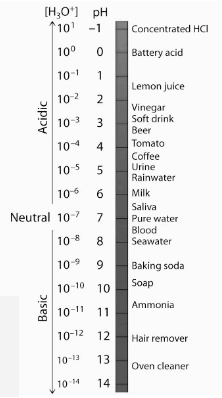
Chapter 14: Acid-Base Equilibria



Chemistry 223
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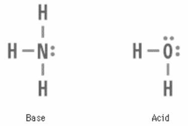
http://mhchem.org/223

MAR Last update: 7/7/25

14.1 - Brønsted-Lowry Acids and Bases

The most general theory for common aqueous acids and bases is the Brønsted - Lowry theory

- * A **Brønsted-Lowry Acid**: A compound that **donates a proton** to another compound
- * A **Brønsted-Lowry Base**: A compound that **accepts a proton** from another compound



The Brønsted definition means **NH_3 is a base** in water - and **water is an acid**

$$\underset{\textbf{Base}}{NH_3} + \underset{\textbf{Acid}}{H_2O} \rightleftharpoons \underset{\textbf{Acid}}{NH_4^+} + \underset{\textbf{Base}}{OH^-}$$

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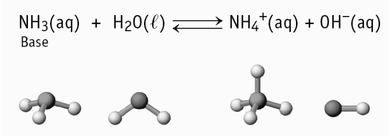
Conjugates of Acids and Bases

NH_3 is a base in water - and water is itself an acid



$$\underset{\text{Base}}{NH_3(aq)} + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

NH_3 / NH_4^+ is a conjugate pair - related by the gain or loss of H^+ *(H_2O and OH^- are another conjugate pair)*

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

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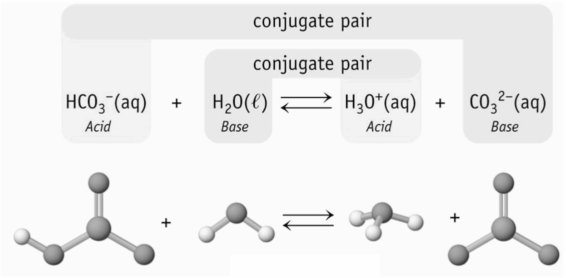
Water as an Acid and a Base

H_2O can function as both an acid *and* a base!



conjugate pair

conjugate pair

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

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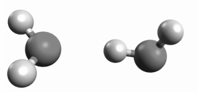
Water and Autoionization



Water can be an acid or a base due to **autoionization**.

Pure water undergoes autoionization into **hydronium (acid) and hydroxide (base) ions.** The **equilibrium constant, K_w,** has been measured for **$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$**

$K_w = [H_3O^+]\ [OH^-] = 1.000 \times 10^{-14}$ at 25 °C

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

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

and so $[H_3O^+] = [OH^-] = \sqrt{K_w} = 1.000 \times 10^{-7}$ M

Memorize $K_W = 1.000 \times 10^{-14}$!

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Acid Ionization

The reaction between a Brønsted-Lowry Acid and water is called acid ionization

Strong acids dissociate **100%** into hydronium and a conjugate base:

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

HNO_3 is about 100% dissociated in water; there is no HNO_3 present, only H_3O^+.

Use single sided arrows for strong acids!

Weak acids do not dissociate completely into hydronium and a conjugate base; *equilibrium*!

$HNO_2(aq) + H_2O(liq) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

Equilibrium constants for weak acids called **acid ionization constants, K_a**:

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

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Base Ionization

The reaction between a Brønsted-Lowry Base and water is called base ionization

Strong bases dissociate **100%** into hydroxide and a conjugate acid:

$NaOH(aq) + H_2O(liq) \rightarrow$

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

NaOH is about 100% dissociated in water; there is no NaOH present, only **OH^-**.

Use single sided arrows for strong bases!

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Weak bases do not dissociate completely into hydroxide and a conjugate acid; *equilibrium*!

$NH_3(aq) + H_2O(liq) \rightleftharpoons$

$OH^-(aq) + NH_4^+(aq)$

Equilibrium constants for weak bases called base ionization constants, K_b:

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

Strong Acids and Bases

There are five strong *monoprotic* acids and three strong *monoprotic* bases

The **five strong acids**:

- * HNO_3
- * HCl
- * HBr
- * HI
- * $HClO_4$

The **three strong bases**:

- * NaOH
- * KOH
- * LiOH

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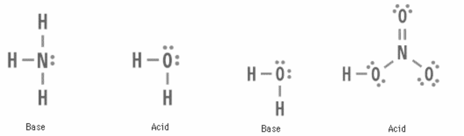

Memorize the eight strong acids and bases!

Assume that all other acids and bases are weak acids and weak bases unless told otherwise!

14.2 - pH and pOH

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ **at 25 °C**

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

Solution:

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

Le Chatelier predicts equilibrium shifts to the ___________.

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

Set up an ICE concentration table:

	H_3O^+	OH^-
initial		
change		
equilib		

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

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

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

$[H_3O^+] = K_w / 0.0010$

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

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14.2 - pH and pOH

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

Solution:

$[OH^-] = 0.0010$ M **and**

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

This solution is consider basic because **$[OH^-] > [H_3O^+]$**

There must be a better way to tell if something is basic or acidic!

A common way to express acidity and basicity is with pH

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

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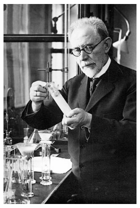

Søren Sørensen, *creator of the pH scale*

In a ***neutral*** solution**,**

$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ *(25 °C)*

$pH = -\log (1.0 \times 10^{-7})$

$= -(-7.00) = 7.00$

pH = 7.00 for neutral solutions!

More on pH

What is the pH of the 0.0010 M NaOH solution?

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

$pH = - \log (1.0 \times 10^{-11}) = 11.00$

Classification	Relative Ion	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

General conclusion -

Basic solution	**pH > 7**
Neutral	pH = 7
Acidic solution	pH < 7

Public Enemy are not scientists!

