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 = 1.3x10^{-5})?

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

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

Concentration (M)	HPr(aq) +	H$_2$O(l) $\rightleftharpoons$	H$_3$O$^+$(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 $x \ll 0.10$ and [HPr] $\approx$ 0.10 M.

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

$x = \sqrt{(0.10)(1.3 \times 10^{-5})}$ = **1.1x10^{-3} M = [H$_3$O$^+$]**   **pH = -log [H$_3$O$^+$] = 2.96**

Check: [HPr]$_{diss}$ = $\dfrac{1.1 \times 10^{-3}\ M}{0.10\ M}$ x 100 = 1.1% (< 5%; 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	$\dfrac{c_{HA}}{K_a}$	$[H_3O^+]$ 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
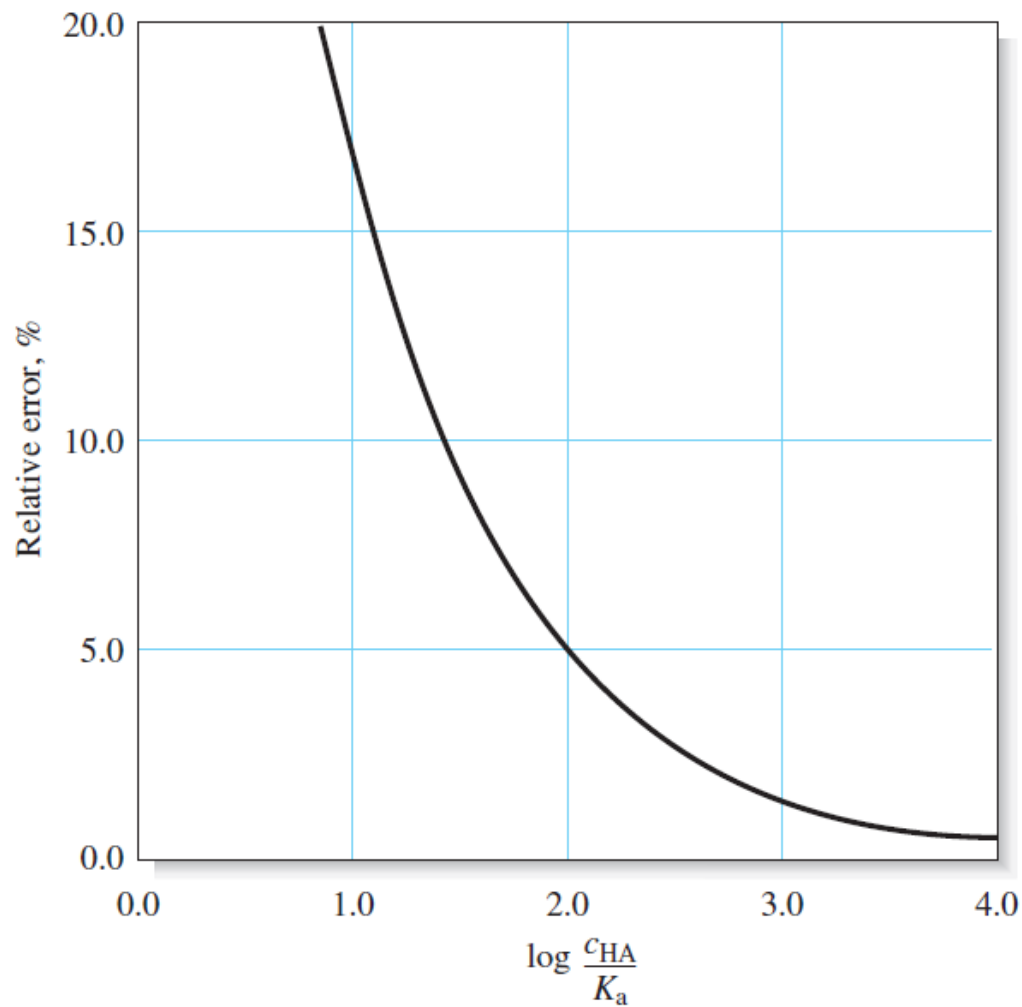
Relative error resulting from the assumption that $[H_3O^+] \ll c_{HA}$

