ **The Intermediate Form (HL)**

- More complicated HL is both an acid and base

$$HL \rightleftharpoons L^- + H^+ \qquad K_a = K_{a2} = 1.80 \times 10^{-10}$$

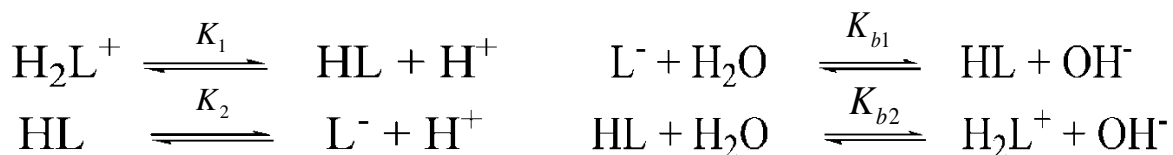$$HL + H_2O \rightleftharpoons H_2L^+ + OH^- \qquad K_b = K_{b2} = 2.13 \times 10^{-12}$$

➢ <u>Amphiprotic</u> – can both donate and accept a proton

➢ Since $K_a > K_b$, expect solution to be acidic

- **Can not ignore base equilibrium**

➢ Need to use Systematic Treatment of Equilibrium

➢ **Step 1:** Pertinent reactions:

$$H_2L^+ \underset{K_2}{\overset{K_1}{\rightleftharpoons}} HL + H^+ \qquad L^- + H_2O \underset{K_{b2}}{\overset{K_{b1}}{\rightleftharpoons}} HL + OH^-$$

$$HL \rightleftharpoons L^- + H^+ \qquad HL + H_2O \rightleftharpoons H_2L^+ + OH^-$$

Step 2:   Charge Balance: Dr. Abdul-Wahab Rjoob

$$[H^+]+[H_2L^+]=[L^-]+[OH^-]$$

Step 3:   Mass Balance:

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

Step 4:   Equilibrium constant expression (one for each reaction):

$$K_2=\frac{[L^-][H^+]}{[HL]} \qquad K_1=\frac{[HL][H^+]}{[H_2L^+]} \qquad K_{b2}=\frac{[H_2L^+][OH^-]}{[HL]} \qquad K_{b1}=\frac{[HL][OH^-]}{[L^-]}$$

Step 6: Solve:

Substitute Acid Equilibrium Equations into charge balance:

$$[H_2L^+]-[L^-]+[H^+]-[OH^-]=0 \qquad [H_2L^+]=\frac{[HL][H^+]}{K_1} \qquad [L^-]=\frac{[HL]K_2}{[H^+]} \qquad [OH^-]=\frac{K_w}{[H^+]}$$

All Terms are related to [H$^+$]

$$\frac{[HL][H^+]}{K_1}-\frac{[HL]K_2}{[H^+]}+[H^+]-\frac{K_w}{[H^+]}=0$$

Multiply by [H$^+$]

$$\frac{[HL][H^+]^2}{K_1}-[HL]K_2+[H^+]^2-K_w=0$$

Factor out [H$^+$]^2:

$$[H^+]^2\left(\frac{[HL]}{K_1}+1\right)=K_2[HL]+K_w$$

Rearrange:

$$[H^+]^2=\frac{K_2[HL]+K_w}{\dfrac{[HL]}{K_1}+1}$$

$$[H^+]^2 = \frac{K_2[HL] + K_w}{\dfrac{[HL]}{K_1} + 1}$$

Multiply by K_1 and take square-root:

$$[H^+] = \sqrt{\frac{K_1 K_2 [HL] + K_1 K_w}{K_1 + [HL]}} \qquad \textbf{(9.10)}$$

Assume [HL] = F, minimal dissociation:
(K_1 & K_2 are small)

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}} \qquad \textbf{(9.11)}$$

➤ **Find the pH of 0.050 M leucine (*HL*)**

$$[H^+] = \sqrt{\frac{(4.70x10^{-3})(1.80x10^{-10})(0.0500) + (4.70x10^{-3})(1.0x10^{-14})}{4.70x10^{-3} + 0.0500}}$$

$$= 8.80x10^{-7} M \Rightarrow pH = 6.06$$

Step 7: Validate Assumptions   Dr. Abdul-Wahab Rjoob

Assume [HL] = F = 0.0500M, minimal dissociation (K_1 & K_2 are small).

Calculate [L⁻] & [H₂L⁺] from K_1 & K_2:

$$[H_2 L^+] = \frac{[HL][H^+]}{K_1} = \frac{(0.0500)(8.80x10^{-7})}{4.70x10^{-3}} = 9.36x10^{-6}$$

$$[L^-] = \frac{[HL]K_2}{[H^+]} = \frac{(0.0500)(1.80x10^{-10})}{8.80x10^{-7}} = 1.02x10^{-5}$$

[HL] = 0.0500M >> 9.36x10⁻⁶ [H₂L⁺] & 1.02x10⁻⁵ [L⁻] <u>Assumption Valid</u>

Summary of results:

> $[L^-] \approx [H_2L^+]$ → two equilibriums proceed equally even though $K_a > K_b$
> Nearly all leucine remained as HL

Solution		pH	[H$^+$] (M)	[H$_2$L$^+$] (M)	[HL] (M)	[L$^-$] (M)
Acid form	0.0500 M H$_2$A	1.88	1.32x10^{-2}	3.68x10^{-2}	1.32x10^{-2}	1.80x10^{-10}
Intermediate Form	0.0500 M HA$^-$	6.06	8.80x10^{-7}	9.36x10^{-6}	5.00x10^{-2}	1.02x10^{-5}
Basic form	0.0500 M A^{2-}	11.21	6.08x10^{-12}	2.13x10^{-12}	1.64x10^{-3}	4.84x10^{-2}

> Simplified Calculation for the Intermediate Form (HL)

$$[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

Assume K$_2$F >> K$_w$:

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$$[H^+] \approx \sqrt{\frac{K_1 K_2 F}{K_1 + F}}$$

Assume K$_1$<< F:

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F}{F}}$$

Cancel F:

$$[H^+] \approx \sqrt{K_1 K_2}$$

Take the -log:

$$-log[H^+] \approx \frac{1}{2}(-logK_1 - logK_2)$$

$$pH \approx \frac{1}{2}(pK_1 + pK_2) \qquad (9.12)$$

(i.e. for 0.0500 M leucine, pH = 6.04 by the above equation
   pH = 6.06 from full calculation)

Independent of concentration: pH of intermediate form of a diprotic acid is close to midway between pK_1 and pK_2

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Example: pH of the Intermediate Form of a Diprotic Acid

Potassium hydrogen phthalate, KHP, is a salt of the intermediate form of phthalic acid. Calculate the pH of 0.10 M and 0.010 M KHP (pK_{a1}= 2.950 and $pK_{a2} = 5.408$)

$K_{a1} = 1.12 \times 10^{-3}$ and $K_{a2} = 3.91 \times 10^{-6}$

$$pH \approx \frac{1}{2}(pK_{a1} + pK_{a2})$$

$$pH \approx \frac{1}{2}(2.950 + 5.408) = 4.18 \; regardless \; of \; concentration$$

$$[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

$$[H^+] = \sqrt{\frac{(1.12 \times 10^{-3})(3.91 \times 10^{-6})(0.10) + (1.12 \times 10^{-3})(1.00 \times 10^{-14})}{1.12 \times 10^{-3} + 0.10}} = 6.58 \times 10^{-5}$$

$$pH = -log \; 6.58 \times 10^{-5} = 4.18$$

$$And \; pH = 4.20 \; for \; 0.010 \; M \; KHP$$

Find the pH of 0.002 M KHP with $[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$
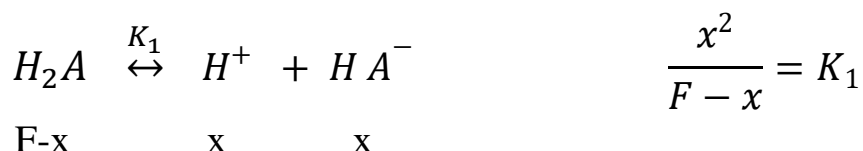
Answer: $pH = 4.28$

Summary of Diprotic Acid Calculations

Here is how we calculate the pH and composition of solutions prepared from different forms of a diprotic acid (H_2A, HA^-, or A_2^-).

Solution of H_2A

1. Treat H_2A as a monoprotic acid with $K_a = K_1$ to find $[H^+]$, $[HA^-]$, and $[H_2A]$.

$$H_2A \overset{K_1}{\leftrightarrow} H^+ + HA^- \qquad\qquad \frac{x^2}{F-x} = K_1$$

$$\text{F-x} \qquad\quad \text{x} \qquad \text{x}$$

2. Use the K_2 equilibrium to solve for $[A_2^-]$.

$$[A_2^-] = \frac{K_2[\cancel{HA^-}]}{[\cancel{H^+}]} = K_2$$

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Solution of HA^-

1. Use the approximation $[HA^-] \approx F$ and find the pH with Equation 9-11.

$$[H^+] \approx \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}} \qquad\qquad \textbf{(9.11)}$$
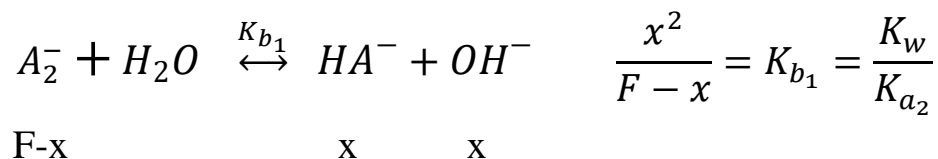
The pH should be close to $\frac{1}{2}(pK_1 + pK_2)$.

2. With $[H^+]$ from step 1 and $[HA^-] = F$, solve for $[H_2A]$ and $[A_2^-]$, using the K_1 and K_2 equilibria.

$$[H_2A] = \frac{[HA^-][H^+]}{K_1} \qquad\qquad [A_2^-] = \frac{K_2[HA^-]}{[H^+]}$$

Solution of A_2^-

1. Treat A_2^- as monobasic, with $K_b = K_{b_1} = \frac{K_w}{K_{a_2}}$ to find $[A_2^-]$, $[HA^-]$, and $[H^+]$.

$$A_2^- + H_2O \overset{K_{b_1}}{\leftrightarrow} HA^- + OH^- \qquad\qquad \frac{x^2}{F-x} = K_{b_1} = \frac{K_w}{K_{a_2}}$$

$$\text{F-x} \qquad\qquad\qquad \text{x} \qquad \text{x}$$

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

2. Use the K_1 equilibrium to solve for $[H_2A]$.

$$[H_2A] = \frac{[H^+][OH^-]}{K_{a_1}} = \frac{\cancel{[HA^-]}\left(K_w/\cancel{[OH^-]}\right)}{K_{a_1}} = K_{b_2}$$

9.2 Diprotic Buffers

1.)   Same Approach as Monoprotic Buffer

➤ Write _two_ Henderson-Hasselbalch equations

$$pH = pK_1 + \log\left(\frac{[HA^-]}{[H_2A]}\right) \qquad pH = pK_2 + \log\left(\frac{[A^{2-}]}{[HA^-]}\right)$$

➤ Both Equations are _always_ true
        Solution only has _one_ pH   Dr. Abdul-Wahab Rjoob
➤ Choice of equation is based on what is known

- [H₂A] and [HA⁻] known use pK_1 equation

- [HA⁻] and [A²⁻] known use pK_2 equation

Find the pH of a solution prepared by dissolving 1.00 g of potassium hydrogen phthalate (204.221 g/mol) and 1.20 g of disodium phthalate (210.094 g/mol) in 50.0 mL of water.
Phthalic acid (H₂P): $pK_{a1} = 2.950$ and $pK_{a2} = 5.408$)

We know [HP⁻] and [P²⁻], so we use the pK_{a2} Henderson-Hasselbalch equation to find the pH:

$$pH = pK_{a2} + \log\frac{[P^{2-}]}{[HP^-]} = 5.408 + \log\frac{(1.20g/210.094g/mol)}{(1.00g/204.221g/mol)} = 5.47$$

Notice that the **volume** of solution was not used to answer the question.