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pH to Hydronium

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

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

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

$= 7.6 \times 10^{-4}$ M

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Logarithms and Sig Figs

Logarithms are exponents with special sig figs rules.

General rule:

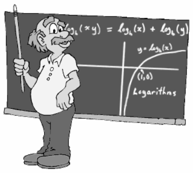
log of experimentally measured number with *N* sig figs give numbers with *N* decimal places *after* the decimal (digit before decimal only indicates magnitude)

***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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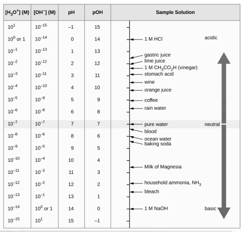
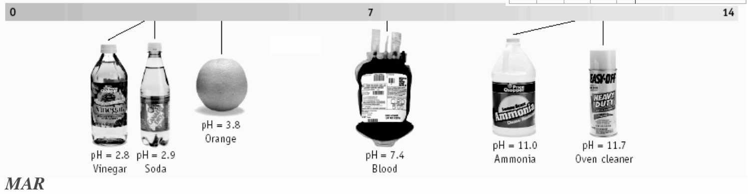
pH of Common Substances

Most foods and drinks are slightly acidic, while most household cleaners are basic



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



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pOH and Other pX Scales

In general **pX = -log X**

and: **$pK_a = -\log K_a$**

and so: **$pOH = -\log [OH^-]$**

$K_w = [H_3O^+][OH^-] = 1.000 \times 10^{-14}$ *at 25 °C*

Take the negative log of both sides

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

$$14.00 = pH + pOH$$

also: $14 = pK_a + pK_b$

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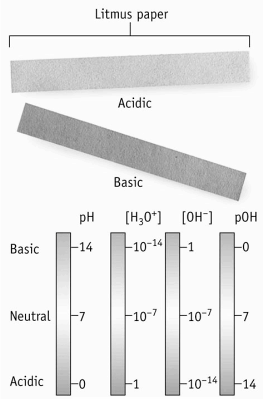

acidic solutions:

pH ↓,

$[H_3O^+]$ ↑,

$[OH^-]$ ↓,

pOH ↑

basic solutions: **pH ↑,**

$[H_3O^+]$ ↓,

$[OH^-]$ ↑,

pOH ↓

$K_w = [H_3O^+][OH^-] = 1.000 \times 10^{-14}$ at 25 °C

pH + pOH = 14

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14.3 - Relative Strengths of Acids and Bases

All weak acids have conjugate bases, *and* **all weak bases have conjugate acids**

Weak acids and bases ionize to a very small extent (< 5%)

Weak acids use **K_a** (acid ionization constants) while weak bases use **K_b** (base ionization constants.)

K_a and K_b values are much less than one

Acid	Conjugate Base
acetic, CH_3CO_2H	$CH_3CO_2^-$, acetate
ammonium, NH_4^+	NH_3, ammonia
bicarbonate, HCO_3^-	CO_3^{2-}, carbonate

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

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

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

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

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Combining Conjugate K_a and K_b Expression

If a weak acid's K_a expression is combined with its conjugate base K_b expression, something interesting happens:

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

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

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_a * K_b = K_w$$

Important relations: $K_a * K_b = K_w$ *and* $pK_a + pK_b = 14$

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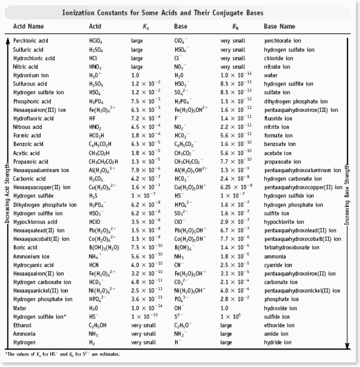
Ionization Constants for Acids/Bases

Acids

Increasing strength



Ionization Constants for Some Acids and Their Conjugate Bases

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaquaaluminum ion	$Al(H_2O)_6^{3+}$	7.9×10^{-6}	$Al(H_2O)_5OH^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$Cu(H_2O)_6^{2+}$	1.6×10^{-7}	$Cu(H_2O)_5OH^+$	6.25×10^{-8}	pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	hydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	sulfite ion
Hypochlorous acid	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	hypochlorite ion
Hexaaqualead(II) ion	$Pb(H_2O)_6^{2+}$	1.5×10^{-8}	$Pb(H_2O)_5OH^+$	6.7×10^{-7}	pentaaquahydroxolead(II) ion
Hexaaquacobalt(II) ion	$Co(H_2O)_6^{2+}$	1.3×10^{-9}	$Co(H_2O)_5OH^+$	7.7×10^{-6}	pentaaquahydroxocobalt(II) ion
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	tetrahydroxoborate ion
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	ammonia
Hydrocyanic acid	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	cyanide ion
Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	3.2×10^{-10}	$Fe(H_2O)_5OH^+$	3.1×10^{-5}	pentaaquahydroxoiron(II) ion
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	carbonate ion
Hexaaquanickel(II) ion	$Ni(H_2O)_6^{2+}$	2.5×10^{-11}	$Ni(H_2O)_5OH^+$	4.0×10^{-4}	pentaaquahydroxonickel(II) ion
Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	phosphate ion
Water	H_2O	1.0×10^{-14}	OH^-	1.0	hydroxide ion
Hydrogen sulfide ion*	HS^-	1×10^{-19}	S^{2-}	1×10^5	sulfide ion
Ethanol	C_2H_5OH	very small	$C_2H_5O^-$	large	ethoxide ion
Ammonia	NH_3	very small	NH_2^-	large	amide ion
Hydrogen	H_2	very small	H^-	large	hydride ion

*The values of K_a for HS^- and K_b for S^{2-} are estimates.

