# Unit 02:
Applications of Chemical Equilibrium

Readings refer to Ch 7 and 8 in
"General Chemistry 152, University of Washington"
by Zumdahl & DeCoste

Lecture 2.1

- Reading
  - Acids and Bases (7.1)
  - Acid Strength (7.2)
  - The pH Scale (7.3)
  - pH of Strong Acid Solutions (7.4)

- Suggested EOC problems
  - Ch 7: 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 115, 119

- Questions we'll answer:
  - What do we mean by "strong" vs. "weak" acids?
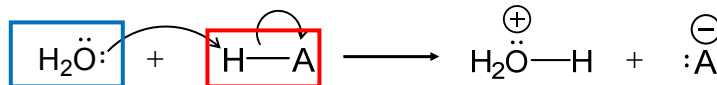 - How do we communicate the concentration of a acid-base solution?
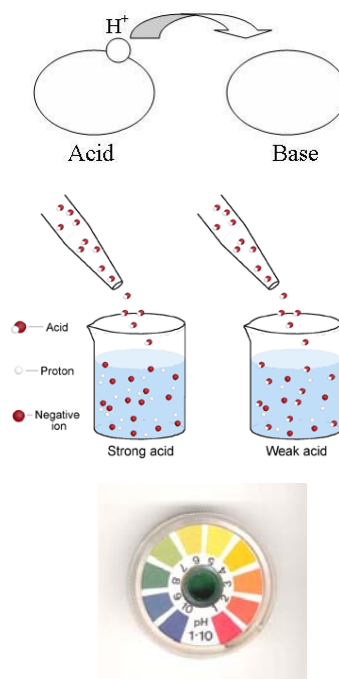
Bronsted-Lowry Theory: acid/base reactions are proton-transfer processes.
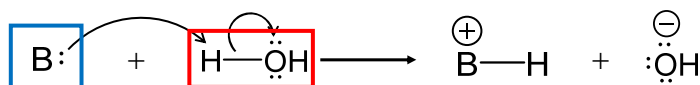
- **Acid** is ***proton-donor*** (H^+ ion donor).
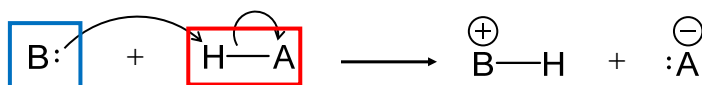
- **Base** is ***proton- acceptor*** (H^+ ion acceptor).

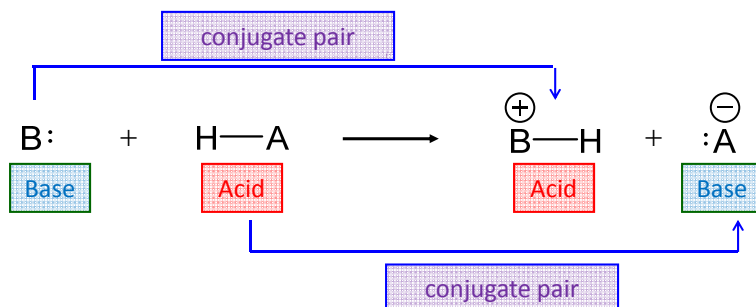- The reaction of HA with H_2O is called **acid ionization**.

- The reaction of B with H_2O is called **base hydrolysis**.

- Acid solutions and base solutions are quantified by the extent of H_3O^+ ("hydronium ion") production. Chemists tend to use "H^+" and "H_3O^+" synonymously.

B L: Conjugate Acid/Base Pairs

conjugate pair

$$B: \quad + \quad H\!-\!A \quad \longrightarrow \quad \overset{\oplus}{B\!-\!H} \quad + \quad \overset{\ominus}{:\!A}$$

Base   Acid   Acid   Base

conjugate pair

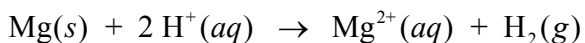*Every **acid** has a conjugate **base**.*

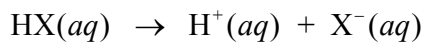These species differ by a single H^+.

*Every **base** has a conjugate **acid**.*

These species differ by a single H^+.

