Chapter 10 in the 9th Edition

Chapter 9 in the 8the Edition

Polyprotic Acid-Base Equilibria

Overview

- Solutions of weak acids and bases

Example:

Propanoic acid (CH_3CH_2COOH, which we simplify as HPr) is a carboxylic acid whose salts are used to retard mold growth in food products. What is the $[H_3O^+]$ of 0.10 *M* HPr ($K_a = 1.3\text{x}10^{-5}$)?

$$HPr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Pr^-(aq)$$

$$K_a = \frac{[H_3O^+][Pr^-]}{[HPr]}$$

Concentration (*M*)	**$HPr(aq)$**	**+ $H_2O(l)$**	**$\rightleftharpoons$**	**$H_3O^+(aq)$**	**+ $Pr^-(aq)$**
Initial	0.10	-		0	0
Change	$-x$	-		$+x$	$+x$
Equilibrium	$0.10 - x$	-		x	x

Since K_a is small, we will assume that $x << 0.10$ and $[HPr] \approx 0.10\ M$.

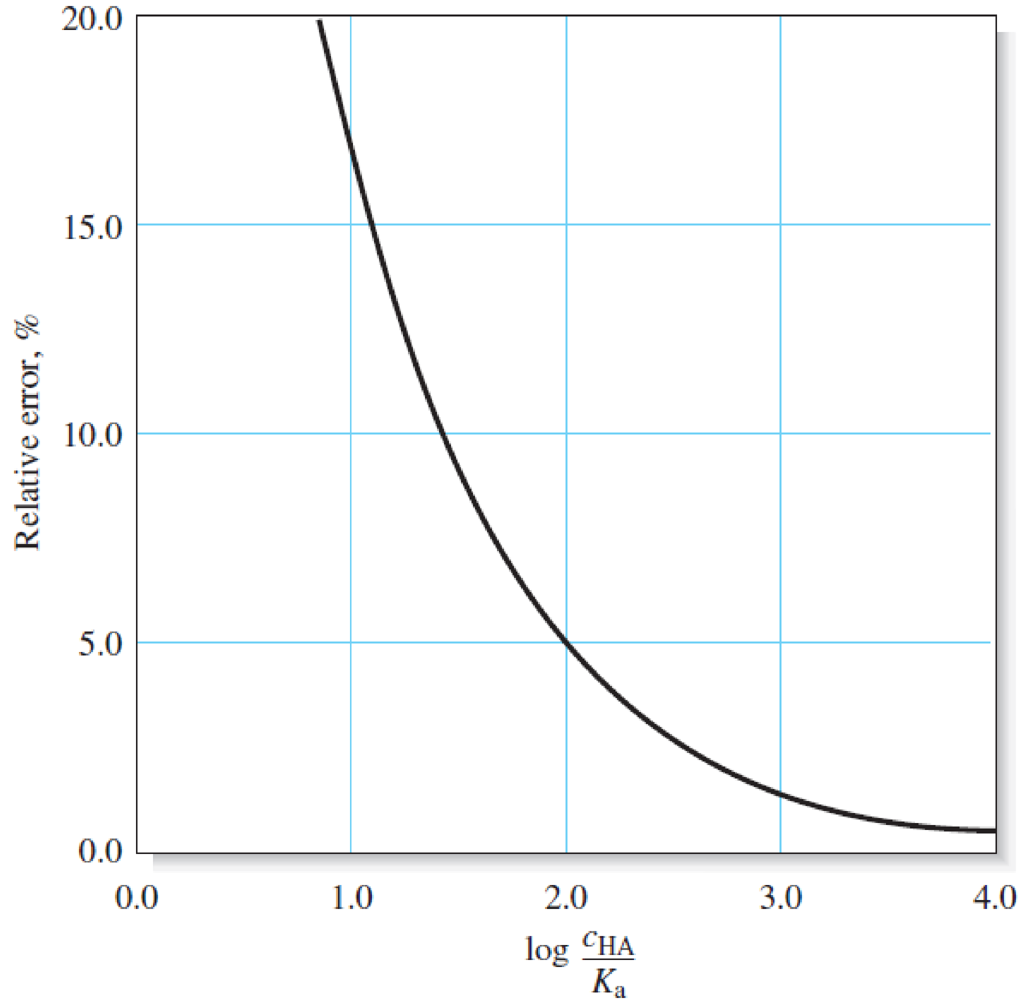
$$K_a = 1.3\text{x}10^{-5} = \frac{[H_3O^+][Pr^-]}{[HPr]} = \frac{x^2}{0.10}$$

$$x = \sqrt{(0.10)(1.3\text{x}10^{-5})} = \mathbf{1.1x10^{-3}\ \mathit{M} = [H_3O^+]} \quad \mathbf{pH = -log\ [H_3O^+] = 2.96}$$

$$\text{Check: } [HPr]_{diss} = \frac{1.1\text{x}10^{-3}\ M}{0.10\ M} \text{ x } 100 = 1.1\%\ (< 5\%;\ \text{assumption is justified.})$$

Error Introduced by Assuming H_3O^+ Concentration Is Small Relative to c_{HA} in Equation 9-16

K_a	c_{HA}	$[H_3O^+]$ Using Assumption	$\frac{c_{HA}}{K_a}$	$[H_3O^+]$ Using More Exact Equation	Percent Error
1.00×10^{-2}	1.00×10^{-3}	3.16×10^{-3}	10^{-1}	0.92×10^{-3}	244
	1.00×10^{-2}	1.00×10^{-2}	10^{0}	0.62×10^{-2}	61
	1.00×10^{-1}	3.16×10^{-2}	10^{1}	2.70×10^{-2}	17
1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	10^{0}	0.62×10^{-4}	61
	1.00×10^{-3}	3.16×10^{-4}	10^{1}	2.70×10^{-4}	17
	1.00×10^{-2}	1.00×10^{-3}	10^{2}	0.95×10^{-3}	5.3
	1.00×10^{-1}	3.16×10^{-3}	10^{3}	3.11×10^{-3}	1.6
1.00×10^{-6}	1.00×10^{-5}	3.16×10^{-6}	10^{1}	2.70×10^{-6}	17
	1.00×10^{-4}	1.00×10^{-5}	10^{2}	0.95×10^{-5}	5.3
	1.00×10^{-3}	3.16×10^{-5}	10^{3}	3.11×10^{-5}	1.6
	1.00×10^{-2}	1.00×10^{-4}	10^{4}	9.95×10^{-5}	0.5
	1.00×10^{-1}	3.16×10^{-4}	10^{5}	3.16×10^{-4}	0.0



Relative error resulting from the assumption that $[H_3O^+] << c_{HA}$

10-1: Diprotic Acids and Bases

- **Polyprotic acids and bases** are those that can donate or accept more than one proton.

