

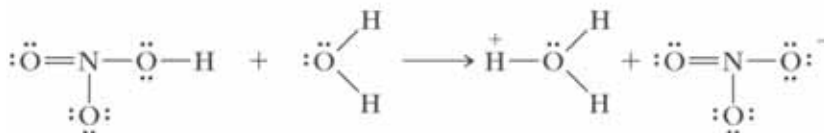
Acid-Base Chemistry

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

Brønsted-Lowry Acids & Bases

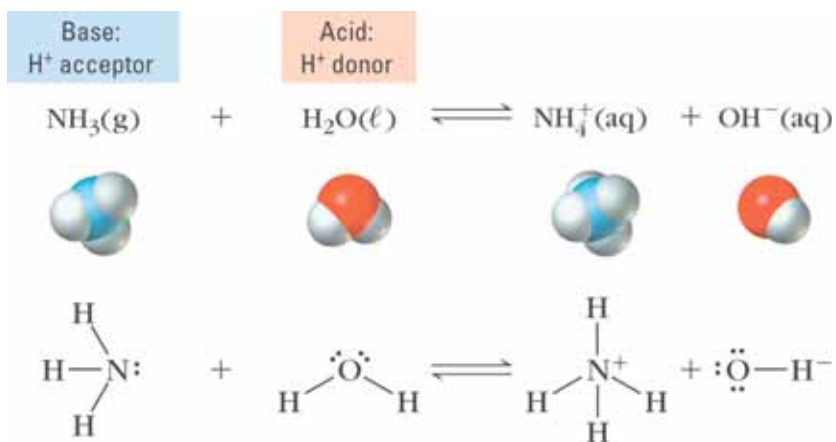
Acid:
H⁺ donor

Base:
H⁺ acceptor



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Brønsted-Lowry Acids & Bases

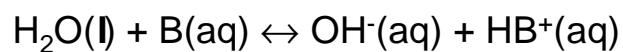


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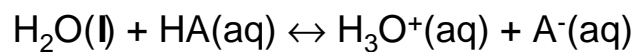
Brønsted-Lowry Acids & Bases

- v 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



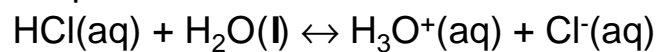
Water as a base



Conjugate Acids & Bases

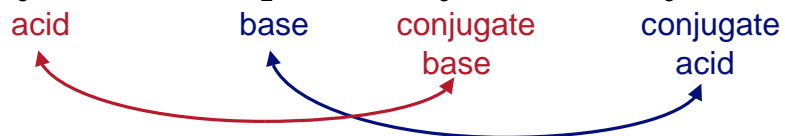
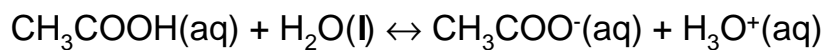
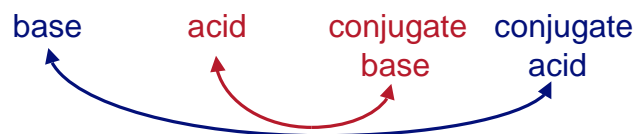
- v Acids react with bases and *vice versa*
- v All acids and bases come with a *conjugate* pair—a base or acid, respectively, that is formed in conjunction with the original species

