Chapter 8: Monoprotic Acid-Base Equilibria

Chapter 6: **Strong acids (SA)** and **strong bases (SB)** ionize completely in water (very large K)

- $[H^+]$ ions produced equals [S.A.]

Example: What is the pH of 0.050 M HCl solution?

- HCl is S.A. so $[HCl] = [H^+]$. Thus, $pH = -\log [H^+] = -\log (0.050)$; $pH = 1.30$
- Similarly, $[OH^-]$ in solution will be equal to [S.B.] x number OH^- per formula unit

Challenge: What is the pH of 1.0×10^{-8} M HCl? What is the pH of 1.0×10^{-8} M NaOH?

- pH = 8 for a 10^{-8} M acid???
- pH = 6 for a 10^{-8} M base???

We are adding an acid to water (at a pH of 7) and then saying that the solution becomes more basic?

- We neglected the dissociation of water!

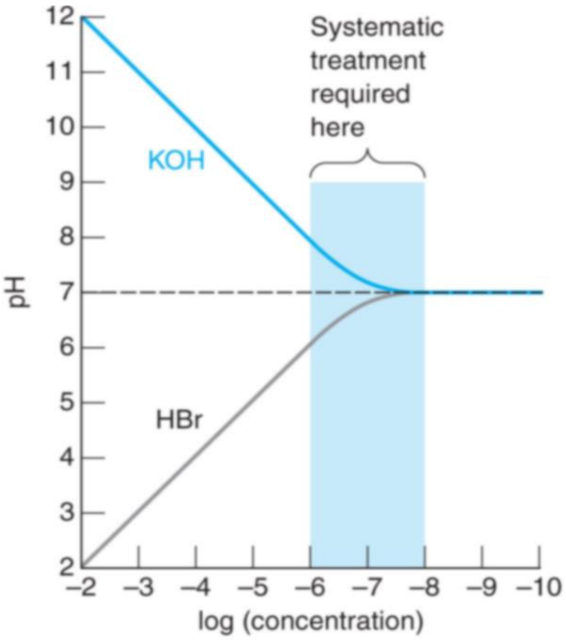

FIGURE 8-1 Calculated pH as a function of concentration of strong acid or strong base in water.

Harris, *Quantitative Chemical Analysis,* 8e

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Summary: **pH calculations of strong acids and strong bases**

1. At relatively high [S.A] or [S.B.], i.e. $\geq 10^{-6}$ M, pH is calculated from [S.A.] or [S.B.]
2. In very dilute [S.A] or [S.B.], i.e. $\leq 10^{-8}$ M, dissociation of water is more important, so the pH is 7.

Question: How do we know if a given acid is strong or weak?

- Know the 6 S.A. and six S.B. by heart

Weak Acids and Weak Bases

- Weak acids (HA) and weak bases (B) *do not dissociate completely*.
- An *equilibrium exists* between reactants and products
- The *equilibrium lies to the left* (K_a for a weak acid is < 1) => mostly HA or B in solution

The ***dissociation (ionization) of a weak acid*, HA**, in water:

$$HA_{(aq)} + H_2O_{(l)} \overset{K_a}{\rightleftharpoons} A^-_{(aq)} + H_3O^+_{(aq)}$$

Weak acid
(H^+ donor)

Conj. base

K_a, the acid dissociation constant, can be written as:

$$\boxed{K_a = \frac{[A^-][H_3O^+]}{[HA]}}$$

Similarly, the ***hydrolysis (ionization) of a weak base*, B**, in water can be written as:

$$B_{(aq)} + H_2O_{(l)} \overset{K_b}{\rightleftharpoons} BH^+_{(aq)} + OH^-_{(aq)}$$

Weak base
(H^+ acceptor)

Conjugate acid
(protonated)

K_b, the **base hydrolysis constant**, can be written as:

$$\boxed{K_b = \frac{[BH^+][OH^-]}{[B]}}$$

Understanding Appendix G: K_a of weak acids

(1) *Acids* are written in their *fully protonated form* (column 2)

(2) *Acidic H's* are indicated in bold

Example: There is only one acidic H in acetic acid, hence it is written as:

Acetic acid (Ethanoic acid) $CH_3CO_2\mathbf{H}$ $pK_a = 4.756$ $K_a = 1.75 \times 10^{-5}$

These 3 are non-acidic H

Acidic H

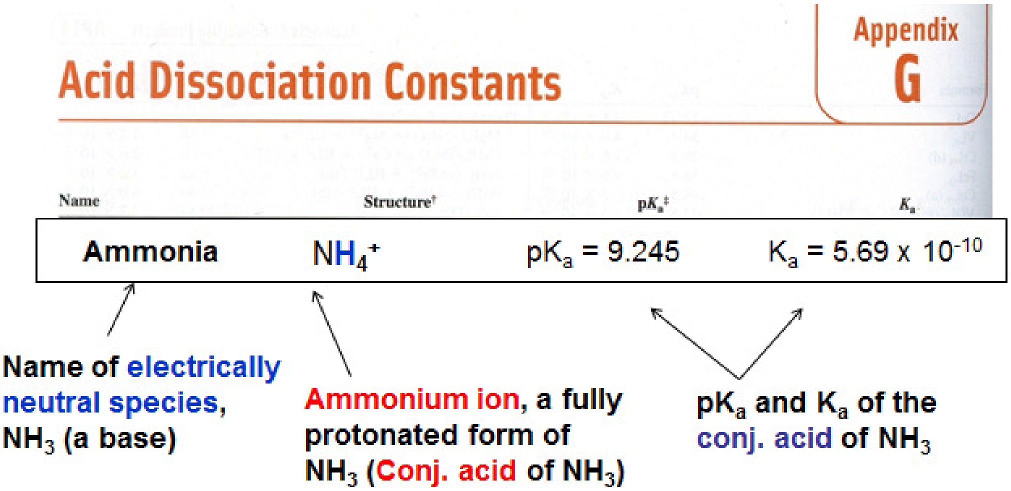
***Remember:* Appendix G is a table of weak acids, not bases!**