- **Diprotic acids and bases** therefore can either donate or accept two protons.

Types of polyprotic acids

1. **H_2B^+**, Amino acids**,** Example: Alanine – H_2A^+

Neutrally charged acids

2. **H_2A** Example: H_2SO_4, H_2CO_3, $H_2C_2O_4$

3. **H_3A** Example: H_3PO_4

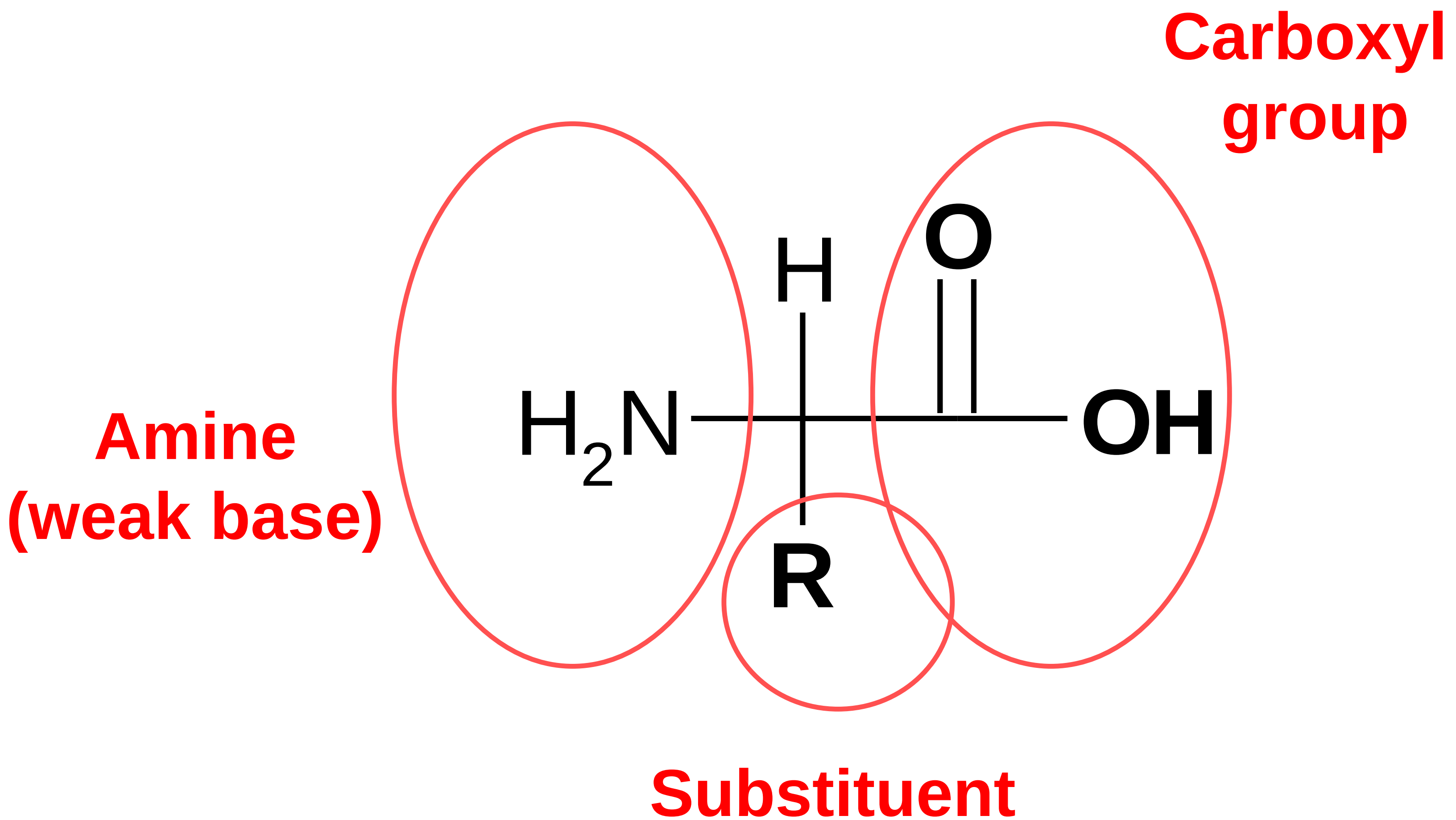
10-1: Diprotic Acids and Bases

- A common class of diprotic acids are **amino acids**, which are the building blocks of proteins.

- They have an acidic **carboxylic acid** group, a basic **amino** group, and a variable **substituent** designated R.

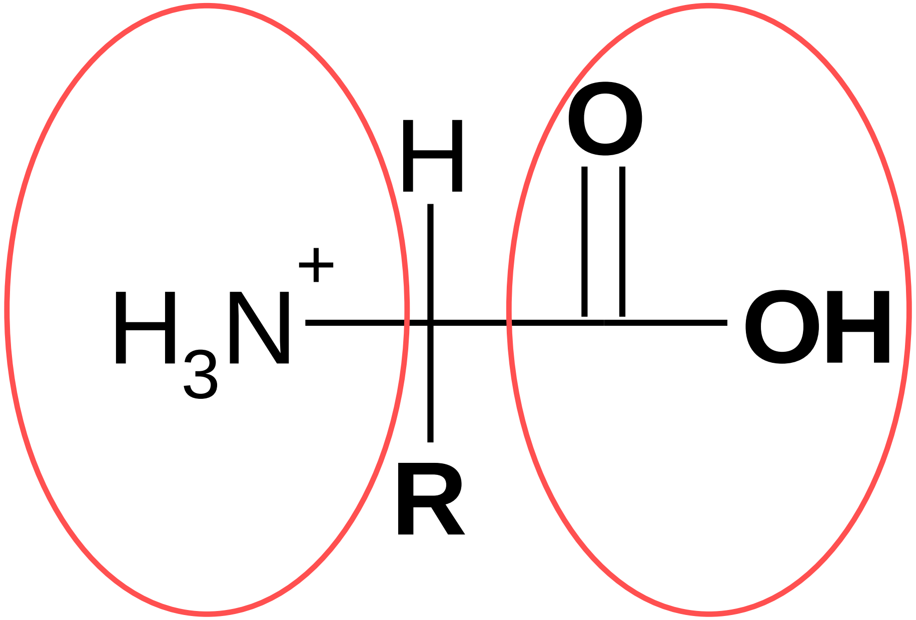
- The carboxyl group is a stronger acid than the ammonium group, so the nonionized form rearranges spontaneously to the **zwitterion,** which has both positive and negative sites.