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

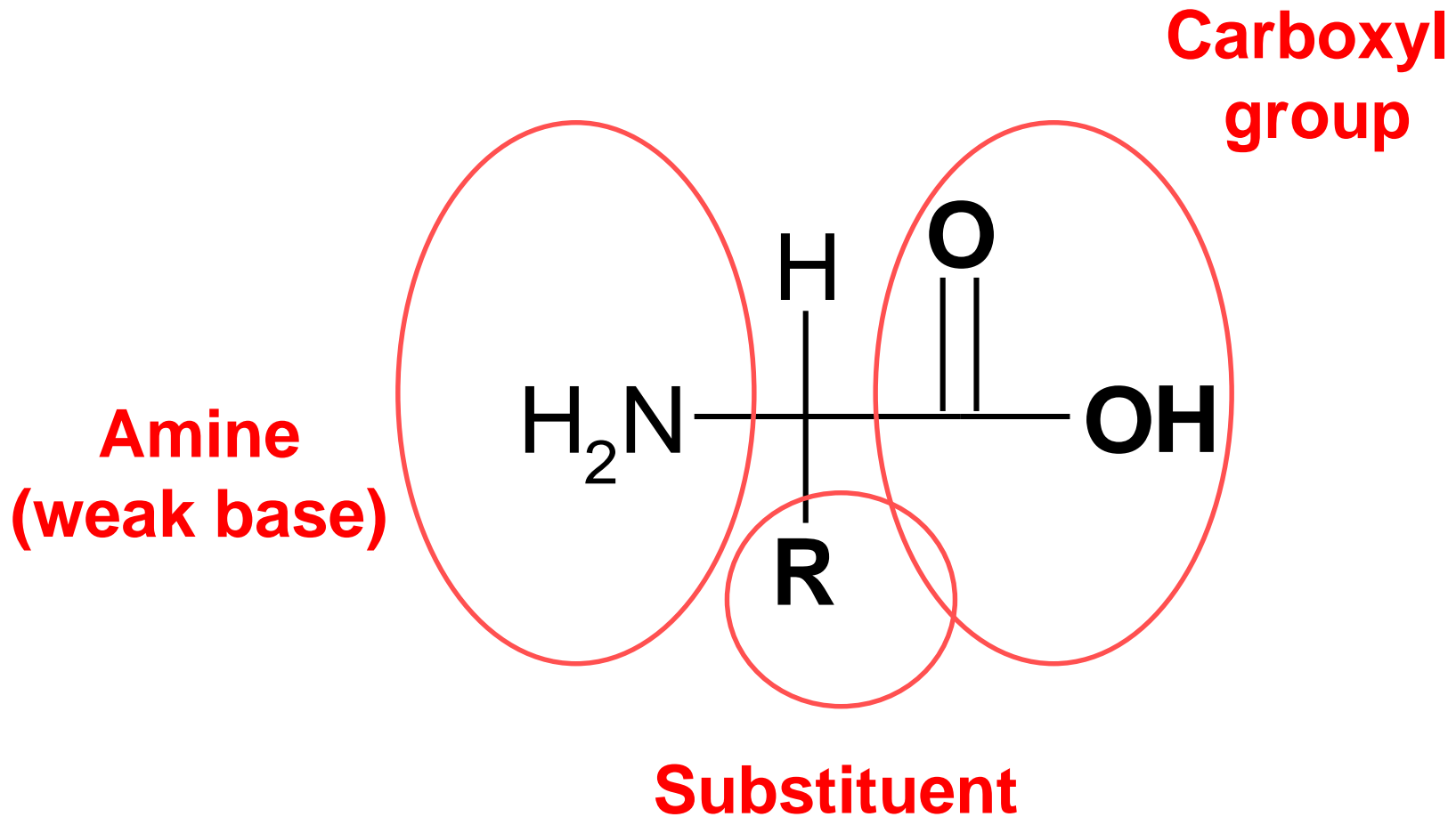1. H_2B^+, Amino acids, Example: Alanine – H_2A^+

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.
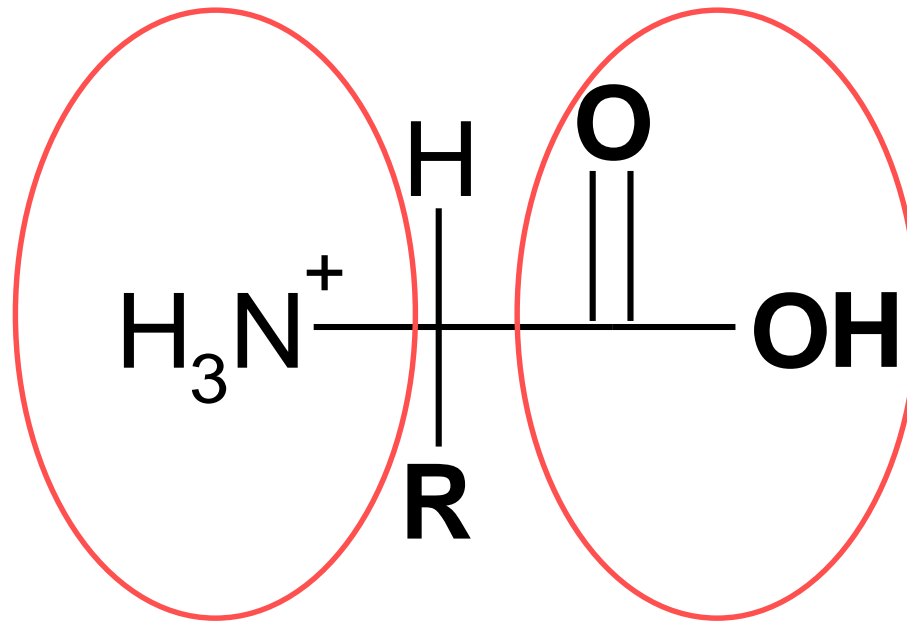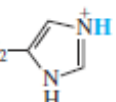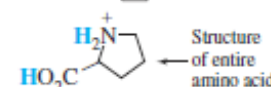
Amino Acid

Carboxyl group

Amine (weak base)

$$H_2N - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} - \overset{\overset{\displaystyle O}{\|}}{C} - OH$$

Substituent
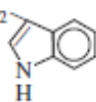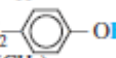
Amino Acid

pK_a ~ 2.5

Ammonium group
pK_a ~ 9.5

$$H_3N^+ - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} - \overset{\displaystyle O}{\underset{}{C}} - OH$$

