The Chemistry of Acids and Bases *Separately*
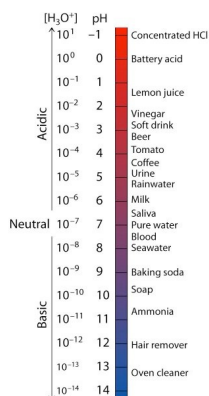
Chapter 14 Part I

Chemistry 223
Professor Michael Russell

*MAR* Last update: 4/29/24

$[H_3O^+]$	pH	
10^1	−1	Concentrated HCl
10^0	0	Battery acid
10^{-1}	1	
10^{-2}	2	Lemon juice
10^{-3}	3	Vinegar / Soft drink / Beer
10^{-4}	4	Tomato / Coffee
10^{-5}	5	Urine / Rainwater
10^{-6}	6	Milk / Saliva
10^{-7}	7	Pure water / Blood
10^{-8}	8	Seawater
10^{-9}	9	Baking soda
10^{-10}	10	Soap
10^{-11}	11	Ammonia
10^{-12}	12	Hair remover
10^{-13}	13	Oven cleaner
10^{-14}	14	

Acidic / Neutral / Basic

Strong and Weak Acids/Bases

Generally divide acids and bases into **STRONG** or **WEAK** categories.

STRONG ACID: $HNO_3(aq) + H_2O(liq) \longrightarrow$

$H_3O^+(aq) + NO_3^-(aq)$
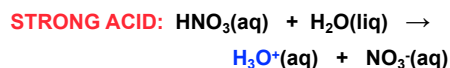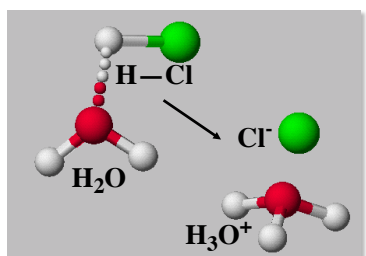
HNO_3 is about 100% dissociated in water. Acids create **hydronium** when they react with water.

MAR
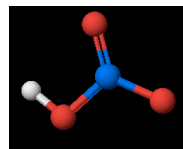
Strong and Weak Acids/Bases

HNO_3, **HCl**, **HBr**, **HI** and $HClO_4$ are among the few known strong *monoprotic* acids.

H—Cl
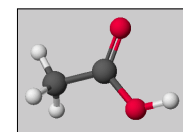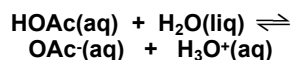
H_2O

Cl^-

H_3O^+

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Memorize these five strong acids!

Strong and Weak Acids/Bases

Weak acids are much less than 100% ionized in water.

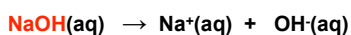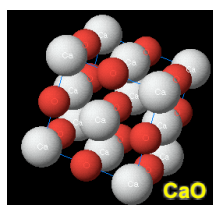One of the best known is **acetic acid** = CH_3CO_2H = **HOAc**

$HOAc(aq) + H_2O(liq) \rightleftharpoons OAc^-(aq) + H_3O^+(aq)$

OAc^- = $CH_3CO_2^-$ = acetate ion

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Strong and Weak Acids/Bases

Strong Base: 100% dissociated in water.

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

Other strong *monobasic* bases: **KOH**, **LiOH**

$Ca(OH)_2$ is a strong *dibasic* system:

CaO (lime) + H_2O -->

$Ca(OH)_2$ (slaked lime)
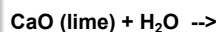
Memorize the three strong monobasic bases!

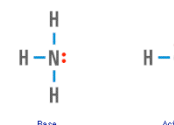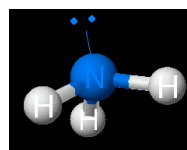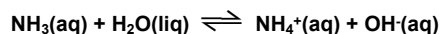*MAR*

Strong and Weak Acids/Bases

Weak base: less than 100% ionized in water

One of the best known weak bases is **ammonia, NH_3**

$NH_3(aq) + H_2O(liq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

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ACID-BASE THEORIES

The most general theory for common aqueous acids and bases is the **BRØNSTED - LOWRY** theory

ACIDS DONATE H⁺ IONS
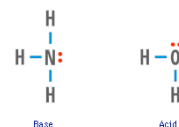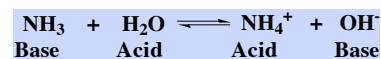
BASES ACCEPT H⁺ IONS

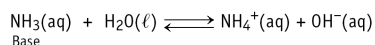*See Brønsted Acids and Bases Handout*

MAR

ACID-BASE THEORIES

The Brønsted definition means NH_3 is a **BASE** in water - and water is itself an **ACID**

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
Base   Acid   Acid   Base

MAR

ACID-BASE THEORIES

NH_3 is a **BASE** in water - and water is itself an **ACID**

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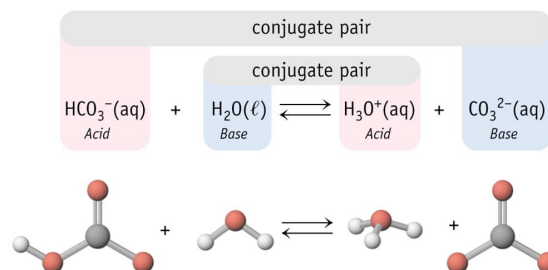Base

NH_3 / NH_4^+ is a **conjugate pair** - related by the gain or loss of H^+

Every acid has a conjugate base - and vice-versa.