Conjugate Bases

Increasing strength

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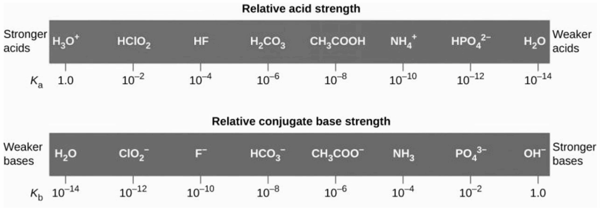
Strengths of Acids and Bases

Acid strength is determined by the amount of **hydronium** it produces; so as K_a increases, the strength of the acid increases.

Base strength is determined by the amount of **hydroxide** it produces; so as K_b increases, the strength of the base increases.



Reactions go from **stronger acids to weaker acids (larger K_a to smaller K_a)** and **stronger bases to weaker bases (larger K_b to smaller K_b)**

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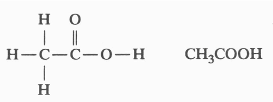
pH Calculations with Weak Acids & Bases



CH_3COOH

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Determining the pH of an acetic acid solution

0.0001 M

0.003 M

0.06 M

2.0 M

a pH meter

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Equilibria and pH of a Weak Acid

Calculate the equilibrium concentrations of HOAc, H_3O^+, OAc^-, and the pH for a 1.00 M HOAc solution.

HOAc = acetic acid,
OAc^- = acetate ion

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

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

	[HOAc]	**$[H_3O^+]$**	**$[OAc^-]$**
initial			
change			
equilib			

Note that we neglect $[H_3O^+]$ from H_2O

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Equilibria and pH of a Weak Acid

Calculate the equilibrium concentrations of HOAc, H_3O^+, OAc^-, and the pH for a 1.00 M HOAc solution.

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

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** *... but there's a better way, sometimes!*

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 = $[H_3O^+]$ = $[OAc^-]$ = $[1.8\text{x}10^{-5} \bullet 1.00]^{1/2}$ = $[K_a \bullet C_a]^{1/2}$

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C_a = concentration (M) of acid

Equilibria and pH of a Weak Acid *(continued)*

Calculate the equilibrium concentrations of HOAc, H_3O^+, OAc^-, and the pH for a 1.00 M HOAc solution.

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

Step 3. **Solve K_a** *approximate* **expression:**

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

x = $[H_3O^+]$ = $[OAc^-]$ = $[1.8\text{x}10^{-5} \bullet 1.00]^{1/2}$

x = $[H_3O^+]$ = $[OAc^-]$ = $4.2 \text{ x } 10^{-3}$ M

pH = - log $[H_3O^+]$ = -log ($4.2 \text{ x } 10^{-3}$) = 2.37

[HOAc] = 1.00 M *no change!*

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

Approximation Method for the pH of a Weak Acid

Consider the approximate expression:

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

For many weak acids

$[H_3O^+] = [\text{conj. base}] = [K_a \bullet C_a]^{1/2}$

where C_a **= initial concentration of acid (M)**

Useful Rule:

If $100 \bullet K_a < C_a$, *then* $[H_3O^+] = [K_a \bullet C_a]^{1/2}$

or pH = - log $[K_a \bullet C_a]^{1/2}$

Important Equation!
Quick method to find pH
of Weak Acids!

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Equilibria Involving A Weak Acid

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

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

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

100 * K_a is not less than C_a!

Approximate solution

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

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Equilibria Involving A Weak Base

Calculate the pH of a 0.010 M NH_3 solution.

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

Step 1. **Define equilibrium concs.**

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

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

As before, assume **x is small** *because*

$100 \bullet K_b < C_b$, *so*

$x = [OH^-] = [NH_4^+] = [K_b \bullet C_b]^{1/2}$

$x = 4.2 \times 10^{-4}$ M

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

$[NH_3] \approx 0.010$ M

Valid approximation!

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

MAR

Equilibria Involving A Weak Base

Calculate the pH of a 0.010 M NH_3 solution.

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

$[OH^-] = 4.2 \times 10^{-4}$ M *(last slide)*

Step 3. **Calculate pH**

pOH = - log $[OH^-]$ = - log $[4.2 \times 10^{-4}]$ = 3.37

Because **pH + pOH = 14.00,**

pH = **14.00 - 3.37** = 10.63

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

Important Equation!
Quick method to find pH
of Weak Bases!

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 $[OH^-]$

Weak acid:

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

Weak base:

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

Memorize!

MAR

Mixing Equimolar Acids and Bases

Mixing **equal moles of strong acids with strong bases** ("**equimolar**") results in a **neutral solution** of water and a 'salt'; **pH = 7**

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

Mixing **equimolar amounts of weak acids with strong bases** results in a **basic solution** due to the conjugate base of the weak acid; **pH > 7**

$CH_3CO_2H(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3CO_2^-(aq)$

Weak base,
pH is basic

Mixing **equimolar amounts of weak bases with strong acids** results in an **acidic solution** due to the conjugate acid of the weak base; **pH < 7**

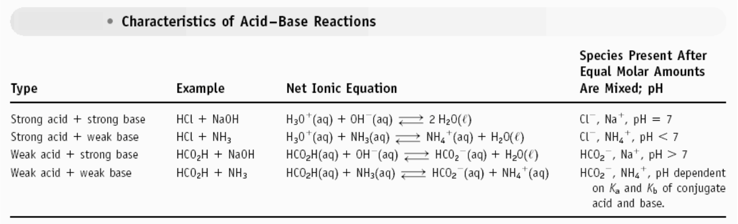
$H_3O^+(aq) + NH_3(aq) \rightarrow H_2O(l) + NH_4^+(aq)$

Weak acid,
pH is acidic

MAR

Types of Acid/Base Reactions: Summary

Knowing the pH when the moles of acid and base are equal ("**equivalence**") can be important



• 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	$HCl + NH_3$	$H_3O^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + H_2O(\ell)$	Cl^-, NH_4^+, pH < 7
Weak acid + strong base	HCO_2H + NaOH	$HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(\ell)$	HCO_2^-, Na^+, pH > 7
Weak acid + weak base	$HCO_2H + NH_3$	$HCO_2H(aq) + NH_3(aq) \rightleftharpoons HCO_2^-(aq) + NH_4^+(aq)$	HCO_2^-, NH_4^+, pH dependent on K_a and K_b of conjugate acid and base.