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)	—$CH_2CH_2CH_2NHC$ $\overset{+}{\underset{}{}}NH_2$ NH_2	1.823	8.991	(12.1[c])	174.20
Asparagine (N)	—$CH_2\overset{O}{\overset{\|}{C}}NH_2$	2.16[c]	8.73[c]		132.12
Aspartic acid (D)	—CH_2CO_2H	1.990	10.002	3.900	133.10
Cysteine (C)	—CH_2SH	(1.7)	10.74	8.36	121.16
Glutamic acid (E)	—$CH_2CH_2CO_2H$	2.16	9.96	4.30	147.13
Glutamine (Q)	—$CH_2CH_2\overset{O}{\overset{\|}{C}}NH_2$	2.19[c]	9.00[c]		146.15
Glycine (G)	—H	2.350	9.778		75.07
Histidine (H)	—CH_2 (imidazole)	(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)	—CH_2⬡	2.20	9.31		165.19
Proline (P)	$H_2\overset{+}{N}$ HO_2C (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)	—CH_2 (indole)	2.37[c]	9.33[c]		204.23
Tyrosine (Y)	—CH_2⬡—OH	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.
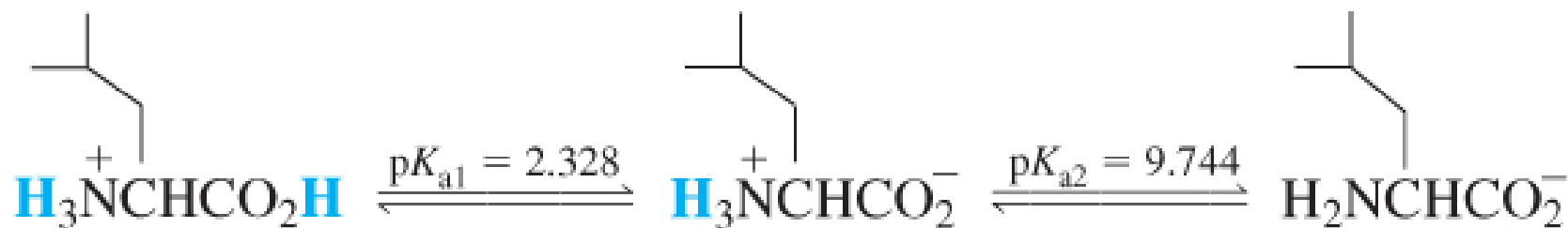
SOURCE: A. E. Martell and R. J. Motekaitis, NIST Database 46 (Gaithersburg, MD: National Institute of Standards and Technology, 2001).
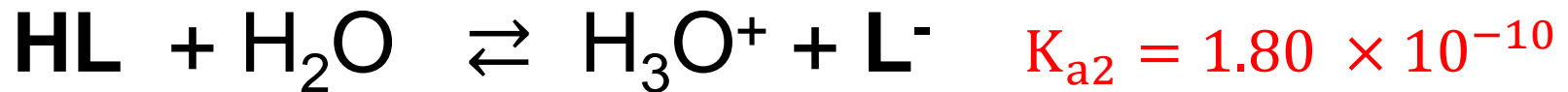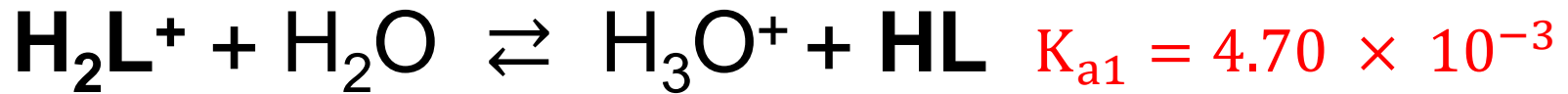
10-1: Diprotic Acids and Bases
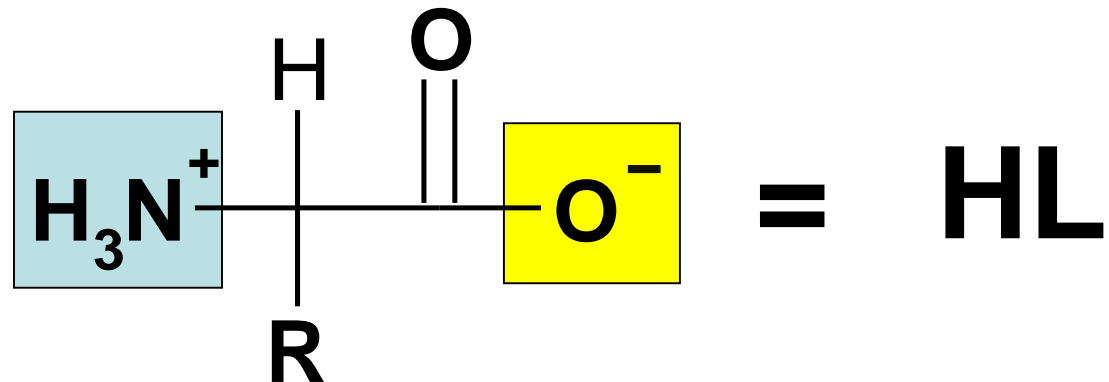
acid   amphiprotic   base

$$\overset{+}{H_3}NCHCO_2H \xrightleftharpoons{pK_{a1} = 2.328} \overset{+}{H_3}NCHCO_2^- \xrightleftharpoons{pK_{a2} = 9.744} H_2NCHCO_2^-$$

Diprotic Acid: Consider the Leucine System

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

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

HL is a **Zwitterion.**

10-2: Diprotic Buffers
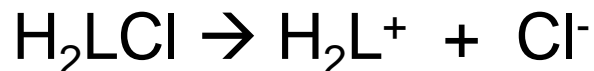
Calculate the pH of the following 0.050 M aqueous solutions:

1. Leucine hydrochloride H_2L^+
2. Sodium leucinate 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^+)
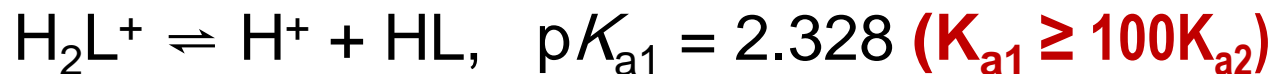
$$H_2LCl \rightarrow H_2L^+ + Cl^-$$

- 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^+)

