H⁺ H⁺ H⁺ H⁺ H⁺ H⁺
H⁺ OH⁻
LOW pH : LOTS OF H⁺

OH⁻ OH⁻ OH⁻ H⁺ OH⁻ OH⁻ OH⁻
LOTS OF OH⁻ : HIGH pH

pH

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Outline

- pH
- Henderson-Hasselbalch Equation
- Monoprotic and polyprotic acids
- Titration

Measuring the acidity of solutions, pH

$$pH = -\log_{10} [H^+]$$

pH Scale

The hydrogen ion and hydroxyl ion concentrations are given in moles per liter at 25°C.

pH		[H⁺]		[OH⁻]	
0	(10^0)	1.0	0.0000000000001	(10^{-14})
1	(10^{-1})	0.1	0.0000000000001	(10^{-13})
2	(10^{-2})	0.01	0.000000000001	(10^{-12})
3	(10^{-3})	0.001	0.00000000001	(10^{-11})
4	(10^{-4})	0.0001	0.0000000001	(10^{-10})
5	(10^{-5})	0.00001	0.000000001	(10^{-9})
6	(10^{-6})	0.000001	0.00000001	(10^{-8})
7	(10^{-7})	0.0000001	0.0000001	(10^{-7})
8	(10^{-8})	0.00000001	0.000001	(10^{-6})
9	(10^{-9})	0.000000001	0.00001	(10^{-5})
10	(10^{-10})	0.0000000001	0.0001	(10^{-4})
11	(10^{-11})	0.00000000001	0.001	(10^{-3})
12	(10^{-12})	0.000000000001	0.01	(10^{-2})
13	(10^{-13})	0.0000000000001	0.1	(10^{-1})
14	(10^{-14})	0.00000000000001	1.0	(10^0)

Dr. Diala Abu-Hassan

Garrett *et al*
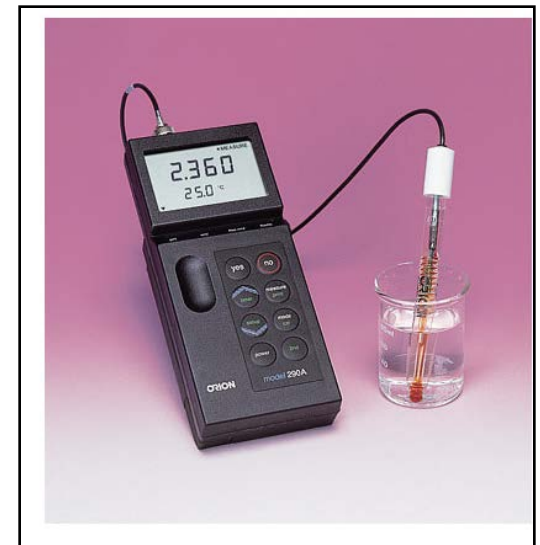
pH

The pH scale is a logarithmic scale.

One pH unit difference implies a 10-fold difference in [H+].

Example: lemon juice at pH 2.0 contains more than 100 times as much H+ as orange juice at pH 4.0

The pH of Various Common Fluids	
Fluid	**pH**
Household lye	13.6
Bleach	12.6
Household ammonia	11.4
Milk of magnesia	10.3
Baking soda	8.4
Seawater	8.0
Pancreatic fluid	7.8–8.0
Blood plasma	7.4
Intracellular fluids	
Liver	6.9
Muscle	6.1
Saliva	6.6
Urine	5–8
Boric acid	5.0
Beer	4.5
Orange juice	4.3
Grapefruit juice	3.2
Vinegar	2.9
Soft drinks	2.8
Lemon juice	2.3
Gastric juice	1.2–3.0
Battery acid	0.35

Measuring acidity in aqueous solutions- pH scale

$pH = - \log [H_3O^+]$

$[H_3O^+] = 10^{-pH}$

Example 1: $[H_3O^+]$ in household bleach is 10^{-12} M

$pH = - \log [10^{-12}] = 12$

Example 2: Orange juice has a pH of 4

$[H_3O^+] = 10^{-4}$ M

pH problem solving

Example 1:

What is the pH of a solution whose hydrogen ion concentration is 3.2×10^{-4} mol/L?