Test Yourself: Find the pH with 1.50 g Na_2P instead of 1.20 g. (***Answer:*** 5.57)

Q1) How many grams of Na_2CO_3 (FM 105.99) should be mixed with 5.00 g of $NaHCO_3$ (FM 84.01) to produce 100 mL of buffer with pH 10.00?
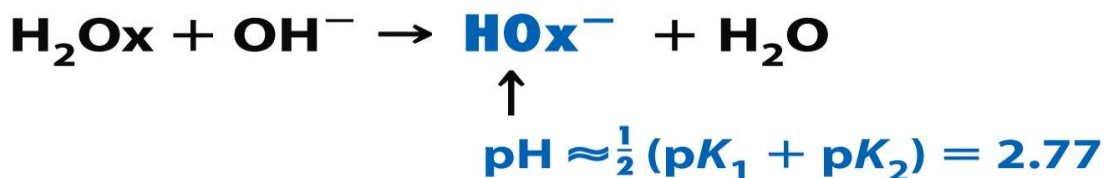

FM =

carbonic acid
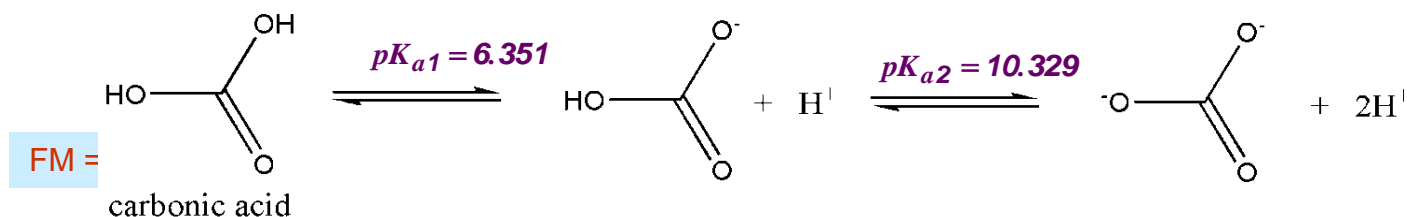
Example: How many milliliters of 0.800 *M* KOH should be added to 3.38 g of oxalic acid to give a pH of 4.40 when diluted to 500 mL?
Oxalic acid: $H_2C_2O_4$ (H_2Ox) FW = 90.035 g/mol; $K_{a1} = 5.62 \times 10^{-2}$ ($pK_{a1} =$ 1.250) and $K_{a2} = 5.42 \times 10^{-5}$ ($pK_{a2} = 4.266$)

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Solution The desired pH is above pK_2. We know that a 1:1 mole ratio of HOx^- : Ox^{2-} would have pH = pK_2 = 4.266. If the pH is to be 4.40, there must be more Ox^{2-} than HOx^- present. We must add enough base to convert all of the H_2Ox into HOx^-, plus enough additional base to convert the right amount of HOx^- into Ox^{2-}.

$$H_2Ox + OH^- \rightarrow HOx^- + H_2O$$

$$\uparrow$$

$$pH \approx \tfrac{1}{2}(pK_1 + pK_2) = 2.77$$

$$HOx^- + OH^- \rightarrow Ox^{2-} + H_2O$$

A 1:1 mixture would have
pH = pK_2 = 4.266

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In 3.38 g of H_2Ox, there are 0.037 54 mol. The volume of 0.800 M KOH needed to react with this much H_2Ox to make HOx^- is (0.037 54 mol)/(0.800 M) = 46.93 mL.

To produce a pH of 4.40 requires more OH^-:   Dr. Abdul-Wahab Rjoob

	HOx^-	+	OH^-	→	Ox^{2-}
Initial moles	0.03754		x		-
Final moles	0.03754 - x		-		x

$$pH = pK_2 + log\frac{[Ox^{2-}]}{[HOx^-]} \rightarrow 4.40 = 4.266 + log\frac{x}{0.03754-x} \rightarrow x = 0.02165 \text{ mol}$$

The volume of KOH needed to deliver 0.021 65 mole is (0.021 65 mol)/(0.800 M) = 27.06 mL.

The total volume of KOH needed to bring the pH to 4.40 is 46.93 + 27.06 = 73.99 mL.