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

We estimate the pH to be less than 2.328.
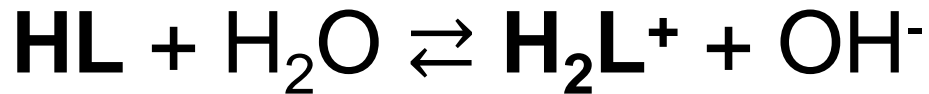
$$\frac{[H^+][HL]}{[H_2L^+]} = \frac{x^2}{F - x} = K_{a1}$$

$$\frac{x^2}{0.050 \text{ M} - x} = 10^{-2.328} = 4.70 \times 10^{-3} \qquad \text{(solve using quadratic equation)}$$
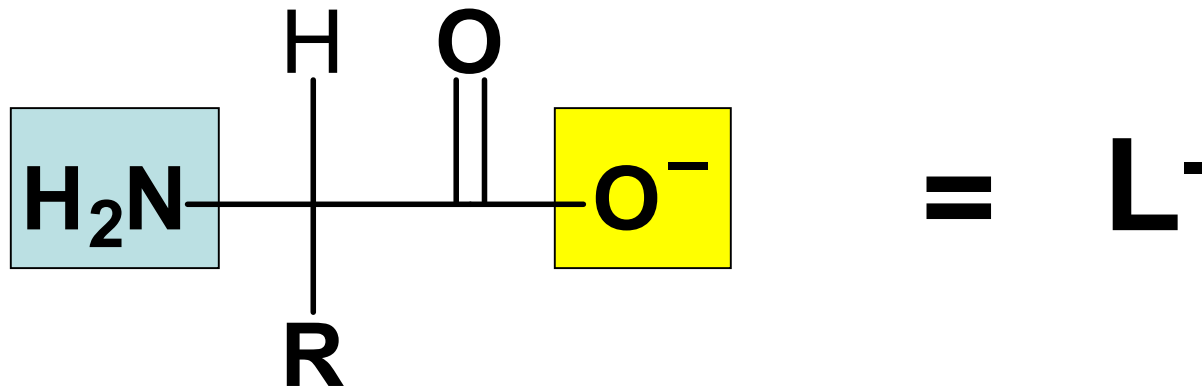
$x = 1.32 \times 10^{-2}$ M

pH = 1.88

2. Sodium leucinate (L⁻)

$$\text{L}^- + \text{H}_2\text{O} \rightleftarrows \text{HL} + \text{OH}^-$$

$$\text{HL} + \text{H}_2\text{O} \rightleftarrows \text{H}_2\text{L}^+ + \text{OH}^-$$

$$K_{b1} = \frac{K_w}{K_{a2}} = 5.55 \times 10^{-5}$$

$$K_{b2} = \frac{K_w}{K_{a1}} = 2.13 \times 10^{-12}$$

$$= \quad \text{L}^-$$

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

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

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? $NaL \rightarrow Na^+ + L^-$

$L^- + H_2O \rightleftharpoons HL + OH^-$, $K_{b1} = 5.55 \times 10^{-5}$ **($K_{b1} \geq 100K_{b2}$)**
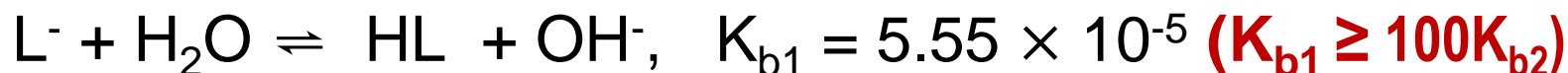
$$\frac{[OH^-][HL]}{[L^-]} = \frac{x^2}{F - x} = K_{b1}$$

$\dfrac{x^2}{0.050\ M - x} = 5.55 \times 10^{-5}$ (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.**

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

$$HL \; + \; H_2O \; \rightleftarrows \; L^- \; + \; H_3O^+$$
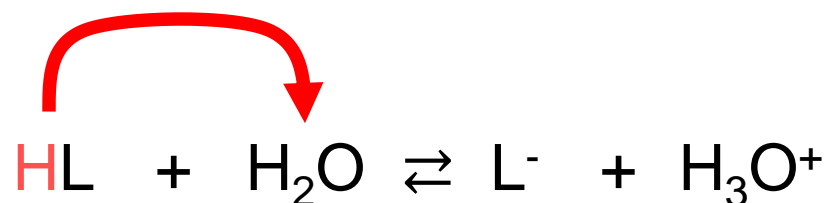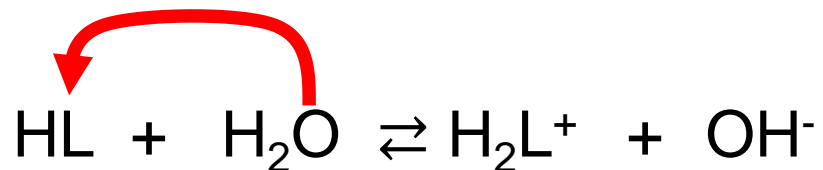
10-2: Diprotic Buffers

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

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

$$pH \sim \tfrac{1}{2}\left(pK_{a1} + pK_{a2}\right)$$

10-2: Diprotic Buffers

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

$$[\mathbf{H^+}] = \sqrt{\frac{(4.7 \times 10^{-3})(1.8 \times 10^{-10})(0.050) + (4.7 \times 10^{-3})(1.0 \times 10^{-14})}{4.7 \times 10^{-3} + 0.050}} = 8.7_9 \times 10^{-7}\,\mathbf{M}$$
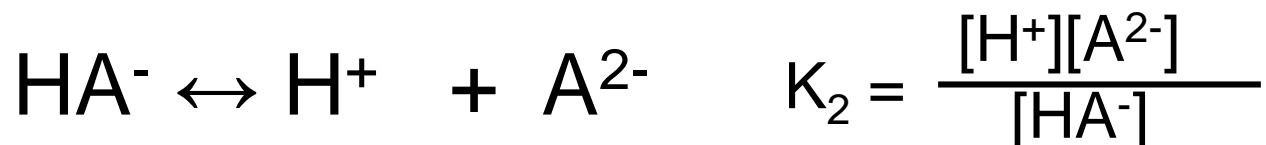
pH = -Log(8.79 × 10^{-7} M) = 6.06

pH ~ ½ (pK_{a1} + pK_{a2}) ~ ½(2.328 + 9.744) ~ 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$^-$	$$[H^+] = \sqrt{\dfrac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$ $$pH \sim \tfrac{1}{2}(pK_{a1} + pK_{a2})$$
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.