$pH = -\log [H^+]$

$\quad = -\log (3.2 \times 10^{-4})$

$\quad = -\log (3.2) - \log (10^{-4})$

$\quad = -0.5 + 4.0$

$\quad = 3.5$

pH in solutions

Acids

Neutral

Bases

[H₃O⁺] and [OH⁻] in Acidic, Neutral, and Basic Solutions
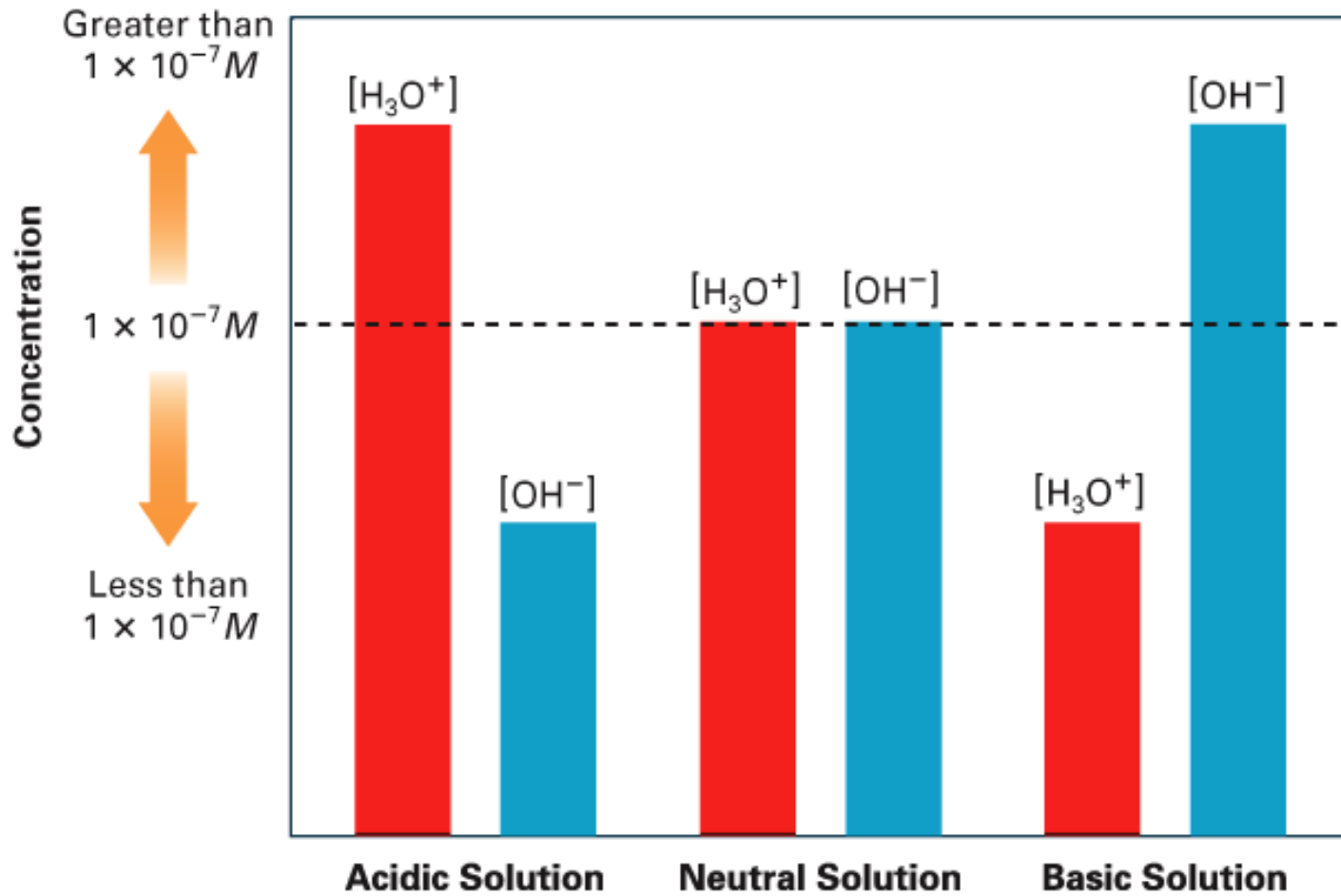
Strong Acids and pH