MAR

14.4 - Hydrolysis of Salts

Salts (ionic compounds) are neutral in water if the hydronium and hydroxide concentrations are equal.

However, often the cation and/or anion are weak acids or bases, which affects the pH of the solution.

$MX + H_2O \rightarrow$ *acidic or basic solution?*

Consider NH_4Cl:

For Chloride:

$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

(a) Reaction of Cl^- with H_2O

$Cl^- \quad + \quad H_2O \rightarrow \quad HCl \quad + \quad OH^-$

base acid acid base

Cl^- ion is a very weak base because its conjugate acid (HCl) is strong.

Therefore, **$Cl^- \rightarrow$ neutral solution**

All conjugates of strong acids (and bases) do not affect the pH of the solution

MAR

Acid-Base Properties of Salts

$MX + H_2O \rightarrow$ acidic or basic solution?

For ammonium:

$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

(b) Reaction of NH_4^+ with H_2O

$NH_4^+ \quad + \quad H_2O \rightarrow \quad NH_3 \quad + \quad H_3O^+$

acid base base acid

NH_4^+ ion is a moderate acid ($K_a = 5.6 \times 10^{-10}$) because its conjugate base (NH_3) is weak.

Therefore, $NH_4^+ \rightarrow$ acidic solution

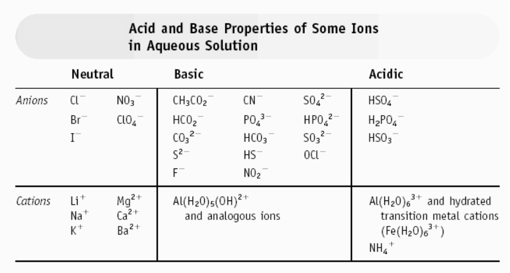
Conclusion:

NH_4Cl in water creates an acidic solution due to the ammonium ion

(chloride is neutral)

MAR

Acid-Base Properties of Salts



Acid and Base Properties of Some Ions in Aqueous Solution

	Neutral		Basic			Acidic
Anions	Cl^- Br^- I^-	NO_3^- ClO_4^-	$CH_3CO_2^-$ HCO_2^- CO_3^{2-} S^{2-} F^-	CN^- PO_4^{3-} HCO_3^- HS^- NO_2^-	SO_4^{2-} HPO_4^{2-} SO_3^{2-} OCl^-	HSO_4^- $H_2PO_4^-$ HSO_3^-
Cations	Li^+ Na^+ K^+	Mg^{2+} Ca^{2+} Ba^{2+}	$Al(H_2O)_5(OH)^{2+}$ and analogous ions			$Al(H_2O)_6^{3+}$ and hydrated transition metal cations ($Fe(H_2O)_6^{3+}$) NH_4^+

MAR

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na_2CO_3

Na^+ **$+ H_2O \rightarrow$ neutral** *(conjugate of NaOH)*

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

base acid acid base

K_b *for carbonate* **$= 2.1 \times 10^{-4}$**

Step 1. Set up ICE concentration table

	$[CO_3^{2-}]$	$[HCO_3^-]$	$[OH^-]$
initial	0.10	0	0
change			
equilib			

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

$100 \bullet K_b < C_b$ so assume

$0.10 - x \approx 0.10$

$x = [HCO_3^-] = [OH^-]$

$x = [K_b \bullet C_b]^{1/2} = 0.0046$ M

Exact solution with quadratic: x = 0.0045, x = -0.0047

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

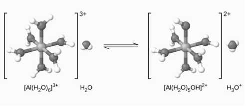
$pH + pOH = 14$,

so pH = 11.66; solution is ________.

MAR

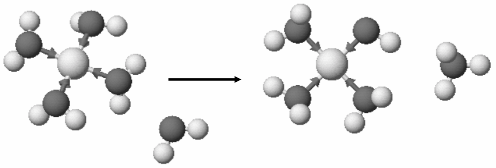
or **$pH = 14 + \log [K_b \bullet C_b]^{1/2} = 11.66$**

Transition Metals and Hydrolysis



Many transition metals (and Al) dissolved in water undergo hydrolysis to give acidic solutions.

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



This is a K_a expression

This explains why water solutions of transition metals and Al are acidic.

MAR

14.5 - Polyprotic Acids

Monoprotic acids have a single ionizable hydrogen. *Examples:* HCl, HF, HNO_2, etc. Weak acids have a single K_a value.

Polyprotic acids have more than one ionizable hydrogens (more than one H capable of forming hydronium) and more than one K_a value. *Examples:* **H_2SO_4** (**diprotic**), **H_3AsO_4** (**triprotic**), *etc.*

Examples: For **triprotic** phosphoric acid **H_3PO_4**:

$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.2\text{x}10^{-3}$$

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

$$K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3\text{x}10^{-8}$$

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$

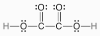
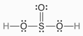
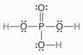
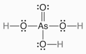
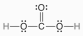
$$K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2\text{x}10^{-13}$$

$$\mathbf{K_{a1} > K_{a2} > K_{a3}}$$

We usually neglect $[H_3O^+]$ produced after the first dissociation.

Polyprotic Acids

Many polyprotic acids known

Name (Formula)	Lewis Structure*	K_{a1}	K_{a2}	K_{a3}
Oxalic acid ($H_2C_2O_4$)		5.6×10^{-2}	5.4×10^{-5}	
Sulfurous acid (H_2SO_3)		1.4×10^{-2}	6.5×10^{-8}	
Phosphoric acid (H_3PO_4)		7.2×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid (H_3AsO_4)		6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Carbonic acid (H_2CO_3)		4.5×10^{-7}	4.7×10^{-11}	
Hydrosulfuric acid (H_2S)		9×10^{-8}	1×10^{-17}	

*Red type indicates the ionizable protons.