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Conjugate Pairs

conjugate pair

conjugate pair

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$
Acid   Base   Acid   Base
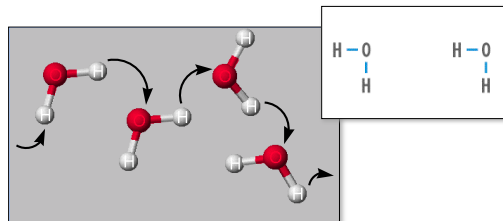
MAR

MORE ABOUT WATER

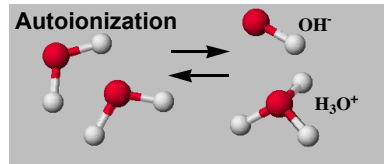H_2O can function as both an **ACID** and a **BASE**.

Pure water undergoes AUTOIONIZATION

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MORE ABOUT WATER

K_w = $[H_3O^+]$ $[OH^-]$ = **1.00 x 10⁻¹⁴ at 25 °C**

In a **neutral** solution $[H_3O^+]$ = $[OH^-]$

so K_w = $[H_3O^+]^2$ = $[OH^-]^2$

and so $[H_3O^+]$ = $[OH^-]$ = $\sqrt{K_w}$ = **1.00 x 10⁻⁷ M**

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Memorize K_W = 1.00 x 10⁻¹⁴!

Calculating [H₃O⁺] & [OH⁻]

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution

$2 H_2O(liq) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
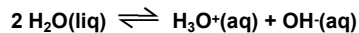
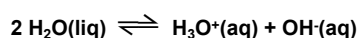Le Chatelier predicts equilibrium shifts to the

_____.

$[H_3O^+] < 10^{-7}$ at equilibrium.

Set up an **ICE** concentration table.

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Calculating [H₃O⁺] & [OH⁻]

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution

$2 H_2O(liq) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

initial

change

equilib

$K_w = (x)(0.0010 + x)$

Because x << 0.0010 M, *assume* $[OH^-]$ = 0.0010 M

$K_w = (x)(0.0010 + x) \approx (x)(0.0010) = [H_3O^+](0.0010)$

$[H_3O^+] = K_w / 0.0010 = 1.0 \times 10^{-11}$ M

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Calculating [H₃O⁺] & [OH⁻]

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution

$2 H_2O(liq) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
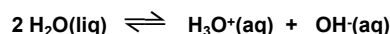
$[H_3O^+] = K_w / 0.0010 = 1.0 \times 10^{-11}$ M

$[OH^-] = 1.0 \times 10^{-3}$ M

This solution is _____

because

$[OH^-] > [H_3O^+]$

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[H₃O⁺], [OH⁻] and pH

A common way to express acidity and basicity is with pH

pH = - log [H₃O⁺]

In a *neutral* solution,

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

1.0×10^{-7} at 25 °C

pH = -log (1.00 × 10⁻⁷)

= - (-7.00) = 7.00

pH = 7.00 for neutral solutions!
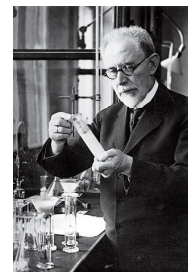
Søren Sørensen, *creator of the pH scale*

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[H₃O⁺], [OH⁻] and pH

What is the pH of the 0.0010 M NaOH solution?

$[H_3O^+] = 1.0 \times 10^{-11}$ M

pH = - log (1.0 × 10⁻¹¹) = 11.00

General conclusion - _____

Basic solution   pH > 7

Neutral   pH = 7

Acidic solution   pH < 7

Public Enemy are not scientists!