Acid Strength

Magnesium metal dissolves in acidic solution according to the following reaction:

$$Mg(s) \;+\; 2\,H^+(aq) \;\rightarrow\; Mg^{2+}(aq) \;+\; H_2(g)$$

where the H^+ ions are one of the products of acid ionization:

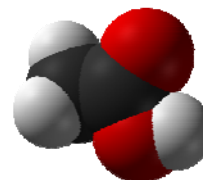$$HX(aq) \;\rightarrow\; H^+(aq) \;+\; X^-(aq)$$

Dissolve _____-g samples of Mg in _____ M hydrochloric (HCl) acid and _____ M acetic (CH₃COOH) acid.
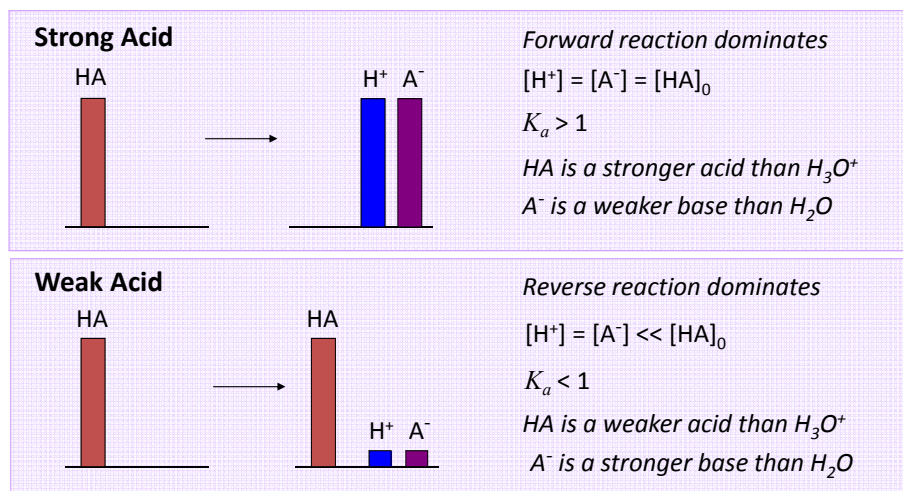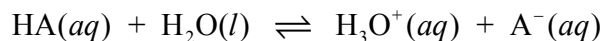
How will the rates of reaction compare?

HCl
(strong)

CH_3COOH
(weak)

4

Acid Strength (cont.)

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Strong Acid

HA   H$^+$ A$^-$

Forward reaction dominates

$[H^+] = [A^-] = [HA]_0$

$K_a > 1$

HA is a stronger acid than H_3O^+

A$^-$ is a weaker base than H_2O

Weak Acid

HA   HA

        H$^+$ A$^-$

Reverse reaction dominates

$[H^+] = [A^-] \ll [HA]_0$

$K_a < 1$

HA is a weaker acid than H_3O^+

A$^-$ is a stronger base than H_2O

$$K_a = \dfrac{\left(\dfrac{[H_3O^+]}{1\ M}\right)\left(\dfrac{[A^-]}{1\ M}\right)}{\left(\dfrac{[HA]}{1\ M}\right)}$$

The magnitude of K_a is a measure of how likely the acid is to dissociate in water.

Acid Strength Comparison

Formula	Name	Value of K_a*
TABLE 14.2	Values of K_a for Some Common Monoprotic Acids	
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
$HOCl$	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

*The units of K_a are customarily omitted.
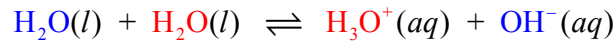
Increasing acid strength

Increasing conjugate base strength

$$K_a = \dfrac{\left(\dfrac{[H_3O^+]}{1\ M}\right)\left(\dfrac{[A^-]}{1\ M}\right)}{\left(\dfrac{[HA]}{1\ M}\right)}$$

Autoionization of Water

- Water also undergoes acid ionization with itself…we call this *autoionization of water*.

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

- The forward reaction occurs to a tiny extent…for pure water at 25°C:

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

$$K_w = \left(\frac{\left[H_3O^+ \right]}{1 \text{ M}} \right) \left(\frac{\left[OH^- \right]}{1 \text{ M}} \right) = 1.0 \times 10^{-14}$$

- We can think of K_w as a measure of how "acidic" a water molecule is.
- The concentration values give us a reference point for acidity.

