CHEMISTRY

Chapter 14 ACID-BASE EQUILIBRIA

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HW problems: 3, 5, 9, 17, 19, 25, 33, 53, 57, 69, 77, 79, 91, 101

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COLLEGE

IMPORTANT INDUSTRIAL PRODUCTS

- 36,000,000 metric tons of sulfuric acid produced annually in the USA
- 8,000,000 metric tons of ammonia
- 10,000,000 metric tons of phosphoric acid
- Nitric acid is a $1billion industry (USA/annually)

CH. 14 OUTLINE

14.1 Brønsted-Lowry Acids and Bases

14.2 pH and pOH

14.3 Relative Strengths of Acids and Bases

14.4 Hydrolysis of Salt Solutions

14.5 Polyprotic Acids

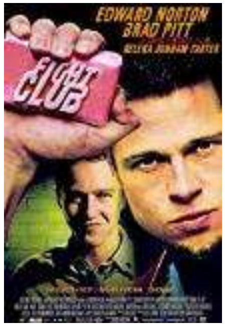
14.6 Buffers

14.7 Acid-Base Titrations

ACIDS AND BASES: QUALITATIVE

- Acids (review)
  - Have a sour taste
    - Vinegar owes its taste to acetic acid
    - Citrus fruits contain citric acid
  - React with certain metals to produce hydrogen gas
  - React with carbonates and bicarbonates to produce carbon dioxide gas

- Bases
  - Have a bitter taste
  - Feel slippery
    - Many soaps contain bases
  - https://www.youtube.com/watch?v=zvtUrjfnSnA



ACID/BASE DEFINITIONS

- Three theories that help us to understand the chemistry of acids and bases
  - Arrhenius theory
  - Brønsted-Lowry theory
  - Lewis theory- especially important if you're taking more chemistry

- An Arrhenius acid is a substance that produces H^+ (or more accurately, the hydronium ion (H_3O^+)) in water

- An Arrhenius base is a substance that produces hydroxide ion (OH^-) in water

ARRHENIUS FAIL

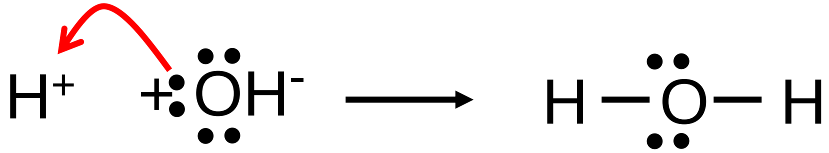
- Where does NH_3 fit?
- When it dissolves in water, there are OH^- ions present, and it has basic properties, but it does not have OH^- ions in the formula
- The next acid-base theory gives us a broader view of acids and bases

ACID/BASE DEFINITIONS (CONT'D)

- A Brønsted acid is a proton donor
- A Brønsted base is a proton acceptor

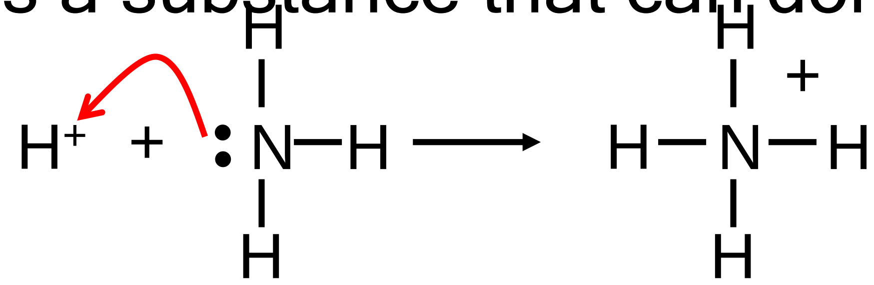
$$\underset{\text{acid}}{HA} + \underset{\text{base}}{B} \rightleftharpoons A^- + HB^+$$

- Can be a neutral molecule or ion
- A Lewis acid is a substance that can accept a pair of electrons



acid base

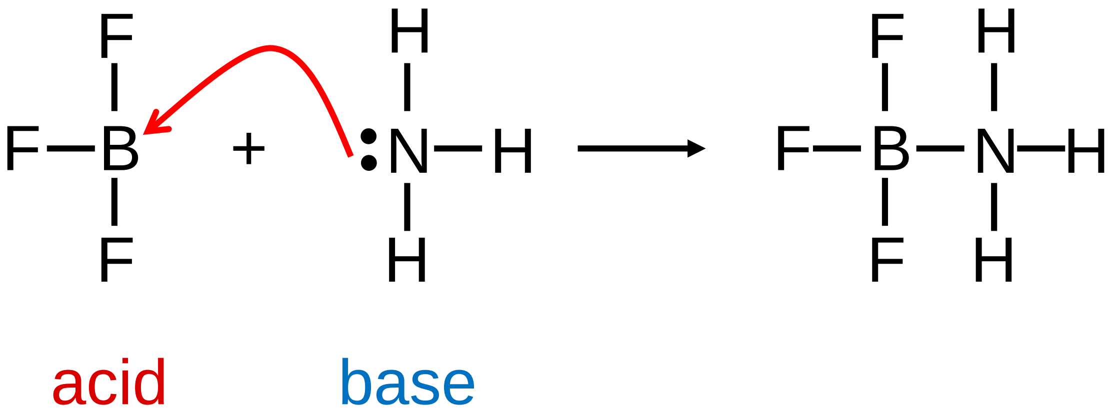
- A Lewis base is a substance that can donate a pair of electrons



acid base

LEWIS ACIDS AND BASES

- No protons required to be donated or accepted!



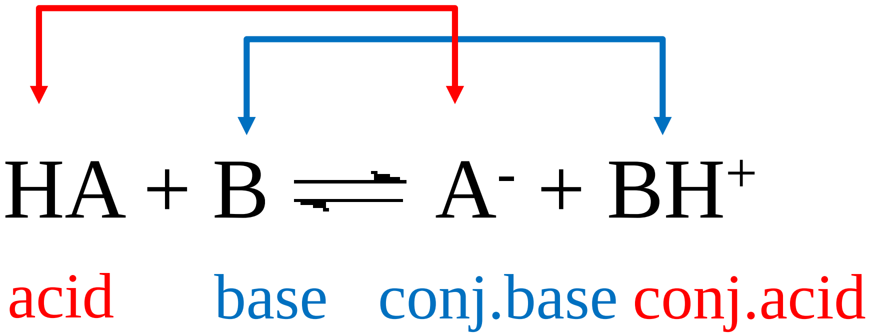
CONJUGATE ACIDS AND BASES

- The acid base reaction can be written in the general form:

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{B} \rightleftharpoons A^- + HB^+$$

- Notice the reversible arrows
  - A Brønsted acid is a proton (H^+) donor
  - A Brønsted base is a proton (H^+) acceptor
- The <u>products</u> are also an acid and base called the *conjugate* acid and base
  - Conjugate base
    - what's left after an acid loses a proton
  - Conjugate acid
    - what you get when a base gains a proton

CONJUGATES (CONT'D)



$$HA + B \rightleftharpoons A^- + BH^+$$

acid base conj.base conj.acid

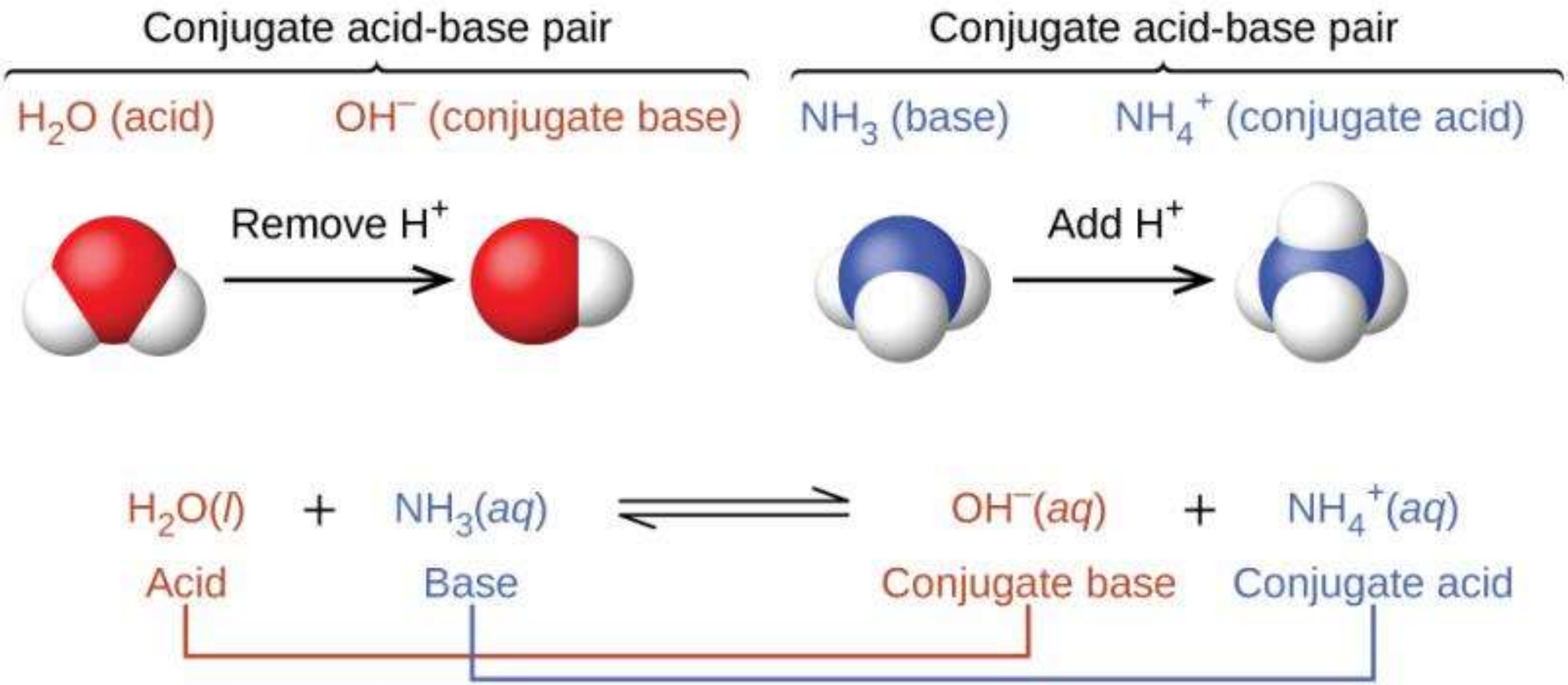
- Conjugate acid - what the base becomes after it accepts a proton.
  - BH^+ is the conjugate acid of the base B
- Conjugate base - what the acid becomes after it donates its proton
  - A^- is the conjugate base of the acid HA
- Conjugate acid-base pair- the acid and base on the opposite sides of the equation
  - HA and A^- constitute a *conjugate acid-base pair*
  - B and BH^+ constitute a *conjugate acid-base pair*

EXAMPLE

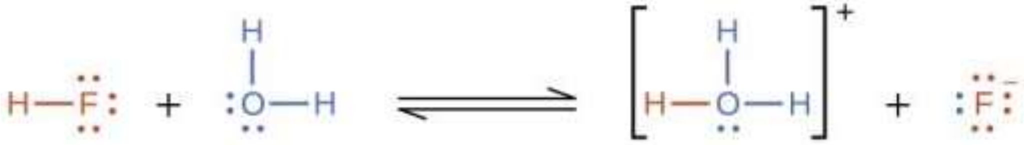
- Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution
- $\mathrm{NH_3}(aq) + \mathrm{HF}(aq) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{F^-}(aq)$

SOLUTION

- NH_3 has one fewer H atom and one fewer positive charge than NH_4^+. F^- has one fewer H atom and one more negative charge than HF. Therefore, the conjugate acid-base pairs are (1) NH_4^+ and NH_3 and (2) HF and F^-.

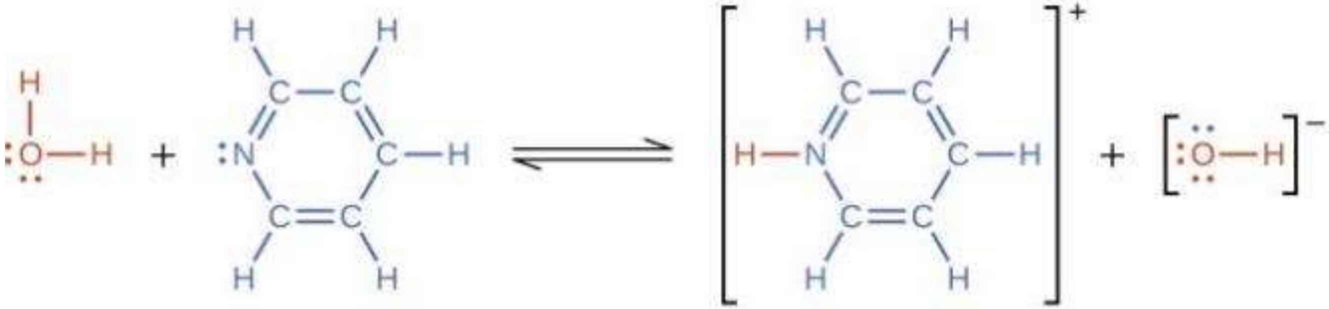


ACID AND BASE IONIZATION



$$\underset{\text{Acid}}{\mathrm{HF}} + \underset{\text{Base}}{\mathrm{H_2O}} \rightleftharpoons \underset{\text{Acid}}{\mathrm{H_3O^+}} + \underset{\text{Base}}{\mathrm{F^-}}$$

$$K = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]}$$



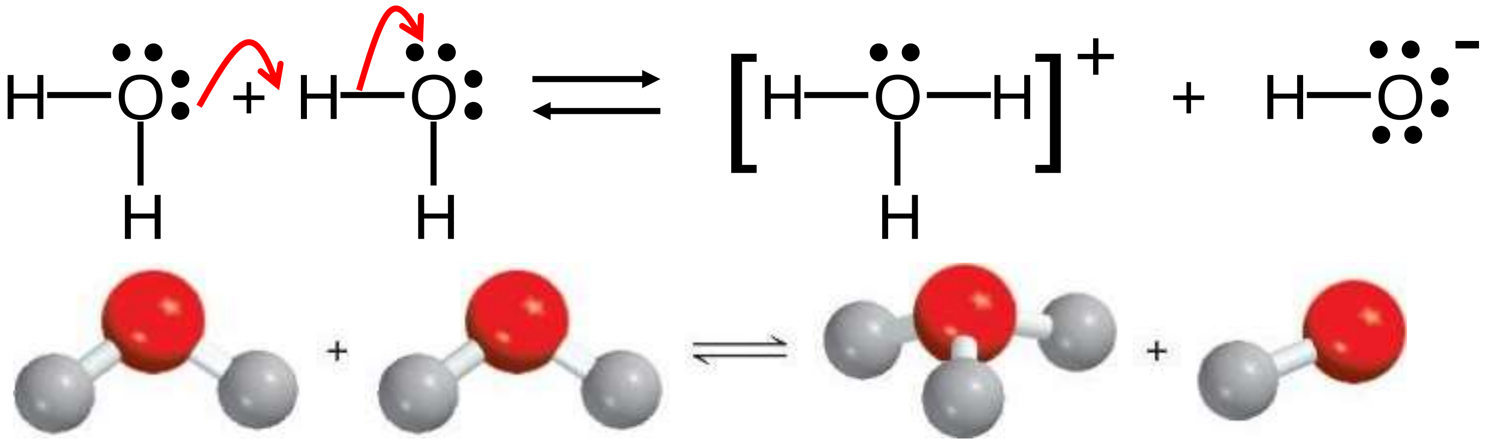
$$\underset{\text{Acid}}{\mathrm{H_2O}} + \underset{\text{Base}}{\mathrm{C_5NH_5}} \rightleftharpoons \underset{\text{Acid}}{\mathrm{C_5NH_6{}^+}} + \underset{\text{Base}}{\mathrm{OH^-}}$$

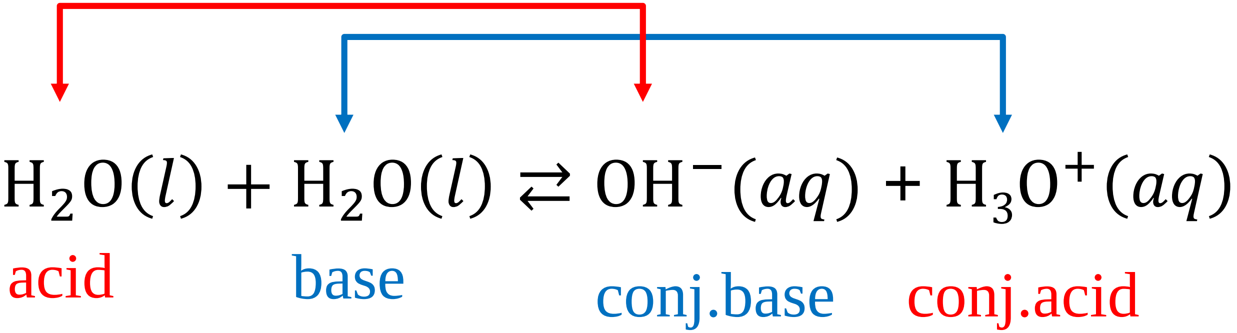
$$K = \frac{[\mathrm{C_5NH_6{}^+}][\mathrm{OH^-}]}{[\mathrm{C_5NH_5}]}$$

ACID-BASE PROPERTIES OF WATER

$$H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq)$$

autoionization of water





$$H_2O(l) + H_2O(l) \rightleftarrows OH^-(aq) + H_3O^+(aq)$$

acid

base

conj.base

conj.acid

SCHIZOPHRENIA

- Water can act as an acid or base
- This is known as being **amphoteric**
- If a compound is amphoteric by the Bronsted definitions (can gain or lose a proton), it is **amphiprotic**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

THE ION PRODUCT OF WATER

$$H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq) \qquad K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

$[H_2O] = \text{constant,}$ so… $\qquad K_c[H_2O] = K_w = [H^+][OH^-]$

The ***ion-product constant*** **(K_w)** is the product of the molar concentrations of H^+ and OH^- ions **at a particular temperature.**

$$\boxed{\begin{gathered}\text{At } 25^\circ\text{ C}\\ K_w = [H^+][OH^-] = 1.0 \times 10^{-14}\end{gathered}}$$

If	Solution Is
$[H^+] < [OH^-]$	basic
$[H^+] = [OH^-]$	neutral
$[H^+] > [OH^-]$	acidic

EXAMPLE

- The concentration of OH^- ions in a certain household ammonia cleaning solution is $0.0025\ M$. Calculate the concentration of H^+ ions.

SOLUTION

- We are given the concentration of the $\mathrm{OH^-}$ ions and asked to calculate $[\mathrm{H^+}]$. The relationship between $[\mathrm{H^+}]$ and $[\mathrm{OH^-}]$ in water or an aqueous solution is given by the ion-product of water, K_w
- Rearranging, we write

$$[\mathrm{H^+}] = \frac{K_\mathrm{w}}{[\mathrm{OH^-}]} = \frac{1.0 \times 10^{-14}}{0.0025} = \mathbf{4.0 \times 10^{-12}}\ \boldsymbol{M}$$

- Because $[\mathrm{H^+}] < [\mathrm{OH^-}]$, the solution is basic, as we would expect.

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14.2 pH and pOH

14.3 Relative Strengths of Acids and Bases

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14.5 Polyprotic Acids

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14.7 Acid-Base Titrations

pH – A RELATIVE MEASURE OF ACIDITY

$$\boxed{\text{pH} = -\log[\text{H}^+]}$$

Solution Is		**At 25°C**	
basic	$[\text{H}^+] < [\text{OH}^-]$	$[\text{H}^+] < 1.0 \times 10^{-7}$	$\text{pH} > 7$
neutral	$[\text{H}^+] = [\text{OH}^-]$	$[\text{H}^+] = 1.0 \times 10^{-7}$	$\text{pH} = 7$
acidic	$[\text{H}^+] > [\text{OH}^-]$	$[\text{H}^+] > 1.0 \times 10^{-7}$	$\text{pH} < 7$

$\text{pH} \uparrow \qquad [\text{H}^+] \downarrow$

OTHER IMPORTANT RELATIONSHIPS

Sample	pH Value
Gastric juice in the stomach	1.0-2.0
Lemon juice	2.4
Vinegar	3.0
Grapefruit juice	3.2
Orange juice	3.5
Urine	4.8-7.5
Water exposed to air*	5.5
Saliva	6.4-6.9
Milk	6.5
Pure water	7.0
Blood	7.35-7.45
Tears	7.4
Milk of magnesia	10.6
Household ammonia	11.5

*Water exposed to air for a long period of time absorbs atmospheric CO_2 to form carbonic acid, H_2CO_3.

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\boxed{[\text{H}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}}$$

$$-\log[\text{H}^+] - \log[\text{OH}^-] = 14.00$$

$$\boxed{\text{pH} + \text{pOH} = 14.00}$$

- pH Meter

EXAMPLE

- The concentration of H^+ ions in a bottle of table wine was $3.2 \times 10^{-4}\ M$ right after the cork was removed. Only half of the wine was consumed. The other half, after it had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to $1.0 \times 10^{-3}\ M$.
- Calculate the pH of the wine on these two occasions.

SOLUTION

- We are given the H^{+} ion concentration and asked to calculate the pH of the solution. What is the definition of pH?
- Since $\mathrm{pH} = -\log[\mathrm{H}^{+}]$, when the bottle was first opened, $[\mathrm{H}^{+}] = 3.2 \times 10^{-4}\ M$, which we substitute into

$$\mathrm{pH} = -\log[\mathrm{H}^{+}] = -\log(3.2 \times 10^{-4}) = \mathbf{3.49}$$

- On the second occasion, $[\mathrm{H}^{+}] = 1.0 \times 10^{-3}\ M$, so that

$$\mathrm{pH} = -\log(1.0 \times 10^{-3}) = \mathbf{3.00}$$

- The increase in hydrogen ion concentration (or decrease in pH) is largely the result of the conversion of some of the alcohol (ethanol) to acetic acid, a reaction that takes place in the presence of molecular oxygen.