*Several **dibasic** ($Sr(OH)_2$) and **tribasic** ($Al(OH)_3$) bases known*

Polyprotic Acids and pH

Example: Diprotic **ascorbic acid** (i.e. **Vitamin C**, **H_2Asc**) has K_{a1} = $1.0\text{x}10^{-5}$ and K_{a2} = $5\text{x}10^{-12}$. Calculate the pH of 0.050 M H_2Asc.

Note: 100* K_{a1} and 100*K_{a2} are less than C_a (0.050 M), so **$[H_3O^+] = \sqrt{K_{ax}*C_a}$**

Find $[H_3O^+]$ from K_{a1} and K_{a2}, *add them up, then* find pH

$$K_{a1} = \frac{[HAsc^-][H_3O^+]}{[H_2Asc]} = 1.0\text{x}10^{-5} = \frac{x^2}{0.050}$$

$$x = [H_3O^+] = [HAsc^-] = \sqrt{(0.050)(1.0\text{x}10^{-5})} = \mathbf{7.1x10^{-4}\ M}$$

$$[H_3O^+]_{\text{from HAsc-}} = \sqrt{[HAsc^-](K_{a2})}$$

$$= \sqrt{(7.1\text{x}10^{-4})(5\text{x}10^{-12})} = \mathbf{6x10^{-8}\ M}$$

$$[H_3O^+]_{\text{Total}} = 7.1\text{x}10^{-4}\text{ M} + 6\text{x}10^{-8}\text{ M} \approx 7.1\text{x}10^{-4}\text{ M}$$

pH = - log ($7.1\text{x}10^{-4}$ M) = **3.15**

Only $[H_3O^+]$ from K_{a1} affects pH,
K_{a2} contributes minor amount of $[H_3O^+]$

14.6 - Buffers

A **buffer** is a solution with both a weak acid and its conjugate base (or a weak base and its conjugate acid.)

Buffers resist drastic changes to the pH of the solution; very helpful in our bodies, living systems, etc.

A 100 mL sample of dilute HCl is adjusted to pH 5.00.

The addition of 1 mL of strong acid (left) or strong base (right) changes the pH by several units.

A 100 mL sample of an acetate buffer is adjusted to pH 5.00.

The addition of 1 mL of strong acid (left) or strong base (right) changes the pH very little.

The acetate buffer is made by mixing 1 M CH_3COOH (a weak acid) with 1 M $NaCH_3COO$ (which provides the conjugate base, CH_3COO^-)

Buffers

Buffers resist strong acids and bases utilizing weak bases and acids within the buffer.

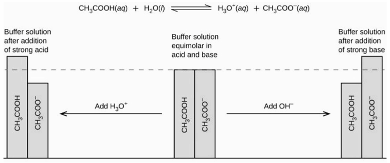
Consider a buffer HA / A^- system:

* Added **strong base** (OH^-) **neutralized by weak acid HA**:

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

* Added **strong acid** (H_3O^+) **neutralized by weak base A^-**:

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



<u>Adding strong acid</u> (H_3O^+) makes solution more acidic due to increased amount of weak acid (acetic acid)!

Likewise, <u>adding strong base</u> (OH^-) makes solution more basic due to increased amount of weak base (acetate)!

Buffer Solutions

The function of a buffer is to resist changes in the pH of a solution.

Buffers always consist of a weak acid and its conjugate base (or a weak base and its conjugate acid)

<u>*Weak Acid*</u>	+	<u>*Conjugate Base*</u>
HOAc	**+**	**OAc^-**
$H_2PO_4^-$	**+**	**HPO_4^{2-}**

HOAc = acetic acid,
OAc^- = acetate ion

<u>*Weak Base*</u>	+	<u>*Conjugate Acid*</u>
NH_3	**+**	**NH_4^+**
NO_2^-	**+**	**HNO_2**

<u>*Buffers and Henderson-Hasselbalch Guide*</u>

Buffer Solutions

HOAc = acetic acid,
OAc^- = acetate ion

Problem: **What is the pH of a buffer that has [HOAc] = 0.700 M and $[OAc^-]$ = 0.600 M?**

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

$K_a = 1.8 \times 10^{-5}$

	[HOAc]	$[OAc^-]$	$[H_3O^+]$
initial			
change			
equilib			

Assuming that x << 0.700 and 0.600, we have

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+](0.600)}{0.700}$$

$[H_3O^+] = 1.8 \times 10^{-5} * (0.700 / 0.600) = 2.1 \times 10^{-5}$

***and* pH = 4.68**

MAR

Buffer Solutions

Notice that the expression for calculating the H^+ concentration of the buffer is:

$$[H_3O^+] = \frac{\text{Orig. conc. of HOAc}}{\text{Orig. conc. of OAc}^-} \bullet K_a$$

$$[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conj. base}]} \bullet K_a \quad \textit{or} \quad [OH^-] = \frac{[\text{Base}]}{[\text{Conj. acid}]} \bullet K_b$$

Notice that $[H_3O^+]$ or $[OH^-]$ depends on K *and* the ratio of acid and base concentrations

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The Henderson-Hasselbalch Equation

$$[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conj. base}]} \bullet K_a$$

Take the negative log of both sides of this equation:

$$pH = pK_a - \log\frac{[\text{Acid}]}{[\text{Conj. base}]}$$

The Henderson - Hasselbalch Eq!

$$\boxed{\mathbf{pH = pK_a + \log\frac{[Conj.\ base]}{[Acid]}}}$$

The pH is determined largely by the pK_a of the acid and then adjusted by the ratio of acid and conjugate base. *Important equation!*