$[H_3O^+] > 1.0 \times 10^{-7}$ M $\rightarrow$ ACIDIC solution

$[H_3O^+] < 1.0 \times 10^{-7}$ M $\rightarrow$ BASIC solution

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

pH = "power of Hydrogen"

- Uses a *logarithmic scale* (powers of 10)

$$pH = -\log_{10}[H_3O^+] \qquad [H_3O^+] = 10^{-pH}$$

- **Sig Fig Rule**: The number of *decimal places* in the log is equal to the number of *significant figures* in the original number.
- pH represents the "order of magnitude" of the hydronium ion concentration.
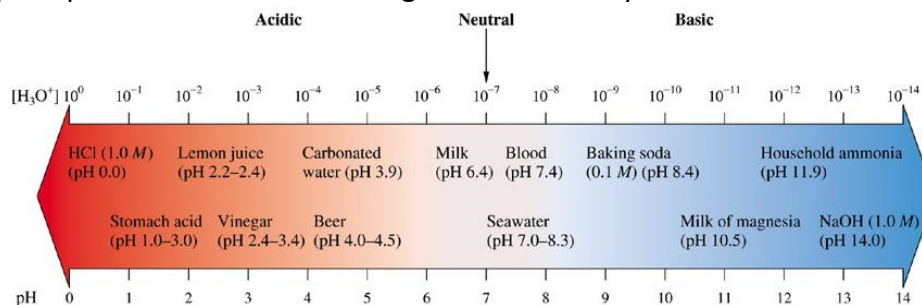
pH of Common Foods: http://www.engineeringtoolbox.com/food-ph-d_403.html
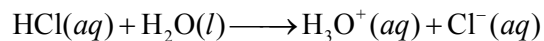
pH of Strong vs Weak Acid Solutions

[HA]$_o$ (M)	HCl $K_a > 1$	HNO$_3$ $K_a > 1$	HF $K_a \sim 10^{-4}$	CH$_3$COOH $K_a \sim 10^{-5}$
10^{-4}	4	4	4.05	4.47
10^{-3}	3	3	3.26	3.91
10^{-2}	2	2	2.64	3.39
10^{-1}	1	1	2.10	2.88
10^{0}	0	0	1.59	2.38
10^{1}	-1	-1	1.09	1.88

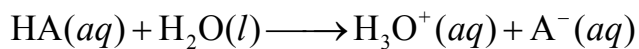Strong acids dissociate "stoichiometrically" to form H$^+$ and A$^-$!

pH of Strong Acid Solutions

Example: What is the pH of a 0.100 M solution of HCl?

HCl is a strong acid; therefore, it complete dissociates to form H$_3$O$^+$ and Cl$^-$.

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

pH of Strong Acid Solutions (cont.)

- The stoichiometric production of H_3O^+ will be true for any strong acid.

$$HA(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$$

Equilibrium lies very, very far to the right!

- Strong acids to know:
    - HCl (hydrochloric acid)
    - HBr (hydrobromic acid)
    - HI (hydroiodic acid)
    - HNO_3 (nitric acid)
    - $HClO_4$ (perchloric acid)
    - H_2SO_4 (sulfuric acid…first proton only)

Concept Quiz

- What is the pH of a 0.010 M solution of nitric acid?

Lecture 2.2

- Reading
  - pH of Weak Acid Solutions (7.5)
  - pH of Base Solutions (7.6)

- Suggested EOC problems
  - Ch 7: 43, 45, 47, 49, 51, 53, 55, 57, 59, 61, 65, 67, 69, 71, 73, 75, 77, 79, 81, 117

- Questions we'll answer:
  - How do we calculate the pH of an acid or base, given its strength and initial concentration?
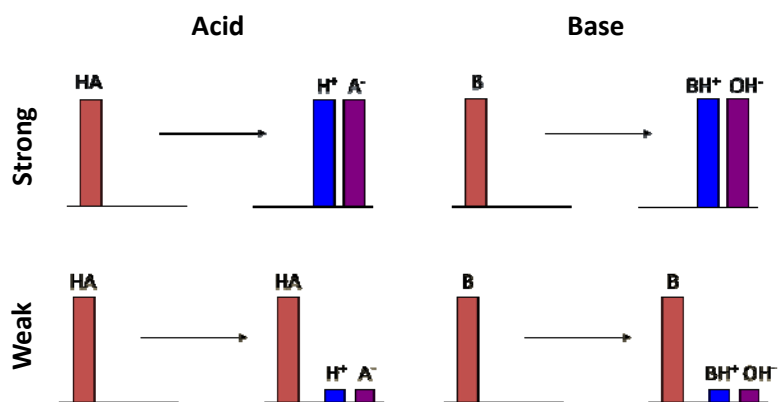
Weak Acids

- For weak acids dissociation is not complete. A mixture of species will be present at equilibrium!

