

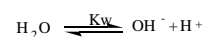
Ch.8 & 9

Systematic Treatment of Equilibrium & Monoprotic Acid-base Equilibrium

Strong acids and bases

Conc. (M)	pH
0.10	1.0
1.0×10^{-3}	3.0
1.0×10^{-5}	5.0
1.0×10^{-8}	8.0?

We have to consider autoprotolysis of water:



Charge Balance

The sum of the positive charges in solution equals the sum of the negative charges in solution.

$$\sum_i n_i C_i^{\text{Cation}} = \sum_j n_j C_j^{\text{anion}}$$

$n \Rightarrow$ charge, $C \Rightarrow$ concentration

Mass Balance

Material balance. The quantity of all species in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution.

Systematic Treatment of Equilibrium - Strong acids and bases

Charge balance. $[\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$

Mass balance. $[\text{Cl}^-] = 1.0 \times 10^{-8} \text{ M}$ $\text{H}_2\text{O} \xrightleftharpoons{K_w} \text{OH}^- + \text{H}^+$

$[\text{OH}^-] = [\text{H}^+] - (1.0 \times 10^{-8} \text{ M})$

$K_w = [\text{H}^+][\text{OH}^-] = [\text{H}^+][(\text{H}^+ - (1.0 \times 10^{-8} \text{ M}))] = 1.0 \times 10^{-14}$

$[\text{H}^+]^2 - (1.0 \times 10^{-8})[\text{H}^+] - K_w = 0$

$[\text{H}^+] = 1.05 \times 10^{-7} \text{ M}, -9.51 \times 10^{-8} \text{ M}$

pH = 6.98

When the (strong) acid or base concentration is around $\sim 10^{-6}$ - 10^{-8} M , we have to be concerned with autoprotolysis.

For extremely low strong acid or base concentration ($< 10^{-8}$), $\text{pH} = 7.00$

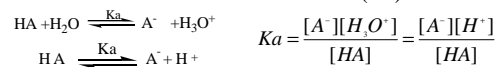
Problem:

What is the pOH, and pH of a $2.48 \times 10^{-7} \text{ M}$ solution of NaOH?

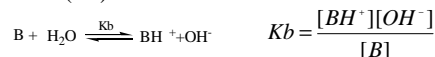
ANS: 6.55; 7.45

Systematic Treatment of Equilibrium - Weak acids and bases

- Weak Acid: acid dissociation constant (K_a)



- Weak Base, hydrolysis reaction: base hydrolysis constant (K_b)

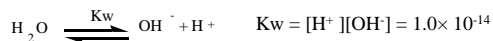
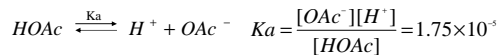


- Relationship between K_a and K_b for conjugate acid/base pairs:

$$K_w = K_a \times K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

A typical weak-acid problem

Example: Calculate the pH of a 1 L solution prepared by dissolving 0.10 moles of acetic acid?



Charge Balance:

$$[H^+] = [OH^-] + [OAc^-]$$

Mass Balance:

$$[HOAc] + [OAc^-] = C = 0.10$$

A typical weak-acid problem

Example: Calculate the pH of a 1 L solution prepared by dissolving 0.10 moles of acetic acid?

Simplifying assumptions

$$(1) \quad K_a = \frac{[A^-][H^+]}{[HA]} \xrightarrow{[H^+] = [A^-]} \frac{[H^+]^2}{C - [H^+]} \xrightarrow{x = [H^+]} \frac{x^2}{C - x}$$

$$C = 0.10 \text{ M and } K_a = 1.75 \times 10^{-5}, x = 1.3 \times 10^{-3} \text{ M}$$

$$(2) \quad K_a = \frac{[A^-][H^+]}{[HA]} = \frac{x^2}{C - x} \xrightarrow{C - x \approx C} \frac{x^2}{C}$$

$$x = \sqrt{K_a \cdot C} = \sqrt{1.75 \times 10^{-5} \times 0.10} = 1.3 \times 10^{-3} \text{ M}$$

A typical weak-acid problem

Example: Calculate the pH of a 1 L solution prepared by dissolving 0.10 moles of acetic acid?