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[H₃O⁺], [OH⁻] and pH

If the pH of Diet Coke is 3.12, it is

_____.

Because pH = - log $[H_3O^+]$ then

log $[H_3O^+]$ = - pH

Take antilog and get

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

$[H_3O^+] = 10^{-3.12}$

= 7.6 × 10⁻⁴ M

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logarithms and sig figs

Logarithms are exponents with special sig figs rules. *General rule:*

log of experimentally measured number with *N* sig figs give numbers with *N* decimal places *after* the decimal (digit before decimal only indicates magnitude)

Examples:

log $3.07*10^{-3}$ = **-2.513** (*3 sigs, 3 places after decimal*)

- log $1.1*10^{-8}$ = **7.96** (*2 sigs, 2 places after decimal*)

$10^{-3.12}$ = **7.6 * 10^{-4}** (*2 places after decimal, 2 sigs*)

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pH of Common Substances
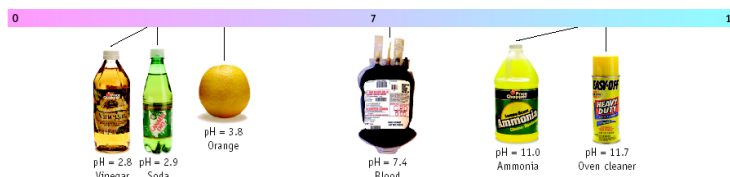
Figure 5.17 pH values of some common substances. Here the "bar" is colored red at one end and blue at the other. These are the colors of litmus paper, commonly used in the laboratory to decide if a solution is acidic (litmus is red) or basic (litmus is blue). *(Charles D. Winters)*

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Other pX Scales

In general   **pX = -log X**

and: **pK_a = - log K_a**

and so: **pOH = - log [OH⁻]**

K_w = [H_3O^+] [OH⁻] = 1.00 x 10^{-14} at 25 °C

Take the negative log of both sides

-log (10^{-14}) = - log [H_3O^+] + (-log [OH⁻])

14 = pH + pOH

also: **14 = pK_a + pK_b**

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K_w = [H_3O^+] [OH⁻] = 1.00 x 10^{-14} at 25 °C

pH + pOH = 14

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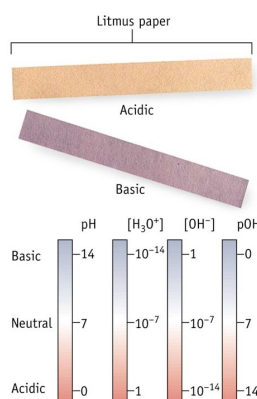
acidic solutions:

pH ↓,

[H_3O^+] ↑,

[OH⁻] ↓,

pOH ↑

basic solutions: **pH ↑,**

[H_3O^+] ↓,

[OH⁻] ↑,

pOH ↓

Equilibria Considerations Involving Weak Acids and Bases
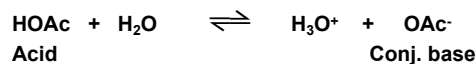
Acid	Conjugate Base
acetic, CH_3CO_2H	$CH_3CO_2^-$, acetate
ammonium, NH_4^+	NH_3, ammonia
bicarbonate, HCO_3^-	CO_3^{2-}, carbonate

A weak acid (or base) is one that ionizes to a VERY small extent (< 5%).

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Equilibria Involving Weak Acids and Bases

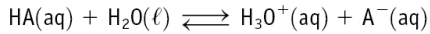Consider acetic acid, CH_3CO_2H (HOAc)

HOAc + H_2O ⇌ H_3O^+ + OAc⁻
Acid   Conj. base

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

(K is designated K_a for ACID)

Because [H_3O^+] and [OAc⁻] are SMALL, K_a << 1.
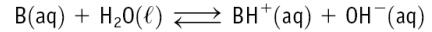
MAR

Equilibrium Constants for Weak Acids (K_a)

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

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

Weak acids have $K_a < 1$
Leads to small $[H_3O^+]$ and a pH of 2 - 7

MAR

Equilibrium Constants for Weak Bases (K_b)

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

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

Weak bases have $K_b < 1$
Leads to small $[OH^-]$ and a pH of 12 - 7

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Equilibrium Constants for Weak Acids and Bases

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad K_b$$

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_a \cdot K_b = K_w$$
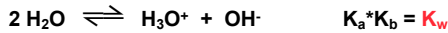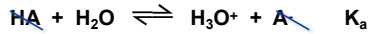
Important relations: $K_a \cdot K_b = K_w$ and
$pK_a + pK_b = 14$

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Ionization Constants for Acids/Bases

Acids

Increase strength

Conjugate Bases

Increase strength

Ionization Constants for Some Acids and Their Conjugate Bases

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K and Acid-Base Reactions

ACIDS	CONJUGATE BASES
STRONG	weak
↑	↓
weak	STRONG

In general, **Reactions always go from the stronger A-B pair (larger K) to the weaker A-B pair (smaller K).**

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K and Acid-Base Reactions

A strong acid is 100% dissociated.