Test Yourself: What volume of KOH would bring the pH to 4.50? (**Answer:** 76.56 mL)
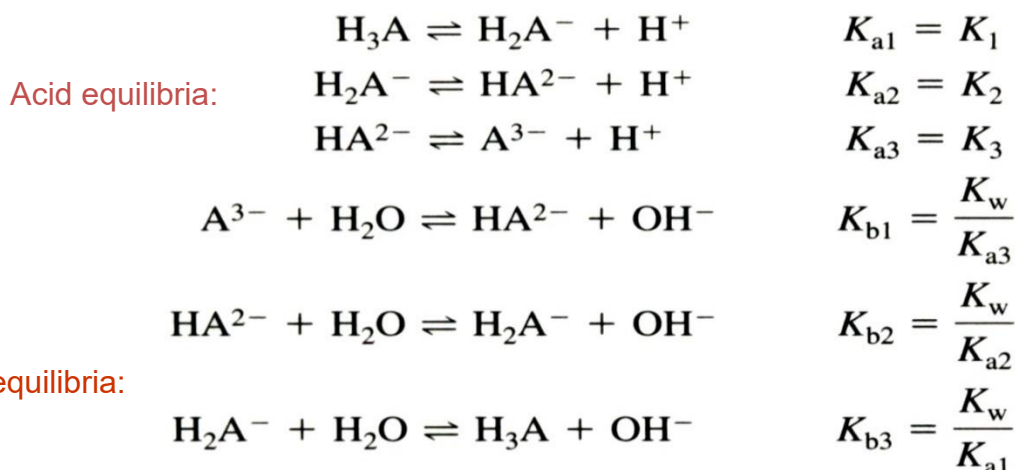
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Q2) How many milliliters of 0.202 M NaOH should be added to 25.0 mL of 0.0233 M of salicylic acid (2-hydroxybenzoic acid) to adjust the pH to 3.50?

salicylic acid
FM = 90.035
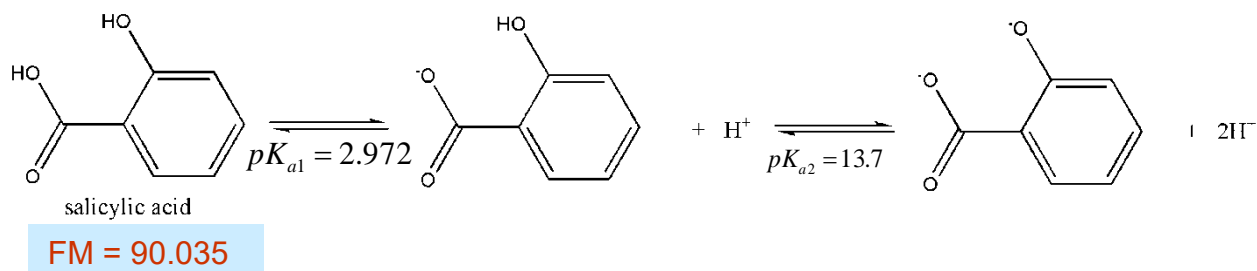
9.3 Polyprotic Acids and Bases

1.) Extend Treatment of Diprotic Acids and Bases to Polyprotic Systems

➤ Equilibria for triprotic system

Acid equilibria:
$$H_3A \rightleftharpoons H_2A^- + H^+ \qquad K_{a1} = K_1$$
$$H_2A^- \rightleftharpoons HA^{2-} + H^+ \qquad K_{a2} = K_2$$
$$HA^{2-} \rightleftharpoons A^{3-} + H^+ \qquad K_{a3} = K_3$$

$$A^{3-} + H_2O \rightleftharpoons HA^{2-} + OH^- \qquad K_{b1} = \frac{K_w}{K_{a3}}$$

$$HA^{2-} + H_2O \rightleftharpoons H_2A^- + OH^- \qquad K_{b2} = \frac{K_w}{K_{a2}}$$

Base equilibria:
$$H_2A^- + H_2O \rightleftharpoons H_3A + OH^- \qquad K_{b3} = \frac{K_w}{K_{a1}}$$

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➤ Rules for triprotic system
➤ Rules for triprotic system

1. H_3A is treated as a monoprotic acid, $K_a = K_1$
2. H_2A^- is treated similarly as an intermediate form of a diprotic acid

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}} \qquad (9.13)$$

3. HA^{2-} is also treated similarly as an intermediate form of a diprotic acid
   a. **Surrounded by H_2A^- and A^{3-}**
   b. **Use K_2 & K_3, instead of K_1 & K_2**

$$[H^+] = \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}} \qquad (9.14)$$

4. A^{3-} is treated as monobasic, with $K_b = K_{b1} = K_w / K_{a3}$

Treat as Monoprotic acid:
$$H_3A \rightleftharpoons H_2A^- + H^+ \qquad K_{a1} = K_1$$

Treat as Intermediate Forms
$$H_2A^- \rightleftharpoons HA^{2-} + H^+ \qquad K_{a2} = K_2$$

Treat as Intermediate Forms
$$HA^{2-} \rightleftharpoons A^{3-} + H^+ \qquad K_{a3} = K_3$$

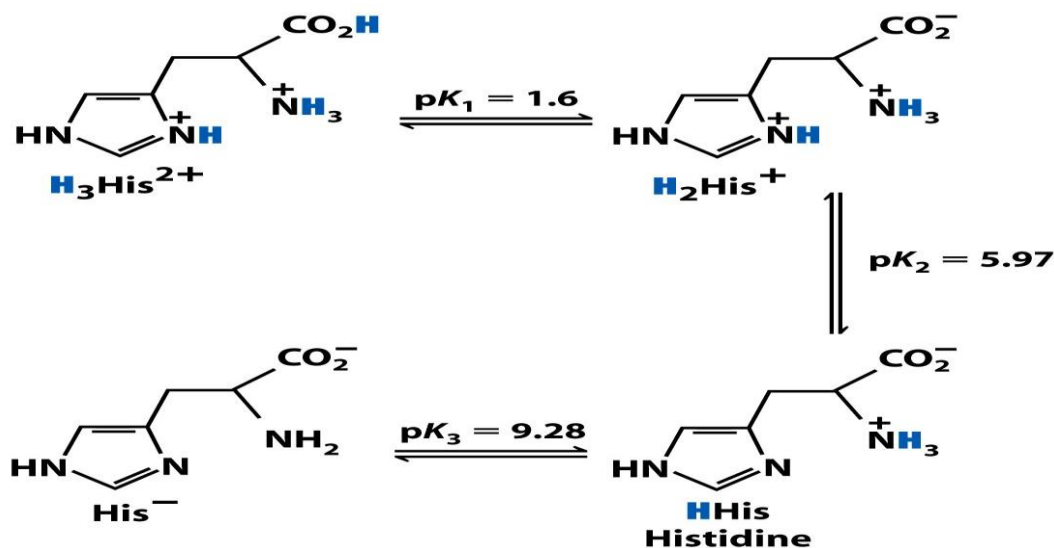Treat as Monoprotic base:
$$A^{3-} + H_2O \rightleftharpoons HA^{2-} + OH^- \qquad K_{b1} = \frac{K_w}{K_{a3}}$$
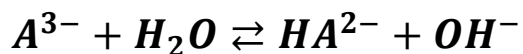
For more complex system, just have additional intermediate forms in-between the two monoprotic acid and base forms at "ends"
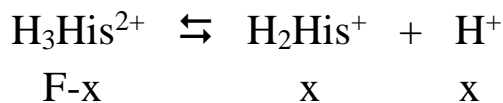
Example: Find the pH of 0.10 M H_3His^{2+}, 0.10 M H_2His^+, 0.10 M HHis, and 0.10 M His⁻, where His stands for the amino acid histidine.