Examples



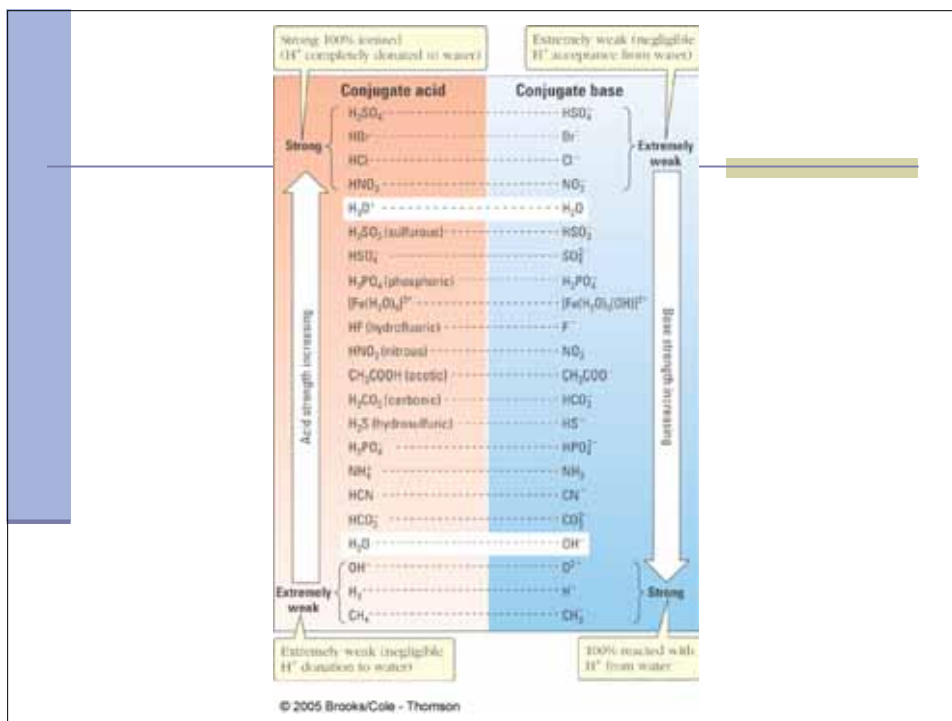
Conjugate Acids & Bases

Examples



Strengths of Acids and Bases

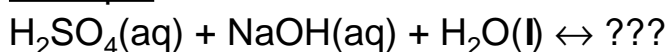
- v Strong acids donate H^+ ions more easily
 - v The stronger the acid, the weaker the conjugate base associated with that acid
- v Strong bases accept H^+ ions more easily
 - v The stronger the base, the weaker the conjugate acid associated with that base



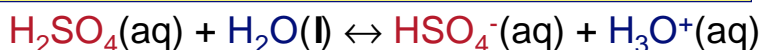
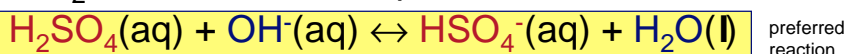
Strengths of Acids and Bases

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

Example

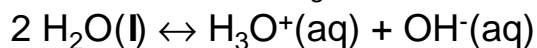


sulfuric acid can react with either OH^- or H_2O —which would it prefer?



Autoionization of Water

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



- v The equilibrium constant for this process at 25 °C is:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

- v In pure water

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

Autoionization of Water

- v K_w is temperature dependent—it increases with increasing temperature

TABLE 16.1 Temperature Dependence of K_w for Water

$T(^{\circ}\text{C})$	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

Example

Determine $[\text{H}_3\text{O}^+]$ in a 0.053 M NaOH solution

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

$$\therefore [\text{OH}^-] = 0.053 \text{ M}$$

Step 2: Use K_w to calculate $[\text{H}_3\text{O}^+]$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.053} = 1.9 \times 10^{-13} \text{ M}$$

The pH Scale

- v pH is a measure of the hydronium ion content of a solution
- v pH is defined as:
$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

log is log base 10, not ln (natural log)
[H₃O⁺] is given in molar units (M)
- v pH of pure water ([H₃O⁺] = 1.0 x 10⁻⁷ M):
$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.0$$
- v pH of last example ([H₃O⁺] = 1.9 x 10⁻¹³ M):
$$\text{pH} = -\log(1.9 \times 10^{-13}) = 12.7$$

The pH Scale

- v Neutral is defined as the pH of pure water:
$$\text{pH} = 7$$
- v Acidic solutions have pH lower than 7:
$$\text{pH} < 7 \Rightarrow \text{acidic}$$
- v Basic solutions have pH larger than 7:
$$\text{pH} > 7 \Rightarrow \text{basic}$$