EXAMPLE

- The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the H^+ ion concentration of the rainwater.

SOLUTION

- Here we are given the pH of a solution and asked to calculate $[\mathrm{H}^+]$.
- Because pH is defined as $\mathrm{pH} = -\log[\mathrm{H}^+]$, we can solve for $[\mathrm{H}^+]$ by taking the antilog of the pH; that is, $[\mathrm{H}^+] = 10^{-\mathrm{pH}}$, $\mathrm{pH} = -\log[\mathrm{H}^+] = 4.82$
- Therefore,

$$\log[\mathrm{H}^+] = -4.82$$

- To calculate $[\mathrm{H}^+]$, we need to take the antilog of -4.82

$$[\mathrm{H}^+] = 10^{-4.82} = \mathbf{1.5 \times 10^{-5}}\ \boldsymbol{M}$$

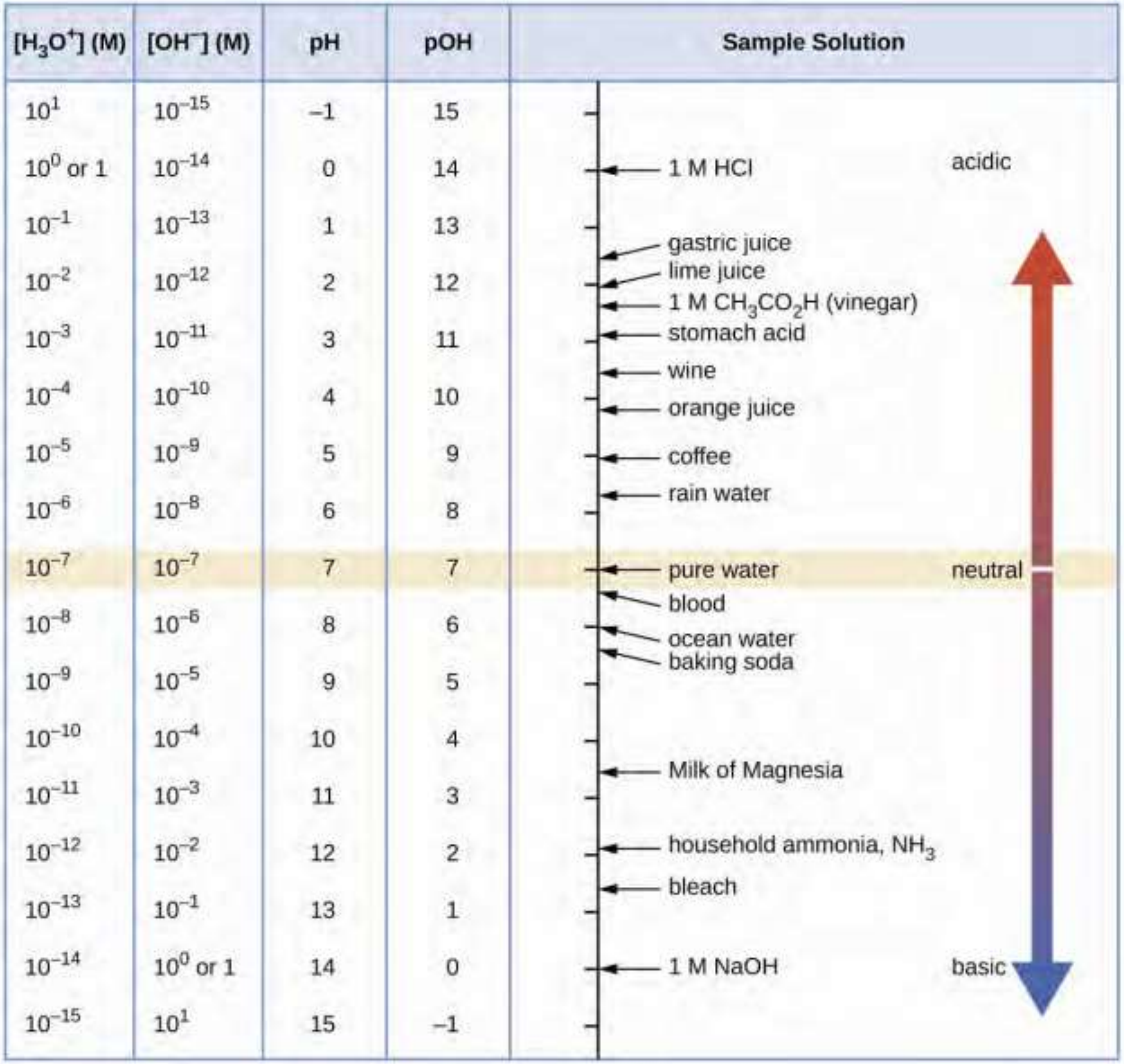
EXAMPLE

- In a NaOH solution $[\mathrm{OH^-}]$ is $2.9 \times 10^{-4}\ M$. Calculate the pH of the solution.

SOLUTION

- Solving this problem takes two steps. First, we need to calculate pOH. Next, we calculate the pH of the solution.
- $\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(2.9 \times 10^{-4}) = 3.54$
- $\text{Since } \mathrm{pH} + \mathrm{pOH} = 14.00,\ \mathrm{pH} = 14.00 - \mathrm{pOH}$
- $\text{Then } 14.00 - 3.54 = \mathbf{10.46}$
- Alternatively, we can use the ion-product constant of water,
- $K_\mathrm{w} = [\mathrm{H^+}][\mathrm{OH^-}]$ to calculate $[\mathrm{H^+}]$, and then we can calculate the pH from the $[\mathrm{H^+}]$. Try it.
- Check: The answer shows that the solution is basic $(\mathrm{pH} > 7)$, which is consistent with a NaOH solution.

FIGURE 14.2



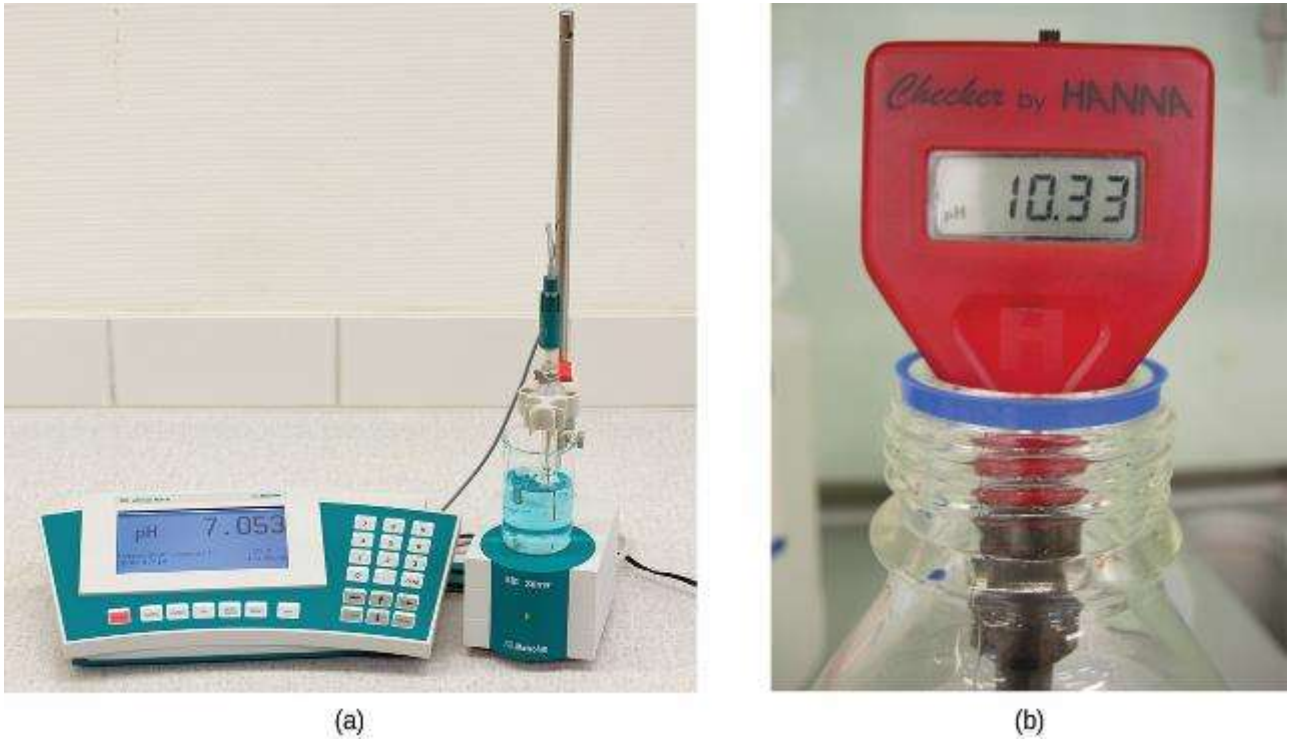
$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH	Sample Solution
10^{1}	10^{-15}	–1	15	
10^{0} or 1	10^{-14}	0	14	1 M HCl acidic
10^{-1}	10^{-13}	1	13	gastric juice
10^{-2}	10^{-12}	2	12	lime juice 1 M CH_3CO_2H (vinegar)
10^{-3}	10^{-11}	3	11	stomach acid
10^{-4}	10^{-10}	4	10	wine orange juice
10^{-5}	10^{-9}	5	9	coffee
10^{-6}	10^{-8}	6	8	rain water
10^{-7}	10^{-7}	7	7	pure water neutral
10^{-8}	10^{-6}	8	6	blood ocean water
10^{-9}	10^{-5}	9	5	baking soda
10^{-10}	10^{-4}	10	4	
10^{-11}	10^{-3}	11	3	Milk of Magnesia
10^{-12}	10^{-2}	12	2	household ammonia, NH_3
10^{-13}	10^{-1}	13	1	bleach
10^{-14}	10^{0} or 1	14	0	1 M NaOH basic
10^{-15}	10^{1}	15	–1	

FIGURE 14.3 – ACID RAIN

(a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil.

(b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

FIGURE 14.4 – MEASURING pH



(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000.

(b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

FIGURE 14.5 – MEASURING pH (CONT’D)

(a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-*M* solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-*M* solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13).

(b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa)

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ELECTROLYTES

- Strong electrolyte - 100% dissociation (section 4.1)

$$\mathrm{NaCl}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

- Weak electrolyte - not completely dissociated

$$\mathrm{CH_3COOH} \rightleftarrows \mathrm{CH_3COO}^-(aq) + \mathrm{H}^+(aq)$$

- Strong acids are strong electrolytes

$$\mathrm{HCl}\ (aq) + \mathrm{H_2O}\ (l) \rightarrow \mathrm{H_3O}^+\ (aq) + \mathrm{Cl}^-\ (aq)$$

$$\mathrm{HNO_3}\ (aq) + \mathrm{H_2O}\ (l) \rightarrow \mathrm{H_3O}^+\ (aq) + \mathrm{NO_3^-}\ (aq)$$

$$\mathrm{HClO_4}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O}^+(aq) + \mathrm{ClO_4^-}(aq)$$

$$\mathrm{H_2SO_4}\ (aq) + \mathrm{H_2O}\ (l) \rightarrow \mathrm{H_3O}^+\ (aq) + \mathrm{HSO_4^-}\ (aq)$$

- (missing: HBr, HI…..but NOT HF!)

ELECTROLYTES (CONT'D)

- Weak acids are weak electrolytes

$$HF\ (aq) + H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + F^-\ (aq)$$

$$HNO_2\ (aq) + H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + NO_2^-\ (aq)$$

$$HSO_4^-\ (aq) + H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + SO_4^{2-}\ (aq)$$

$$H_2O\ (l) + H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + OH^-\ (aq)$$

- Strong bases are strong electrolytes

$$NaOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq)$$

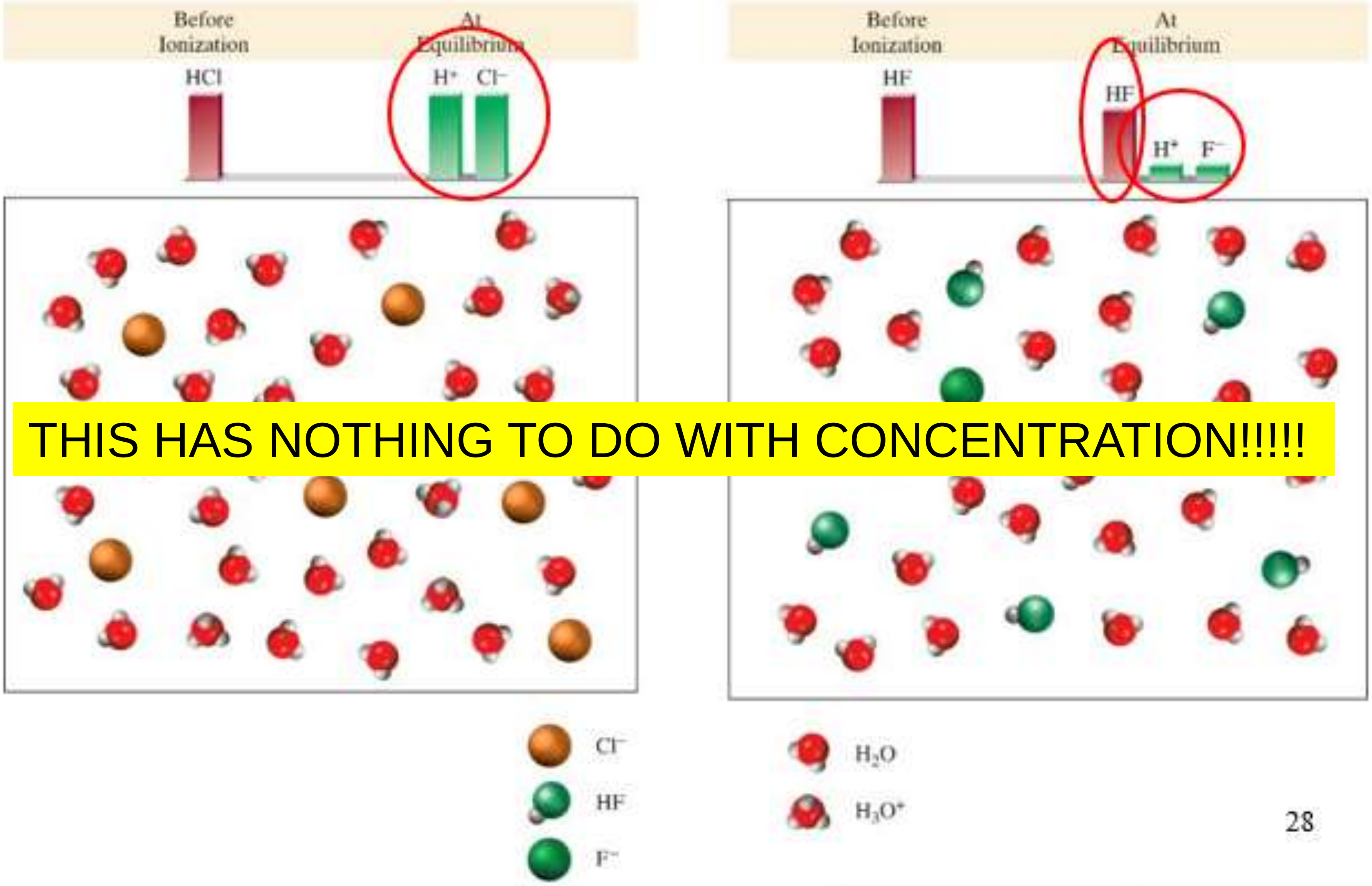
$$KOH\ (s) \xrightarrow{H_2O} K^+\ (aq) + OH^-\ (aq)$$

$$Ba(OH)_2\ (s) \xrightarrow{H_2O} Ba^{2+}\ (aq) + 2OH^-\ (aq)$$

STRONG VS. WEAK ACIDS

Strong acid (HCl)

Weak acid (HF)



THIS HAS NOTHING TO DO WITH CONCENTRATION!!!!!

ELECTROLYTES (CONT'D)

- Weak bases are weak electrolytes

$$F^- \,(aq) + H_2O\,(l) \rightleftarrows OH^- \,(aq) + HF\,(aq)$$

$$NO_2^- \,(aq) + H_2O\,(l) \rightleftarrows OH^- \,(aq) + HNO_2\,(aq)$$

- Conjugate acid-base pair strength
  - The conjugate base of a strong acid has no measurable strength.
  - The conjugate acid of a strong base is similarly weak.
- H_3O^+ is the strongest acid that can exist in aqueous solution.
- The OH^- ion is the strongest base that can exist in aqueous solution.

FIGURE 14.9

- pH paper indicates that a 0.l-*M* solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+] = 0.1\ M$. A 0.1-*M* solution of CH_3CO_2H (beaker on right) is has a pH of 3 ($[H_3O^+] = 0.001\ M$) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

FIGURE 14.10

- pH paper indicates that a 0.1-*M* solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-] = 0.001\ M$) because the weak base NH_3 only partially reacts with water. A 0.1-*M* solution of NaOH (right) has a pOH of 1 because NaOH is a strong base. (credit: modification of work by Sahar Atwa)

ACID/CONJ. BASE STRENGTH

- The conjugate base of a strong acid MUST be weak

$$\mathrm{HCl}\ (aq) + \mathrm{H_2O}\ (l) \rightarrow \mathrm{H_3O^+}\ (aq) + \mathrm{Cl^-}\ (aq)$$

- The conjugate base of a weak acid must be “strong”

$$\mathrm{CH_3COOH} \rightleftarrows \mathrm{CH_3COO^-}(aq) + \mathrm{H^+}(aq)$$

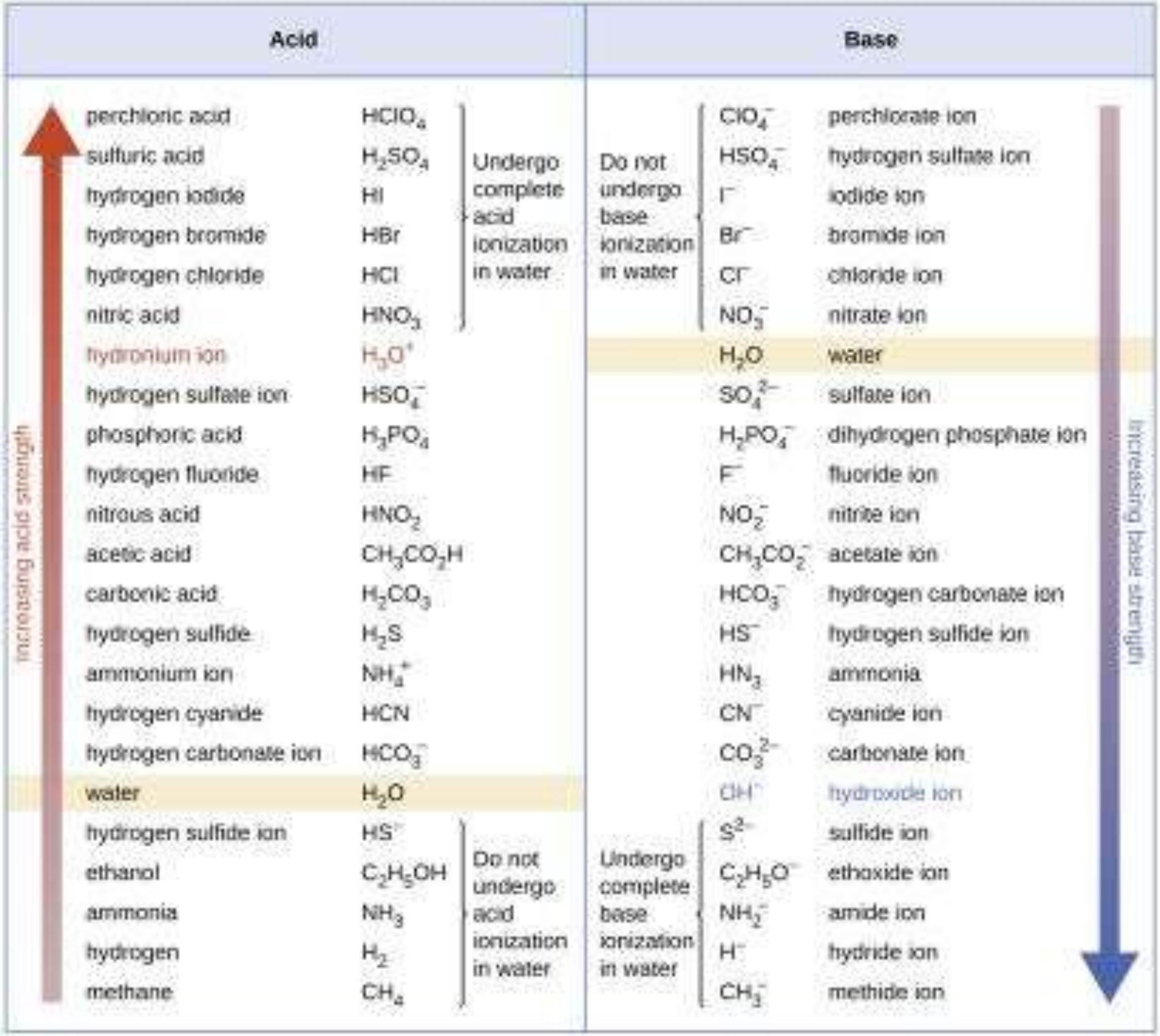
- The conjugate acid of a strong base MUST be weak

$$\mathrm{NaOH}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

- The conjugate acid of a weak base must be “strong”

$$\mathrm{NH_3(aq) + H_2O \rightleftarrows NH_4{}^+\ (aq) + OH^-(aq)}$$

ACID/CONJ. BASE STRENGTH



Acid			Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			HN_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

increasing acid strength

increasing base strength

EXAMPLE

Predict the direction of the following reaction in aqueous solution:

$$\mathrm{HNO_2}(aq) + \mathrm{CN^-}(aq) \rightleftharpoons \mathrm{HCN}(aq) + \mathrm{NO_2^-}(aq)$$

SOLUTION

Strategy- The problem is to determine whether, at equilibrium, the reaction will be shifted to the right, favoring HCN and NO_2^-, or to the left, favoring HNO_2 and CN^-. Which of the two is a stronger acid and hence a stronger proton donor: HNO_2 or HCN? Which of the two is a stronger base and hence a stronger proton acceptor: CN^-or NO_2^-? Remember that the stronger the acid, the weaker its conjugate base.