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Solution *0.10 M H₃His²⁺*: Treating **H₃His²⁺** as a monoprotic acid, we write

$$H_3His^{2+} \rightleftharpoons H_2His^+ + H^+$$
$$\quad F\text{-}x \qquad\qquad x \qquad\ x$$

$$K_1 = 10^{-1.6} = \frac{x^2}{0.10 - x} \rightarrow x = 3.9 \times 10^{-2}M \rightarrow pH = 1.41$$

0.10 M H₂His⁺ : Using Equation $[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$ $(9 - 13)$, we find

$$[H^+] = \sqrt{\frac{(10^{-1.6})(10^{-5.97})(0.10) + (10^{-1.6})(10^{-14})}{(10^{-1.6}) + (0.10)}} = 1.47 \times 10^{-4}M \rightarrow pH = 3.83$$

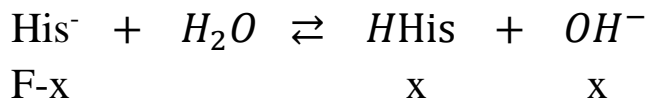which is close to $\frac{1}{2}(pK_{a1} + pK_{a2}) = 3.78$

0.10 M HHis: Using Equation (9-14) $[H^+] = \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}}$ gives

$$[H^+] = \sqrt{\frac{(10^{-5.97})(10^{-9.28})(0.10) + (10^{-5.97})(10^{-14})}{(10^{-5.97}) + (0.10)}} = 2.37 \times 10^{-8}M \rightarrow pH = 7.62$$

Which is the same as $\frac{1}{2}(pK_{a2} + pK_{a3}) = 7.62$

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0.10 M His⁻: Treating **His⁻** as monobasic, we can write

$$His^- + H_2O \rightleftharpoons HHis + OH^-$$
$$F\text{-}x \qquad\qquad\qquad x \qquad\ x$$

$$K_{b1} = \frac{K_w}{K_{a3}} = 1.9 \times 10^{-5} = \frac{x^2}{0.10 - x} \rightarrow x = 1.37 \times 10^{-3}M = [OH^-]$$

$$pH = -log\left(\frac{K_w}{[OH^-]}\right) = 11.14$$

Test Yourself: Compute the pH of 0.010 M HHis. (***Answer:*** 7.62)

9.4 Which is the Principal Species?

We sometimes must identify which species of acid, base, or intermediate predominates under given conditions. For example, "What is the principal form of benzoic acid at pH 8?"

Benzoic acid (C_6H_5COOH) is a monoprotic acid with $pK_a = 4.20$

pK_a for benzoic acid is 4.20. So, at pH 4.20, there is a 1:1 mixture of benzoic acid (HA) and benzoate ion (A^-). At $pH = pKa + 1$ ($= 5.20$), the quotient $[A^-]/[HA]$ is 10:1. At $pH = pKa + 2$ ($= 6.20$), the quotient $[A^-]/[HA]$ is 100:1. As pH increases, the quotient $[A^-]/[HA]$ increases still further.

For a monoprotic system, the basic species A^- is the predominant form when $pH > pK_a$. The acidic species, HA, is the predominant form when $pH < pK_a$. The predominant form of benzoic acid at pH 8 is the benzoate anion, $C_6H_5CO_2^-$.

EXAMPLE Principal Species - Which One and How Much?
What is the predominant form of ammonia in a solution at pH 7.0? Approximately what fraction is in this form?
Solution In Appendix G, we find $pK_a = 9.24$ for the ammonium ion (NH_4^+, the conjugate acid of ammonia, NH_3). At $pH = 9.24$, $[NH_4^+] = [NH_3]$. Below pH 9.24, NH_4^+ will be the predominant form. Because $pH = 7.0$ is about 2 pH units below pK_a, the quotient $[NH_4^+]/[NH_3]$ will be about 100:1. More than 99% is in the form NH_4^+.

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Test Yourself Approximately what fraction of ammonia is in the form NH_3 at pH 11? (Answer: somewhat less than 99% because pH is almost 2 units above pK_a)

For polyprotic systems, our reasoning is similar, but there are several values of pKa. Consider oxalic acid, H_2Ox, with $pK_1 = 1.25$ and $pK_2 = 4.27$. At $pH = pK_1$, $[H_2Ox] = [HOx^-]$. At $pH = pK_2$, $[HOx^-] = [Ox^{2-}]$.

EXAMPLE Principal Species in a Polyprotic System
The amino acid arginine has the following forms:

$$H_3Arg^{2+} \xrightleftharpoons[]{pK_1=1.82} H_2Arg^+ \xrightleftharpoons[]{pK_2=8.99} HArg \xrightleftharpoons[]{pK_3=12.1} Arg^-$$
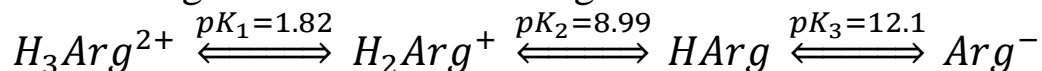
What is the principal form of arginine at pH 10.0? Approximately what fraction is in this form? What is the second most abundant form at this pH?