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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:

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

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_2A^+
2. Alanine HA
3. Sodium alanate 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:

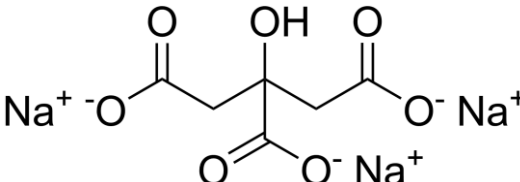| Name	Form	Strategy	Calculated pH
Alanine chloride	H_2A^+	Monoprotic acid	1.71
Alanine	HA	Amphiprotic	6.11
Sodium alanate	A^-	Monoprotic base	11.44

10-2: Diprotic Buffers

Describe **how you would calculate the pH of the following 0.10 M aqueous solutions:**
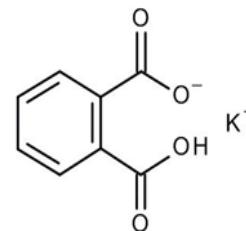
- sodium monohydrogen phosphate: Na_2HPO_4

- 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.

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

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

$$pH = pK_1 \pm \text{Log} \frac{[HA^-]}{[H_2A]} \qquad pH = pK_2 \pm \text{Log} \frac{[A^{2-}]}{[HA^-]}$$

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:

$$pH = pK_2 + \log \frac{[P^{2-}]}{[HP^-]} = 5.408 + \log \frac{(1.20 \text{ g})/(210.094 \text{ g/mol})}{(1.00 \text{ g})/(204.221 \text{ g/mol})} = 5.47$$

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.
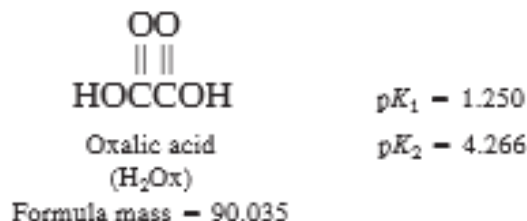
TEST YOURSELF Find the pH with 1.50 g Na_2P instead of 1.20 g. (*Answer:* 5.57)
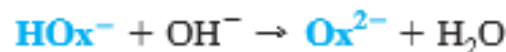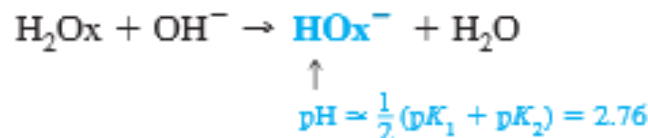
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10-3: Polyprotic Acids and Bases

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?

$$\underset{\substack{\text{Oxalic acid}\\(H_2Ox)\\ \text{Formula mass} = 90.035}}{HOC\overset{\displaystyle OO}{\overset{\displaystyle \| \|}{C}}COH}$$

$pK_1 = 1.250$

$pK_2 = 4.266$

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$_2$Ox into HOx$^-$, plus enough additional base to convert the right amount of HOx$^-$ into Ox^{2-}.

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

$$\uparrow$$

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

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

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

$$pH = pK_2 + \log \frac{[Ox^{2-}]}{[HOx^-]}$$

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

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)

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10-4: Which Is the Principal Species?

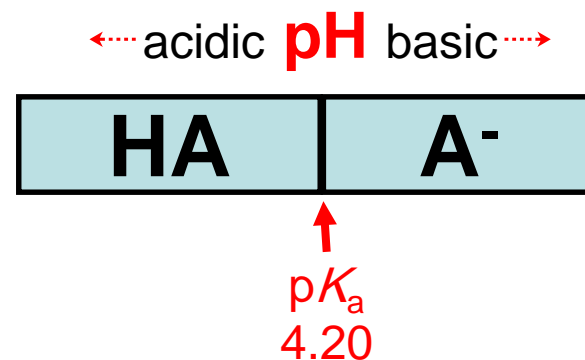What is the principal form of benzoic acid (pK_a 4.20) at pH 8?

From the Henderson-Hasselbalch equation:

$$pH = pK_a \pm Log\frac{[A^-]}{[HA]}$$

$$pH = 4.20 \pm Log\frac{[A^-]}{[HA]}$$

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

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

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

←----acidic **pH** basic----→

HA	A$^-$

pK_a
4.20

At pH 8.0, base form A$^-$ predominates.
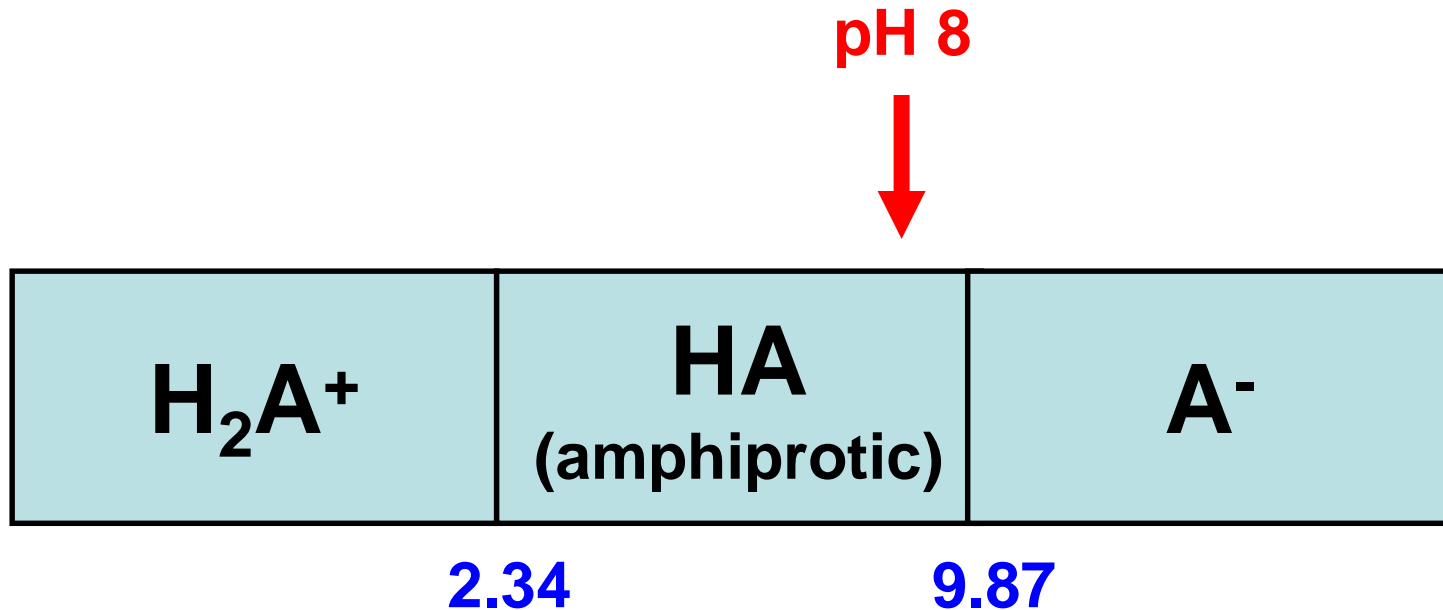
10-4: Which Is the Principal Species?

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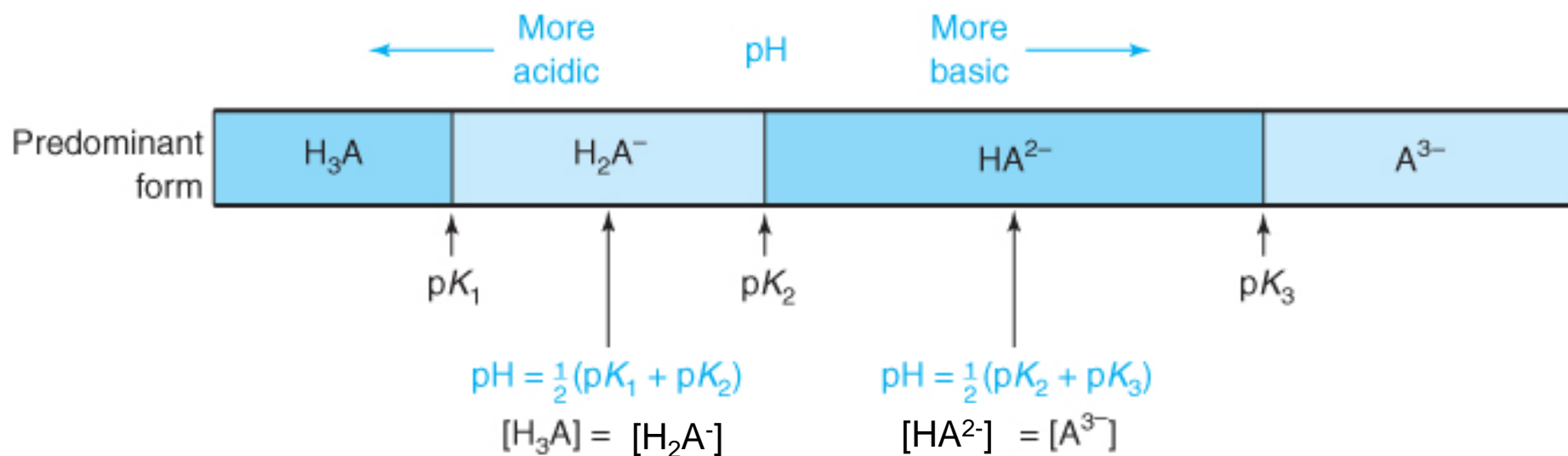
TEST YOURSELF Approximately what fraction of ammonia is in the form NH_3 at pH 11? (*Answer:* somewhat less than 99% because pH is almost 2 units above pK_a)

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

pH 8

H_2A^+	HA (amphiprotic)	A^-

2.34   **9.87**

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:

$$\alpha_{HA} = \frac{[HA]}{[F]} = \frac{[H^+]}{[H^+] + K_a} \qquad \alpha_{A-} = \frac{[A^-]}{[F]} = \frac{K_a}{[H^+] + K_a}$$
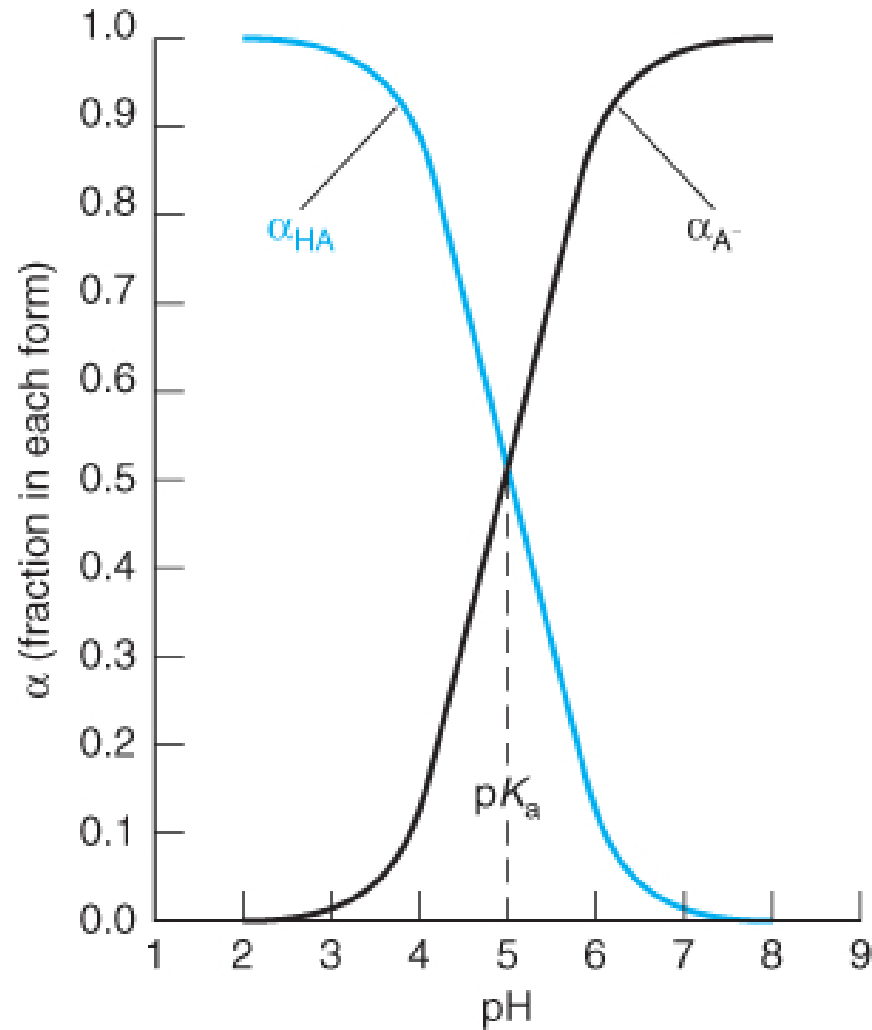
Example:
What fraction of benzoic acid exists as benzoate at pH 8.0?

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

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
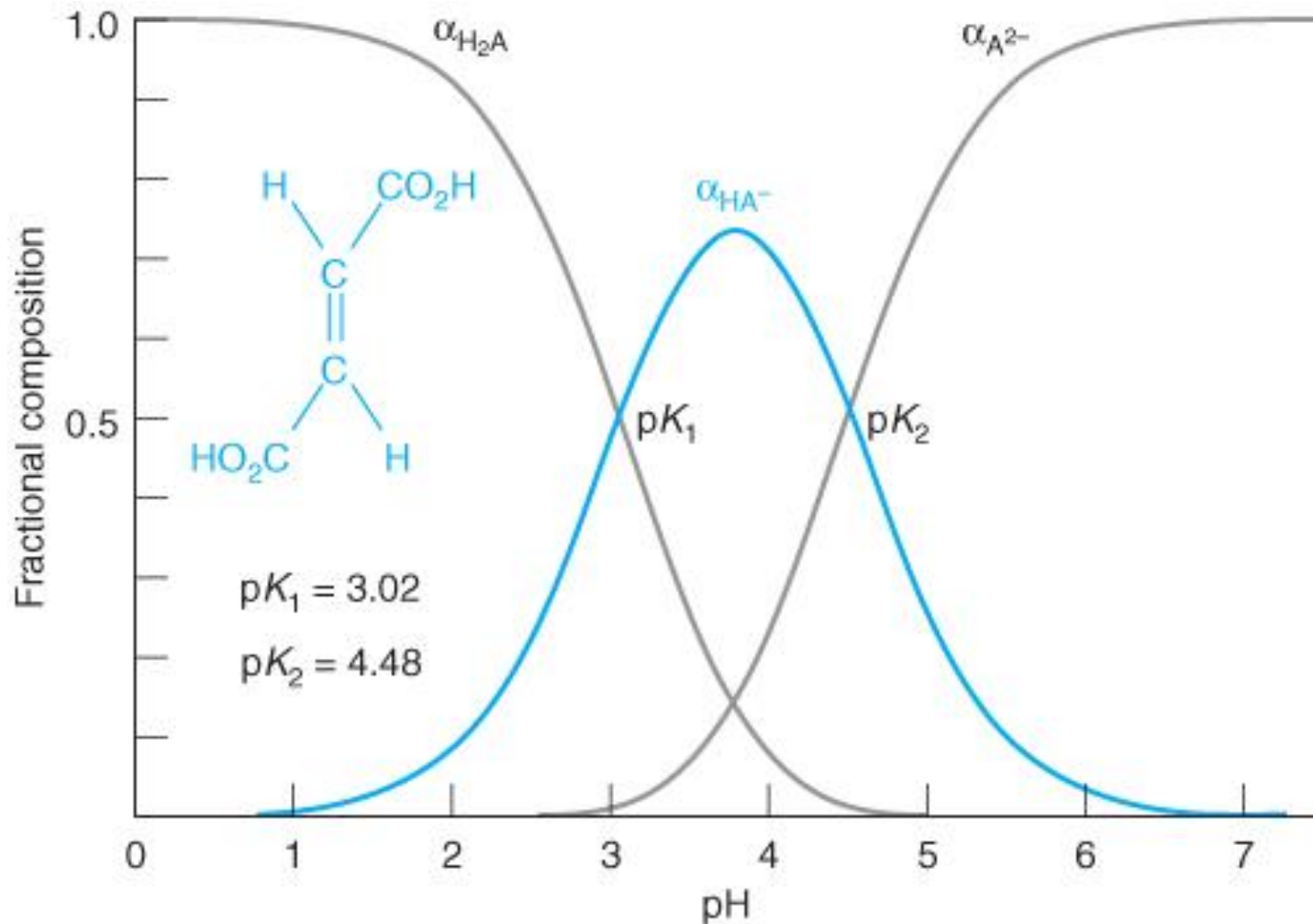
10-5: Fractional Composition Equations