In the table, we see that HNO_2 is a stronger acid than HCN. Thus, CN^- is a stronger base than NO_2^-. The net reaction will proceed from left to right as written because HNO_2 is a better proton donor than HCN (and CN^- is a better proton acceptor than NO_2^-).

WEAK ACID IONIZATION CONSTANTS

$$\mathrm{HA}\ (aq) + \mathrm{H_2O}\ (l) \rightleftarrows \mathrm{H_3O^+}\ (aq) + \mathrm{A^-}\ (aq)$$

$$\mathrm{HA}(aq) \rightleftarrows \mathrm{H^+}(aq) + \mathrm{A^-}(aq)$$

$$K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

K_a is the ***acid ionization constant***

K_a ↑ weak acid strength ↑

ACID IONIZATION CONSTANTS

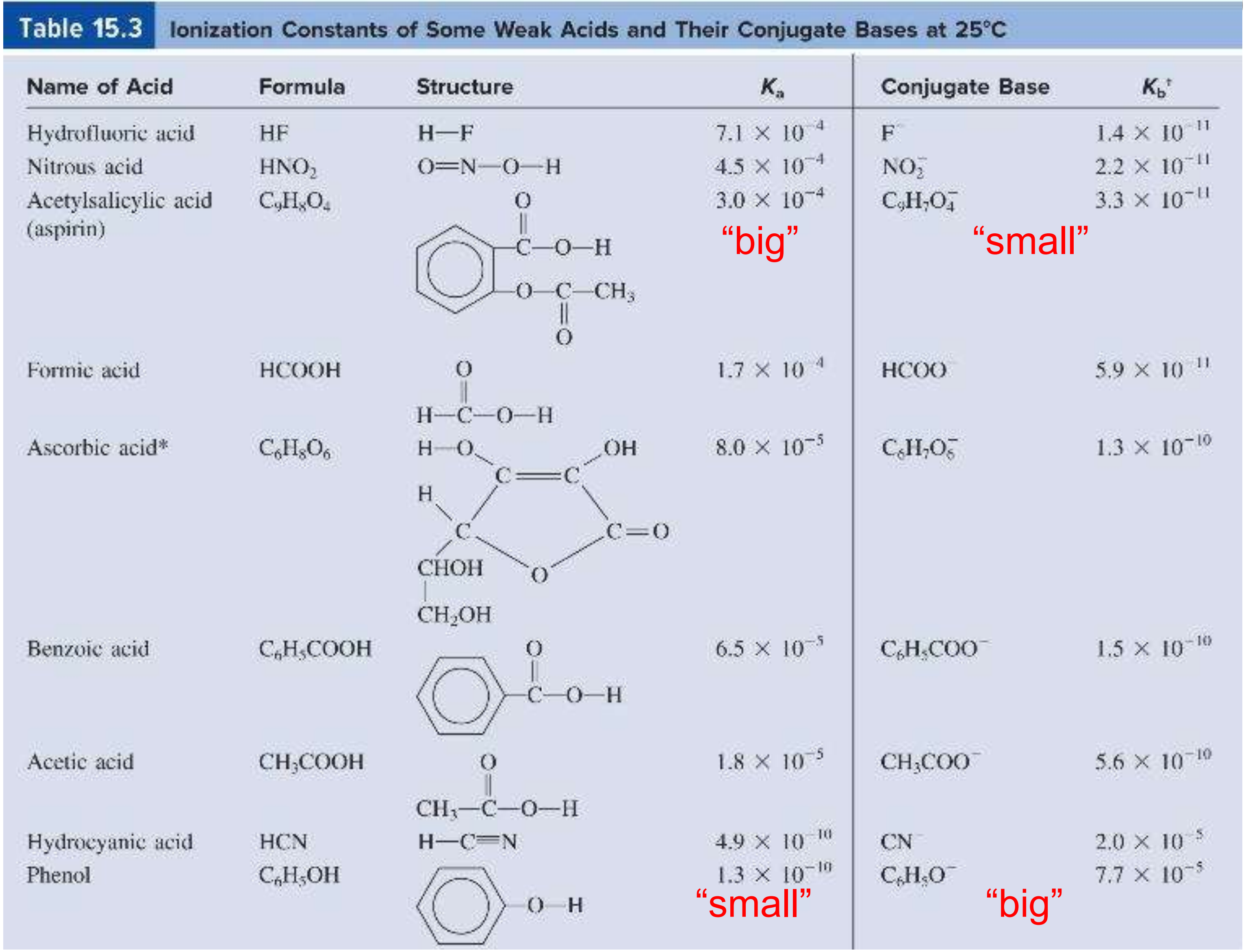


Table 15.3 Ionization Constants of Some Weak Acids and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b†
Hydrofluoric acid	HF	H—F	7.1×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	O=N—O—H	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	$C_9H_7O_4^-$	3.3×10^{-11}
Formic acid	$HCOOH$	$H-\overset{\overset{O}{\Vert}}{C}-O-H$	1.7×10^{-4}	$HCOO^-$	5.9×10^{-11}
Ascorbic acid*	$C_6H_8O_6$		8.0×10^{-5}	$C_6H_7O_6^-$	1.3×10^{-10}
Benzoic acid	C_6H_5COOH		6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}
Acetic acid	CH_3COOH	$CH_3-\overset{\overset{O}{\Vert}}{C}-O-H$	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
Hydrocyanic acid	HCN	H—C≡N	4.9×10^{-10}	CN^-	2.0×10^{-5}
Phenol	C_6H_5OH		1.3×10^{-10}	$C_6H_5O^-$	7.7×10^{-5}

“big” “small”

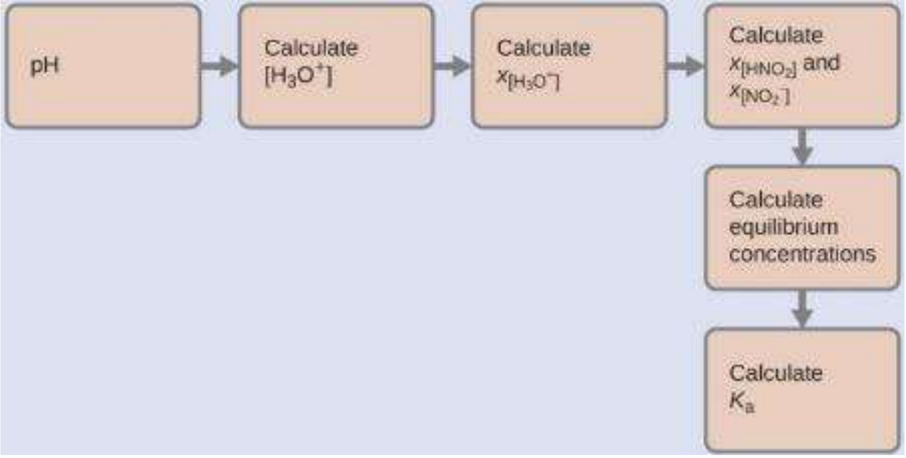
“small” “big”

*For ascorbic acid it is the upper left hydroxyl group that is associated with this ionization constant.

The base ionization constant K_b is discussed in Section 15.6.

SOLVING WEAK ACID IONIZATION PROBLEMS

- Identify the major species that can affect the pH.
  - In most cases, you can ignore the autoionization of water.
  - Ignore $[\mathrm{OH}^-]$ because it is determined by $[\mathrm{H}^+]$.
- Use an ICE table to express the equilibrium concentrations in terms of single unknown x.
- Write K_a in terms of equilibrium concentrations.
- Solve for x by the approximation method.
  - If approximation is not valid, solve for x exactly.
- Calculate concentrations of all species and/or pH of the solution.



pH

Calculate $[H_3O^+]$

Calculate $x_{[H_3O^+]}$

Calculate $x_{[HNO_2]}$ and $x_{[NO_2^-]}$

Calculate equilibrium concentrations

Calculate K_a

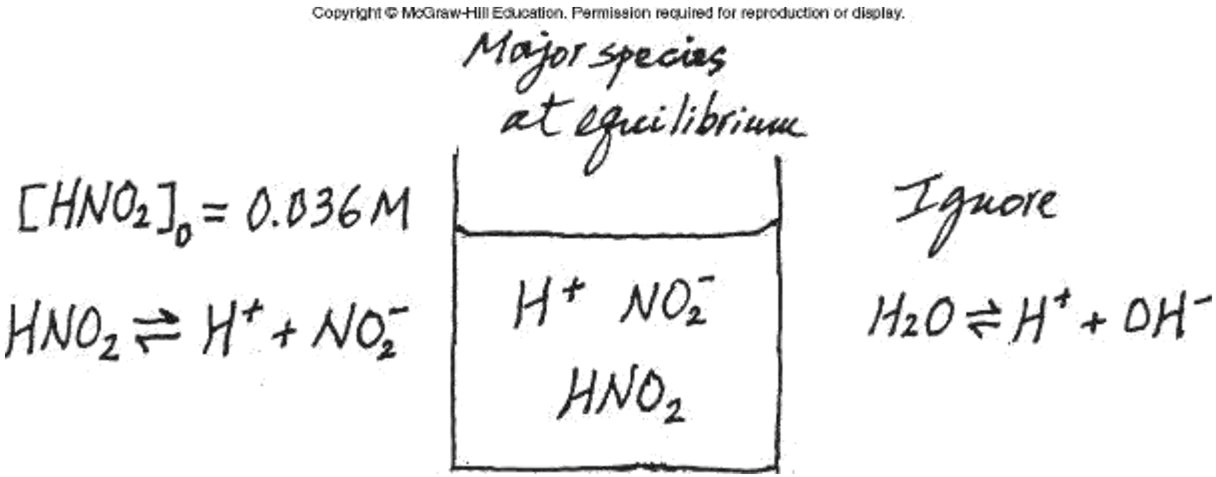
EXAMPLE

Calculate the pH of a $0.036\ M$ nitrous acid $(\mathrm{HNO_2})$ solution:

$$\mathrm{HNO_2}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{NO_2^-}(aq)$$

SOLUTION

Strategy Recall that a weak acid only partially ionizes in water. We are given the initial concentration of a weak acid and asked to calculate the pH of the solution at equilibrium. It is helpful to make a sketch to keep track of the pertinent species.



- As in Example 15.6, we ignore the ionization of H_2O so the major source of H^+ ions is the acid. The concentration of OH^- ions is very small as we would expect from an acidic solution so it is present as a minor species.

SOLUTION (CONT'D)

Step 3: From Table 15.3 we write

$$K_a = \frac{[\mathrm{H}^+][\mathrm{NO}_2^-]}{[\mathrm{HNO}_2]}$$

$$4.5 \times 10^{-4} = \frac{x^2}{0.036 - x}$$

Applying the approximation $0.036 - x \approx 0.036$, we obtain

$$4.5 \times 10^{-4} = \frac{x^2}{0.36 - x} \approx \frac{x^2}{0.036}$$

$$x^2 = 1.62 \times 10^{-5}$$

$$x = 4.0 \times 10^{-3}\ M$$

SOLUTION (CONT'D)

Solution We follow the procedure already outlined.

Step 1: The species that can affect the pH of the solution are $\mathrm{HNO_2}$, $\mathrm{H^+}$, and the conjugate base $\mathrm{NO_2^-}$. We ignore water's contribution to $[\mathrm{H^+}]$.

Step 2: Letting *x* be the equilibrium concentration of $\mathrm{H^+}$ and $\mathrm{NO_2^-}$ ions in $\mathrm{mol/L}$, we summarize:

- $\mathrm{HNO_2}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{NO_2^-}(aq)$

Initial (*M*):	0.036	0.00	0.00
Change (*M*):	-*x*	+*x*	+*x*
Equilibrium (*M*):	0.036-*x*	*x*	*x*

SOLUTION (CONT'D)

To test the approximation,

$$\frac{4.0 \times 10^{-3}\ M}{0.036\ M} \times 100\% = 11\%$$

Because this is greater than 5%, our approximation is **not** valid and we must solve the quadratic equation, as follows:

$$x^2 + 4.5 \times 10^{-4}x - 1.62 \times 10^{-5} = 0$$

$$\mathrm{x} = \frac{-4.5 \times 10^{-4} \pm \sqrt{(4.5 \times 10^{-4})^2 - 4(1)(-1.62 \times 10^{-5})}}{2(1)}$$

$= 3.8 \times 10^{-3}\ M$ or $-4.3 \times 10^{-3}\ M$

SOLUTION (CONT'D)

The second solution is impossible, because the concentration of ions produced as a result of ionization cannot be negative. Therefore, the solution is given by the positive root,
$x = 3.8 \times 10^{-3}\ M.$

Step 4: At equilibrium

$$[\mathrm{H}^+] = 3.8 \times 10^{-3}\ M$$

$$\mathrm{pH} = -\log(3.8 \times 10^{-3})$$

$$= \mathbf{2.42}$$

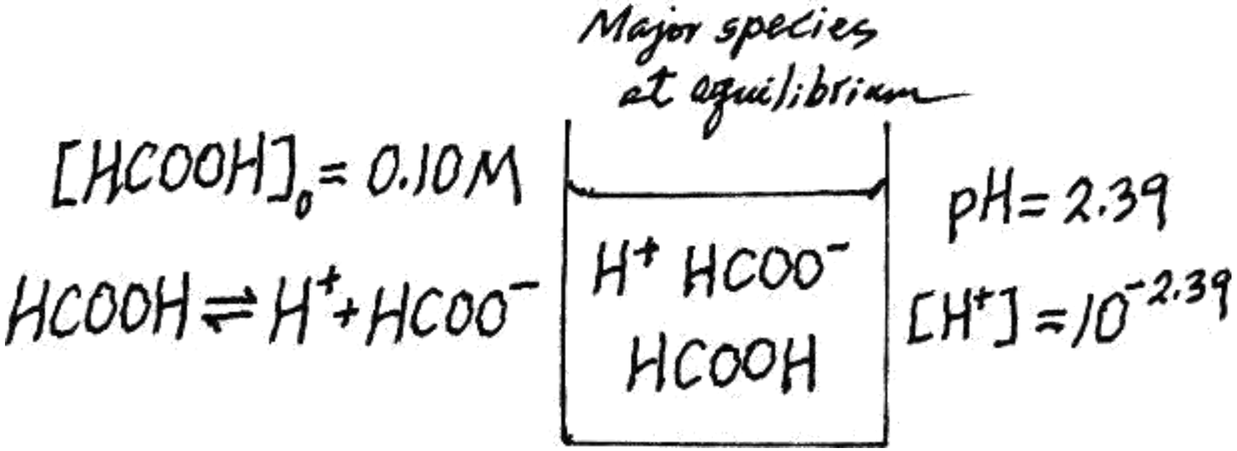
Check Note that the calculated pH indicates that the solution is acidic, which is what we would expect for a weak acid solution. **Compare the calculated pH with that of a $\mathbf{0.036}\ M$ strong acid solution such as HCl to convince yourself of the difference between a strong acid and a weak acid.**

EXAMPLE

The pH of a $0.10\ M$ solution of formic acid (HCOOH) is 2.39. What is the K_a of the acid?

SOLUTION

Strategy Formic acid is a weak acid. It only partially ionizes in water. Note that the concentration of formic acid refers to the initial concentration, before ionization has started. The pH of the solution, on the other hand, refers to the equilibrium state. To calculate K_a, then, we need to know the concentrations of all three species: $[\mathrm{H}^+]$, $[\mathrm{HCOO}^-]$, and $[\mathrm{HCOOH}]$ at equilibrium. As usual, we ignore the ionization of water. The following sketch summarizes the situation.



SOLUTION (CONT'D)

Solution We proceed as follows.

Step 1: The major species in solution are HCOOH, $\mathrm{H^+}$, and the conjugate base $\mathrm{HCOO^-}$.

Step 2: First we need to calculate the hydrogen ion concentration from the pH value

$$\mathrm{pH} = -\log[\mathrm{H^+}]$$
$$2.39 = -\log[\mathrm{H^+}]$$

Taking the antilog of both sides, we get

$$[\mathrm{H^+}] = 10^{-2.39} = 4.1 \times 10^{-3}\ M$$

SOLUTION (CONT'D)

Next we summarize the changes:

$$\mathrm{HCOOH}(aq) \rightleftharpoons \mathrm{H}^{+}(aq) + \mathrm{HCOO}^{-}(aq)$$

Initial (*M*):	0.10	0.00	0.00
Change (*M*):	-4.1×10^{-3}	$+4.1 \times 10^{-3}$	$+4.1 \times 10^{-3}$
Equilibrium (*M*):	$(0.10 - 4.1 \times 10^{-3})$	4.1×10^{-3}	4.1×10^{-3}

Note that because the pH and hence the H^{+} ion concentration is known, it follows that we also know the concentrations of HCOOH and HCOO^{-} at equilibrium.

SOLUTION (CONT'D)

Step 3: The ionization constant of formic acid is given by

The pain of an ant's sting is caused by formic acid. (credit: John Tann)

$$K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}$$

$$= \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})}$$

$$= \mathbf{1.8 \times 10^{-4}}$$

Check

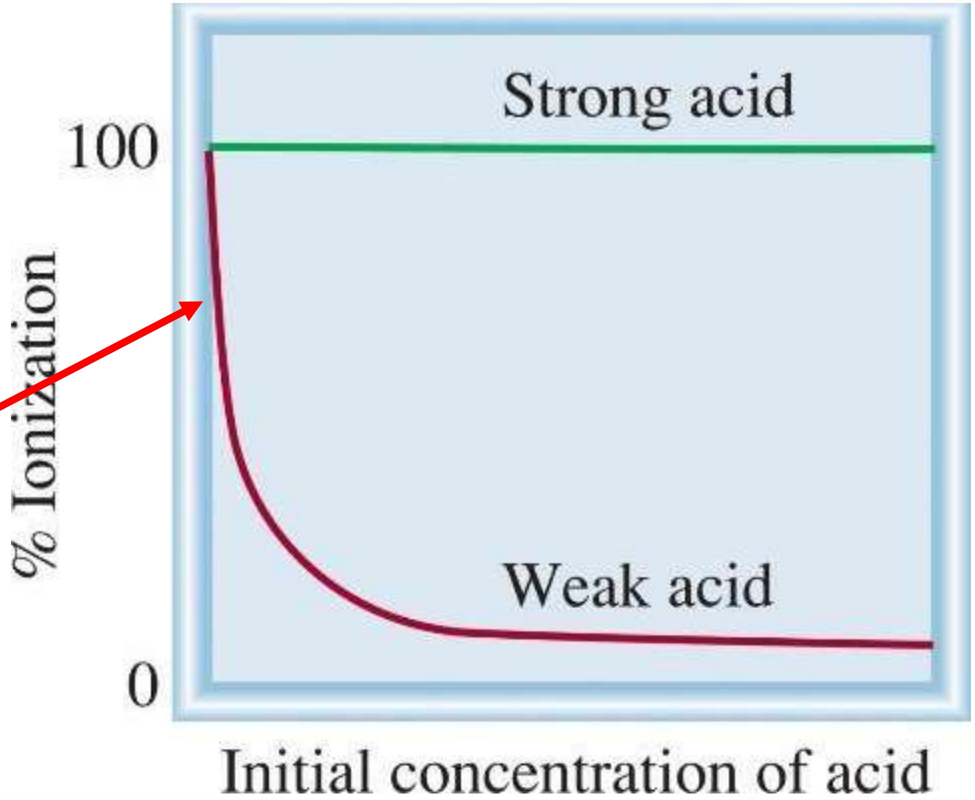
The K_a value differs slightly from the one listed in Table 15.3 because of the rounding-off procedure we used in the calculation.

PERCENT IONIZATION

$$\boldsymbol{percent\ ionization} = \frac{\text{Ionized acid concentration at equillibrium}}{\text{Initial concentration of acids}} \times 100\%$$

For a monoprotic acid HA,

Percent Ionization$= \dfrac{[\mathrm{H}^+]}{[\mathrm{HA}]_0} \times 100\%$ $[\mathrm{HA}]_0 =$ initial concentration



Ostwald dilution law

EXAMPLE

Example 14.7

Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is: $HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2{}^-(aq) + H_3O^+(aq)$. Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}$ *M*, so that percent ionization is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Check Your Learning

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89.

Answer: 1.3% ionized

BASE IONIZATION CONSTANTS

$$\mathrm{NH_3}\ (aq) + \mathrm{H_2O}\ (l) \rightleftarrows \mathrm{NH_4^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

$$K_b = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]}$$

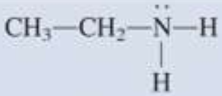
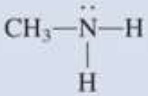
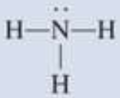
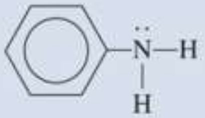
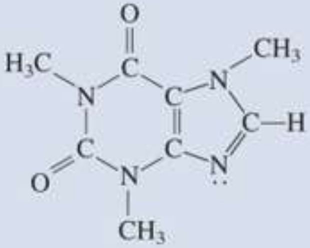
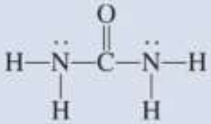
K_b is the ***base ionization constant***

K_b ↑ weak base strength ↑

Solve weak base problems like weak acids ***except***
solve for $[\mathrm{OH^-}]$ instead of $[\mathrm{H^+}]$.

