Topic 7

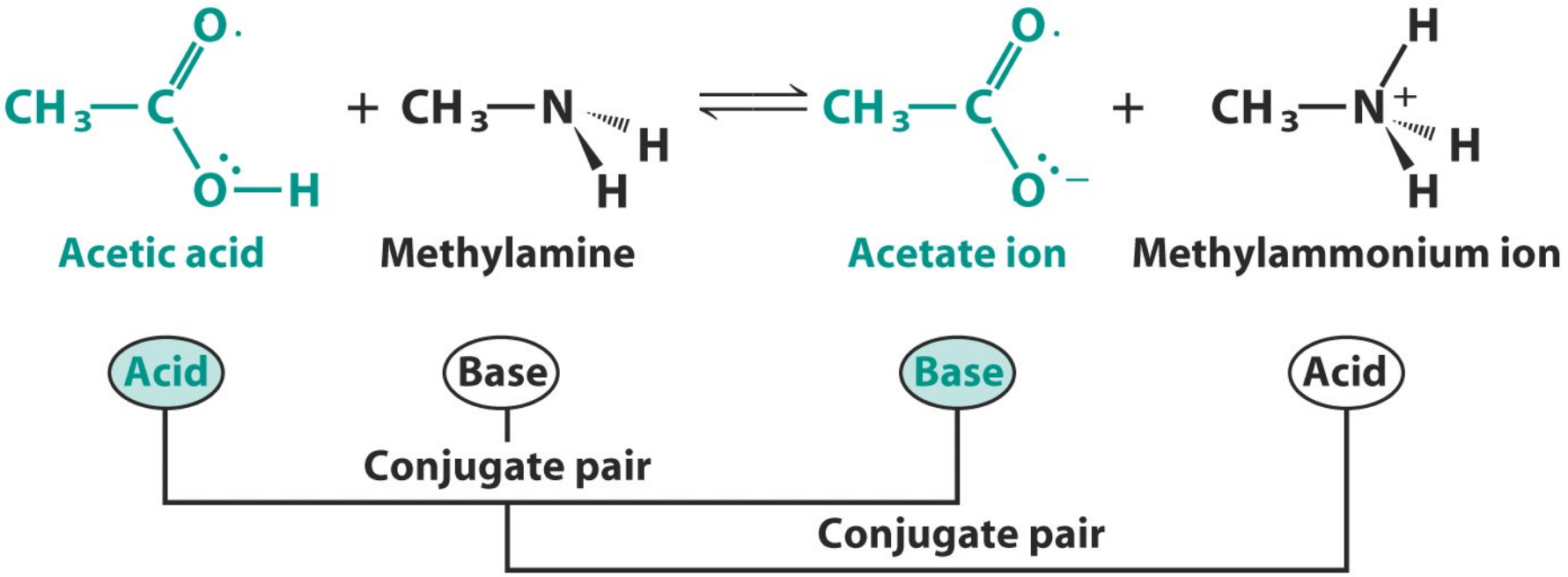
Acids, Bases,

Buffers,

Titrations,

Polyprotic acids

Conjugate acids & bases



Strengths of acids & bases

- A strong acid or strong base is completely dissociated in aqueous solution.

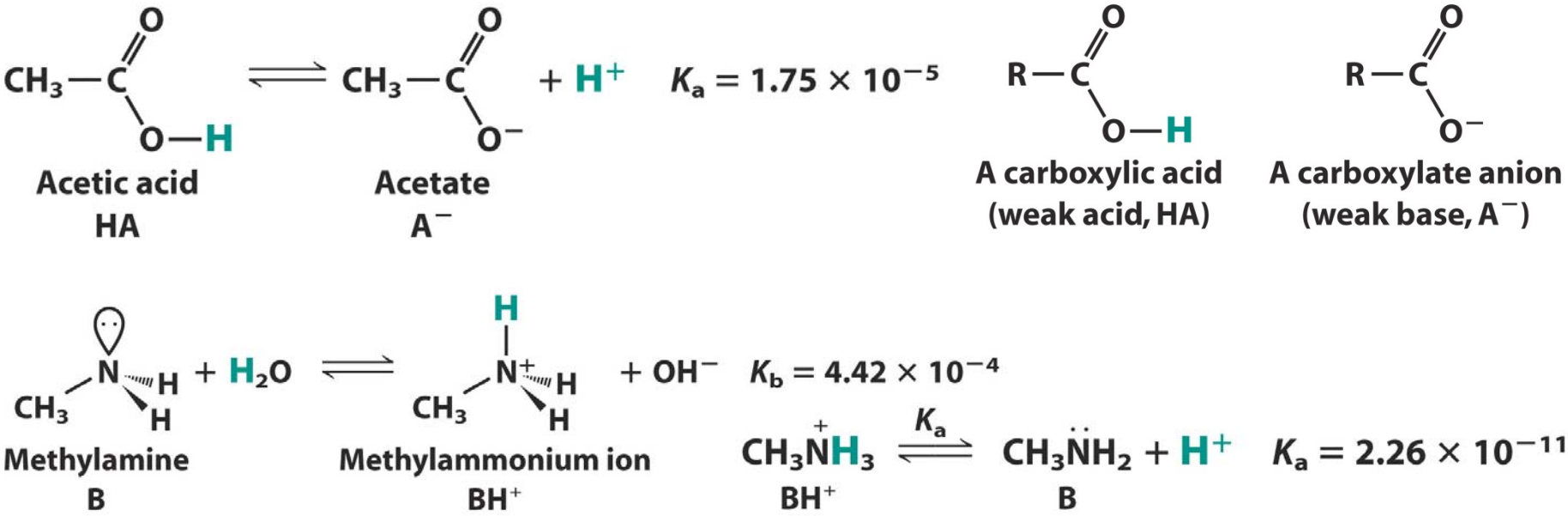
$$HCl(aq) \longrightarrow H^+ + Cl^-$$
$$KOH(aq) \longrightarrow K^+ + OH^-$$

- Weak Acids and Weak Bases

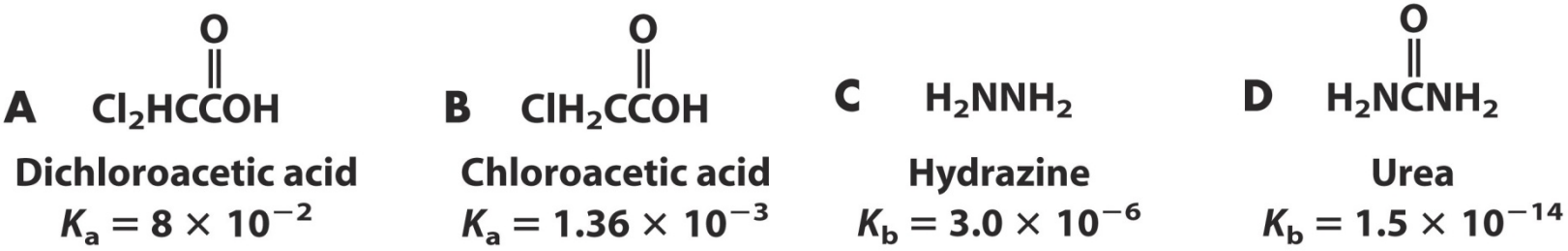
$$HA \overset{K_a}{\rightleftharpoons} H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$B + H_2O \overset{K_b}{\rightleftharpoons} BH^+ + OH^- \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

Carboxylic Acids Are Weak Acids and Amines Are Weak Bases

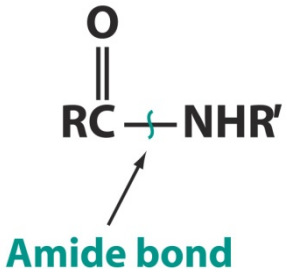


- Ask yourself

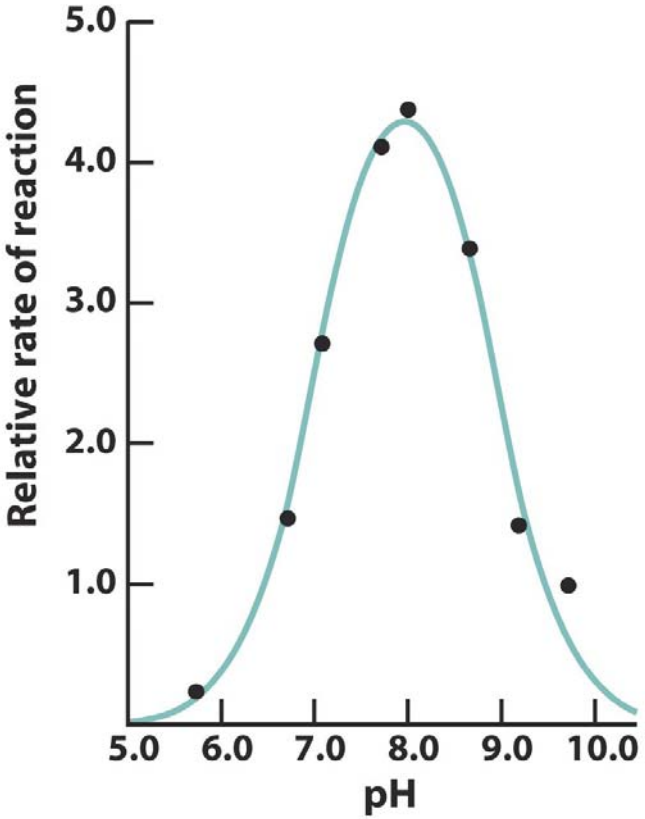


Buffers

Buffered solution resists changes in pH when small amounts of acids or base are added or when dilution occurs.