Amino Acid



Amino Acid

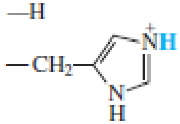
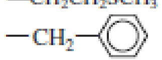
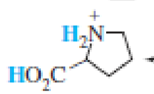
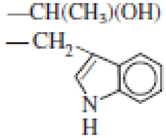
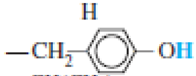
pK_a ~ 2.5



Ammonium group
pK_a ~ 9.5

10-1: Diprotic Acids and Bases

TABLE 10-1 Acid dissociation constants of amino acids

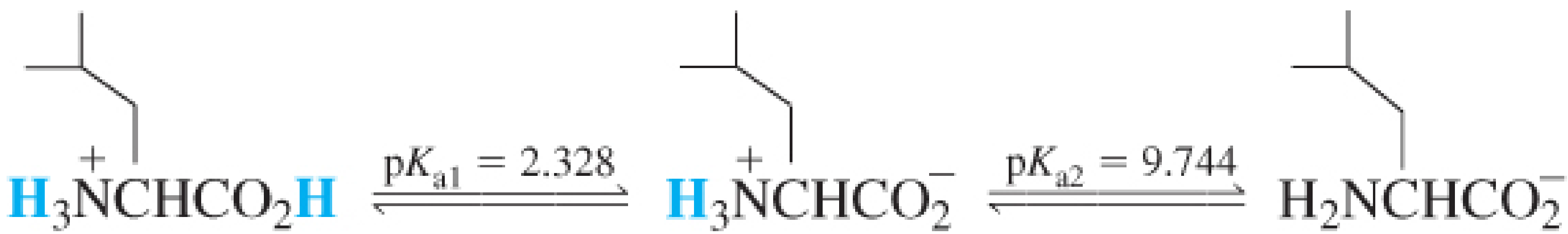
Amino acid[a]	Substituent[a]	Carboxylic acid[b] pK_a	Ammonium[b] pK_a	Substituent[b] pK_a	Formula mass
Alanine (A)	$—CH_3$	2.344	9.868		89.09
Arginine (R)	$—CH_2CH_2CH_2NHC(=\overset{+}{N}H_2)NH_2$	1.823	8.991	(12.1[c])	174.20
Asparagine (N)	$—CH_2C(=O)NH_2$	2.16[c]	8.73[c]		132.12
Aspartic acid (D)	$—CH_2CO_2$**H**	1.990	10.002	3.900	133.10
Cysteine (C)	$—CH_2S$**H**	(1.7)	10.74	8.36	121.16
Glutamic acid (E)	$—CH_2CH_2CO_2$**H**	2.16	9.96	4.30	147.13
Glutamine (Q)	$—CH_2CH_2C(=O)NH_2$	2.19[c]	9.00[c]		146.15
Glycine (G)	—H	2.350	9.778		75.07
Histidine (H)		(1.6)	9.28	5.97	155.16
Isoleucine (I)	$—CH(CH_3)(CH_2CH_3)$	2.318	9.758		131.17
Leucine (L)	$—CH_2CH(CH_3)_2$	2.328	9.744		131.17
Lysine (K)	$—CH_2CH_2CH_2CH_2NH_3^+$	(1.77)	9.07	10.82	146.19
Methionine (M)	$—CH_2CH_2SCH_3$	2.18[c]	9.08[c]		149.21
Phenylalanine (F)		2.20	9.31		165.19
Proline (P)	 Structure of entire amino acid	1.952	10.640		115.13
Serine (S)	$—CH_2OH$	2.187	9.209		105.09
Threonine (T)	$—CH(CH_3)(OH)$	2.088	9.100		119.12
Tryptophan (W)		2.37[c]	9.33[c]		204.23
Tyrosine (Y)		2.41[c]	8.67[c]	11.01[c]	181.19
Valine (V)	$—CH(CH_3)_2$	2.286	9.719		117.15

a. The acidic protons are shown in **bold** type. Each amino acid is written in its fully protonated form. Standard abbreviations are shown in parentheses.
b. pK_a values refer to 25°C and zero ionic strength unless marked by c. Values considered to be uncertain are enclosed in parentheses. Appendix G gives pK_a for $\mu = 0.1$ M.
c. For these entries, the ionic strength is 0.1 M, and the constant refers to a product of concentrations instead of activities.

SOURCE: A. E. Martell and R. J. Motekaitis, NIST Database 46 (Gaithersburg, MD: National Institute of Standards and Technology, 2001).

10-1: Diprotic Acids and Bases

acid amphiprotic base

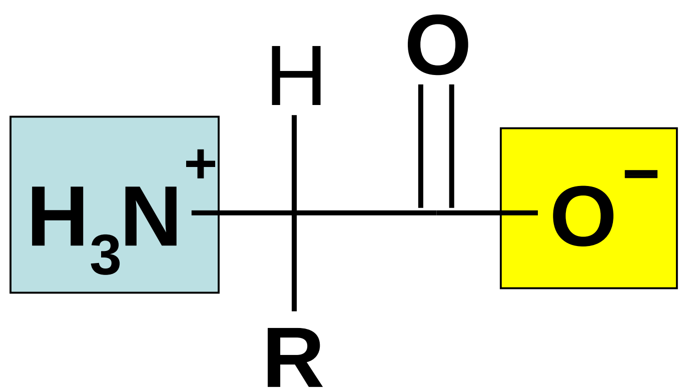


Diprotic Acid: Consider the Leucine System

$$\mathbf{H_2L^+} + H_2O \rightleftarrows H_3O^+ + \mathbf{HL} \qquad K_{a1} = 4.70 \times 10^{-3}$$

$$\mathbf{HL} + H_2O \rightleftarrows H_3O^+ + \mathbf{L^-} \qquad K_{a2} = 1.80 \times 10^{-10}$$

HL is a **Zwitterion.**



= HL

10-2: Diprotic Buffers

Calculate the pH of the following 0.050 M aqueous solutions:

1. Leucine hydrochloride $H_2\mathbf{L}^+$
2. Sodium leucinate $\mathbf{L}^-$
3. Leucine **HL**

pK_a's = 2.328 and 9.744

(1) Estimate answer

(2) Calculate it!