(3) The *chemical names* (alphabetized; Column 1) pertain to the *electrically neutral species*, and

(4) *Bases* are *__derived__* from their *conjugate acids; Their K_b* is derived from K_a.

Example: What is the pH of 0.050 M ammonia?

- At this point, you should know that ammonia is a base
- Using Appendix G, you find ammonia on the first page with the following entry:



Acid Dissociation Constants

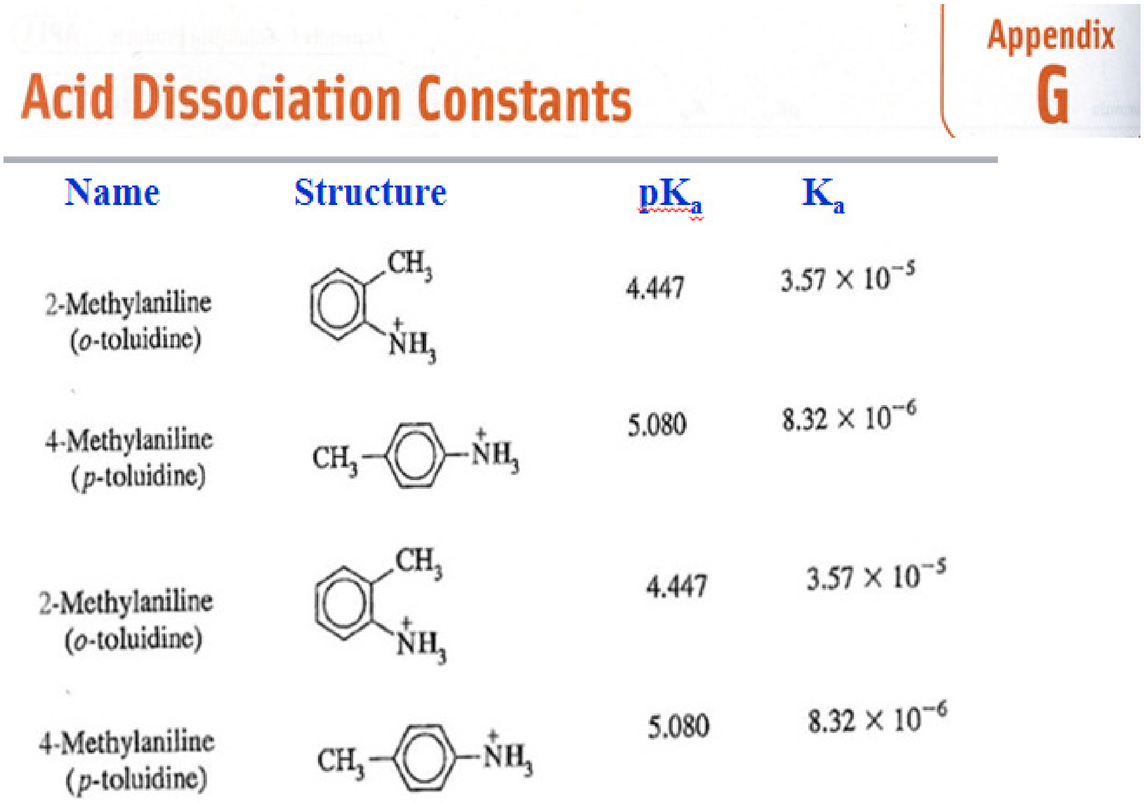
Appendix G

Name	Structure†	pK_a‡	K_a
Ammonia	NH_4^+	$pK_a = 9.245$	$K_a = 5.69 \times 10^{-10}$

Name of electrically neutral species, NH_3 (a base)

Ammonium ion, a fully protonated form of NH_3 (Conj. acid of NH_3)

pK_a and K_a of the conj. acid of NH_3



Appendix G

Acid Dissociation Constants

Name	Structure	pKa	K_a
2-Methylaniline (*o*-toluidine)		4.447	3.57×10^{-5}
4-Methylaniline (*p*-toluidine)		5.080	8.32×10^{-6}
2-Methylaniline (*o*-toluidine)		4.447	3.57×10^{-5}
4-Methylaniline (*p*-toluidine)		5.080	8.32×10^{-6}

Exercise: Using part of App. G above:
(a) draw the structure of 4-methylaniline.
(b) Is alanine an acid or a base?
(c) Draw the dissociation of 4-methylaniline and write the corresponding K (K_a if acid or K_b if base) expression.