BASE IONIZATION CONSTANTS

Table 15.4 **Ionization Constants of Some Weak Bases and Their Conjugate Acids at 25°C**

Name of Base	Formula	Structure	K_b*	Conjugate Acid	K_a
Ethylamine	$C_2H_5NH_2$		5.6×10^{-4}	$C_2H_5\overset{+}{N}H_3$	1.8×10^{-11}
Methylamine	CH_3NH_2		“big” $4.[illegible] \times 10^{-4}$	$CH_3\overset{+}{N}H_3$	“small” $[illegible].3 \times 10^{-11}$
Ammonia	NH_3		1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Pyridine	C_5H_5N		1.7×10^{-9}	$C_5H_5\overset{+}{N}H$	5.9×10^{-6}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}	$C_6H_5\overset{+}{N}H_3$	2.6×10^{-5}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}	$C_8H_{11}\overset{+}{N}_4O_2$	0.19
Urea	$(NH_2)_2CO$		1.5×10^{-14} “small”	$H_2NCO\overset{+}{N}H_3$	0.67 “big”

*The nitrogen atom with the lone pair accounts for each compound’s basicity. In the case of urea, K_B can be associated with either nitrogen atom.

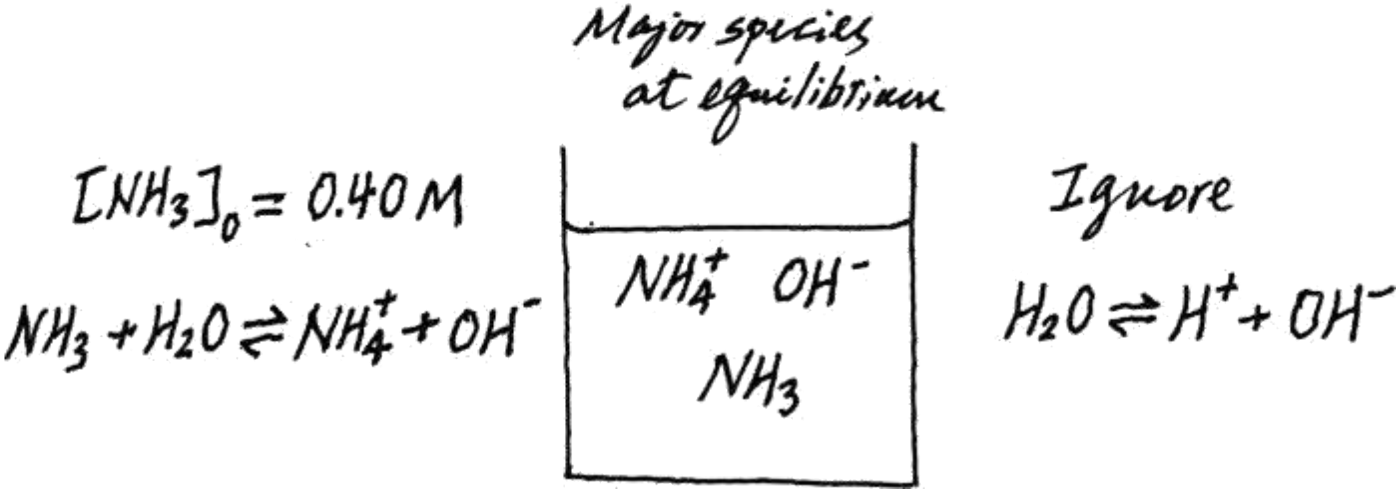
EXAMPLE

What is the pH of a $0.40\ M$ ammonia solution?

SOLUTION

Strategy The procedure here is similar to the one used for a weak acid (see Example 15.8). From the ionization of ammonia, we see that the major species in solution at equilibrium are

NH_3, NH_4^+,and OH^-. The hydrogen ion concentration is very small as we would expect from a basic solution, so it is present as a minor species. As before, we ignore the ionization of water. We make a sketch to keep track of the pertinent species as follows:



SOLUTION (CONT'D)

Solution We proceed according to the following steps.

Step 1: The major species in an ammonia solution are $\mathrm{NH_3}$, $\mathrm{NH_4^+}$, and $\mathrm{OH^-}$. We ignore the very small contribution to $\mathrm{OH^-}$ concentration by water.

Step 2: Letting *x* be the equilibrium concentration of $\mathrm{NH_4^+}$ and $\mathrm{OH^-}$ ions in $\mathrm{mol/L}$, we summarize:

- $\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$

Initial (*M*):	0.40	0.00	0.00
Change (*M*):	-*x*	+*x*	+*x*
Equilibrium (*M*):	0.40-*x*	*x*	*x*

SOLUTION (CONT'D)

Step 3: Table 15.4 gives us K_b:

$$K_\text{b} = \frac{[\text{NH}_4^+][\text{OH}]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x}$$

Applying the approximation $0.40 - x \approx 0.40$, we obtain

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40}$$

$$x^2 = 7.2 \times 10^{-6}$$

$$x = 2.7 \times 10^{-3}\ M$$

SOLUTION (CONT'D)

To test the approximation, we write

$$\frac{2.7 \times 10^{-3}\ M}{0.40\ M} \times 100\% = 0.68\%$$

Therefore, the approximation is valid.

Step 4: At equilibrium, $[\mathrm{OH^-}] = 2.7 \times 10^{-3}\ M$. Thus,

$$\begin{aligned} \mathrm{pOH} &= -\log(2.7 \times 10^{-3}) \\ &= 2.57 \\ \mathrm{pH} &= 14.00 - 2.75 \\ &= \mathbf{11.43} \end{aligned}$$

SOLUTION (CONT’D)

Check

Note that the pH calculated is basic, which is what we would expect from a weak base solution. Compare the calculated pH with that of a $0.40\ M$ strong base solution, such as KOH, to convince yourself of the difference between a strong base and a weak base.

IONIZATION CONST OF CONJ ACID-BASE PAIRS

$$\cancel{\mathrm{HA}}\,(aq) \rightleftarrows \mathrm{H}^+\,(aq) + \cancel{\mathrm{A}^-}\,(aq) \qquad K_a$$

$$\cancel{\mathrm{A}^-}\,(aq) + \mathrm{H_2O}\,(l) \rightleftarrows \mathrm{OH}^-\,(aq) + \cancel{\mathrm{HA}}\,(aq) \qquad K_b$$

$$\mathrm{H_2O}\,(l) \rightleftarrows \mathrm{H}^+(aq) + \mathrm{OH}^-(aq) \qquad K_w$$

$$\boxed{K_\mathrm{a}\,K_b = K_W}$$

For a weak acid and its conjugate base:

$$K_\mathrm{a} = \frac{K_W}{K_b} \qquad\qquad K_b = \frac{K_W}{K_\mathrm{a}}$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w.

MOLECULAR STRUCTURE AND ACID STRENGTH

$$\mathrm{H - X \rightarrow H^{+} + X^{-}}$$

The stronger the bond

The weaker the acid

$$\mathrm{HF \ll HCl < HBr < HI}$$

Bond Enthalpies for hydrogen halides and acid strengths for hydrohalic acids

Bond	Bond Enthalpy $(\mathrm{kJ/mol})$	Acid Strength
$\mathrm{H - F}$	568.2	weak
$\mathrm{H - Cl}$	431.9	strong
$\mathrm{H - Br}$	366.1	strong
$\mathrm{H - I}$	298.3	strong

Why is the HI bond so weak?

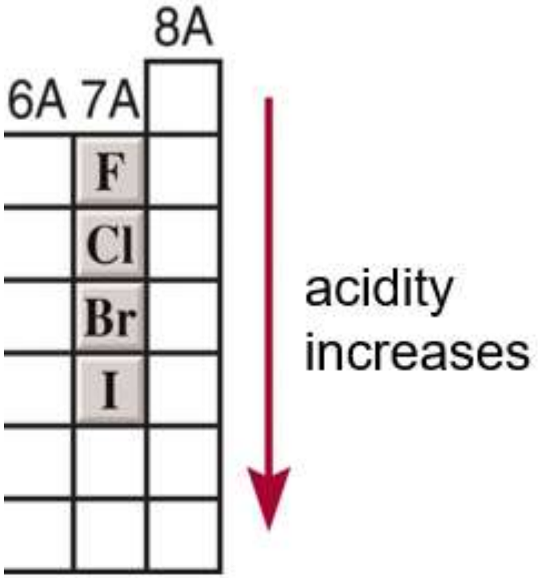
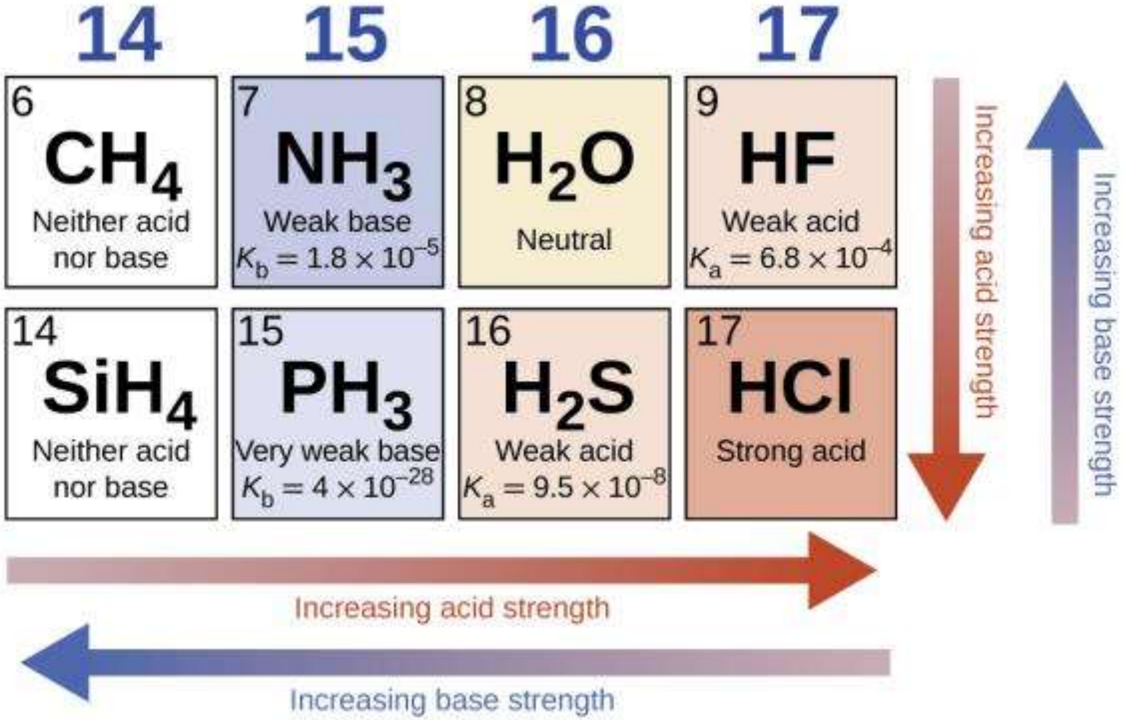


FIGURE 14.13



- As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

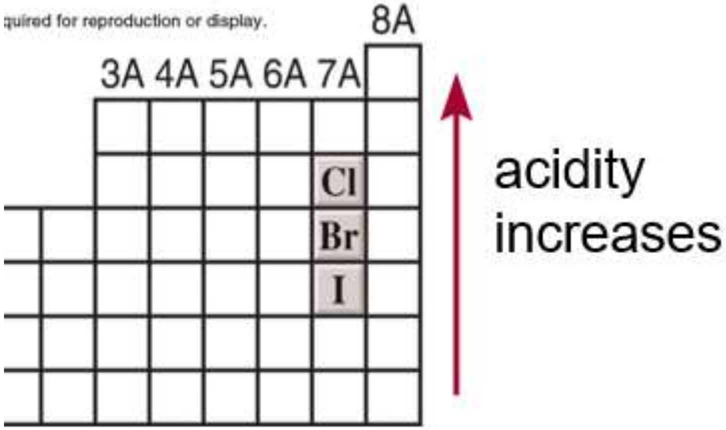
MOLECULAR STRUCTURE & OXOACID STRENGTH

For oxoacids having different central atoms (Z) that **are from the same group** and that have the **same oxidation number**:

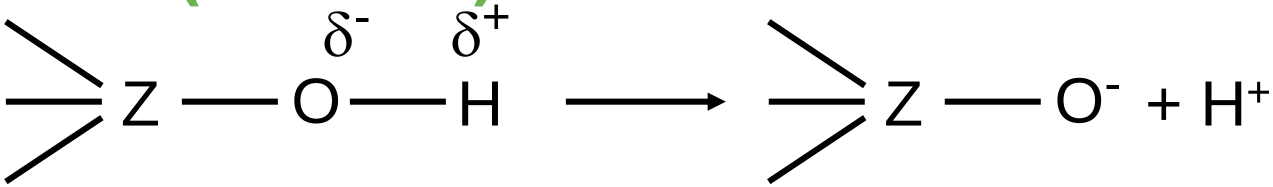
Acid strength increases with increasing electronegativity of Z

Cl is more electronegative than Br

$$HClO_3 > HBrO_3 > HIO_3$$

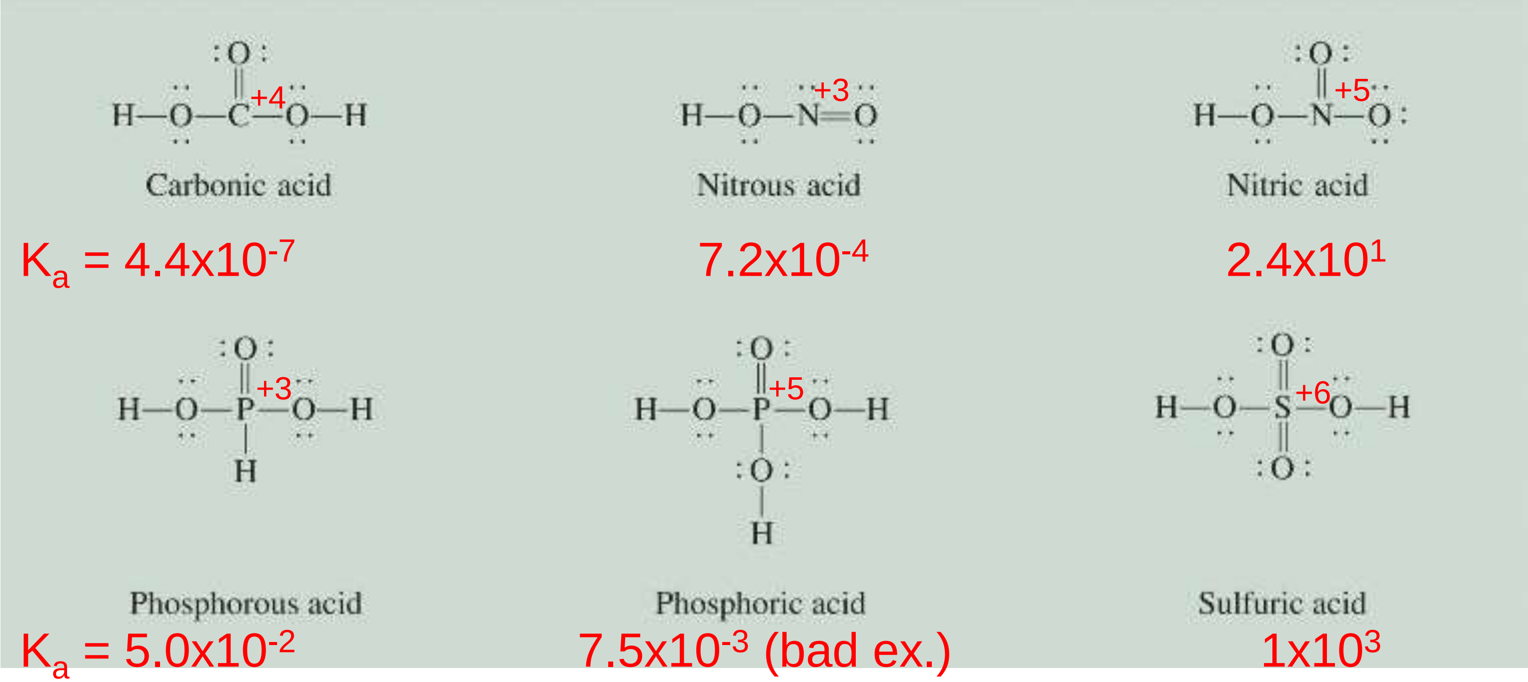


MOLECULAR STRUCTURE & OXOACID STRENGTH (CONT'D)



The O-H bond will be more polar and easier to break if:

- Z is very electronegative or
- Z is in a high oxidation state



$K_a = 4.4\text{x}10^{-7}$ $7.2\text{x}10^{-4}$ $2.4\text{x}10^{1}$

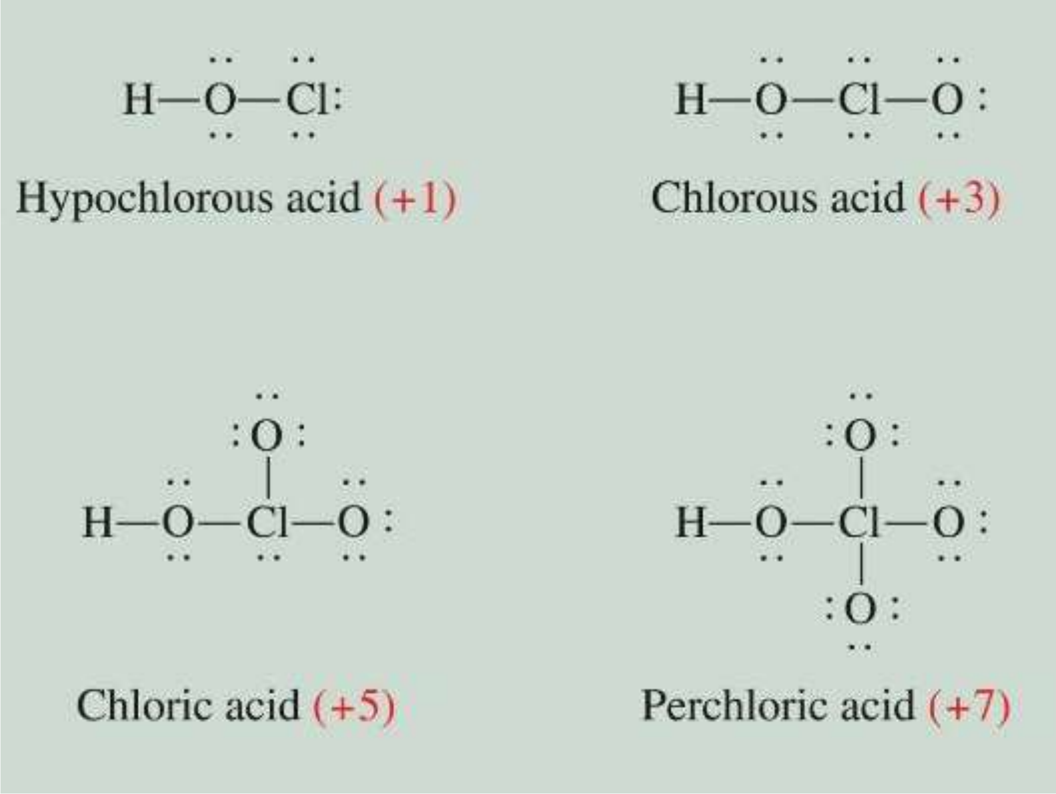
$K_a = 5.0\text{x}10^{-2}$ $7.5\text{x}10^{-3}$ (bad ex.) $1\text{x}10^{3}$

vs $1.6\text{x}10^{-2}$ for sulfurous

MOLECULAR STRUCTURE & OXOACID STRENGTH (CONT’D)

For oxoacids having the same central atom (Z) but different numbers of attached groups:

Acid strength increases as the oxidation number of Z increases.



$HClO_4 > HClO_3 > HClO_2 > HClO$

EXAMPLE

Predict the relative strengths of the oxoacids in each of the following groups:

(a) $HClO$, $HBrO$, and HIO

(b) HNO_3 and HNO_2

SOLUTION

Strategy

Examine the molecular structure. In (a) the two acids have similar structure but differ only in the central atom (Cl, Br, and I). Which central atom is the most electronegative? In (b) the acids have the same central atom (N) but differ in the

number of O atoms. What is the oxidation number of N in each of these two acids?

SOLUTION (CONT'D)

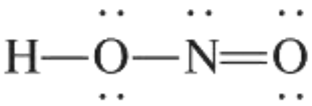
Solution

(a) These acids all have the same structure, and the halogens all have the same oxidation number (+1). Because the electronegativity decreases from Cl to I,the Cl atom attracts the electron pair it shares with the O atom to the greatest extent. Consequently, the $\mathrm{O-H}$ bond is the most polar in HClO and least polar in HIO. Thus, the acid strength decreases as follows:

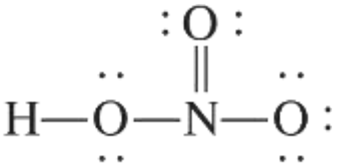
$$\mathrm{HClO} > \mathrm{HBrO} > \mathrm{HIO}$$

SOLUTION (CONT'D)

(b) The structures of HNO_3 and HNO_2 are shown in Figure 15.5. Because the oxidation number of N is +5 in HNO_3 and +3 in HNO_2, HNO_3 is a stronger acid than HNO_2.