Therefore, a STRONG ACID - a good H^+ donor- must have a WEAK CONJUGATE BASE - a poor H^+ acceptor.

$$HNO_3(aq) + H_2O(liq) \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$$

STRONG A   base   acid   weak B

Every A-B reaction has two acids and two bases. Equilibrium always lies *toward the weaker pair.* Here K is *very* large... should write:

$$HNO_3(aq) + H_2O(liq) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

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K and Acid-Base Reactions

Acetic acid is only 0.42% ionized when [HOAc] = 1.0 M. It is a **WEAK ACID**

$$HOAc \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ \quad + \quad OAc^-$$

WEAK A   **base**   **acid**   **STRONG B**
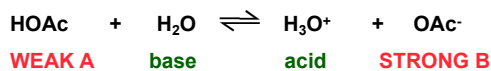
Because $[H_3O^+]$ is small, this must mean

1. H_3O^+ is a stronger acid than HOAc

2. OAc^- is a stronger base than H_2O

3. K for this reaction is small

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Types of Acid/Base Reactions

1. Strong acid + Strong base (SA + SB) reactions:

$$HCl(aq) + NaOH(aq) \quad \rightleftharpoons \quad H_2O(l) \ + \ NaCl(aq)$$

$$H^+ + Cl^- + Na^+ + OH^- \quad \rightleftharpoons \quad H_2O + Na^+ + Cl^-$$

Net ionic equation:

$$H^+(aq) + OH^-(aq) \quad \rightleftharpoons \quad H_2O(liq)$$
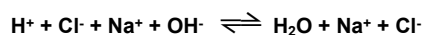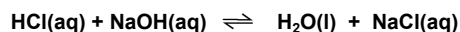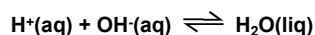
$K = 1/K_w = 1 \times 10^{14}$ *very product favored K!*

> Mixing equal molar quantities of a strong acid and strong base produces a neutral solution.
> *should write:*
> $HCl(aq) + NaOH(aq) \ \rightarrow \ H_2O(l) \ + \ NaCl(aq)$

MAR
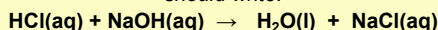
Types of Acid/Base Reactions

2. Weak acid + Strong base (WA + SB) reactions:

$$CH_3CO_2H + OH^- \quad \rightleftharpoons \quad H_2O + CH_3CO_2^-$$
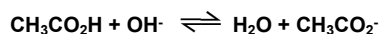
This is the reverse of the reaction of $CH_3CO_2^-$ (conjugate base) with H_2O.

OH^- stronger base than $CH_3CO_2^-$

$K = 1/K_b = 1.8 \times 10^9$ *very product favored K!*

> Mixing equal molar quantities of a weak acid and strong base produces the acid's conjugate base. The solution is basic.

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Types of Acid/Base Reactions

3. Weak base + Strong acid (WB + SA) reactions:

$$H_3O^+ + NH_3 \quad \rightleftharpoons \quad H_2O + NH_4^+$$
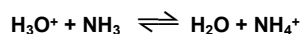
This is the reverse of the reaction of NH_4^+ (conjugate acid of NH_3) with H_2O.

H_3O^+ stronger acid than NH_4^+

$K = 1/K_a = 1.8 \times 10^9$ *very product favored K!*

> Mixing equal molar quantities of a strong acid and weak base produces the base's conjugate acid. The solution is acidic.

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Types of Acid/Base Reactions

4. Weak acid + weak base (WA + WB) reactions:
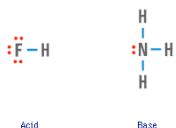
Acid   Base

Product cation = conjugate acid of weak base.
Product anion = conjugate base of weak acid.
pH of solution depends on relative strengths of cation and anion (larger K → smaller K).

MAR   *We will not be studying WA + WB reactions in CH 223*

Types of Acid/Base Reactions: Summary

• **Characteristics of Acid–Base Reactions**

Type	Example	Net Ionic Equation	Species Present After Equal Molar Amounts Are Mixed; pH
Strong acid + strong base	HCl + NaOH	$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2 H_2O(\ell)$	Cl^-, Na^+, pH = 7
Strong acid + weak base	HCl + NH₃	$H_3O^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + H_2O(\ell)$	Cl^-, NH_4^+, pH < 7
Weak acid + strong base	HCO₂H + NaOH	$HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(\ell)$	HCO_2^-, Na^+, pH > 7
Weak acid + weak base	HCO₂H + NH₃	$HCO_2H(aq) + NH_3(aq) \rightleftharpoons HCO_2^-(aq) + NH_4^+(aq)$	HCO_2^-, NH_4^+, pH dependent on K_a and K_b of conjugate acid and base.

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0.0001 M

0.003 M

Equilibria Involving A Weak Acid

0.06 M
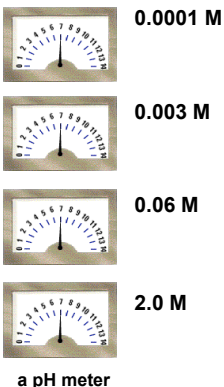
Determining the pH of an acetic acid solution

2.0 M

a pH meter

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Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc-, and the pH.

Step 1. Define **ICE** equilibrium using K_a.

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

$$[HOAc] \qquad [H_3O^+] \qquad [OAc^-]$$

initial

change

equilib

Note that we neglect $[H_3O^+]$ from H_2O.
HOAc = acetic acid, OAc- = acetate ion

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc-, and the pH.