pH dependence of the rate of a particular enzyme-catalyzed reaction. The rate near pH 8 is twice as the rate at pH 7 or 9



The Henderson-Hasselbalch eqn

$$HA_{(aq)} \longleftrightarrow H^+_{(aq)} + A^-_{(aq)} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$-\log K_a = -\log [H^+] - \log \frac{[A^-]}{[HA]}$$

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

$$\Rightarrow pH = pK_a + \log \frac{[base]}{[acid]}$$

$$pH = pK_a \qquad \text{when } [A^-] = [HA]$$

If pH = pKa, $[HA] = [A^-]$

If pH < pKa, $[HA] > [A^-]$

If pH > pKa, $[HA] < [A^-]$

$[A^-] / [HA]$	pH
100:1	$pK_a + 2$
10:1	$pK_a + 1$
1:1	pK_a
1:10	$pK_a - 1$
1:100	$pK_a - 2$

Preparing a Buffer in Real Life

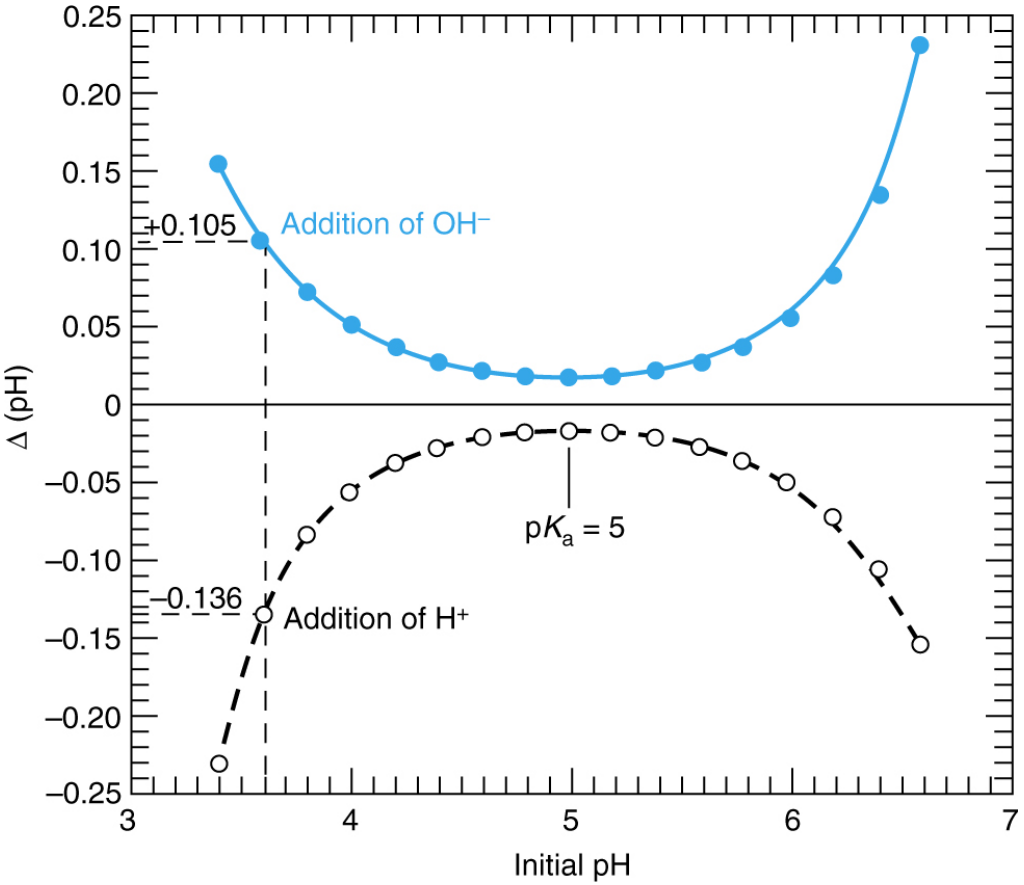
- *Suppose you wish to prepare 1.00 L of buffer containing 0.100 M tris at pH 7.60. When we say 0.100 M tris, we mean that the total concentration of tris plus tris H+ will be 0.100M.*

1. Weigh out 0.100 mol tris hydrochloride and dissolve it in a beaker containing about 800 mL water and a stirring bar.
2. Place a pH electrode in the solution and monitor the pH.
3. Add NaOH solution until the pH is exactly 7.60. The electrode does not respond instantly.
4. Transfer the solution to a volumetric flask and wash the beaker and stirring bar a few times. Add the washings to the volumetric flask.
5. Dilute to the mark and mix.

Buffer capacity

Buffer capacity measures how well a solution resists changes in pH when acid or base is added. The greater the buffer capacity, the less the pH changes.

The amount of H^+ or OH^- that buffered solution can absorb without a significant change in pH



Buffer capacity

2) Magnitudes of [HA] and [A^-]

$\Rightarrow$ the capacity of a buffered soln.

Ex : soln A : 5.00 M HOAc + 5.00 M NaOAc

soln B : 0.05 M HOAc + 0.05 M NaOAc

pH change when 0.01 mol of HCl(g) is added

A :

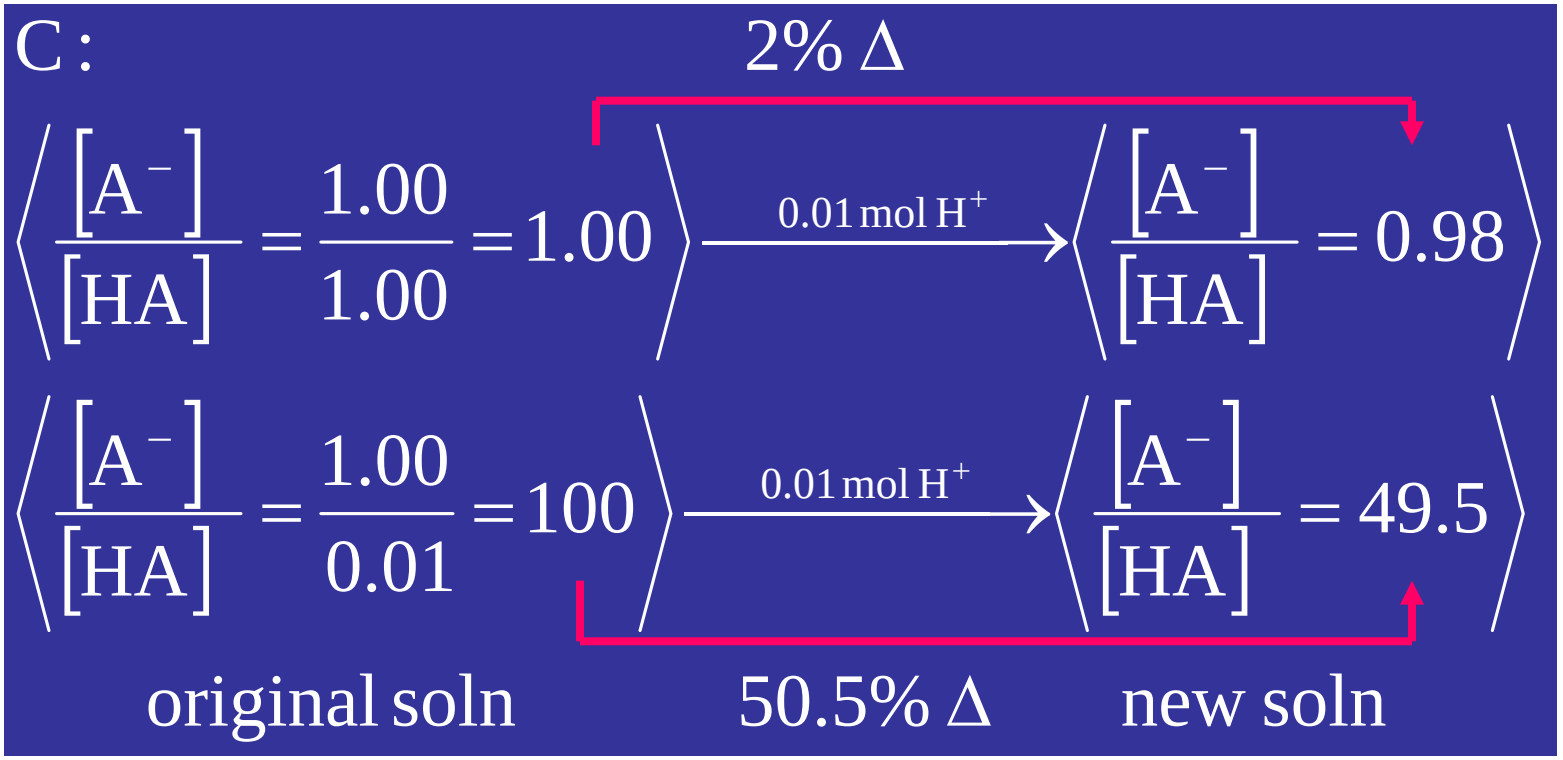
$$\left\langle \frac{[A^-]}{[HA]} = \frac{5.00}{5.00} = 1 \right\rangle \xrightarrow{+0.01\,\text{mol}\,H^+} \left\langle \frac{[A^-]}{[HA]} = \frac{4.99}{5.01} = 0.996 \right\rangle$$

B :

$$\left\langle \frac{[A^-]}{[HA]} = \frac{0.05}{0.05} = 1 \right\rangle \xrightarrow{+0.01\,\text{mol}\,H^+} \left\langle \frac{[A^-]}{[HA]} = \frac{0.04}{0.06} = 0.67 \right\rangle$$

Buffer capacity

3) $[A^-]$ / [HA] ratio $\Rightarrow$ the pH of a buffered soln.