Nitrous acid



Nitric acid

CH. 14 OUTLINE

14.1 Brønsted-Lowry Acids and Bases

14.2 pH and pOH

14.3 Relative Strengths of Acids and Bases

14.4 Hydrolysis of Salt Solutions

14.5 Polyprotic Acids

14.6 Buffers

14.7 Acid-Base Titrations

ACID-BASE PROPERTIES OF SALTS

Type of salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	$\mathrm{NaCl, KI, KNO_3, RbBr, BaCl_2}$	None	≈ 7
Cation from strong base; anion from weak acid	$\mathrm{CH_3COONa, KNO_2}$	Anion	> 7
Cation from weak base; anion from strong acid	$\mathrm{NH_4Cl, NH_4NO_3}$	Cation	< 7
Cation from weak base; anion from weak acid	$\mathrm{NH_4NO_2, CH_3COONH_4, NH_4CN}$	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small , highly charged cation; anion from strong acid	$\mathrm{AlCl_3, Fe(NO_3)_3}$	Hydrated cation	< 7

Entirely more confusing than it needs to be!!!

ACID-BASE PROPERTIES OF SALTS: NEUTRAL AND BASIC SOLUTIONS

- Neutral solutions:
  - Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (*e.g.* Cl^-, Br^-, and NO_3^-).

- Basic solutions:
  - Salts derived from a strong base **and** a **weak** acid.

$$\mathrm{CH_3COONa}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}\ (aq) + \mathrm{CH_3COO^-}\ (aq)$$

$$\mathrm{CH_3COO^-}\ (aq) + \mathrm{H_2O}\ (l) \rightleftarrows \mathrm{CH_3COOH}\ (aq) + \enclose{circle}{\mathrm{OH^-}}\ (aq)$$

$$\mathrm{Na^+(aq)} + \mathrm{H_2O(l)} \cancel{\rightleftarrows} \mathrm{NaOH(aq)} + \mathrm{H^+(aq)}$$

EXAMPLE

Calculate the pH of a $0.15\ M$ solution of sodium acetate $(\mathrm{CH_3COONa})$. What is the percent hydrolysis?

SOLUTION

Strategy

What is a salt? In solution, CH_3COONa dissociates completely into Na^+ and CH_3COO^- ions. The Na^+ ion, as we saw earlier, does not react with water and has no effect on the pH of the solution. The CH_3COO^- ion is the conjugate base of the weak acid CH_3COOH. Therefore, we expect that it will react to a certain extent with water to produce CH_3COOH and OH^-, and the solution will be basic.

SOLUTION (CONT'D)

Solution

Step 1: Because we started with a $0.15\ M$ sodium acetate solution, the concentrations of the ions are also equal to $0.15\ M$ after dissociation:

- $CH_3COONa(aq) \rightleftharpoons Na^+(aq) + CH_3COO^-(aq)$

Initial (*M*):	0.15	0	0
Change (*M*):	-0.15	+0.15	+0.15
Final (*M*):	0	0.15	0.15

- Of these ions, only the acetate ion will react with water
  - $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

SOLUTION (CONT'D)

At equilibrium, the major species in solution are $\mathrm{CH_3COOH}$, $\mathrm{CH_3COO^-}$, and $\mathrm{OH^-}$. The concentration of the $\mathrm{H^+}$ ion is very small as we would expect for a basic solution, so it is treated as a minor species. We ignore the ionization of water.

Step 2: Let *x* be the equilibrium concentration of $\mathrm{CH_3COOH}$ and $\mathrm{OH^-}$ ions in $\mathrm{mol/L}$, we summarize:

- $\mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{CH_3COOH}(aq) + \mathrm{OH^-}(aq)$

Initial (*M*):	0.15	0.00	0.00
Change (*M*):	-*x*	+*x*	+*x*
Equilibrium (*M*):	0.15-*x*	*x*	*x*

SOLUTION (CONT'D)

Step 3: From the preceding discussion and Table 15.3 we write the equilibrium constant of hydrolysis, or the base ionization constant, as

$$K_{\mathrm{b}} = \frac{[\mathrm{CH_3COOH}][\mathrm{OH^-}]}{[\mathrm{CH_3COO^-}]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x}$$

Because K_b is very small and the initial concentration of the base is large, we can apply the approximation $0.15 - x \approx 0.15$:

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$x = 9.2 \times 10^{-6}$$

SOLUTION (CONT'D)

Step 4: At equilibrium:

$$[\mathrm{OH^-}] = 9.2 \times 10^{-6}\ M$$

$$\mathrm{pOH} = -\log(9.2 \times 10^{-6})$$

$$= 5.04$$

$$\mathrm{pH} = 14.00 - 5.04$$

$$= 8.96$$

- Thus the solution is basic, as we would expect. The percent
- hydrolysis is given by
- $$\%\ \text{hydrolysis} = \frac{9.2\times10^{-6}\ M}{0.15\ M} \times 100\%$$
- $$= \mathbf{0.0061\%}$$

SOLUTION (CONT'D)

Check

The result shows that only a very small amount of the anion undergoes hydrolysis. Note that the calculation of percent hydrolysis takes the same form as the test for the approximation, which is valid in this case.

ACID-BASE PROPERTIES OF SALTS: ACIDIC SOLUTIONS

- Salts derived from a strong acid and a weak base.

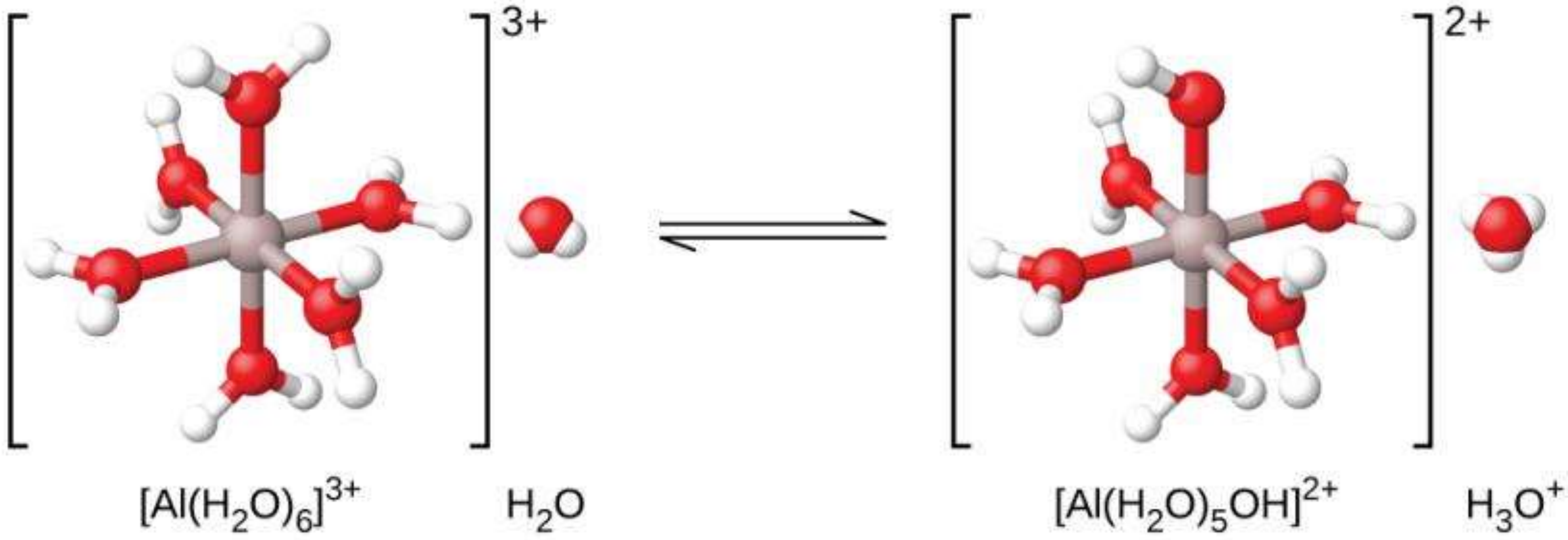
$$\mathrm{NH_4Cl}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{NH_4^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{NH_4^+}(aq) \rightleftarrows \mathrm{NH_3}(aq) + \boxed{\mathrm{H^+}}(aq)$$

- Salts with small, highly charged metal cations (*e.g.* $\mathrm{Al^{3+}}$, $\mathrm{Cr^{3+}}$, and $\mathrm{Be^{2+}}$) and the conjugate base of a strong acid.

$$\mathrm{Al(H_2O)_6^{3+}}\ (aq) \rightleftarrows \mathrm{Al(OH)(H_2O)_5^{2+}}\ (aq) + \mathrm{H^+}(aq)$$

FIGURE 14.16



- When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

ACID-BASE PROPERTIES OF SALTS (CONT'D)

- Solutions in which both the cation and the anion hydrolyze:
  - K_b for the anion $>$ K_a for the cation, solution will be basic
  - K_b for the anion $<$ K_a for the cation, solution will be acidic
  - K_b for the anion $\approx$ K_a for the cation, solution will be neutral

EXAMPLE

Predict whether the following solutions will be acidic, basic, or nearly neutral:

(a) NH_4I

(b) $NaNO_2$

(c) $FeCl_3$

(d) NH_4F

SOLUTION

Strategy

In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or an ammonium ion? Is the anion the conjugate base of a weak acid? If yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of K_a for the cation and K_b for the anion.

SOLUTION (CONT'D)

Solution

We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

(a) The cation is NH_4^+, which will hydrolyze to produce NH_3 and H^+.The I^- anion is the conjugate base of the strong acid HI. Therefore, I^- will not hydrolyze and the solution is acidic.

(b) The Na^+ cation does not hydrolyze. The NO_2^- is the conjugate base of the weak acid HNO_2 and will hydrolyze to give HNO_2 and OH^-.The solution will be basic.

SOLUTION (CONT'D)

(c) Fe^{3+} is a small metal ion with a high charge and hydrolyzes to produce H^{+} ions. The Cl^{-} does not hydrolyze. Consequently, the solution will be acidic.

(d) Both the NH_4^{+} and F^{-} ions will hydrolyze. From Tables 15.3 and 15.4 we see that the K_a of NH_4^{+} (5.6×10^{-10}) is greater than the K_b for $\mathrm{F}^{-}(1.4 \times 10^{-11})$. Therefore, the solution will be acidic.

CH. 14 OUTLINE

14.1 Brønsted-Lowry Acids and Bases

14.2 pH and pOH

14.3 Relative Strengths of Acids and Bases

14.4 Hydrolysis of Salt Solutions

14.5 Polyprotic Acids

14.6 Buffers

14.7 Acid-Base Titrations

DIPROTIC AND TRIPROTIC ACIDS

- May yield more than one hydrogen ion per molecule.
- Ionize in a *stepwise* manner; that is, they lose one proton at a time.
- An ionization constant expression can be written for each ionization stage.
- Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution (each one subsequently smaller).

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

IONIZATION CONSTANTS OF SOME POLYPROTIC ACIDS

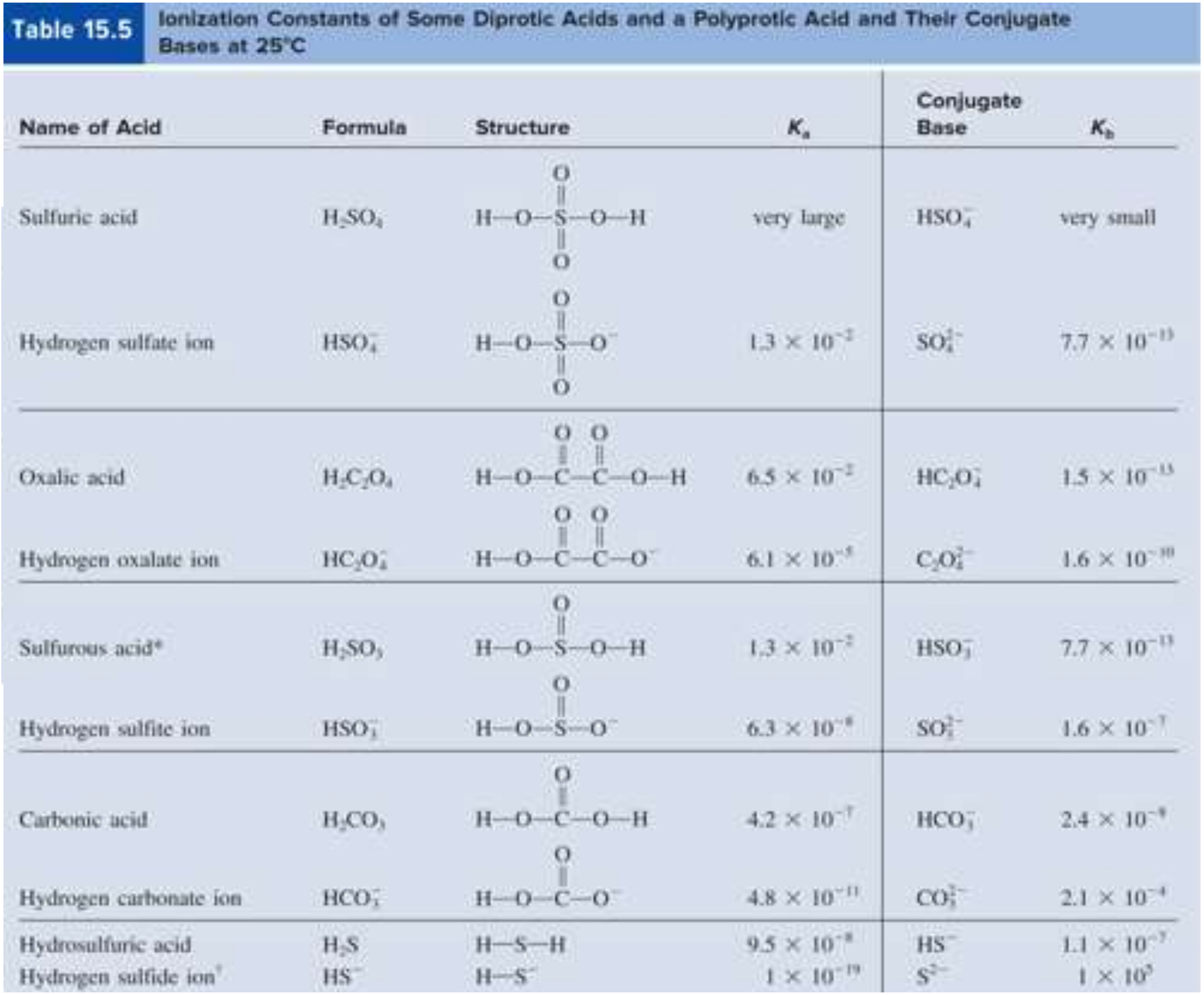


Table 15.5 **Ionization Constants of Some Diprotic Acids and a Polyprotic Acid and Their Conjugate Bases at 25°C**

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Sulfuric acid	H_2SO_4	$H{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O{-}H$	very large	HSO_4^-	very small
Hydrogen sulfate ion	HSO_4^-	$H{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O^-$	1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
Oxalic acid	$H_2C_2O_4$	$H{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}H$	6.5×10^{-2}	$HC_2O_4^-$	1.5×10^{-13}
Hydrogen oxalate ion	$HC_2O_4^-$	$H{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O^-$	6.1×10^{-5}	$C_2O_4^{2-}$	1.6×10^{-10}
Sulfurous acid*	H_2SO_3	$H{-}O{-}\overset{\overset{O}{\|}}{S}{-}O{-}H$	1.3×10^{-2}	HSO_3^-	7.7×10^{-13}
Hydrogen sulfite ion	HSO_3^-	$H{-}O{-}\overset{\overset{O}{\|}}{S}{-}O^-$	6.3×10^{-8}	SO_3^{2-}	1.6×10^{-7}
Carbonic acid	H_2CO_3	$H{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}H$	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
Hydrogen carbonate ion	HCO_3^-	$H{-}O{-}\overset{\overset{O}{\|}}{C}{-}O^-$	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrosulfuric acid	H_2S	$H{-}S{-}H$	9.5×10^{-8}	HS^-	1.1×10^{-7}
Hydrogen sulfide ion†	HS^-	$H{-}S^-$	1×10^{-19}	S^{2-}	1×10^{5}

* H_2SO_2 has never been isolated and exists in only minute concentration in aqueous solution of SO_2. The K_a value here refers to the process $SO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$.

†The ionization constant of HS^- is very low and difficult to measure. The value listed here is only an estimate.

EXAMPLE

Oxalic acid $(\mathrm{H_2C_2O_4})$ is a poisonous substance used chiefly as a bleaching and cleansing agent (for example, to remove bathtub rings). Calculate the concentrations of all the species present at equilibrium in a $0.10\ M$ solution.

SOLUTION

Strategy

Determining the equilibrium concentrations of the species of a diprotic acid in aqueous solution is more involved than for a monoprotic acid. We follow the same procedure as that used for a monoprotic acid for each stage, as in Example 15.8. Note that the conjugate base from the first stage of ionization becomes the acid for the second stage ionization.

SOLUTION (CONT'D)

Solution We proceed according to the following steps.

Step 1: The major species in solution at this stage are the nonionized acid, H^+ ions, and the conjugate base, $HC_2O_4^-$.

Step 2: Letting *x* be the equilibrium concentration of H^+ and $HC_2O_4^-$ ions in mol/L, we summarize:

- $H_2C_2O_4(aq) \rightleftharpoons H^+(aq) + HC_2O_4^-(aq)$

Initial (*M*):	0.10	0.00	0.00
Change (*M*):	-*x*	+*x*	+*x*
Equilibrium (*M*):	0.10-*x*	*x*	*x*

SOLUTION (CONT’D)

Step 3: Table 15.5 gives us

$$K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{HC_2O_4^-}]}{[\mathrm{H_2C_2O_4}]}$$

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

Applying the approximation $0.10 - x \approx 0.10$, we obtain

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x^2 = 6.5 \times 10^{-3}$$

$$x = 8.1 \times 10^{-2}\ M$$

SOLUTION (CONT'D)

To test the approximation,

$$\frac{8.1 \times 10^{-2}\ M}{0.10\ M} \times 100\% = 81\%$$

Clearly the approximation is **not** valid. Therefore, we must solve the quadratic equation

$$x^2 + 6.5 \times 10^{-2}x - 6.5 \times 10^{-3} = 0$$

The result is $x = 0.054\ M$.

SOLUTION (CONT'D)

Step 4: When the equilibrium for the first stage of ionization is reached, the concentrations are

$$[\mathrm{H^+}] = 0.054\ M$$
$$[\mathrm{HC_2O_4^-}] = 0.054\ M$$
$$[\mathrm{H_2C_2O_4}] = (0.10 - 0.054)\ M = 0.046\ M$$

Next we consider the second stage of ionization.

Step 1: At this stage, the major species are $\mathrm{HC_2O_4^-}$, which acts as the acid in the second stage of ionization, $\mathrm{H^+}$, and the conjugate base $\mathrm{C_2O_4^{2-}}$.

SOLUTION (CONT'D)

Step 2: Letting *y* be the equilibrium concentration of $\mathrm{H^+}$ and $\mathrm{C_2O_4^{2-}}$ ions in $\mathrm{mol/L}$, we summarize:

- $\mathrm{HC_2O_4^-}\ (aq) \rightleftharpoons \mathrm{H^+}\ (aq) + \mathrm{C_2O_4^{2-}}\ (aq)$

Initial (*M*):	0.054	0.054	0.00
Change (*M*):	-*y*	+*y*	+*y*
Equilibrium (*M*):	0.054-*y*	0.054+*y*	*y*

Step 3: Table 15.5 gives us

$$K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{C_2O_4^{2-}}]}{[\mathrm{HC_2O_4^-}]}$$

$$6.1 \times 10^{-5} = \frac{(0.054 + y)(y)}{(0.054 - y)}$$

SOLUTION (CONT'D)

Applying the approximation $0.054 + y \approx 0.054$ and $0.054 - y \approx 0.054$, we obtain

$$\frac{(0.054)(y)}{(0.054)} = y = 6.1 \times 10^{-5}\ M$$

and we test the approximation,

$$\frac{6.1 \times 10^{-5}\ M}{0.054\ M} \times 100\% = 0.11\%$$

The approximation is valid

SOLUTION (CONT'D)

Step 4: At equilibrium,

$$[\mathrm{H_2C_2O_4}] = \mathbf{0.046}\ \boldsymbol{M}$$
$$[\mathrm{HC_2O_4^-}] = (0.054 - 6.1 \times 10^{-5})M = \mathbf{0.054}\ \boldsymbol{M}$$
$$[\mathrm{H^+}] = (0.054 + 6.1 \times 10^{-5})M = \mathbf{0.054}\ \boldsymbol{M}$$
$$[\mathrm{C_2O_4^{2-}}] = \mathbf{6.1 \times 10^{-5}}\ \boldsymbol{M}$$
$$[\mathrm{OH^-}] = 1.0 \times 10^{-14}/0.054 = \mathbf{1.9 \times 10^{-13}}\ \boldsymbol{M}$$

CH. 14 OUTLINE

14.1 Brønsted-Lowry Acids and Bases

14.2 pH and pOH

14.3 Relative Strengths of Acids and Bases

14.4 Hydrolysis of Salt Solutions

14.5 Polyprotic Acids

14.6 Buffers

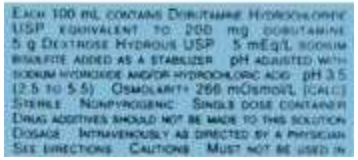
14.7 Acid-Base Titrations

BUFFERS

A buffer solution is a solution of:

1. A weak acid or a weak base and
2. The salt of the weak acid or weak base

Both must be present!
(a weak acid AND its conj. base OR
a weak base AND its conj. acid)



Each 100 mL contains Dobutamine Hydrochloride
USP equivalent to 200 mg dobutamine
5 g Dextrose Hydrous USP 5 mEq/L sodium
bisulfite added as a stabilizer pH adjusted with
sodium hydroxide and/or hydrochloric acid pH 3.5
(2.5 to 5.5) Osmolarity 266 mOsmol/L (calc)
Sterile Nonpyrogenic Single dose container
Drug additives should not be made to this solution
Dosage Intravenously as directed by a physician
See directions Cautions Must not be used in

A buffer solution has the ability to resist large changes in pH upon the addition of small amounts of either acid or base.