MAR

The Henderson-Hasselbalch Equation

$$\boxed{\mathbf{pH = pK_a + \log\frac{[Conj.\ base]}{[Acid]}}}$$

Note that the **concentrations of the acid and conjugate base are *not* important**

It is the ratio of the number of moles that affects pH

Result: **diluting a buffer solution does not change its pH**

Result: **You can use moles *or* molarity when using Henderson-Hasselbalch!**

See: Buffers and Henderson-Hasselbalch Guide

MAR

Adding an Acid to a Buffer

Problem: **What is the pH when 1.00 mL of 1.00 M HCl is added to**

a) 1.00 L of pure water (before HCl, pH = 7.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M *(pH = 4.68 before HCl, earlier problem)*

Solution to Part a:

pH of strong acid **= - log $[H_3O^+]$ = - log [HCl]**

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

$$1.00\text{ M} * 1.00\text{ mL} = M_2 \bullet 1001\text{ mL}$$

$$M_2 = 9.99 \times 10^{-4}\text{ M} = [H_3O^+]$$

$$pH = -\log(9.99 \times 10^{-4}) = 3.000$$

MAR

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water *(pH = 7.00; after HCl, pH = 3.000)*

b) 1.00 L of buffer with [HOAc] = 0.700 M and [OAc-] = 0.600 M *(pH = 4.68 before HCl)*

Solution to Part b:

***Step 1:* via stoichiometry,**

H_3O^+ (from HCl) + OAc^- (from buffer) → HOAc (from buffer)

	$[H_3O^+]$	$[OAc^-]$	[HOAc]
Initial			
Change			
After rxn			

Now we need to calculate pH using our new buffer solution

MAR

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water *(pH = 7.00; after HCl, pH = 3.000)*

b) 1.00 L of buffer with [HOAc] = 0.700 M and [OAc-] = 0.600 M *(pH = 4.68 before HCl)*

Solution to Part b:

Step 2: Equilibrium: **$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$**

	[HOAc]	**[OAc-]**	**[H$_3$O+]**
Initial			
Change			
Equilibrium			

$$[H_3O^+] = \frac{[HOAc]}{[OAc^-]} \bullet K_a = \frac{0.701}{0.599} \bullet (1.8 \text{ x } 10^{-5})$$

$[H_3O^+]$ = 2.1 x 10^{-5} M → pH = 4.68

Ignore x relative to 0.701 and 0.599

x = $[H_3O^+]$

The pH has not changed upon adding HCl to the buffer!

MAR

Adding an Acid to a Buffer Using HH Equation

The **Henderson-Hasselbalch equation** can be used to calculate the pH when 1.00 mL of 1.00 M HCl is added to 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc-] = 0.600 M

We can use an *alternate* form of the H-H equation:

$$\text{pH} = \text{p}K_a + \log \frac{(\textbf{mol}_{\textbf{Conj base}} - \textbf{mol}_{\textbf{strong acid}})}{(\textbf{mol}_{\textbf{weak acid}} + \textbf{mol}_{\textbf{strong acid}})}$$

$\text{p}K_a = -\log(1.8 * 10^{-5}) = 4.74$

$$\text{pH} = 4.74 + \log \frac{(0.600 - 0.00100)}{(0.700 + 0.00100)} = 4.67$$

Answer in good agreement with "double ice" method (4.68)

See: Buffers and Henderson-Hasselbalch Guide

MAR

Adding Acids and Bases to Buffers

For adding strong acids to buffers:

$$\text{pH} = \text{p}K_a + \log \frac{(\textbf{mol}_{\textbf{Conj base}} - \textbf{mol}_{\textbf{strong acid}})}{(\textbf{mol}_{\textbf{weak acid}} + \textbf{mol}_{\textbf{strong acid}})}$$

For adding strong bases to buffers:

$$\text{pH} = \text{p}K_a + \log \frac{(\textbf{mol}_{\textbf{Conj base}} + \textbf{mol}_{\textbf{strong base}})}{(\textbf{mol}_{\textbf{weak acid}} - \textbf{mol}_{\textbf{strong base}})}$$

*Very useful **for calculating pH changes in buffers!***

See: Buffers and Henderson-Hasselbalch Guide

MAR

Preparing a Buffer


Henderson

You want to create a buffer solution with a pH = 4.30.

This means **$[H_3O^+] = 10^{-pH}$ = 5.0 x 10^{-5} M**

It is *best* to choose an acid such that:

- *$[H_3O^+] \approx K_a$, **or***
- *pH ≈ pK_a*

You get the *exact* $[H_3O^+]$ (or pH) by **adjusting the *ratio* of weak acid to conjugate base.**

For a pH = 4.30 buffer, we will look for a value of K_a ≈ 5.0 x 10^{-5} or a pK_a ≈ 4.30


Hasselbalch

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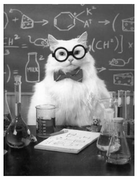
Preparing a Buffer



Which of the following three systems would be best to create a buffer solution at pH = 4.30 (*or* $[H_3O^+]$ = 5.0 x 10^{-5} M)?

Possible Buffers	K_a	pK_a
HSO_4^- / SO_4^{2-}	**1.2 x 10^{-2}**	**1.92**
HOAc / OAc^-	**1.8 x 10^{-5}**	**4.74**
HCN / CN^-	**4.0 x 10^{-10}**	**9.40**

Best choice is acetic acid / acetate - closest in $[H_3O^+]$ to K_a *or* pH to pK_a!

MAR

Preparing a Buffer

Create a buffer solution at pH = 4.30 *(or $[H_3O^+]$ = 5.0 x 10^{-5} M)* **using HOAc and OAc^-.**

Equal moles of acid (HOAc) and base (OAc^-) would create pH = 4.74 (= pK_a). What ratio of acid to base is needed to get the buffer to 4.30?