How indicators work

1) Usually a weak organic acid or base that has distinctly different colors in its nonionized & ionized forms.

$$HIn_{(aq)} \leftrightarrows H^+_{(aq)} + In^-_{(aq)} \qquad pK_{HIn}$$

nonionized form — ionized form

How indicators work

2)

$$\frac{[HIn]}{[In^-]} \geq 10 \Rightarrow \begin{cases} \text{show the color of HIn} \\ pH \leq pK_{HIn} - 1 \end{cases}$$

$$\frac{[In^-]}{[HIn]} \geq 10 \Rightarrow \begin{cases} \text{show the color of } In^- \\ pH \geq pK_{HIn} + 1 \end{cases}$$

$$[HIn] \approx [In^-]$$

$$\Rightarrow \text{combination of the color of HIn \& } In^-$$

How indicators work

3) The useful pH range for indicator is

$pK_{HIn} \pm 1$

↓

encompass the pH at equivalence point of titration curve

4) Not all indicators change color at the same pH.

TABLE 14-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a*	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R – Y	1
	8.0–9.6	8.96§	Y – B	
Methyl yellow	2.9–4.0		R – Y	2
Methyl orange	3.1–4.4	3.46§	R – O	2
Bromocresol green	3.8–5.4	4.66§	Y – B	1
Methyl red	4.2–6.3	5.00§	R – Y	2
Bromocresol purple	5.2–6.8	6.12§	Y – P	1
Bromothymol blue	6.2–7.6	7.10§	Y – B	1
Phenol red	6.8–8.4	7.81§	Y – R	1
Cresol purple	7.6–9.2		Y – P	1
Phenolphthalein	8.3–10.0		C – R	1
Thymolphthalein	9.3–10.5		C – B	1
Alizarin yellow GG	10–12		C – Y	2

*At ionic strength of 0.1.

†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

‡(1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type: $In + H_2O \rightleftharpoons InH^+ + OH^-$

§For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$

Acid-Base Titrations

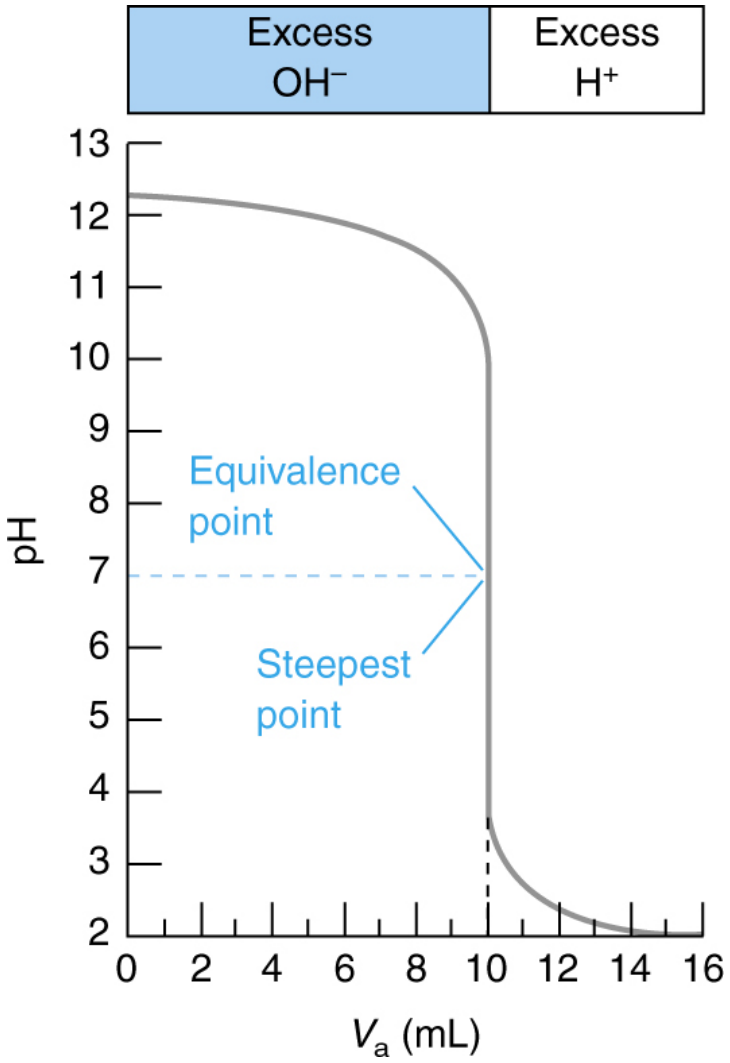
1) Strong base +
Strong acid

3 regions :

a) excess base

b) equivalence point
(pH = 7.00)

c) excess acid



2) Weak acid + Strong base

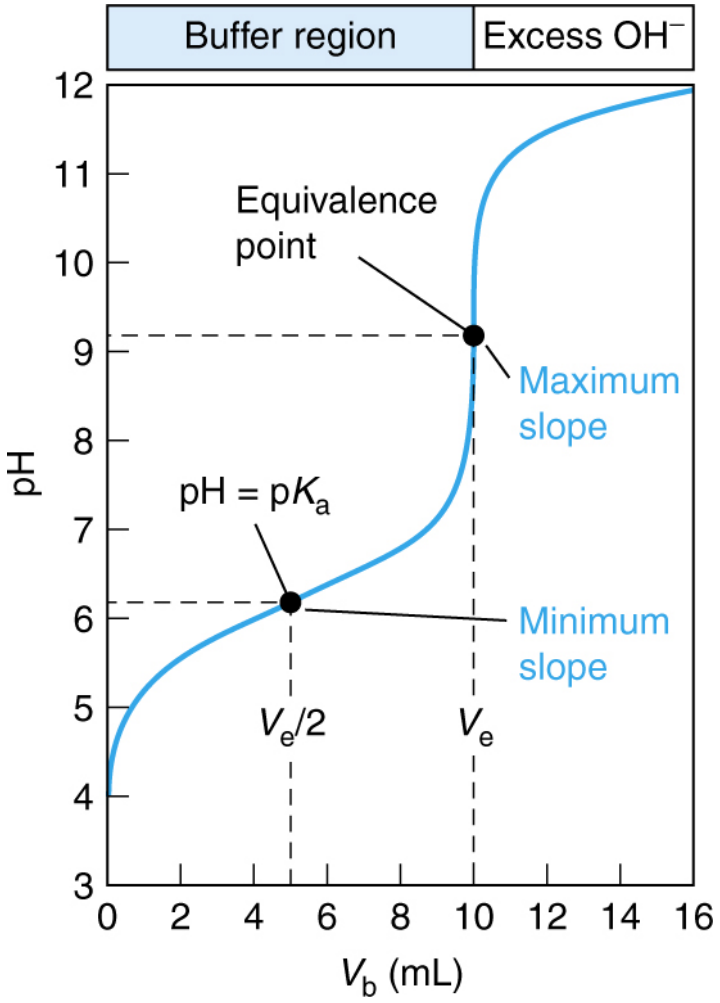
4 regions:

a) excess weak acid

b) buffer region

c) equivalence point (pH > 7.0)

d) excess base



3) Weak base + Strong acid

4 regions:

a) excess weak base

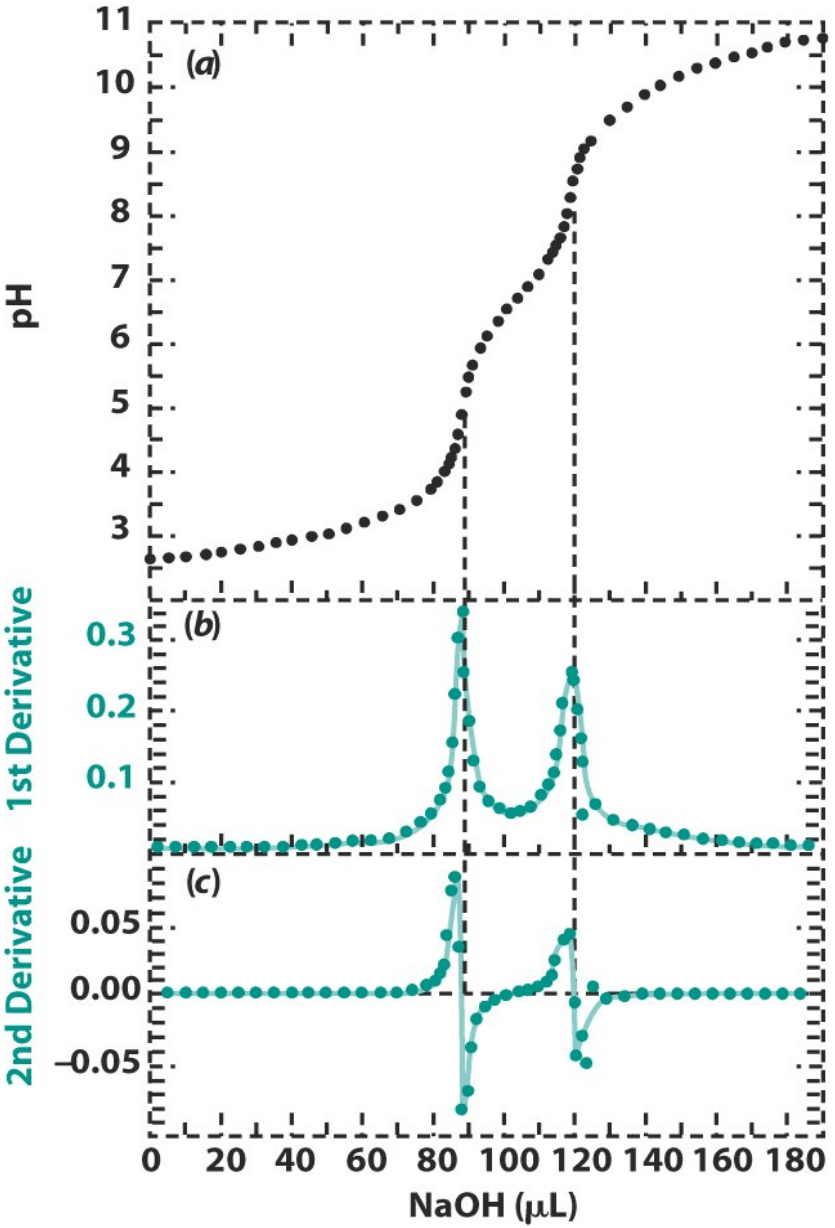
b) buffer region

c) equivalence point (pH < 7.00)

d) excess acid

b) Using a pH Electrode to Find the End Point

using titration curve



Practical Notes

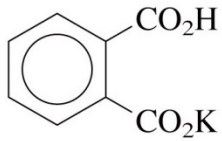
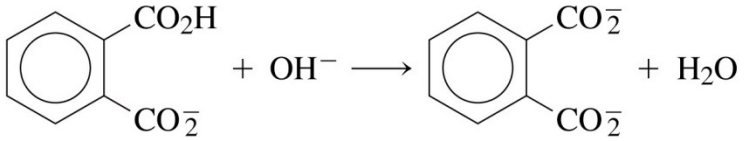
- Primary standards: Acids and bases can be purchased in forms pure enough.
- NaOH, KOH must be standardized against a primary standard
- Alkaline solutions: (ex: NaOH)

$$OH^- + CO_2 \rightarrow HCO_3^-$$

- Strong base attacks glass.

Practical Notes

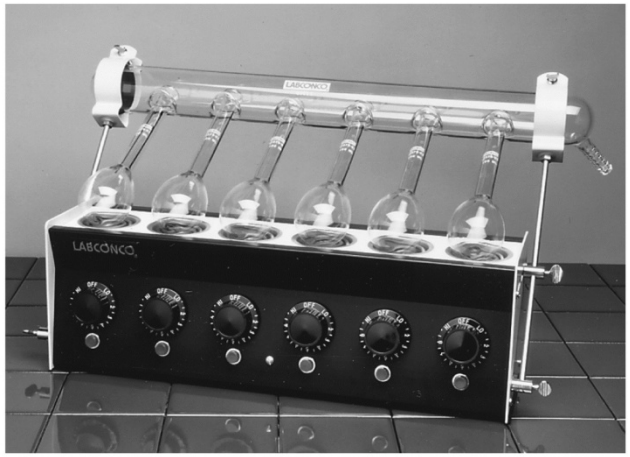
TABLE 10-4 Primary standards

Compound	Formula mass	Notes
ACIDS		
 Potassium hydrogen phthalate	204.22	The pure solid is dried at 105°C and used to standardize base. A phenolphthalein end point is satisfactory. 
$KH(IO_3)_2$ Potassium hydrogen iodate	389.91	This is a strong acid, so any indicator with an end point between ~5 and ~9 is adequate.
BASES		
$H_2NC(CH_2OH)_3$ Tris(hydroxymethyl)aminomethane (also called tris or tham)	121.14	The pure solid is dried at 100°–103°C and titrated with strong acid. The end point is in the range pH 4.5–5. $H_2NC(CH_2OH)_3 + H^+ \longrightarrow H_3\overset{+}{N}C(CH_2OH)_3$
Na_2CO_3 Sodium carbonate	105.99	Primary standard grade Na_2CO_3 is titrated with acid to an end point of pH 4–5. Just before the end point, the solution is boiled to expel CO_2.
$Na_2B_4O_7 \cdot 10H_2O$ Borax	381.37	The recrystallized material is dried in a chamber containing an aqueous solution saturated with NaCl and sucrose. This procedure gives the decahydrate in pure form. The standard is titrated with acid to a methyl red end point. $\text{“}B_4O_7^{2-} \cdot 10H_2O\text{”} + 2H^+ \longrightarrow 4B(OH)_3 + 5H_2O$

Typical applications of neutralization titrations : Kjeldahl Nitrogen Analysis

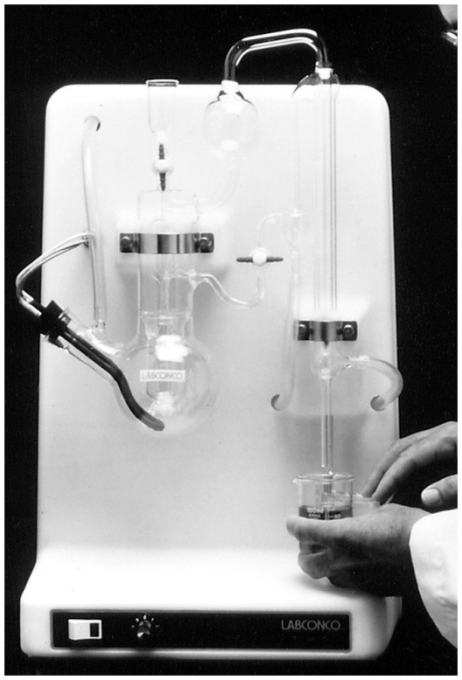
Developed in 1883, the analysis remains one of the most widely used methods for determining nitrogen in organic substances such as protein, cereal, and flour. The solid is digested (decomposed and dissolved) in boiling sulfuric acid to convert nitrogen into ammonium ion, NH_4^+, in a long-neck Kjeldahl flask

(*a*)

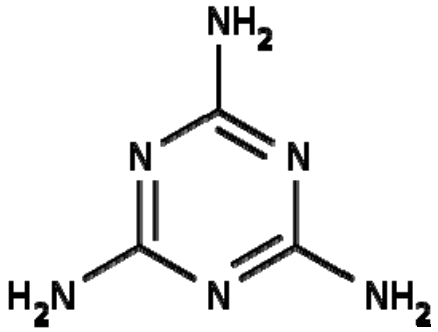


(*b*)

Kjeldahl digestion: $$\text{organic C, H, N} \xrightarrow[H_2SO_4]{\text{boiling}} NH_4^+ + CO_2 + H_2O$$



Melamine contaminated milk



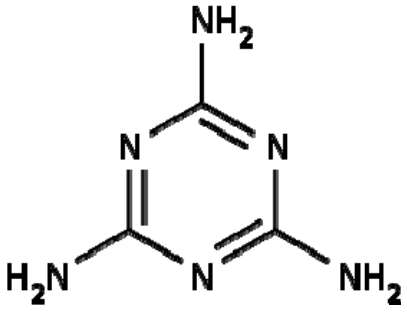
Neutralization of NH_4^+: $NH_4^+ + OH^- \longrightarrow NH_3(g) + H_2O$ (10-5)

Distillation of NH_3 into standard HCl: $NH_3 + H^+ \longrightarrow NH_4^+$ (10-6)

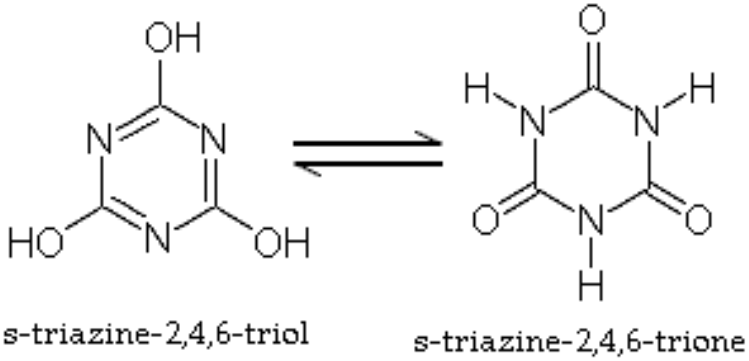
Titration of unreacted HCl with NaOH: $H^+ + OH^- \longrightarrow H_2O$ (10-7)

Kjeldahl Nitrogen Analysis: Chemistry Behind the Health

- Melamine (66.6wt% nitrogen)



- Cyanuric acid (32.6 wt% N)