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
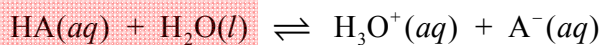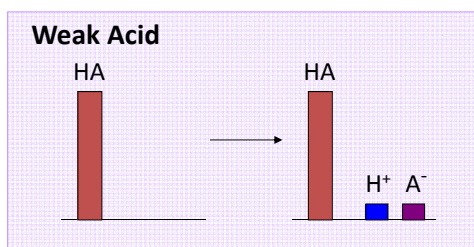
Dominant species in solution

$$K_a = \frac{\left(\dfrac{[H_3O^+]}{1\,M}\right)\left(\dfrac{[A^-]}{1\,M}\right)}{\left(\dfrac{[HA]}{1\,M}\right)}$$

The magnitude of K_a is a measure of how likely the acid is to dissociate in water.

- Need to use our equilibrium chemistry techniques.

pH of Weak Acid Solutions

- **Example**: Calculate the pH of a 0.100 M solution of nitrous acid HNO_2 (K_a = 4.0 x 10^{-4}).

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$
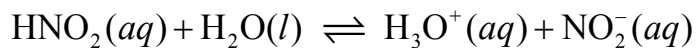
- This is a weak acid; therefore we will treat this just like a standard equilibrium problem.

- Reaction is balanced; therefore, we can construct the equilibrium expression:

$$K_a = 4.0 \times 10^{-4} = \frac{\left(\dfrac{\left[H_3O^+\right]}{1\,M}\right)\left(\dfrac{\left[NO_2^-\right]}{1\,M}\right)}{\left(\dfrac{\left[HNO_2\right]}{1\,M}\right)}$$

pH of Weak Acid Solutions (cont.)

- Next: ICE Table!

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$
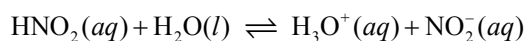
- Sub into K_a and solve.

- Let's trying solving this two ways: with and without approximation.

pH of Weak Acid Solutions (cont.)

- First, no approximations. Use quadratic formula:

pH of Weak Acid Solutions (cont.)

- Next, let's assume x is really small:
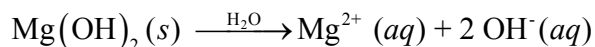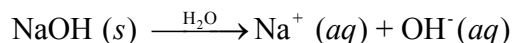
Approximation Check

- There are two assumptions we've made in the past two calculations:

  - Extent of dissociation is modest such that we can just use the initial concentration of the weak acid.
  - The amount of H_3O^+ produced from HNO_2 is significantly greater than the amount present due to autoionization.

- Checking:

  1. For $[HNO_2]_{dissoc}$: $\dfrac{0.006\underline{3}2\ M}{0.100\ M}$ x 100 = 6.3 %

  2. For $[H_3O^+]_{from\ water}$: $\dfrac{1\ x\ 10^{-7}\ M}{0.006\underline{3}2\ M}$ x 100% = 1.6 x 10^{-3} %

- Both assumptions are reasonable.

pH of Weak Acid Solutions (cont.)

- **Example**: A 0.150 M solution of hydrofluoric acid HF has a pH of 1.98. Use this data to approximate the K_a for this weak acid.

What is a Base?

- According to Arrhenius theory, a base is a substance that produces OH⁻ ions in solution.
- Within this definition, the metal hydroxide salts are bases:

$$\text{NaOH } (s) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+ (aq) + \text{OH}^- (aq)$$

$$\text{Mg(OH)}_2 (s) \xrightarrow{\text{H}_2\text{O}} \text{Mg}^{2+} (aq) + 2\text{ OH}^- (aq)$$

- In the Bronsted-Lowry theory, a base is a substance that can accept a proton from an acid. When the acid is water, [OH⁻] increases:

$$\text{B } (aq) + \text{H}_2\text{O } (l) \rightleftharpoons \text{BH}^+ (aq) + \text{OH}^- (aq)$$
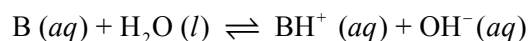
- This more general definition includes the strong base hydroxide, which is the conjugate base of water.