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]}, \textit{ or rearranged}:$$

$$[H_3O^+] = 5.0 \text{ x } 10^{-5} = \frac{[HOAc]}{[OAc^-]}\,(1.8 \text{ x } 10^{-5})$$

Solve for [HOAc] / [OAc^-] ratio:

= $[H_3O^+]$ / K_a = 2.8 / 1

MAR

Preparing a Buffer

Create a buffer solution at pH = 4.30 (or $[H_3O^+] = 5.0 \times 10^{-5}$ M) using HOAc and OAc^-.

[HOAc] / [OAc^-] **ratio =** 2.8 / 1 *(previous slide)*

Therefore, if you use **0.10 mol** of NaOAc and **0.28 mol** of HOAc**, you will have pH = 4.30.**

Could have also used Henderson Hasselbalch:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{Conj. base}]}{[\text{Acid}]}$$

$$4.30 = 4.74 + \log\frac{[\text{Conj. base}]}{[\text{Acid}]}$$

$$10^{-0.44} = 0.36 = {[base]}/{[acid]},\ invert:$$

$$[acid]/[base] = 2.8$$

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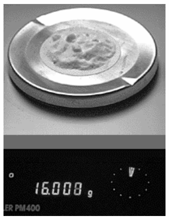
Preparing a Buffer Solution



Buffer prepared from

8.4 g $NaHCO_3$

weak acid

16.0 g Na_2CO_3

conjugate base

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

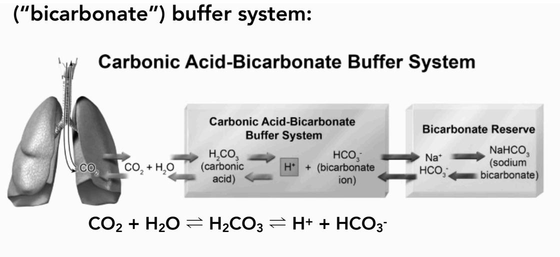
What is the pH?

Check yourself! Answer: ***10.50***

MAR

Buffers in Our Bodies

The blood pH in our bodies is regulated by a carbonic acid / hydrogen carbonate ("bicarbonate") buffer system:



$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

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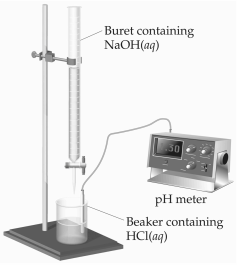
Exhaling CO_2 raises the pH of our blood!

14.7 - Acid-Base Titrations

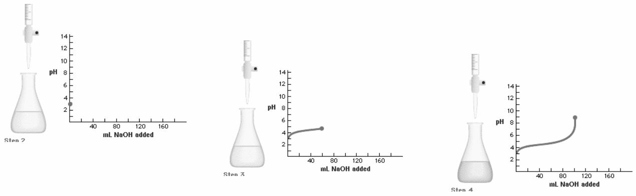


In an **acid-base titration** a known concentration of base (or acid) is slowly added to a solution of acid (or base)

A **pH meter** (or **indicator**) is used to determine when the solution has reached the **equivalence point** (where moles of acid = moles of base)

MAR

Titrations



Adding NaOH **from the buret to** acetic acid**:**

Initially the pH increases very slowly, then rises dramatically at equivalence point (midpoint of the vertical part of the curve

pH rises, then levels off as equivalence point passed

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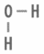
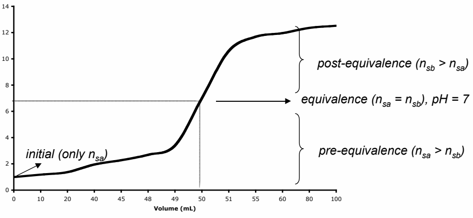
Strong Acid + Strong Base



$$\begin{array}{l} O-H \\ | \\ H \end{array}$$

Titration calculations divided into four regions: initial, pre-equivalence, equivalence and post-equivalence

A strong acid + strong base titration



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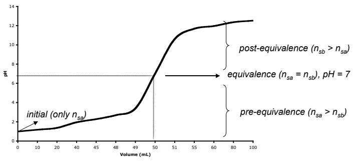
Strong Acid + Strong Base



Initial: $\mathrm{pH} = -\log\,[n_{sa} / V_{sa}]$

Pre-equivalence: $\mathrm{pH} = -\log\left(\dfrac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)$

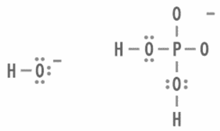
Equivalence: pH = 7 (neutral salt + water)

Post-equivalence: $\mathrm{pH} = 14 + \log\left(\dfrac{n_{sb} - n_{sa}}{V_{sb} + V_{sa}}\right)$

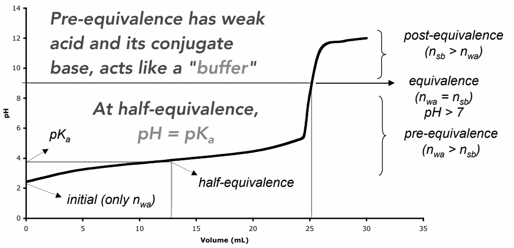
MAR

Weak Acid + Strong Base

Equivalence point dominated by conjugate base of weak acid



A weak acid + strong base titration



Pre-equivalence has weak acid and its conjugate base, acts like a "buffer"

At half-equivalence, pH = pK_a

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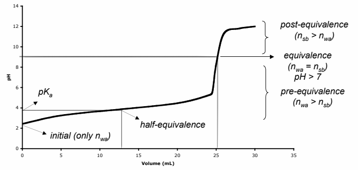
Weak Acid + Strong Base



Initial: $\mathrm{pH} = -\log\sqrt{K_a C_{wa}}$

Pre-equivalence: $\mathrm{pH} = pK_a + \log\left(\dfrac{n_{sb}}{n_{wa} - n_{sb}}\right)$

Equivalence: $\mathrm{pH} = 14 + \log\sqrt{\left(\dfrac{K_w}{K_a}\right)\left(\dfrac{n_{wa}}{V_{wa} + V_{sb}}\right)}$

