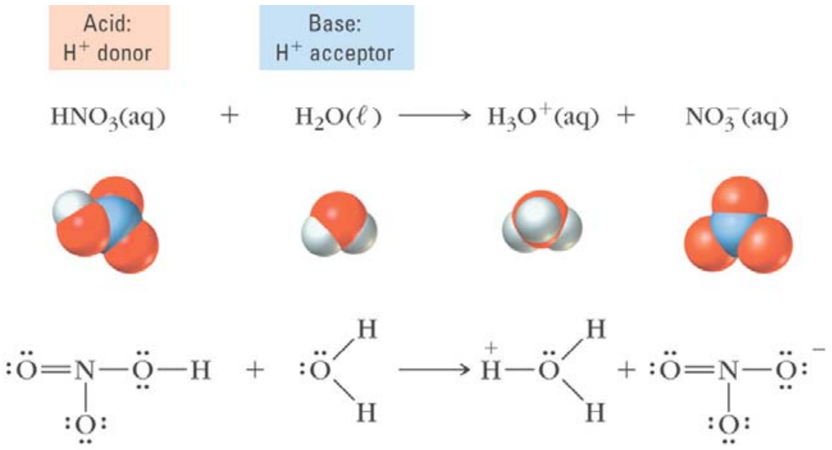
Acid-Base Chemistry

- There are a couple of ways to define acids and bases
- Brønsted-Lowry acids and bases
  - Acid: H^+ ion donor
  - Base: H^+ ion acceptor
- Lewis acids and bases
  - Acid: electron pair acceptor
  - Base: electron pair donor

Brønsted-Lowry Acids & Bases



$$HNO_3(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

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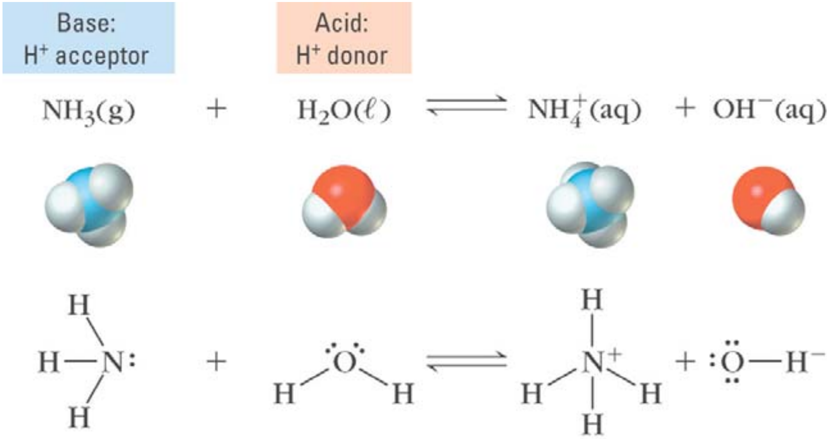
Brønsted-Lowry Acids & Bases



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Brønsted-Lowry Acids & Bases

- In most acid-base systems, water may play a role as either an acid (H^+ donor) or a base (H^+ acceptor)

Water as an acid

$H_2O(\ell) + B(aq) \leftrightarrow OH^-(aq) + HB^+(aq)$

Water as a base

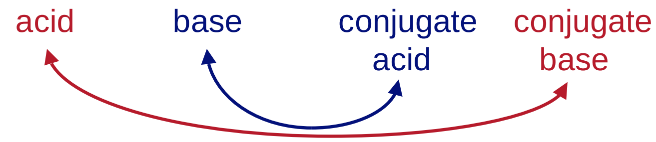
$H_2O(\ell) + HA(aq) \leftrightarrow H_3O^+(aq) + A^-(aq)$

Conjugate Acids & Bases

- Acids react with bases and *vice versa*
- All acids and bases come with a *conjugate* pair—a base or acid, respectively, that is formed in conjunction with the original species