$$HCl \rightarrow H^+ + Cl^-$$

$$Ka = \frac{[H^+]\,[Cl^-]}{[HCl]}$$

$$[H^+] = [acid]$$

Ex.1 M solution of HCl has a pH of 0

1 mM HCl solution has a pH of 3

0.1 M NaOH solution has a pH of 13

Dissociation of water

- $K_w = [H^+][OH^-] = 10^{-14}$

- Valid for acidic, basic, neutral and pure H_2O

  - $pH = -\log[H^+]$
  - $pOH = -\log[OH^-]$

  - $pH + pOH = 14$

Example: A solution has an $[OH^-] = 10^{-9}$ M

$[H_3O^+] = 10^{-5}$ M $\rightarrow$ pH = 5

pH scale for some common substances

Relationship among [H$^+$], [OH$^-$], and pH

	[H$^+$] (mol/L)	[OH$^-$] (mol/L)	pH	Aqueous system
Increasing acidity	1×10^0	1×10^{-14}	0.0	1M HCl
	1×10^{-1}	1×10^{-13}	1.0	0.1M HCl
	1×10^{-2}	1×10^{-12}	2.0	Gastric juice / Lemon juice
	1×10^{-3}	1×10^{-11}	3.0	
	1×10^{-4}	1×10^{-10}	4.0	Tomato juice
	1×10^{-5}	1×10^{-9}	5.0	Black coffee
	1×10^{-6}	1×10^{-8}	6.0	Milk
Neutral	1×10^{-7}	1×10^{-7}	7.0	Pure water
Increasing basicity	1×10^{-8}	1×10^{-6}	8.0	Blood
	1×10^{-9}	1×10^{-5}	9.0	Sodium bicarbonate, sea water
	1×10^{-10}	1×10^{-4}	10.0	
	1×10^{-11}	1×10^{-3}	11.0	Milk of magnesia / Household ammonia
	1×10^{-12}	1×10^{-2}	12.0	Washing soda
	1×10^{-13}	1×10^{-1}	13.0	0.1M NaOH
	1×10^{-14}	1×10^0	14.0	1M NaOH

# Enzyme activity and pH
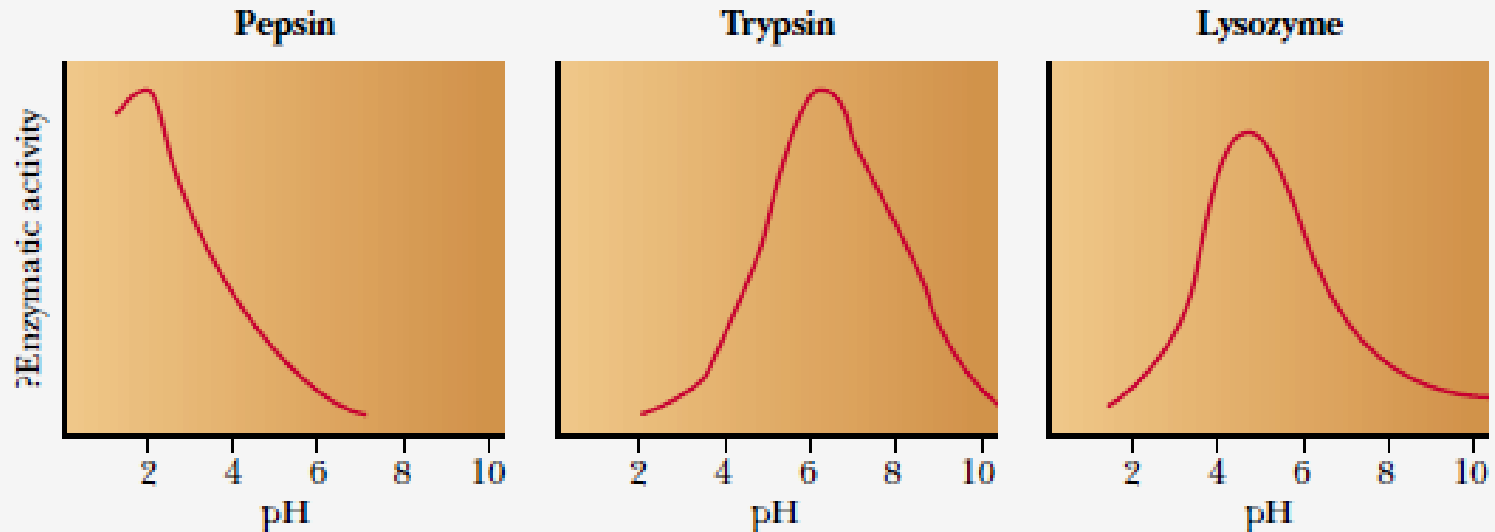
■ FIGURE 2.12 pH versus enzymatic activity. Pepsin, trypsin, and lysozyme all have steep pH optimum curves. Pepsin has maximum activity under very acidic conditions, as would be expected for a digestive enzyme that is found in the stomach. Lysozyme has its maximum activity near pH 5, while trypsin is most active near pH 6.
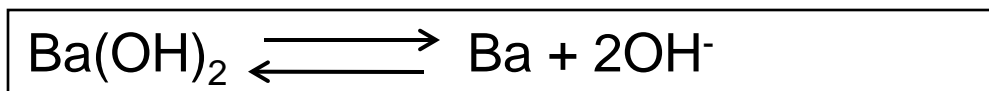
Example:

Find the K_a of a 0.04 M weak acid HA whose pH is 4.0?