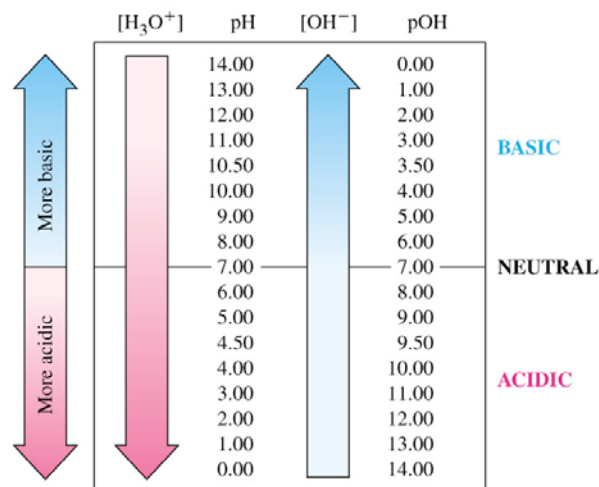# pH and pOH

We can define an expression similar to pH for "power of hydroxide":

$$pOH = -\log_{10}[\text{OH}^-]$$

In aqueous solution at 25° C

$$pH + pOH = 14.00$$

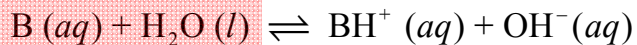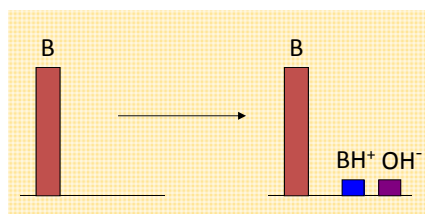| [H₃O⁺]	pH	[OH⁻]	pOH	
	14.00		0.00	
	13.00		1.00	
	12.00		2.00	
	11.00		3.00	BASIC
	10.50		3.50	
	10.00		4.00	
	9.00		5.00	
	8.00		6.00	
	7.00		7.00	NEUTRAL
	6.00		8.00	
	5.00		9.00	
	4.50		9.50	
	4.00		10.00	ACIDIC
	3.00		11.00	
	2.00		12.00	
	1.00		13.00	
	0.00		14.00	

More basic / More acidic

2017-01-12

Hydroxide: A Strong Base

- **Example**: What is the pH of a 0.010 M solution of KOH?

- Since KOH is a soluble salt of the strong base OH⁻, complete dissociation occurs:

Weak Bases

- When a weak base B reacts with water, hydroxide ions are produced, a lot of unreacted B remains at equilibrium:


$$K_b = \frac{\left(\dfrac{[BH^+]}{1\,M}\right)\left(\dfrac{[OH^-]}{1\,M}\right)}{\left(\dfrac{[B]}{1\,M}\right)}$$

$$B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH^-\,(aq)$$

Dominant species in solution

*The magnitude of K_b is a measure of how likely the base is to hydrolyze water.*

- To determine the concentration of OH⁻, we are going to have to use our equilibrium chemistry techniques (just like we did for weak acids).

Weak Bases

- Typical weak bases include amines (nitrogen-bearing compounds) of which the simplest is ammonia.

$$\text{NH}_3 \; (aq) + \text{H}_2\text{O} \; (l) \; \rightleftharpoons \; \text{NH}_4^+ \; (aq) + \text{OH}^- (aq)$$
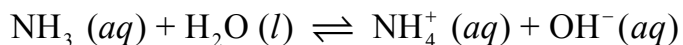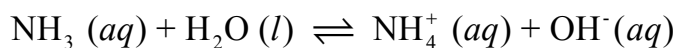
- The reaction involves the lone pair of electrons on the nitrogen that forms a bond with a proton to form the protonated amine.
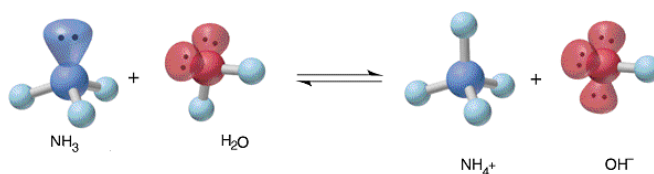
- Other amines include methylamine (CH_5N) and triethylamine (C_3H_9N).

pH of Weak Base Solutions

- **Example**: Calculate the pH of a 0.100 M solution of ammonia NH_3 ($K_b = 1.8 \times 10^{-5}$).

$$\text{NH}_3 \; (aq) + \text{H}_2\text{O} \; (l) \; \rightleftharpoons \; \text{NH}_4^+ \; (aq) + \text{OH}^- (aq)$$

- Since ammonia is a weak base we treat this just like a standard equilibrium problem.

- Reaction is balanced; therefore, we can construct the equilibrium expression:

- Next: ICE Table!

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-(aq)$$
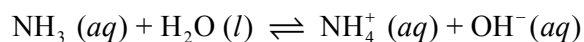
- Sub into K_b and solve.