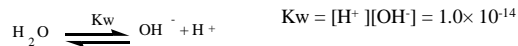
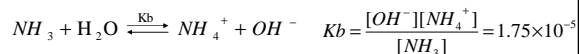
- Fraction of dissociation (α)
- For a monoprotic weak acid:

$$\alpha_{(A^-)} = \frac{[A^-]}{[A^-] + [HA]} = \frac{[A^-]}{[A^-] + (C - [A^-])} = \frac{x}{x + (C - x)} = \frac{x}{C}$$

$$\alpha = \frac{x}{C} = \frac{1.3 \times 10^{-3}}{0.10} = 0.013$$

A typical weak-base problem

Example: Find the pH of 0.10 M ammonia.



Charge Balance:

$$[OH^-] = [H^+] + [NH_4^+]$$

Mass Balance:

$$[NH_3] + [NH_4^+] = C = 0.10$$

A typical weak-base problem

Example: Find the pH of 0.10 M ammonia.

Simplifying assumptions

$$(1) \quad K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} \xrightarrow{[OH^-] = [NH_4^+]} \frac{[OH^-]^2}{C - [OH^-]} \xrightarrow{x = [OH^-]} \frac{x^2}{C - x}$$

$$C = 0.10 \text{ M and } K_b = 1.76 \times 10^{-5}, x = 1.3 \times 10^{-3} \text{ M}$$

$$(2) \quad K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} = \frac{x^2}{C - x} \xrightarrow{C - x \approx C} \frac{x^2}{C}$$

$$x = \sqrt{K_b \cdot C} = \sqrt{1.76 \times 10^{-5} \times 0.10} = 1.3 \times 10^{-3} \text{ M}$$

A typical weak-base problem

Example: Find the pH of 0.10 M ammonia.

- Fraction of dissociation (α)
- For a monoprotic weak base:

$$\alpha = \frac{[NH_4^+]}{[NH_4^+] + [NH_3]} = \frac{[NH_4^+]}{[NH_4^+] + (C - [NH_4^+])} = \frac{x}{x + (C - x)} = \frac{x}{C}$$

$$\alpha = \frac{x}{C} = \frac{1.3 \times 10^{-3}}{0.10} = 0.013$$

Buffers

- A buffer solution resists changes in pH when acids or bases are added or when dilution occurs.
- A buffer solution generally consists of a mixture of an acid and its conjugate base.

Henderson-Hasselbalch Equation

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad K_b = \frac{[OH^-][HB^+]}{[B]}$$

For a buffer solution containing a weak acid and its conjugate base:

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

For a buffer solution containing a weak base and its conjugate acid,

$$pH = pK_a + \log \frac{[B]}{[HB^+]} \quad \text{or} \quad pOH = pK_b + \log \frac{[HB^+]}{[B]}$$

Henderson-Hasselbalch Equation

- $pH = pK_a \rightarrow [A^-] = [HA]$ $pH = pK_a + \log \frac{[A^-]}{[HA]}$
- For every power of 10 change in the ratio $[A^-]/[HA]$, the pH changes by one unit.
- As the acid increases, the pH goes down.

Table 9-1 Effect of $[A^-]/[HA]$ on pH

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

Effect of adding acid to a buffer

Example 1. Calculate the pH of a buffer prepared by adding 10.00 mL of 0.10 M acetic acid and 20.00 mL of 0.10 M sodium acetate.

ANS : 5.06

Example 2. What is the pH if 10.00 mL of 0.0050 M HCl is added to the above buffer solution?