HA $\rightleftharpoons$ $H^+ + A^-$
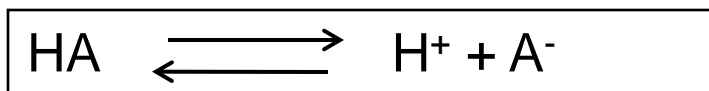
$K_a = [A^-][H^+] / [HA] = [H^+]^2 / [HA] = 10^{-4} \times 10^{-4} / 0.04 = 2.5 \times 10^{-7}$

Example 2:

What is the pH of a 0.05 M $Ba(OH)_2$?

$Ba(OH)_2 \rightleftharpoons Ba + 2OH^-$

$[OH^-] = 2 \times 0.05 = 0.10 \ M = 1 \times 10^{-1}$
$pOH = - \log 1 \times 10^{-1} = 1$

Remember $pOH = -\log [OH^-]$

$pH = 14 - 1 = 13$
$[H^+] = 1 \times 10^{-13}$

Example:

The K_b for ammonia is 1.8×10^{-5} M. What is the pH of 1×10^{-2} M of ammonia?

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
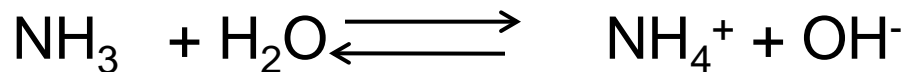
$K_b = [NH_4^+] [OH^-] / [NH_3]$

$1.8 \times 10^{-5} = [OH^-]^2 / 0.01$

$[OH^-] = 4.24 \times 10^{-4}$ M

$pOH = -\log 4.24 \times 10^{-4} = 3.37$

$pH = 14 - 3.37 = 10.63$

Henderson-Hasselbalch Equation

– The dissociation of a weak acid is as follows:

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

The acid dissociation constant is as follows:

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

Rearranging this expression in terms of the parameter of interest [H+] gives the following:

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

Henderson-Hasselbalch Equation

Take the log of both sides:

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

Change the signs , remember $pK_a = -\log K_a$:

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

or

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

What happens when .....

pH = pKa

Substance protonation and deprotanation are in equillibruim.

pH < pKa

H^+ on, substance protonated

pH > pKa

H^+ off, substance deprotonated

pH= pKa -1

Base/acid = 0.1

pH=pKa + 1

Base/acid = 10

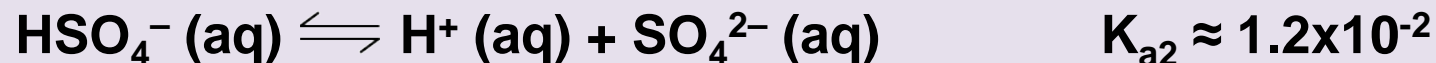| Table 2.7	
pH Values and Base/Acid Ratios for Buffers	
If the pH equals	The ratio of base form/acid form equals
$pK_a - 3$	1/1000
$pK_a - 2$	1/100
$pK_a - 1$	1/10
pK_a	1/1
$pK_a + 1$	10/1
$pK_a + 2$	100/1
$pK_a + 3$	1000/1

Monoprotic- and PolyproticAcids

1. Monoprotic acids have only one ionizable proton.
2. Polyprotic acids have more than one ionizable proton.
3. The protons are removed in steps, not all at once.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COO^-Na^+ + H_2O$$

$$H_3PO_4 \quad \underset{}{\overset{pK_{a1} = 2.14}{\rightleftharpoons}} \quad H_2PO_4^- \quad \underset{}{\overset{pK_{a2} = 7.20}{\rightleftharpoons}} \quad HPO_4^{-2} \quad \underset{}{\overset{pK_{a3} = 12.4}{\rightleftharpoons}} \quad PO_4^{-3}$$

H₂PO₄⁻ + H⁺   HPO₄⁻² + H⁺   PO₄⁻³ + H⁺
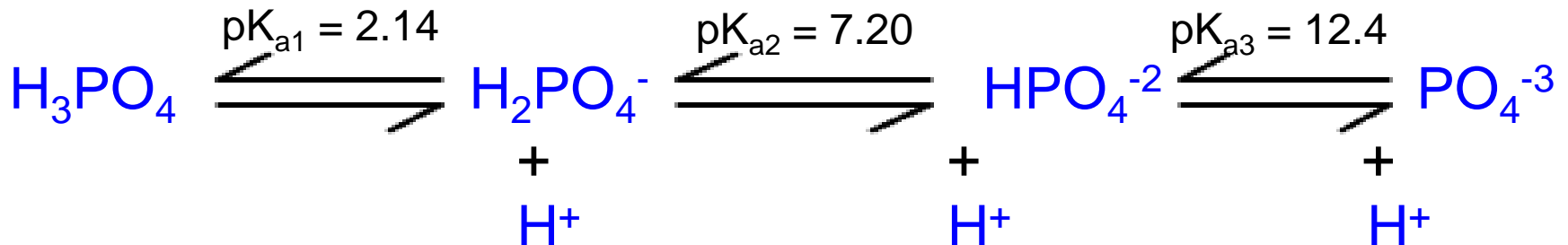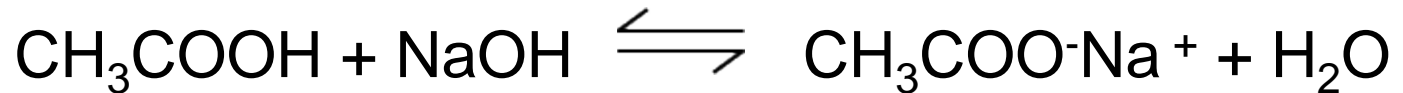
Polyprotic Acids