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

Step 2. Write K_a expression

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{x^2}{1.00 - x}$$

This is a quadratic equation; solve using the quadratic formula.

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc-, and the pH.

Step 3. Solve K_a expression

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{x^2}{1.00 - x}$$

First assume x is *very small* because K_a is so small. If so:

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00}$$

Therefore,

x = $[H_3O^+]$ = [OAc-] = [1.8x10⁻⁵ • 1.00]¹/² = $[K_a • C_a]^{1/2}$

C_a = concentration (M) of acid

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc-, and the pH.

Step 3. Solve K_a *approximate* expression:

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00}$$

x = $[H_3O^+]$ = [OAc-] = [1.8x10⁻⁵ • 1.00]¹/²

x = $[H_3O^+]$ = [OAc-] = 4.2 x 10⁻³ M

pH = - log $[H_3O^+]$ = -log (4.2 x 10⁻³) = 2.37

MAR

Exact solution with quadratic: x = 0.0042, x = -0.0043   MAR

Equilibria Involving A Weak Acid

Consider the approximate expression:

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00} \qquad x = [H_3O^+] = [K_a • 1.00]^{1/2}$$

For many weak acids

[H₃O⁺] = [conj. base] = [Kₐ · Cₐ]¹/²

where C_a = initial conc. of acid

Useful Rule of Thumb:

If 100·Kₐ < Cₐ, then [H₃O⁺] = [Kₐ·Cₐ]¹/²

or pH = – log [Kₐ·Cₐ]¹/²

MAR

Equilibria Involving A Weak Acid

Calculate the pH of a 0.0010 M solution of formic acid, HCO_2H.

$$HCO_2H + H_2O \rightleftharpoons HCO_2^- + H_3O^+$$

$K_a = 1.8 \times 10^{-4}$
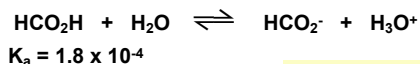
Approximate solution

> *100 * K_a is not less than C_a!*

$[H_3O^+] = [K_a \bullet C_a]^{1/2} = 4.2 \times 10^{-4}$ M, **pH = 3.37**

Exact Solution

$[H_3O^+] = [HCO_2^-] = 3.4 \times 10^{-4}$ M

$[HCO_2H] = 0.0010 - 3.4 \times 10^{-4} = 0.0007$ M

pH = 3.47

MAR

Weak Bases

Ammonia, NH_3
$K_b = 1.8 \times 10^{-5}$

Caffeine, $C_8H_{10}N_4O_2$
$K_b = 2.5 \times 10^{-4}$

Benzoate ion, $C_6H_5CO_2^-$
$K_a = 1.6 \times 10^{-10}$

Phosphate ion, PO_4^{3-}
$K_b = 2.8 \times 10^{-2}$

MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
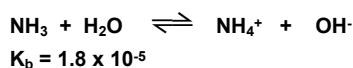
$K_b = 1.8 \times 10^{-5}$

Step 1. Define equilibrium concs.

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial			
change			
equilib			

MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
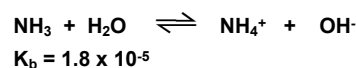
$K_b = 1.8 \times 10^{-5}$

Step 2. Solve the equilibrium expression

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.010 - x}$$

Assume x is small ($100 \bullet K_b < C_b$), so

$x = [OH^-] = [NH_4^+] = [K_b \bullet C_b]^{1/2} = 4.2 \times 10^{-4}$ M

check: $[NH_3] = 0.010 - 4.2 \times 10^{-4} \approx 0.010$ M

Valid approximation!

Exact solution with quadratic: x = 0.00042, x = -0.00043

MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$K_b = 1.8 \times 10^{-5}$
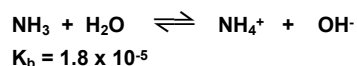
Step 3. Calculate pH

$[OH^-] = 4.2 \times 10^{-4}$ M

so **pOH** = - log $[OH^-]$ = **3.37**

Because pH + pOH = 14,

pH = 10.63

or **pH = 14 + log $[K_b \bullet C_b]^{1/2}$ = 10.63**

MAR

Overview: Calculating pH of Acids & Bases

Strong acid: **pH = - log C_a = - log $[H_3O^+]$**

Strong base:
pH = 14 + log C_b = 14 + log $[OH^{-1}]$

Weak acid:
pH = - log $[K_a \bullet C_a]^{1/2}$ *(100 * $K_a < C_a$)*

Weak base:
pH = 14 + log $[K_b \bullet C_b]^{1/2}$ *(100 * $K_b < C_b$)*

MAR   ***Memorize!***

Acid-Base Properties of Salts

MX + H$_2$O ----> acidic or basic solution?