Solution We know that at pH = pK_2 = 8.99, $[H_2Arg^+]$ = [HArg]. At pH = pK_3 = 12.1, [HArg] = [Arg^-]. At pH = 10.0, the major species is HArg. Because pH 10.0 is about one pH unit higher than pK_2, we can say that [HArg] / $[H_2Arg^+]$ ≈10:1. About 90% of arginine is in the form HArg. The second most important species is H_2Arg^+, which makes up about 10% of the arginine.

Test Yourself What is the predominant form of arginine at pH 11? What is the second major species? (Answer: HArg, Arg^-)

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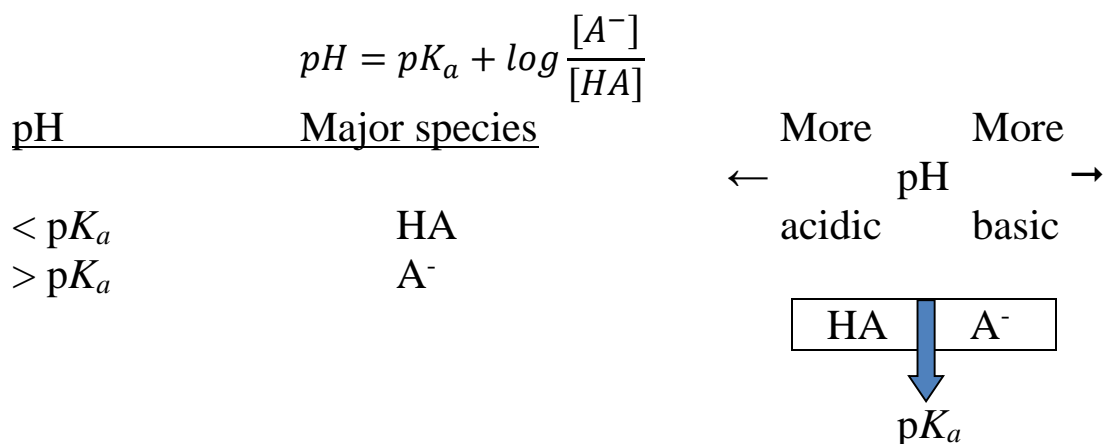
EXAMPLE More on Polyprotic Systems
In the pH range 1.82 to 8.99, H_2Arg^+ is the principal form of arginine. Which is the second most prominent species at pH 6.0? at pH 5.0?

Solution We know that the pH of the pure intermediate (amphiprotic) species, H_2Arg^+, is

$$\text{pH of } H_2Arg^+ \approx \frac{1}{2}(pK_{a1} + pK_{a2}) = 5.40$$

Above pH 5.40 (and below pH = pK_2), HArg, the conjugate base of H_2Arg^+, will be the second most important species. Below pH 5.40 (and above pH = pK_1), H_3Arg^{2+} will be the second most important species.

Test Yourself At what pH does $[H_2Arg^+]$ = [Arg^-]? (Answer: 10.54)

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

pH	Major species
< pK_a	HA
> pK_a	A$^-$

More   More

←   pH   →

acidic   basic

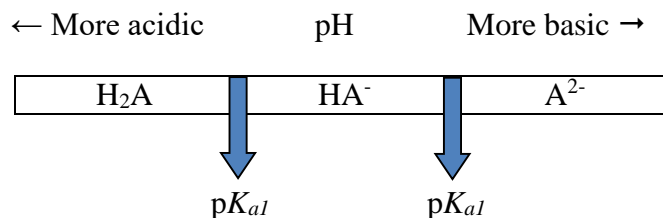| HA	A$^-$

↓

pK_a

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➤ Depends on the pH of the sample and the pK_a values

- **For monoprotic, At pH = pK_a, 1:1 mixture of HA and A$^-$**

- **For monoprotic, A$^-$ is predominant when pH > pK_a**

- **For monoprotic, HA is predominant when pH < pK_a**
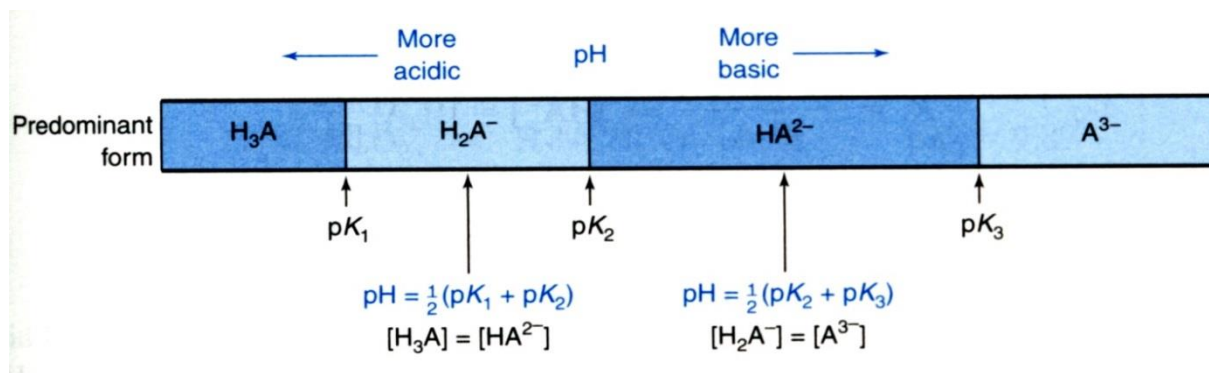
➤ Similar for polyprotic, but several pK_a values