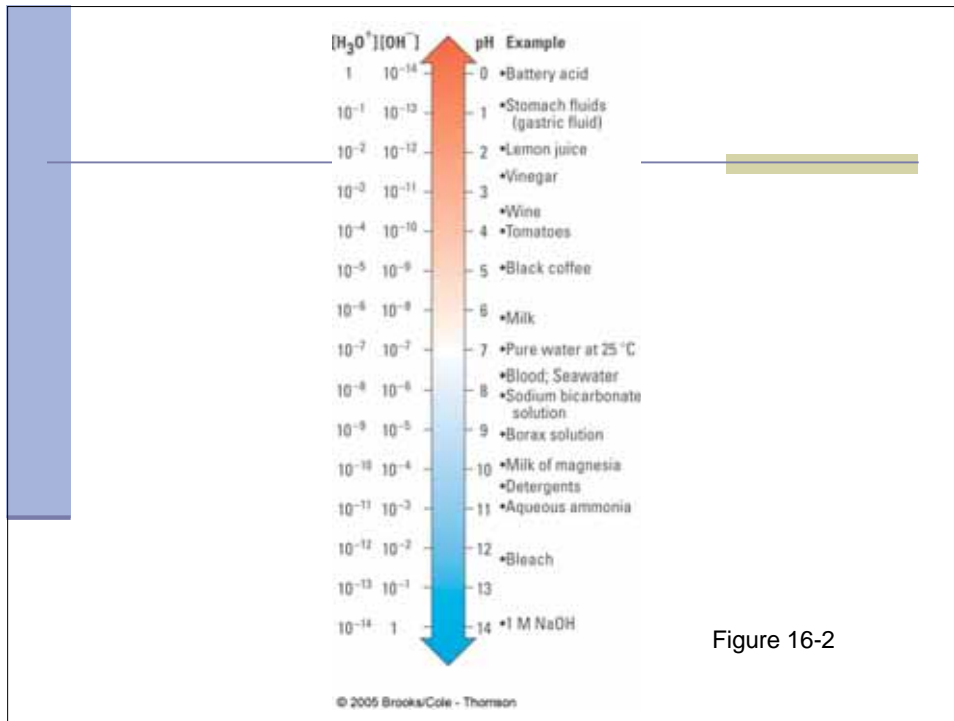


Figure 16-2

The pH Scale

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

$$\text{pOH} = -\log[\text{OH}^-]$$
- v The sum of pH and pOH must equal 14

$$\text{pH} + \text{pOH} = 14$$
 assuming room temperature (25 °C)

The pH Scale

Example

Find $[\text{H}_3\text{O}^+]$ of a solution that has $\text{pOH} = 9.37$

Method 1: Calculate pH, then $[\text{H}_3\text{O}^+]$

Step 1: Determine pH

$$\text{pH} = 14 - \text{pOH} = 14.00 - 9.37 = 4.63$$

Step 2: Determine $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.63} = 2.34 \times 10^{-5} \text{ M}$$

The pH Scale

Example (con't.)

Find $[\text{H}_3\text{O}^+]$ of a solution that has $\text{pOH} = 9.37$

Method 2: Calculate $[\text{OH}^-]$, then $[\text{H}_3\text{O}^+]$ using K_w

Step 1: Determine $[\text{OH}^-]$

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

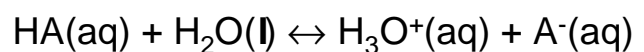
Step 2: Determine $[\text{H}_3\text{O}^+]$ using K_w

$$\begin{aligned} [\text{H}_3\text{O}^+] &= K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (4.27 \times 10^{-10}) \\ &= 2.34 \times 10^{-5} \text{ M} \end{aligned}$$

Ionization Constants

v The extent of dissociation of an acid or base in H₂O can be quantified using its *ionization constant*

v Acids:



acid base c. acid c. base

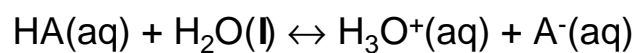
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+][\text{conjugate base}]}{[\text{acid}]}$$

[HA] = undissociated acid in solution

Ionization Constants

v K_a is a specific equilibrium constant

v Acids:



acid base c. acid c. base

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+][\text{conjugate base}]}{[\text{acid}]}$$

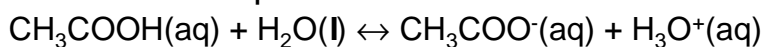
[HA] = undissociated acid in solution

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



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.):

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

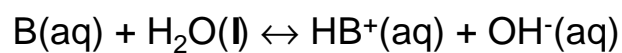
$$1.8 \times 10^{-5} = \frac{x^2}{.2 - x} \Rightarrow x = 0.0019 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(.0019) = 2.7$$

Ionization Constants

v K_b is a specific equilibrium constant for bases

v Bases:



base acid c. acid c. base

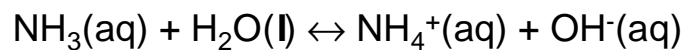
$$K_b = \frac{[HB^+][OH^-]}{[B]} = \frac{[OH^-][\text{conjugate acid}]}{[\text{base}]}$$