10-2: Diprotic Buffers

1. Calculating the pH of weak diprotic acids (H_2L^+)

$$H_2LCl \rightarrow H_2L^+ + Cl^-$$

- The weak acid H_2L^+ dissociates only a little and the even weaker acid HL dissociates hardly at all.
- Treat as a **monoprotic acid.**
- For the reaction $H_2L^+ \rightleftharpoons H^+ + HL$, we set up and solve the equation

$$\frac{[H^+][HL]}{[H_2L^+]} = \frac{x^2}{F - x} = K_{a1}$$

where $[H^+] = [HL] = x$, and $[H_2L^+] = F - x$.

10-2: Diprotic Buffers

1. Calculating the pH of weak diprotic acids (H_2L^+)

$H_2L^+ \rightleftharpoons H^+ + HL$, $pK_{a1} = 2.328$ **($K_{a1} \geq 100K_{a2}$)**

We estimate the pH to be less than 2.328.

$$\frac{[H^+][HL]}{[H_2L^+]} = \frac{x^2}{F - x} = K_{a1}$$

$$\frac{x^2}{0.050\ M - x} = 10^{-2.328} = 4.70 \times 10^{-3}$$ (solve using quadratic equation)

$x = 1.32 \times 10^{-2}$ M

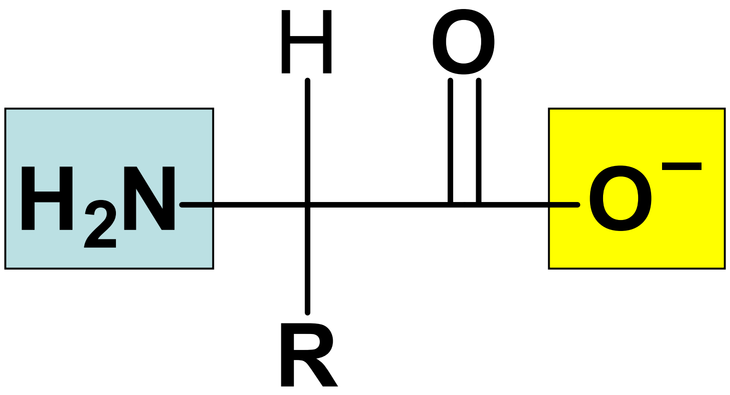
pH = 1.88

10-2: Diprotic Buffers

2. Sodium leucinate (L^-)

$L^- + H_2O \rightleftarrows \mathbf{HL} + OH^-$ $\qquad K_{b1} = \frac{K_w}{K_{a2}} = 5.55 \times 10^{-5}$

$\mathbf{HL} + H_2O \rightleftarrows \mathbf{H_2L^+} + OH^-$ $\qquad K_{b2} = \frac{K_w}{K_{a1}} = 2.13 \times 10^{-12}$



$= \ L^-$

10-2: Diprotic Buffers

2. Calculating the pH of weak diprotic bases (L^-)

- The weak base L^- ionizes by hydrolysis only a little and the even weaker base HL ionizes hardly at all.
- Therefore, treat L^- as a **monoprotic base.**
- For the reaction $L^- + H_2O \rightleftharpoons HL + OH^-$, we set up and solve the equation

$$\frac{[\mathrm{HL}][\mathrm{OH}^-]}{[\mathrm{L}^-]} = \frac{x^2}{\mathrm{F} - x} = \mathrm{K_{b1}}$$

where $[OH^-] = [HL] = x$, and $[L^-] = F - x$.

10-2: Diprotic Buffers

What is the pH of an aqueous 0.050 M sodium leucinate solution? $NaL \rightarrow Na^+ + L^-$

$L^- + H_2O \rightleftharpoons HL + OH^-$, $K_{b1} = 5.55 \times 10^{-5}$ **($K_{b1} \geq 100K_{b2}$)**

$$\frac{[\mathrm{OH}^-][HL]}{[\mathrm{L}^-]} = \frac{x^2}{\mathrm{F} - x} = \mathrm{K_{b1}}$$

$$\frac{x^2}{0.050\ \mathrm{M} - x} = 5.55 \times 10^{-5}$$ (solve using quadratic equation)

$x = 1.6_4 \times 10^{-3}$ M = $[OH^-]$

$pOH = 2.78_6$; $pH = 14.00 - pOH$; **pH = 11.21**

10-2: Diprotic Buffers

A molecule that can both donate and accept a proton is said to be **amphiprotic.**

$$HL + H_2O \rightleftarrows H_2L^+ + OH^-$$

$$HL + H_2O \rightleftarrows L^- + H_3O^+$$

10-2: Diprotic Buffers

Using the systematic treatment of equilibrium, an equation for calculating the $[H^+]$ of amphiprotics can be derived (see text).

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

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

10-2: Diprotic Buffers

What is the pH of a 0.05 M leucine (HL) solution?

$$[\mathrm{H^+}] = \sqrt{\frac{(4.7\times10^{-3})(1.8\times10^{-10})(0.050)+(4.7\times10^{-3})(1.0\times10^{-14})}{4.7\times10^{-3}+0.050}} = 8.7_9\times10^{-7}\,\mathrm{M}$$

$$\mathrm{pH} = -\mathrm{Log}(8.79\times10^{-7}\ \mathrm{M}) = 6.06$$

$$\mathrm{pH} \sim \tfrac{1}{2}(\mathrm{p}K_{a1} + \mathrm{p}K_{a2}) \sim \tfrac{1}{2}(2.328 + 9.744) \sim 6.04$$

Calculating pH

H_2L^+ or H_2A $H_2A + HA^-$ ($H_2L^+ + HL$) and $K_{a1} \geq 100K_{a2}$ L^- ($K_{b1} \geq 100K_{b2}$)	monoprotic acid Monoprotic base hydrolysis
HL or HA^-	$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$ pH ~ ½(pK_{a1} + pK_{a2})
HA^- + A^{2-} $K_{a1} \geq 100K_{a2}$	The pH is calculated using K_{a2}

- Solutions of Polyprotic acids

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

$$HA^- \leftrightarrow H^+ + A^{2-} \qquad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]}$$

1. A solution containing H_2A, or H_2A+HA^-

If K_1 is a hundred times or so greater than K_2, the second ionization constant will have very little effect and can be ignored. The pH of the solution is calculated from K_1 expression.