Consider an equal molar mixture of $\mathrm{CH_3COOH}$ and $\mathrm{CH_3COONa}$...

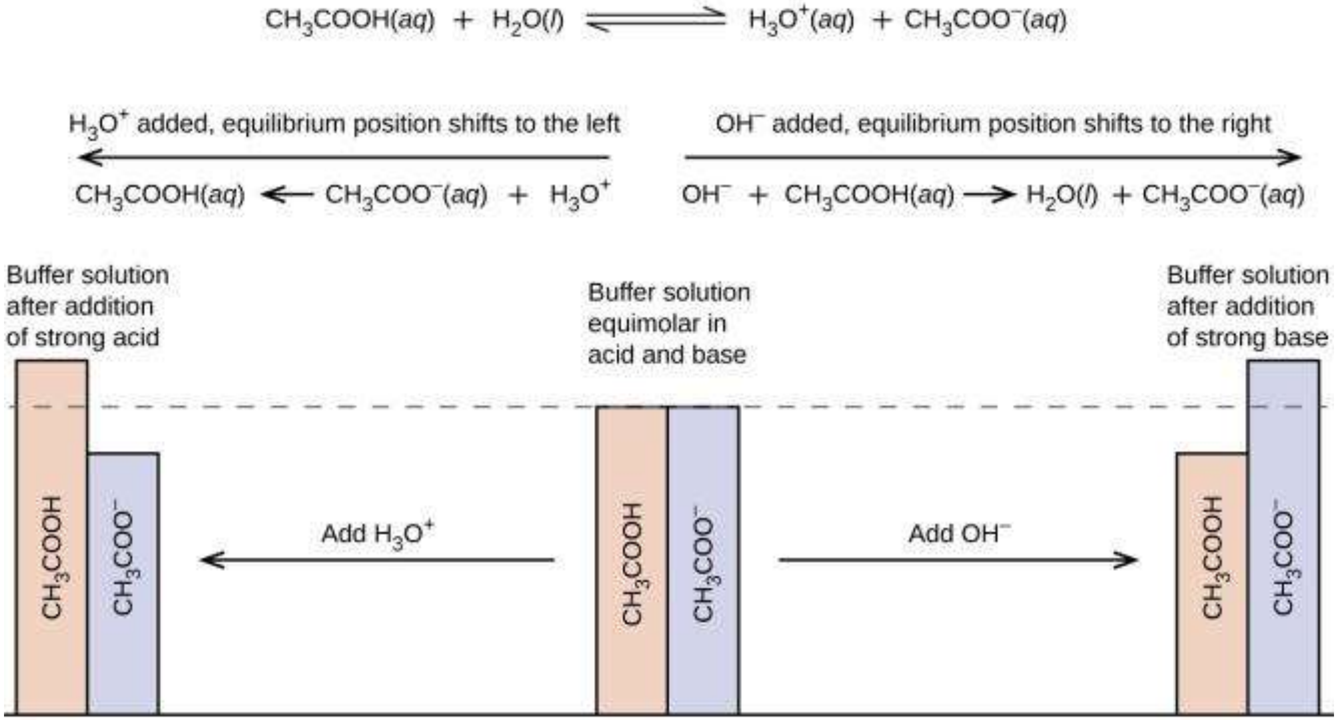
Add strong acid, then:

$$\mathrm{H^+}(aq) + \mathrm{CH_3COO^-}(aq) \rightarrow \mathrm{CH_3COOH}(aq)$$

Add strong base, then:

$$\mathrm{OH^-}(aq) + \mathrm{CH_3COOH}\ (aq) \rightarrow \mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l)$$

FIGURE 14.18



$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

H_3O^+ added, equilibrium position shifts to the left

$CH_3COOH(aq) \leftarrow CH_3COO^-(aq) + H_3O^+$

OH^- added, equilibrium position shifts to the right

$OH^- + CH_3COOH(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$

- This diagram shows the buffer action of these reactions.

EXAMPLE

Which of the following solutions can be classified as buffer systems?

(a) KH_2PO_4/H_3PO_4

(b) $NaClO_4/HClO_4$

(c) C_5H_5N/C_5H_5NHCl(C_5H_5N is pyridine; its K_b is given in Table 15.4)

Explain your answer.

SOLUTION

Strategy

What constitutes a buffer system? Which of the preceding solutions contains a weak acid and its salt (containing the weak conjugate base)? Which of the preceding solutions contains a weak base and its salt (containing the weak conjugate acid)? Why is the conjugate base of a strong acid not able to neutralize an added acid?

SOLUTION (CONT'D)

Solution The criteria for a buffer system is that we must have a weak acid and its salt (containing the weak conjugate base) or a weak base and its salt (containing the weak conjugate acid).

(a) H_3PO_4 is a weak acid, and its conjugate base, $H_2PO_4^-$,is a weak base (see Table 15.5). Therefore, this is a buffer system.

(b) Because $HClO_4$ is a strong acid, its conjugate base, ClO_4^-, is an extremely weak base. This means that the CIO_4^- ion will not combine with a H^+ ion in solution to form $HClO_4$. Thus, the system cannot act as a buffer system.

(c) As Table 15.4 shows, C_5H_5N is a weak base and its conjugate acid, $C_5H_5N^+H$ (the cation of the salt C_5H_5NHCl), is a weak acid. Therefore, this is a buffer system.

EXAMPLE

(a) Calculate the pH of a buffer system containing $1.0\ M$ $\mathrm{CH_3COOH}$ and $1.0\ M$ $\mathrm{CH_3COONa}$.

(b) What is the pH of the buffer system after the addition of 0.10 mole of gaseous HCl to $1.0\ \mathrm{L}$ of the solution? Assume that the volume of the solution does not change when the HCl is added.

SOLUTION

Strategy

(a) The K_a of CH_3COOH is 1.8×10^{-5}

(b) It is helpful to make a sketch of the changes that occur in this case:

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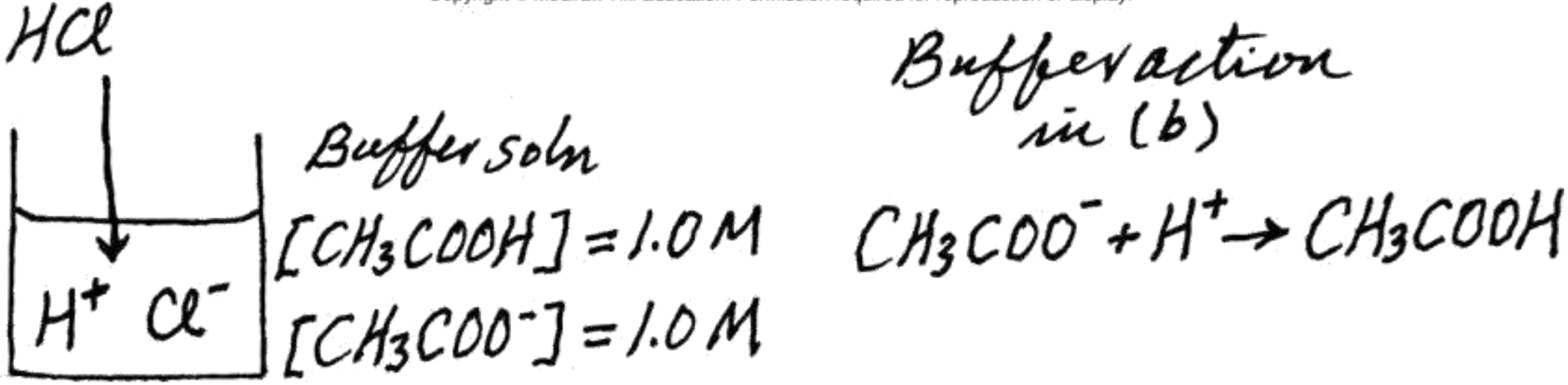


SOLUTION (CONT'D)

Solution (a) We summarize the concentrations of the species at equilibrium as follows:

- $CH_3COOH(aq) \rightleftarrows H^+(aq) + \ CH_3COO^-(aq)$

Initial (M):	1.0	0	1.0
Change (M):	$-x$	$+x$	$+x$
Equilibrium(M)	$1.0 - x$	x	$1.0 + x$

- $$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$
- $$1.8 \times 10^{-5} = \frac{(x)(1.0+x)}{(1.0-x)}$$

SOLUTION (CONT'D)

Assuming $1.0 + x \approx 1.0$ and $1.0 - x \approx 1.0$, we obtain

$$1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)} \approx \frac{x(1.0)}{1.0}$$

or $\quad x = [\mathrm{H}^+] = 1.8 \mathrm{~x}\, 10^{-5}\, M$

Thus, $\quad \mathrm{pH} = -\log(1.8 \times 10^{-5}) = \mathbf{4.74}$

SOLUTION (CONT'D)

- (b) When HCl is added to the solution, the initial changes are

$$\mathrm{HCl}(aq) \quad \rightarrow \quad \mathrm{H}^{+}(aq) \qquad \mathrm{Cl}^{-}(aq)$$

Initial (mol):	0.10	0	0
Change (mol):	−0.10	+0.10	+0.10
Final(mol):	0	0.10	0.10

  - The Cl^{-} ion is a spectator ion in solution because it is the conjugate base of a strong acid. The H^{+} ions provided by the strong acid HCl react completely with the conjugate base of the buffer, which is $\mathrm{CH_3COO^{-}}$. At this point it is more convenient to work with moles rather than molarity. The reason is that in some cases the volume of the solution may change when a substance is added. A change in volume will change the molarity, but not the number of moles.

SOLUTION (CONT'D)

The neutralization reaction is summarized next:

- $CH_3COO^-(aq) \quad + \; H^+(aq) \quad \rightarrow CH_3COOH(aq)$

	$CH_3COO^-(aq)$	$H^+(aq)$	$CH_3COOH(aq)$
Initial (mol):	1.0	0.10	1.0
Change (mol):	−0.10	−0.10	+0.10
Final(mol):	0.90	0	1.1

- Finally, to calculate the pH of the buffer after neutralization of the acid, we convert back to molarity by dividing moles by 1.0 L of solution.

SOLUTION (CONT'D)

$$\mathrm{CH_3COOH}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CH_3\ COO^-}(aq)$$

$$K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.90 + x)}{(1.1 - x)}$$

Initial (M):	1.1	0	0.90
Change (M):	$-x$	$+x$	$+x$
Equilibrium(M):	$1.1 - x$	x	$0.90 + x$

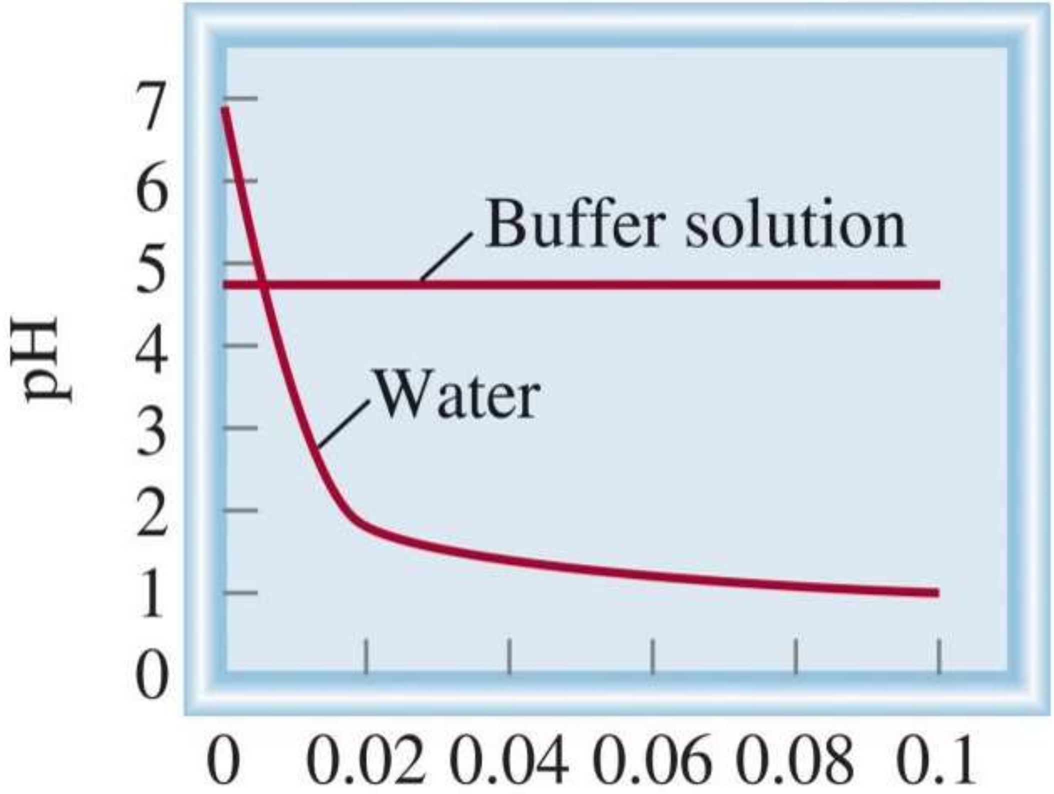
SOLUTION (CONT'D)

Assuming $0.90 + x \approx 0.90$ and $1.1 - x \approx 1.1$, we obtain

- $1.8 \times 10^{-5} = \frac{(x)(0.90+x)}{(1.1-x)} \approx \frac{x(0.90)}{1.1}$
- or
  - $x = [\mathrm{H}^+] = 2.2 \times 10^{-5}\ M$
- Thus,
  - $\mathrm{pH} = -\log(2.2 \times 10^{-5}) = \mathbf{4.66}$
- ***Check*** The pH decreases by only a small amount upon the addition of HCl. This is consistent with the action of a buffer solution.

ADDITION OF STRONG ACID TO A BUFFER

- $HCl \rightarrow H^+ + Cl^-$
- $HCl + CH_3COO^- \rightarrow CH_3COOH + Cl^-$



# of moles of HCl added

EXAMPLE

Describe how you would prepare a “phosphate buffer” with a pH of about 7.40.

SOLUTION

Strategy

For a buffer to function effectively, the concentrations of the acid component must be roughly equal to the conjugate base component. According to Equation (16.4), when the desired pH is close to the $\mathrm{p}K_\mathrm{a}$ of the acid, that is, when

$\mathrm{pH} \approx \mathrm{p}K_\mathrm{a}$,

$$\log \frac{[\text{conjugate base}]}{[\text{acid}]} \approx 0$$

or

- $\dfrac{[\text{conjugate base}]}{[\text{acid}]} \approx 1$

SOLUTION (CONT’D)

Solution

Because phosphoric acid is a triprotic acid, we write the three stages of ionization as follows. The K_a values are obtained from Table 15.5 and the $\mathrm{p}K_\mathrm{a}$ values are found by applying Equation (16.3).

- $\mathrm{H_3PO_4}(aq)\ f\ \mathrm{H^+}(aq) + \mathrm{H_2PO_4^-}(aq) \quad K_{\mathrm{a}_1} = 7.5 \times 10^{-3}; \mathrm{p}K_{\mathrm{a}_1} = 2.12$
- $\mathrm{H_2PO_4^-}(aq)\ f\ \mathrm{H^+}(aq) + \mathrm{HPO_4^{2-}}(aq) \quad K_{\mathrm{a}_2} = 6.2 \times 10^{-8}; \mathrm{p}K_{\mathrm{a}_2} = 7.21$
- $\mathrm{HPO_4^{2-}}(aq)\ f\ \mathrm{H^+}(aq) + \mathrm{PO_4^{3-}}(aq) \quad K_{\mathrm{a}_3} = 4.8 \times 10^{-13}; \mathrm{p}K_{\mathrm{a}_3} = 12.32$

SOLUTION (CONT'D)

The most suitable of the three buffer systems is $HPO_4^{2-}/H_2PO_4^-$, because the pK_a of the acid $H_2PO_4^-$ is closest to the desired pH. From the Henderson-Hasselbalch equation we write

- $pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$
- $7.40 = 7.21 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$
- $\log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.19$

SOLUTION (CONT'D)

Taking the antilog, we obtain

$$\frac{[\mathrm{HPO_4^{2-}}]}{[\mathrm{H_2PO_4^-}]} = 10^{0.19} = 1.5$$

Thus, one way to prepare a phosphate buffer with a pH of 7.40 is to dissolve disodium hydrogen phosphate $(\mathrm{Na_2HPO_4})$ and sodium dihydrogen phosphate $(\mathrm{Na_2HPO_4})$ in a mole ratio of $1.5{:}\,1.0$ in water. For example, we could dissolve $1.5\ \mathrm{moles}$ of $\mathrm{Na_2HPO_4}$and $1.0\ \mathrm{mole}$ of $\mathrm{Na_2HPO_4}$ in enough water to make up a $1-\mathrm{L}$ solution.

COMMON ION EFFECT (LATE CH15)

- The common ion effect is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

- The presence of a common ion suppresses the ionization of a weak acid or a weak base. (LeChatelier!)

Consider mixture of CH_3COONa (strong electrolyte) and CH_3COOH (weak acid).

$$CH_3COONa(s) \rightarrow Na^+(aq) + \boxed{CH_3COO^-(aq)}$$

$$CH_3COOH(aq) \rightleftarrows H^+(aq) + \boxed{CH_3COO^-(aq)}$$

$$\xleftarrow{\hspace{8em}}$$

common ion

HENDERSON-HASSELBALCH EQUATION

Consider mixture of salt NaA and weak acid HA.

$$\mathrm{NaA}(s) \rightarrow \mathrm{Na}^+(aq) + \mathrm{A}^-(aq)$$

$$\mathrm{HA}(aq) \rightleftarrows \mathrm{H}^+(aq) + \mathrm{A}^-(aq)$$

$$K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$[\mathrm{H}^+] = \frac{K_\mathrm{a}[\mathrm{HA}]}{[\mathrm{A}^-]}$$

Henderson-Hasselbalch equation

$$-\log[\mathrm{H}^+] = -\log K_\mathrm{a} - \log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

$$-\log[\mathrm{H}^+] = -\log K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

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

EXAMPLE

(a) Calculate the pH of a $0.20\ M\ \mathrm{CH_3COOH}$ solution.

(b) What is the pH of a solution containing both $0.20\ M\ \mathrm{CH_3COOH}$ and $0.30\ M\ \mathrm{CH_3COONa}$? The K_a of $\mathrm{CH_3COOH}$ is 1.8×10^{-5}.

SOLUTION

Strategy

(a) We calculate $[\mathrm{H}^+]$ and hence the pH of the solution by following the procedure in Example 15.8.

(b) $\mathrm{CH_3COOH}$ is a weak acid ($\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+}$), and $\mathrm{CH_3COONa}$ is a soluble salt that is completely dissociated in solution ($\mathrm{CH_3COONa} \rightarrow \mathrm{Na^+} + \mathrm{CH_3COO^-}$). The common ion here is the acetate ion, $\mathrm{CH_3COO^-}$. At equilibrium, the major species in solution are $\mathrm{CH_3COOH}$, $\mathrm{CH_3COO^-}$, $\mathrm{Na^+}$, $\mathrm{H^+}$, and $\mathrm{H_2O}$. The $\mathrm{Na^+}$ ion has no acid or base properties and we ignore the ionization of water. Because K_a is an equilibrium constant, its value is the same whether we have just the acid or a mixture of the acid and its salt in solution. Therefore, we can calculate $[\mathrm{H^+}]$ at equilibrium and hence pH if we know both $\mathrm{CH_3COOH}$ and $[\mathrm{CH_3COO^-}]$ at equilibrium.

SOLUTION (CONT’D)

Solution

(a) In this case, the changes are

- $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

Initial (M):	0.20	0	0
Change (M):	$-x$	$+x$	$+x$
Equilibrium(M):	$0.20 - x$	x	x

- $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$
- $1.8 \times 10^{-5} = \frac{x^2}{0.20-x}$

SOLUTION (CONT’D)

Assuming $0.20 - x \approx 0.20$, we obtain

$$1.8 \times 10^{-5} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

or

$$x = [\mathrm{H}^+] = 1.9 \times 10^{-3}\ M$$

Thus,

$$\mathrm{pH} = -\log(1.9\ \mathrm{x}\ 10^{-3}) = \mathbf{2.72}$$

SOLUTION (CONT'D)

Sodium acetate is a strong electrolyte, so it dissociates completely in solution:

- $CH_3COONa(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$
- $0.30\ M \qquad 0.30\ M$

- The initial concentrations, changes, and final concentrations of the species involved in the equilibrium are

- $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

Initial (M):	0.20	0	0.30
Change (M):	$-x$	$+x$	$+x$
Equilibrium(M):	$0.20 - x$	x	$0.30 + x$

SOLUTION (CONT'D)

From Equation (16.1),

- $$K_a = \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$
- $$1.8 \times 10^{-5} = \frac{(x)(0.30+x)}{0.20-x}$$
- Assuming that $0.30 + x \approx 0.30$ and $0.20 - x \approx 0.20$, we obtain
- $$1.8 \times 10^{-5} = \frac{(x)(0.30+x)}{0.20-x} \approx \frac{(x)(0.30)}{0.20}$$

or

$$x = [\mathrm{H^+}] = 1.2 \text{ x } 10^{-5}\ M$$

Thus,

$$\mathrm{pH} = -\log[\mathrm{H^+}]$$

$$= -\log(1.2 \text{ x}10^{-5}) = \mathbf{4.92}$$

SOLUTION (CONT'D)

Check

Comparing the results in (a) and (b), we see that when the common ion $(\mathrm{CH_3COO^-})$ is present, according to Le Châtelier's principle, the equilibrium shifts from right to left. This action decreases the extent of ionization of the weak acid.