Sulfuric acid is a **strong acid** in its first dissociation step and a **weak acid** in its second step.

$$H_2SO_4 \ (aq) \longrightarrow H^+ \ (aq) + HSO_4^- \ (aq) \qquad K_{a1} \approx 1.0 \times 10^2$$

$$HSO_4^- \ (aq) \rightleftharpoons H^+ \ (aq) + SO_4^{2-} \ (aq) \qquad K_{a2} \approx 1.2 \times 10^{-2}$$

Polyprotic Acids

TABLE 7.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid*	H_2CO_3	4.3×10^{-7}	4.8×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid[†]	H_2S	1.0×10^{-7}	$\approx 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

*This is really $CO_2(aq)$.

[†]The K_{a_2} value for H_2S is quite uncertain. Its small size makes it very difficult to measure.

It is <u>always</u> easier to remove the first proton in a polyprotic acid than the second. That is, $K_{a1} > K_{a2} > K_{a3}$

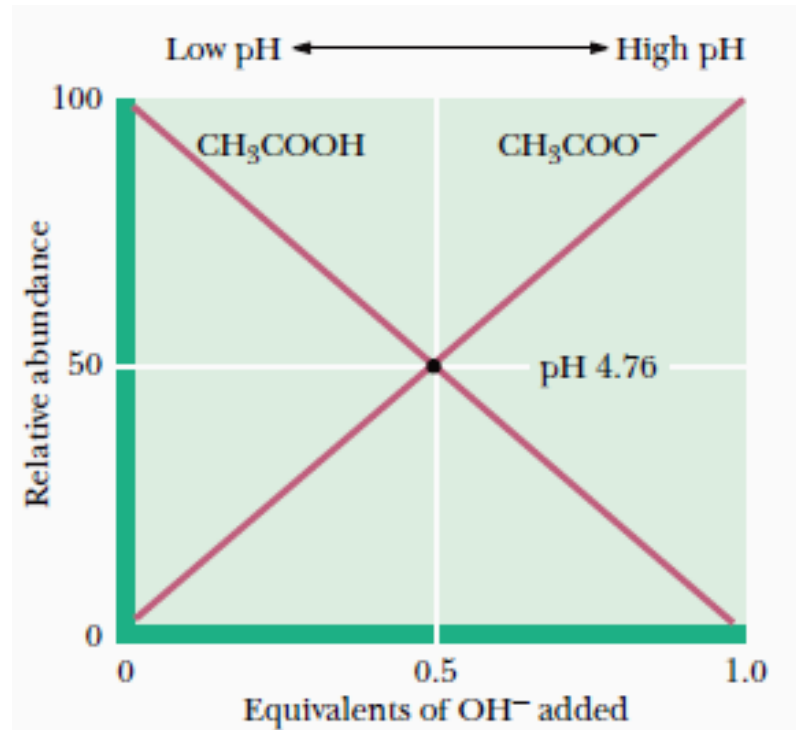# A plot of the fractions of H_2CO_3, HCO^-_3 and CO_3^{2-}