ANS : 5.03

Buffer Capacity

$$\beta = \frac{dC_b}{dpH} = -\frac{dC_a}{dpH}$$

- Buffer capacity is a maximum when $pH = pK_a$
- Best to choose a buffer system whose pK_a is within ± 1 pH unit of your desired pH

Diprotic Buffers

- For H_2A , we can write two Henderson-Hasselbalch equations:

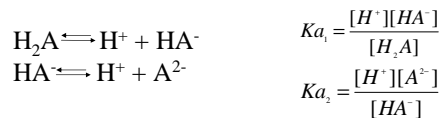
$$pH = pK_1 + \log \frac{[HA^-]}{[H_2A]} \quad pH = pK_2 + \log \frac{[A^{2-}]}{[HA^-]}$$

Ex: What is the pH of a solution prepared by dissolving 1.0 g KHP and 1.20 g Na_2P in 50.0 mL water?

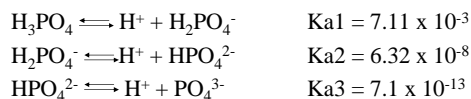
ANS : 5.47

Ch.10 Polyprotic Acid-base Equilibrium

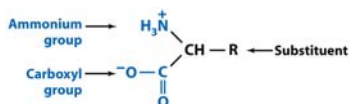
Diprotic acids/Dibasic bases Polyprotic acids/Polybasic bases



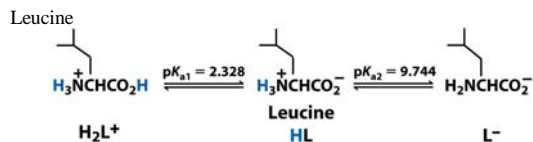
Ka1, Ka2 ...



Amino Acid

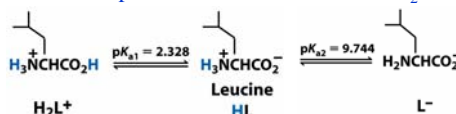


A **zwitterion**: a molecule with both positive and negative charges



H_2L^+ (Acidic form)

What's the pH of a 0.0500 M solution of H_2L^+ ?



Assume that H_2L^+ acts as a monoprotic acid

$$K_{a1} = \frac{[\text{H}^+][\text{HL}]}{[\text{H}_2\text{L}^+]} = \frac{x^2}{C-x}$$

$$x = 1.32 \times 10^{-2} \text{ M}, \text{pH} = 1.88$$

Check our assumption by calculating $[\text{L}^-]$

$$K_{a2} = \frac{[\text{H}^+][\text{L}^-]}{[\text{HL}]} \Rightarrow [\text{L}^-] = \frac{K_{a2}[\text{HL}]}{[\text{H}^+]} = K_{a2} = 1.80 \times 10^{-10} \text{ M}$$

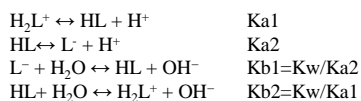
L^- (Basic form)

What's the pH of a 0.0500 M solution of L^- ?

The relations between acid and base equilibrium constants for a diprotic acid/base:

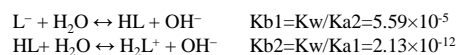
$$K_{a1} K_{b2} = K_w$$

$$K_{a2} K_{b1} = K_w$$



L^- (Basic form)

What's the pH of a 0.0500 M solution of L^- ?



assume that L^- acts as a monobasic species with $K_b = K_{b1}$

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

$$x = 1.64 \times 10^{-3} \text{ M}, [\text{OH}^-] = K_w/x = 6.08 \times 10^{-12} \text{ M}, \text{pH} = 11.22$$

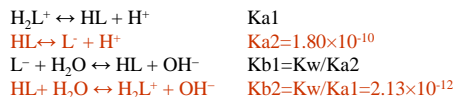
Check our assumption by calculating $[\text{H}_2\text{L}^+]$

$$K_{b2} = \frac{[\text{H}_2\text{L}^+][\text{OH}^-]}{[\text{HL}]} \Rightarrow [\text{H}_2\text{L}^+] = \frac{K_{b2}[\text{HL}]}{[\text{OH}^-]} = K_{b2} = 2.13 \times 10^{-12} \text{ M}$$

HL (Intermediate Form)

What's the pH of a 0.0500 M solution of HL ?