[B] = undissociated base in solution

Ionization Constants

Example:

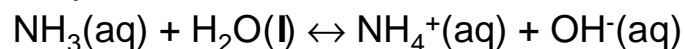
Determine [B] in a 1.82×10^{-3} M solution of NH_3



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

Ionization Constants

Example:



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{1.82 \times 10^{-3} - x}$$

$$x = 1.72 \times 10^{-4} \text{ M} = [\text{NH}_4^+] = [\text{OH}^-]$$

$$\begin{aligned} [\text{NH}_3] &= 1.82 \times 10^{-3} \text{ M} - 1.72 \times 10^{-4} \text{ M} \\ &= 1.65 \times 10^{-3} \text{ M} \end{aligned}$$

Polyprotic Acids

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

- v Each H atom has a unique K_a associated with its release to form H^+ ion
- v Consider phosphoric acid:
 $H_3PO_4(aq) + H_2O(l) \leftrightarrow H_2PO_4^-(aq) + H_3O^+(aq)$ 1st
 $K_{a1} = 7.5 \times 10^{-3}$
 $H_2PO_4^-(aq) + H_2O(l) \leftrightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$ 2nd
 $K_{a2} = 6.2 \times 10^{-8}$
 $HPO_4^{2-}(aq) + H_2O(l) \leftrightarrow PO_4^{3-}(aq) + H_3O^+(aq)$ 3rd
 $K_{a3} = 3.6 \times 10^{-13}$
- v The first H atom is easiest to pull off, so it has the higher K_a value

Strengths of Acids

- v Acid strength is determined by a combination of factors:
 - v 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

v Acid strength is determined by a combination of factors:

v 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 x 10 ⁻⁴
HCl	427 kJ/mol	~10 ⁶
HBr	362 kJ/mol	~10 ⁸
HI	295 kJ/mol	~10 ⁹

Strengths of Acids

v Oxoacids are those with a H-O-Z linkage

v Electronegativity of Z—the higher the electronegativity of Z, the stronger the acid

Acid	χ _Z	K _a
HOCl	3.0	3.5 x 10 ⁻⁸
HOBr	2.8	2.5 x 10 ⁻⁹
HOI	2.5	2.3 x 10 ⁻¹¹

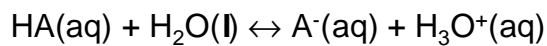
Strengths of Acids

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

Acid	O atoms	K_a
HOCI	1	3.5×10^{-8}
HOCIO	2	1.1×10^{-2}
HOCIO ₂	3	$\sim 10^3$
HOCIO ₃	4	$\sim 10^8$

Relationship Between K_a and K_b

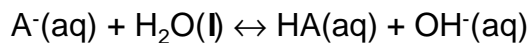
- v The K_a of an acid and the K_b of its conjugate base are related:



acid

c. base

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$



base

c. acid

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

Relationship Between K_a and K_b

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

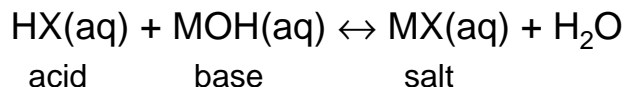
v The product $K_a \times K_b = K_w$

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

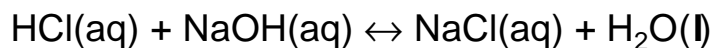
This is true of any conjugate pair of acid and base

Salts of Acids and Bases

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

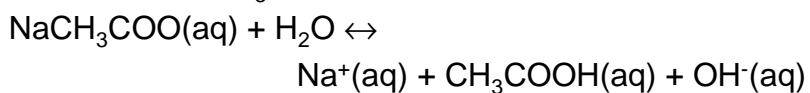


v If a strong base is neutralized with a strong acid, the resulting solution contains only the salt

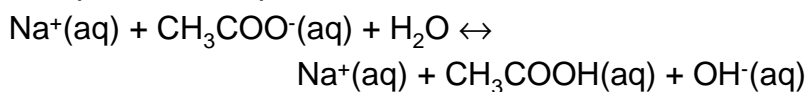


Salts of Acids and Bases

Determine the pH of 0.284 M solution of sodium acetate, NaCH₃COO



Complete ionic equation:



$$K = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a} = 5.56 \times 10^{-10}$$