Diprotic acid

pH	Major Species
pH < pK_1	H$_2$A
pK_1 < pH < pK_2	HA$^-$
pH > pK_2	A^{2-}

← More acidic   pH   More basic →

H$_2$A	HA$^-$	A^{2-}

↓   ↓

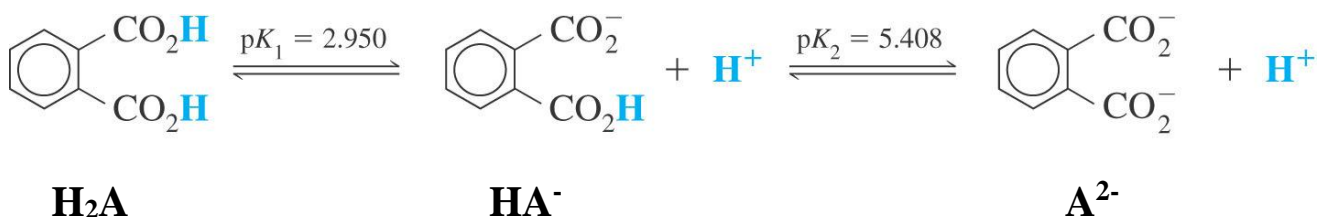pK_{a1} pK_{a1}

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Triprotic acid

Determine Principal Species by Comparing the pH of the Solution with the pK_a Values

What is the **major species** at a given pH?

$$\text{H}_2\text{A} \qquad\qquad \text{HA}^- \qquad\qquad\qquad \text{A}^{2-}$$

1. When $pH < pK_1$, H_2A predominates
2. When $pH = pK_1$, $[H_2A] = [HA^-]$
3. When $pK_1 < pH < pK_2$, $[HA^-]$ predominates
4. When $pH = pK_2$, $[HA^-] = [A^{2-}]$
5. When $pH > pK_2$, $[A^{2-}]$ predominates
Q. Which of the species above predominate at pH 6.50? pH 4.00? pH 2.00?
Answer: A^{2-}, HA^-, H_2A

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9.5 Fractional Composition Equations

➤ Fraction of Each Species at a Given pH

➤ Useful for:
- **Acid-base titrations**
- **EDTA titrations**

- **Electrochemical equilibria**

Monoprotic Systems

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

➢ Combine Mass Balance and Equilibrium Constant

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

$$K_a = \frac{[H^+](F\text{-}[HA])}{[HA]}$$

Rearrange:

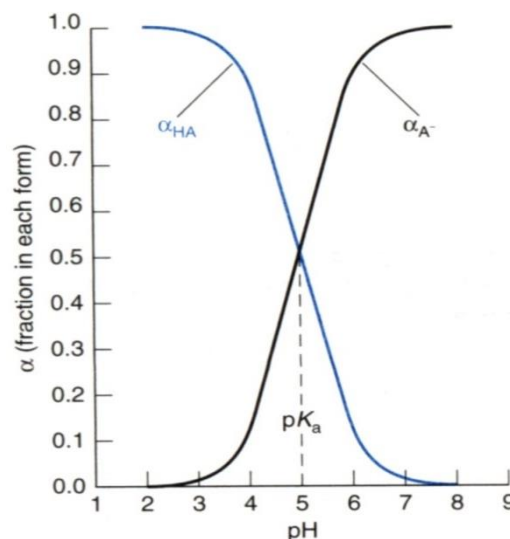$$[HA] = \frac{[H^+]F}{[H^+] + K_a}$$

<u>Recall</u>: fraction of molecule in the form HA is: $\alpha_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{[HA]}{F}$

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

Divide by F:

Fraction in the form HA: $\alpha_{HA} = \frac{[HA]}{F} = \frac{[H^+]}{[H^+] + K_a}$

Fraction in the form A⁻: $\alpha_{A^-} = \frac{[A^-]}{F} = \frac{K_a}{[H^+] + K_a}$

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Fractional composition diagram of a monoprotic system with pKa = 5.00. Below pH 5, HA is the dominant form, whereas, above pH 5, A⁻ dominates.

➢ Diprotic Systems   Dr. Abdul-Wahab Rjoob

➢ Follows same process as monoprotic systems

Fraction in the form H₂A:

$$\alpha_{H_2A} = \frac{[H_2A]}{F} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

Fraction in the form HA⁻:

$$\alpha_{HA^-} = \frac{[HA^-]}{F} = \frac{K_1[H^+]}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

Fraction in the form A²⁻:

$$\alpha_{A^{2-}} = \frac{[A^{2-}]}{F} = \frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$
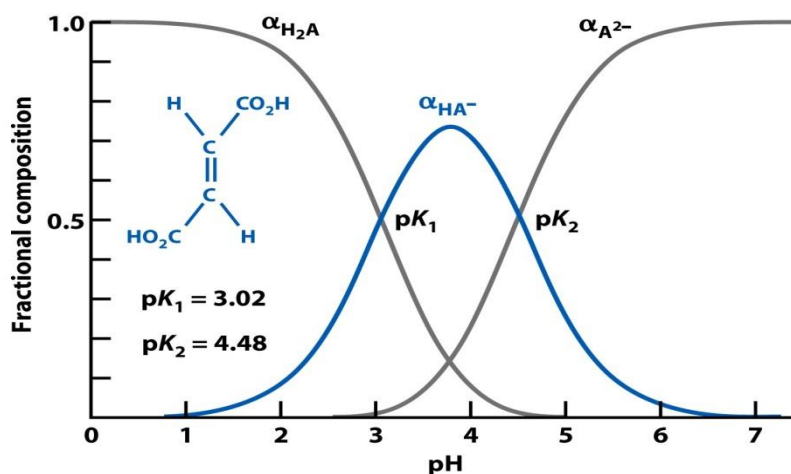

Figure 10-3
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Fractional composition diagram for fumaric acid (*trans*-butenedioic acid). At low pH, H₂A is dominant. At intermediate pH, HA⁻ is dominant; and, at high pH, A²⁻ dominates. Because pK_1 and pK_2 are not separated very much, the fraction of HA⁻ never gets very close to unity.