Examples

$HCl(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + Cl^-(aq)$



acid

base

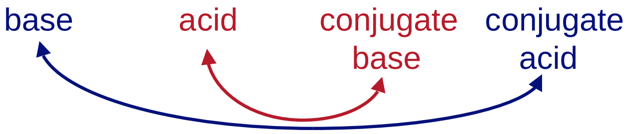
conjugate acid

conjugate base

Conjugate Acids & Bases

Examples

$NaOH(aq) + H_2O(\ell) \leftrightarrow OH^-(aq) + H_2O(\ell) + Na^+(aq)$



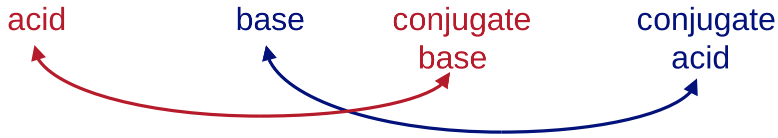
base

acid

conjugate base

conjugate acid

$CH_3COOH(aq) + H_2O(\ell) \leftrightarrow CH_3COO^-(aq) + H_3O^+(aq)$



acid

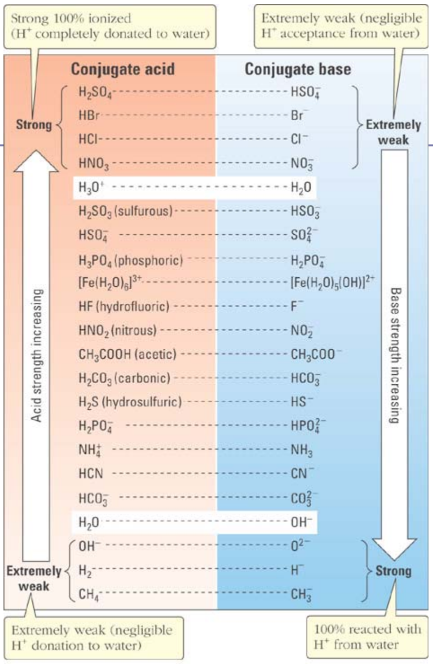
base

conjugate base

conjugate acid

Strengths of Acids and Bases

- Strong acids donate H^+ ions more easily
  - The stronger the acid, the weaker the conjugate base associated with that acid
- Strong bases accept H^+ ions more easily
  - The stronger the base, the weaker the conjugate acid associated with that base



Strong 100% ionized (H^+ completely donated to water)

Extremely weak (negligible H^+ acceptance from water)

Conjugate acid	Conjugate base
H_2SO_4	HSO_4^-
HBr	Br^-
HCl	Cl^-
HNO_3	NO_3^-
H_3O^+	H_2O
H_2SO_3 (sulfurous)	HSO_3^-
HSO_4^-	SO_4^{2-}
H_3PO_4 (phosphoric)	$H_2PO_4^-$
$[Fe(H_2O)_6]^{3+}$	$[Fe(H_2O)_5(OH)]^{2+}$
HF (hydrofluoric)	F^-
HNO_2 (nitrous)	NO_2^-
CH_3COOH (acetic)	CH_3COO^-
H_2CO_3 (carbonic)	HCO_3^-
H_2S (hydrosulfuric)	HS^-
$H_2PO_4^-$	HPO_4^{2-}
NH_4^+	NH_3
HCN	CN^-
HCO_3^-	CO_3^{2-}
H_2O	OH^-
OH^-	O^{2-}
H_2	H^-
CH_4	CH_3^-

Extremely weak (negligible H^+ donation to water)

100% reacted with H^+ from water

Strengths of Acids and Bases

- Stronger acids will always react to form weaker conjugate bases
- Stronger bases will always react to form weaker conjugate acids

Example

$H_2SO_4(aq) + NaOH(aq) + H_2O(\ell) \leftrightarrow ???$

sulfuric acid can react with either OH^- or H_2O—which would it prefer?