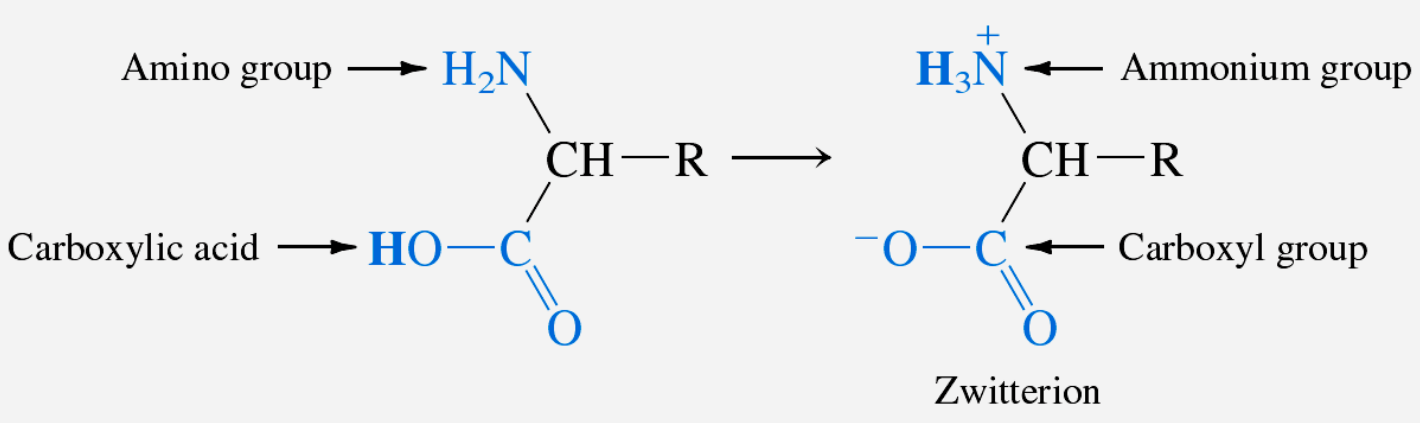
s-triazine-2,4,6-triol s-triazine-2,4,6-trione

Protein source	Weight% nitrogen
Meat	**16.0**
Blood plasma	**15.3**
Milk	**15.6**
Flour	**17.5**
Egg	**14.9**

Polyprotic Acids and Bases

Amino acids are polyprotic

Amino acids from which proteins are built have an acidic carboxylic acid group, a basic amino group, and a variable substituent designated R:



The resulting structure, with positive and negative sites, is called a zwitterion.

Amino acids are polyprotic

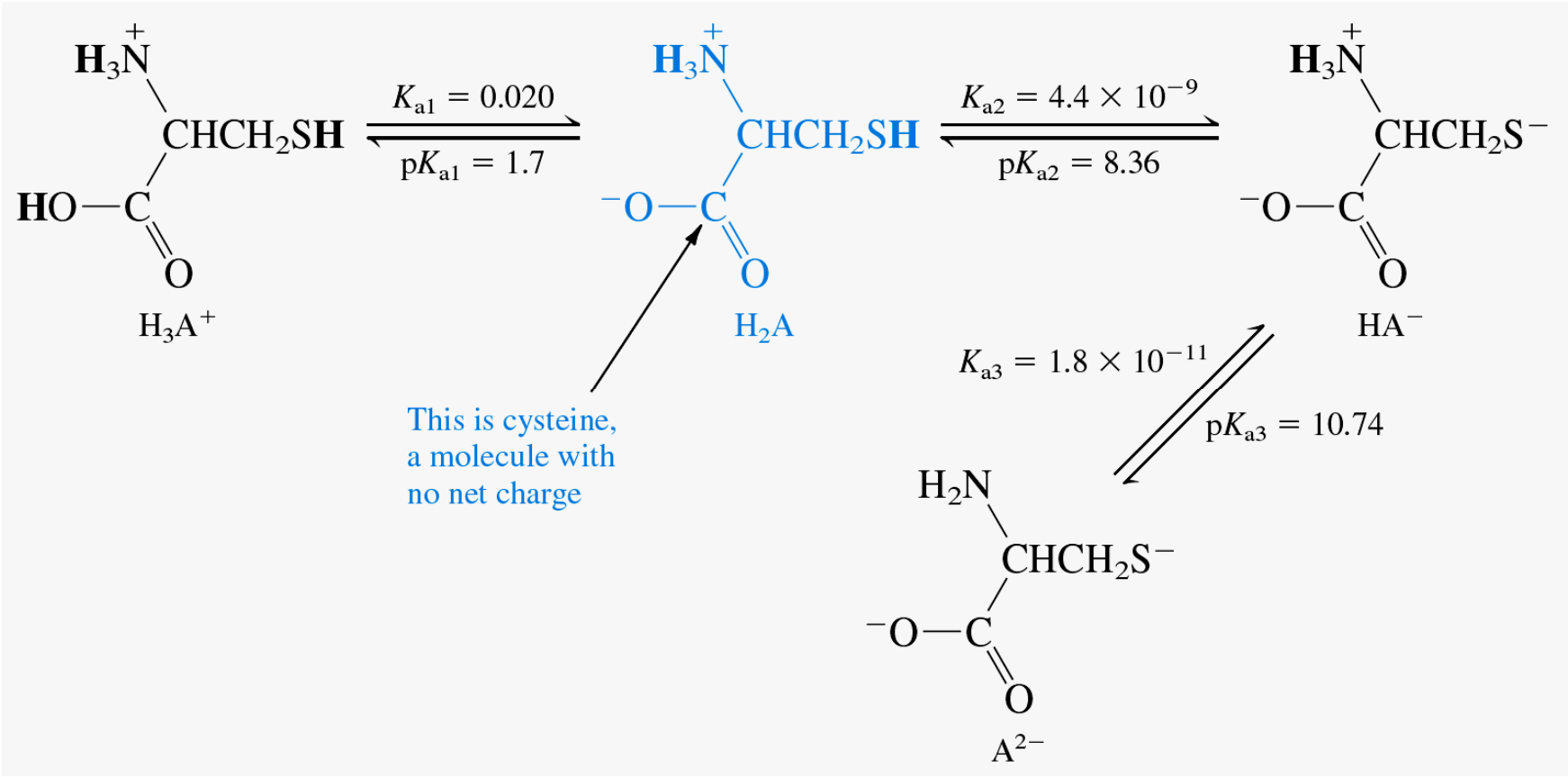
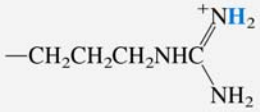
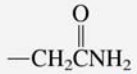
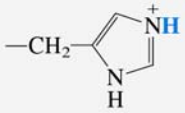
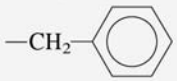
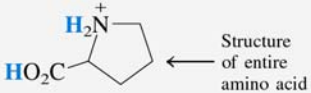
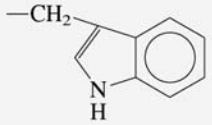
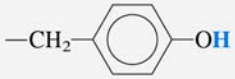


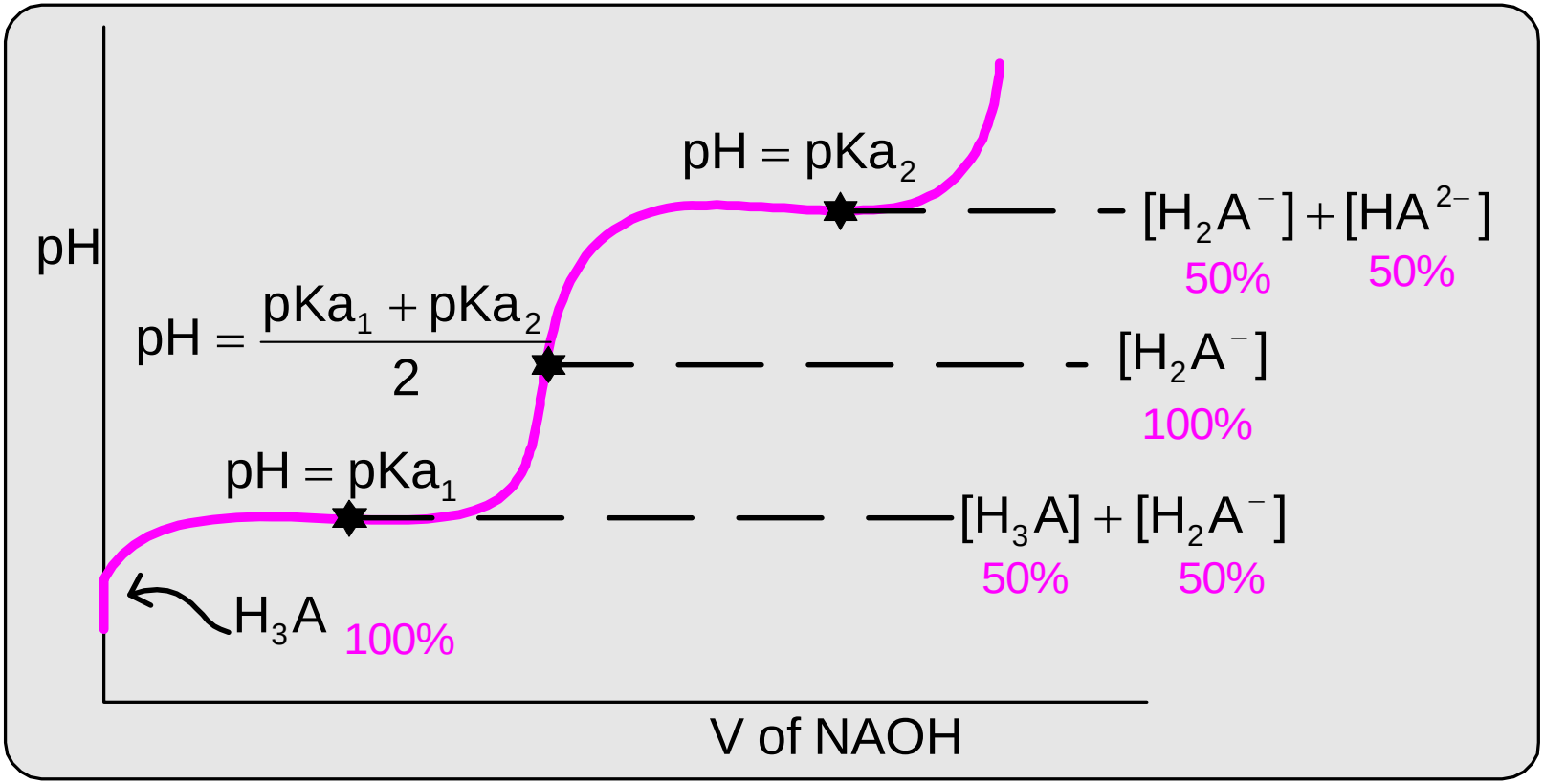
Table 11-1 Acid dissociation constants of amino acids[a]