Approximation Check

- We made two assumptions we made in the last calculation:

  - Extent of dissociation is modest such that we can just use the initial concentration of the weak base.
  - The amount of OH⁻ produced is significantly greater than the amount present due to autoionization.

- Checking:

  1. For $[NH_3]_{hydrolysis}$: $\dfrac{0.00134\ M}{0.100\ M}$ x 100 = 1.3 %

  2. For $[OH^-]_{from\ water}$: $\dfrac{1 \times 10^{-7}\ M}{0.00134\ M}$ x 100% = 0.00746 %

- Both assumptions are reasonable.

Lecture 2.3

- Reading
  - Acid-Base Properties of Salts (7.8)

- Suggested EOC Problems
  - Ch 7: 91, 93, 97, 99, 101, 103, 107, 121

- Questions we'll answer:
  - What is the relationship between K_a and K_b?
  - How does the strength of a acid/base conjugate affect the pH of solution?
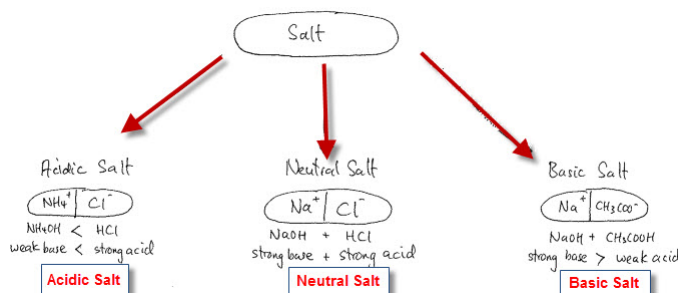

TABLE 17.1   Relative Strengths of Some Common Brønsted–Lowry Acid and Bases

Acid		Conjugate Base	
Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-
Hydroiodic acid	HI	Iodide ion	I^-
Hydrobromic acid	HBr	Bromide ion	Br^-
Hydrochloric acid	HCl	Chloride ion	Cl^-
Sulfuric acid	H_2SO_4	Hydrogen sulfate ion	HSO_4^-
Nitric acid	HNO_3	Nitrate ion	NO_3^-
Hydronium ion[a]	H_3O^+	Water[a]	H_2O
Hydrogen sulfate ion	HSO_4^-	Sulfate ion	SO_4^{2-}
Nitrous acid	HNO_2	Nitrite ion	NO_2^-
Acetic acid	$HC_2H_3O_2$	Acetate ion	$C_2H_3O_2^-$
Carbonic acid	H_2CO_3	Hydrogen carbonate ion	HCO_3^-
Ammonium ion	NH_4^+	Ammonia	NH_3
Hydrogen carbonate ion	HCO_3^-	Carbonate ion	CO_3^{2-}
Water	H_2O	Hydroxide ion	OH^-
Methanol	CH_3OH	Methoxide ion	CH_3O^-
Ammonia	NH_3	Amide ion	NH_2^-

Increasing acid strength / Increasing base strength

[a] The hydronium ion–water combination refers to the ease with which a proton is passed from one water molecule to another; that is, $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$

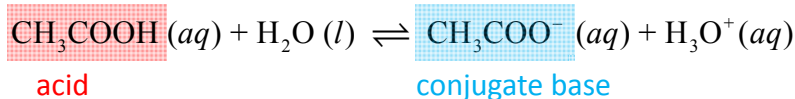acids that are stronger than H_3O^+ have conjugate bases that are weaker than H_2O

acids that are weaker than H_3O^+ and stronger than H_2O have conjugate bases that are stronger than H_2O and weaker than OH^-

acids that are weaker than water have conjugate bases that are stronger than OH^-

Acid/Base Conjugates

- Consider the dissociation of acetic acid (CH_3COOH) where $K_a = 1.8 \times 10^{-5}$):

$$\underset{\text{acid}}{CH_3COOH} \, (aq) + H_2O \, (l) \rightleftharpoons \underset{\text{conjugate base}}{CH_3COO^-} \, (aq) + H_3O^+ (aq)$$

- Notice that the acetate ion is capable of accepting a proton; therefore, it is a base.

- The resulting base formed from the dissociation of an **acid** is called the **conjugate base** of the acid.
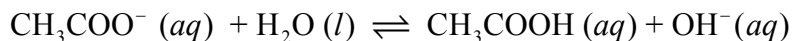
Acid/Base Conjugates (cont.)