At pH = 9.00 $H_2CO_3 \approx 0\%$, $HCO^-_3 = 95\%$ and $CO_3^{2-} = 5\%$

At pH = 10.00 $H_2CO_3 \approx 0\%$, $HCO^-_3 = 68\%$ and $CO_3^{2-} = 32\%$

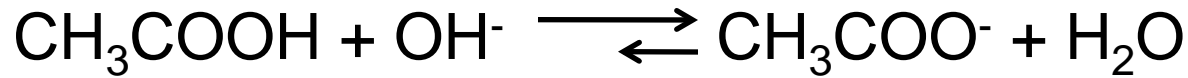$K_{a1} = $ **4.3 x10^{-7}** $K_{a2} = $ **4.8 x10^{-11}**
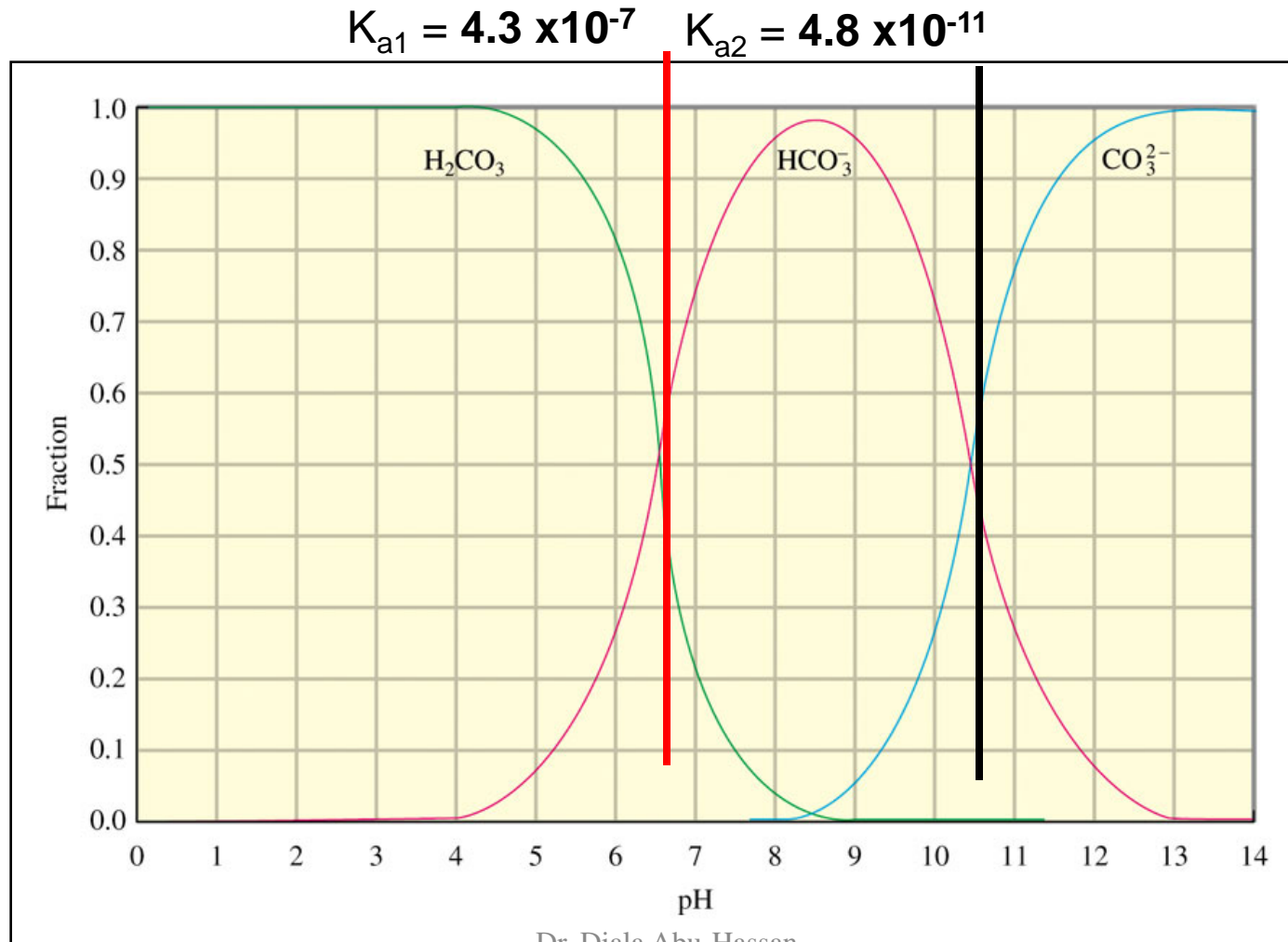
Titration

Titration is an experiment in which measured amounts of base are added to a measured amount of acid while following up changes in pH using a pH meter.
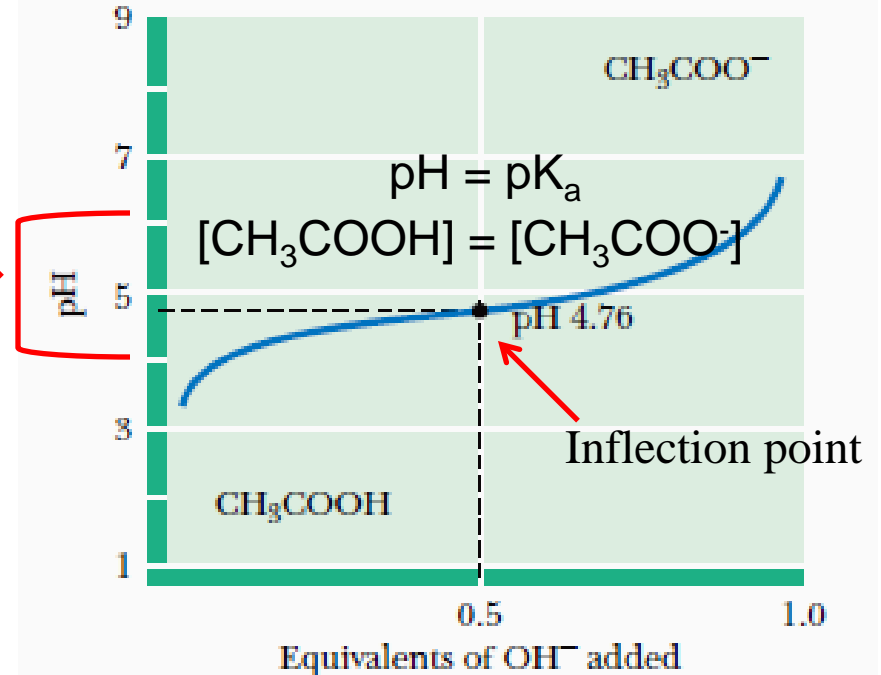
Titration curves