2. A solution containing HA- : Here both ionization affect the composition of the solution and must be considered.

$$pH = (pK_1 + pK_2) / 2$$

3. A solution containing $HA^- + A^{2-}$: If K_1 100 times or more greater than K_2, there will be very little H_2A in the solution at equilibrium and the first ionization constant need not be used. The pH is calculated using K_2.

1. Example: Calculate the pH of a 0.15M solution of malonic acid, $CH_2(COOH)_2$. The ionization constants for malonic acids are, $K_{a1} = 1.40 \times 10^{-3}$, and $K_{a2} = 2.2 \times 10^{-6}$.

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

$$K_{a1} = \frac{[H^+]^2}{0.15 - [H^+]}$$

Solving this equation by the quadratic formula:

$$[H^+] = 1.38 \times 10^{-2}\ M$$

pH = 1.86

2. Example: Calculate the pH of a solution of sodium hydrogen malonate. The ionization constants for malonic acid are pK_{a1} = 2.85, pK_{a2} = 5.66

pH = (2.85 + 5.66) / 2 = 4.26

3. Example: Calculate the pH of a solution having, at equilibrium a hydrogen malonate ion (HA^-) concentration of 0.15M and a malonate ion A^{-2} concentration of 0.05M.

$$K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} \qquad 2.2 \times 10^{-6} = \frac{[H^+](0.05)}{(0.15)}$$

pH= 5.18

10-2: Diprotic Buffers

Calculate the pH of the following 0.10 M aqueous solutions:

1.	Alanine chloride	$H_2\mathbf{A}^+$
2.	Alanine	$H\mathbf{A}$
3.	Sodium alanate	$\mathbf{A}^-$

pK_a's = 2.34 and 9.87

(1) Estimate answer

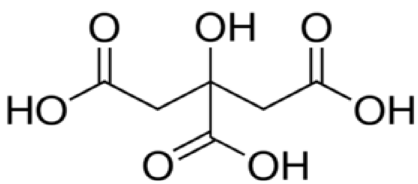
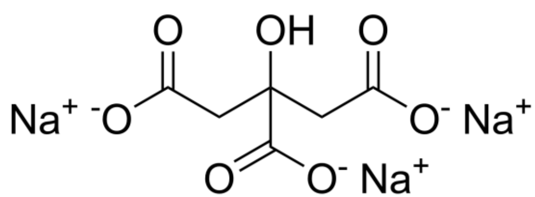
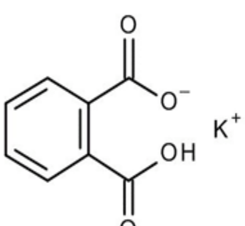
(2) Calculate it!

Calculate the pH of the following 0.10 M aqueous solutions:

Name	**Form**	**Strategy**	**Calculated pH**
Alanine chloride	$H_2\mathbf{A}^+$	Monoprotic acid	1.71
Alanine	$H\mathbf{A}$	Amphiprotic	6.11
Sodium alanate	$\mathbf{A}^-$	Monoprotic base	11.44

10-2: Diprotic Buffers

Describe how you would calculate the pH of the following 0.10 M aqueous solutions:

- sodium monohydrogen phosphate: Na_2HPO_4
- glycine hydrochloride: $H_2G^+.Cl^-$
- citric acid: 
- trisodium citrate: 
- potassium hydrogen phthalate, (KHP): 

10-2: Diprotic Buffers

Describe how you would calculate the pH of the following 0.10 M aqueous solutions:

Solution:

Chemical Formula	Acid or base form	Strategy
Na_2HPO_4	$HPO_4{}^{2-}$	amphiprotic, K_{a2}, K_{a3}
H_2GCl or $HG \cdot HCl$	H_2G^+	monoprotic acid, K_{a1}
$H_3C_6H_5O_7$	$H_3C_6H_5O_7$	monoprotic acid, K_{a1}
$Na_3C_6H_5O_7$	$C_6H_5O_7{}^{3-}$	monoprotic base, K_{b1}
$KHC_8H_4O_4$	$HC_8H_4O_4{}^-$	amphiprotic, K_{a1}, K_{a2}

10-2: Diprotic Buffers

- A buffer made from a diprotic (or polyprotic) acid is treated in the same way as a buffer made from a monoprotic acid.
- For the acid H_2A, we can write *two* Henderson-Hasselbalch equations, both of which are **always** true.
- If we know $[H_2A]$ and $[HA^-]$, then use the pK_1 equation. If we know $[HA^-]$ and $[A^{2-}]$, use the pK_2 equation.

$$H_2A \rightleftarrows HA^- + H^+ \qquad pK_1$$

$$HA^- \rightleftarrows A^{2-} + H^+ \qquad pK_2$$

$$\mathrm{pH} = \mathrm{p}K_1 \pm \mathrm{Log}\frac{[\mathrm{HA}^-]}{[\mathrm{H_2A}]} \qquad \mathrm{pH} = \mathrm{p}K_2 \pm \mathrm{Log}\frac{[\mathrm{A}^{2-}]}{[\mathrm{HA}^-]}$$

10-2: Diprotic Buffers

Example: A Diprotic Buffer System

- Find the pH of a solution prepared by dissolving 1.00 g of potassium hydrogen phthalate and 1.20 g of disodium phthalate in 50.0 mL of water.

EXAMPLE **A Diprotic Buffer System**

Find the pH of a solution prepared by dissolving 1.00 g of potassium hydrogen phthalate and 1.20 g of disodium phthalate in 50.0 mL of water.

Solution Monohydrogen phthalate and phthalate were shown in the preceding example. The formula masses are KHP $= C_8H_5O_4K = 204.221$ and $Na_2P = C_8H_4O_4Na_2 = 210.094$. We know $[HP^-]$ and $[P^{2-}]$, so we use the pK_2 Henderson-Hasselbalch equation to find the pH:

$$\text{pH} = \text{p}K_2 + \log\frac{[\text{P}^{2-}]}{[\text{HP}^-]} = 5.408 + \log\frac{(1.20\text{ g})/(210.094\text{ g/mol})}{(1.00\text{ g})/(204.221\text{ g/mol})} = 5.47$$

K_2 is the acid dissociation constant of HP^-, which appears in the denominator of the log term. 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)

10-3: Polyprotic Acids and Bases

Example: A diprotic System

EXAMPLE **Preparing a Buffer in a Diprotic System**

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?