Q. If we are dealing with a base, how do find its K_b? (App. G only gives K_a)

Consider then two reactions: The *dissociation of a weak acid, HA*, and *hydrolysis of its conjugate base, A-*

$$\cancel{HA} + H_2O \overset{K_a}{\rightleftharpoons} \cancel{A^-} + H_3O^+$$

$$\cancel{A^-} + H_2O \overset{K_{b\,(A-)}}{\rightleftharpoons} \cancel{HA} + OH^-$$

Sum of 2 equations: $$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

Since $H_3O^+ = H_2O + H^+$, the equation above reduces to $H_2O \rightleftharpoons H^+ + OH^-$ What is the equilibrium constant for this reaction?

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^- \quad \textit{or} \quad 2H_2O \overset{K_w}{\rightleftharpoons} H_3O^+ + OH^-$$

Since we added 2 equations, K_w is also equal to:

$$K_w = K_a \times K_b$$

$$K_w = \frac{[\cancel{A^-}]\,[H_3O^+]}{[\cancel{HA}]} \times \frac{[\cancel{HA}]\,[OH^-]}{[\cancel{A^-}]}$$

$$K_w = [H_3O^+] \times [OH^-] = 1.00 \times 10^{-14} \text{ at } 25\ ^0\text{C}$$

Thus, $$\boxed{\begin{aligned} K_w &= K_a \times K_b \\ 1.00 \times 10^{-14} &= K_a \times K_b \end{aligned}}$$ at 25 ^{0}C

Types of Acids and Bases

Acids and bases can be classified as electrically neutral or charges species
(1) **Electrically neutral** species – *Examples:*
Acids: All 6 strong acids, $HC_2H_3O_2$ (acetic), H_2CO_3 (carbonic)
Bases: All 6 strong bases, NH_3, CH_3NH_2 (methyl amine)

(2) **Electrically charged** species – *Examples:*
Acids: $H_2PO_4^-$, HSO_4^-, HCO_3^- (from polyprotic acids; each has at least *1 acidic H left*); NH_4^+ (conj. acid of NH_3)
Bases: $C_2H_3O_2^-$, PO_4^{-3}, SO_4^{-2}, CO_3^{-2} $H_2PO_4^-$, HSO_4^-, HCO_3^- (conj. bases of acids)

Some species can act as an acid or a base. These substances are called **amphoteric**.
Example: $H_2PO_4^-$, HSO_4^-, HCO_3^- are all amphoteric

Exercise: Write the equilibria involved when HCO_3^- acts as (a) an acid and (b) a base.

Acid dissociation:

$$\underset{\textit{Acid}}{HCO_3^-} + H_2O \overset{K_a}{\Longleftrightarrow} \underset{\textit{Conj. base}}{CO_3^{-2}} + H_3O^+$$

Base hydrolysis:

$$\underset{\textit{Base}}{HCO_3^-} + H_2O \overset{K_b}{\Longleftrightarrow} \underset{\textit{Conj. acid}}{H_2CO_3} + OH^-$$

Weak Acid Equilibria and *pH Calculations*

Example: Calculate $[H_3O^+]$ and pH of 0.10 M aqueous solution of hypochlorous acid ($K_a = 3.5 \times 10^{-8}$)?

- Note that K_a is a very small number (i.e. HOCl is a very weak acid). To begin the problem, write down the equilibrium involved:

$$HOCl + H_2O \overset{K_a}{\Longleftrightarrow} H_3O^+ + OCl^-$$

- Since HOCl is a weak acid, only a fraction of the 0.10 M solution will dissociate to form *x* M of OCl^-, i.e. we can set up our ICE table:

$$\mathbf{HOCl + H_2O \overset{K_a}{\rightleftharpoons} H_3O^+ + OCl^-}$$

I:	0.10	0	0
C:	$-x$	$+x$	$+x$
E:	$(0.10 - x)$	x	x

❖ The K_a expression is:

$$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]} = \frac{(x)(x)}{(0.10 - x)}$$

$$3.5 \times 10^{-8} = \frac{x^2}{(0.10 - x)}$$

Assuming $x << 0.10$ (since K_a is very small) and solving for x, we get:

$x = 5.9_2 \times 10^{-5}$ M Q. What does x represent?

$x = \mathbf{[H_3O^+] = 5.9_2 \times 10^{-5} M} = [OCl^-]$

Since $5.9 \times 10^{-5} << 0.10$ our assumption is valid. We calculate pH as:

$pH = -\log [H_3O^+] = -\log (5.9_2 \times 10^{-5})$

$$\boxed{\mathbf{pH = 4.23}}$$

- If HOCl dissociates by an *x* amount, its actual concentration is not 0.10 M, right?
- The given concentration of HOCl, 0.10 M, is called its formal concentration.

Formal concentration, F (or **formality**), refers to the *total number of moles* of a compound dissolved *per liter of solution*, regardless of the number of species it forms upon dissociation.