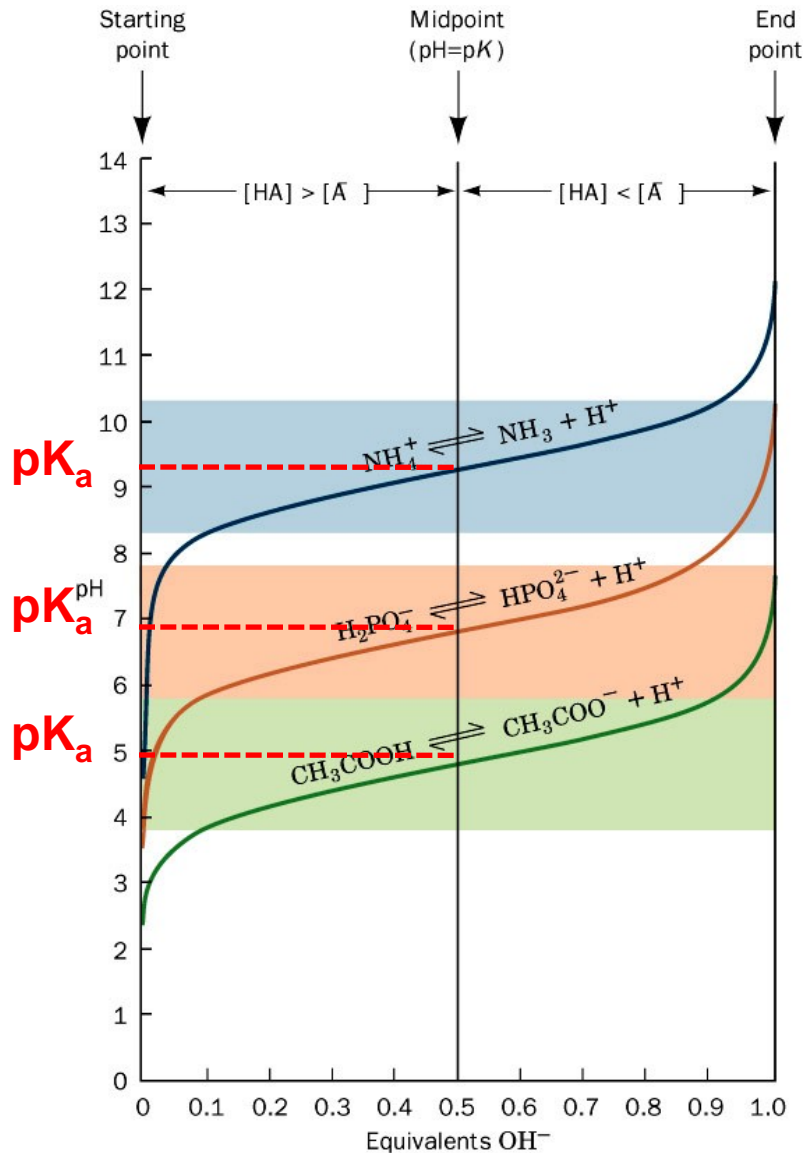$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

In the region small pH changes upon addition of acid or base, the acid/base ratio varies within a narrow range (10:1 at one end and 1:10 at the other end).