Consider NH$_4$Cl

NH$_4$Cl(aq) ----> NH$_4$$^+$(aq) + Cl$^-$(aq)

(a)   Reaction of Cl$^-$ with H$_2$O

  Cl$^-$ +   H$_2$O ----> HCl   +   OH$^-$

  base   acid   acid   base

Cl$^-$ ion is a VERY weak base because its conjugate acid is strong.

Therefore, Cl$^-$ ----> neutral solution

MAR

Acid-Base Properties of Salts

MX + H$_2$O ----> acidic or basic solution?

NH$_4$Cl(aq) ----> NH$_4$$^+$(aq) + Cl$^-$(aq)
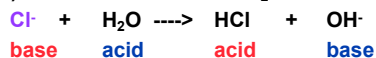
(b)   Reaction of NH$_4$$^+$ with H$_2$O

  NH$_4$$^+$ + H$_2$O ----> NH$_3$ +   H$_3$O$^+$
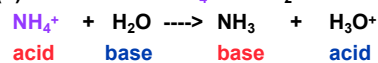
  acid   base   base   acid

NH$_4$$^+$ ion is a moderate acid (K$_a$ = 5.6 x 10^{-10}) because its conjugate base is weak.

Therefore, NH$_4$$^+$ ----> acidic solution

MAR

Acid-Base Properties of Salts

Acid and Base Properties of Some Ions in Aqueous Solution

	Neutral		Basic			Acidic	
Anions	Cl$^-$	NO$_3$$^-$	CH$_3$CO$_2$$^-$	CN$^-$	SO$_4$$^{2-}$	HSO$_4$$^-$	
	Br$^-$	ClO$_4$$^-$	HCO$_2$$^-$	PO$_4$$^{3-}$	HPO$_4$$^{2-}$	H$_2$PO$_4$$^-$	
	I$^-$		CO$_3$$^{2-}$	HCO$_3$$^-$	SO$_3$$^{2-}$	HSO$_3$$^-$	
			S^{2-}	HS$^-$	OCl$^-$		
			F$^-$	NO$_2$$^-$			
Cations	Li$^+$	Mg^{2+}	Al(H$_2$O)$_5$(OH)$^{2+}$			Al(H$_2$O)$_6$$^{3+}$ and hydrated	
	Na$^+$	Ca^{2+}	and analogous ions			transition metal cations	
	K$^+$	Ba^{2+}				(Fe(H$_2$O)$_6$$^{3+}$)	
						NH$_4$$^+$	

MAR

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na$_2$CO$_3$.

Na$^+$ + H$_2$O ---> neutral

CO$_3$$^{2-}$ +   H$_2$O ⇌ HCO$_3$$^-$ +   OH$^-$

base   acid   acid   base

   K$_b$ = 2.1 x 10^{-4}

Step 1.   Set up ICE concentration table

	[CO$_3$$^{2-}$]	[HCO$_3$$^-$]	[OH$^-$]
initial			
change			
equilib			

MAR

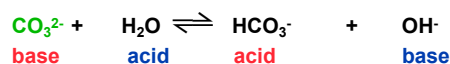## Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na$_2$CO$_3$.

Na$^+$ + H$_2$O ---> neutral

CO$_3$$^{2-}$ +   H$_2$O ⇌ HCO$_3$$^-$ +   OH$^-$

base   acid   acid   base

   K$_b$ = 2.1 x 10^{-4}

Step 2.   Solve the equilibrium expression

$$K_b = 2.1 \text{ x } 10^{-4} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x^2}{0.10 - x}$$

Assume 0.10 - x ≈ 0.10, because 100•K$_b$ < C$_b$

x = [HCO$_3$$^-$] = [OH$^-$] = [K$_b$ • C$_b$]$^{1/2}$ = 0.0046 M
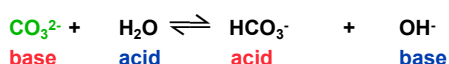
Exact solution with quadratic: x = 0.0045, x = -0.0047   *MAR*

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na$_2$CO$_3$.

Na$^+$ + H$_2$O ---> neutral

CO$_3$$^{2-}$ +   H$_2$O ⇌ HCO$_3$$^-$ +   OH$^-$

base   acid   acid   base
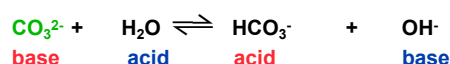
   K$_b$ = 2.1 x 10^{-4}

Step 3.   Calculate the pH

[OH$^-$] = 0.0046 M

pOH = - log [OH$^-$] = 2.34

pH + pOH = 14,

so pH = 11.66, and the solution is _____.

  or pH = 14 + log [K$_b$•C$_b$]$^{1/2}$ = 11.66

MAR

Lewis Acids & Bases

Nickel bis(dimethylglyoximate)
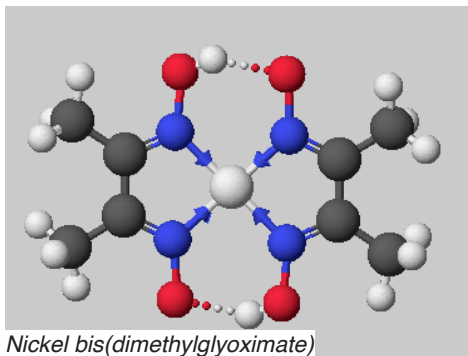
Clifford and Aiden with red Nickel bis(dimethylglyoximate) solution (April 2023)

MAR

Lewis Acids & Bases

Lewis acid = electron pair acceptor (BF$_3$)

BF$_3$, the boron atom is surrounded by only three electron pairs.