$H_2SO_4(aq) + OH^-(aq) \leftrightarrow HSO_4^-(aq) + H_2O(\ell)$ preferred reaction

$H_2SO_4(aq) + H_2O(\ell) \leftrightarrow HSO_4^-(aq) + H_3O^+(aq)$

Autoionization of Water

- Water always undergoes some degree of dissociation to form H_3O^+ ions and OH^- ions

  $2\ H_2O(\ell) \leftrightarrow H_3O^+(aq) + OH^-(aq)$
- The equilibrium constant for this process at 25 °C is:

  $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$
- In pure water

  $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M

Autoionization of Water

- K_w is temperature dependent—it increases with increasing temperature

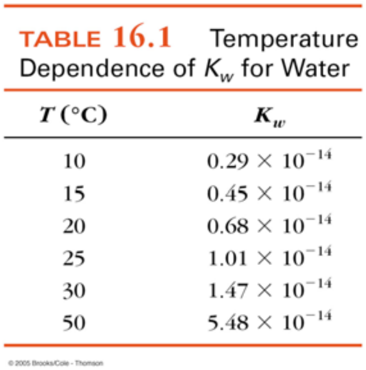


TABLE 16.1 Temperature Dependence of K_w for Water

T (°C)	K_w
10	0.29×10^{-14}
15	0.45×10^{-14}
20	0.68×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
50	5.48×10^{-14}

Autoionization of Water

<u>Example</u>

Determine $[H_3O^+]$ in a 0.053 M NaOH solution

Step 1: since NaOH is a strong base, dissociation is complete

$\therefore$ $[OH^-] = 0.053$ M

Step 2: Use K_w to calculate $[H_3O^+]$

$$K_w = [H_3O^+][OH^-] = 1.0 \text{ x } 10^{-14}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \text{ x } 10^{-14}}{0.053} = 1.9 \text{ x } 10^{-13} \text{ M}$$

The pH Scale

- pH is a measure of the hydronium ion content of a solution
- pH is defined as:

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

  log is log base 10, not ln (natural log)

  $[H_3O^+]$ is given in molar units (M)
- pH of pure water ($[H_3O^+] = 1.0 \times 10^{-7}$ M):

  pH = $-\log(1.0\times10^{-7}) = 7.0$
- pH of last example ($[H_3O^+] = 1.9 \times 10^{-13}$ M):

  pH = $-\log(1.9\times10^{-13}) = 12.7$

The pH Scale

- Neutral is defined as the pH of pure water:

  pH = 7
- Acidic solutions have pH lower than 7:

  pH < 7 ⇒ acidic
- Basic solutions have pH larger than 7:

  pH > 7 ⇒ basic

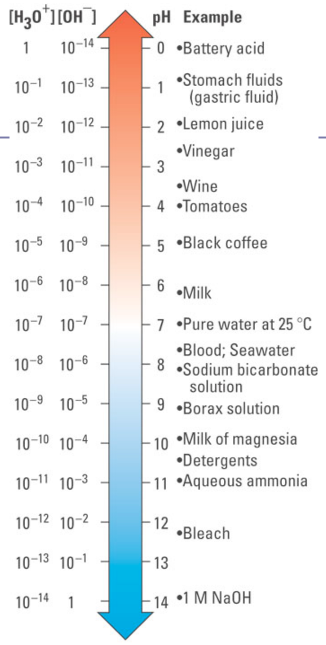


Figure 16-2

The pH Scale

- We can also use pOH to describe a solution
- pOH is defined as:

  pOH = -log[OH^-]
- The sum of pH and pOH must equal 14

  pH + pOH = 14

  assuming room temperature (25 °C)

The pH Scale

Example

Find $[H_3O^+]$ of a solution that has pOH = 9.37

Method 1: Calculate pH, then $[H_3O^+]$

Step 1: Determine pH

pH = 14 – pOH = 14.00 – 9.37 = 4.63

Step 2: Determine $[H_3O^+]$

$[H_3O^+] = 10^{-pH} = 10^{-4.63} = 2.34 \times 10^{-5}$ M

The pH Scale

Example (con't.)