Salts of Acids and Bases

Determine the pH of 0.284 M solution of sodium acetate, NaCH₃COO

	[CH ₃ COO ⁻]	[CH ₃ COOH]	[OH ⁻]
initial	0.284	0	0
Δ	-x	x	x
equil	0.284 - x	x	x

$$5.56 \times 10^{-10} = \frac{x^2}{0.284 - x} \quad \text{assume } x \text{ is negligible}$$

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

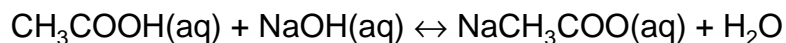
$$\text{pOH} = -\log(1.26 \times 10^{-5}) = 4.90 \quad \text{pH} = 9.1$$

Salts of Acids and Bases

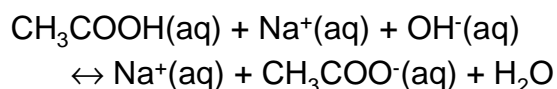
Weak acid and salt of a strong base:

- v 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

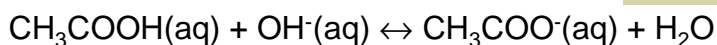


Complete ionic equation:



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

Salts of Acids and Bases

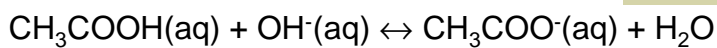


	CH_3COOH	OH^-	CH_3COO^-
initial	0	0	0.020
Δ	x	x	-x
equil	x	x	0.020 - x

$$K = 1.8 \times 10^9 = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{OH}^-]} = \frac{0.020 - x}{x^2} \quad \text{assume } x \text{ is negligible}$$

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

Salts of Acids and Bases



$$[\text{OH}^-] = [\text{CH}_3\text{COOH}] = 3.3 \times 10^{-6} \text{ M}$$

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

$$\text{pH} = 14.0 - 5.5 = 8.5$$

Salts of Acids and Bases

Salts of weak bases:

A principle ingredient of chlorine bleach is sodium hypochlorite, NaOCl

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

$$\text{MW} = 74.44 \text{ g/mol}$$

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

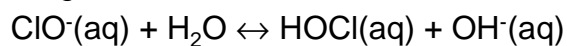
$$(1.00 \text{ g NaOCl}) / (74.44 \text{ g/mol}) = .0134 \text{ mol NaOCl}$$

$$(99.00 \text{ g H}_2\text{O}) / (.9971 \text{ g/mL}) = 99.29 \text{ mL H}_2\text{O}$$

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

Salts of Acids and Bases

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

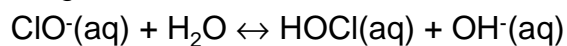


$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{ClO}^-]} = 2.9 \times 10^{-7}$$

	[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



$$2.9 \times 10^{-7} = \frac{x^2}{.135 - x} \Rightarrow x = 1.98 \times 10^{-4} \quad \text{assume } x \text{ is negligible}$$

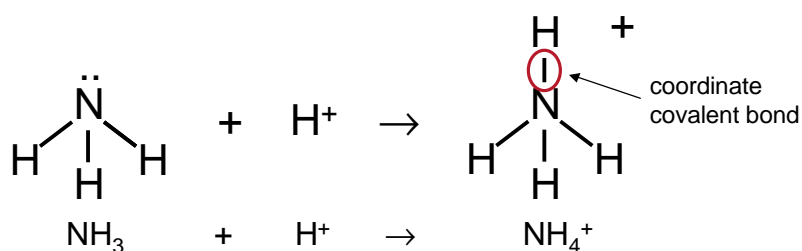
$$[\text{OH}^-] = 1.98 \times 10^{-4} \text{ M}$$

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

$$\text{pH} = 10.30$$

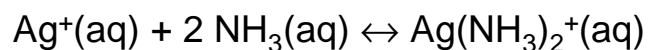
Lewis Acids and Bases

- 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



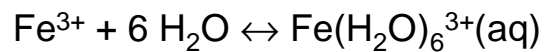
Lewis Acids and Bases

- 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*

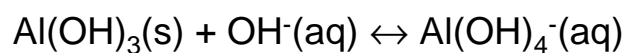


Lewis Acids and Bases

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



- v OH^- is a good Lewis base



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