Lewis base = electron pair donor (NH$_3$)

MAR
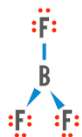
Lewis Acids & Bases

New bond formed using electron pair from the Lewis base.

Coordinate covalent bond

Notice geometry change on reaction.

MAR

Lewis Acids & Bases

Lewis Acid		Lewis Base		Adduct
H$^+$	+	H$_2$O	→	H$_3$O$^+$
H$^+$	+	NH$_3$	→	NH$_4^+$

MAR
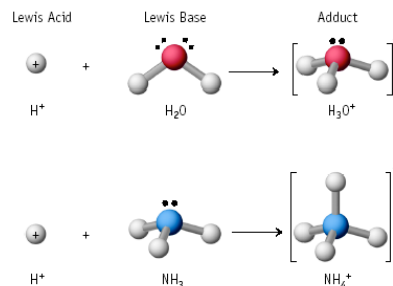
Lewis Acids & Bases

The combination of metal ions (Lewis acids) with Lewis bases such as H$_2$O and NH$_3$ ------>
COMPLEX IONS

All metal ions form complex ions with water and are of the type [M(H$_2$O)$_x$]$^{n+}$ where **x** = 4 and 6.

[Co(H$_2$O)$_6$]$^{3+}$

[Cu(NH$_3$)$_4$]$^{2+}$

MAR
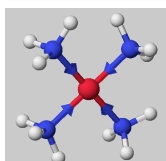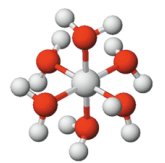
Lewis Acids & Bases

Add NH$_3$ to light blue [Cu(H$_2$O)$_4$]$^{2+}$ ------>
light blue Cu(OH)$_2$ and then deep blue [Cu(NH$_3$)$_4$]$^{2+}$

Ammonia   Water

MAR
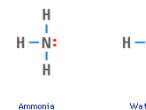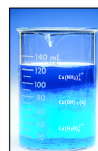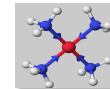
Lewis Acids & Bases

The Fe^{2+} in heme can interact with O_2 or CO in a Lewis acid-base reaction.

MAR
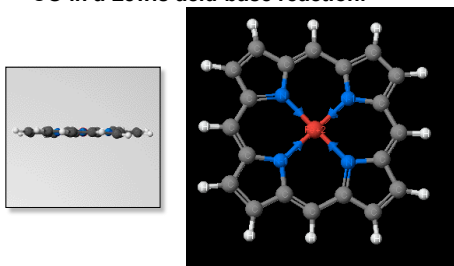
Lewis Acids & Bases

Many complex ions containing water undergo HYDROLYSIS to give acidic solutions.

$[Cu(H_2O)_4]^{2+} + H_2O \longrightarrow [Cu(H_2O)_3(OH)]^+ + H_3O^+$

This is a K_a expression
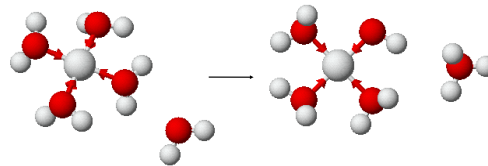
This explains why water solutions of transition metals are acidic.

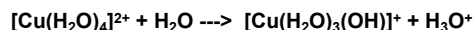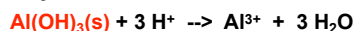MAR

Lewis Acids & Bases

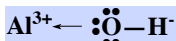Lewis acid & base theory explains AMPHOTERIC nature of some metal hydroxides.

$Al(OH)_3(s) + 3 H^+ \longrightarrow Al^{3+} + 3 H_2O$

Here $Al(OH)_3$ is a Brønsted base.

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

Here $Al(OH)_3$ is a Lewis acid.

$Al^{3+} \longleftarrow :\ddot{O}-H^-$

MAR

Lewis Acids & Bases

Many complex ions are very stable.

$Cu^{2+} + 4 NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$
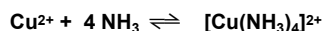
K for the reaction is called

$K_{formation}$

or a "formation constant"

Here $K_f = 6.8 \times 10^{12}$. Reaction is strongly product-favored.

$$K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$
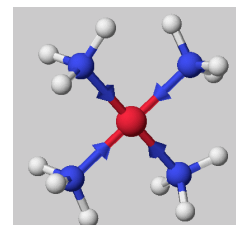
MAR

Lewis Acids & Bases

Formation of complex ions explains why you can dissolve a precipitate by forming a complex ion.