Find $[H_3O^+]$ of a solution that has pOH = 9.37

Method 2: Calculate $[OH^-]$, then $[H_3O^+]$ using K_w

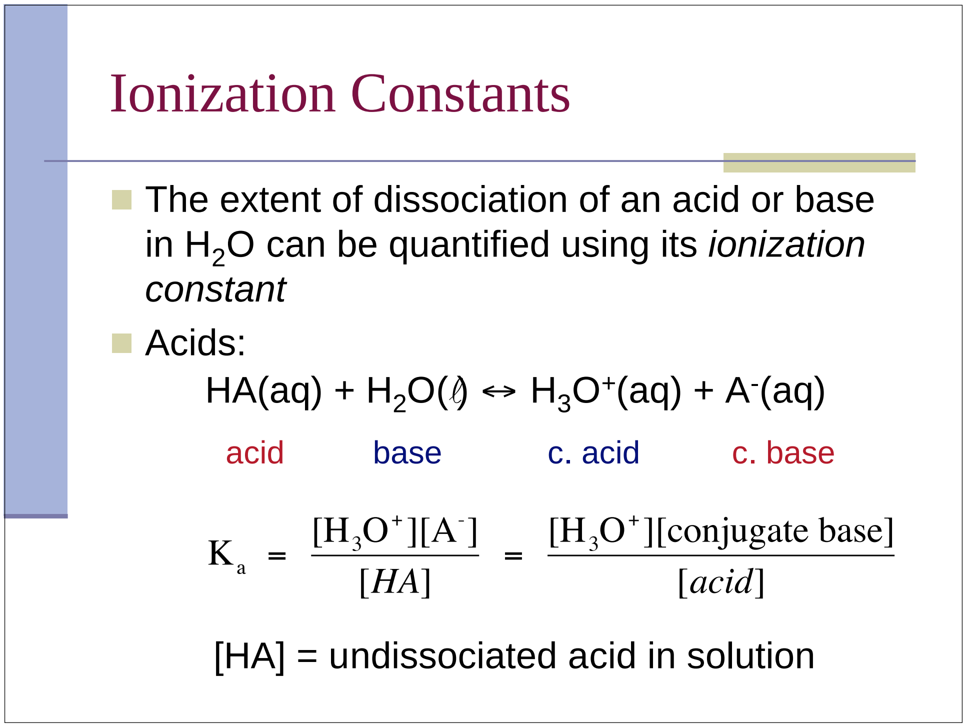
Step 1: Determine $[OH^-]$

$[OH^-] = 10^{-pOH} = 10^{-9.37} = 4.27 \times 10^{-10}$ M

Step 2: Determine $[H_3O^+]$ using K_w

$[H_3O^+] = K_w/[OH^-] = (1.0\times10^{-14})/(4.27\times10^{-10})$

$= 2.34 \times 10^{-5}$ M



Ionization Constants

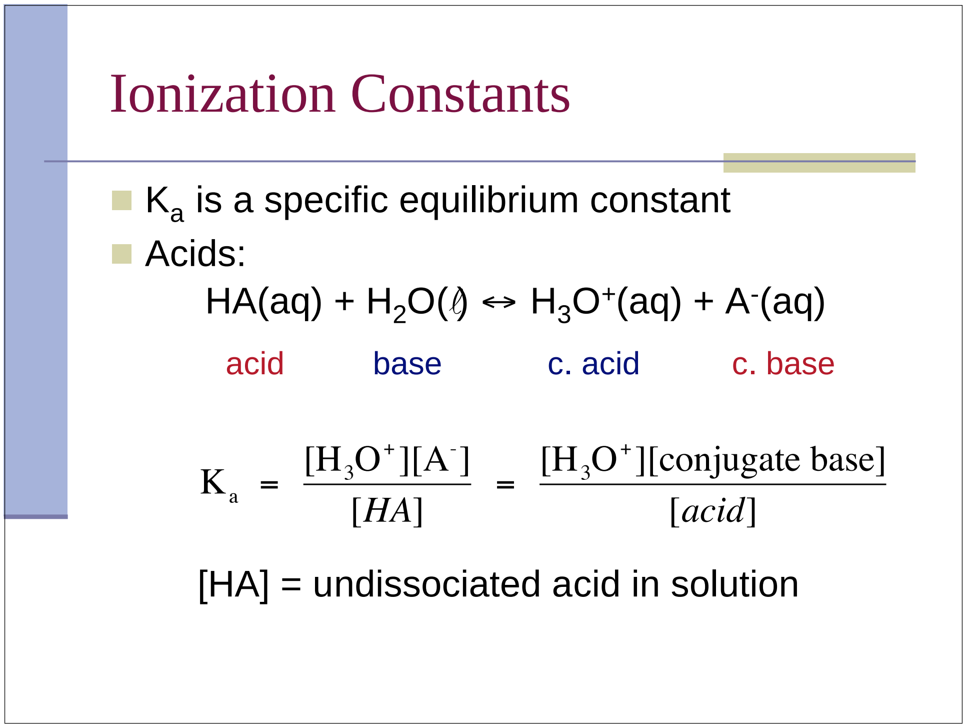
- The extent of dissociation of an acid or base in H_2O can be quantified using its *ionization constant*
- Acids:

$$HA(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + A^-(aq)$$

acid base c. acid c. base

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+][\text{conjugate base}]}{[acid]}$$

[HA] = undissociated acid in solution



Ionization Constants

- K_a is a specific equilibrium constant
- Acids:

$$HA(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + A^-(aq)$$

acid base c. acid c. base

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+][\text{conjugate base}]}{[acid]}$$

[HA] = undissociated acid in solution

Ionization Constants

Example:

Acetic acid has a $K_a = 1.8 \times 10^{-5}$

Determine the pH of a 0.2 M acetic acid solution

$CH_3COOH(aq) + H_2O(\ell) \leftrightarrow CH_3COO^-(aq) + H_3O^+(aq)$

We can approach this like any equilibrium problem from Chap. 15

	CH_3COOH	CH_3COO^-	H_3O^+
initial	0.2	0	0
Δ	-x	x	x
equil	.2 – x	x	x

Ionization Constants

Example (con't.):

$$K_a = 1.8 \times 10^{-5} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{.2 - x} \quad \Rightarrow \quad x = 0.0019 \text{ M}$$

pH = $-\log[H_3O^+] = -\log(.0019) = 2.7$

Ionization Constants

- K_b is a specific equilibrium constant for bases
- Bases:

$$B(aq) + H_2O(\ell) \leftrightarrow HB^+(aq) + OH^-(aq)$$

base acid c. acid c. base

$$K_b = \frac{[HB^+][OH^-]}{[B]} = \frac{[OH^-][\text{conjugate acid}]}{[base]}$$

[B] = undissociated base in solution

Ionization Constants

Example:

Determine [B] in a 1.82×10^{-3} M solution of NH_3

$$NH_3(aq) + H_2O(\ell) \leftrightarrow NH_4^+(aq) + OH^-(aq)$$

	NH_3	NH_4^+	OH^-
initial	$1.82\text{x}10^{-3}$	0	0
Δ	-x	x	x
equil	$1.82\text{x}10^{-3} - x$	x	x

Ionization Constants

Example:

$NH_3(aq) + H_2O(\ell) \leftrightarrow NH_4^+(aq) + OH^-(aq)$

$$K_b = 1.8x10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{1.82x10^{-3} - x}$$

$x = 1.72 \times 10^{-4}$ M = $[NH_4^+]$ = $[OH^-]$

$[NH_3]$ = 1.82×10^{-3} M – 1.72×10^{-4} M

= 1.65×10^{-3} M

Polyprotic Acids

- Some acids contain more than one hydrogen atom that may be donated to form H^+ ion
- These are called *polyprotic acids*
- Examples include:

H_2SO_4	sulfuric acid (2 H^+ ions)
H_3PO_4	phosphoric acid (3 H^+ ions)
H_2CO_3	carbonic acid (2 H^+ ions)

Polyprotic Acids

- Each H atom has a unique K_a associated with its release to form H^+ ion
- Consider phosphoric acid:

$H_3PO_4(aq) + H_2O(\ell) \leftrightarrow H_2PO_4^-(aq) + H_3O^+(aq)$ 1st

$K_{a1} = 7.5 \times 10^{-3}$

$H_2PO_4^-(aq) + H_2O(\ell) \leftrightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$ 2nd

$K_{a2} = 6.2 \times 10^{-8}$

$HPO_4^{2-}(aq) + H_2O(\ell) \leftrightarrow PO_4^{3-}(aq) + H_3O^+(aq)$ 3rd

$K_{a3} = 3.6 \times 10^{-13}$

- The first H atom is easiest to pull off, so it has the higher K_a value

Strengths of Acids

- Acid strength is determined by a combination of factors:
  - Bond polarity—the H-A bond must be polar in order for the H atom to be transferred to water as H^+