- Let's write down the equilibrium expression for the acid:

$$CH_3COOH \, (aq) + H_2O \, (l) \rightleftharpoons CH_3COO^- \, (aq) + H_3O^+ (aq)$$
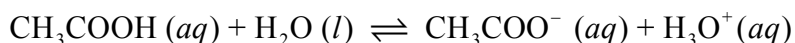
$$K_a = \frac{\left(\dfrac{\left[CH_3COO^-\right]}{1 \, M}\right)\left(\dfrac{\left[H_3O^+\right]}{1 \, M}\right)}{\left(\dfrac{\left[CH_3COOH\right]}{1 \, M}\right)}$$

- Let's write down the equilibrium expression for the base:

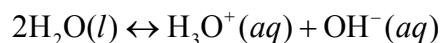$$CH_3COO^- \, (aq) + H_2O \, (l) \rightleftharpoons CH_3COOH \, (aq) + OH^- (aq)$$

$$K_b = \frac{\left(\dfrac{\left[CH_3COOH\right]}{1 \, M}\right)\left(\dfrac{\left[OH^-\right]}{1 \, M}\right)}{\left(\dfrac{\left[CH_3COO^-\right]}{1 \, M}\right)}$$

Acid/Base Conjugates (cont.)

- Finally, let's look at the product of K_a and K_b:

$$K_a K_b = \frac{\left(\frac{[CH_3COO^-]}{1\text{ M}}\right)\left(\frac{[H_3O^+]}{1\text{ M}}\right)}{\left(\frac{[CH_3COOH]}{1\text{ M}}\right)} \times \frac{\left(\frac{[CH_3COOH]}{1\text{ M}}\right)\left(\frac{[OH^-]}{1\text{ M}}\right)}{\left(\frac{[CH_3COO^-]}{1\text{ M}}\right)} = \left(\frac{[H_3O^+]}{1\text{ M}}\right)\left(\frac{[OH^-]}{1\text{ M}}\right)$$

- This last expression is equivalent to the equilibrium constant for the autoionization of water:

$$2H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-(aq)$$

$$K_w = \left(\frac{[H_3O^+]}{1\text{ M}}\right)\left(\frac{[OH^-]}{1\text{ M}}\right) = 1.0 \times 10^{-14}$$
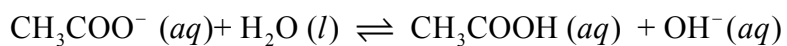
Acid/Base Conjugates (cont.)

- Generalizing this result:

$$K_a K_b = K_w = 1.0 \times 10^{-14} \quad \textit{at 25}^o\textit{C}$$

- The K_a for an acid and the K_b for its conjugate base are directly related through the above expression.

- If one is given the K_a for an acid, then K_b for the conjugate base is readily determined.

- Same goes for a base and its conjugate acid, the product of K_b and K_a is K_w.

Acid/Base Conjugates (cont.)

- Consider the product of the dissociation of acetic acid (CH_3COOH), for which $K_a = 1.8 \times 10^{-5}$. What is the pH of a 0.350 M solution of acetate?

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

- First, the reaction is balanced. Next, we write the equilibrium expression:

$$K_b = \frac{\left(\dfrac{[CH_3COOH]}{1 \ M}\right)\left(\dfrac{\left[OH^-\right]}{1 \ M}\right)}{\left(\dfrac{\left[CH_3COO^-\right]}{1 \ M}\right)}$$

Acid/Base Conjugates (cont.)

- Next, we can use the K_a for acetic acid to calculate K_b for acetate.

- ICE table time:

Ions of Strong Acid/Base

- To finish our introduction to acid/base chemistry, we return to ionic compounds (aka "salts") in solution, such as NaCl.

- Water simply "solvates" the Na^+ and Cl^- ions, and there is no reaction with H^+ or OH^-

- For example, Cl^- does not react with H_2O to make HCl and OH^-:

$$Cl^-(aq) + H_2O(l) \xrightarrow{\quad\times\quad} HCl(aq) + OH^-(aq)$$
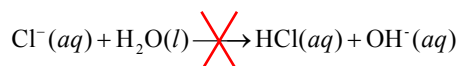
- In fact, the equilibrium lies on the reactant side (since the products are a strong acid and a strong base).