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

$$\underset{\substack{\text{Alanine cation}\\ \text{H}_2\text{A}^+}}{\text{H}_3\overset{+}{\text{N}}\text{CHCO}_2\text{H}} \rightleftharpoons \underset{\substack{\text{Neutral zwitterion}\\ \text{HA}}}{\text{H}_3\overset{+}{\text{N}}\text{CHCO}_2^-} + \text{H}^+ \qquad \text{p}K_1 = 2.34$$

(with CH$_3$ groups attached above each structure)

$$\underset{\text{Alanine anion}}{\text{H}_3\overset{+}{\text{N}}\text{CHCO}_2^-} \rightleftharpoons \underset{\text{A}^-}{\text{H}_2\text{N}\text{CHCO}_2^-} + \text{H}^+ \qquad \text{p}K_2 = 9.87$$

(with CH$_3$ groups attached above each structure)

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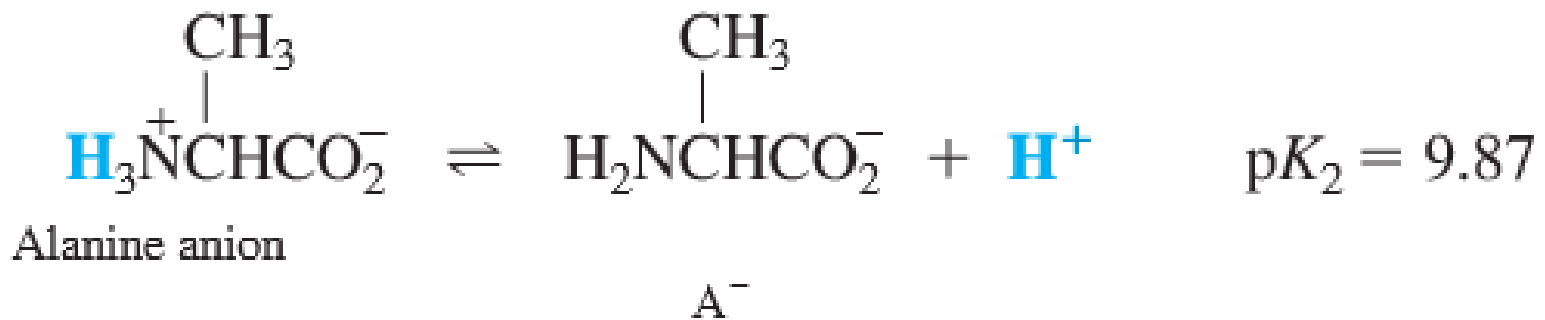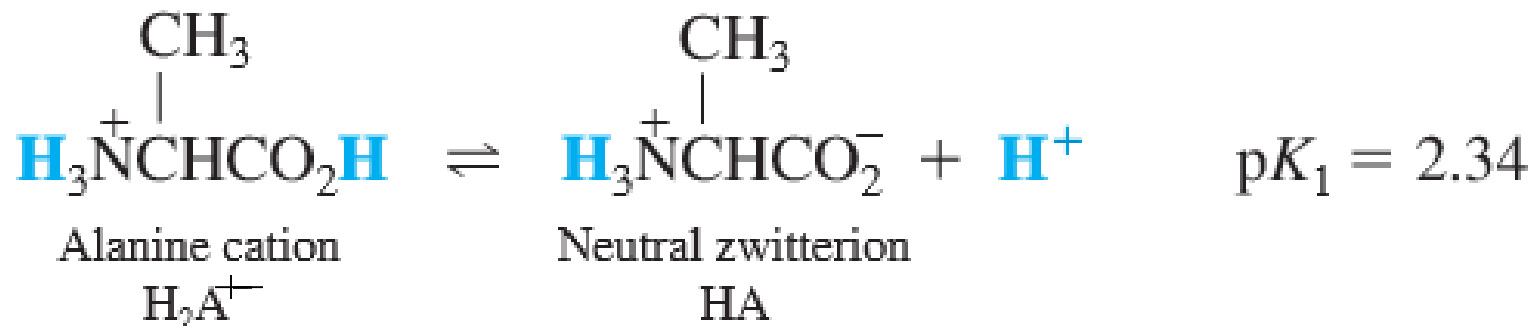
10-6: Isoelectric and Isoionic pH

- **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.

    $$[H_2A^+] = [A^-]$$
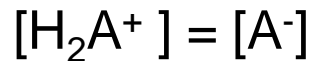
- If a pure sample of neutral alanine (pK_1 2.34, pK_2 9.87) is dissolved in water, the $[A^-]$ would be slightly larger than the $[H_2A^+]$.

- 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. $$pH = \tfrac{1}{2}(pK_{a1} + pK_{a2})$$

- Can be used to separate proteins from one another.

10-3: Polyprotic Acids and Bases

- 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 :

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

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

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:

$$[H+] = [(K_2 K_3 F + K_2 K_w)/(K_1 + F)]^{1/2}$$

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

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