    The H atom in CH_4 is non-acidic because the C-H bond is not polar

    The H-Cl bond in HCl is polar, and HCl is a strong acid

Strengths of Acids

- Acid strength is determined by a combination of factors:
  - Bond strength—the stronger the bond, the weaker the acid—it is harder to pull away the H atom to form H^+

Acid	Bond Energy	K_a
HF	617 kJ/mol	7.2×10^{-4}
HCl	427 kJ/mol	$\sim 10^{6}$
HBr	362 kJ/mol	$\sim 10^{8}$
HI	295 kJ/mol	$\sim 10^{9}$

Strengths of Acids

- Oxoacids are those with a H-O-Z linkage
  - Electronegativity of Z—the higher the electronegativity of Z, the stronger the acid

Acid	χ_Z	K_a
HOCl	3.0	3.5×10^{-8}
HOBr	2.8	2.5×10^{-9}
HOI	2.5	2.3×10^{-11}

Strengths of Acids

- Oxoacids are those with a H-O-Z linkage
  - The more O atoms attached to Z, the stronger the acid

Acid	O atoms	K_a
HOCl	1	3.5×10^{-8}
HOClO	2	1.1×10^{-2}
$HOClO_2$	3	$\sim 10^{3}$
$HOClO_3$	4	$\sim 10^{8}$

Relationship Between K_a and K_b

- The K_a of an acid and the K_b of its conjugate base are related:

$HA(aq) + H_2O(\ell) \leftrightarrow A^-(aq) + H_3O^+(aq)$

acid c. base

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

$A^-(aq) + H_2O(\ell) \leftrightarrow HA(aq) + OH^-(aq)$

base c. acid

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

Relationship Between K_a and K_b

- The K_a of an acid and the K_b of its conjugate base are related:
  - The product K_a x K_b = K_w

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

$$= [H_3O^+][OH^-] = K_w$$

This is true of any conjugate pair of acid and base

Salts of Acids and Bases

- When an acid and a base undergo an exchange reaction, the result is a salt and water:

  $HX(aq) + MOH(aq) \leftrightarrow MX(aq) + H_2O$

  acid base salt

- If a strong base is neutralized with a strong acid, the resulting solution contains only the salt

  $HCl(aq) + NaOH(aq) \leftrightarrow NaCl(aq) + H_2O(\ell)$

Salts of Acids and Bases

Determine the pH of 0.284 M solution of sodium acetate, $NaCH_3COO$

$NaCH_3COO(aq) + H_2O \leftrightarrow$

$Na^+(aq) + CH_3COOH(aq) + OH^-(aq)$

Complete ionic equation:

$Na^+(aq) + CH_3COO^-(aq) + H_2O \leftrightarrow$

$Na^+(aq) + CH_3COOH(aq) + OH^-(aq)$

$$K = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{K_w}{K_a} = 5.56 \text{ x } 10^{-10}$$

Salts of Acids and Bases

Determine the pH of 0.284 M solution of sodium acetate, $NaCH_3COO$

	$[CH_3COO^-]$	$[CH_3COOH]$	$[OH^-]$
initial	0.284	0	0
Δ	-x	x	x
equil	0.284 – x	x	x

$$5.56 \text{ x } 10^{-10} = \frac{x^2}{0.284 - x}$$

assume x is negligible

$$x^2 = 1.58 \text{ x } 10^{-10} \Rightarrow x = 1.26 \text{ x } 10^{-5} \text{ M} = [OH^-]$$

pOH = -log(1.26x10^{-5}) = 4.90 pH = 9.1

Salts of Acids and Bases

Weak acid and salt of a strong base:

- If stoichiometric amounts are combined, the solution will be slightly basic

Determine pH of a solution with 0.020 M NaOH and 0.020 M acetic acid

$CH_3COOH(aq) + NaOH(aq) \leftrightarrow NaCH_3COO(aq) + H_2O$

Complete ionic equation:

$CH_3COOH(aq) + Na^+(aq) + OH^-(aq)$
$\leftrightarrow Na^+(aq) + CH_3COO^-(aq) + H_2O$

Sodium is a spectator ion and does not actively participate in the reaction

---

Salts of Acids and Bases

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

	CH_3COOH	OH^-	CH_3COO^-
initial	0	0	0.020
Δ	x	x	-x
equil	x	x	0.020 – x

$$K = 1.8 \times 10^9 = \frac{[CH_3COO^-]}{[CH_3COOH][OH^-]} = \frac{0.020 - x}{x^2}$$

assume x is negligible

$$x^2 = \frac{0.020}{1.8 \times 10^9} = 1.11 \times 10^{-11} \qquad x = 3.33 \times 10^{-6}$$

Salts of Acids and Bases

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

$[OH^-] = [CH_3COOH] = 3.3 \times 10^{-6}$ M

pOH = $-\log(3.3 \times 10^{-6}) = 5.5$

pH = 14.0 – 5.5 = 8.5

Salts of Acids and Bases

<u>Salts of weak bases:</u>

A principle ingredient of chlorine bleach is sodium hypochlorite, NaOCl

Determine the pH of a solution containing 1.00% by weight NaOCl

MW = 74.44 g/mol

$K_b(ClO^-) = 2.9 \times 10^{-7}$

(1.00 g NaOCl)/(74.44 g/mol) = .0134 mol NaOCl

(99.00 g H_2O)/(.9971 g/mL) = 99.29 mL H_2O

$[ClO^-]$ = (.0134 mol)/(.09929 L) = .135 M

Salts of Acids and Bases

Determine the pH of a solution containing 1.00% by weight NaOCl

$ClO^-(aq) + H_2O \leftrightarrow HOCl(aq) + OH^-(aq)$

$$K_b = \frac{[HOCl][OH^-]}{[ClO^-]} = 2.9 \times 10^{-7}$$

	$[ClO^-]$	$[HOCl]$	$[OH^-]$
initial	.135	0	0
Δ	-x	x	x
equil	.135 – x	x	x

Salts of Acids and Bases

Determine the pH of a solution containing 1.00% by weight NaOCl

$ClO^-(aq) + H_2O \leftrightarrow HOCl(aq) + OH^-(aq)$

$$2.9 \times 10^{-7} = \frac{x^2}{.135 - x} \Rightarrow x = 1.98 \times 10^{-4}$$

assume x is negligible

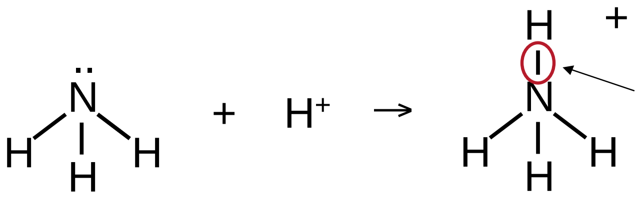
$[OH^-] = 1.98 \times 10^{-4}$ M

pOH = $-\log(1.98 \times 10^{-4}) = 3.70$

pH = 10.30

Lewis Acids and Bases

- Remember:
  - Lewis Acid = electron pair acceptor
  - Lewis Base = electron pair donor
- A Lewis acid reacts with a Lewis base to form a coordinate covalent bond



coordinate covalent bond

$NH_3 + H^+ \rightarrow NH_4^+$

Lewis Acids and Bases

- Metal cations are potential Lewis acids
- Any empty valence orbitals can accept an electron pair from a Lewis base to form a coordinate covalent compound
- If the coordinate covalent compound is an ion, it is called a *complex ion*

$$Ag^+(aq) + 2\ NH_3(aq) \leftrightarrow Ag(NH_3)_2^+(aq)$$

Lewis Acids and Bases

- One electron pair on the oxygen atom in water can act a Lewis base to hydrated metal ions

  $Fe^{3+} + 6\ H_2O \leftrightarrow Fe(H_2O)_6^{3+}(aq)$

- OH^- is a good Lewis base

  $Al(OH)_3(s) + OH^-(aq) \leftrightarrow Al(OH)_4^-(aq)$

  electron pair from OH^- inserts into the empty 2p orbital on aluminum to form covalent bond