Consequently, fewer $\mathrm{H^+}$ ions are produced in (b) and the pH of the solution is higher than that in (a). As always, you should check the validity of the assumptions.

CH. 14 OUTLINE

14.1 Brønsted-Lowry Acids and Bases

14.2 pH and pOH

14.3 Relative Strengths of Acids and Bases

14.4 Hydrolysis of Salt Solutions

14.5 Polyprotic Acids

14.6 Buffers

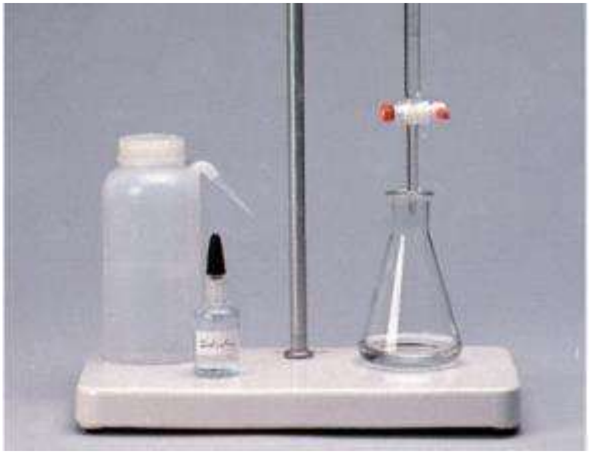
14.7 Acid-Base Titrations

TITRATIONS

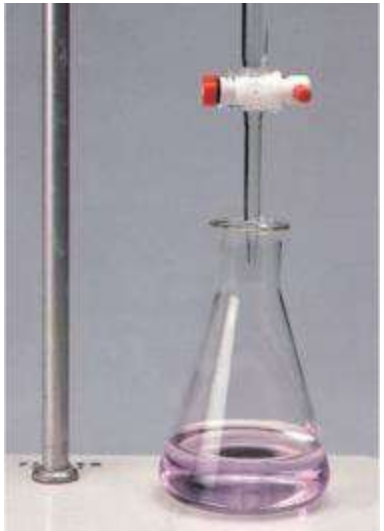
In a titration, a solution of accurately known concentration is gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Equivalence point – *the point at which the reaction is complete*

Indicator – substance that changes color at (or near) the equivalence point



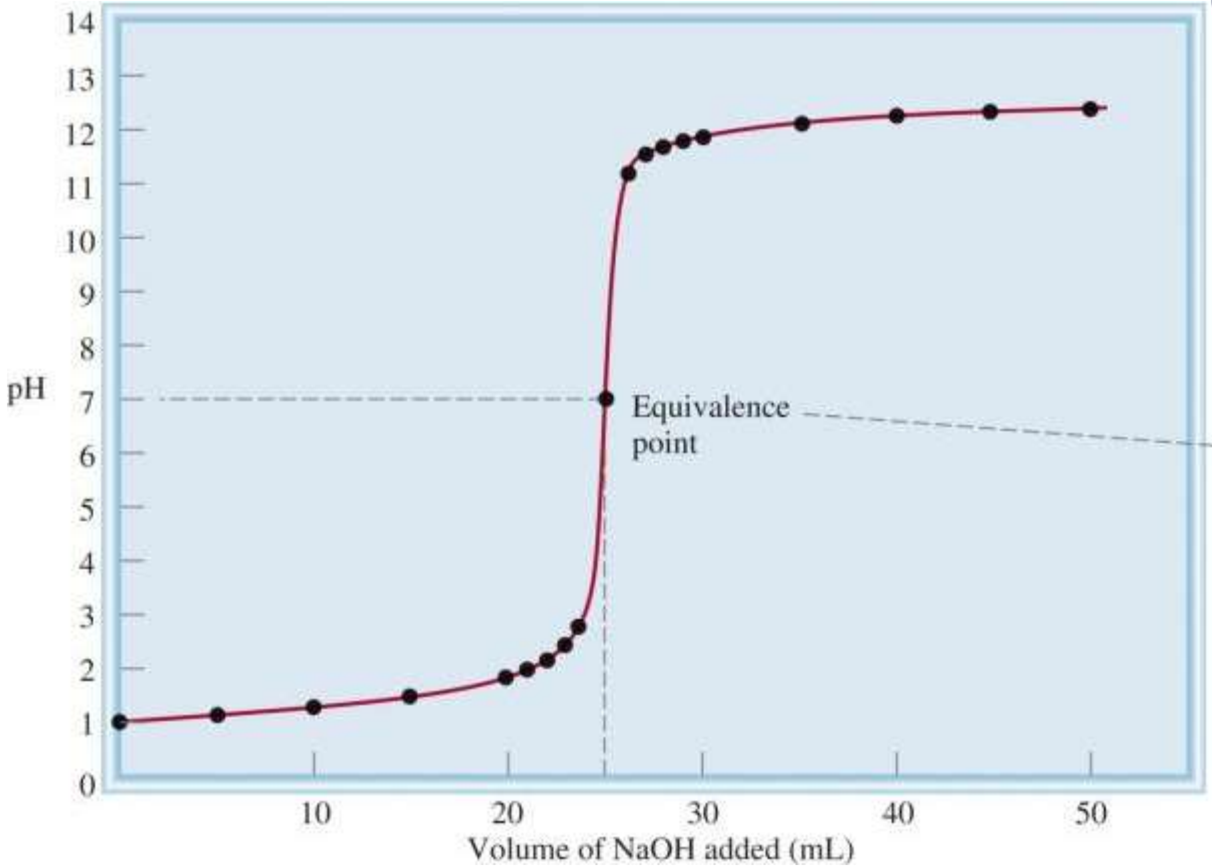
Slowly add base
to unknown acid
UNTIL
the indicator
changes color
(pink)



STRONG ACID - STRONG BASE TITRATIONS

$$NaOH(aq) + HCl(aq) \rightarrow H_2O(l) + NaCl(aq)$$

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$



Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

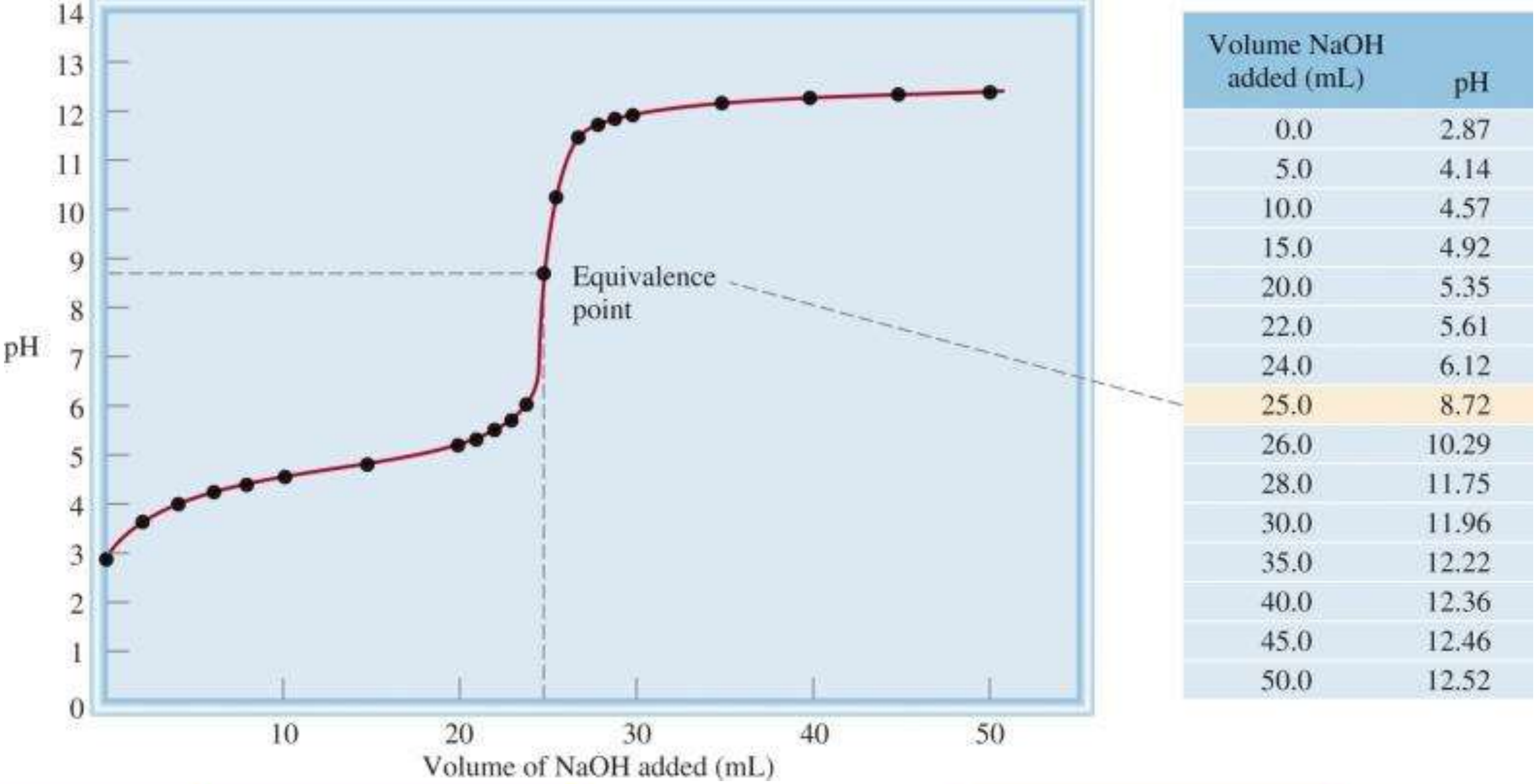
WEAK ACID - STRONG BASE TITRATIONS

$$\mathrm{CH_3COOH}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{CH_3COONa}(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{CH_3COOH}\,(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l)$$ (net ionic)

At equivalence point ($\mathrm{pH} > 7$)
(a weak acid has a strong conj. base…):

$$\mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l) \rightleftarrows \mathrm{OH^-}(aq) + \mathrm{CH_3COOH}(aq)$$



Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

EXAMPLE

Calculate the pH in the titration of 25.0 mL of 0.100 *M* acetic acid by sodium hydroxide after the addition to the acid solution of

(a) 10.0 mL of 0.100 M NaOH

(b) 25.0 mL of 0.100 M NaOH

(c) 35.0 mL of 0.100 M NaOH

SOLUTION

Strategy

The reaction between $\mathrm{CH_3COOH}$ and NaOH is

$$\mathrm{CH_3COOH}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{CH_3COONa}(aq) + \mathrm{H_2O}(l)$$

- We see that $1\ \mathrm{mol\ CH_3COOH} = 1\ \mathrm{mol\ NaOH}$. Therefore, at every stage of the titration we can calculate the number of moles of base reacting with the acid, and the pH of the
- solution is determined by the excess acid or base left over. At the equivalence point, however, the neutralization is complete and the pH of the solution will depend on the extent of the hydrolysis of the salt formed, which is $\mathrm{CH_3COONa}$.

SOLUTION (CONT'D)

Solution

(a)The number of moles of NaOH in $10.0\ \mathrm{mL}$ is

$$10.0\ \mathrm{mL} \times \frac{0.100\ \mathrm{mol\ NaOH}}{1\ \mathrm{L\ NaOH\ soln}} \times \frac{1\ \mathrm{L}}{1000\ \mathrm{mL}} = 1.00 \times 10^{-3}\ \mathrm{mol}$$

The number of moles of $\mathrm{CH_3COOH}$ originally present in $25.0\ \mathrm{mL}$ of solution is

$$25.0\ \mathrm{mL} \times \frac{0.100\ \mathrm{mol\ CH_3COOH}}{1\mathrm{L\ CH_3COOH\ soln}} \times \frac{1\ \mathrm{L}}{1000\ \mathrm{mL}} = 2.50 \times 10^{-3}\mathrm{mol}$$

We work with moles at this point because when two solutions are mixed, the solution volume increases. As the volume increases, molarity will change but the number of moles will remain the same.

SOLUTION (CONT'D)

The changes in number of moles are summarized next:

- $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$

	CH_3COOH	$NaOH$	CH_3COONa
Initial (mol):	2.50×10^{-3}	1.00×10^{-3}	0
Change (mol):	-1.00×10^{-3}	-1.00×10^{-3}	$+1.00 \times 10^{-3}$
Final (mol):	1.50×10^{-3}	0	1.00×10^{-3}

- At this stage we have a buffer system made up of CH_3COOH and CH_3COO^- (from the salt, CH_3COONa).

SOLUTION (CONT'D)

To calculate the pH of the solution, we write

$$K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{CH_3COO}^-]}{[\mathrm{CH_3COOH}]}$$

$$[\mathrm{H}^+] = \frac{[\mathrm{CH_3COOH}]K_\mathrm{a}}{[\mathrm{CH_3COO}^-]}$$

$$= \frac{(1.50 \times 10^{-3})(1.8 \times 10^{-5})}{1.00 \times 10^{-3}} = 2.7 \times 10^{-5}\ M$$

Therefore,

$$\mathrm{pH} = -\log(2.7 \text{ x } 10^{-5}) = \mathbf{4.57}$$

SOLUTION (CONT'D)

(b) These quantities (that is, $25.0\ \text{mL}$ of $0.100\ M\ \text{NaOH}$ reacting with $25.0\ \text{mL}$ of $0.100\ M\ \text{CH}_3\text{COOH}$) correspond to the equivalence point. The number of moles of NaOH in 25.0 mL of the solution is

- $25.0\ \text{mL} \times \frac{0.100\ \text{mol NaOH}}{1\text{LNaOH soln}} \times \frac{1\text{L}}{1000\text{mL}} = 2.50 \times 10^{-3}\ \text{mol}$

- The changes in number of moles are summarized next:

- $\text{CH}_3\text{COOH}(aq) + \text{NaOH}(aq) \longrightarrow \text{CH}_3\text{COONa}(aq) + \text{H}_2\text{O}(l)$

Initial (mol):	$2.50\ \text{x}10^{-3}$	$2.50\text{x}10^{-3}$	0
Change (mol):	$-2.50\ \text{x}10^{-3}$	$-2.50\ \text{x}10^{-3}$	$+2.50\ \text{x}10^{-3}$
Final (mol):	0	0	$2.50\ \text{x}10^{-3}$

SOLUTION (CONT'D)

At the equivalence point, the concentrations of both the acid and the base are zero. The total volume is $(25.0 + 25.0)\ \mathrm{mL}$ or $50.0\ \mathrm{mL}$, so the concentration of the salt is

- $$[\mathrm{CH_3COONa}] = \frac{2.50\times10^{-3}\mathrm{mol}}{50.0\ \mathrm{mL}} \times \frac{1000\ \mathrm{mL}}{1\mathrm{L}}$$
- $$= 0.0500\ \mathrm{mol/L} = 0.0500\ M$$

- The next step is to calculate the pH of the solution that results from the hydrolysis of the $\mathrm{CH_3COO^-}$ ions.

SOLUTION (CONT'D)

Following the procedure described in Example 15.13 and looking up the base ionization constant (K_b) for $\mathrm{CH_3COO^-}$ in Table 15.3, we write

- $K_\mathrm{b} = 5.6 \times 10^{-10} = \frac{[\mathrm{CH_3COOH}][\mathrm{OH^-}]}{[\mathrm{CH_3COO^-}]} = \frac{x^2}{0.0500 - x}$
  - $x = [\mathrm{OH^-}] = 5.3 \times 10^{-6}\ M, \mathrm{pH} = \mathbf{8.72}$

SOLUTION (CONT'D)

(c) After the addition of $35.0\ \text{mL}$ of NaOH, the solution is well past the equivalence point. The number of moles of NaOH originally present is

- $35.0\ \text{mL} \times \frac{0.100\ \text{mol NaOH}}{1\ \text{L NaOH soln}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 3.50 \times 10^{-3}\ \text{mol}$

- The changes in number of moles are summarized next:
  - $\text{CH}_3\text{COOH}(aq) + \text{NaOH}(aq) \rightarrow \text{CH}_3\text{COONa}(aq) + \text{H}_2\text{O}(l)$

Initial (mol):	$2.50\ \text{x}10^{-3}$	$3.50\text{x}10^{-3}$	0
Change (mol):	$-2.50\ \text{x}10^{-3}$	$-2.50\ \text{x}10^{-3}$	$+2.50\ \text{x}10^{-3}$
Final (mol):	0	1.00×10^{-3}	$2.50\ \text{x}10^{-3}$

SOLUTION (CONT'D)

At this stage we have two species in solution that are responsible for making the solution basic: OH^- and CH_3COO^- (from CH_3COONa). However, because OH^- is a much stronger base than CH_3COO^-, we can safely neglect the hydrolysis of the CH_3COO^- ions and calculate the pH of the solution using only the concentration of the OH^- ions. The total volume of the combined solutions is $(25.0 + 35.0)\ \mathrm{mL}$ or $60.0\ \mathrm{mL}$, so we calculate OH^- concentration as follows:

$$[\mathrm{OH^-}] = \frac{1.00 \times 10^{-3}\ \mathrm{mol}}{60.0\ \mathrm{mL}} \times \frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}$$

$$= 0.0167\ \mathrm{mol/L} = 0.0167\ M$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log 0.0167 = 1.78$$

$$\mathrm{pH} = 14.00 - 1.78 = \mathbf{12.22}$$

STRONG ACID - WEAK BASE TITRATIONS

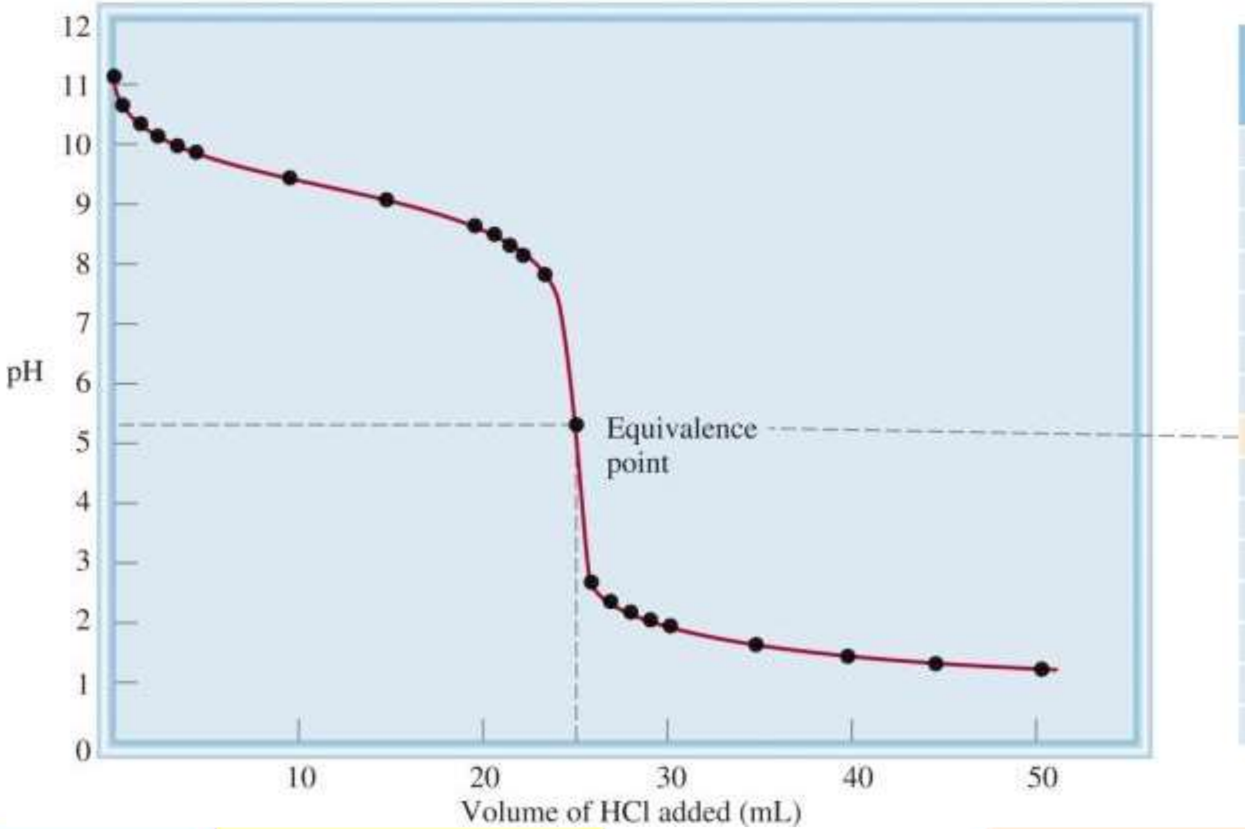
$$HCl\ (aq)\ + NH_3(aq) \rightarrow NH_4Cl\ (aq)$$

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)\ \text{(net ionic)}$$

At equivalence point (pH <7)

(a weak base has a strong conj. acid):

$$NH_4^+ + H_2O(l) \rightleftarrows NH_3(aq) + H^+(aq)$$



Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

EXAMPLE

Calculate the pH at the equivalence point when $25.0\ \mathrm{mL}$ of $0.100\ M\ \mathrm{NH_3}$ is titrated by a $0.100\ M\ \mathrm{HCl}$ solution.