Post-equivalence: $\mathrm{pH} = 14 + \log\left(\dfrac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}}\right)$

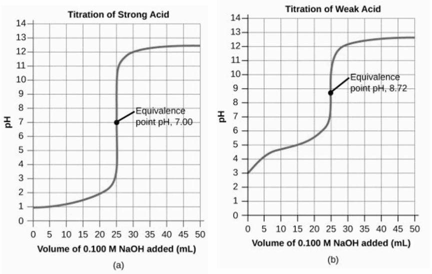
MAR

Differences in Titration Curves

With strong acids, equivalence point always equal to 7

With weak acids, equivalence point will be basic (> 7)

Half Equivalence Point important with weak acids; at that point, **pH = pK_a** *(great method to find K_a!)*



(a) (b)

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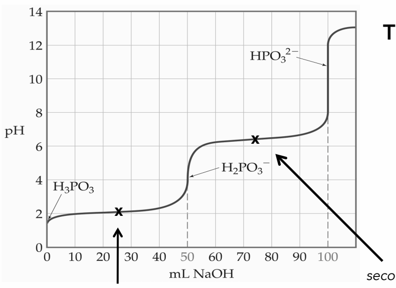
Polyprotic Acids



first half equivalence (pH = pKa for H_3PO_3)

second half equivalence (pH = pKa for $H_2PO_3^{1-}$)

Titrations of polyprotic acids with bases have multiple equivalence points (and half equivalence points) for each dissociation.

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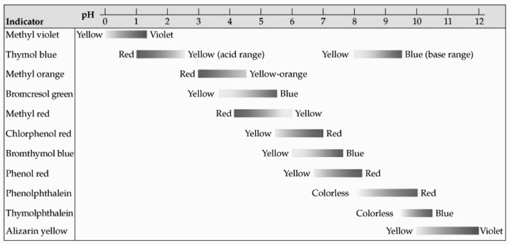
pH Indicators



Equivalence point important in titration, can use an indicator to signify equivalence point

Indicator color change must reflect equivalence point to be useful!

Bromthymol Blue

pH < 6.0 ***pH > 7.5***

pH = 6.0-7.5

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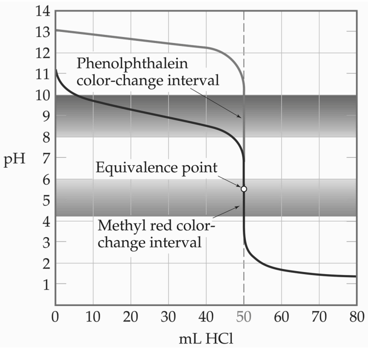
pH Indicators

Which indicator to use?
Phenolphthalein or Methyl Red?

The pH at the equivalence point in this titration is **< 7.**

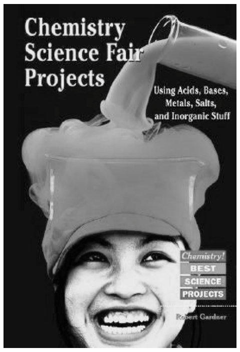
Methyl red **is the indicator of choice here.**



End of Chapter 14

See:

- *Chapter Fourteen Study Guide*
- *Chapter Fourteen Concept Guide*
- *Types of Equilibrium Constants (handout)*
- *Buffers and Henderson-Hasselbalch Guide (handout)*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



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)

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*
- *Buffers and Henderson-Hasselbalch Guide*

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

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

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

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

$$pH = pK_a + \log\frac{[Conj.\ base]}{[Acid]}$$

$$pH = pK_a + \log\frac{(mol_{Conj\ base} - mol_{strong\ acid})}{(mol_{weak\ acid} + mol_{strong\ acid})}$$

$$pH = pK_a + \log\frac{(mol_{Conj\ base} + mol_{strong\ base})}{(mol_{weak\ acid} - mol_{strong\ base})}$$

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 $K_b = 4.7 \times 10^{-11}$. 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: $Fe^{2+}(aq)$, CH_3NH_2
8. Does the pH of the solution increase, decrease, or stay the same when you: a) Add solid ammonium chloride to a dilute aqueous solution of NH_3; b) Add solid sodium acetate to a dilute aqueous solution of acetic acid; c) Add solid NaCl to a dilute aqueous solution of NaOH?
9. For each of the following cases, decide whether the pH is less than 7, equal to 7, or greater than 7: a) equal volumes of 0.10 M acetic acid, CH_3CO_2H, and 0.10 M KOH are mixed; b) 25 mL of 0.015 M NH_3 is mixed with 25 mL of 0.015 M HCl; c) 150 mL of 0.20 M HNO_3 is mixed with 75 mL of 0.40 M NaOH
10. What is the pH of a solution that consists of 0.20 M ammonia, NH_3, and 0.20 M ammonium chloride, NH_4Cl? ($K_a = 5.6 \times 10^{-10}$)
11. What mass of sodium acetate, $NaCH_3CO_2$, must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50? ($K_a = 1.8 \times 10^{-5}$)

End of Chapter Problems: *Answers*

1. $[H_3O^+] = 1.8 \times 10^{-4}$ M, $[OH^-] = 5.6 \times 10^{-11}$ M, acidic
2. 11.48
3. 3.0×10^{-10}
4. 2.1×10^{-4}
5. 0.0021 M, 3.6×10^{-4} ($K_a = 3.0 \times 10^{-4}$ using short method)
6. $[H_3O^+] = 8.1 \times 10^{-11}$ M, $[OH^-] = 1.2 \times 10^{-4}$ M, $K_b = 9.7 \times 10^{-7}$
7. $Fe^{2+}(aq)$ would be a Lewis acid, CH_3NH_2 would be a Lewis base
8. a) pH decreases; b) pH increases; c) no change to pH
9. a. pH > 7 b. pH < 7 c. pH = 7
10. pH = 9.25
11. 4.7 g