Amino acid[b]	Substituent	Carboxylic acid pK_a	Ammonium pK_a	Substituent pK_a	Molecular mass
Alanine (A)	—CH_3	2.344	9.868		89.09
Arginine (R)		1.823	8.991	12.1	174.20
Asparagine (N)		2.16	8.73		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)		2.19	9.00		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	9.08		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	9.33		204.23
Tyrosine (Y)		2.41	8.67	11.01	181.19
Valine (V)	—$CH(CH_3)_2$	2.286	9.719		117.15

Finding the pH

1) Titration of polyprotic acids

(ex) H_3PO_4 (H_3A)



Finding the pH

2) solutions containing Amphoteric Anions (H_2A^-) as the only A-B major species

$$H_2A^-_{(aq)} + H_2A^-_{(aq)} \leftrightarrow H_3A_{(aq)} + HA^{2-}_{(aq)}$$

$$K = \frac{[H_3A][HA^{2-}]}{[H_2A^-]^2} = \frac{K_{a_2}}{K_{a_1}}$$

$$[H_3A] = [HA^{2-}]$$

Finding the pH

① $$\Rightarrow K = \frac{[H_3A]^2}{[H_2A^-]^2} = \frac{K_{a_2}}{K_{a_1}}$$

from $H_3A_{(aq)} \leftrightarrow H^+ + H_2A^-$

$$K_{a_1} = \frac{[H^+][H_2A^-]}{[H_3A]}$$

② $$K_{a_1} = \frac{[H^+][H_2A^-]}{[H_3A]} \quad \Rightarrow \frac{[H^+]}{K_{a_1}} = \frac{[H_3A]}{[H_2A^-]}$$

Finding the pH

① & ②

$$\Rightarrow \frac{K_{a_2}}{K_{a_1}} = \left(\frac{\left[H^+\right]}{K_{a_1}} \right)^2$$

$$\left[H^+\right] = \sqrt{K_{a_1} K_{a_2}}$$

$$\Rightarrow pH = \frac{pK_{a_1} + pK_{a_2}}{2}$$

Which is the principle species ?

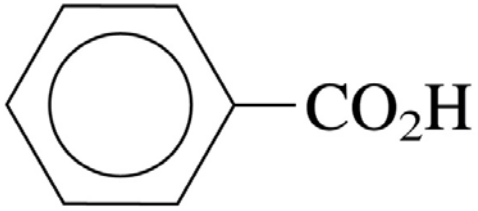
1) .

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

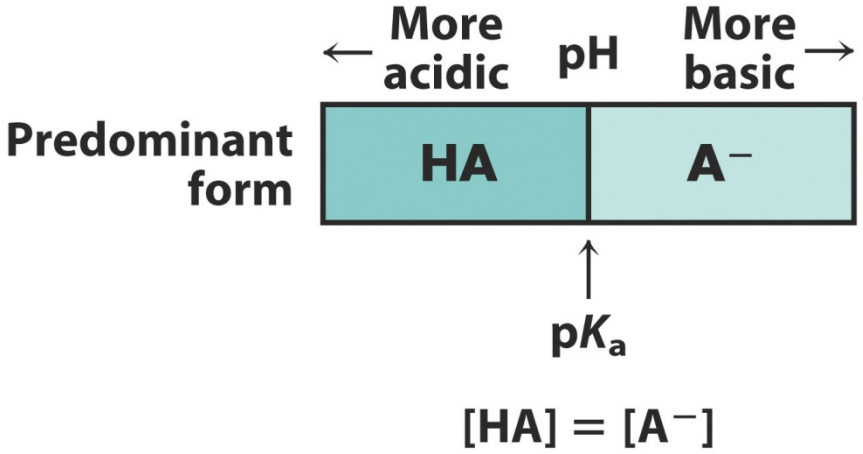
$$\therefore \text{at } pH = 4.20 \qquad \frac{[A^-]}{[HA]} = 1$$

$$pH > pK_a \qquad [A^-] > [HA]$$

$$pH < pK_a \qquad [A^-] < [HA]$$



Benzoic acid
$pK_a = 4.20$

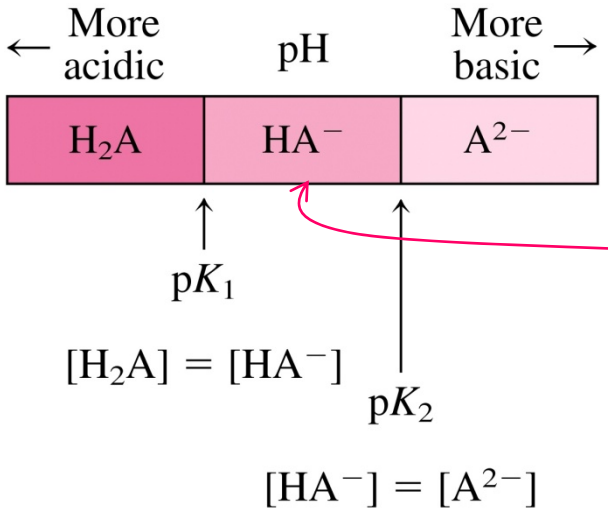


Which is the principle species ?

2) For H_2A

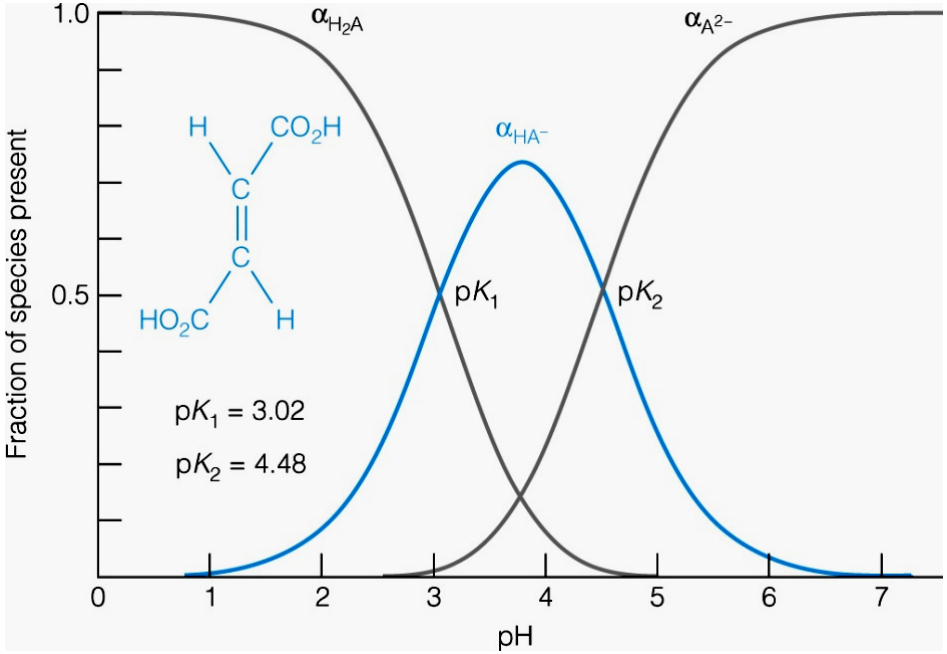
$$pH = pK_{a_1} + \frac{[HA^-]}{[H_2A]}$$