- In summary: Anions (Cl^-) from strong acids (HCl) have no affect on pH. The same is true for the cations (Na^+) from strong bases (NaOH).
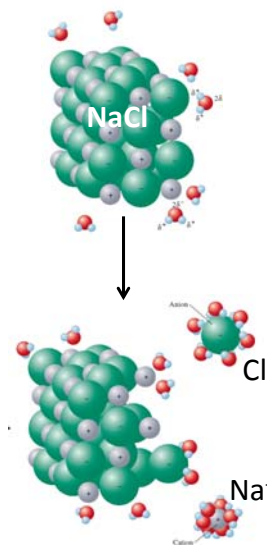

Ions of Strong Acid/Base (cont.)

- There are a variety of ions from strong acids and bases that simply form solvated ions in solution and do not affect pH.

- Correspondingly, the salts of these ions will not affect pH when dissolved in water.

- Examples include KNO_3, $NaNO_3$, KCl, NaCl, $NaClO_4$.

$$KCl(s) \xrightarrow{\quad H_2O \quad} K^+(aq) + Cl^-(aq)$$
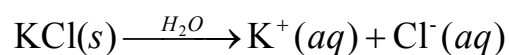
- Sulfate salts are also "neutral" salts: Na_2SO_4, K_2SO_4.

pH of Salts

- What happens when the anion of the salt is also a weak base?

- Consider placing sodium acetate ($NaC_2H_3O_2$) into solution:

$$NaC_2H_3O_2(s) \xrightarrow{\;H_2O\;} Na^+(aq) + C_2H_3O_2^{\;-}(aq)$$
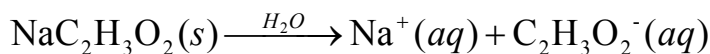
- We have three species in solution: Na^+, $C_2H_3O_2^{\;-}$, and H_2O. Which species can affect the pH?

- Notice that **sodium acetate** contains the conjugate base of **acetic acid** (a weak acid).

$$HC_2H_3O_2(aq) + H_2O(l) \;\rightleftharpoons\; H_3O^+(aq) + C_2H_3O_2^{\;-}(aq)$$
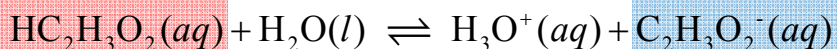
pH of Salts (cont.)

- Sodium acetate acts as a base, and is the "strongest" species present (since neither Na^+ nor H_2O affect pH).

- Therefore, the reaction of interest is:

$$C_2H_3O_2^{\;-}(aq) + H_2O(l) \;\rightleftharpoons\; HC_2H_3O_2(aq) + OH^-(aq)$$
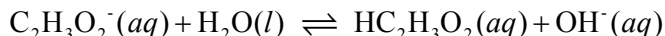
- We can determine the pH by simply applying the techniques developed earlier. The equilibrium expression is:

$$K_b = \frac{\left(\dfrac{[HC_2H_3O_2]}{1\,M}\right)\left(\dfrac{[OH^-]}{1\,M}\right)}{\left(\dfrac{[C_2H_3O_2^{\;-}]}{1\,M}\right)} = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

- Recall:　　$K_a K_b = K_w = 1.0\times10^{-14}$

pH of Salts (cont.)

- **Example**: Calculate the pH of a 0.45 M NaCN solution where the K_a value for HCN is 6.2 x 10^{-10}.

- First step: Determine what the strongest species in solution is.

- Next, write down the acid/base reaction for this species.
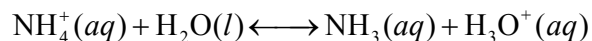
pH of Salts (cont.)

- Finally, ICE table and solve.

pH of Salts (cont.)

- There are salts that produce acidic solutions as well.

- Salts where the cation is the conjugate acid of a weak base will produce solutions that are acidic.

- Example: ammonuium chloride

$$\mathrm{NH_4Cl}(s) \xrightarrow{\;H_2O\;} \mathrm{NH_4^+}(aq) + \mathrm{Cl^-}(aq)$$
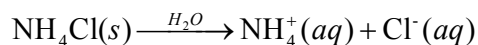
- Chloride ($\mathrm{Cl^-}$) does not affect pH, but ammonium ion acts as a weak acid:

$$\mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l) \longleftrightarrow \mathrm{NH_3}(aq) + \mathrm{H_3O^+}(aq)$$

pH of Salts (cont.)

- **Example**: What is the pH of a solution that is 0.10 M in $\mathrm{NH_4Cl}$? K_b for $\mathrm{NH_3}$ is 1.8 x 10^{-5}.

- $\mathrm{NH_4^+}$ is the strongest species in solution and dictates pH.

- Next, write down the equilibrium expression for $\mathrm{NH_4^+}$:

pH of Salts (cont.)

- Finally, ICE table and solve.