Formality, F

- Accounts for all forms of a species

  Ex. Forms of H_2CO_3 in solution = H_2CO_3, HCO_3^- and CO_3^{2-}

- Thus, $F_{H2CO3} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

Thus, **for a weak monoprotic acid, HA**, at equilibrium:

$$\begin{array}{lccccccc} & \mathrm{HA} & + & \mathrm{H_2O} & \overset{K_a}{\rightleftarrows} & \mathrm{H_3O^+} & + & \mathrm{A^-} \\ \mathrm{E:} & (F_{HA} - x) & & & & x & & x \end{array}$$

$$\boxed{K_a = \frac{x^2}{(F_{HA} - x)}} \quad \text{and} \quad \boxed{\mathrm{pH} = -\log x}$$

Exercise: Calculate the pH of a 1.50 x 10^{-2} M formic acid, HCO_2H. ($pK_a = 3.745$).
HINT: You must first determine K_a from pK_a. *How?*

Answer: pH = 2.808

Weak Acid Equilibria: *Fraction of Dissociation*

The ***fraction of dissociation***, **α** *(Greek: alpha)*, of a weak acid HA refers to the fraction of HA in the dissociated form A^-, i.e.

$$\alpha_{HA} = \frac{[A^-]}{\underbrace{[HA] + [A^-]}_{= F_{HA}}} \qquad \text{Thus,} \quad \boxed{\alpha_{HA} = \frac{x}{F_{HA}}}$$

Exercise: You calculated the pH of a 1.50 x 10^{-2} M formic acid, HCO_2H, in the previous exercise. What fraction of formic acid in this solution has dissociated?

Answer: α_{HA} = 0.10 or 10 % dissociated

Fraction of dissociation:

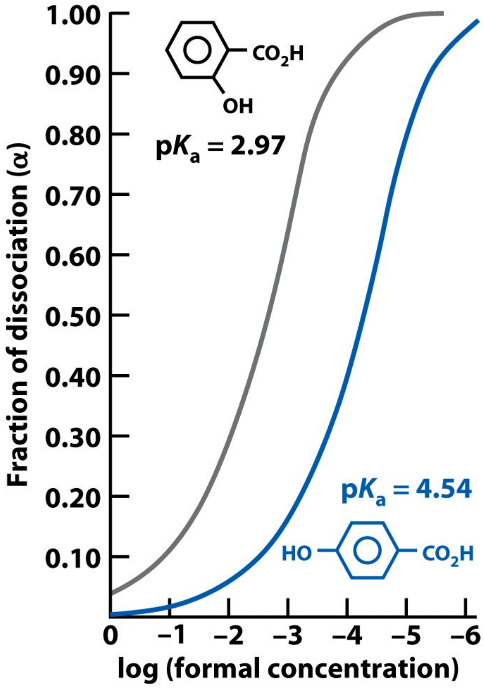


Figure 9-2
Quantitative Chemical Analysis, Seventh Edition

Weak Base Equilibria and *pH Calculations*

For a monobasic species, B, the ***hydrolysis equation*** is:

$$\mathbf{B} \;+\; H_2O \;\overset{\mathbf{K_b}}{\Longleftrightarrow}\; \mathbf{BH^+} \;+\; OH^-$$

Weak base **Conj. acid**
(H$^+$ acceptor)

I:	F_B	0	0
C:	$-y$	$+y$	$+y$
E:	$(F_B - y)$	y	y

K_b and pH can be expressed as:

$$\boxed{\mathbf{K_b = \frac{y^2}{(F_B - y)}}}$$

and $pH = 14.00 - pOH = 14.00 - (-\log\,[OH^-])$

or $\boxed{\mathbf{pH = 14.00 - \log\,(y)}}$

Exercise: Calculate the pH and fraction of association of 1.5×10^{-1} M ethylamine.
HINT: You must first recognize that ethylamine is a base.
[NOTE: Amines are organic bases. Their names end in –*ine*]

From Appendix G

Name	Structure	Ionic strength (μ) = 0 pK_a	 K_a
Ethylamine	$CH_3CH_2NH_3^+$	10.673	2.12×10^{-11}

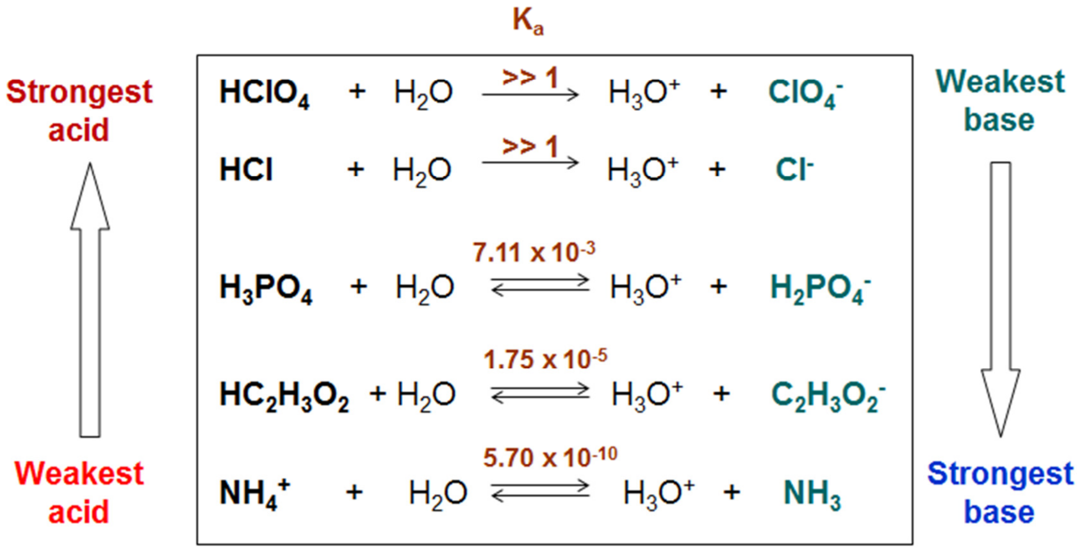
$$RNH_2 + H_2O \overset{K_b}{\Leftrightarrow} RNH_3^+ + OH^-$$