$AgCl(s) + 2 NH_3 \rightleftharpoons$

$Ag(NH_3)_2^+ + Cl^-$

AgCl(s)

MAR

Lewis Acids & Bases

Formation of complex ions explains why you can dissolve a precipitate by forming a complex ion.

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$ $K_{sp} = 1.8 \times 10^{-10}$

$Ag^+ + 2 NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $K_{form} = 1.6 \times 10^7$

$AgCl(s) + 2 NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$
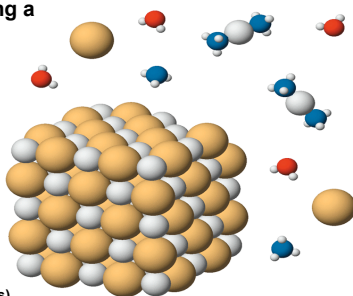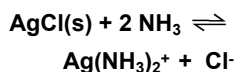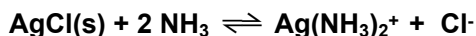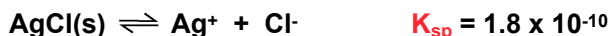
$K_{net} = K_{sp} \cdot K_{form} = 2.9 \times 10^{-3}$

MAR

Hints for This Chapter

$pH_{(strong\ acid)}$ = - log C_a

$pH_{(strong\ base)}$ = 14 + log C_b

$pH_{(weak\ acid)}$ = - log $[K_a*C_a]^{1/2}$

$pH_{(weak\ base)}$ = 14 + log $[K_b*C_b]^{1/2}$

14 = pH + pOH = pK_a + pK_b

K_w = 1.00 * 10^{-14} = $[H_3O^+][OH^-]$ = K_a*K_b (25 °C)

Know equivalence point pH values for different titrations

Know how to use formation constants

Understand Lewis acid/base theory

MAR

End of Chapter 14 Part I

See:
- *Chapter Fourteen Part I Study Guide*
- *Chapter Fourteen Part I Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

MAR

Important Equations, Constants, and Handouts from this Chapter:
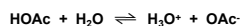
$pH_{(strong\ acid)}$ = - log C_a

$pH_{(strong\ base)}$ = 14 + log C_b

$pH_{(weak\ acid)}$ = - log $[K_a*C_a]^{1/2}$

$pH_{(weak\ base)}$ = 14 + log $[K_b*C_b]^{1/2}$

14 = pH + pOH = pK_a + pK_b

K_w = 1.00 * 10^{-14} = $[H_3O^+][OH^-]$ = K_a*K_b (25 °C)

HOAc + H_2O ⇌ H_3O^+ + OAc⁻

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} ;$$

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
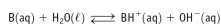
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Acid-Base Theory: Brønsted theory, conjugate acid *and* base, strong *and* weak acids *and* bases, *know* the 8 strong acids *and* bases!, autoionization, Lewis theory, electron pair acceptor *and* donator, salt acidity/basicity, formation constants (K_f)

Handouts:
- *Manipulating Equilibrium Constant Expressions*
- *Types of Equilibrium Constants*
- *Table of K_a and K_b values in Problem Set #2*

MAR

End of Chapter Problems: *Test Yourself*

1. An aqueous solution has a pH of 3.75. What is the hydronium ion concentration of the solution? What is the hydroxide ion concentration of the solution? Is it acidic or basic?
2. What is the pH of a 0.0015 M solution of Ba(OH)₂?
3. Epinephrine hydrochloride has a pK_a value of 9.53. What is the value of K_a?
4. A weak base has K_b = 4.7 x 10⁻¹¹. What is the value of K_a for the conjugate acid?
5. A 0.015 M solution of hydrogen cyanate, HOCN, has a pH of 2.67. What is the hydronium ion concentration in the solution? What is the ionization constant, K_a, for the acid?
6. A 0.015 M solution of a base has a pH of 10.09. What are the hydronium and hydroxide ion concentrations of this solution? What is the value of K_b for this base?
7. Which of the following substances should be classified as a Lewis acid and a Lewis base: Fe²⁺(aq), CH₃NH₂

MAR

End of Chapter Problems: *Answers*

1. $[H_3O^+]$ = 1.8 × 10⁻⁴ M, $[OH^-]$ = 5.6 × 10⁻¹¹ M, acidic
2. 11.48
3. 3.0 x 10⁻¹⁰
4. 2.1 x 10⁻⁴
5. 0.0021 M, 3.6 x 10⁻⁴ (K_a = 3.0 x 10⁻⁴ using short method)
6. $[H_3O^+]$ = 8.1 × 10⁻¹¹ M, $[OH^-]$ = 1.2 × 10⁻⁴ M, K_b = 9.7 x 10⁻⁷
7. Fe²⁺(aq) would be a Lewis acid, CH₃NH₂ would be a Lewis base

MAR