$$pH = pK_{a_2} + \frac{[A^{2-}]}{[HA^-]}$$

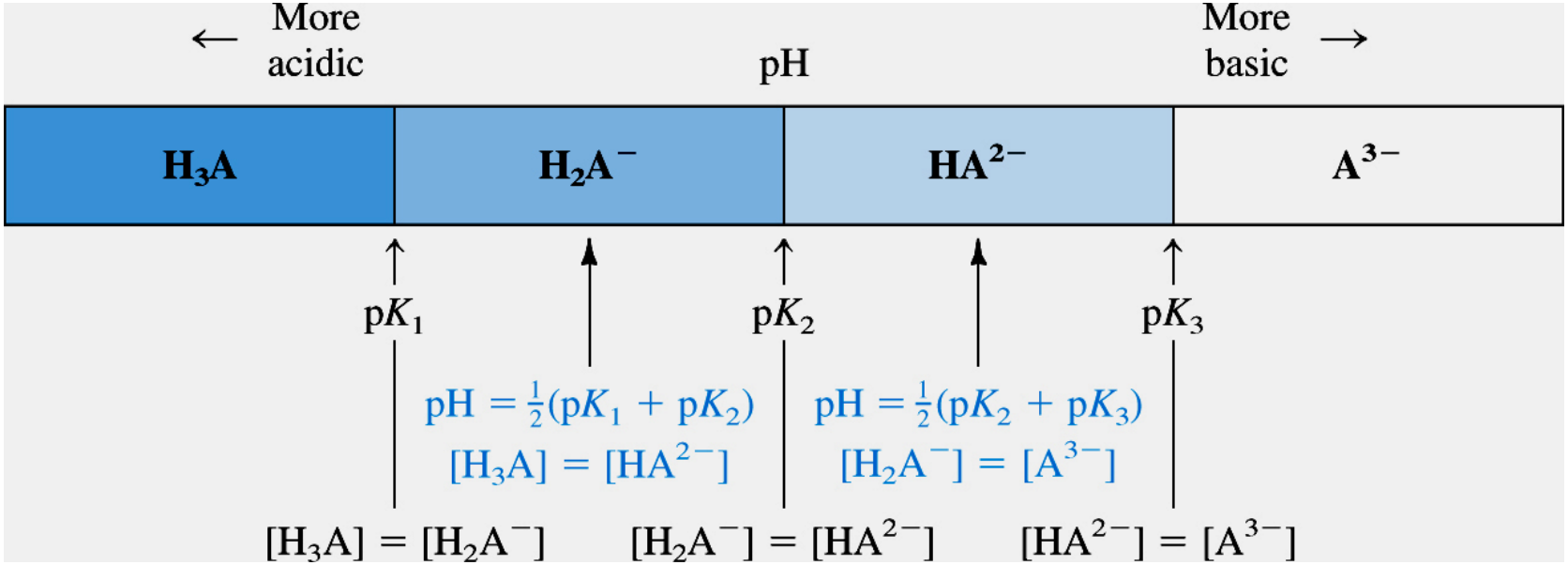


$$pH = \frac{1}{2}(pK_1 + pK_2)$$

$$[H_2A] = [A^{2-}]$$

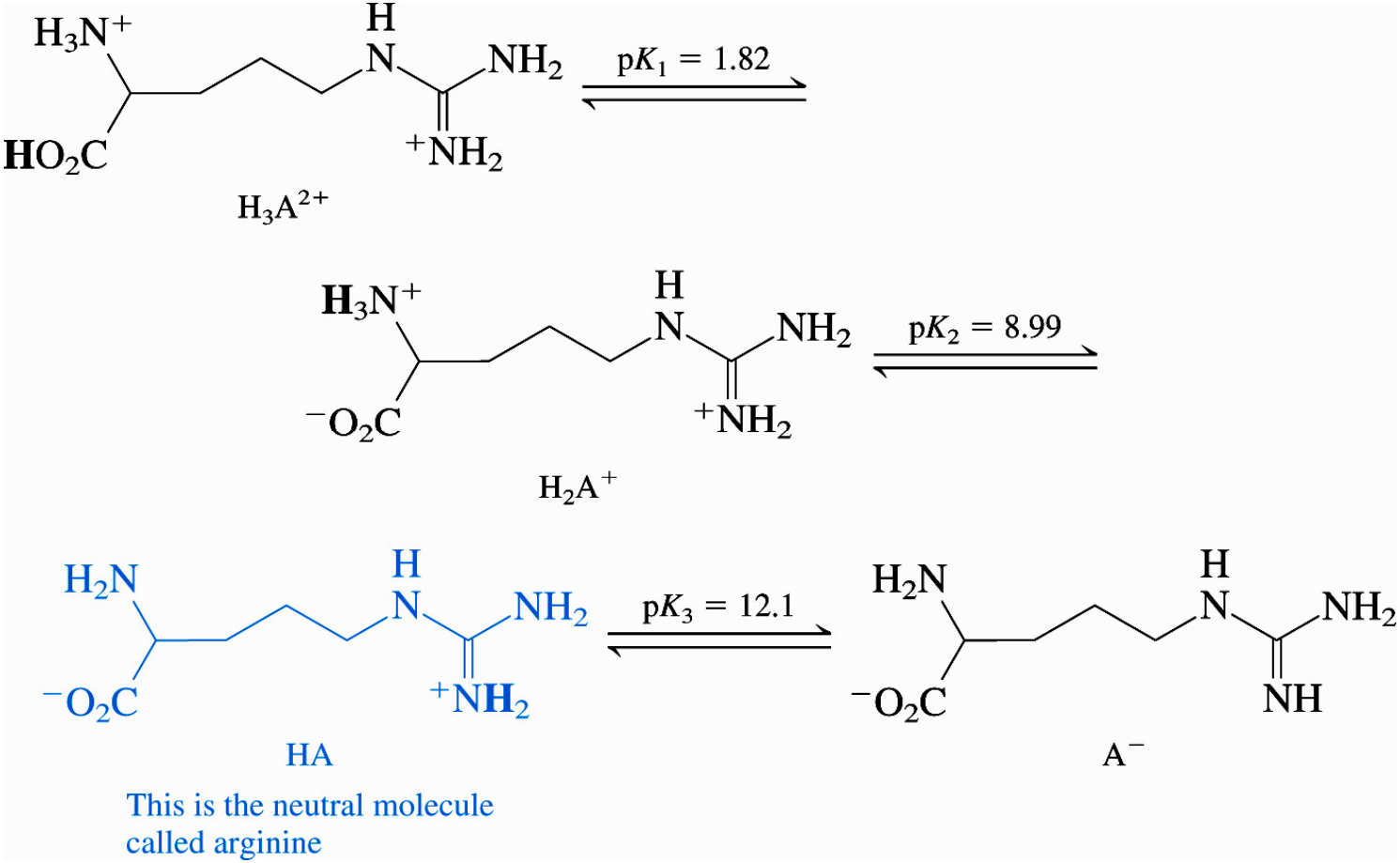


- 3) For H_3A

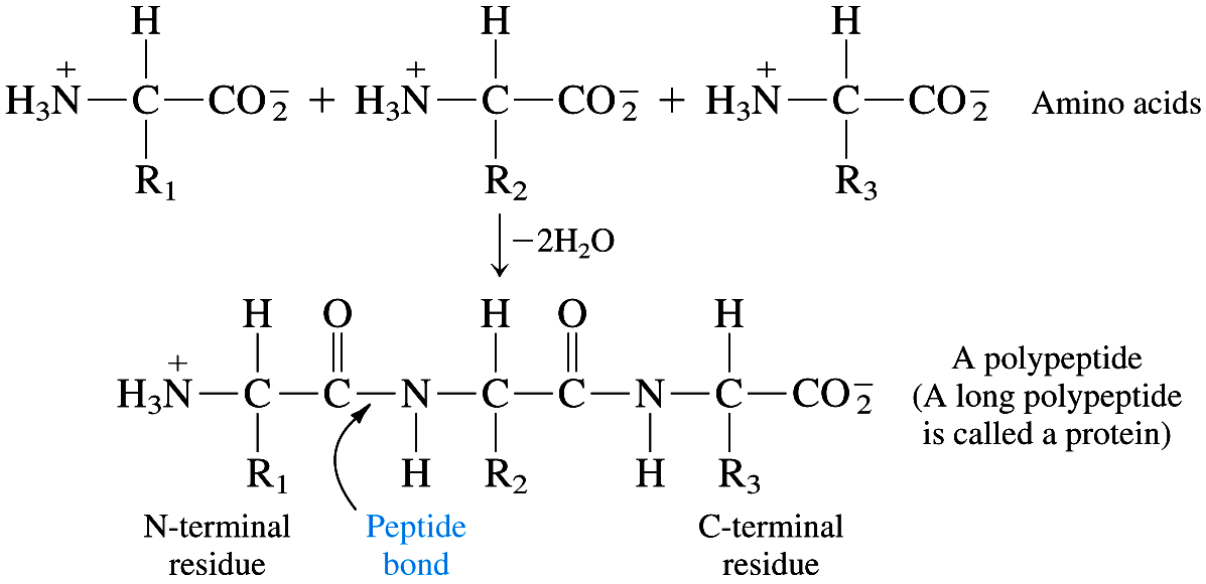

← More acidic
pH
More basic →
H3A
H2A−
HA2−
A3−
pK1
pK2
pK3
pH = ½(pK1 + pK2)
[H3A] = [HA2−]
pH = ½(pK2 + pK3)
[H2A−] = [A3−]
[H3A] = [H2A−]
[H2A−] = [HA2−]
[HA2−] = [A3−]

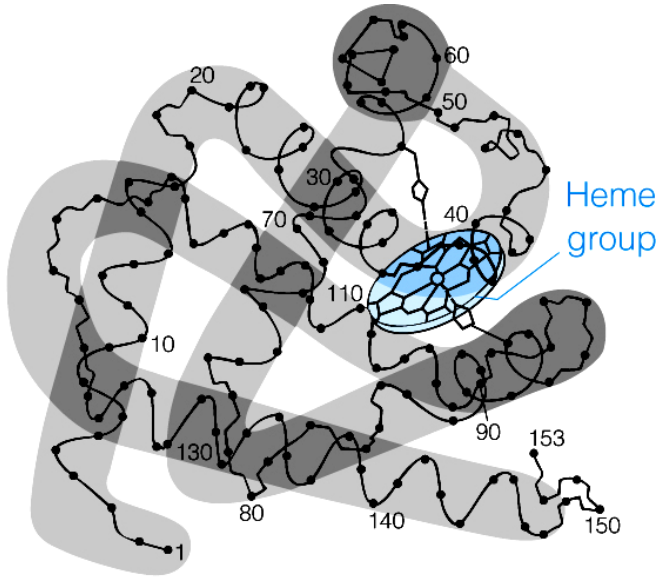
Ex

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?