$$\begin{array}{ccc} 0.15 - y & y & y \end{array}$$

$$K_b = \frac{y^2}{F - y} \qquad \frac{K_w}{K_a} = \frac{y^2}{0.15 - y}$$

Relative strengths of acids/bases

- *The stronger the acid the weaker its conjugate base; the stronger the base the weaker its conjugate acid. How?*
- *If K_a is large in the forward direction, the reverse reaction will have a low K*



$$HClO_4 + H_2O \xrightarrow{>> 1} H_3O^+ + ClO_4^-$$

$$HCl + H_2O \xrightarrow{>> 1} H_3O^+ + Cl^-$$

$$H_3PO_4 + H_2O \overset{7.11 \times 10^{-3}}{\rightleftharpoons} H_3O^+ + H_2PO_4^-$$

$$HC_2H_3O_2 + H_2O \overset{1.75 \times 10^{-5}}{\rightleftharpoons} H_3O^+ + C_2H_3O_2^-$$

$$NH_4^+ + H_2O \overset{5.70 \times 10^{-10}}{\rightleftharpoons} H_3O^+ + NH_3$$

Q. Which is a stronger base, NH_3 or $H_2PO_4^-$? Which is a stronger acid, NH_4^+ or $H_2PO_4^-$?

Answer: **NH_3 is a stronger base; $H_2PO_4^-$ is a stronger acid than NH_4^+.**

SALTS

The term ***salt*** refers to the ionic compound produced from acid-base reaction.

Q. What is the pH of an aqueous solution of a salt?

- The anion or the cation of a salt, or both, can react with water (= hydrolysis)
- The **pH of the salt** depends on the strengths of the original acids and bases

Acid	Base	Salt pH	Example of salt
Strong	Strong	7 (Neutral)	NaCl, KNO_3, $CaBr_2$
Weak	Strong	> 7 (Basic)	Na_2CO_3, K_3PO_4
Strong	Weak	< 7 (Acidic)	NH_4Cl, CH_3NH_3Br
Weak	Weak	Depends on which is stronger	NH_4ClO, $(NH_4)_2CO_3$

Exercise: Show that Na_2CO_3 hydrolyzes in water to form a basic solution.

Solution: First, recognize that Na_2CO_3 in water produces **Na^+** and **CO_3^{2-}**

From S.B; does not react with water = *spectator ion*, **S.I.**

Will hydrolyze; acts as **W.B.**

Hydrolysis of CO_3^{2-}

$$CO_3^{2-} + H_2O \longleftrightarrow HCO_3^- + \underbrace{OH^-}_{\text{Basic!}}$$

Exercise: Show that ammonium chloride hydrolyzes in water to form an acidic solution.

$$NH_4Cl_{(aq)} \longrightarrow NH_4^+ \text{ and } Cl^-$$

NH_4^+: **W.A.** *Hydrolyzes* to form H^+ = **acidic!**

Cl^-: **S.I.**

$$NH_4^+ \quad + \quad H_2O \longleftrightarrow NH_3 + \mathbf{H_3O^+}$$

Acidic!

Practice: *Problem 8-20.* Find the pH of 0.050 M NaCN. *What constant do you need?* K_a? K_b? *What kind of species (acidic, basic or neutral) are produced in solution?*

BUFFERS

A ***buffer*** solution resists drastic changes in pH when a small amount of acid or base is added, or when diluted.

Composition of a buffer:

- A buffer consists of a weak acid and its conjugate base (more common), or:
- a weak base and its conjugate acid

Q. How does a buffer resist changes in pH?

- *Effect of adding a small amount of base* (OH^-) to a buffer:

Reacts with HA, forming A-; [HA] decreases a little bit, [A-] increases a little bit

- *Effect of adding a small amount of acid* (H_3O^+) to a buffer:

Reacts with A^-, forming HA; [A^-] decreases a little bit, [HA] increases a little bit

Some common buffers

Buffer Name	**Composition**	**Useful pH (Approx.)**
Acetate	$HC_2H_3O_2/NaC_2H_3O_2$	5
Carbonate	$H_2CO_3/NaHCO_3$	7
Phosphate	NaH_2PO_4/Na_2HPO_4	7
Ammonia	NH_4Cl/NH_3	10

Importance of Buffers

The Carbonic-Acid-Bicarbonate Buffer in the Blood

By far the most important buffer for maintaining acid-base balance in the blood is the carbonic-acid-bicarbonate buffer. The simultaneous equilibrium reactions of interest are:

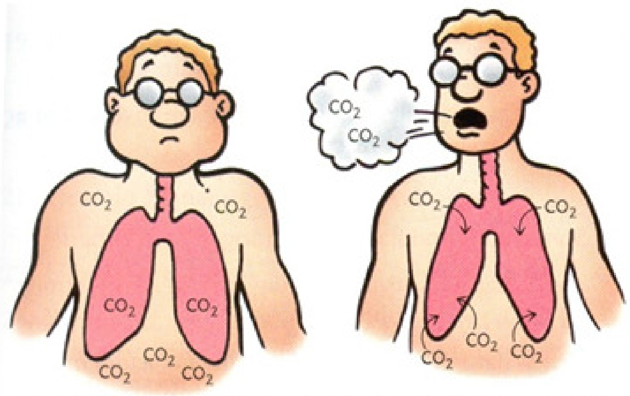
$$H^+ (aq) + HCO_3^- (aq) \rightleftharpoons H_2CO_3 (aq) \rightleftharpoons H_2O (l) + CO_2 (g)$$

During ***acidosis***, the pH of blood drops below its normal level of ~ 7.4. What can be done to bring the pH back to 7.4?

- Induce <u>hyperventilation</u> (Expel CO_2 at a faster rate)
- Equilibrium shifts to the right to use up H^+, producing more CO_2)

During ***alkalosis***, the pH of blood rises. What can be done to bring the pH back to 7.4?

- <u>Hypoventilate</u> **(Keep CO_2 in your lungs by holding your breath)**
- Equilibrium shifts to the left to replenish H^+)



Hypoventillation and **hyperventillation**

Image available at J. Suchocki, "Conceptual Chemistry: Understanding Our World Of Atoms and Molecules." 3rd Edition, Benjamin Cummings, Wesley: San Francisco, 2007.

Calculating pH of buffers: *The Henderson-Hasselbalch Equation*

- Relates the pH of a buffer solution to the concentration of buffer components
- Simply a rearranged version of the K_a expression for the acid component

Derivation:

$$\mathbf{HA_{(aq)} + H_2O_{(l)} \overset{K_a}{\rightleftharpoons} H_3O^+_{(aq)} + A^-_{(aq)}}$$

$$\mathbf{K_a = \frac{[A^-]\,[H_3O^+]}{[HA]}}$$

Taking the logarithm of both sides of the equation we get:

$$\mathbf{\log K_a = \log [H_3O^+] + \log ([A^-]/[HA])}$$

$$\mathbf{-\log [H_3O^+] = -\log K_a + \log ([A^-]/[HA])}$$

Henderson-Hasselbalch (H-H) equation

$$\mathbf{pH = \underbrace{pK_a}_{\text{Applies to HA}} + \log \frac{[A\text{-}]}{[HA]}}$$

Conj. base

Weak acid

Similarly, for BH^+/B buffer systems:

$$pH = \underbrace{pK_a}_{\text{For the conjugate acid, BH}^+} + \log\frac{[B]}{[BH^+]}$$

Properties of the H-H equation:

1. When **[A-] = [HA]**

$$\mathbf{pH = pK_a}$$

2. For *every power-of-10 change in the ratio $[A^-]/[HA]$*, the **pH changes** by **1 unit** (See Table 8-1, p. 173)

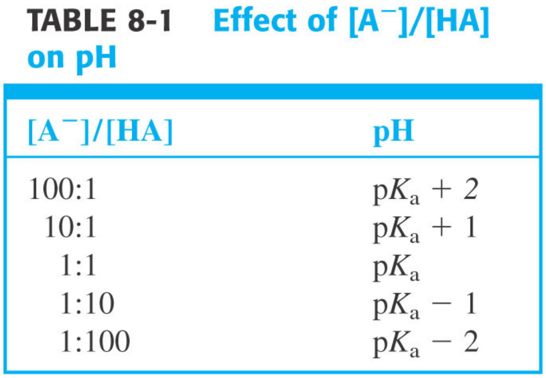


TABLE 8-1 Effect of $[A^-]/[HA]$ on pH

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

Harris, *Quantitative Chemical Analysis*, 8e

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Understanding Table 8-2: Structures and pKa of common buffers

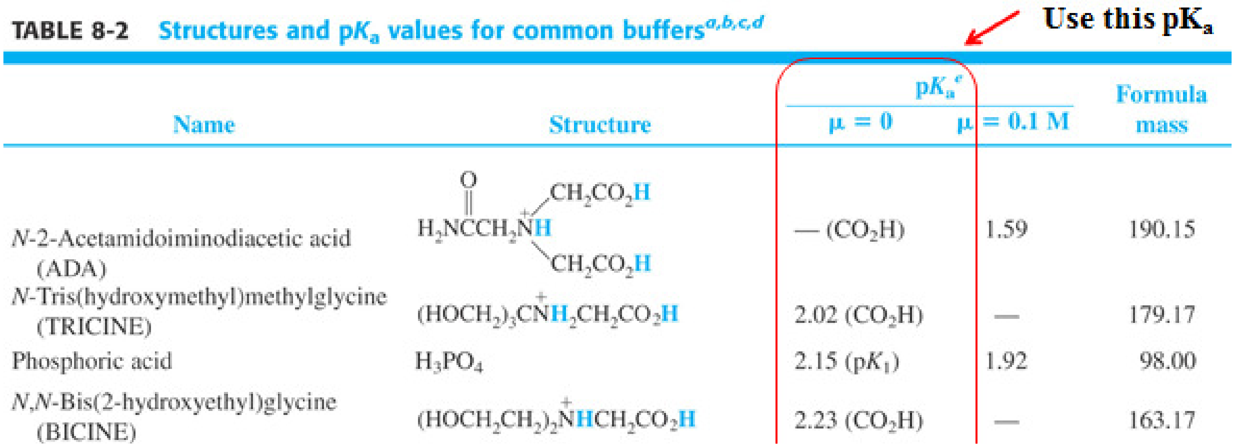

TABLE 8-2 Structures and pK_a values for common buffers[a,b,c,d]