OO
|| ||
HOCCOH

Oxalic acid
(H_2Ox)
Formula mass = 90.035

$pK_1 = 1.250$
$pK_2 = 4.266$

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 H_2Ox into HOx^-, plus enough additional base to convert the right amount of HOx^- into Ox^{2-}.

$$H_2Ox + OH^- \rightarrow \underset{\uparrow}{HOx^-} + H_2O$$

$pH = \frac{1}{2}(pK_1 + pK_2) = 2.76$

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

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

10-3: Polyprotic Acids and Bases

Example: A diprotic System

In 3.38 g of H_2Ox, there are $0.037\,5_4$ mol. The volume of 0.800 M KOH needed to react with this much H_2Ox to make HOx^- is $(0.037\,5_4 \text{ mol})/(0.800 \text{ M}) = 46.9_3$ mL.

To produce a pH of 4.40 requires an additional x mol of OH^-:

	HOx^-	$+\ OH^-$	$\rightarrow Ox^{2-}$
Initial moles	$0.037\,5_4$	x	—
Final moles	$0.037\,5_4 - x$	—	x

$$\text{pH} = \text{p}K_2 + \log \frac{[Ox^{2-}]}{[HOx^-]}$$

$$4.40 = 4.266 + \log \frac{x}{0.037\,5_4 - x} \Rightarrow x = 0.021\,6_6 \text{ mol}$$

The volume of KOH needed to deliver $0.021\,6_6$ mole is $(0.021\,6_4 \text{ mol})/(0.800 \text{ M}) = 27.0_5$ mL. The total volume of KOH needed to bring the pH to 4.40 is $46.9_3 + 27.0_5 = 73.9_8$ mL.

TEST YOURSELF What volume of KOH would bring the pH to 4.50? (*Answer:* 76.5_6 mL)

10-4: Which Is the Principal Species?

What is the principal form of benzoic acid (pK_a 4.20) at pH 8?

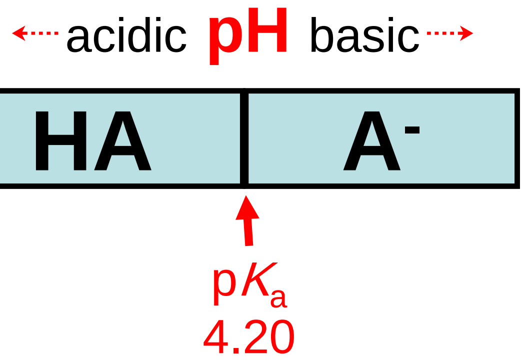
From the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a \pm \mathrm{Log}\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \qquad \mathrm{pH} = 4.20 \pm \mathrm{Log}\frac{\mathbf{[A^-]}}{\mathbf{[HA]}}$$

pH = 4.20, [HA] = [A$^-$]

pH < 4.20, [HA] > [A$^-$]

pH > 4.20, [HA] < [A$^-$]



At pH 8.0, base form A$^-$ predominates.

10-4: Which Is the Principal Species?

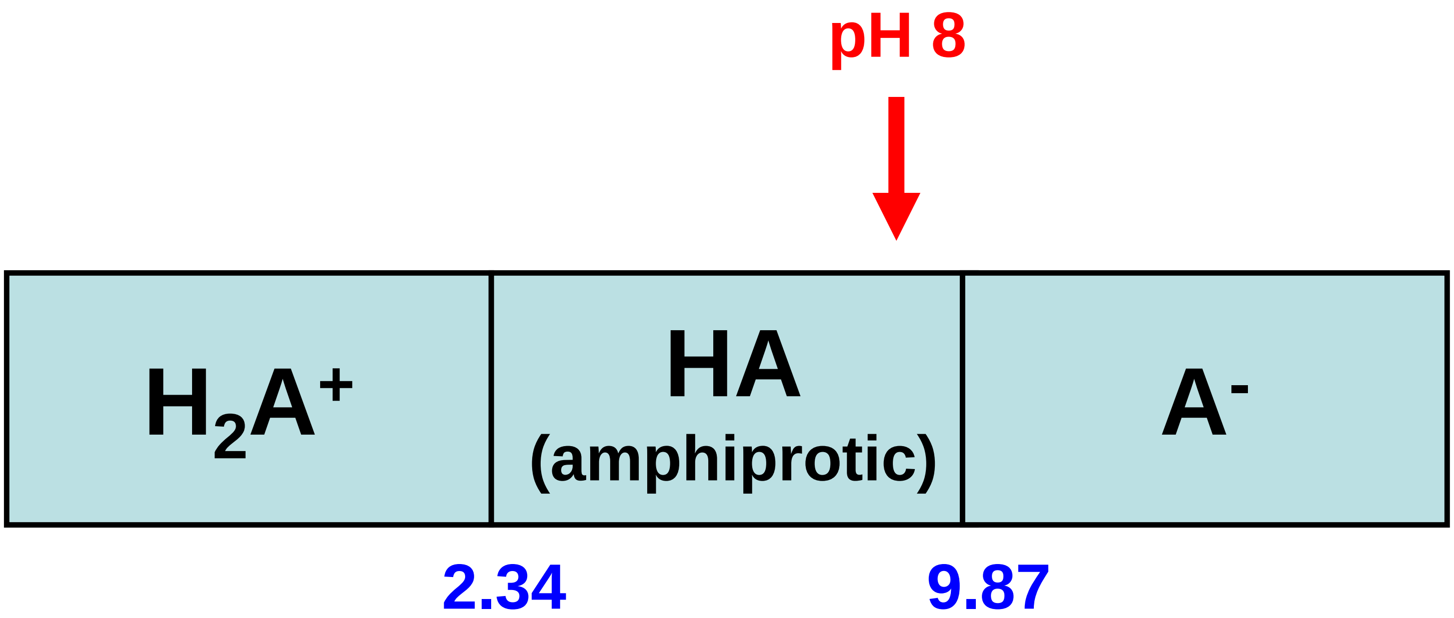
EXAMPLE **Principal Species—Which One and How Much?**

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^+.