SOLUTION

Strategy

The reaction between $\mathrm{NH_3}$ and HCl is

$$\mathrm{NH_3}(aq) + \mathrm{HCl}(aq) \rightarrow \mathrm{NH_4Cl}(aq)$$

We see that $1\ \mathrm{mol\ NH_3} = 1\ \mathrm{mol\ HCl}$. At the equivalence point, the major species in solution are the salt $\mathrm{NH_4Cl}$ (dissociated into $\mathrm{NH_4^+}$ and $\mathrm{Cl^-}$ ions) and $\mathrm{H_2O}$. First, we determine the concentration of $\mathrm{NH_4Cl}$ formed. Then we calculate the pH as a result of the $\mathrm{NH_4^+}$ ion hydrolysis. The $\mathrm{Cl^-}$ ion, being the conjugate base of a strong acid HCl, does not react with water. As usual, we ignore the ionization of water

SOLUTION (CONT'D)

Solution The number of moles of NH_3 in 25.0 mL of $0.100\ M$

solution is

- $$25.0 \text{ mL} \times \frac{0.100 \text{ mol NH}_3}{1 \text{ L NH}_3} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

- At the equivalence point the number of moles of HCl added equals the number of moles of NH_3. The changes in number of moles are summarized below:

- $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

Initial (mol):	2.50×10^{-3}	2.50×10^{-3}	0
Change (mol):	-2.50×10^{-3}	-2.50×10^{-3}	$+2.50 \times 10^{-3}$
Final (mol):	0	0	2.50×10^{-3}

SOLUTION (CONT'D)

At the equivalence point, the concentrations of both the acid and the base are zero. The total volume is $(25.0 + 25.0)\ \mathrm{mL}$, or $50.0\ \mathrm{mL}$, so the concentration of the salt is

$$[\mathrm{NH_4Cl}] = \frac{2.50 \times 10^{-3}\ \mathrm{mol}}{50.0\ \mathrm{mL}} \times \frac{1000\ \mathrm{mL}}{1\mathrm{L}}$$

$$= 0.0500\,\mathrm{mol/L} = 0.0500\mathrm{M}$$

The pH of the solution at the equivalence point is determined by the hydrolysis of $\mathrm{NH_4^+}$ ions.

SOLUTION (CONT'D)

Step 1: We represent the hydrolysis of the cation NH_4^+, and let x be the equilibrium concentration of NH_3 and H^+ ions in mol/L:

- $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$

Initial (*M*):	0.0500	0.000	0.000
Change (*M*):	-*x*	+*x*	+*x*
Equillibrium(*M*):	(0.0500-*x*)	*x*	*x*

SOLUTION (CONT'D)

Step 2: From Table 15.4 we obtain the K_a for $\mathrm{NH_4^+}$:

$$K_\mathrm{a} = \frac{[\mathrm{NH_3}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x}$$

Applying the approximation $0.0500 - x \approx 0.0500$, we get

$$5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

$$x = 5.3 \times 10^{-6}\ M$$

Thus, the pH is given by

$$\mathrm{pH} = -\log(5.3 \times 10^{-6})$$

$$= \mathbf{5.28}$$

SOLUTION (CONT’D)

Check

Note that the pH of the solution is acidic. This is what we would expect from the hydrolysis of the ammonium ion.

ACID-BASE INDICATORS

$$\mathrm{HIn}(aq) \rightleftarrows \mathrm{H}^+(aq) + \mathrm{In}^-(aq)$$

$$\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \geq 10 \text{ Color of acid } (\mathrm{HIn}) \text{ predominates}$$

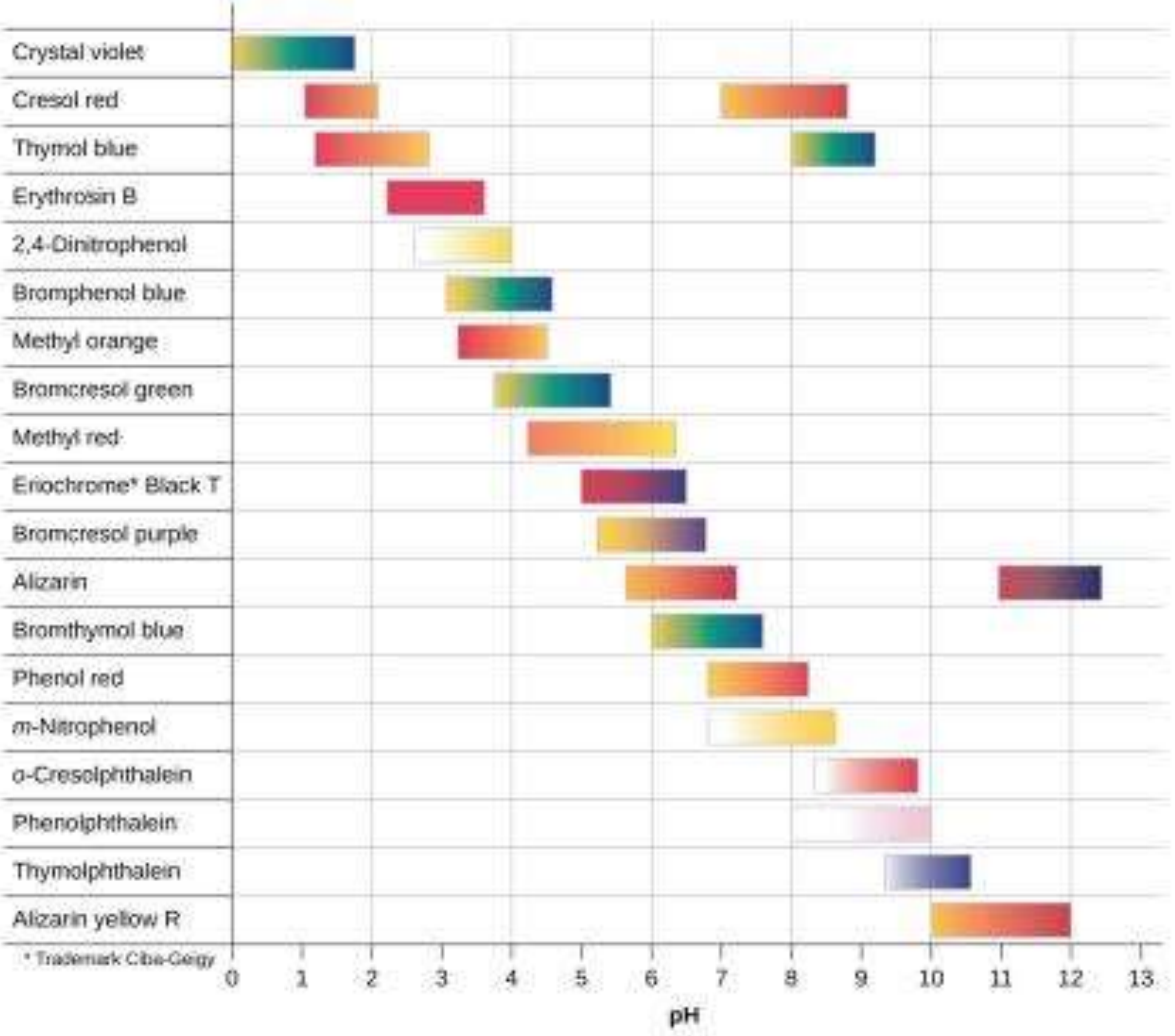
$$\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \leq 10 \text{ Color of conjugate base } (\mathrm{In}^-) \text{ predominates}$$

Table 16.1 Some Common Acid-Base Indicators

Indicator	In Acid *Color*	In Base *Color*	pH Range*
Thymol blue	Red	yellow	1.2-2.8
Bromophenol blue	Yellow	Blueish purple	3.0-4.6
Methyl orange	Orange	Yellow	3.1-4.4
Methyl red	Red	Yellow	4.2-6.3
Chlorophenol blue	Yellow	Red	4.8-6.4
Bromothymol blue	Yellow	Blue	6.0-7.6
Cresol red	Yellow	Red	7.2-8.8
phenolphthalein	Colorless	Reddish pink	8.3-10.0

*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

FIGURE 14.22



This chart illustrates the ranges of color change for several acid-base indicators.

SOLUTIONS OF RED CABBAGE EXTRACT

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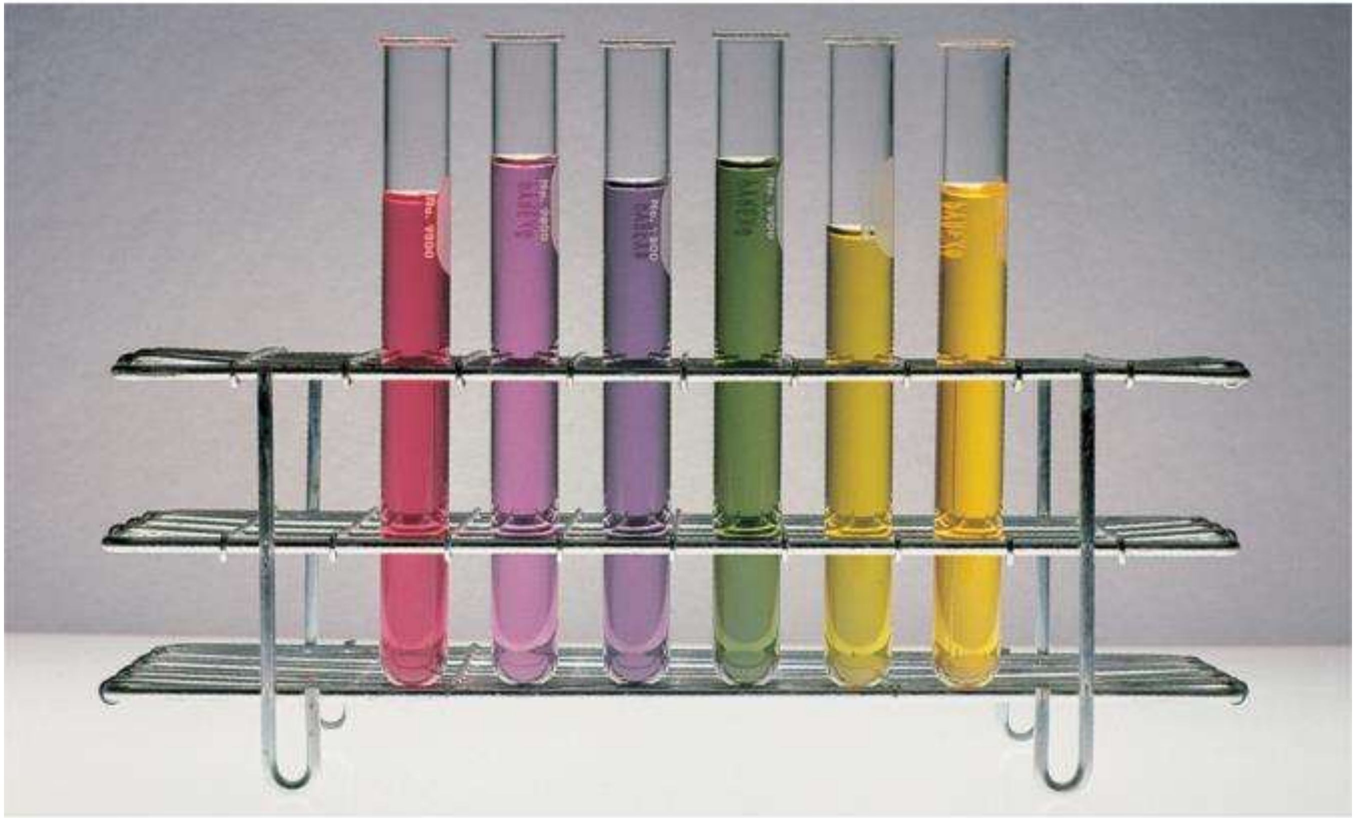

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$\xrightarrow{\hspace{2em}}$ pH $\xrightarrow{\hspace{2em}}$

INDICATORS IN THE TITRATION OF A STRONG ACID WITH A STRONG BASE

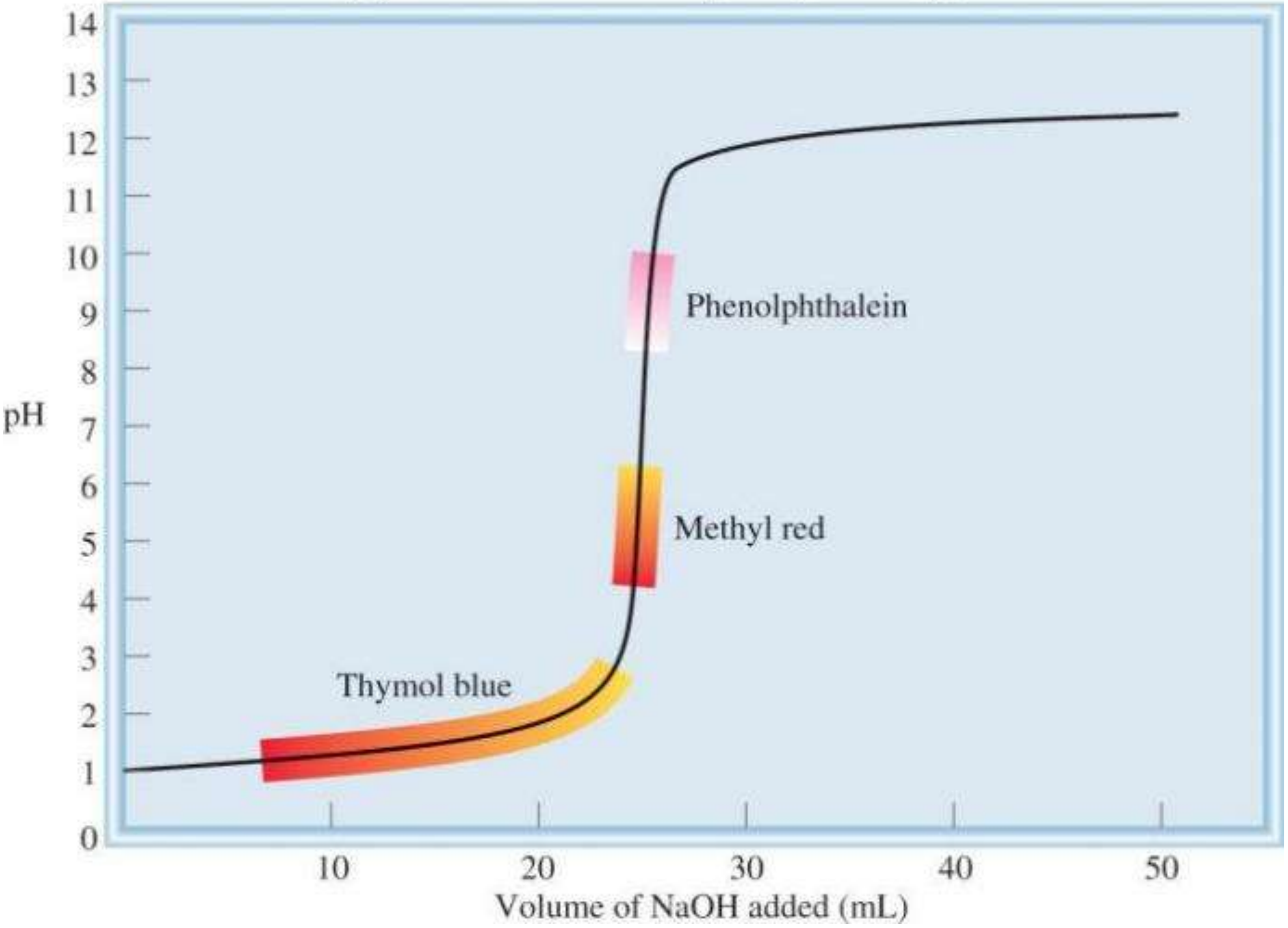
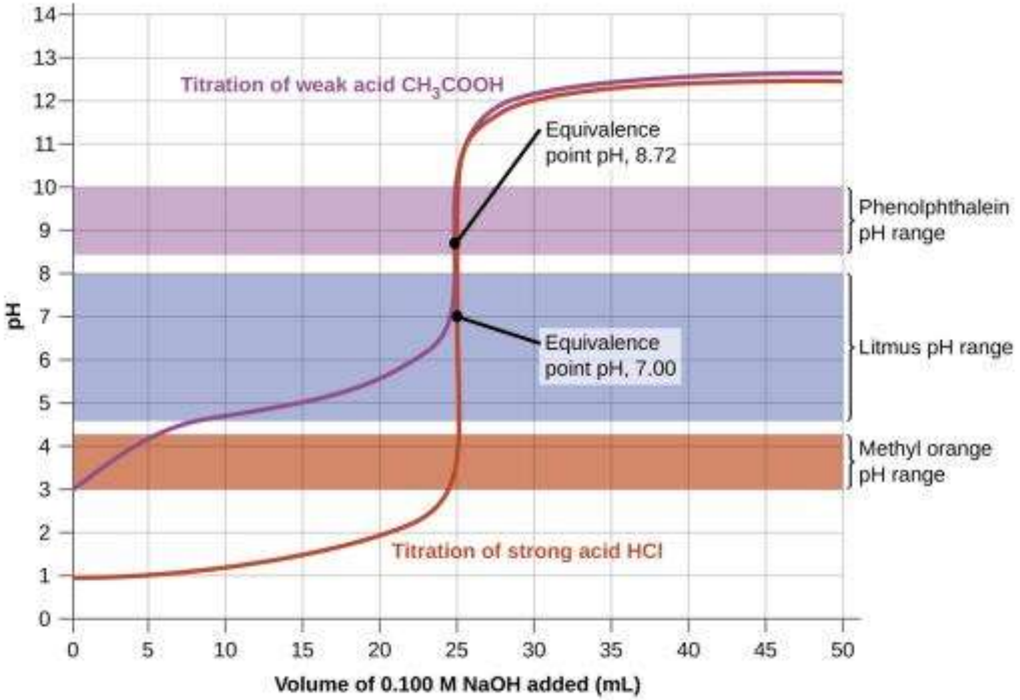


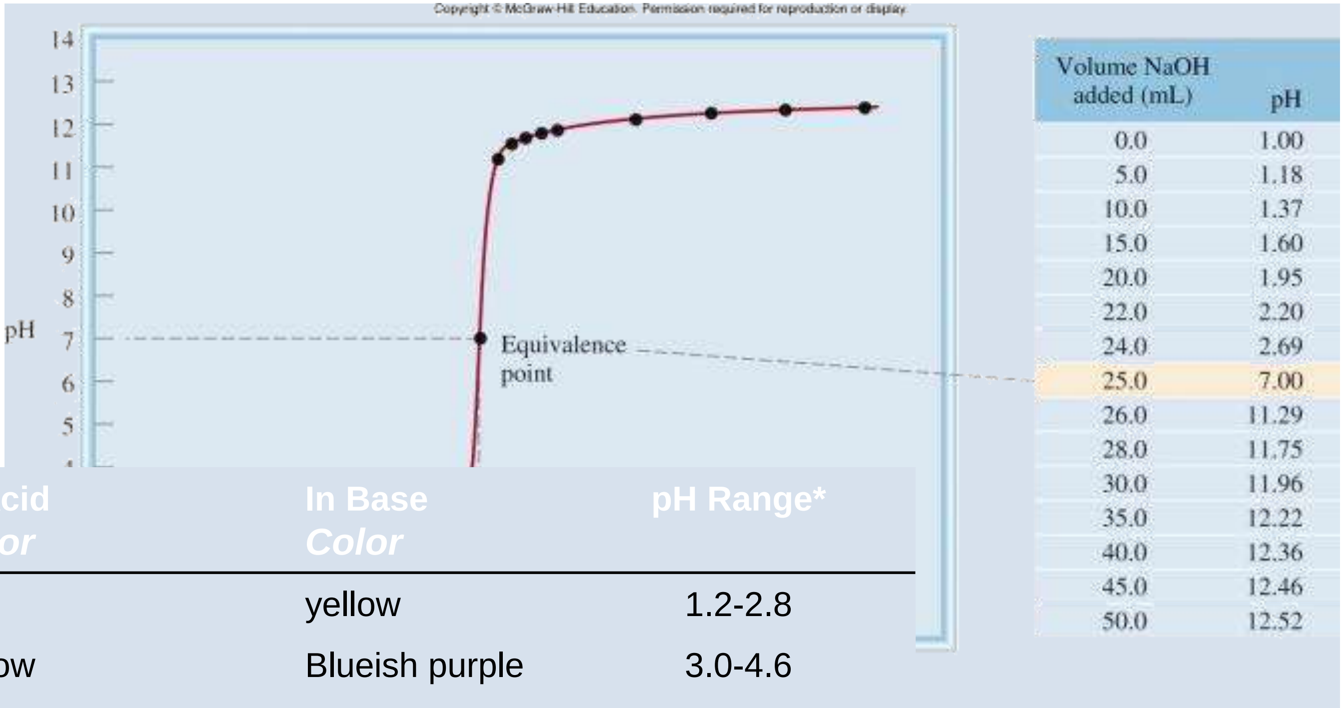
FIGURE 14.23



- The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

EXAMPLE

Which indicator or indicators listed would you use for the acid-base titrations shown in this figure?



Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Indicator	In Acid *Color*	In Base *Color*	pH Range*
Thymol blue	Red	yellow	1.2-2.8
Bromophenol blue	Yellow	Blueish purple	3.0-4.6
Methyl orange	Orange	Yellow	3.1-4.4
Methyl red	Red	Yellow	4.2-6.3
Chlorophenol blue	Yellow	Red	4.8-6.4
Bromothymol blue	Yellow	Blue	6.0-7.6
Cresol red	Yellow	Red	7.2-8.8
phenolphthalein	Colorless	Reddish pink	8.3-10.0

SOLUTION

Strategy

The choice of an indicator for a particular titration is based on the fact that its pH range for color change must overlap the steep portion of the titration curve. Otherwise we cannot use the color change to locate the equivalence point.

SOLUTION (CONT’D)

Solution

Near the equivalence point, the pH of the solution changes abruptly from 4 to 10. Therefore, all the indicators except thymol blue, bromophenol blue, and methyl orange are suitable for use in the titration.

Chapter 14 Acid-base Equilibria

HW problems: 3, 5, 9, 17, 19, 25, 33, 53, 57, 69, 77, 79, 91, 101