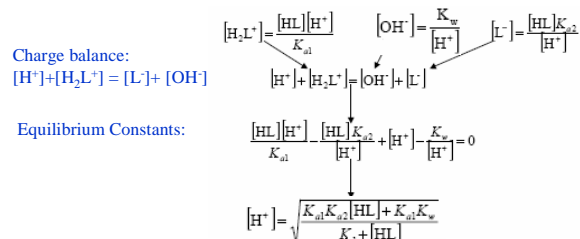
HL is **amphiprotic**, meaning it can both donate and accept a proton



We have to use the systematic treatment to determine pH.

HL (Intermediate Form)

What's the pH of a 0.0500 M solution of HL ?



HL (Intermediate Form)

What's the pH of a 0.0500 M solution of HL ?



$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}[\text{HL}] + K_{a1}K_w}{K_{a1} + [\text{HL}]}} \quad [\text{HL}] = C \quad [\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}C + K_{a1}K_w}{K_{a1} + C}}$$

$$[\text{H}^+] = \sqrt{\frac{(4.69 \times 10^{-3})(1.80 \times 10^{-10})(0.050) + (4.69 \times 10^{-3})(1.0 \times 10^{-14})}{4.69 \times 10^{-3} + 0.050}} = 8.76 \times 10^{-7} \text{ M}$$

pH = 6.06

Check our assumptions:

$$[\text{H}_2\text{L}^+] = \frac{[\text{HL}][\text{H}^+]}{K_{a1}} = \frac{(0.050)(8.67 \times 10^{-7})}{4.69 \times 10^{-3}} = 9.34 \times 10^{-6} \text{ M}$$

$$[\text{L}^-] = \frac{[\text{HL}]K_{a2}}{[\text{H}^+]} = \frac{(1.79 \times 10^{-10})(0.050)}{8.76 \times 10^{-7}} = 1.02 \times 10^{-3} \text{ M}$$

HL (Intermediate Form)

What's the pH of a 0.0500 M solution of HL ?



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

If $K_{a2}C \gg K_w$, then the 2nd term in the numerator can be dropped and if $K_{a1} \ll C$, the 1st term in the denominator can also be neglected:

$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}C}{C}} = \sqrt{K_{a1}K_{a2}}$$

pH = 1/2 (pK₁ + pK₂)

ANS: 6.04

For diprotic weak acid

For $\text{H}_2\text{A} = \text{H}^+ + \text{HA}^-$ and $\text{HA}^- = \text{H}^+ + \text{A}^{2-}$

$$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}_2\text{A}]}{[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

$$\alpha_{\text{HA}^-} = \frac{[\text{HA}^-]}{[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]} = \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

$$\alpha_{\text{A}^{2-}} = \frac{[\text{A}^{2-}]}{[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

- Isoionic Point: The pH of pure, neutral polyprotic acid (the natural zwitterion)
- Isoelectric Point: pH when average charge is zero (amino acids)

Type	Keq	Formula	Example
Strong acids	$K_{eq}=\infty$	$[H_3O^+] = C_a$	HCl, HNO ₃ , HClO ₄
Strong Bases	$K_{eq}=\infty$	$[OH^-]=C_b$	NaOH, KOH
Weak Acids	$K_a = \frac{[H_3O^+][A^-]}{[HA]}$	$[H_3O^+] = \sqrt{CK_a}$	HAc, HCOOH, HClO
Weak Bases	$K_b = \frac{[OH^-][B]}{[BOH]}$	$[OH^-] = \sqrt{CK_b}$	NH ₄ OH
Buffer	$K_a = \frac{[H_3O^+][A^-]}{[HA]}$	$[H_3O^+] = K_a \frac{C_{HA}}{C_{NaA}}$	HAc-NaAc, NH ₄ ⁺ - NH ₃ H ₂ O
Amphiprotic salt(NaHA)	$K_{a1} = \frac{[H_3O^+][HA]}{H_2A}$ $K_{a2} = \frac{[H_3O^+][A^-]}{[HA]}$	$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$	NaHCO ₃ , NaHPO ₄ , NaH ₂ PO ₄ , amino acid
Polyprotic acids		Treated as monoprotic weak acids	