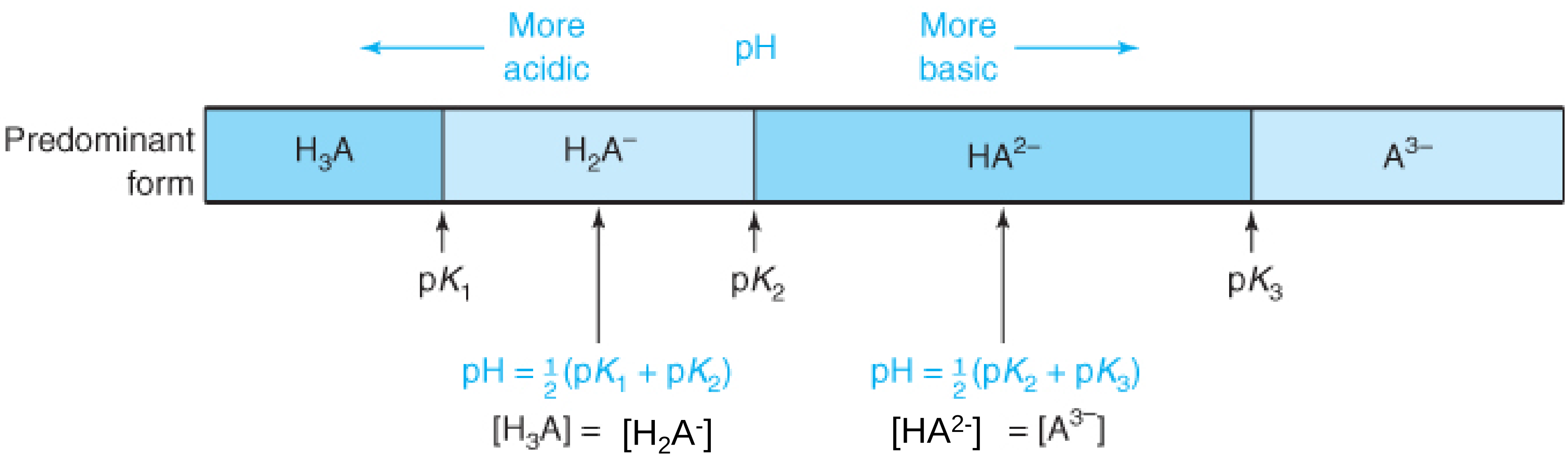
TEST YOURSELF Approximately what fraction of ammonia is in the form NH_3 at pH 11? (***Answer:*** somewhat less than 99% because pH is almost 2 units above pK_a)

What is the principal form of alanine (pK_a 2.34 and 9.87) at pH 8?



The principal form of alanine pH 8 is the amphiprotic form, HA.

10-4: Which Is the Principal Species?



10-5: Fractional Composition Equations

We can derive equations that give the fraction of each species of acid or base at a given pH.

Monoprotic Systems:

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

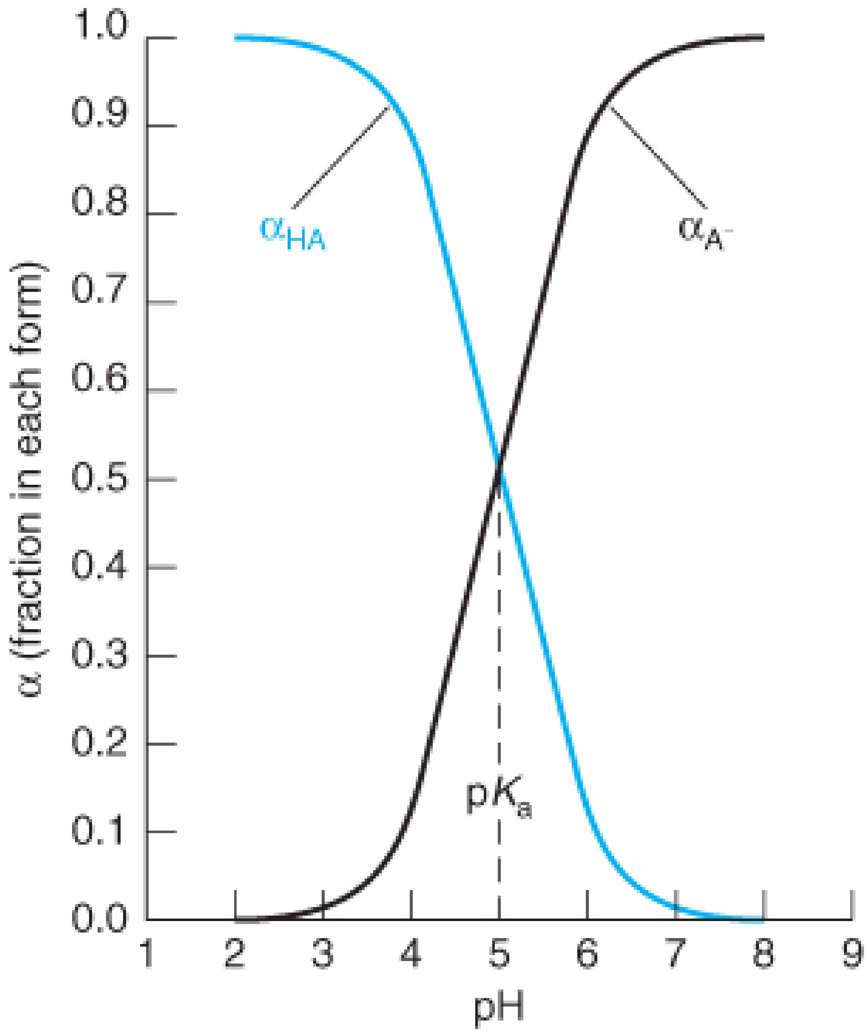
Example:

What fraction of benzoic acid exists as benzoate at pH 8.0?

$$\alpha_{A-} = \frac{K_a}{[H^+] + K_a} = \frac{10^{-4.20}}{10^{-8.0} + 10^{-4.20}} = 0.9_{998}$$

At pH 8.0, almost all of the benzoic acid exists in the basic form!