The point in the titration at which the acid is exactly neutralized is called the **equivalence point.**

Titration curves

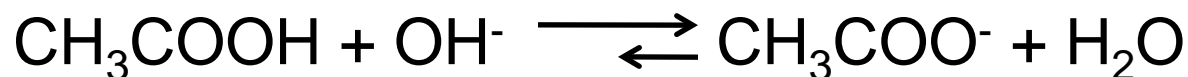– Once OH^- is added to the reaction, it reacts completely with HA to form A^-

$$[A^-] = \frac{X}{V}$$

x = the equivalents of OH^- added

V represents the volume of the solution.

$$[HA] = \frac{[HA_i]\text{-}[Base]}{V}$$

$$pH = pK_a + log\left(\frac{[Base]}{[HA_i]\text{-}[Base]}\right)$$

Example:

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

Calculate the relative amounts of acetic acid and acetate ion present and pH values when 1 mol of acetic acid is titrated with sodium hydroxide.
0.1 mol of NaOH is added

When 0.1 mol of NaOH is added, 0.1 mol of acetic acid reacts with it to form 0.1 mol of acetate ion, leaving 0.9 mol of acetic acid. The composition is 90% acetic acid and 10% acetate ion.
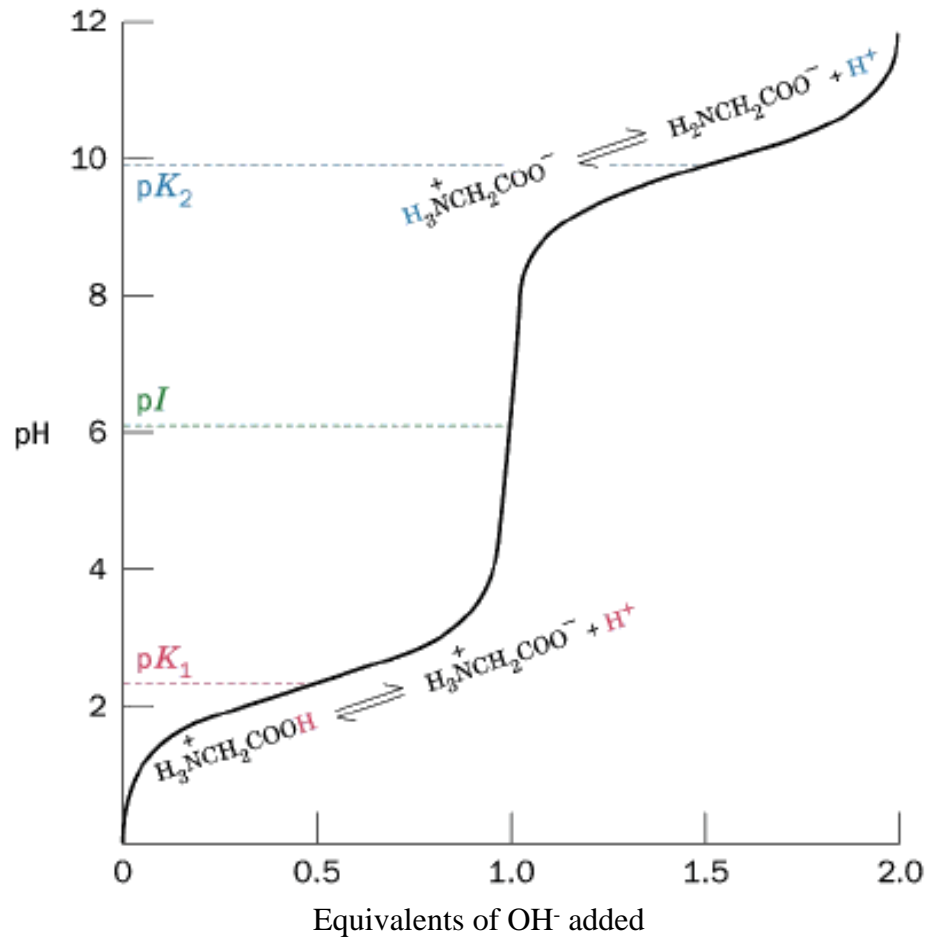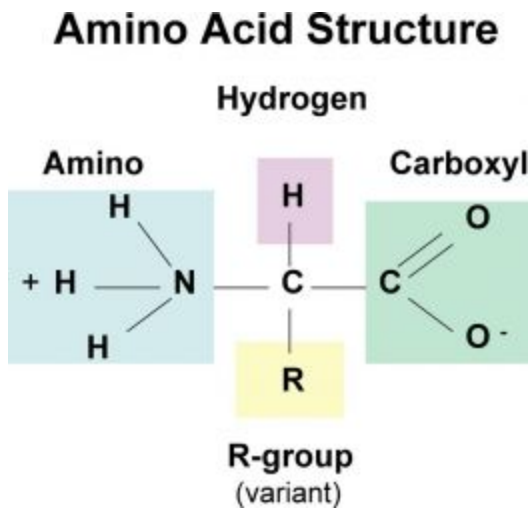
pH = pKa + log 0.1/0.9
pH = 4.76 + log 0.1/0.9
pH = 4.76 - 0.95
pH = 3.81

Titration curve of Glycine

Amino Acid Structure