The general form of α for the polyprotic acid H_nA is

$$\alpha_{H_nA} = \frac{[H^+]^n}{D}$$

$$\alpha_{H_{n-1}A} = \frac{K_1[H^+]^{n-1}}{D}$$

$$\alpha_{H_{n-j}A} = \frac{K_1K_2...K_j[H^+]^{n-j}}{D}$$

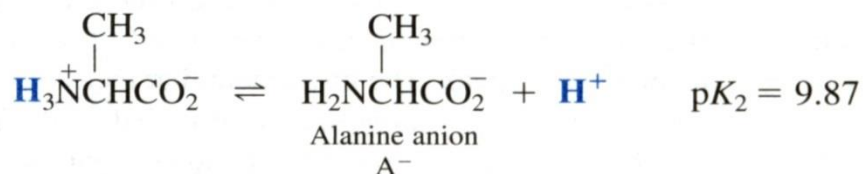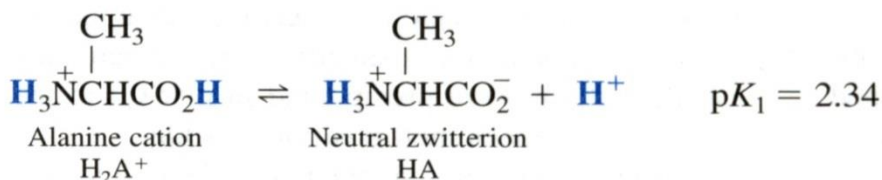where $D = [H^+]^n + K_1[H^+]^{n-1} + K_1K_2[H^+]^{n-2} + \ldots + K_1K_2K_3 \ldots K_n$.

The above equations apply equally well to B, BH^+, and BH_2^{2+} obtained from the base B. The fraction α_{H2A} applies to the acidic form BH_2^{2+}. α_{HA^-} applies to BH^+, and $\alpha_{A^{2-}}$ applies to B. The constants K_1 and K_2 are the *acid* dissociation constants of BH_2^{2+} ($K_1 = K_w/K_{b2}$ and $K_2 = K_w/K_{b1}$).

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9.6 Isoelectric and Isoionic pH

1) Isoionic point (or isoionic pH) – is the pH obtained when the pure, neutral polyprotic acid HA (the neutral zwitterion) is dissolved in water

- The only ions are H_2A^+, A^-, H^+ and OH^-. Most alanine is in the form of HA, and the concentrations of H_2A^+ and A^- are *not* equal to each other.

$$H_3\overset{+}{N}CHCO_2H \quad \rightleftharpoons \quad H_3\overset{+}{N}CHCO_2^- + H^+ \qquad pK_1 = 2.34$$

Alanine cation H_2A^+ Neutral zwitterion HA

$$H_3\overset{+}{N}CHCO_2^- \quad \rightleftharpoons \quad H_2NCHCO_2^- + H^+ \qquad pK_2 = 9.87$$

Alanine anion A^-

When alanine is dissolved in water, the pH of the solution, by definition, is the *isoionic* pH. Because alanine (HA) is the intermediate form of the diprotic acid, H_2A^+, $[H^+]$ is given by

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Isoionic point: $$[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

pH obtained by simply dissolving alanine

where F is the formal concentration of alanine. For 0.10 *M* alanine, the isoionic pH is found from

$$[H^+] = \sqrt{\frac{K_1 K_2 (0.10) + K_1 K_w}{K_1 + (0.10)}} = 7.7 \times 10^{-7} M \rightarrow pH = 6.11$$

From $[H^+]$, K_1, and K_2, you could calculate $[H_2A^+] = 1.68 \times 10^{-5}$ *M* and $[A^-] = 1.76 \times 10^{-5}$ *M* for pure alanine in water (the *isoionic* solution).

Remember: Net Charge of Solution is Always Zero!

➢ 2) Isoelectric point – is the pH at which the *average* charge of the polyprotic acid is 0 or the pH at which $[H_2A^+] = [A^-]$

Always some A^- and H_2A^+ in equilibrium with HA

➢ Most of molecule is in uncharged HA form   Dr. Rjoob

➢ To go from isoionic point (all HA) to isoelectric point, add acid to decrease $[A^-]$ and increase $[H_2A^+]$ until equal

$pK_1 < pK_2$ ➔ isoionic point is acidic➔ excess $[A^-]$

➢ At isoelectric point: $[A^-] = [H_2A^+]$

$$[H_2A^+] = \frac{[HA][H^+]}{K_1} \qquad\qquad [A^-] = \frac{K_2[HA]}{[H^+]}$$

$$\frac{[HA][H^+]}{K_1} = \frac{K_2[HA]}{[H^+]} \Rightarrow [H^+] = \sqrt{K_1 K_2}$$

Isoelectric point: $$pH = \tfrac{1}{2}(pK_1 + pK_2)$$

Example:

➢ Determine isoelectric and isoionic pH for 0.10 M alanine ($pK_1 = 2.34$, $pK_2 = 9.87$).

   ➢ Solution:

   ➢   For isoionic point:

$$[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}} = \sqrt{\frac{(10^{-2.34})(10^{-9.87})(0.10) + (10^{-2.34})(1 \times 10^{-14})}{10^{-2.34} + 0.10}}$$

$$= 7.7 \times 10^{-7} M \Rightarrow pH = 6.11$$

For isoelectric point:
$$pH = \frac{1}{2}(pK_1 + pK_2) = \frac{1}{2}(2.34 + 9.87) = 6.10$$

Isoelectric and isoionic points for polyprotic acid are almost the same

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