10-5: Fractional Composition Equations



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

10-5: Fractional Composition Equations

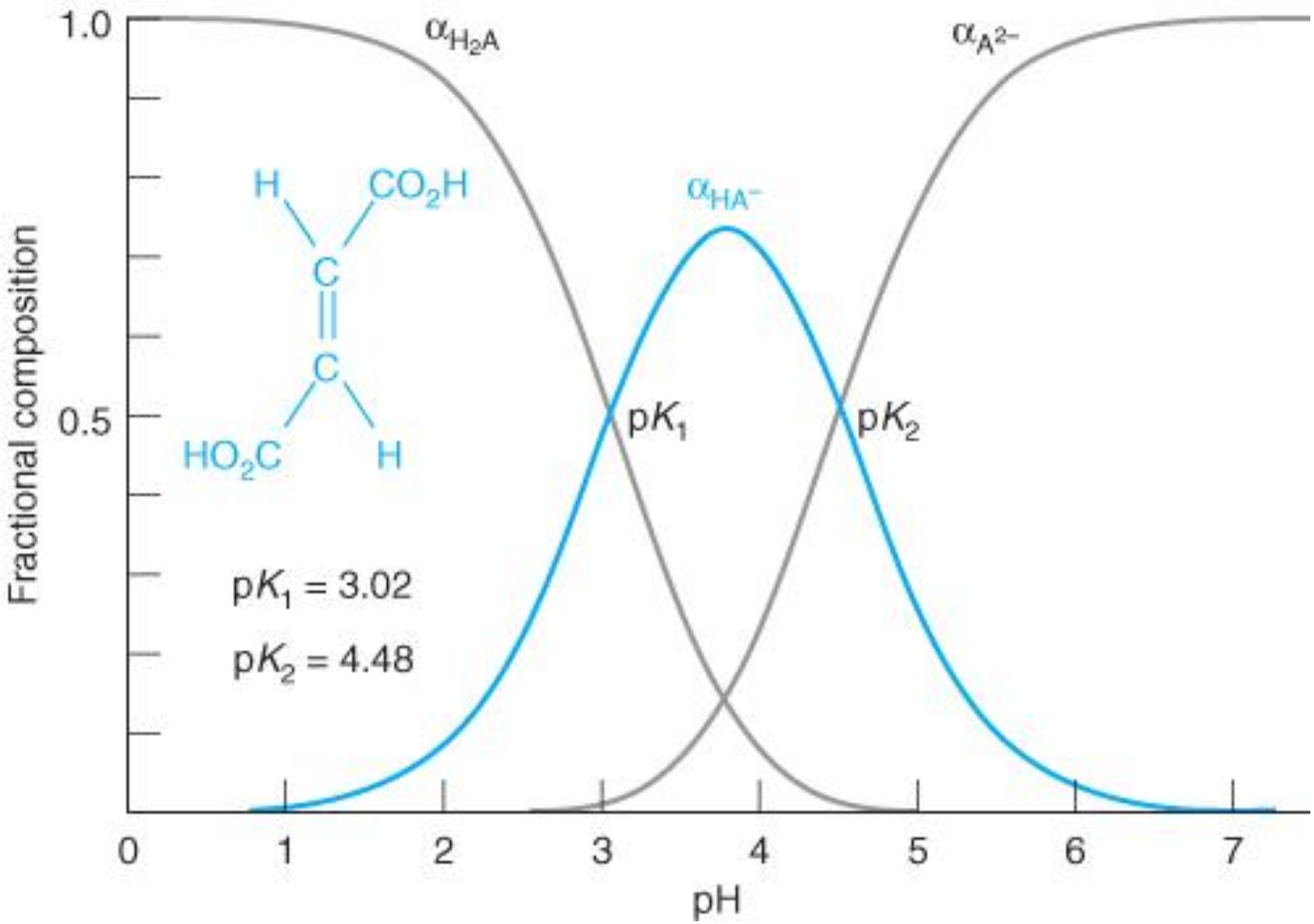
Diprotic Systems:

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

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

$$\alpha_{A2-} = \frac{[A^{2-}]}{[F]} = \frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

10-5: Fractional Composition Equations



10-6: Isoelectric and Isoionic pH

$$\mathrm{H_3\overset{+}{N}CH(CH_3)CO_2H} \rightleftharpoons \mathrm{H_3\overset{+}{N}CH(CH_3)CO_2^-} + \mathrm{H^+} \qquad \mathrm{p}K_1 = 2.34$$

Alanine cation H_2A^+

Neutral zwitterion HA

$$\mathrm{H_3\overset{+}{N}CH(CH_3)CO_2^-} \rightleftharpoons \mathrm{H_2NCH(CH_3)CO_2^-} + \mathrm{H^+} \qquad \mathrm{p}K_2 = 9.87$$

Alanine anion

A^-

10-6: Isoelectric and Isoionic pH

- The **isoionic point** (or isoionic pH):
  - 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 HA, and the concentrations of H_2A^+ and A^- are *not* equal to each other.
  - For neutral alanine, HA, dissolved in water, the pH would be somewhere between 2.234 and 9.87. The $[A^-]$ would be slightly larger than the $[H_2A^+]$. This is the **isoionic pH**.

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

10-6: Isoelectric and Isoionic pH

- The **isoelectric point** (or isoelectric pH):
  - pH at which the **average charge** of the polyprotic acid is 0.
  - Most of the molecules are in the uncharged form HA, and the concentrations of H_2A^+ and A^- ***are*** **equal** to each other.

$$[H_2A^+] = [A^-]$$

- If a pure sample of neutral alanine (pK_1 2.34, pK_2 9.87) is dissolved in water, the $[A^-]$ would be slightly larger than the $[H_2A^+]$.
- By adding a small amount of acid, some A^- would be converted to H_2A^+ until the concentrations are equal. This is the isoelectric pH.

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

- Can be used to separate proteins from one another.

10-3: Polyprotic Acids and Bases

Example: A triprotic System, page 221 (9th Edition)

- 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.

1. H_3A is treated as monoprotic acid, with ka = k_1.

2. H_2A^- is tretaed as the intermediate form of a diprotic acid :

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

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

10-3: Polyprotic Acids and Bases

3. HA^{2-} is treated as the intermediate form of a diprotic acid. However, HA^{2-} is "surrounded" by H_2A^- and A^{3-}, so the equilibrium constants to use are K_2 and K_3, instead of K_1 and K_2:

$$[H+] = [(K_2K_3F + K_2K_w)/(K_1 + F)]^{1/2}$$

$$\boxed{pH \approx \tfrac{1}{2}\,(pK_{a2} + pK_{a3})}$$

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