Use this pK_a

Name	Structure	pK_a[e] $\mu = 0$	pK_a[e] $\mu = 0.1$ M	Formula mass
N-2-Acetamidoiminodiacetic acid (ADA)	$H_2N\overset{O}{\overset{\Vert}{C}}CH_2\overset{+}{N}H(CH_2CO_2H)_2$	— (CO_2H)	1.59	190.15
N-Tris(hydroxymethyl)methylglycine (TRICINE)	$(HOCH_2)_3C\overset{+}{N}H_2CH_2CO_2H$	2.02 (CO_2H)	—	179.17
Phosphoric acid	H_3PO_4	2.15 (pK_1)	1.92	98.00
N,N-Bis(2-hydroxyethyl)glycine (BICINE)	$(HOCH_2CH_2)_2\overset{+}{N}HCH_2CO_2H$	2.23 (CO_2H)	—	163.17

Example 1: Sodium hypochlorite (NaOCl), the active ingredient of almost all bleaches, was dissolved in a solution buffered to pH 6.80. Find the ratio [OCl]/[HOCl] in this solution.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[A^-]}{[HA]}$$

Note: From App. G, $\mathrm{p}K_a$ of HOCl = 7.53

$$6.80 = 7.53 + \log\frac{[A^-]}{[HA]}$$

$$6.80 - 7.53 = \log\frac{[A^-]}{[HA]}$$

$$-0.73 = \log\frac{[A^-]}{[HA]}$$

$$10^{-0.73} = 10^{\log\frac{[A^-]}{[HA]}}$$

Note: $10^{\log x} = x$

$$0.186 = \frac{[A^-]}{[HA]}$$

$$\boxed{\text{Thus, } \frac{[OCl^-]}{[HOCl]} = 0.186}$$

Example 2: Find the pH of a 750-mL aqueous solution prepared by dissolving 15.50 g TRIS (MM 121.135) plus 5.23 g TRIS hydrochloride (MM 157.596).

Means the protonated, or **HA**, form. Thus, TRIS = A-

$$[A^-] = \frac{(15.50\,\mathrm{g})/(121.135\,\mathrm{g\,mol^{-1}})}{0.750\,\mathrm{L}} = \frac{0.1280\,\mathrm{mol}}{0.750\,\mathrm{L}}$$

$$= 0.1706\,\mathrm{M}$$

$$[HA] = \frac{(5.23\,\mathrm{g})/(157.596\,\mathrm{g\,mol^{-1}})}{0.750\,\mathrm{L}} = \frac{0.03319\,\mathrm{mol}}{0.750\,\mathrm{L}}$$

$$= 0.04425\,\mathrm{M}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[A^-]}{[HA]} \qquad \mathrm{pH} = 8.07 + \log\frac{[0.1706]}{[0.04425]}; \quad \boxed{\mathrm{pH} = 8.66}$$

Note: From Table 8-2, $\mathrm{p}K_a$ of TRIS.HCl = 8.07.

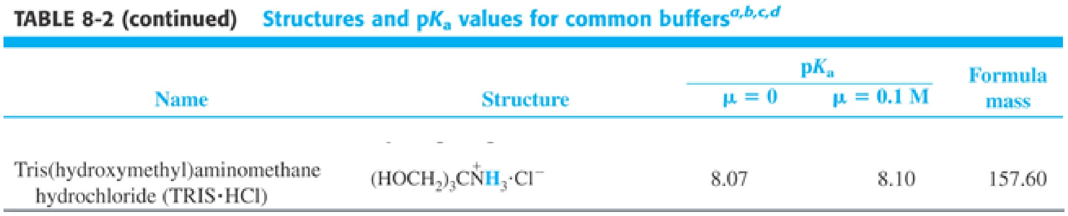

TABLE 8-2 (continued) Structures and $\mathrm{p}K_a$ values for common buffers[a,b,c,d]

Name	Structure	$\mathrm{p}K_a$ $\mu = 0$	$\mathrm{p}K_a$ $\mu = 0.1$ M	Formula mass
Tris(hydroxymethyl)aminomethane hydrochloride (TRIS·HCl)	$(HOCH_2)_3C\overset{+}{N}H_3 \cdot Cl^-$	8.07	8.10	157.60

The pH of a buffer is nearly independent of volume

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{(\text{moles of }A^-/\cancel{\text{L of solution}})}{(\text{moles of HA}/\cancel{\text{L of solution}})}$$

Note: *L of solution* cancel out

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{\text{moles of }A^-}{\text{moles of HA}}$$

Effect of Adding and Acid or a Base to a Buffer

Example 1: If we add 10.50 mL of 1.00 M HCl to the solution in the previous example, what will be the new pH?