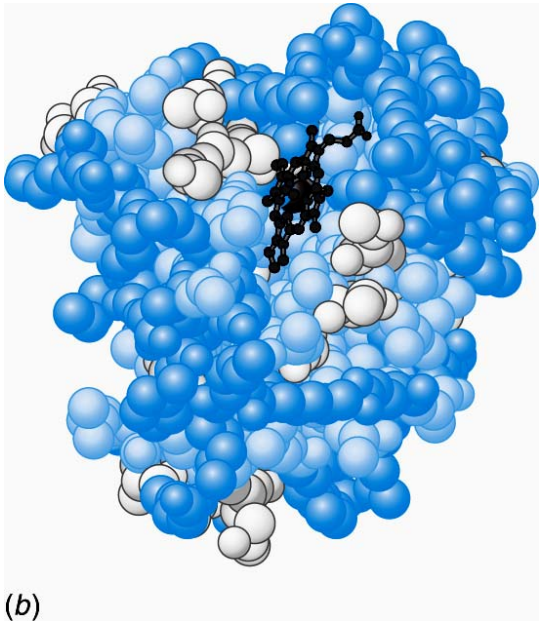


Proteins are polyprotic acids and bases





(*a*)



(*b*)

myoglobin

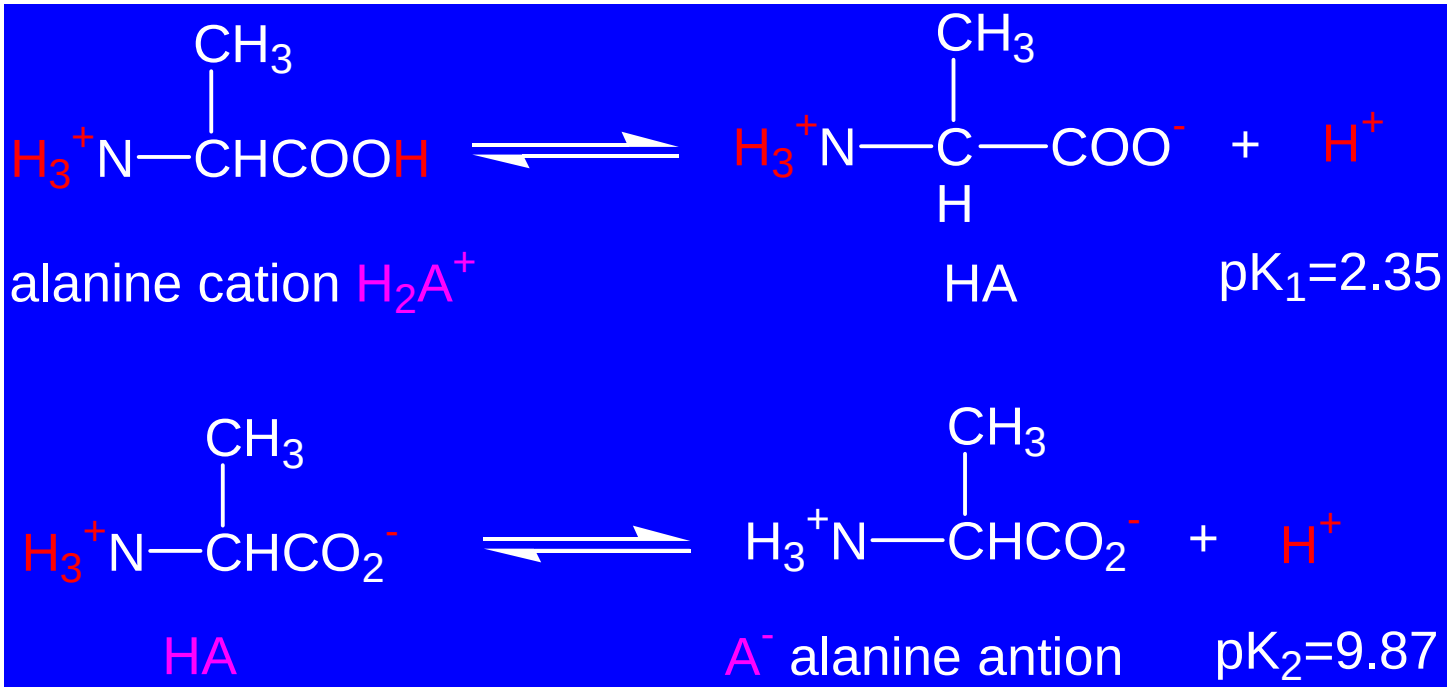
Titrations in Polyprotic Systems

Isoelectric pH (isoionic pH)

The pH at which the average charge of the polyprotic acid is zero

Titrations in Polyprotic Systems

(ex)



isoelectric pH : most form as HA & $\left[H_2A^+\right] \approx \left[A^-\right]$

where $pH = \frac{1}{2}\left(pK_1 + pK_2\right)$

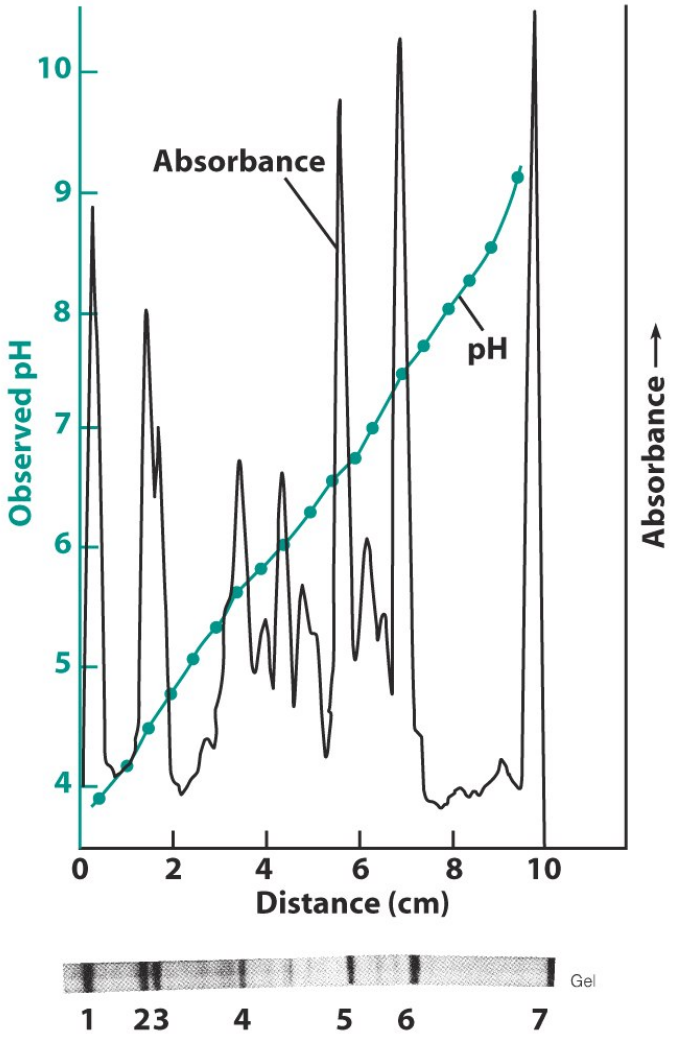
Titrations in Polyprotic Systems

Isoelectric focusing :

A technique of protein separation

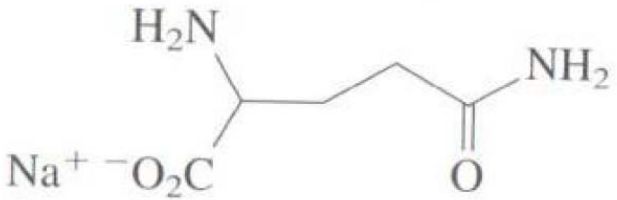
pH gradient design

Protein stop migrating in an electric field at isoelectric pH

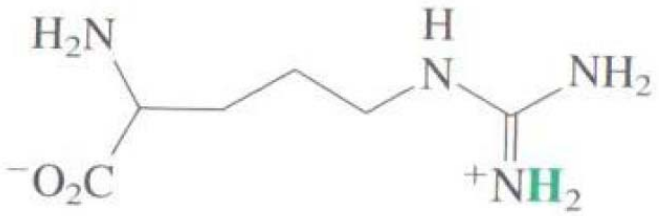


Homework

1. Draw the structures of the predominant forms of glutamine acid and tyrosine at pH 9.0 and pH 10.0. What is the second most abundant species at each pH?
2. Calculate the pH of 0.10M solution of each of the following amino acids in the form drawn:



(a) Sodium salt of glutamine



(b) Arginine