Hint: Which buffer component will react with HCl? This is the time to set up an ICF table.

$$\text{mol added H}^+ = (0.01050\ \text{L})(1.00\,\text{mol}/\text{L} = \underbrace{0.0105\,\text{mol H}^+}_{\text{Will react w/ }A^-}$$

	$HA_{(aq)}$ ⇌	$H^+_{(aq)}$ +	$A^-_{(aq)}$
Initial **mol** (**I**):	0.03319	0.0105	0.1280
Change (**C**):	+0.0105	-0.0105	- 0.0105
Final (**F**):	+0.04369	0	0.1175

$$\text{pH} = 8.07 + \log\frac{[0.1175]}{[0.04369]};\ \boxed{\text{pH} = 8.50}$$

vs. original **pH = 8.66**

- ➢ pH drops a little bit since [HA] increases while the numerator, [A-], decreases

Example 2: If we add 5.00 mL of 1.00 M NaOH to the original TRIS buffer solution in Example 2 above, what will be the new pH?

$$\text{mol added OH}^- = (0.00500\ \text{L})(1.00\,\text{mol}/\text{L} = \underbrace{0.00500\,\text{mol OH}^-}_{\text{Will react w/ HA}}$$

$$\text{pH} = 8.07 + \log\frac{[0.133]}{[0.02819]};\quad \textbf{pH = 8.74}$$

vs. original pH = 8.66

- ➢ Added base increases the buffer's pH a little bit.

NOTE: If you know the desired pH of solution and the pK_a of HA, you should be able to determine how much 0.100 M HCl or 0.100 M NaOH is needed to adjust the pH of a buffer.

8-41. Calculate how many milliliters of 0.626 M KOH should be added to 5.00 g of MOBS (Table 8-2) to give a pH of 7.40.

Preparing Buffers in Real Life

In real life, we don't really mix *x* g of NaA with *y* g of HA to prepare a buffer.
Remember that a buffer has two components:

- a weak acid (HA) and its salt (NaA), or
- a weak base (B) and its salt (BHCl)

Preparing a buffer**:**
1. To prepare a buffer, start with one component and dissolve it in water.
2. Then add either HCl or NaOH to form the conjugate species until the desired pH is reached.

> *Example:* You wish to prepare 1.00 L of buffer containing TRIS at a pH of 7.60. You have available solid TRIS hydrochloride and 1 M NaOH. How would you do it?

Buffer Capacity

Buffer capacity, β, is a measure of how well a solution resists changes in pH when a strong acid or a strong base is added.
Mathematical definition of buffer capacity:

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

where C_a and C_b are the number of moles of strong acid and strong base per liter needed to produce a unit change in pH.

- The greater the buffer capacity, the more resistant the solution is to pH change, the better the buffer.

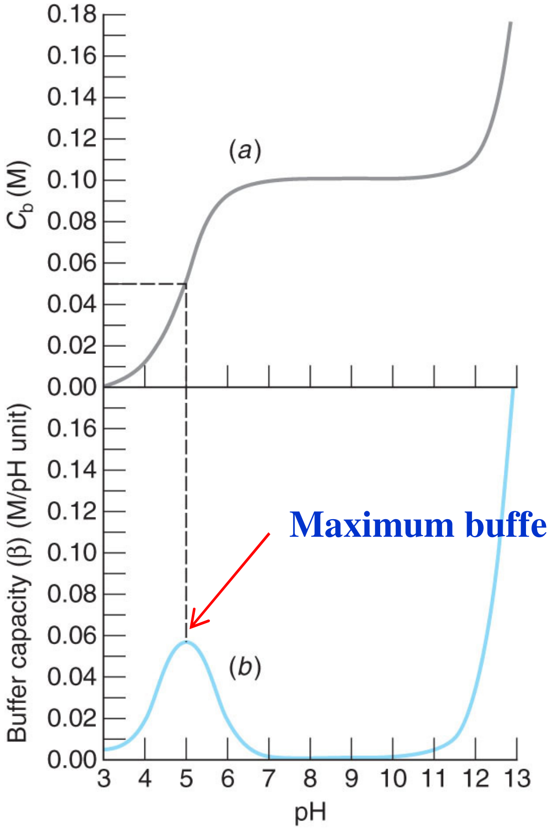

FIGURE 8-4 (*a*) C_b versus pH for a solutic containing 0.100 F HA with pK_a = 5.00. (*b*) Buffer capacity versus pH for the same system reaches a maximum when pH = pK_a. The lower curve is the derivative of the upper curve.

Harris, *Quantitative Chemical Analysis*, 8e

Maximum buffer capacity when **[HA] = [A$^-$]**

Q. What is the pH of a buffer equal to when [HA] = [A$^-$]?

$$\mathrm{pH} = \mathrm{p}K_a + \log \cancel{\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}}$$

$$\boxed{\mathbf{pH = pK_a}}$$

Maximum buffer capacity

- Thus, a buffer works best (max. buffer capacity) when pH = pK_a
- When choosing a buffer, *select one whose pK_a is as close as possible to the desired pH*

Useful pH range of a buffer: **pH = pK_a ± 1**

Exercise 1: Using Table 8-2, suggest the best buffer for each of the following pHs: (a) 4.00, (b) 5.50, (c) 7.30 and (d) 12.00.